Effects of Wood Ash-Based Alkaline Treatment on Nitrogen, Carbon, and Phosphorus Availability in Food Waste and Agro-Industrial Waste Digestates

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Abstract
Handling of food waste and agro-industrial waste digestates, and fly and bottom wood ashes represents an economic and environmental problem for society and industries where they are produced due to the requirement of large capacity storage facilities with special conditions. Since both materials contain important nutrients for crops, two different blending combinations were examined as potential slow-release fertilizers to enhance the circular economy. High share of biomass ashes were selected aiming the chemical alkaline stabilization of the digestates. The concentrations of nitrogen, carbon, and phosphorus in the water-soluble extract of the blends, which was obtained by adding ten parts of milli-Q® per each part of sample and subsequent solid–liquid separation, were measured during a 10-h incubation at 22 °C and 100 rpm. The volatilization of ammonia was the main route of losing nitrogen, with the greatest rate of volatilization at the time of blending and approximately 50 mg NH₃-N/kg blend/hour by the end of the incubation. The hydrolysis taking place at alkaline pH was found responsible of the conversion of organic nitrogen to ammoniacal nitrogen and of the increase of the amount of water-soluble carbon, which rose progressively during the incubation. The release of CO₂ was prevented by the high pH (> 10) of the blends. The drop in the concentration of water-soluble orthophosphate at the time of preparing the mixtures
was driven by adsorption onto the ashes. The desorption of some of the orthophosphate was found to be inversely related to the amount of ashes added to the digestates.

**Graphic Abstract**

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**Keywords** Waste-derived fertilizer · Chemical alkaline stabilization · Hydrolysis · Ammonia volatilization · Orthophosphate sorption

**Statement of Novelty**

This work contributed to the development of the technology of alkaline stabilization of organic wastes. Considering the interrelations between the three levels of stabilization, a holistic approach was proposed for the intensification of the process of manufacturing of advanced fertilizers. In this way, the mixing ratios of low-pollutant fly and bottom wood ashes with food waste and agro-industrial waste digestates, which were primarily selected to assess the chemical stability of the blends (i.e. the availability of carbon and nutrients), also seek positive impacts on biological and physical stabilities. In addition to reduce the demand of inorganic fertilizers, the granules for easy-spreading of nutrient-balanced controlled-release amendent would contain recalcitrant stable organic matter to restore the soil as a natural carbon sink.

**Introduction**

The management of digestates and ashes represents a problem for the industries where they are produced. Whilst both issues are operational expenditure challenges, for ashes it is predominantly related to the gate-fee for disposal in landfills. For both digestates and the ashes, large spaces with special conditions (i.e. collection of gases and leachate) are required for the storage of these waste streams [1]. The use of low-pollutant digestates as an organic soil amendments is limited because of transporta- tion (due to the moisture content higher than 90%), the season of application, the nitrogen quota [2]. Whole diges- tates (i.e. which have not undergone any solid–liquid sepa- ration) are usually employed when nutrients are expected to be safely stored in the soil or effectively uptaken by the plants. Organic slow-release fertilizers are known for hav- ing low nutrient availability, which is typically enough for the utilization by the soil biota while preventing important losses due to runoff waters and gas exchange [3].

The use of ashes as soil amendment is largely dependent on their nature. In the UK, only poultry litter ash can be directly applied to soil, under the conditions indicated by
the Quality Protocol [4], due to their low content of pollutants (e.g. heavy metals). On the other hand, the direct use of biomass ashes is also accepted as alkaline and liming agent, and/or as a source of potassium comparable to the K chemical fertilizers [5]. Digestates and ashes could be combined to improve the handling of these wastes and to enhance their properties as fertilizers (e.g. nutrient profile).

The term stability is applied in literature indistinctly to a number of parameters which provide completely different information about waste materials. In this work, the differences between biological, chemical, and physical stabilities have been established. The biological stability [6] of organic wastes is a critical factor when deciding on the land application of these materials and this parameter is not limited to the pathogen content. According to the UK regulations, it is determined by the amount of carbon mineralized as biogas or CO₂ release due to microbial respiration, depending on the methodology used [7, 8]. Steenari and Lindqvist [9] employed the term chemical stabilization of the biomass ashes to refer to the process of self-hardening which is achieved by adding water or other suitable binders. However, since one of the objectives of employing this phenomenon is to improve the mechanical properties of the granules and pellets produced with ashes, in this manuscript it is regarded as physical stabilization. In the present work, the term chemical stability refers to how much the composition of the wastes changes overtime. The three types of stability are interrelated since the availability of the nutrients, which is the key parameter for determining chemical stability, also impacts on the microbial growth and the hardening process. A discussion is offered below on how ashes can be employed to maximize the stabilization of digestates to produce a novel fertilizer.

First of all, there is evidence that the use of ash as source of nutrients affects the carbon utilization during the anaerobic digestion (AD) of organic waste [10]. Guerrero et al. [11] tested doses up to 200 mg of thermoelectric fly ash per litre of digester prepared with 2 g of chemical oxygen demand (COD) of secondary sludge and 2.5 g of volatile suspended solids of inoculum. Similarly, Huiliñir et al. [12] studied how concentrations of coal fly ash up to 500 mg/L would enhance the digestion of sewage sludge in a bioreactor containing 5.87 ± 0.87 g soluble COD/L of substrate and 2.2 ± 0.42 g soluble COD/L of inoculum. If these doses were expressed as gram of ash per gram of sewage sludge, they would be slightly higher because of the water and the inoculum added to carry out the AD. Nevertheless, the highest doses are associated with other type of anaerobic systems, such as landfills. Lo et al. [13] employed up to 20 g of municipal solid waste (MSW) fly ash per kg of MSW (94% moisture) to enhance the biogas production.

Combinations of digestates and biomass ashes have been also tested in the soil to assess the biological stability. Bougnom et al. [14] employed three different rates of wood ash (0, 1, and 3 t/ha) together with manure digestate (67 t/ha) as fertilizer for pastures. They did not found significant difference in terms of carbon assimilation by the microbes in the soil compared to the application of the same doses of ash with undigested manure (74 t/ha). Similarly, Fernández-Delgado et al. [15] concluded that the carbon assimilation was not affected by the dose of wood ash (0, 1, and 3 t/ha), but in their study lower losses of carbon due to microbial respiration were found when using the manure digestate (52 t/ha) as organic amendment compared to the undigested cattle manure (41 t/ha).

The biological stabilization in not limited to improve the carbon utilization in the soil but high doses of ashes could be used prior to land application, to reduce the number of pathogens in the organic waste. The lime stabilization of liquid sludge is described to occur at pH above 12 when it is operated for at least two hours [16], for which is required a dose of 3.9 g Ca(OH)₂ per kg of sewage sludge (1.3% solid concentration) [17]. Jamali et al. [18] reported a ratio of 50 g CaO per kg sewage sludge, although they only reached a pH 9.1 due to the 25% content of solids. It should be noted the moderate (i.e. ~18%) calcium content of biomass ashes [5] at the time of proposing the amounts of these materials to be added to the organic wastes. Calcium and magnesium are not very soluble that is why the adsorption of the organic matter takes place onto these elements. Thus the chemical stability also increases because of the lower availability of carbon and nutrients.

Fivelman et al. [19] employed the adsorption technology to enhance the solid–liquid separation of the liquid fraction (i.e. liquor) of the digestate (AD FerTech). The main powder adsorbent that they used was dolomite (CaMg(CO₃)₂) in doses ranging from 10 to 200 g/L (mixed for 5 min at 20 °C), which was able to retain around 250 mg nitrogen and 300 mg phosphorus per gram of dolomite. Biomass ashes are a source of magnesium which can be used to decrease the availability of nutrients like nitrogen and phosphorus in the digestate due to the formation of struvite (MgNH₄PO₄·6H₂O). The adsorption is faster than the precipitation and it requires less amount of soluble nutrients. However, these two processes can take place simultaneously in a range of concentrations of the adsorbate [20]. Similarly, the concentration of adsorbent also determines the predominant phenomenon. Mor et al. [21] found the greatest adsorption in a 10 mg PO₄³⁻/L synthetic wastewater when using 2 g activated rice husk ash per litre. They tested higher ash doses, up to 4 g/L, but resulted in less PO₄³⁻ removed from the wastewater because of the aggregation of the adsorbent and the consequent decrease in the number of active sites. This fact does not agree with the results of Ma et al. [22], who tested concentration of adsorbent (prepared from wheat straw) in doses up to 6 g/L. They found that for a 25 mg...
PO$_4^{3-}$/L solution, the greatest adsorption was obtained when using the highest dose of adsorbent. However, the adsorption in a 50 mg NH$_4^+$-L solution followed the opposite trend.

In the soil, the adsorption phenomena could be coupled with the microbial growth to immobilize the carbon and the nutrients which further reduce the leaching and enhance the chemical stability. Insam et al. [23] reported that the wood ash tested in three different rates (0, 8.2, and 24.7 t/ha), together with vermiculite (24.6 t/ha), did not reduce the nitrate leaching resulting from the application of 96 t/ha thermophilic digestate (of manure, apple residues, and rice husk) during the fertilization of a 350 kg/ha mixture of seeds (85% grass and 15% legume). The characterization of the water-soluble (WS) extract of the blends digestates and ashes before land application (i.e. without dilution due to elements of soil) would represents a more conservative scenario to assess the readily available nutrients, since more leaching and volatilization are expected due to the higher concentration of carbon and nutrients compared to amended soil. Furthermore, the characterization of the blend, is less subjective to decrease the availability of the elements due to microbial assimilation. The assessment of the availability of carbon and nutrients in the blend could provide with key information to optimize the processing towards minimization of resources and better properties of the waste-derived fertilizer. The most common approach in the adsorption studies is to focus on the removal of adsorbate from the WS phase rather than monitoring the change of composition of the adsorbent [20–22]

Doses of ash added to organic waste resulting in a pH beyond 13 lead to chemical hydrolysis [24], which has a negative impact on the chemical stability to the liquid blend. This effect is desired for purposes that are different from the production of a fertilizer. Concentrations between 50 and 150 g Ca(OH)$_2$ per kg biomass (5 to 20% solid loading) are usually employed as caustic pre-treatment of the bioconversion of lignocellulosic biomass in the ethanol production [25]. The solubilization of organic carbon [26] enhances the subsequent fermentation [12], although it is necessary the previous neutralization with an acid agent to reach an appropriate pH for microbial activity. The physical stabilization of the organic wastes to produce a granular fertilizer is achieved even with higher doses of ashes [27, 28], but the moisture level of the final pellets should be less than around 3% [19, 28], which reduces the extent of the hydrolysis of the organic matter.

Steenari and Lindqvist [9] explained that the self-hardening of 1 g of wood ash when adding between 0.3 and 0.5 g of water as binder depends on a number of on-going reactions which can last from days to months. The hydration of CaO to produce Ca(OH)$_2$ is the main responsible of the curing since the subsequent formation of CaCO$_3$ is a much slower reaction due to the mass transfer resistance, which limits diffusion of CO$_2$ from the atmosphere. In addition to the solidification, Steenari and Lindqvist [9] claimed that other reason for which the curing of ashes would be necessary is the presence of the reactive oxides and soluble salts which might have adverse effects in plants (e.g. pH shock and burning tissues). Moilanen et al. [29] studied the use of self-hardened wood ash before and after granulation in the forest. They concluded that the amount of nutrients provided to soil is the most important factor to enhance the tree growth, despite the lower solubilization rates of the self-hardened ash and the granulated ash with regard to the untreated powder ash. Thereby, advanced manufacturing (e.g. pelletization) is encouraged to make easier spreading (i.e. prevent the formation of dust during land application) and to avoid excessive leaching of nutrients after land application.

Pesonen et al. [28] reported the smell of ammonia during the granulation of a fertilizer based on biomass ash and dewatered sludge. Although they included Ca(OH)$_2$ in the blends, the compressive strength of the granules did not increase. Mudryk et al. [27] assessed three agglomeration techniques for blends ranging from 0.33 to 3 g of waste wood ash per gram of dewatered digestate, with moisture content of 10%, 15%, and 18% required for binding. Based on the results of Mudryk et al. [27], Jewiarz et al. [30] proposed the entire process for the production of this granular fertilizer. In this process, the combustion of biomass is used to dry up the digestate until acceptable levels for the subsequent granulation of the blend with the ash. Other way of using the ashes to enhance the dewatering of the digestate was tested by Zheng et al. [31], who used coal fly ash as physical conditioner to reduce the filter cake compressibility. These are examples of synergies which need to be implemented to achieve the process intensification because there is a lack of a holistic approach when proposing the manufacturing of the blended fertilizer.

The aim of the present study was to evaluate how high doses of biomass ashes of wood origin affect the availability of nitrogen, carbon, and phosphorus in household food debris and post-harvest vegetable waste digestates to be able to propose further connected processing steps for the production of a novel fertilizer. In this way, the samples were blended without previous dewatering to promote the interaction between the components of the ashes and the digestates. This allowed focusing on the initial stages of the production of a blended fertilizer rather than on the self-hardening and granulation, which will be addressed in future studies. It was expected to identify and potentially take advantage of any ongoing phenomenon to minimize the cost of isolating carbon and nutrients to produce an organic fertilizer.
Materials and Methods

Materials

The samples were obtained from a variety of sources, including food waste digestate (FWD), post-harvest vegetable waste digestate (PVWD), woody biomass derived fly ash (WFA), and woody biomass derived bottom ash (WBA). The description of each sample from various sourced plants is illustrated in Table 1. The FWD was produced in compliance with the PAS 110, thus fulfilled the criteria towards the end-of-waste status according to the UK regulations [32]. It is important to highlight that the composition of the FWD was variable due to the different foods consumed during the different seasons of the year. Similarly, the maize was only fed from October to June as plant feedstock for the preparation of the PVWD. The sampling of the digestates and the ashes took place on September 2016.

Each digestate sample consisted on 5 kg of material, which was sourced at the end of the process line of the AD plant with a jerry can. Cooling down of the samples was allowed before placing them in suitable containers with ice for their transport by courier. Once received by the staff of Lancaster University, the samples were stored in a cold room (< 4 °C) until further use. These were considered “fresh” samples. A subsample of each digestate was sent out externally to Natural Resource Management (NRM) certified laboratory for determination of complementary analyses (nitrogen, phosphorus, and trace elements).

Each ash sample received consisted of 10 kg of material, which was sent by the producer in a sealed plastic box to minimize the contact with the open atmosphere. Once at the university, each sample was milled to pass a 1 mm mesh, sieved, and placed in zip bags which were left under room temperature until further use. These were considered “fresh” samples.

The samples were blended in order to achieve ashes-to-digestates ratios of 1:4.6 and 1:2.3 (Table 2). Usually, alkaline stabilization requires a ratio of g Ca(OH)$_2$/g solid of 1:10 [25]. It should be noted the significant amount (~10%) of Ca presented in the wood ashes (Online resource 1) and the low dry matter of the digestates (Table 3) when comparing the blending ratios. Both blends have a nutrient profile around C/N/P:10/1/1 (Table 3), hence low carbon mineralization would be expected after land application. The ashes were used directly without any prior treatment/activation to enhance the sorption process.

Methods

The preparation of the 3 g of each mixture was done in 50-mL Corning® flasks (Fig. 1) by following the weight percentages shown in Table 2. Therefore, the closed system had a headspace of ~47 mL which allowed the gas exchange of the blends during incubation. The factors assessed in the experiments were; (a) the type of blend (composition of blend 1 and blend 2 shown in Table 3), and (b) the length of the incubation at 22 °C (0, 0.5, 1, 3, 6 and 10 h). Under such working conditions and incubation time, the changes in the composition of the blend because of the microbial activity were assumed to be negligible compared to the physico-chemical phenomena. Up to sixteen repetitions in each of the twelve conditions (i.e. two blends and six incubation times) were done.

The assessment of the WS fraction of each material was considered since most of the short-term physico-chemical transformation would be reflected in this phase and also because was the phase where risks (e.g. nutrients leaching)
could be better understood [33]. The parameters measured were the pH, EC, concentrations of ammonium and ammonia (WS \( \text{NH}_4^+ \) and WS \( \text{NH}_3 \)), nitrate and nitrite (WS \( \text{NO}_3^- \) and WS \( \text{NO}_2^- \)), orthophosphate (WS \( \text{PO}_4^{3-} \)), total nitrogen (WS TN), and total carbon (WS TC). Two steps were required for the isolation of the WS extract (Fig. 1).

The procedures available in the literature for the determination of pH and EC mainly differ in the dilution ratio used (Online resource 2). The values of pH and EC are generally reported for the leachates. The digestate samples did not require addition of water for the measurement of pH and EC [34] but it was performed to match the procedure employed for the characterization of the ashes. In agreement with the procedure used by NRM laboratory, the WS extract was prepared following a sample-to-extractant (S:E) ratio of 10 parts of extractant per each part of sample (1:10). In this way, after the incubation, each blend of 3 g was mixed with 30 mL of ultrapure milli-Q water. The 50-mL tubes were placed horizontally in the rotary shaker for 1 h at 100 rpm. Finally, the lixiviation was achieved via centrifugation for 5 min at 4000 rpm and subsequently filtered down to pass 3 µm. Unlike the other parameters measured in the WS extract for the initial characterization (Table 3), the pH and the EC of the samples were measured in the WS extract of the samples generated using a S:E ratio 1:5 (i.e. one part of sample and five parts of ultrapure milli-Q water) rather than a S:E ratio 1:10.

The measurement of the pH and the EC of the WS extracts of the blends were done with a Mettler Toledo® Seven Compact™ S220 pH/Ion meter and a Jenway® 4510 bench conductivity/total dissolved solids meter, respectively. The determination of the concentrations of WS \( \text{NH}_4^+ \) and WS \( \text{NH}_3 \) (methods DIN 38,406 and ISO/DIN 11,732), WS \( \text{NO}_3^- \) and WS \( \text{NO}_2^- \) (methods DIN 38,405 and ISO/DIS 13,395), and WS \( \text{PO}_4^{3-} \) (methods DIN/EN/ISO 15,681-2) was done with the Autoanalyzer (AA3, SEAL analytical), by using the colorimetry based on the salicylate, hydrazine, and molybdate reactions, respectively. On the other hand, the concentrations of WS TN and WS TC were measured with the TOC-L Shimadzu via combustion of the sample and detection of CO\(_2\) and NO gases. The TC of all the samples and the TN of the ashes (Table 3) were measured in the elemental analyser (Elementar vario EL cube) in dried and ground samples. For the digestates, it was considered that there was no losses of carbon during the drying at 105 °C. The TN of the digestates together with the total phosphorus (TP) of all the samples were determined by the NRM laboratory. The estimated expanded uncertainty calculated as per the NORTTEST 537 method was 10% for the values provided by NRM.

In order to build the mass balance for the nitrogen, the theoretical TN of the blends at time zero (Table 3) was divided into the TN of the blend (TN\(_{\text{blend}}\)), ammonia nitrogen gas lost (NH\(_3\)-N), and nitrous oxide nitrogen gas lost (N\(_2\)O-N). Furthermore, the TN\(_{\text{blend}}\) was divided into water-insoluble (WI) TN and WS TN. It is important to highlight that although the WI TN\(_{\text{org}}\) of the digestates presented different availability (i.e. different solubilization rates) than the WI TN of the ashes, this distinction was not considered in the present study. With regard to the WS TN, the following fractions were considered as the fate of the nitrogen in the WS extract: WS organic nitrogen (WS \( \text{N}_{\text{org}} \)), ammoniacal nitrogen (WS \( \text{NH}_4^+\)-N), and nitric nitrogen (WS \( \text{NO}_3^-\)-N). The WS \( \text{N}_{\text{org}} \) was calculated as the difference between the WS TN and the sum of WS \( \text{NH}_4^+\)-N and WS \( \text{NO}_3^-\)-N [35]. It should be noted that the WS \( \text{NH}_4^+\)-N represented the nitrogen contained in both aqueous species WS \( \text{NH}_4^+ \) and WS \( \text{NH}_3 \) (i.e. \( \text{NH}_4^+_{\text{aq}} \) and \( \text{NH}_3_{\text{aq}} \)), while \( \text{NH}_3\)-N stood for the ammoniacal nitrogen gas form (\( \text{NH}_3_{\text{gas}} \)) that has been lost by volatilization. A widely used procedure is the calculation of the \( \text{NH}_3_{\text{aq}} \) volatilization based on the decrease of the concentration of \( \text{NH}_4^+\)-N in the digestates [36, 37]. In the
present study, the increase in the formation of NH$_3$ gas was accounted for the decrease in all the other forms of nitrogen, with the exception of WS NO$_3^-$ and WS NO$_2^-$, for which the decrease was expressed as an increase of the N$_2$O gas. In this way, the rate of formation of NH$_3$-N during the incubation of the samples was calculated based on reduction of the TN$_{blend}$ for both blends, since the variation in the concentration of the NH$_4^+$-N was not representative of the nitrogen lost because of the pool of both WS N$_{org}$ and WI N$_{org}$. The approach of Ukwuani and Tao [38] to this problem was to begin the calculation of the NH$_3$-N volatilized once the WS NH$_4^+$-N has started to decrease. In their study about the development of a vacuum thermal stripping up, the WS NH$_4^+$-N increased during the first hour of heating up the digestates and the content of the WS NH$_4^+$-N started to decrease progressively once reached the desired temperature for the next 4 h which lasted the for ammonia stripping.

Results and Discussion

Initial Characterization

The characterization of the samples, in terms of the parameters concerning the present work, is shown in Table 3. While the values for the samples were determined empirically, the characterization of the blends at time zero was estimated based on the data of each sample and their share in each blend (Table 2).

The digestates were the main source of nitrogen in the blends. The NH$_4^+$-N, which was higher in the FWD because of the higher protein content, was an important contributor to the electric conductivity (EC) [39], together with other elements (Online resource 4), such as sodium (Na$^+$). Although there was no significant difference between the pH values of the digestates, it was expected that the FWD would have greater buffer capacity to prevent the increase of the pH when adding the ashes because of the greater content of NH$_4^+$-N (Eq. (1)).

The ashes were the main source of (insoluble) TP and they were also loaded with alkali and alkaline earth metals (Online resource 1), which conferred them high pH. It should be noted that less than 1% of the phosphorus contained in the ashes was soluble (Table 3) because it was in the form of insoluble calcium compounds, such as hydroxyapatite (Ca$_5$(PO$_4$)$_3$OH) [9]. The fate of most of the phytotoxic elements, such as heavy metals (e.g. As, Cd, Pb, and Zn [9]), usually are the finer fractions of ashes. The reason could be that the fly ash account for most ashes (around 80%) generated during combustion, although the exact mass distribution

| Sample | FWD | PVWD | WFA | WBA | Blend 1 | Blend 2 |
|--------|-----|------|-----|-----|--------|--------|
| pH     | 8.8 ± 0.0 | 8.8 ± 0.0 | 12.9 ± 0.0 | 13.4 ± 0.0 | 9.5 ± 0.0 | 10.2 ± 0.0 |
| EC     | 8.6 ± 0.1 | 2.4 ± 0.0 | 20.6 ± 0.6 | 57.9 ± 1.0 | 9.9 ± 0.2 | 13.8 ± 0.2 |
| Dry matter/(wt.%) | 6.3 ± 0.5 | 7.6 ± 0.3 | 90.0 ± 0.5 | 98.9 ± 0.6 | 21.4 ± 0.5 | 34.3 ± 0.4 |
| TC/(mg/kg) | 21332.3 ± 805.1 | 31959.3 ± 43.6 | 41398.7 ± 575.2 | 41398.7 ± 575.2 | 22069.7 ± 1145.8 | 26390.5 ± 1145.8 |
| WS TC/(mg/kg) | 4073.6 ± 252.0 | 2041.5 ± 87.7 | 3773.6 ± 516.0 | 1825 ± 113.6 | 3737.0 ± 276.2 | 2266.9 ± 156.0 |
| TN/(mg/kg) | 8500.0 ± 380.0 | 3800.0 ± 380.0 | 1061.2 ± 152.6 | 3316 ± 191.6 | 6519.0 ± 660.2 | 2923.1 ± 316.3 |
| WS TN/(mg/kg) | 8799.5 ± 246.6 | 2062.7 ± 18.9 | 61.1 ± 3.3 | 46.6 ± 13.9 | 6303.0 ± 171.5 | 1445.9 ± 15.8 |
| WS NH$_4^+$ & WS NH$_3^-$/(mg/kg) | 4375.1 ± 151.2 | 886.8 ± 111.6 | 5.3 ± 0.3 | 5.5 ± 1.0 | 3110.0 ± 118.8 | 616.2 ± 77.5 |
| WS NO$_3^-$ & WS NO$_2^-$/(mg/kg) | 7.5 ± 1.0 | 83.9 ± 2.9 | 29.9 ± 0.5 | 5.7 ± 0.1 | 22.1 ± 1.2 | 63.5 ± 2.1 |
| TP/(mg/kg) | 1004.0 ± 100.4 | 1119.0 ± 111.9 | 23968 ± 2396.8 | 12359.0 ± 1235.9 | 5114.5 ± 511.5 | 6308.7 ± 630.9 |
| WS PO$_4^{3-}$/(mg/kg) | 168.1 ± 11.4 | 119.5 ± 8.4 | 68.9 ± 0.7 | 68.2 ± 4.6 | 143.7 ± 9.0 | 103.9 ± 6.6 |
depends on the type of incinerator [9]. It is important to highlight that there are different fractions of fly ash, each separated at different stages (e.g. cyclone ash, electrostatic precipitator ash, filter ash, etc. [9]) of the flue gas treatment system, depending on the particle size. The ashes employed in the present work were generated in a grate combustion chamber, thereby the bottom ash represented the main fraction (Table 1) and more pollutants could end up in the WBA. The samples of both ashes were collected on the same day, but the WFA presented more surface area, which made it more reactive [40] and fostered faster kinetic and greater extent of the water sorption during the storage. This could be the reason for which the WFA had higher moisture content (i.e. lower dry matter) than the WBA. Similarly, the neutralization and carbonation, that took place during storage, were enhanced in the WFA, leading to a greater total carbon (TC) and lower pH of the WFA compared to the WBA (Table 3). Values with an uncertainty greater than 10%, such as the TC of the WBA, are explained by the heterogeneity of the samples.

It could be possible that the WBA was cooled down via quenching, as this fraction was reported by the producer as wet ash (Table 1), and was subsequently dried. Firstly, adding water to the WBA promoted hydration and in this process the alkalinity of the WBA decreased because the oxides of the alkaline metals were converted to hydroxides. Secondly, the alkalinity was further reduced because of the lower mass transfer resistance of the atmospheric CO₂ towards the alkaline aqueous solution, leading to the formation of carbonates [9]. Thirdly, the drying at high temperature decreased the moisture content, restored the alkalinity (because of the decomposition of carbonates and even hydroxides) [5], and would be responsible of the clumping and formation of greater particle size compared to the WFA.

The EC of the ashes was measured following the same procedure as for the digestates, in the S:E ratio 1:5 WS extract (Table 3). The higher content of potassium (K⁺) explained the higher conductivity of the WBA in spite of its lower moisture content (Online resource 1). Generally, the EC of the ashes increases with the moisture content but beyond the water sorption saturation level, which corresponds to a S:E ratio of 1:0.4 [41, 42], the EC decreases because of the dilution effect and the lack compaction. The level of self-hardening of the ashes affected the measurement of the EC [43], which was determined by the amount of mobile ions. According to Karoline [44] sulfate (SO₄²⁻), chloride (Cl⁻), and PO₄³⁻ were the main anions provided by the wood ash. While the low WS PO₄³⁻ in the ashes of the present study (Table 3) was associated with the low solubility of calcium (Ca²⁺) and magnesium (Mg²⁺), the SO₄²⁻ and the Cl⁻ were the counter ions associated with the potassium. The potassium salts are very soluble and are rarely related to the hardening phenomenon, with the exception of K₂Ca(SO₄)₂*H₂O [9].

**pH and EC Profiles**

As illustrated in Fig. 2, the blend 2 had a higher pH and EC than the blend 1 because of the higher share of ashes, which were the driving force for the change of the composition of the digestates. Moreover, the blend 1 had higher content of NH₄⁺-N (Table 3) with buffer effect, which prevented a drastic increase of the pH. These two characteristics (i.e. content of ashes and NH₄⁺-N of the blends) were responsible for the more time required for the blend 1 to reach a steady level of pH and EC than for the blend 2. In fact, the ANOVA test indicated that the EC of the blend 2 was constant during the whole incubation period. The larger error bars of the EC of the blend 2 (Fig. 2b) could be related to the greater particle size of the WBA which made this sample more susceptible to be affected by sampling errors and, therefore, less homogenous than the WFA. Moreover, as the EC of the

![Fig. 2 Changes of the pH (a) and the EC (b) of the ~ 30 mL WS extracts (S:E ratio 1:10) of each of the blends (Table 2) obtained after the incubation at 100 rpm and 22 °C](image-url)
WBA was higher than the one of WFA (Table 3), any change in the composition of the bottom ash had greater impact on the EC of the blend. It should be noted that only the blend 2 contained WBA while WFA had a similar share in both blends (Table 2).

The mobility of H⁺ ions, explained by the Grotthuss mechanism, is almost twice as those of OH⁻ ions [45]. Thereby, strongly acidic solutions have more EC than the highly basic ones. At the pH of the blends (Fig. 2a), the amount of H⁺ was negligible compared to the OH⁻. Therefore, the higher the pH, the higher the EC. Following the same reasoning, moderate alkaline pH reduces the amount of ions [46], such as NH₄⁺, Na⁺, and K⁺, but greater basicity could even promote the solubilization of organic matter [47]. The EC of both blends matched with saline soils (>4 dS/m) [48], which could give an idea of their potential purposes. It is possible that the dose of ashes used to prepare the blend 1 fell in the range of chemical alkaline stabilization while the behaviour of the blend 2 was ruled by the chemical hydrolysis. Both blends had high pH which is desired to decrease microbial growth in the blend [24].

The straight forward comparison of the pH and EC values obtained for the WS extracts of the incubated blends (Fig. 2) with the pH and EC values of the initial characterization (Table 3) was not possible because different S:E ratios were used for the preparation of the WS extract. The increase of the EC of the digestates when the ashes were added, was less significant than the increase of the pH, considering the wider range for the variation of EC. Garfí et al. [49] reported a value of EC as low as 6.88 × 10⁻³ dS/m for digested guinea pig manure determined with a standard method for the characterization of wastewater. On the other hand, Walker et al. [7], using a standard method for the characterization of waste, found 145 dS/m in a digestate based on agricultural waste and animal slurry. Unlike the pH, the EC was very dependent on the S:E ratio used to produce the WS extract [41]. The pH was less affected by the dilution (i.e. 1:5 to 1:10) because the decrease of the concentration of H₂O⁻ was smoothed by the logarithmic calculation. On the other hand, the measurement of the resistance, which was a proxy of the EC, was directly related to the concentration of ions.

**WS NH₄⁺ and WS NH₃ profiles**

The amount of WS NH₄⁺ and WS NH₃ in blend 1 was greater than in the blend 2 (Fig. 3a) in agreement with the higher share of digestates (Table 2) and the large concentration of these species in the FWD (Table 3). The results of the single factor analysis of variance for both blends were that F > F_critical = 2.36. Thereby, it was possible to claim with a 95% of certainty (α = 0.05) that, during the 10 h of incubation at 22 °C, the concentration of WS NH₄⁺ and WS NH₃ in both blends was not constant.

The fluctuations of the concentration of WS NH₄⁺ and WS NH₃ in both blends (Fig. 3a) could be related to the mineralization of the Norg due to abiotic factors. Given the high concentration of calcium in the ash samples (Online resource 1), the hydrolysis with the exchangeable calcium was possible [50]. Consequently, the NH₄⁺ would be released and then neutralized into NH₃_aq owing to the high pH of the medium as per the reaction pathway (1). The formation of NH₃_aq implies the acidification of the medium, which could be one of the reasons explaining the lower pH of the blend 1 (Fig. 2a), since the FWD had more WS NH₄⁺ and WS NH₃, together with the lower share of ashes compared to the blend 2 (Table 2). Furthermore, the FWD had a greater pool of NH₄⁺ than the PVWD, in agreement with the higher peak of the concentration of WS NH₄⁺ and WS NH₃ at the 30 min of incubation (Fig. 3a), confirming a greater protein content of the materials used as feedstock for AD. The WS NH₄⁺

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**Fig. 3** Concentration of WS NH₄⁺ & WS NH₃ (a) and WS NO₃⁻ & WS NO₂⁻ (b) in 3 g of each of the blends (Table 2) measured after the incubation at 100 rpm and 22 °C.
and WS NH₃ could build up because the rate of hydrolysis of the N-org was faster than the volatilization of NH₃ gas. At a pH value of 11, all WS NH₄⁺-N in the blends would be in the form of NH₃ aq [46]. Thereby, it was considered that what limited the flux of NH₃ aq from the blends to the air was the mass transfer step (1).

\[
N_{\text{org}} \xrightarrow{\text{Auto-bio-mineralization}} NH_4^+ \xrightarrow{\text{Neutralization}} NH_3 aq + H^+ \xrightarrow{\text{Mass transfer}} NH_3 gas
\]  

(1)

The theoretical content of WS NH₄⁺ and WS NH₃ in the blends (Table 3) was higher than the content of WS NH₄⁺ and WS NH₃ measured at time zero (Fig. 3a). Both blends have lost around 50% of the theoretical content of WS NH₄⁺ and WS NH₃ at the time of blending the samples. It was considered that a minimum amount of nitrogen was lost during the storage of the digestates at (<4°C). The optimum pH for the formation of indophenol during the determination of the NH₃ aq content in the blends via the salicylate method is 12 [51]. This pH was meant to be achieved after the WS extract (S:E ratio 1:10) interacted with the reagents for the development. Moreover, it is worth to mention that low molecular weight amines could react similarly to NH₃ aq, resulting in an overestimation of the concentration of WS NH₄⁺ and WS NH₃ [52].

Méndez et al. [53] reported a 4.99% loss of NH₄⁺-N when adding 600 g of quicklime (81.5% CaO) to 2 kg municipal wastewater sludge after 2 h of incubation at 300 rpm and 20 °C in an open system. They did not provide information on how the measurement was performed, which would be required to understand how much of the of the NH₄⁺-N was adsorbed and why there were no losses in the closed systems. Although the size of their system was 1000 times bigger than the 3-g blends of the present study, the concentration of WS NH₄⁺ and WS NH₃ in their wastewater sludge was 1000 times lower (i.e. 0.120 mg NH₄⁺-N/kg sludge) than the ones of the blends in this work (Table 3). Whelan et al. [37] reported a loss of 1925 mg WS NH₄⁺ and WS NH₃ in 120 g of digestate (mixture of ruminant slurry and food waste) during three weeks of incubation at 25 °C. The initial WS NH₄⁺ and WS NH₃ content was 7425 mg/kg digestate and the enhancement in the release of NH₃ was given by a 10 mL 1 M H₂SO₄ trap placed in the 1 L headspace of the kilner jar for trapping the NH₃ gas. The amount of NH₃ aq volatilized in their system with the H₂SO₄ trap for more than 3 weeks, was similar to the loss of NH₃ aq in the blend 1 at time zero (2348 mg NH₃ aq/kg blend; Fig. 5a). On the other hand, in this work their model has been used to predict that ~6% of the initial WS NH₄⁺ and WS NH₃ would be lost at the time of blending. It is important to mention that mass transfer coefficients of environmental models were employed for this calculation. It was considered that the conditions of turbulence would be a more similar approach to represent the enhancement of NH₃ aq volatilization given by the addition of the ashes to the digestates. The NH₃ aq volatilization was also estimated using the values of the vapour pressure tables available for the aqua ammonia (NH₄OH) solutions [54]. For the calculation, it was considered that the concentration of NH₃ aq in the blend was 10 wt.% (i.e. approximately 10 times higher compared to the initial composition of the blends; Table 3), to take into account the enhancement in the volatilization of NH₃ aq because of the addition of the ashes. The calculated losses at the time of blending were 1.9% and 9.5% of the initial WS NH₄⁺ and WS NH₃ in the blend 1 and blend 2, respectively.

Other possible routes for the decrease of concentration of WS NH₄⁺ and WS NH₃ would be adsorption and precipitation. This would be reflected by a translocation of a share of the TN from the WS phase to the WI phase. Ma et al. [22] studied the removal of NH₄⁺ and NH₃ and PO₄³⁻ from water with concentrations up to 200 and 250 mg/L, respectively. In their study, the optimum pH required for adsorption in a 50 mg NH₄⁺ and NH₃/L solution was between 3 and 9, and higher pH could lead to losses via NH₃ aq volatilization. With regard to the precipitation, the formation of struvite could explain a share of the decrease in the concentration of WS NH₄⁺ and WS NH₃. Changes in the concentration of NH₄⁺-N lower than 15% have been reported by Sakthivel et al. [55], during the incubation at 25 °C of 11.4 g of wood ash with 1 L of ureolysed urine with an initial content of 3497 mg NH₄⁺ and NH₃ per litre. Similarly, Huang et al. [56] tested the dose of plant ash up to 28.5 g per litre of swine wastewater with 529 mg NH₄⁺ and NH₃ per litre. Although the precipitation of the 97% of the 267 mg PO₄³⁻/L in a 500 mL swine wastewater was found after 1 h using a dose of plant ash of 12.5 g/L, they did not report which share of PO₄³⁻ in the precipitate corresponded to struvite. This information was necessary for the calculation of the amount of precipitated NH₄⁺, since in their study the PO₄³⁻ also precipitated with the calcium, as hydroxyapatite, and with the potassium, as K-struvite (MgKPO₄·6H₂O).

**WS NO₃⁻ and WS NO₂⁻ Profiles**

In both blends, the same levels of WS NO₃⁻ and WS NO₂⁻ were constant during the incubation (Fig. 3b). The low value of 6–7 mg WS NO₃⁻ and WS NO₂⁻ per kg blend could be associated with the low reactivity of these species at low concentrations [57]. Other explanation for the constant levels of WS NO₃⁻ and WS NO₂⁻ in both blends during the incubation could be the detection limit of the analytical procedure. It should be noted that the concentration of WS NO₃⁻ and WS NO₂⁻ shown in the Fig. 3b is expressed in terms of fresh base of the blend (Online resource 4), and the concentration in the WS extract (S:E ratio 1:10) was around...
0.65 mg WS NO$_3^-$ and WS NO$_2^-$/L. Nevertheless, according to the manufacturer of the Autoanalyzer, the method used in the present study has a detection limit of 1 µg WS NO$_3^-$ and WS NO$_2^-$/L [52].

Similarly to WS NH$_4^+$ and WS NH$_3$, there was a loss of the WS NO$_3^-$ and WS NO$_2^-$ at the time of blending. It was not very likely that the nitrate remained in the system adsorbed in the ashes [58] or in the digestates fibres [59], since these materials have not been activated for that purpose. Also, the biological desnitrification [60] should not be possible in the blends due to the high pH and short incubation (Fig. 2a). However, the N$_2$O gas has been reported as the main product of abiotic reduction of WS NO$_3^-$ [61] and WS NO$_2^-$ [62] to presence of iron around pH 7 ± 1. The reducing effect of the alkali and alkaline earth metals depended on the forms in which these elements were presented in the ashes (Online resource 1), which were set by the temperature of incineration and the conditions of storage.

**WS TN and WS TC profiles**

The blends had opposite trends both for the WS TN and the WS TC (Fig. 4). The blend 2 had a constant WS TN during the whole incubation period, while its WS TC significantly increased. On the other hand, the blend 1 had a decrease in the WS TN during the first 3 h of incubation and the WS TC increased less than the blend 2. These trends could be explained by the initial composition of the samples. The higher protein content of the feedstock used to prepare the FWD provided with a fraction of N$_{org}$ more easily converted to WS NH$_4^+$ and WS NH$_3$ in the conditions of chemical alkaline stabilization that were tested. The N$_{org}$ could be an important component of both, the WI N and the WS TN, and it was taken into account to explain the changes in the concentrations of WS NH$_4^+$ and WS NH$_3$ and WS TN, in both blends (Fig. 5).

The content of WS NH$_4^+$ and WS NH$_3$ in the blends was between one and two orders of magnitude greater than the WS NO$_3^-$ and WS NO$_2^-$ (Table 3). Therefore, the loss of WS TN at the time of blending was mainly given by the reduction of the concentration of WS NH$_4^+$ and WS NH$_3$.
in both blends. In an open system (e.g., after applying the blended fertilizer to land), the leaching of WS N\textsubscript{org} could be the main way of losing N [63]. Because of the high concentration of WS NH\textsubscript{4}\textsuperscript{+} and NH\textsubscript{3} in the blend 1, resulting from the conversion of the N\textsubscript{org}, it took longer to reach a stable level (Fig. 3a).

The carbon losses via gas exchange (e.g., CO\textsubscript{2} release), were considered minimal given the high pH of the blends. On the other hand, the increase of the carbon content of the blends because of the absorption of the CO\textsubscript{2} available in the atmosphere during the incubation and the analysis of the WS extract (S:E ratio 1:10) was assumed to be negligible considering the amount of carbon presented in the blends (Table 3).

The trends found for the WS TC of both blends (Fig. 4b) could be explained based on the type of carbon containing compounds in each sample and the blending ratio. While the FWD contained more easily degradable labile organic matter, the stable fraction of organic matter abounded in the PVWD [64]. The initial WS TC of blend 1 was therefore higher than the initial WS TC of the blend 2 in spite of the lower carbon content of the blend 1 (Table 2). The carbon provided by the ashes was less reactive (i.e., less soluble) and can be regarded as the inert fraction of the organic matter [65]. Furthermore, since both blends had similar share of the WFA, the increase of the WS TC because of the carbonates is similar for both blends. Only the blend 2 further included the WBA to promote the hydrolysis of the stable organic matter of the PVWD [6]. Under the conditions of chemical alkaline stabilization attained in the blend 1, the Ca\textsuperscript{2+} could promote the neutralization and sorption of organic matter [26]. In this way, the organic acids could undergo saponification reactions [66] which increased the yield of the WI material. This organic salts were expected to remain in the WI material due to the low solubility of calcium and magnesium. The slight increase in the WS TC of blend 1 (Fig. 4b) with respect to the initial (Table 3) could be explained by the short chains of low molecular weight organic compounds that ended up in the WS extract because they were not absorbed by the alkali metals.

**Nitrogen Profile**

Based on the empirical results obtained for nitrogen, the speciation of blend 1 and blend 2 were represented in Fig. 5. A detailed description of the assumptions made for this simulation is offered in the section of this manuscript describing the methodology. It should be noted that no mechanism for the translocation of the TN from the WS phase to the WI phase, such as sorption or precipitation, has been considered since the ashes have not been activated, thus this could lead to an underestimation of the WI TN. The greater concentration of WI N in the blend 2 (Fig. 5b) compared to the blend 1 (Fig. 5a), was in agreement with the lower NH\textsubscript{3}-N losses in the blend 2. The N\textsubscript{2}O\textsubscript{gas} emissions were higher in the blend 2 than in the blend 1, but any of these losses were negligible compared to the NH\textsubscript{3}\textsubscript{aq} volatilization. In this way, NH\textsubscript{3}\textsubscript{gas} was the main form in which the N was lost, with the highest volatilization rate of NH\textsubscript{3}\textsubscript{aq} at the time of blending the samples (Fig. 6a). However, the determination of the rate of volatilization of NH\textsubscript{3}\textsubscript{aq} at time zero was not possible because of the negligible time interval. It took 6 h to have similar rates in both blends (around 90 mg NH\textsubscript{3}-N/kg blend/hour), which continued to decrease after the 10 h of incubation until reaching a minimum NH\textsubscript{3}\textsubscript{aq} concentration. Ukwuani and Tao [38] found similar volatilization rates, ranging from 151 to 1284 mg NH\textsubscript{3}-N/kg digestate/hour, in 15 L municipal sludge digestate and 10 L retenrate of landfill leachate, respectively. In their experiment, the incubation of each waste took place for 2 h at 65–70 °C and 25.3–34.7 kPa of absolute pressure. Other NH\textsubscript{3}\textsubscript{aq} volatilization rates available in the literature were lower than the values found for the two blends (Fig. 6a). Whelan et al. [37] found a rate of volatilization of 2.6 mg NH\textsubscript{3}-N/kg digestate/hour during the first two hours.

![Fig 6](image-url)  
*Fig. 6* Calculated rate of NH\textsubscript{3}-N loss in each blend (a). Concentration of WS PO\textsubscript{4}\textsuperscript{3−} (b) in 3 g of each of the blends (Table 2) measured after the incubation at 100 rpm and 22 °C.
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weeks of incubation. Besides, it was possible to calculate a rate of volatilization of 0.0023 mg NH₃-N/kg sludge/hour with the results of Méndez et al. [53].

**WS PO₄³⁻ Profile**

The result of the single factor analysis of variance for blend 1, was that F = 6.39 > Fₜₐₜ = 2.35. Thereby, it was possible to claim with a 95% of certainty (α=0.05) that, during the 10 h of incubation at 22 °C, the concentration of WS PO₄³⁻ of blend 1 increased (Fig. 6b). The reason for the lower concentration of WS PO₄³⁻ in both blends, compared to their initial characterization (Table 3), would be the gradual process of adsorption and precipitation as described by Yagi and Fukushi [20]. The kinetic of adsorption was faster than precipitation, therefore the concentration as described by Yagi and Fukushi [20]. The kinetic of adsorption was faster than precipitation, therefore the gradual process of adsorption and precipitation as described by Yagi and Fukushi [20].

Mor et al. [21] had the greatest adsorption of WS PO₄³⁻ at pH 2. On the other hand, Ma et al. [22] found that the pH required for the adsorption in a 25 mg PO₄³⁻/L solution was between 4 and 11. In the study of Huang et al. [56], the pH of the 500 mL swine wastewater raised from 7.1 to >9 after they added 14.25 g of plant ash followed by 30-min mixing and 30-min precipitation. Sakthivel et al. [55] reported an increase of the pH, from 8.77 to 9.21, of the ureolysed urine with an initial content of WS PO₄³⁻ of 573 mg/L after 15 min of mixing and 4 h of settling. They used an ash-to-urine ratio of 1:88, which is lower than the dose of wood ashes used in the present study (Table 2), in spite of the higher concentration of PO₄³⁻ in their urine solution compared to the digestates of the this work (Table 3). They only considered the WS fractions of the elements to achieve the ratio 1.5 mol (Mg + Ca)/mol P for the production of struvite and octacalcium phosphate (Ca₈H₂(PO₄)₆*5H₂O), without taking into account the excess of WS NH₃-N in the urine. The 53% of the Mg in their wood ash was soluble. According to Drog et al. [68], a nutrient ratio of Mg/N/P:1.3/1/0.9 is necessary to maximize the precipitation of struvite. Because of the high ammonium content of the digestates, the addition of magnesium oxide and phosphoric acid is a common procedure. The Mg/N/P total nutrient ratios 1.1/1/0.4 and 2.5/1/1 correspond to the blend 1 and blend 2, respectively.

Comparing the values of Fig. 6b) with the initial characterization (Table 3), it was possible to conclude that both doses of ashes used in this work (Table 2) decreased the availability of phosphorus. Approximately 1 mmol of PO₄³⁻ was removed from the WS phase in 1 kg of each blend at the time of blending. On the other hand, 87 and 20 mmol of WS NH₃⁺ were discounted from 1 kg of the blend 1 and the blend 2, respectively (Fig. 3a). Although the 77% of the potassium of the ashes was soluble, the formation of either struvite or K-struvite in the blends was unlikely because less than 1% of the magnesium provided by the ashes was soluble (Online resource 1). Moreover, given the high content of calcium of the ashes, it was expected that the decrease of the WS PO₄³⁻ was due to a mixture of sorption and precipitation reactions [69]. However, since less than 1% of the calcium of the ashes was soluble, the precipitation of a calcium phosphate compound was less feasible. Sakthivel et al. [55] reported calcite (CaCO₃) as the main compound in the precipitate and struvite as the only phosphate compound detected. Other compounds such as hydroxyapatite and octacalcium phosphate were described as intermediates because they were not found in the precipitate. According to Yagi and Fukushi [20], calcium phosphates with lower concentrations than 1 wt.% could not be detected from the XRD patterns. Yagi and Fukushi [20] studied the adsorption and precipitation by adding 100 mg monohydrocalcite (CaCO₃*H₂O) to 50 mL solutions ranging form 0.95 to 19.95 mg PO₄³⁻/L under continuous stirring for 6 to 216 h. The lower chemical stability of the CaCO₃*H₂O make this material more reactive and more suitable for decreasing the availability of the WS PO₄³⁻. The initial pH of their blend of 10.3, decreased until 8.3–8.8 after 24 h due to the diffusion of the atmospheric CO₂. They reported a decrease of 88% in the concentration of WS PO₄³⁻ after 120 h. Sakthivel et al. [55] reported a decrease of WS PO₄³⁻ in less time (i.e. 87% removal after 0.5 h, 97% removal after 1.5 h, and 99.5% removal after 4 h of adding the ash). In the present study, reductions of the concentration of the WS PO₄³⁻ of 66% and 95% were achieved at the time of preparing the blend 1 and the blend 2, respectively (Fig. 6b).
In the study of Yagi and Fukushi [20], the most effective way of removing the $\text{PO}_4^{3-}$ from the WS phase was via precipitation rather than adsorption onto Ca. In order to promote precipitation of calcium phosphates in their system, it was required a concentration of $\text{WS PO}_4^{3-}$ higher than 10.45 mg/L and a soluble sorption agent, such as CaCO$_3$·H$_2$O. Other process parameter that could reduce the availability of the WS $\text{PO}_4^{3-}$ is the operating temperature. Yagi and Fukushi [20] found the greatest removal of the WS $\text{PO}_4^{3-}$ at the highest temperature that they tested (15, 25, and 35 °C). On the other hand, Mor et al. [21] found that the removal of WS $\text{PO}_4^{3-}$ was better at 30 °C than at any of the other temperature that they tested (25, 35, and 40 °C). Moreover, it is necessary to take into account that the increase of the temperature of the blends could lead to higher NH$_3$$_{aq}$ volatilization [38].

The phosphorus was not expected to be lost via gas exchange under the conditions of incubation of this work (i.e. 10 h at 100 rpm and 22 °C) and the total initial amount would thereby be expected to remain split into the WS phase and the WI phase of each blend. The phosphorus in the ashes was in the form of $\text{PO}_4^{3-}$ and the WI phase of each blend. The phosphorus in the ashes would thereby be expected to remain split into the WS phase (i.e. 10 h at 100 rpm and 22 °C) and the total initial amount exchange under the conditions of incubation of this work of the particulate P and WS $\text{Porg}$ were anticipated to be hydro-

tic way of removing the $\text{PO}_4^{3-}$ of the digestates were determined by the amount of ashes in the blends. Herein, it was possible to identify the best samples for the preparation of a slow-release fertilizer. Digestates with high content of NH$_4^+$-N or other easily converted forms, such as FWD, were anticipated to have greater losses via NH$_3$$_{aq}$ volatilization. In this way, the PVWD was the most suitable digestate for the production of a controlled-release fertilizer. In terms of ashes, the WFA could be preferred due to its better properties as sorbent (i.e. smaller particle size and greater concentration of calcium and magnesium). On the other hand, the WBA was the main fraction produced in grate combustion chamber, hence using this fraction would have a greater positive impact on the circular economy. Furthermore, the higher pH of WBA could be used to enhance the NH$_3$$_{aq}$ stripping from the digestates which would be recovered with a H$_2$SO$_4$ trap. Although the pH of WFA is lower, still required the use of acid to prevent the loss of nitrogen and the carbon solubilisation. Finally, since ashes are an important source of nutrients (i.e. the WFA was richer in phosphorus while WBA was richer in potassium), the blending ratio should not be entirely based on reducing the availability of the components of organic wastes to improve the dewatering and to produce slow-release fertilizers nor on the self-hardening to improve the granulation process.

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Conclusions

The changes in the availabilities of nitrogen, carbon, and phosphorus in food waste and agro-industrial waste digestates due to the addition of wood ashes, were monitored for ten hours of incubation. It was proposed that the NO$_3^-$-N was lost as N$_2$O$_{gas}$ due to the reducing effect of the alkali and alkaline earth metals contained in the ashes. The high pH of the blends (>$10$), promoted the volatilization of NH$_4^+$-N and the solubilization of carbon. The extents of these phenomena were related to the composition of the digestates and the ashes. The greatest loss of nitrogen took place at the time of blending and during the first three hours after the preparation of the mixtures. On the other hand, the loss of carbon via CO$_2$ release was regarded as negligible at the high pH of the blends. In terms of phosphorus availability, the sorption kinetic and equilibrium of the WS $\text{PO}_4^{3-}$ of the digestates were determined by the amount of ashes in the blends. Herein, it was possible to identify the best samples for the preparation of a slow-release fertilizer. Digestates with high content of NH$_4^+$-N or other easily converted forms, such as FWD, were anticipated to have greater losses via NH$_3$$_{aq}$ volatilization. In this way, the PVWD was the most suitable digestate for the production of a controlled-release fertilizer. In terms of ashes, the WFA could be preferred due to its better properties as sorbent (i.e. smaller particle size and greater concentration of calcium and magnesium). On the other hand, the WBA was the main fraction produced in grate combustion chamber, hence using this fraction would have a greater positive impact on the circular economy. Furthermore, the higher pH of WBA could be used to enhance the NH$_3$$_{aq}$ stripping from the digestates which would be recovered with a H$_2$SO$_4$ trap. Although the pH of WFA is lower, still required the use of acid to prevent the loss of nitrogen and the carbon solubilisation. Finally, since ashes are an important source of nutrients (i.e. the WFA was richer in phosphorus while WBA was richer in potassium), the blending ratio should not be entirely based on reducing the availability of the components of organic wastes to improve the dewatering and to produce slow-release fertilizers nor on the self-hardening to improve the granulation process.

References

1. UK government. Clean air strategy 2019. Department for Environment, Food & Rural Affairs. 2019. https://www.gov.uk/government/publications/clean-air-strategy-2019. Accessed 15 July 2020
2. Northern Ireland Department of Agriculture Environment and Rural Affairs: nitrate Directive partial derogation. https://www.daera-ni.gov.uk/articles/nitrates-directive (2019). Accessed 8 February 2019
3. Rop, K., Karuku, G.N., Mbu, D., Michira, I., Njomo, N.: Formulation of slow release NPK fertilizer (cellulose-graft-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer)
composite and evaluating its N mineralization potential. Ann. Agric. Sci. 63(2), 163–172 (2018)
4. WRAP: Quality Protocol Poultry Litter Ash. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/296435/geho0812wbpk-e-ep.pdf (2012). Accessed 18 November 2016
5. Demeyer, A., Vouidi Nkana, J.C., Verloo, M.G.: Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. Bioresour. Technol. 77(3), 287–295 (2001)
6. Tambone, F., Orzi, V., Zilio, M., Adani, F.: Measuring the organic amendment properties of the liquid fraction of digestate. Waste Manag. 88, 21–27 (2019)
7. Walker, M., Banks, C., Heaven, S., Frederickson, J.: Residual biogas potential test for digestates. https://www.wrap.org.uk/sites/wrap/Residual Biogas Potential.pdf (2010). Accessed 20 November 2016
8. WRAP: PAS 100:2011 Specification for composted materials. https://www.wrap.org.uk/system/files/private/PAS-100-2011.pdf (2011). Accessed 3 December 2016
9. Steenari, B.M., Lindqvist, O.: Stabilisation of biofuel ashes for recycling to forest soil. Biomass. Bioenerg. 13(1–2), 39–50 (1997)
10. Romero-Guiza, M.S., Vila, J., Mata-Alvarez, J., Chimenos, J.M., Astals, S.: The role of additives on anaerobic digestion: a review. Renew. Sustain. Energy Rev. 58, 1486–1499 (2016)
11. Guerrero, L., Da Silva, C., Barahona, A., Montalvo, S., Huilinü, C., Borja, R., Peirano, E., Toledo, M., Carvajal, A.: Fly ash as stimulant for anaerobic digestion: effect over hydrolytic stage and methane generation rate. Water Sci. Technol. 80(7), 1384–1391 (2019)
12. Huilinü, C., Pinto-Villegas, P., Castillo, A., Montalvo, S., Guerrero, L.: Biochemical methane potential from sewage sludge: effect of an aerobic pretreatment and fly ash addition as source of trace elements. Waste Manag. 64, 140–148 (2017)
13. Lo, H.M., Liu, M.H., Pai, T.Y., Liu, W.F., Lin, C.Y., Wang, S.C., Banks, C.J., Hung, C.H., Chiang, C.F., Lin, K.C., Chen, P.H., Chen, J.K., Chiu, H.Y., Su, M.H., Kurniawan, T.A., Wu, K.C., Hsieh, C.Y., Hsu, H.S.: Biostabilization assessment of MSW co-disposed with MSWI fly ash in anaerobic bioreactors. J Hazard Mater. 162(2–3), 1233–1242 (2009)
14. Bougnom, B.P., Niederkofler, C., Knapp, B.A., Stimpfl, E., Insam, H.: Residues from renewable energy production: their value for fertilizing pastures. Biomass Bioenerg. 39, 290–295 (2012)
15. Fernández-Delgado Juárez, M., Waldbhuber, S., Knapp, A., Partl, C., Gómez-Brandón, M., Insam, H.: Wood ash effects on chemical and microbiological properties of digestate- and manure-amended soils. Biol. Fertil. Soils. 49(5), 575–585 (2013)
16. UK government: Sewage sludge in agriculture: code of practice for England, Wales and Northern Ireland. https://www.gov.uk/government/publications/sewage-sludge-in-agriculture-code-of-practice/sewage-sludge-in-agriculture-code-of-practice-for-england-wales-and-northern-ireland (2018). Accessed 13 February 2017
17. Metcalf & Eddy: AECOM: Advanced alkaline stabilisation technologies. In: Tchobanoglous, G., Stensel, H.D., Tsichlassihi, R., Burton, F. (eds.) Wastewater Engineering: Treatment and Resource Recovery, 5th edn, pp. 1501–1502. McGraw Hill, New York (2002)
18. Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Memon, A.R., Jaltani, N., Shah, A.: Use of sewage sludge after liming as fertiliser for maize growth. Pedosphere 18(2), 203–213 (2008)
19. Fivelman, Q.: Granular fertiliser from anaerobic digestate liquor. https://www.wrap.org.uk/sites/files/wrap/ADFerTech - DIAD 2 feasibility study.pdf. Accessed 26 January 2018
20. Yagi, S., Fukushima, K.: Removal of phosphate from solution by adsorption and precipitation of calcium phosphate onto monohydrocalcite. J. Colloid Interface Sci. 384(1), 128–136 (2012)
21. Mor, S., Chhodan, K., Ravindra, K.: Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. J. Clean Prod. 129, 673–680 (2016)
22. Ma, Z., Li, Q., Yue, Q., Gao, B., Li, W., Xu, X., Zhong, Q.: Adsorption removal of ammonium and phosphate from water by fertilizer controlled release agent prepared from wheat straw. Chem. Eng. J. 171(3), 1209–1217 (2011)
23. Insam, H., Franke-Whittle, I.H., Knapp, B.A., Plank, R.: Use of wood ash and anaerobic sludge for grassland fertilization: effects on plants and microbes. Die Bodenkultur. 60(2), 39–51 (2009)
24. Randall, D.G., Krähenbühl, M., Köpping, I., Larsen, T.A., Uerd, K.M.: A novel approach for stabilizing fresh urine by calcium hydroxide addition. Water Res. 95, 361–369 (2016)
25. Kim, J.S., Lee, Y.Y., Kim, T.H.: A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. Bioresour. Technol. 199, 42–48 (2018)
26. Tavakkoli, E., Rengasamy, P., Smith, E., Meldonald, G.K.: The effect of cation-anion interactions on soil pH and solubility of organic carbon. Eur. J. Soil Sci. 66(6), 1054–1062 (2015)
27. Mudryk, K., Fąrczek, J., Wróbel, M., Jewiarz, M., Dziedzic, K.: Agglomeration of ash-based fertilizer mixtures from biomass combustion and digestate. In: Mudryk, K., Werle, S. (eds.) Renewable Energy Sources: Engineering, Technology, Innovation, pp. 823–834. Springer (2018)
28. Pesonen, J., Kuokkanen, V., Kuokkanen, T., Ilikainen, M.: Co-granulation of bio-ash with sewage sludge and lime for fertilizer use. J. Environ. Chem. Eng. 5(4), 4817–4821 (2016)
29. Mozianen, M., Saarsalmi, A., Kukkola, M., Issakainen, J.: Effects of stabilized wood ash on nutrient status and growth of Scots pine—comparison between uplands and peatlands. For. Ecol. Manage. 295, 136–144 (2013)
30. Jewiarz, M., Wróbel, M., Fąrczek, J., Mudryk, K., Dziedzic, K.: Digestate, ash and Trichoderma based fertilizer-production line concept design. MATEC Web Conf. 168, 1–6 (2018)
31. Zheng, Y., Ke, L., Xia, D., Zheng, Y., Wang, Y., Li, H., Qingbiao, L.: Enhancement of digestates dewaterability by CTAB combined with CFA pretreatment. Sep. Purif. Technol. 163, 282–289 (2016)
32. WRAP: PAS 110:2014 Specification for whole digestate, separated liquid and separated fibre derived from the anaerobic digestion of source-segregated biodegradable materials. https://www.wrap.org.uk/content/bi-si-pas-110-specification-2014 (2014). Accessed 20 November 2016
33. Schwab, P.: Soil solution. In: Huang, P.M., Li, Y., Sumner, M.E. (eds.) Handbook of soil sciences: properties and processes, 2nd edn, pp. 353–376. CRC Press, Boca Raton Florida (2012)
34. Alburquerque, J.A., de la Fuente, C., Bernal, M.P.: Chemical properties of anaerobic digestates affecting C and N dynamics in amended soils. Agric. Ecosyst. Environ. 160, 15–22 (2012)
35. Urgun-Demirtas, M., Sattayatwaa, C., Papilla, K.R.: Bioavailability of dissolved organic nitrogen in treated effluents. Water Environ. Res. 80(5), 397–406 (2008)
36. Ndegwa, P.M., Vaddella, V.K., Hristov, A.N., Joo, H.S.: Measuring concentrations of ammonia in ambient air or exhaust air stream using acid traps. J. Environ. Qual. 38(2), 647–653 (2009)
37. Whelan, M.J., Everitt, T., Villa, R.: A mass transfer model of ammonia volatilisation from anaerobic digestate. Waste Manag. 30(10), 1808–1812 (2010)
38. Ukwuani, A.T., Tao, W.: Developing a vacuum thermal stripping – acid absorption process for ammonia recovery from anaerobic digestor effluent. Water Res. 106, 108–115 (2016)
39. Shcherbakov, V.V., Artemkina, Y.M., Ponomareva, T.N., Kirillov, A.D.: Electrical conductivity of the ammonia-water system. Russ. J. Inorg. Chem. 54(2), 277–279 (2009)
40. Chindaprasirt, P., Jaturapitakkul, C., Chalee, W., Rattanasak, U.: Comparative study on the characteristics of fly ash and bottom ash geopolymers. Waste Manag. 29(2), 539–543 (2009)
41. Sakai, E., Miyahara, S., Ohsawa, S., Lee, S.H., Daimon, M.: Hydration of fly ash cement. Cem. Concr. Res. 35(6), 1135–1140 (2005)

42. Wei, X., Li, Z.: Study on hydration of Portland cement with fly ash using electrical measurement. Mater. Struct. Constr. 38(277), 411–417 (2005)

43. Maresca, A., Krüger, O., Herzel, H., Adam, C., Kalbe, U., Astrup, T.F.: Influence of wood ash pre-treatment on leaching behaviour, liming and fertilising potential. Waste Manag. 83, 113–122 (2019)

44. Karoline, K.: Chemistry of wood ash leachates and the filter effect of soil columns on leachate composition. University of Natural Resources and Life Sciences Vienna. https://eupub.boku.ac.at/urn:nbn:at:at-ubbw:1-4762 (2012). Accessed 5 March 2019

45. Agmon, N.: The grotthuss mechanism. Chem. Phys. Lett. 244(5–6), 456–462 (1995)

46. Fanguiero, D., Hjorth, M., Gioelli, F.: Acidification of animal slurry—a review. J. Environ. Manage. 149, 46–56 (2015)

47. López Torres, M., Espinosa Lloréns, M. del C.: Effect of alkaline pretreatment on anaerobic digestion of solid wastes. Waste Manag. 28(11), 2229–2234 (2008)

48. Conklin, A.R., Vitha, M.F.: Electrical measurements. In: Introduction to Soil Chemistry: Analysis and Instrumentation, p. 188. John Wiley & Sons, New Jersey (2014)

49. Tunesi, S., Poggi, V., Gessa, C.: Phosphate adsorption and precipitation in calcareous soils: the role of calcium ions in solution and carbonate minerals. Nutr. Cycl. Agroecosyst. 53(3), 219–227 (1999)

50. Jones, C.A., Koenig, R.T., Ellsworth, J.W., Brown, B.D., Jackson, G.D.: Extension Soil Fertility Specialist Management of Urea Fertilizer to Minimize Volatilization. Montana State University. https://www.extension.uidaho.edu/Nutrient/pdf/smallgrain/New/Management of Urea fertilizer to minimize volatilization.pdf (2007). Accessed 18 September 2018

51. Márquez, A., Pfab, M., Einfalt, D., Hasyyati, F.I.: Calcium soap from palm fatty acid distillate for nutrient recovery by biogas digestate processing. IEA Bioenergy. https://www.iea-biogas.net/files/daten-redaktion/download/Technical%2520Brochures/NUTRIENT_RECOVERY_RZ_web2.pdf. Accessed 2 October 2016

52. Maresca, A., Hyks, J., Astrup, T.F.: Recirculation of biomass ash onto forest soils: ash composition, mineralogy and leachability of wood ash and plant materials on soil microbial community and emission of CO₂ and N₂O. Appl. Soil Ecol. 63, 36–44 (2013)

53. Perakis, S.S., Hedin, L.O.: Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature 415(6870), 416–419 (2002)

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