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

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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

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 transportation (due to the moisture content higher than 90%), the season of application, the nitrogen quota [2]. Whole digestates (i.e. which have not undergone any solid–liquid separation) 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 having 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 is 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 (ADFerTech). The main powder adsorbent that they added 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 represent 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 $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ 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 focussing 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 ($< 4^{\circ}\text{C}$) 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 $\text{g Ca(OH)}_2/\text{g solid}$

Table 2 Mass percentage (wt.%) of each fresh sample for the preparation of approximately 3 g of each blend

Sample	Blend 1	Blend 2
FWD/(wt.%)	68.3	0
PVWD/(wt.%)	13.9	69.3
WFA/(wt.%)	17.8	15.0
WBA/(wt.%)	0	15.7
Ashes:digestates/(g/g)	1:4.6	1:2.3

of 1:10 [25]. It should be noted the significant amount ($\sim 10\%$) 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)

Table 1 Description of the samples used in this study

Sample	Plant and feedstock composition
FWD	17,600 t/year source segregated food waste (mainly household)
PVWD	Maize Silage(10,000 t/year), vegetables waste(5000 t/year), sweet-corn waste (15,000 tons per year), aerobically treated food waste (10,000 t/year), and other biodegradable sludge (2000 t/year)
WFA and WBA	Virgin wood bark and chipped timber (generally 85% sitka spruce and 15% larch, but the blending ratio depended on the availability of these materials) to produce 256 t/year of WFA and 295 t/year of WBA

Fig. 1 Stepwise methodology for the characterization of the WS extract of the blends after the 10-hour incubation at 100 rpm and 22 °C

could be better understood [33]. The parameters measured were the pH, EC, concentrations of ammonium and ammonia (WS NH_4^+ and WS NH_3), nitrate and nitrite (WS NO_3^- and WS NO_2^-), orthophosphate (WS 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 NH_4^+ and WS NH_3 (methods DIN 38,406 and ISO/DIN 11,732), WS NO_3^- and WS NO_2^- (methods DIN 38,405 and ISO/DIS 13,395), and WS 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 NORTEST 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_{blend}), ammonia nitrogen gas lost ($\text{NH}_3\text{-N}$), and nitrous oxide nitrogen gas lost ($\text{N}_2\text{O-N}$). Furthermore, the TN_{blend} was divided into water-insoluble (WI) TN and WS TN. It is important to highlight that although the WI TN_{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 N_{org}), ammoniacal nitrogen (WS $\text{NH}_4^+\text{-N}$), and nitric nitrogen (WS $\text{NO}_3^-\text{-N}$). The WS N_{org} was calculated as the difference between the WS TN and the sum of WS $\text{NH}_4^+\text{-N}$ and WS $\text{NO}_3^-\text{-N}$ [35]. It should be noted that the WS $\text{NH}_4^+\text{-N}$ represented the nitrogen contained in both aqueous species WS NH_4^+ and WS NH_3 (i.e. $\text{NH}_4^+_{\text{aq}}$ and NH_3_{aq}), while $\text{NH}_3\text{-N}$ stood for the ammoniacal nitrogen gas form (NH_3_{gas}) that has been lost by volatilization. A widely used procedure is the calculation of the NH_3_{aq} volatilization based on the decrease of the concentration of $\text{NH}_4^+\text{-N}$ 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_2O 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.

Whether the experimental results were referred to the S:E ratio 1:10 WS extract (i.e. no units for pH and dS/m for EC) or were expressed in terms of the fresh base (i.e. mg of WS NH_4^+ and WS NH_3 , WS NO_3^- and WS NO_2^- , WS PO_4^{3-} , WS TN , and WS TC , per kg fresh blend), the average value of all the measurements in each condition and the standard deviation were calculated. The procedure for the calculation of the concentration of WS species in the fresh samples is on the Online resource 3. It was assumed that the data obtained for each blend during the 10-hour incubation followed a normal distribution. The single factor analysis of variance ($\alpha=0.05$) was performed with MS excel to decide whether the measured parameters remained constant during the incubation period.

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 ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) [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

Table 3 Characterization of the four samples and the two type of blends evaluated in terms of the relevant parameters for this study. The average and standard deviation ($n=3$) for all the measurements are expressed in fresh weight

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	22069.7 ± 1145.8	26390.5 ± 658.1	31818.7 ± 296.5
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 ± 850.0	3800.0 ± 380.0	1061.2 ± 152.6	831.6 ± 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 CO_2 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 (SO_4^{2-}), chloride (Cl^-), and PO_4^{3-} were the main anions provided by the wood ash. While the low WS PO_4^{3-} in the ashes of the present study (Table 3) was associated with the low solubility of calcium (Ca^{2+}) and magnesium (Mg^{2+}), the SO_4^{2-} 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 $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ [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 $\text{NH}_4^+\text{-N}$ (Table 3) with buffer effect, which prevented a drastic increase of the pH. These two characteristics (i.e. content of ashes and $\text{NH}_4^+\text{-N}$ 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

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 NH_4^+ , 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. Garfi et al. [49] reported a value of EC as low as $6.88 \cdot 10^{-3}$ 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 H_3O^+ 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 NH_4^+ and WS NH_3 profiles

The amount of WS NH_4^+ and WS NH_3 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 $F > F_{crit} = 2.36$. Thereby, it was possible to claim with a 95% of certainty ($\alpha = 0.05$) that, during the 10 h of incubation at 22 °C, the concentration of WS NH_4^+ and WS NH_3 in both blends was not constant.

The fluctuations of the concentration of WS NH_4^+ and WS NH_3 in both blends (Fig. 3a) could be related to the mineralization of the N_{org} 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 NH_4^+ would be released and then neutralized into NH_3_{aq} owing to the high pH of the medium as per the reaction pathway (1). The formation of NH_3_{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 NH_4^+ and WS NH_3 , together with the lower share of ashes compared to the blend 2 (Table 2). Furthermore, the FWD had a greater pool of NH_4^+ than the PVWD, in agreement with the higher peak of the concentration of WS NH_4^+ and WS NH_3 at the 30 min of incubation (Fig. 3a), confirming a the greater protein content of the materials used as feedstock for AD. The WS NH_4^+

Fig. 3 Concentration of WS NH_4^+ & WS NH_3 (a) and WS NO_3^- and WS NO_2^- (b) in 3 g of each of the blends (Table 2) measured after the incubation at 100 rpm and 22 °C

and WS NH_3 could build up because the rate of hydrolysis of the N_{org} was faster than the volatilization of NH_3_{gas} . At a pH value of 11, all WS $\text{NH}_4^+\text{-N}$ in the blends would be in the form of NH_3_{aq} [46]. Thereby, it was considered that what limited the flux of NH_3_{aq} from the blends to the air was the mass transfer step (1).

The theoretical content of WS NH_4^+ and WS NH_3 in the blends (Table 3) was higher than the content of WS NH_4^+ and WS NH_3 measured at time zero (Fig. 3a). Both blends have lost around 50% of the theoretical content of WS NH_4^+ and WS NH_3 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 ($<4^\circ\text{C}$). The optimum pH for the formation of indophenol during the determination of the NH_3_{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 of the blue colour, thus the initial pH of the samples affected the determination. Moreover, it is worth to mention that low molecular weight amines could react similarly to NH_3_{aq} , resulting in an overestimation of the concentration of WS NH_4^+ and WS NH_3 [52].

Méndez et al. [53] reported a 4.99% loss of $\text{NH}_4^+\text{-N}$ 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 a 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 $\text{NH}_4^+\text{-N}$ 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 NH_4^+ and WS NH_3 in their wastewater sludge was 1000 times lower (i.e. 0.120 mg $\text{NH}_4^+\text{-N/kg}$ sludge) than the ones of the blends in this work (Table 3). Whelan et al. [37] reported a loss of 1925 mg WS NH_4^+ and WS NH_3 in 120 g of digestate (mixture of ruminant slurry and food waste) during three weeks of incubation at 25°C . The initial WS NH_4^+ and WS NH_3 content was 7425 mg/kg digestate and the enhancement in the release of NH_3 was given by a 10 mL 1 M H_2SO_4 trap placed in the 1 L headspace of the kilner jar for trapping the NH_3 gas. The amount of NH_3_{aq} volatilized in their system with the H_2SO_4 trap for more than 3 weeks, was similar to the loss of NH_3_{aq} in the blend 1 at time zero (2348 mg $\text{NH}_3_{\text{aq/kg}}$ blend; Fig. 5a). On the other hand, in this work their model has been used to predict that ~6% of the initial WS NH_4^+ and WS NH_3 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 NH_3_{aq} volatilization given by the addition of the ashes to the digestates. The NH_3_{aq} volatilization was also estimated using the values of the vapour pressure tables available for the aqua ammonia (NH_4OH) solutions [54]. For the calculation, it was considered that the concentration of NH_3_{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 NH_3_{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 NH_4^+ and WS NH_3 in the blend 1 and blend 2, respectively.

Other possible routes for the decrease of concentration of WS NH_4^+ and WS NH_3 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 NH_4^+ and NH_3 and PO_4^{3-} 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 NH_4^+ and NH_3/L solution was between 3 and 9, and higher pH could lead to losses via NH_3_{aq} volatilization. With regard to the precipitation, the formation of struvite could explain a share of the decrease in the concentration of WS NH_4^+ and WS NH_3 . Changes in the concentration of $\text{NH}_4^+\text{-N}$ 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 NH_4^+ and NH_3 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 NH_4^+ and NH_3 per litre. Although the precipitation of the 97% of the 267 mg $\text{PO}_4^{3-}/\text{L}$ 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 PO_4^{3-} in the precipitate corresponded to struvite. This information was necessary for the calculation of the amount of precipitated NH_4^+ , since in their study the PO_4^{3-} also precipitated with the calcium, as hydroxyapatite, and with the potassium, as K-struvite ($\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$).

WS NO_3^- and WS NO_2^- Profiles

In both blends, the same levels of WS NO_3^- and WS NO_2^- were constant during the incubation (Fig. 3b). The low value of 6–7 mg WS NO_3^- and WS NO_2^- 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 NO_3^- and WS NO_2^- in both blends during the incubation could be the detection limit of the analytical procedure. It should be noted that the concentration of WS NO_3^- and WS NO_2^- 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 denitrification [60] should not be possible in the blends due to the high pH and short incubation (Fig. 2a). However, the $\text{N}_2\text{O}_{\text{gas}}$ 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

Fig. 4 Concentration of WS TN (a) and WS TC (b) in 3 g of each the blends (Table 2) measured after the incubation at 100 rpm and 22 °C

Fig. 5 Calculated profiles of nitrogen species in 3 g of blend 1 (a) and 3 g of blend 2 (b) during the incubation at 100 rpm and 22 °C (Table 2)

in both blends. In an open system (e.g. after applying the blended fertilizer to land), the leaching of WS N_{org} could be the main way of losing N [63]. Because of the high concentration of WS NH_4^+ and NH_3 in the blend 1, resulting from the conversion of the N_{org} , it took longer to reach a stable level (Fig. 3a).

The carbon losses via gas exchange (e.g. CO_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_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], leading to a greater increase of the WS TC. Under the conditions of chemical alkaline stabilization attained in the blend 1, the Ca^{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_3 -N losses in the blend 2. The N_2O_{gas} emissions were higher in the blend 2 than in the blend 1, but any of these losses were negligible compared to the NH_3_{aq} volatilization. In this way, NH_3_{gas} was the main form in which the N was lost, with the highest volatilization rate of NH_3_{aq} at the time of blending the samples (Fig. 6a). However, the determination of the rate of volatilization of NH_3_{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_3 -N/kg blend/hour), which continued to decrease after the 10 h of incubation until reaching a minimum NH_3_{aq} concentration. Ukwuani and Tao [38] found similar volatilization rates, ranging from 151 to 1284 mg NH_3 -N/kg digestate/hour, in 15 L municipal sludge digestate and 10 L retentate 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_3_{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_3 -N/kg digestate/hour during the first two

Fig. 6 Calculated rate of NH_3 -N loss in each blend (a). Concentration of WS PO_4^{3-} (b) in 3 g of each of the blends (Table 2) measured after the incubation at 100 rpm and 22 °C

weeks of incubation. Besides, it was possible to calculate a rate of volatilization of 0.0023 mg $\text{NH}_3\text{-N/kg}$ sludge/hour with the results of Méndez et al. [53].

WS PO_4^{3-} Profile

The result of the single factor analysis of variance for blend 1, was that $F = 6.39 > F_{\text{crit}} = 2.35$. Thereby, it was possible to claim with a 95% of certainty ($\alpha = 0.05$) that, during the 10 h of incubation at 22 °C, the concentration of WS PO_4^{3-} of blend 1 increased (Fig. 6b). The reason for the lower concentration of WS PO_4^{3-} 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 continuous 100 rpm shaking prevented the formation of new crystals. Millero et al. [67] found that the optimum pH for the adsorption of WS PO_4^{3-} onto aragonite (CaCO_3) was 8.6 at 25 °C. Considering the high content of calcium of both types of ash (Online resource 1), similar pH would be desired in both blends to promote the adsorption. Unlike the increase of the content of WS NH_4^+ and WS NH_3 (Fig. 3a), the raise of WS PO_4^{3-} in blend 1 (Fig. 6b) was due to desorption rather than chemical hydrolysis. The kinetic control of the desorption was only seen in the solubilization of PO_4^{3-} in blend 1 (Fig. 6b), which had a pH slightly higher than 10 but lower than the blend 2 (Fig. 2). Therefore, the greater decrease in the WS PO_4^{3-} found in the blend 2 (Fig. 6b) in spite of its higher pH and its higher ionic strength of the solution (i.e. greater salinity due to higher content of ashes), which are factors that affect negatively the adsorption process, occurred because of the twice more content of ashes compared to blend 1 (Table 2). This conclusion is in agreement with the results of Pesonen et al. [28], who obtained the greatest WS TP when the lowest amount of ash (40%) was used to prepare the blend with dewatered sewage sludge (30%) and $\text{Ca}(\text{OH})_2$ (30%). In the present study, the amounts of WS PO_4^{3-} sorbed were 20 and 10 mmol/g Ca in blend 1 and blend 2, respectively.

Mor et al. [21] had the greatest adsorption of WS PO_4^{3-} at pH 2. On the other hand, Ma et al. [22] found that the pH required for the adsorption in a 25 mg $\text{PO}_4^{3-}/\text{L}$ 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 PO_4^{3-} 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 PO_4^{3-} in their urine solution compared to the digestates of 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 ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), without taking into account the excess of WS $\text{NH}_4^+\text{-N}$ in the urine. The 53% of the Mg in their wood ash was soluble. According to Drosig 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 PO_4^{3-} 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 NH_4^+ 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 PO_4^{3-} 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 (CaCO_3) 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 ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$) to 50 mL solutions ranging from 0.95 to 19.95 mg $\text{PO}_4^{3-}/\text{L}$ under continuous stirring for 6 to 216 h. The lower chemical stability of the $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ make this material more reactive and more suitable for decreasing the availability of the WS PO_4^{3-} . 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 CO_2 . They reported a decrease of 88% in the concentration of WS PO_4^{3-} after 120 h. Sakthivel et al. [55] reported a decrease of WS PO_4^{3-} 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 PO_4^{3-} 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 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 WS PO_4^{3-} higher than 10.45 mg/L and a soluble sorption agent, such as $\text{CaCO}_3 \cdot \text{H}_2\text{O}$. Other process parameter that could reduce the availability of the WS PO_4^{3-} is the operating temperature. Yagi and Fukushi [20] found the greatest removal of the WS 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 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 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 PO_4^{3-} [70], whether it was part of the WS TP or the WI TP. On the other hand, the phosphorus of the digestates was a mixture PO_4^{3-} , polyphosphates and phosphorus associated to organic molecules (P_{org}). Unlike the WS N_{org} , the WS P_{org} is minimal (i.e. less than 25% of the WS TP) in organic amendments [71]. In this way, the determination of the dissolved reactive phosphorus, which is the WS PO_4^{3-} that responds to the molybdate colorimetric test without previous hydrolysis [72], could give a good idea of the WS TP in the blends. It should be noted that some of the particulate P and WS P_{org} were anticipated to be hydrolysed easily [73], even with the reagents of the improved colorimetric method of Murphy and Riley [72] which was used in the present study.

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 $\text{N}_2\text{O}_{\text{gas}}$ 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 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 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 stripping from the digestates which would be recovered with a H_2SO_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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