

Impact of sulphuric, hydrochloric, nitric, and lactic acids in the preparation of a blend of agro-industrial digestate and wood ash to produce a novel fertiliser

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PVWD, Post-harvest vegetable (agro-industrial) waste digestate; WBA, Woody biomass derived bottom ash; S:E, Solid-to-extractant ratio; WS, Water-soluble; WI, Water-insoluble; wt. %, weight percentage; α , Statistical significance level; TP, Total phosphorus; PO_4^{3-} , Orthophosphate; $\text{PO}_4^{3-}\text{-P}$, Phosphorus in the form of orthophosphate; P_{org} , Organic phosphorus; TC, Total carbon; CO_3^{2-} , Carbonate; $\text{CO}_3^{2-}\text{-C}$, Carbon in the form of carbonate; C_{inert} , Inert carbon; C_{org} , Organic carbon; TN, Total nitrogen; N_{org} , Organic nitrogen; NH_4^+ & NH_3 , Ammonium and ammonia; $\text{NH}_4^+\text{-N}$, Ammoniacal nitrogen; NO_3^- & NO_2^- , Nitrate and nitrite; $\text{NO}_3^-\text{-N}$, Nitric nitrogen.

Abstract

Anaerobic digestate is a waste product of biogas generation which is produced in large amounts and, because of its high water content, it is expensive to store, transport, and spread to land. Additionally, special conditions are required for land application to minimise the losses of nutrients. This material is primarily used as source of organic matter for soil while farmers continue to rely on NPK chemical fertilisers, which are produced using energy intensive processes. This work evaluated the use of low-pollutant biomass bottom ash as an adsorbent to decrease the availability and the losses of carbon and nutrients. A number of acidification conditions were tested to enhance the adsorption and to improve the dewaterability of the organic waste. The final blend was intended to have a more balanced nutrient profile and to offer better performance in terms of crop growth than the digestate alone. The severe acidifications of the digestate and ash using sulphuric, hydrochloric, nitric, and lactic acids increased more than twice the amount of ammonia which remained in the digestate-ash blend. Hydrochloric acid was found to be the best option for preparation of the ash as sorbent, before mixing with the digestate, and to promote dehydration of the blend to enhance solid-liquid separation. This acid did not reduce the number of active sites in the ash, to promote the chemical stabilisation of the digestate; the addition of the acidified ash reduced the pH below that of the digestate thereby reducing the volatilisation of NH_3 from the blend.

1. Introduction

Moving from a linear to a circular economy requires better resource management and a reduction of waste, placing less of a burden on the environment. Within the resource recover from waste paradigm, the valorisation of organic waste via anaerobic digestion (AD) is widely accepted as a reliable source of renewable energy which can be implemented in the geographic points (i.e. decentralised treatment) at which the organic wastes are produced [1]. Moreover, the resulting digestate potentially has a significant role to play in recycling key plant nutrients (e.g. nitrogen and phosphorus) back to land [2,3]. The use of this organic amendment with low pathogen content offers opportunities to restore the soil as a natural carbon sink as well as promoting soil health and fertility for greater crop yield [4]. However, the high moisture content of digestate poses problems of high capital investment and operational costs (i.e. storage and haulage) [5] due to the large volume of this material. Due to the high availability of carbon and nutrients in the digestate, losses via leaching and volatilisation are expected to occur prior to, during, and after spreading this material to land.

To offset some of these challenges, dewatering of digestate has become a critical step in the processing of this soil amendment, similarly to organic wastes (e.g. animal manure and slurry, and sewage sludge), and the performances of several technologies have been evaluated [5]. In operations such as flotation, centrifugation, and filtration the enhancement of the solid-liquid separation relies on the use of flocculating and precipitating agents. However, the nature of these additives might limit the application of the solid and liquid streams produced from chemo-mechanical separation [6,7] and further downstream treatment technologies may be required. Hence, most farm businesses can only afford the use of low-efficiency separation equipment (e.g. screw press) before applying their organic residues to land [5]. In the case of the agro-industrial digestate, the fibres can be employed as bedding material for animals while the liquor requires expensive low emission spreading techniques (e.g. soil injection) [8].

Additives, such as aluminium sulphate, ferric chloride, acetic acid, and sulphuric acid, can be used to minimise the release of atmospheric contaminants during storage [9] and application [10] of animal manure and slurry to soil. This technology aim to ease the handling of agro-industrial residues and might to improve their performance in terms of crop growth, but farmers continue to rely on NPK chemical fertilisers [11]. For this reason biomass ashes have been used to supplement the nutrients of digestate [2,3]. This is not the only potential benefit provided by ashes but rather contributing to dewatering by decreasing the compressibility of the cake formed during the filtration, as highlighted by Zheng et al. [12]. They found that the

effectiveness of the filtration was higher when a surfactant was included in the blend of agro-industrial digestate and coal fly ash, as this resulted in release of the water which was bounded to the fibre of digestate.

The granulation of sewage sludge [13] and digestate [14] together with biomass ash has also been investigated as a way of obtaining an user-friendly product with superior aesthetic properties. To the best of our knowledge, the steps involved in the processing of digestates with ash – to favour a balanced nutrient content, to enhance dewatering, and to enable the granulation – have been studied individually but have not been connected in order to reduce the consumption of energy and resources. We aim to develop a manufacturing process with a number of synergies to achieve the three levels of stabilisation: (a) chemical stabilisation based on the adsorption of carbon and nutrients to reduce their availability and allow economically viable solid-liquid separation; (b) physical stabilisation relying on the self-hardening of the blend after the dewatering and prior to the granulation; and (c) biological stability based on the moderate fermentation in the soil avoiding carbon and nutrient losses due to excessive mineralisation (e.g. N_2O emissions and NO_3^- leaching).

The present work contains two studies about the chemical stabilisation of an agro-industrial digestate by means of blending it with wood ash under different acidification conditions (i.e. different moles of H^+ and anions supplied). The intended role of the wood ash was not only to increase the nutrient content (e.g. phosphorus) of the digestate but to decrease the availability of all elements in order to enhance the properties of the blends of these organic wastes as slow-release fertiliser. The role of the acids would be to prevent the release of NH_3 and to promote dehydration in order to reduce the requirements of storage (e.g. covered facilities) and land application. The availabilities of phosphorus, carbon, and nitrogen were monitored before and after blending the two waste streams, under different acidification conditions.

2. Materials and methods

2.1. Materials

Wood bottom ash (WBA) was selected because it represented the main share of the ashes generated in the grate combustion chamber of the sawmill cogeneration plant (Table 1). Generally, the bottom ash fraction contains fewer and/or less available toxic elements than the fly ash fraction, thus it is comparatively considered less hazardous waste [15]. It should be noted that the fate of pollutants (e.g. heavy metals) in ashes depends on the type of input resource (e.g. coal, biomass, etc.) and the configuration of incinerator [16]. The WBA was

stored in a sealed plastic box to minimise the contact with the open atmosphere during its transportation by courier. The metal oxides present in the ashes could react with moisture and CO₂ of the environment, leading to a decrease of alkalinity due to formation of hydroxides and carbonates (CO₃²⁻), respectively [17]. These types of absorption reactions (e.g. neutralisation, carbonation, etc.) are widely used for cleaning flue gases [18]. Once the 10 kg of WBA was received at Lancaster University, a composite sub-sample was prepared by milling and sieving to pass a 1 mm mesh, being stored in a zip-bag and was stored at room temperature until further use. This was considered a “fresh” sample.

Table 1 Description of the feedstock used in the production plants from which the digestate and the ash were sampled.

Sample	Production plant feedstock composition and capacity
WBA	Virgin wood, bark, and chipped timber. Usually mixture ratio 85 wt. % sitka spruce and 15 wt. % larch. 256 ton/year fly ash and 295 ton/year WBA.
PVWD	Maize Silage (10000 t/year), vegetables waste (5000 t/year), sweet-corn waste (15000 tons per year), aerobically treated food waste (10000 t/year), and biodegradable sludge (2000 t/year). 40000 ton/year PVWD.

The post-harvest vegetable waste digestate (PVWD) was selected based on its moderate amount of NH₄⁺-N (Table 2) resulting from the limited degradation undergone by fibrous vegetable material during the AD [19]. The 10 kg of PVWD was sourced from an industrial scale AD plant (Table 1), collected in a jerry can and allowed to cool down prior to its transportation in a refrigerated cool box (sample preservation). After arriving at Lancaster University, the sample was placed in a cold room (< 4 °C) until further use. This was considered a “fresh” sample. A subsample was sent out externally to Natural Resource Management (NRM) certified laboratory for complementary analyses (nitrogen, phosphorus, and trace elements).

The characterisation of the samples, in terms of the parameters concerning the present studies, is shown in Table 2. The water-soluble (WS) fraction of phosphorus, carbon, and nitrogen were measured using a solid-to-liquid (S:E) ratio 1:10 (i.e. 1 part of sample and 10 parts of ultrapure [milli-Q] water). A detailed explanation of the calculations to express the concentration of the

WS species in fresh basis is illustrated in the Supplementary material. Only in this initial characterisation (Table 2), the pH and the EC of the samples were determined in the WS extract of the samples generated using a S:E ratio 1:5. The theoretical values of the characterisation of the blend were calculated considering that the mixture was prepared with approximately 0.5 g of WBA and 3 g of PVWD (Table 2). In the section of Results and Discussion, the experimental values of the characterisation of the samples during their incubation at 100 rpm and 20 °C, and their blending at the 96 hours, were compared to the data in Table 2, which was used as reference. In this way, it was possible to elucidate any undergoing phenomena which might have affected the masses of the WS and water-insoluble (WI) fractions of the blend or the availability the phosphorus, carbon, and nitrogen.

The samples were blended in order was to achieve an approximate C/N/P ratio of 10/1/1 (Table 2). The PVWD was the main source of nitrogen (96 wt. %) and carbon (89 wt. %) in the blend and provided as well with other elements (Table S.1). On the other hand, the WBA was the main source of phosphorus (66 wt. %), alkali, and alkaline-earth metals (Table S.2). The electrical conductivity of WBA was higher because of the greater content of Na⁺ and K⁺, since both calcium and magnesium had lower effect on the EC due to their low solubility (Table S.1). SO₄²⁻, Cl⁻, and PO₄³⁻ were the main anions provided by the wood ashes [20].

Table 2 Initial characterisation expressed in fresh basis of the samples and the blend.

Sample		WBA		PVWD		WBA + PVWD ^a	
Parameter	Units	Average	St. deviation	Average	St. deviation	Average	St. deviation
pH	-	13.29	0.03	7.85	0.12	7.98	0.00
Electrical conductivity	dS/m	57.90	0.96	2.37	0.04	16.28	5.49
Dry matter	wt. %	98.90	0.58	7.57	0.32	30.45	9.40
TC	mg/kg	22,069.71	1,145.77	31,959.34	43.60	29,482.21	3,687.73
WS TC	mg/kg	1,825.00	113.57	2,041.50	87.73	1,987.27	260.86
TN	mg/kg	832.00	83.20	3,800.00	380.00	3,058.58	369.11
WS TN	mg/kg	46.58	13.88	2,062.70	18.89	1,557.71	195.37
WS NH ₄ ⁺ -N	mg/kg	4.29	0.77	689.74	86.78	518.05	65.66
WS NO ₃ ⁻ -N	mg/kg	1.30	0.02	18.94	0.65	14.52	1.90
TP	mg/kg	12,359.00	1,235.90	1,119.00	111.90	3,934.36	1,214.83
WS PO ₄ ³⁻ -P	mg/kg	22.25	1.51	38.99	2.74	34.80	4.44

^a Calculated using the experimental composition of the samples in the blend (0.87 ± 0.40 g WBA and 2.59 ± 0.55 g PVWD; n=3). A detailed description of the procedure for the estimation of the propagation of uncertainty is shown in the Supplementary material.

2.2. Methodology

In favour of minimising the cost of the processing and building up the knowledge on the underlying chemistry, our approach to develop this technology was to carry out increasingly complexity studies. This would allow (1) to find the cheapest technologies to reduce the carbon and nutrient availability in the organic wastes in order to improve their properties as controlled-release fertiliser, in case this material is applied directly to the soil; (2) to reach a more efficient solid-liquid separation using cheap technologies (e.g. sedimentation), as part of the first manufacturing operation. In our previous study we evaluated the scenario of dispensing with the acid medium [21].

In the present two studies, we have tested several acidification conditions to enhance the sorption processes that take place in the blend of PVWD and WBA. It is important to highlight that the WBA was used directly without any further treatment or activation. It would be expected that a prior activation via milling and sieving, acid wash, and calcination would further enhance adsorption but would also lead to a more energy and resource intensive process. The activation of WBA before preparation of the blend might be addressed in future work.

2.2.1. Factorial design of each study

The two factors which were assessed in both experiments were the conditions of acidification and the time of incubation, although the levels are different. Each experimental unit assessing the preparation of the blended fertiliser was comprised by certain masses of the PVWD, the WBA, and an acid solution which acted both as acidifying agent and extractant at the same time (Table 3). Because of the destructive sampling procedure used in the first and second studies, 210 experimental units were prepared (i.e. 7 blends, each with 3 replicates, to be measured over 10 incubations times) and 90 (i.e. 5 blends, each with 3 replicates, to be measured over 6 incubations times), respectively.

In the first study, the acid doses for PVWD were based on information taken from the literature relating to the treatment of manure and slurry (Table S.3) since digestates have been traditionally treated in the same way [22]. The WBA was not acidified before mixing with the PVWD. The composition of the samples was measured at 0, 24, 48, 72, 96 (before and after adding the WBA), 120, 144, 168, and 192 hours of incubation. In the second study, the dose of each acid (Table 3) was based on preliminary titrations of the PVWD and the WBA, to ensure the target pH value (around 5.5; [23]) was reached after the blending the acidified samples. The

composition of the samples was measured at 0, 24, 48, 96 (before and after blending), and 144 hours of incubation.

Two-factor analysis of variance (ANOVA) with replication was performed with Microsoft® Excel 2016 ($\alpha = 0.05$) for the balanced design of experiments (i.e. each blending condition studied has the same number of observations) to identify any significant change in the variables measured over the incubation time and to decide whether the trends found for the samples were significantly different. This analysis interrogated any changes in the composition of the samples during the incubation under the different acidification conditions and the impact of the blending operation on the availability of phosphorus, carbon, and nitrogen. Furthermore, this statistical analysis enabled the rigorous selection of the best acidifying agent and optimum concentration to be used. It is important to mention that, in order to apply the ANOVA test, it was assumed that the data obtained in the two studies followed a normal distribution.

Table 3 Blends characterised during the incubation at 100 rpm shaking and 20 °C in the two studies.

Study	WBA	Extractant WBA	PVWD	Extractant PVWD
First/(g)	0.51 ± 0.05	^a 5	2.24 ± 0.09	^a 20.5
Solutions/	H ₂ SO ₄	0		0.08
		0		0.24
(mmol H ⁺ /	HCl	0	(mmol H ⁺ /	0.08
g WBA)		0	g PVWD)	0.24
	HNO ₃	0		0.08
		0		0.24
	-	0		0
Second/(g)	1.28 ± 0.15	10.50 ± 0.22	3.40 ± 0.20	30.19 ± 0.20
Solutions	H ₂ SO ₄	6.29		0.12
	HCl	15.21	(mmol H ⁺ /	0.19
(mmol H ⁺ /	HNO ₃	11.97	g PVWD)	0.14
g WBA)	CH ₃ CH(OH)COOH	^b 0.16		^b 0.03
	-	0		0

^a Mass of the extractants added to the samples using a dispenser to achieve the WS extraction following a S:E ratio 1:10. The specific amount added to each experimental unit was not recorded.

^b It should be noted the large volume of commercial (90 wt. %) lactic acid required to reach these proton concentrations of the extractant solutions.

2.2.2. Blend preparation and fractionation

A detailed description of the amount of each sample and extractants used for the preparation of the blends is shown in the Figures S.1. and S.5. The volume of the extractant (i.e. acidifying agent) that was added to each sample before blending, followed an approximate S:E ratio 1:10 (Table 3). Our previous studies have proven that adding the extractant before the incubation did not significantly affect the composition of 2.5 g blend undergoing incubation at 100 rpm and 20 °C [21]. The acid solutions prepared with ultrapure milli-Q water and reagent grade H₂SO₄, HCl, HNO₃, and CH₃CH(OH)COOH had several purposes: (a) fluidise both waste streams to make easier the blending process and reduce the losses after weighting the samples, (b) enhance the contact between the components of the WBA and the PVWD, (c) control of pH, and (d) extract nutrients for fractionation of the samples and the blend. The term

fractionation refers to the analytical (i.e. at higher performance than what would be expected for farm processing equipment) solid-liquid separation. The fluidised samples and blends were incubated (i.e. extraction) at 100 rpm and 20 °C in closed 50-mL Corning® tubes with stopper (Fig. 1). It is important to highlight that in the first study the incubation of the 0.51 ± 0.05 g of WBA with the 5 mL milli-Q® was not monitored before mixing with the acidified 2.24 ± 0.09 g PVWD.

After the incubation of each destructive sample, the solid-liquid separation was performed via 5 minutes centrifugation at 4000 rpm and filtration of the supernatant using Whatman No 44 filter paper (3 µm). The gravity was the driving force of the filtration rather than vacuum to minimise the release of the gases (e.g. NH₃) solubilised in the WS extract, since the gaseous fraction of the samples after the incubation was not characterised. For the isolation of the WI material, both the pellet and the cake that remained in the filter paper were dried at 105 °C for 24 hours (Fig. 1).

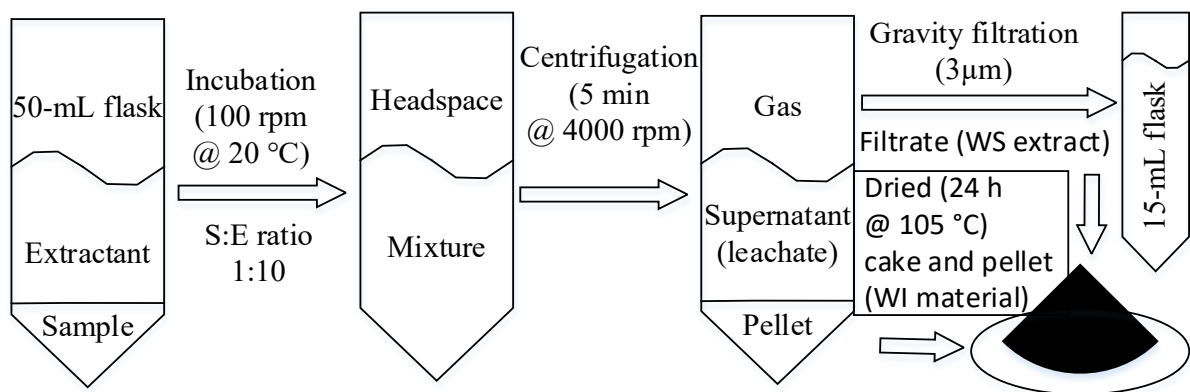


Fig. 1. Stepwise methodology for the characterisation of the WS extract and the WI material of the samples and their blend after the incubation at 100 rpm and 20 °C.

In the first study, the theoretical volumes of the WS extracts of the blends were determined considering the moisture of each sample (Table 2), in addition to the volume of extractant used to prepare the blends (Table 3). For this calculation, it was considered a density of 1 g/mL for both the moisture of the samples and the extractant. The theoretical masses of WI materials were assumed to be the dry matter of the blend (Table 2). For the second study, the experimental WI material recovered after the incubation was weighed and the experimental WS extract was calculated based on this value, the moisture of the samples, and the amount of extractant used for the fluidisation of the blend. The comparisons between the theoretical and

the experimental masses of WS extracts and WI materials of the second study are shown in Fig. S.6.

2.2.3. Characterisation of the fractions of the blend

The two studies rely on measurement of the availability (i.e. distribution between WS and WI fractions) of phosphorus, carbon, and nitrogen to elucidate any reaction mechanism and kinetics. Elements present in the WS phase to the soil biota and more prone to be lost via leaching and volatilisation. It is important to mention that the content of phosphorus in the WI material was not measured in the first study.

The parameters measured in WS extract were the pH, and the concentrations of ammonium and ammonia (WS NH_4^+ & WS NH_3), nitrate and nitrite (WS NO_3^- & WS NO_2^-), orthophosphate (WS PO_4^{3-}), total nitrogen (WS TN), and total carbon (WS TC). Similarly, for WI material, mass and concentrations of nitrogen (WI TN), carbon (WI TC), and phosphorus (WI TP) were determined. The calculation procedure of the WS and the WI species is offered in the Supplementary material.

Measurement of WS extract pH was performed with a Mettler Toledo® Seven Compact™ S220 pH/Ion meter. Determination of concentrations of WS NH_4^+ & WS NH_3 and WS NO_3^- & WS NO_2^- (methods DIN 38405 and ISO/DIS 13395 for both parameters), and WS PO_4^{3-} (methods DIN/EN/ISO 15681-2) was done with the Autoanalyser (AA3, SEAL analytical), by using colorimetry based on salicylate, hydrazine, and molybdate reactions, respectively. The standards used were ammonium sulphate, potassium nitrate, and potassium dihydrogen phosphate, all chemicals were analytical grade. On the other hand, 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. Thus, the WS organic nitrogen (WS N_{org}) could be calculated as the difference between the WS TN and the WS $\text{NH}_4^+\text{-N}$ + WS $\text{NO}_3^-\text{-N}$ [24]. Although digestates could contain significant amounts of bicarbonate buffer [25], most of the TC of the PVWD was in the organic form (C_{org}). On the other hand, a greater proportion of $\text{CO}_3^{2-}\text{-C}$ was expected in the WBA with regard to the inert carbon (C_{inert}).

Phosphorus in ashes is generally in the form of PO_4^{3-} [26], in both WS extract and WI material. On the other hand, phosphorus of digestates is generally a mixture of PO_4^{3-} , polyphosphates and phosphorus associated to organic molecules (P_{org}). Unlike WS N_{org} , which can be an important fraction [27], the WS P_{org} was expected to be minimal (i.e. $\leq 12\%$ of the TP) in manures [28]. In this way, determination of dissolved reactive phosphorus, which is the WS

phosphorus that responds to molybdate colorimetric test without previous hydrolysis [29], would give good idea of total phosphorus in WS extract. It should be noted however that some of the particulate phosphorus and WS P_{org} were anticipated to be hydrolysed easily [30], even with reagents of the improved colorimetric method of Pote & Daniel [29].

The samples of WI material were milled before doing any characterisation. Measurement of WI TN and WI TC was done in elemental analyser (Elemental vario EL cube) using acetanilide as standard. Sulphuric-peroxide digestion of the WI material at 400 °C for 2 hours was done following the method described by Grimshaw [31] to obtain the phosphate-rich extract which was measured in the Autoanalyser to determine the WI TP, following the calculation procedure illustrated in the Supplementary material.

2.2.4. Empirical and theoretical concentrations and mass balances of each element

Whether the experimental results were referred to the WS extract (S:E ratio 1:10) without units for pH, or were expressed in terms of fresh base (mg of WS NH₄⁺-N, WS NO₃⁻-N, WS PO₄³⁻-P, WS TN, WS TC, WI TN, WI TC, and WI TP, per kg fresh blend), the average value of the 3 repetitions of each condition and their standard deviation (n=3) were calculated and plotted in scatter charts. Besides, the average value and standard deviation (n=3) of the masses of phosphorus, carbon, and nitrogen WS and WI species were calculated to represent the mass balances of these elements in the Supplementary material. The calculation of concentrations and masses of the chemical species in the first study was based on the theoretical masses of the WS extracts and WI materials. On the other hand, the results of the second study rely on the experimental WS extracts and WI materials recovered for each blend after the incubation. The reason for the different calculation procedures of the two studies was that the procedure of the first study was improved for the second one, because it was considered more accurate the use of the experimental masses of the WS extracts and WI materials. This would allow to identify more easily non-ideal behaviours (e.g. sorption processes) of the samples and the blend during the incubation.

Losses during the blending process were estimated via comparison of the total amounts (i.e. sum of WS and WI species) of phosphorus, carbon, and nitrogen recovered for each blend over the incubation period against the initial amount of each element (Table 2) Particularly, the average recovery effectiveness, which was expressed as weight percentage (wt. %) for each

acidification condition and sample type, was calculated as the final amount of a element divided by the initial one.

3. Results and discussion

3.1. First study

3.1.1. pH, WS phosphate, and carbon speciation

The decrease of the pH in the PVWD due to acidification (Fig. 2 a) promoted processes such as the solubilisation of phosphorus before the addition of the WBA (Fig. 2 b) and the depletion of the carbon from the WS phase (Fig. 2 d). The different doses of acidification did not affected significantly ($\alpha=0.05$) to the WI TC of the PVWD (Fig. 2 e), therefore it was not possible to claim that the acidification promoted the adsorption of some of the WS TC carbon onto the solid fraction (i.e. fibre). It should be noted that the excessive solubilisation of phosphorus would lead to eutrophication of inland and coastal waters [32].

Despite the acidification of the PVWD, the addition of the WFA at the 96 hours of incubation drastically increased the pH to a value of 12.69 ± 0.14 , which remained constant until the end of the incubation (Fig. 2 a). This agrees with the results of Wróbel et al. [33], who described that only 3 hours of stabilisation after the blending of agricultural waste digestate and biomass ash is required before pelletisation. It is important to mention that for the preparation of the blend, they employed dewatered digestate in order to have a final blend with a moisture content of 18 wt. %. The stabilisation that Wróbel et al. [33] referred to in their study was regarded in our present work as physical stabilisation, which is mainly the result of the hydration of oxides to hydroxides and, to a lesser extent, later the subsequent formation of carbonates. In this way, this self-hardening process which is required prior to the granulation relies on the alkalinity of the ashes and specially on the calcium content [34].

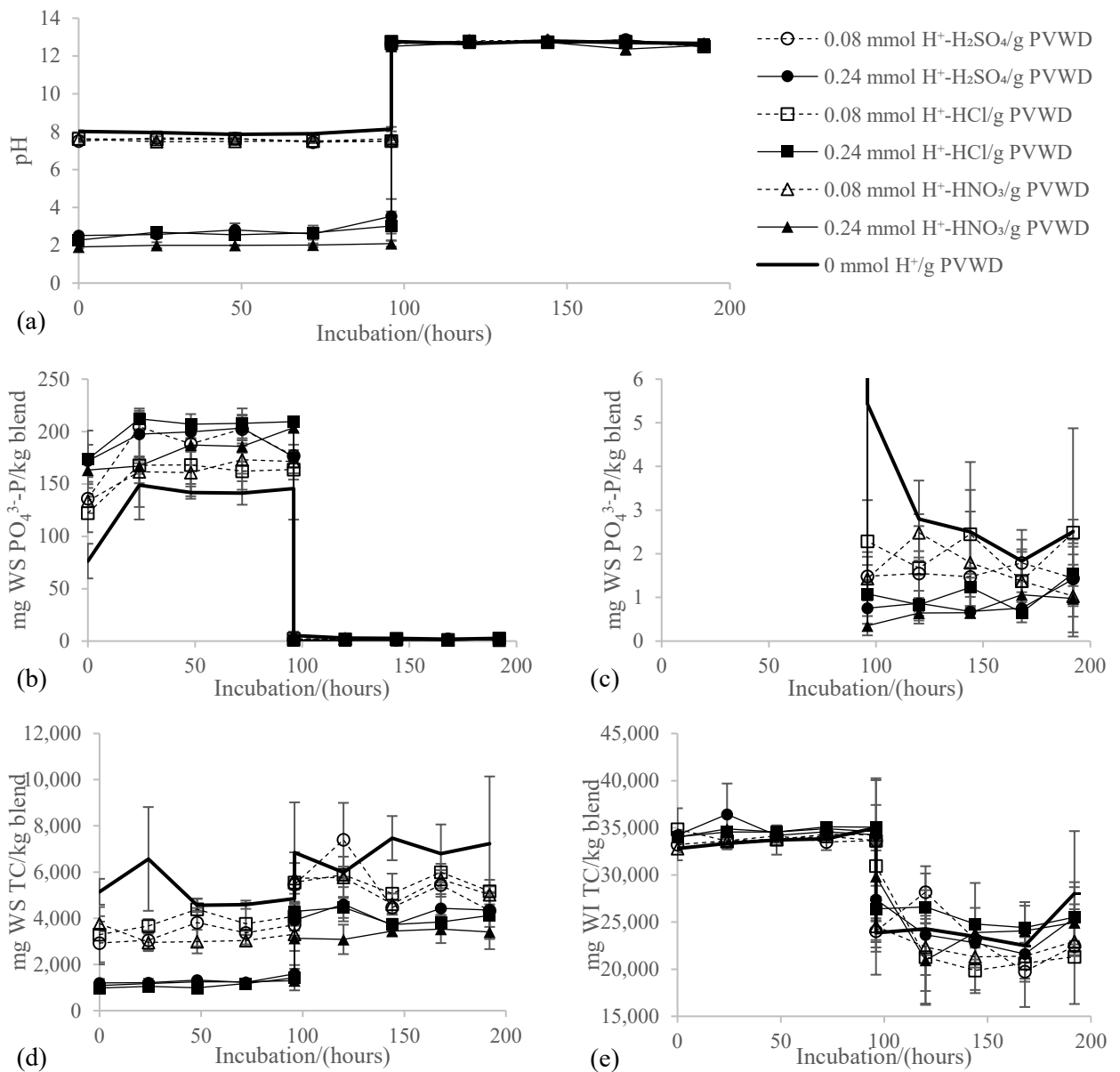


Fig. 2. Characterisation in terms of (a) pH, (b) WS PO₄³⁻-P, (c) zoom in WS PO₄³⁻-P, (d) WS TC, and (e) WI TC, 2.24 ± 0.09 g of PVWD acidified with 2 dose (0.08 and 0.24 mmol H⁺/g PVWD) of 3 acids (H₂SO₄, HCl, and HNO₃) and without acidification, followed by the addition of 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-hour incubation.

Calcium also plays a key role in the chemical stabilisation as it precipitates the phosphorus effectively while the blend remains at pH above 8.5 [35]. In the blend of the first study, most of the phosphorus was sorbed in the WI fraction, remaining at only 1.56 ± 1.22 mg WS PO₄³⁻-P/kg blend. Fig. 2 (c) illustrates how acidification promoted the sorption of WS PO₄³⁻-P onto the WBA. Similarly, the effect of acidification on the WS TC could be seen even after the addition of the WBA. As expected, increases in pH resulted in greater amounts of carbon in the WS fraction of the blend. Although there was significant difference ($\alpha=0.05$) in terms of

WI TC of the blend due to the doses of acid, no clear trend was identified that could be explained by the adsorption process. It should be noted that the decrease in the amount of carbon in the WI fraction was due to the lower content of carbon of the WBA, which was the main contributor to the dry matter of the blend (Table 2).

As can be seen in the theoretical carbon balances (Fig. S.2), which are shown in the Supplementary material, the average recovery effectiveness of carbon for all the acidification conditions was 105.47 ± 3.60 wt. %. The reason was that the WI TC was the main form of carbon in the samples and the blend, thus the losses WS TC in the form of CO_2 were regarded as negligible. This could be related to the weak acidification or to the fact that the carbon was predominantly in forms different from $\text{CO}_3^{2-}\text{-C}$ [36,37], such as C_{org} and C_{inert} in PVWD and WBA, respectively. Both these forms of carbon are important to maintain a healthy soil and maximize crop productivity. For example, Bhogal et al. [4] reported the relevance of the stable fraction of the organic matter that remains in the biologically stabilised organic wastes, via AD or composting, to restore the soil as a natural carbon sink. The results of their study show that the application of food waste compost to land over a period of 9 years increased the soil organic carbon as much as the application of farm yard manure for 20 years. However, when looking at the carbon speciation in the soil, the carbon immobilised in microbial biomass was more than twice in the case of manure. Thus, the stable organic matter prevented the excessive growth of microbes in the soil. It is important to mention that in the study of Bhogal et al. [4], the food waste digestate offered similar results to the compost when they were applied for 3 years. The land spreading of livestock slurry for 20 years provided with a lower increase in soil organic carbon compared to the same rate of application of manure but with the same relative increase in the microbial growth. Although controlling diseases, pathogens, and odours is not among the main concerns of farmers [38], the procedures for combating antibiotic resistance are regulated and demanded by the governments [39].

3.1.2. Nitrogen speciation

The content of WS $\text{NH}_4^+\text{-N}$ increased ($\alpha=0.05$) progressively during the first 96 hours of incubation (Fig. 3 a), especially with the acidification. The reason could be the microbial activity of ammonification [40] or the hydrolysis of N_{org} [41] which took place in the acid conditions. Abiotic mineralisation processes such as the photolysis [42] were not considered significant under the conditions of the incubation. It should be noted that these levels of WS $\text{NH}_4^+\text{-N}$ in the PVWD were slightly overestimated because the samples would require further dilution to fit in the calibration range of the Autoanalyser. This explains why that the

concentrations of WS $\text{NH}_4^+\text{-N}$ in Fig. 3 (a) were similar to the WS TN in Fig. 3 (c), since the WS TN should include as well other forms of nitrogen, such as the WS N_{org} .

High level of WS $\text{NO}_3^-\text{-N}$ (246.63 ± 28.75 mg/kg PVWD) were only found when using HNO_3 for acidification (Fig. 3 b). A lower concentration of WS $\text{NO}_3^-\text{-N}$ (4.75 ± 2.31 mg/kg PVWD) was found for all the other conditions. The measurement of the concentration of WS $\text{NO}_3^-\text{-N}$ in the PVWD acidified with HNO_3 affected the characterisation of the PVWD acidified with H_2SO_4 and HCl , leading to an apparent increase in the concentration overtime due to the carry-over error in the Autoanalyser [43]. It should be noted that the best conditions for nitrification include a neutral pH [44], therefore it was unlikely that the progressive increase in the concentration of WS $\text{NO}_3^-\text{-N}$ for the H_2SO_4 and HCl acidifications was due to this biological process. Only the HNO_3 acidification affected significantly WS TN of PVWD (Fig. 3 c) but the impact on the WI TN of the PVWD was less significant. (Fig. 3 d).

The addition of the WBA at the 96 hours of incubation significantly decreased the concentration of all forms of nitrogen in the blend. Only the dose 0.24 mmol $\text{H}^+\text{-HNO}_3/\text{g}$ PVWD did not show significant decrease in the level of WS $\text{NO}_3^-\text{-N}$, because the concentration was out of the calibration range of the Autoanalyser. This also explains why a greater difference of the concentration of WS TN was found for the doses 0.08 and 0.24 mmol $\text{H}^+\text{-HNO}_3/\text{g}$ PVWD in Fig. 3 (c). The values of WS TN provided by the TOC machine were used to establish the nitrogen balances, which are shown in the Supplementary material (Fig. S.3). The average recovery effectiveness found was 68.38 ± 3.23 % because of the decrease of the nitrogen content of the PVWD after adding the WBA at the 96 hours of incubation, which was explained by the volatilisation of NH_3 . Only when the HNO_3 was used, the losses of nitrogen due to N_2O release need to be considered as well. The N_2O is product of the denitrification [45], although this compound can be generated due to the abiotic reduction of WS NO_3^- [46] and WS NO_2^- [47], given the reducing effect of the alkaline metals contained in the WBA (Table S.2). It could be considered as well that the denitrification yielded N_2 as well, since the reduction potentials for the $\text{NO}_3^-/\text{NO}_2^-$, NO_2^-/NO , $\text{NO}/\text{N}_2\text{O}$, $\text{N}_2\text{O}/\text{N}_2$ are 0.42 , 0.38 , 1.18 , and 1.36 . Hence, the conversion of N_2O to N_2 is not a limiting step as the more positive the reduction potential, the more spontaneous is reaction [48].

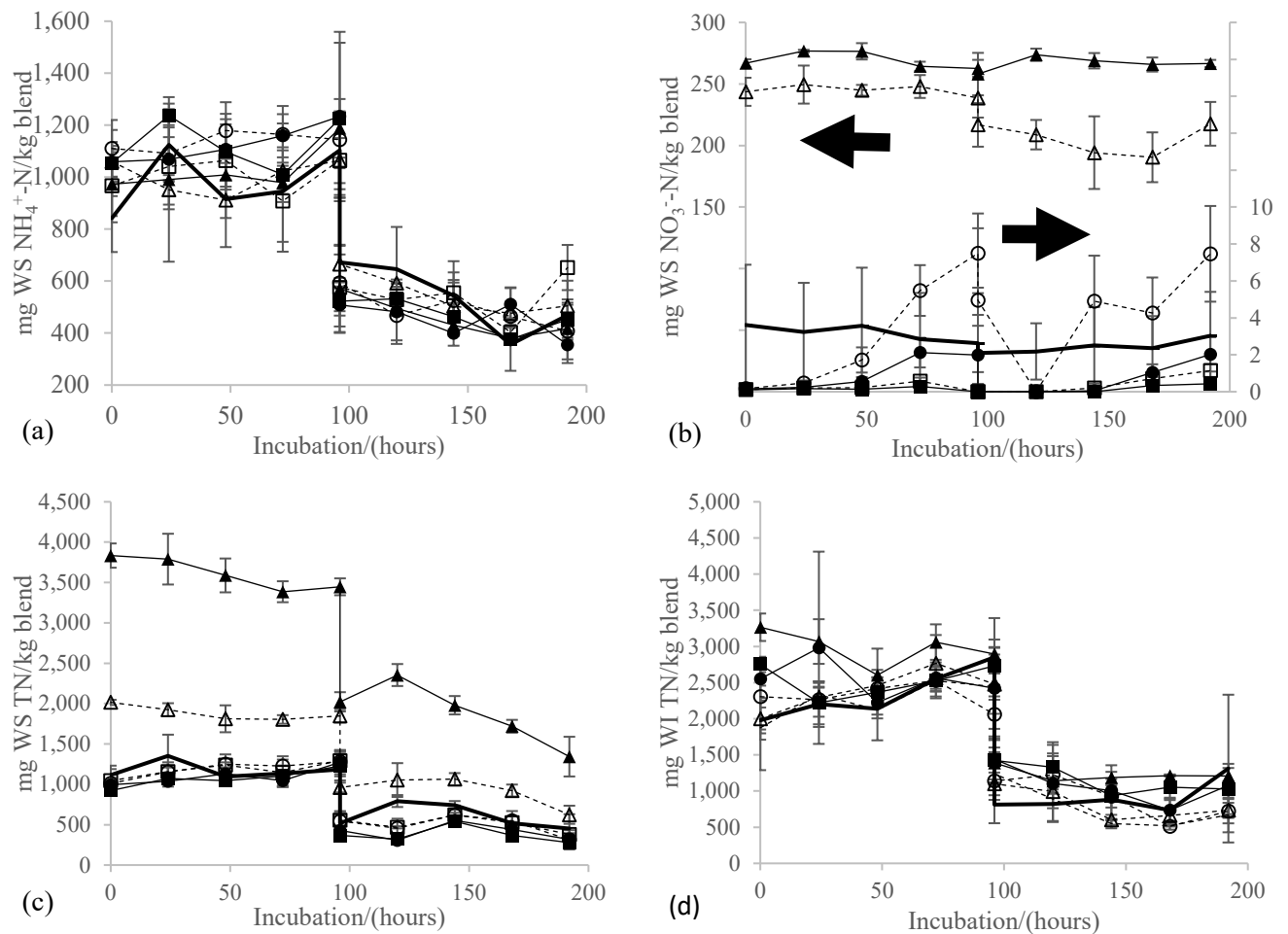


Fig. 3. Characterisation in terms of (a) WS NH_4^+ -N, (b) WS NO_3^- -N, (c) WS TN, and (d) WI TN, 2.24 ± 0.09 g of PVWD acidified with 2 dose (0.08 and 0.24 mmol H^+ /g PVWD) of 3 acids (H_2SO_4 , HCl , and HNO_3) and without acidification, followed by the addition of 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-hour incubation.

--○-- 0.08 mmol H^+ - H_2SO_4 /g PVWD
 ● 0.24 mmol H^+ - H_2SO_4 /g PVWD
 --□-- 0.08 mmol H^+ - HCl /g PVWD
 ■ 0.24 mmol H^+ - HCl /g PVWD
 --△-- 0.08 mmol H^+ - HNO_3 /g PVWD
 ▲ 0.24 mmol H^+ - HNO_3 /g PVWD
 — 0 mmol H^+ /g PVWD

Since agricultural soils have been identified as one of the major sources of the greenhouse gas, N_2O [49], a number of regulations and technologies has been developed to address emission to the atmosphere. The designation of Nitrate Vulnerable Zones as per the Nitrate Directive (91/676/EEC) or its corresponding legislation for countries outside of the European Union such as United Kingdom [50], aims to limit the rate of application to 170 kg N/ha/y . The development of nitrification inhibitors aims to address this environmental [51] as well as economic problems, since crops generally prefer NH_4^+ -N to grow [52]. Advocates for organic

agriculture claim that the excess of nitrogen is also responsible of health issues as the high crop yields lead to food containing less nutrients in the human diet [53].

The technology that we are proposing, which enables the easier handling (i.e. store, transport, and spread to land) of organic waste, is in agreement with the perception of farmers and other stakeholders (e.g. public authorities, agricultural advisors, and consultants) [38]. At both sides of the supply and demand of slurry, these groups see the pressure from environmental policies as the main stimulant for the adoption of organic waste processing technologies. Moreover, they have identified the lack of capital investment and the high processing costs as the most important barriers for wider implementation of technologies. Our CATNAP (cheapest available technology narrowly avoiding prosecution) approach aims to bridge the gaps, preventing the efficient recycling of carbon and nutrients. Both in the EU and the UK regulatory frameworks, there is flexibility to design the national or regional action programmes in order to comply with the Emission Ceiling Directive (2001/81/EC) or the Clean Air Strategy 2019 [54], respectively.

In terms on nitrogen management, biomass ash should act as sorbent of NH_4^+ -N under the acid conditions of processing and minimising the nitrification/denitrification once in the soil, due to the reduced availability of this inorganic form of nitrogen. Although considering the increase in pH of the PVWD after the addition of the WBA, acidification might be better performed after carrying out the ammonia stripping following the strategy evaluated by Limoli et al. [55]. Other procedure for activation of the ashes would be the synthesis of zeolites prior to addition to digestates to produce a slow-release fertiliser. Nevertheless for this purpose, coal ash is better suited than wood ash due to its higher content in aluminosilicates and lower content of calcium which prevent the crystallisation of the zeolite structure during the cooling stage of the hydrothermal synthesis [56]. Although the levels of toxic elements (e.g. heavy metals) in the coal ash might limit the application as fertiliser.

3.2. Second study

3.2.1. pH, phosphorus and carbon speciation

The acidification of the WBA before its addition to the PVWD prevented the increase in the pH above a value of 8 (Fig. 4 a). It should be noted that in spite of the high dose of each acid, the pH of the WBA progressively increased during the first 96 hours of incubation due to the high content of alkaline elements of this material (Table S.2). This resulted in a decrease of WS PO_4^{3-} -P, which had been solubilised due to the severe acidification of the WBA (Fig. 4 b).

After the blending at the 96 hours, the pH was not constant under all acidification conditions because there was not enough time for the chemical stabilisation of the WBA before the blending. The final concentration of WS $\text{PO}_4^{3-}\text{-P}$ in the blends at the 144 hours of incubation was 74.53 ± 52.43 mg/kg blend (Fig. S.7 a). This concentration was higher than what was found in the first study (1.56 ± 1.22 mg WS $\text{PO}_4^{3-}\text{-P}$ /kg blend; Fig. 2 c), due to the lower pH of the blends at the end of incubation. This level of availability would provide the crops with enough $\text{PO}_4^{3-}\text{-P}$ while preventing the excessive leaching. In fact, most phosphorus in the blend was in the form of WI TP (Fig. 4 c), since the WBA was the main source of phosphorus and the main contributor to the WI fraction (Table 2). The mass balances (Fig. S.8), show that only 38.22 ± 5.71 % and 26.49 ± 2.06 % of the phosphorus initially present in the WBA and the PVWD, respectively, were measured in all conditions (i.e. with and without acidification). These low average recovery effectiveness could be related to other forms of WS phosphorus different from $\text{PO}_4^{3-}\text{-P}$ (e.g. P_{org}) which were not determined. Furthermore, similarly to the mass balances of carbon and nitrogen, the losses of WI material and WS extract during the fractionation of the samples and the blend would affect the recovery effectiveness of phosphorus. Nevertheless, only the WBA acidified with sulphuric and lactic acids showed significant deviations from the ideal behaviour (Fig. S.6). It was particularly noteworthy the increase in the WI material and the decrease in the WS fraction of the WBA due to the adsorption of the $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.

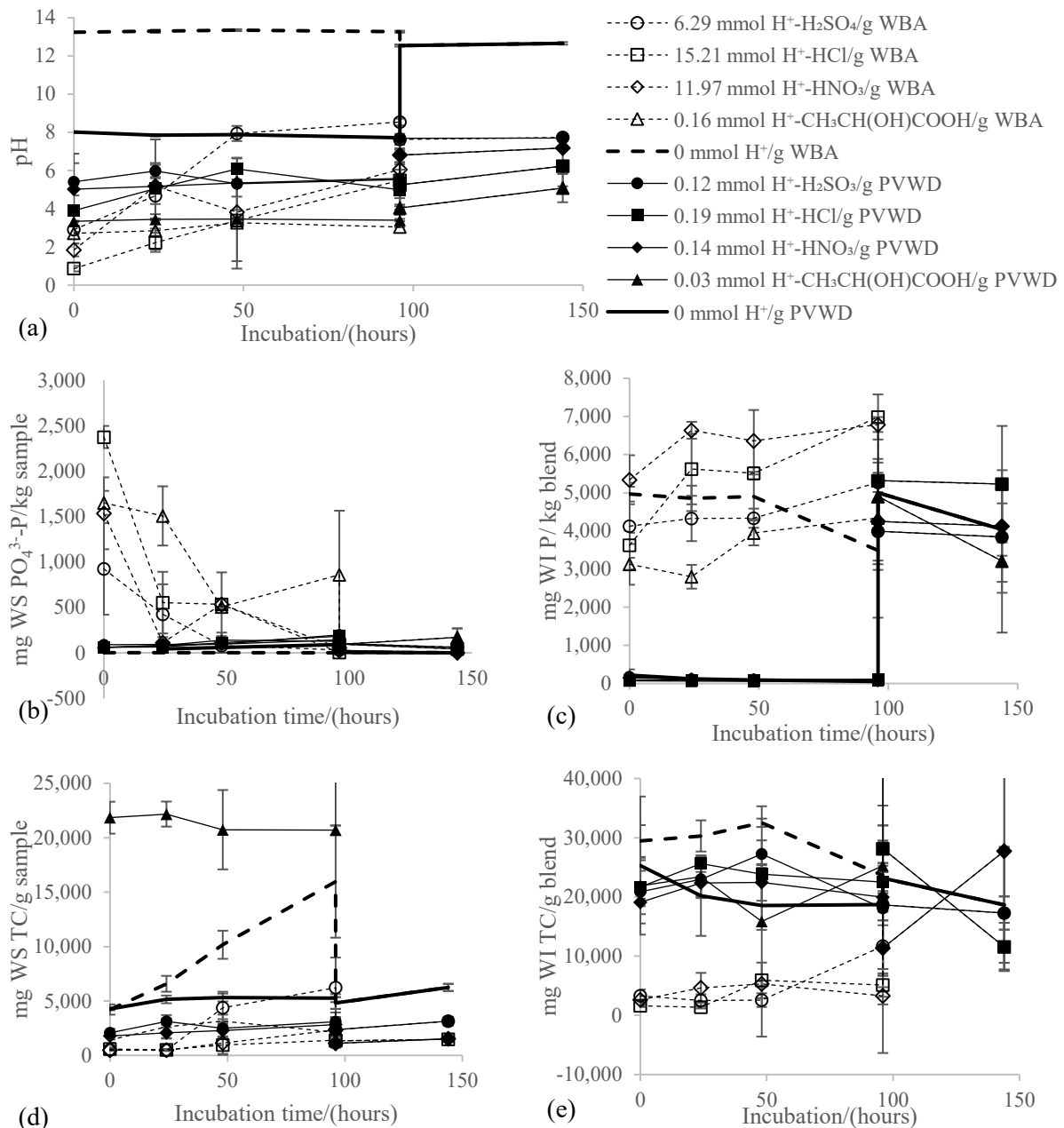


Fig. 4. Characterisation in terms of (a) pH, (b) WS PO₄³⁻⁻P, (c) WI TP, (d) WS TC, and (e) WI TC of 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD acidified with 4 acids (i.e. H₂SO₄, HCl, HNO₃, and CH₃CHCOOH) and without acidification before and after blending (at the 96 hours) during the 144-hour incubation.

The high concentration of the WS TC due to the acidification of the ash with lactic acid (259,917 ± 94,320 mg/kg WBA; Fig. S.9 a) might be responsible of the carry-over error in the measurement of the experimental blank WBA (i.e. no acidification) and the WBA acidified with H₂SO₄ (Fig. 4 d). It should be noted that this type of analytical error is less likely to happen in the TOC instrument than in the Autoanalyser because of the type of determination (i.e. combustion rather than colorimetry) and because the washing between the samples is done for

longer time. We saw that both the base line and the analytical blanks were less affected by the high concentration of analyte given by the severe acidification with lactic acid. Of all acidifications, the H₂SO₄ gave to the WBA and the PVWD the highest pH. Similarly to the samples which were not acidified (i.e. experimental blank), this could explain the greater content of WS TC, since the carbon would not be lost as CO₂ due to the dissociation of the carbonic acid in water which takes place at low pH. The results of WI TC obtained in the second study (Fig. 4 d) agree with the data of the first study (Fig. 2 c). The WI TC found for the WBA without any acidification during the first 96 hour of incubation ($28,965 \pm 6,320.1$ mg WI TC/kg WBA; Fig. 4 e) was significantly higher than the value of the initial characterisation ($20,245 \pm 1,032$ mg WI TC/kg WBA; Table 2). There is not possible carry-over error in the measurements of the WI TC with the Elemental Analyser, despite the high amount of carbon which ended up in the WI fraction of the WBA acidified with lactic acid ($679,467 \pm 253,462$ mg/kg; Fig. S.9 b) due to adsorption. Unlike the moderate acidification of the PVWD, which did not promote the loss of CO₂, the severe acidification of the WBA significantly decreased the carbon content in the WI fraction. This could be related to the fact that most of the carbon in the PVWD was in the form of C_{org} rather than CO₃²⁻-C. After the blending at the 96 hours, the level of WI TC raised (Fig. 4 e) to a similar level as in the previous study (Fig. 2 d), despite the final pH of the blends of the second study was lower than 8 (Fig. 4 a). Nevertheless, these lower levels of the WI TC in the WBA acidified with H₂SO₄, HCl, and HNO₃ were reflected in their mass balance for carbon (Fig. S.10) with an average recovery effectiveness (58.11 ± 1.09 %), which was lower than the 109 % recovery of carbon in the WBA which was not acidified. It should be noted that there was not significant difference ($\alpha=0.05$) in the concentration of WI TC in each blend by the end of the 144-hour incubation, with the exception of the blend acidified with lactic acid. The average value of $18,810 \pm 11,468$ mg WI TC/kg blend (Fig. 4 e) found in the second study was similar to the one found in the first study ($24,380 \pm 3,821$ mg WI TC/kg blend; Fig. 1 d).

The cheapest option for restoring the levels of carbon in the soil is via restoration with vegetation. This strategy can be applied in remote areas which are not subjected to intensive agricultural practices [57]. Even on farm land, the use of cover crops is considered as a valuable resource, although reduced tillage is not widely applied in the agro-industry [58]. Primary market research carried out by Hou et al. [38] exposed the level of readiness of producers and users of manure and slurry to employ AD and even solid-liquid separation, despite transport not being seen as a burden for the utilisation of these organic wastes.

The phases of development of the technology for processing organic wastes with the ash address the current needs and fit in the machinery employed in the fertilisation of agricultural soils for the cultivation of crops. Although the chemical stabilisation is essential to enhance the separation of the fractions of organic waste and ash blends, this step does not rely on the physical stabilisation to prevent the release of greenhouse gas during application to land. The ash-based additive can improve the utilisation of the whole digestate or the liquor without modification of the traditional splash plate. In fact, there are a number of chemicals and materials that have been investigated to minimise loss of greenhouse gases due to the broadcast spreading [10] and open storage of manure and slurry [9]. An analysis made by the Teagasc Greenhouse Gas Working Group [8] on the strategies for the abatement of this problem, highlighted that the low emission spreading techniques (e.g. soil injection) coming into force are the most expensive technologies. The farmers need to hire these equipment due to the lack of capital investment [38]. Furthermore, the use of these machineries is economically inefficient since their operation cost are more expensive than reasonable carbon prices [8].

Wróbel et al. [33] proposed an economical way of achieving the granulation of the organic wastes treated with ashes by means of creating a mobile granulation unit (i.e. decentralised plant). Our investigation aims to reinforce the synergies between the steps of the process of production of this granular organic amendment in order to reduce the use of energy and resources. We rely on the understanding of the underlying phenomena to propose a connection between chemical and physical stabilisations. If the dewatering is achieved by thermal drying and the active ash could be produced onsite from the combustion of virgin wood. It should be noted that the reactivity and the sorption capacity of biomass ash decrease from the moment it is produced because of reactions with atmospheric moisture and CO₂. On the other hand, the CO₂ produced during the combustion might be enough to be used as an acidifying agent to promote the adsorption onto the ashes of the WS elements of the organic waste, while preventing the volatilisation of NH₃. Even if the solid-liquid separation of the digestate is done prior to the blending with biomass ash, acidification would be required to prevent NH₃ volatilisation. This has been reported by Pesonen et al. [13] when they attempted to produce granules of dried (i.e. 45 % moisture) sewage sludge and wood ash.

3.2.2. Nitrogen speciation

In the second study, the levels of WS NH₄⁺-N in the PVWD (Fig. 5 a) were in agreement with the initial characterisation (689.74 ± 86.78 mg/kg; Table 2), because appropriate dilution of the samples was done for the measurement in the Autoanalyser. The acidification of the PVWD

made a clear difference in preserving the WS $\text{NH}_4^+\text{-N}$, although this effect could not be seen in the WS TN (Fig. 5 c) due to the impact of the samples acidified with HNO_3 in the measurements (Fig. S.11 c). While it is confirmed that the carry-over error occurred in the first study using the Autoanalyser, the values of the WS TN in the second study are less likely to be affected by the carry over.

The concentrations of WS $\text{NO}_3^-\text{-N}$ in the PVWD before and after the blending found in the second study (1.60 ± 2.46 mg/kg blend; Fig. 5 b), with the exception of the blend prepared with HNO_3 , agree with the values found the first study (1.49 ± 2.34 mg/kg sample; Fig. 3 b). The characterisation of the WBA in terms of WS $\text{NO}_3^-\text{-N}$ was not possible due to interactions with the reagents of the colorimetric procedure employed by the Autoanalyser. The undesired reactions also affected the PVWD and reduced the replicates of some conditions. Thus the two-way ANOVA test for balanced design experiments could not be applied to know whether the concentration of WS $\text{NO}_3^-\text{-N}$ in the lactic acid extract was significantly different from the other conditions used to prepare the blend of the WBA with the PVWD (Fig. 5 b).

The amount of WI TN in the PVWD was greater than in the WBA (Fig. 5 d), except when the acidification was done with HNO_3 , because of the adsorption of the WS $\text{NO}_3^-\text{-N}$ onto the WBA (Fig. S.11 c). This effect could not be seen significantly ($\alpha=0.05$) in the first study (Fig. 3 d) and the losses as N_2O were the main effect observed (Fig. 3 c). Herein the procedure followed to prepare the blend (i.e. whether the WBA is acidified before mixing with the PVWD) determined the fate of the nitrogen. This explains the greater nitrogen recovery effectiveness found for the blend prepared with HNO_3 in the second study (Fig. S.12 c). It should be noted that the N_2O release due to abiotic mineralisation could be also present in the second study, as per the progressive decrease in the WS TN shown in Fig. S.11 (b) for the WBA acidified with HNO_3 . On the other hand, the WBA acidified with the HNO_3 showed a significant concentration of WS $\text{NH}_4^+\text{-N}$ (Fig. 5 a). The reason would be the reducing effect of the WBA and the high oxidation capacity of the WS $\text{NO}_3^-\text{-N}$.

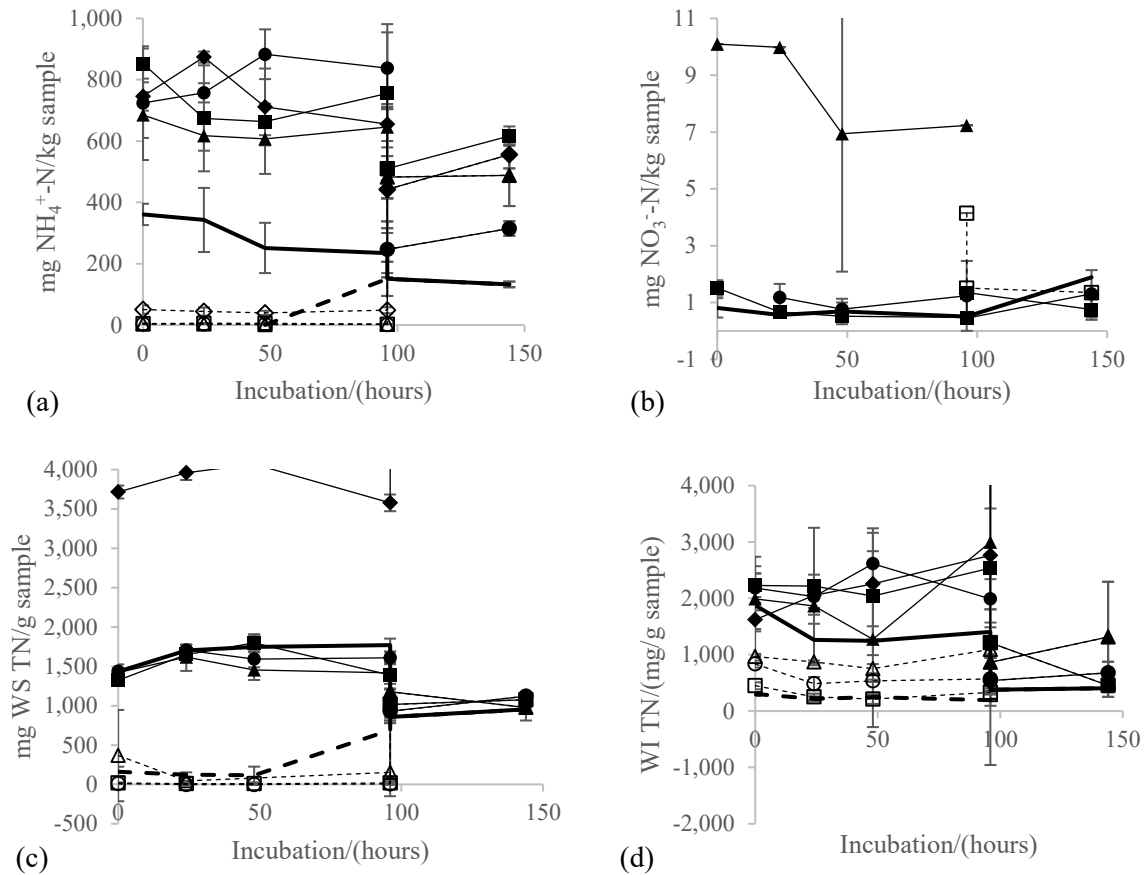


Fig. 5. Characterisation in terms of (a) WS $\text{NH}_4^+\text{-N}$, (b) WS $\text{NO}_3^-\text{-N}$, (c) WS TN, and (d) WI TN of the 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours), under 4 acidification conditions (i.e. H_2SO_4 , HCl , HNO_3 , and CH_3CHCOOH) and no acidification, during the 144-hour incubation.

- 6.29 mmol $\text{H}^+\text{-H}_2\text{SO}_4/\text{g}$ WBA
- 15.21 mmol $\text{H}^+\text{-HCl}/\text{g}$ WBA
- ◇-- 11.97 mmol $\text{H}^+\text{-HNO}_3/\text{g}$ WBA
- △-- 0.16 mmol $\text{H}^+\text{-CH}_2\text{CH}(\text{OH})\text{COOH}/\text{g}$ WBA
- - - 0 mmol H^+/g WBA
- 0.12 mmol $\text{H}^+\text{-H}_2\text{SO}_3/\text{g}$ PVWD
- 0.19 mmol $\text{H}^+\text{-HCl}/\text{g}$ PVWD
- ◆ 0.14 mmol $\text{H}^+\text{-HNO}_3/\text{g}$ PVWD
- ▲ 0.03 mmol $\text{H}^+\text{-CH}_2\text{CH}(\text{OH})\text{COOH}/\text{g}$ PVWD
- 0 mmol H^+/g PVWD

The mass balances of the 3 elements (phosphorus, carbon, and nitrogen), which are offered in the Supplementary material (Fig. S.8, Fig. S.10, and Fig. S.12, respectively), show that only for the nitrogen, the WS fraction is present in similar amounts to the WI fraction in both the PVWD and the blend with the WBA. The same distribution of nutrients (i.e. the nitrogen is the most available element) was found in the mass balances of the first study for carbon and nitrogen (Fig. S.2 and Fig. S.3; respectively). Thus, the treatment of the PVWD with the acids and the WBA need to be improved to reduce the availability of nitrogen as much as all the other elements, to reduce losses before and after land application. The sorption capacity of the

WBA could be enhanced before being added to the PVWD in a similar way the $\text{Ca}(\text{OH})_2$ is prepared with HCl to produce CaCl_2 . The activation with HNO_3 would result in the formation of $\text{Ca}(\text{NO}_3)_2$, which may increase the denitrification to produce N_2O after land application, due to the excessive content of nitrogen in the blended fertiliser [59]. In addition to calcium, the WBA contained other elements such as Mg (Table S.2) and C_{inert} (Table 2) which might be responsible of sorption processes as well.

We are currently carrying out a market research to improve the stabilisation of the organic waste by means of the treatment with ashes. According to this project agricultural advisors, even in high clay soils where the adsorption of $\text{NH}_4^+\text{-N}$ is common, the slurry or digestate injected under very dry conditions (i.e. with cracks in the soil or more than 1 m depth) could potentially run down through and end up in the ground water. The intensification of the manufacturing process of the organic amendment to include the physical stabilisation and pelletisation can improve the control of excess of nitrogen in the soil because of the easier and more accurate spreading [60]. The study of Hou et al. [38] suggested that the willingness of the farmers in using processed organic fertiliser due to the increasing cost of chemical fertilisers and the need to facilitate the export of manure from farm.

The utilisation of the ash to treat the organic waste has also been proposed as technology to achieve the biological stabilisation organic waste before (i.e. killing of pathogens) and after application to land (i.e. promoting beneficial microbial activity in the soil to ensure the supply of nutrient to the crops). The reason might be the high temperatures during the thermal drying, the high pH for the ammonia stripping, and/or the high salinity of biomass ash that mean that microbes cannot thrive in that environment. In fact, Jewiarz et al. [61] could not include a biofertiliser (fungal strains of *Trichoderma* species) in the blend agricultural waste digestate and biomass ash because the microbes would not survive. Ideally the blend would be pasteurised rather than sterilised, to allow the presence of unharmed microorganism [62]. On the other hand, it is expected beneficial microbes will proliferate around the granules of the fertiliser once applied to the soil to improve the fermentation and the supply of nutrients in the rhizome. That is the reason for which the improvements in carbon and nitrogen use efficiency have been investigated when applying simultaneously digestate and wood ash [63–66]. Taking into account the nutrient profile of the ashes, another objective of the treatment was to make the organic waste more competitive with chemical NPK fertiliser.

The AD is regarded as a technology to achieve the biological stabilisation of organic waste [62,67]. Furthermore, it allows a more sustainable bioenergy production compared to the incineration of the dried organic waste which leads to the formation and release to the atmosphere of NO_x . In terms of processing the organic waste, the fermentation also improves the mixing with the ashes. The mineralisation of the organic nutrients makes that the inorganic forms of these nutrient to be more suitable for adsorption onto the ashes and the preparation of a slow release fertiliser. This organic amendment would be less likely to putrefy in the soil. For these reasons, the processing of the organic wastes firstly via AD and secondly with the ash treatment, whether this material is sourced from somewhere else or produced onsite, could be regarded as a good ecological practice.

4. Conclusions

In terms of time required for the chemical stabilisation, in the first study the composition of the blend remained constant straight after the mixing. The severe acidification of the WBA in the second study prevented the increase of the pH of the blend above the initial value of the digestate, thus minimising the losses of NH_3 . Both the sulphuric and the lactic acids decreased the sorption capacity of the WBA and minimised the potential decrease in the availability of the phosphorus, carbon, and nitrogen of the PVWD. It is important to mention that both sulphuric and nitric acids are able to oxidise the organic matter, enhancing the losses of CO_2 . Although the incubation with nitric acid as extractant did not increase the WI fraction of the WBA, the excessive content of nitrogen in the organic amendment would boost the losses of this nutrient before and after land application. Therefore, the hydrochloric acid was considered to be the best option for the acidification of the PVWD and the WBA before the mixing. This would enhance the subsequent solid-liquid separation by means of promoting the dehydration of the WI fraction of the blend. It should be noted that in order to confirm that the hydrochloric acid enhances the adsorption, it would be necessary to determine the content of the Cl^- in both fractions (i.e. WS and WI) of the blend. Alternatively, the HCl could be used in an acid wash pre-treatment, instead of as reactive medium, to minimise the chlorine attached to the surface of the WBA. In this way, the acid wash would be performed after milling, sieving, and calcination of the WBA, as part of the activation of this material, prior to the addition to the PVWD. The impact of the conditions of the chemical stabilisation on the stages of physical and biological stabilisations need to be assessed via measuring the mechanical properties of the pellets (e.g. compressibility strength) and the fate of the nutrients once in the soil.

The results obtained prove the technical feasibility of the chemical treatment of PVWD with WBA but the analysis of the economic viability remains unclear. Further downstream treatments, such as the solid-liquid separation via filtration of the acidified blend of digestate and ash, could be tested to enhance the quality of the final product. The investigation of different waste streams configurations – for example, drying the digestate by direct contact with the combustion gases and the activated ashes from the combustion of the wood pellets – is proposed to achieve optimal capital and operating costs. In parallel to the techno-economical assessment, a primary research market is currently carried out to make sure our investigation addresses the problems of the stakeholders of the agro-industry at both sides of the supply and demand chain of organic wastes. It is necessary to take into account the economic aspects which limit the implementation of the AD (e.g. investment capital, processing cost, and payback period), at the time of designing business-friendly processes for the manufacturing of novel soil amendment. Therefore, it would be worth exploring the ash treatment on materials which have undergone poor fermentation (e.g. manure and slurry) or even waste types that have not been biologically processed (e.g. crushed organic waste).

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