Chemical stabilisation of anaerobic digestate *via* wood ash-based treatment

Alejandro Moure Abelenda (MEng, AFHEA)

This thesis is submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

February 2022

Supervisor:

Dr Farid Aiouache

Co-supervisors:

Prof George Aggidis

Prof Kirk T. Semple

Dr Ben M. J. Herbert

School of Engineering & Lancaster Environment Centre

Faculty of Science and Technology

Lancaster University

Engineering and Physical Sciences Research Council

Declaration

The candidate declares that this thesis is his own work and he has not submitted it elsewhere for the award of a PhD degree. This thesis is the result of joint research by the School of Engineering and the Lancaster Environment Centre. The chapters that have been published are specified in the thesis with an authorship statement for each of them.

Alejandro Moure Abelenda

Abstract

The depletion of world´s mineral resources increases the cost of production of chemical fertilisers for agriculture, due to the need for extraction of raw materials in poorly accessible and inconvenient sites. An enhancement of the circular economy by means of reprocessing clean nutrient-rich waste materials will also address environmental challenges associated with the low use efficiency of the nutrients, which leads to pollution of water, soil and air due to the excessive fertilisation of fields to maintain crop yields and provide enough foodstuff. This thesis investigates the treatment of anaerobic digestate with wood ash and commercial acids (*i.e.* sulphuric, hydrochloric, nitric and lactic acids) for the preparation of a stable slow-released fertiliser and mineral products, such as ammonium sulphate. The extraction of the biogas from the anaerobic digestate implies the mineralisation of some organic nutrients (*e.g.* organic nitrogen; N_{org}), thus becoming more available for plants (*e.g.* formation of ammoniacal nitrogen; NH_4^+-N). The application of this material to land represents a problem due to the volatilisation of ammonia and leaching of nitrate (after nitrification of ammonium in the soil) and phosphate. The role of the wood ash as sorbent could be used to control the availability of the nutrients already present in the anaerobic digestate. Moreover, the wood ash provides additional phosphorus to generate a more balanced organic fertiliser, according to the type of crop. The investigation of the wood ash treatment of the anaerobic digestate under different pHs was necessary to find the best blending conditions of these two waste streams. A food waste digestate (FWD) and a post-harvest vegetable waste digestate (PVWD) were the two types of organic material considered. A wood fly ash (WFA) and a wood bottom ash (WBA) were the two types of sorbents employed and they were produced in the same combined heat and power plant. Among these samples, the best controlled-release soil organic amendment was found to be produced by blending the PVWD, which has a lower ratio NH_4^+-N/N_{org}, and the WFA, which is the finer fraction of the ashes with more black carbon content and surface area to enhance the sorption processes. The pH of zero charge of WFA (11.90 ± 0.50) was found to be the optimum and it could be attained by mild acidification with HCl, maintaining a blending ratio lower than 3 g total solids (TS) WFA/g TS FWD or using non-invasive H_2SO_4 acidification (*i.e.* closed chamber) to recover the NH_3 volatilised. The solid-liquid separation of the blend of wood ash and anaerobic digestate was performed as part of the analyses of the availability of the nutrients (N, C and P). Nevertheless, a more detailed study needs to be conducted on whether this share of wood ash is enough to produce a granular fertiliser with sufficient mechanical properties (*e.g.* durability) for packaging commercialisation.

Acknowledgements

The candidate would like to acknowledge the support that received from the School of Engineering, the Lancaster Environment Centre and the Faculty of Science and Technology of Lancaster University to write this thesis. Furthermore, the candidate would like to express his sense of gratefulness for the unconditional support of the supervisory team of this PhD thesis Dr Farid Aiouache, Prof George Aggidis, Prof Kirk T. Semple and Dr Ben M. J. Herbert. Special mention is due to the leading role of Dr Aiouache, who coordinated this project and make possible the submission of this thesis. Dr Aiouache was awarded with a scholarship from the Engineering and Physical Sciences Research Council (EPSRC) of the United Kingdom and he used the funding to cover the tuition fees of Lancaster University and provide the candidate with a stipend for 3.5 years. His role as coordinator of the previous AVAnD project involved the supervision of two postdoctoral research associates, Dr Alfonso Lag Brotons and Dr Rachel Marshall, who assisted the PhD candidate in the design of experiments and the laboratory training on analytical techniques. Dr Aiouache sought for additional funds to allow the candidate to complete the experiments for this thesis, in the plant-soil lab of the Lancaster Environment Centre. Last but not least, the candidate would like to recognise the importance of the parental support received from Manuel Moure Beiroa and María Dolores Abelenda Mallo.

Table of contents

List of tables

List of figures

List of equations

Abbreviations

AC	Activated Carbon
AD	Anaerobic Digestion
AF	Anaerobic Filters
Anammox	Anaerobic Ammonium Oxidation
ANOVA	Analysis of Variance
AVAnD	Adding Value to Ash and Digestate
BET	Brunauer, Emmett and Teller
BC	Black Carbon
BMP	Biochemical Methane Potential
BSI PAS 110:2014	British Standards Institution's Publicly Available Specification for Anaerobic Digestate
BOD	Biological Oxygen Demand
C	Carbon
CATNAP	Cheapest Available Technology Narrowly Avoiding Prosecution
CFA	Coal Fly Ash
CHP	Combined Heat and Power
CSTR	Continuous Stirred Tank Reactor
COD	Chemical Oxygen Demand
CO_3^{2-}-C	Carbon in the Form of Carbonate
CUE	Carbon Use Efficiency
C/N/P	Nutrient Ratio
DM	Dry Matter
EC	Electric Conductivity

EoW	End-of-Waste
EPSRC	Engineering & Physical Sciences Research Council
FWD	Food Waste Digestate
GHGs	Greenhouse Gases
H_2SO_4 trap	Trap for NH_3 Containing a Solution of H_2SO_4
K	Potassium
K-struvite	$MgKPO_4 \cdot 6H_2O$
Lime	Mixure of CaO, $Ca(OH)_2$ and $CaCO_3$
Limestone	$CaCO_3$
mEq	MilliEquivalent
MSDS	Material Safety Data Sheet
MSW	Municipal Solid Waste
N	Nitrogen
NERC	Natural Environment Research Council
NH_4^+-N	Ammoniacal Nitrogen Contained the Species NH_4^+ & NH_3
NRM	Natural Resources Management
N_{org}	Organic Nitrogen
NO_3^--N	Nitric Nitrogen Contained in the Species NO_3^- & NO_2^-
NPK fertiliser	Synthetic Material Containing Nitrogen, Phosphorus and Potassium
OLR	Organic Loading Rate
OM	Organic Matter
P	Phosphorus
pH_{zpc}	pH of Zero-Point Charge
PLA	Poultry Litter Ash

P_{org}	Organic Phosphorus
PVWD	Post-harvest Vegetable Waste Digestate
qCO_2	Metabolic Quotient
QPAD	Quality Protocol of Anaerobic Digestate
QPPLA	Quality Protocol of Poultry Litter Ash
Quicklime	CaO
SEM-EDX	Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy
RBP	Residual Biogas Potential
rpm	Revolutions Per Minute
SS	Sewage Sludge
Struvite	$MgNH_4PO_4 \cdot 6H_2O$
S/E	Sample to Extractant Ratio
S/I	Substrate-to-Inoculum Ratio
Slaked lime	$Ca(OH)_2$
t	Metric Tonne
TOC	Total Organic Carbon
TS	Total Solids
VFA	Volatile Fatty Acid
vol.%	Percentage in Volume
VS	Volatile Solids
WBA	Wood Bottom Ash
WFA	Wood Fly Ash
WI	Water-Insoluble
WRAP	Waste and Resources Action Programme

WS	Water-Soluble

1. Introduction, research aim and objectives, and outline of the thesis

The growth of human population and the change in the diet (*e.g.* more consumption of animal products) implies to devote more land for food production at an alarming rate (Banwart, 2011). The problem of the current agricultural practices is not limited to the land management but also to the unsustainable consumption of essential nutrient for plants, such as phosphorus (P) (Elser & Bennett, 2011; Vaccari, 2009). In terms of mineral resources, the total amount of raw materials in the earth crust are known as deposits; however, only the economically and technically exploitable deposits at a given time are regarded as reserves (Roberts & Stewart, 2002). This means that the depletion of some reserves encourages the search for new ores which augments the available deposits and reserves (USA Geological Survey, 2021). The fluctuation of the prices helps to preserve the long term availability of these mineral resources (Cordell *et al.*, 2009). On the other hand, this idea is opposite to the general understanding that the free market of the capitalism economic system, in absence of any government regulation, does not help to reduce the consumption of materials (Korczynski, 2005). In the present situation, the development of profitable strategies for the utilisation of the waste materials is the only way to achieve a sustainable development of the society (Hsu, 2021).

1.1. Waste management system

The recycling technologies are alternatives to resource-intensive processes and prevent the depletion of raw materials (Dela Piccolla *et al.*, 2021). They are components of the waste management systems (Figure 1.1) and can be divided into physical, biological and thermo-chemical treatments. It is important to highlight that when designing a waste management system, prevention and minimisation of waste should be considered before any reprocessing technology (Demirbas, 2011). The industrial symbiosis in Kalundborg (Denmark) is an example of a waste management system which was designed to reduce the disposal materials while enhancing the economy of the process (Chertow, 2000). Once a material is regarded as waste, its utilisation is constrained by the regulations (European Parliament, 2018). In Europe, all the waste-derived products need to comply with the Directive 2018/851 but there are short cuts to achieve the end-of-waste (EoW) status. Generally, when a residue is produced in large amounts and has a composition suitable for a particular application, the European parliament rules EoW regulations do not need to be transposed by the governments of each member state and they are directly in force (Saveyn & Eder, 2014). The European Commission estimated that production of both manure and slurry in the EU27, before Croatia's accession in 2013, was about 1.4 billion tonnes per year (AMEC Environment & Infrastructure UK limited, 2014). Production of digestate and compost were around 180 and 17.3 million tonnes per year respectively, in the EU28, before the UK withdrawal in 2020 (Corden *et al.*, 2019). In 2009 (Blumenthal, 2014), the EU27 produced 256 million tonnes of municipal solid waste (MSW). Much more animal manure is applied to land as soil amendment than anaerobic digestate, because of the high capital expenditure (CAPEX) and operational expendinture (OPEX) associated with the implementation of the anaerobic digestion (AD) in the farms (Hou *et al.*, 2018). In the UK, 7.5 million tonnes of anaerobic digestate and 2.7 million tonnes of compost were produced in 2018 (Victor, 2020). A common policy is being developed to improve the management of all nitrogenous materials employed as soil amendments (Wood *et al.*, 2020).

In total about 95 – 97 % of the world's bioenergy is currently produced by direct combustion of biomass. It was estimated that approximately 480 million tonnes of biomass ash could be generated worldwide annually if the burned biomass is assumed to be 7 billion tonnes, hence this quantity is comparable to that of coal ash, namely 780 million tonnes (Vassilev *et al.*, 2013). The wood ash production in the UK could be estimated considering that the 1 % of the wood incinerated is left as ash (Pitman, 2006). According to the UK Forestry Commission (2016), 2.68 million tonnes of woodfuel were used in 2016. Even if the combustion of other types of biomasses is considered, the amount of biomass ash currently produced in the UK is lower than the one coming from the coal power plants. In 2016, the amount of coal ash produced in the UK was around 6 million tonnes (UK Quality Ash Association, 2016). However, this scenario is changing and by the 2025 is expected the amount of biomass ashes to be greater than that of coal ash (UK Quality Ash Association, 2021). In 2007, Sweden produce 0.3 million tonnes of wood ash and most of this material was disposed in landfills (Andersson, 2007).

After the end of the Brexit (Britain's exit of the European Union) transition period (*i.e.* 1st January 2021), the UK kept the EU regulations on iron, steel and aluminium scrap, glass cullet and copper scrap. The UK Government has also produced quality protocols with the same purpose of easing and speeding up the utilisation of these materials and preventing its accumulation (UK Government, 2021b). For example, the UK Government created the quality protocol of poultry litter ash (QPPLA), since this type of ash is produced in large amounts and is suitable to be used as fertiliser due to its high content of P and low content of pollutants (Codling *et al.*, 2017; Fahimi *et al.*, 2020; WRAP, 2012a). Developing countries aspire to have similar waste management systems with reprocessing technologies for clean, source segregated materials (Demirbas, 2011). Nevertheless, technologies with great potential to enhance the circular economy, such as AD, are yet to be fully widespread in Europe due to the high capital investment (Hou *et al.*, 2018).

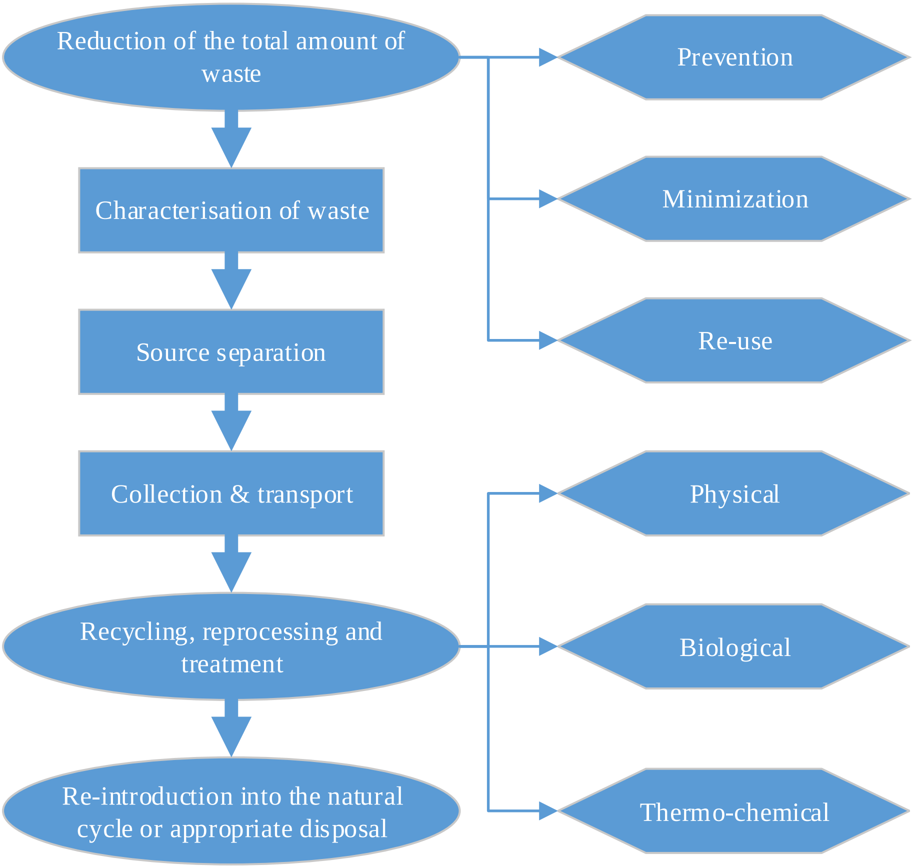


Figure 1.1. Components of a waste management system. Elaborated from Demirbas (2011) and European Parliament (2018).

1.2.Anaerobic digestion (AD)

The biological treatment of organic residues *via* AD is a promising technology for energy recovery, in the form of biogas, and for the production of fertilisers (Holm-Nielsen *et al.*, 2009). The AD was firstly applied to deal with the sewage sludge (SS) produced during the primary and secondary treatment of wastewater but its use to deal with the agrowaste and with the MSW with around 70 % of organic material has been subsequently encouraged (Bond & Templeton, 2011; Dagnall, 1995). The AD technology fits with the current trends of using the biorefinery to sustainably satisfy the needs of the society, which used to be covered by the petrochemical industry (Madsen *et al.*, 2011).

The AD process is also known as biogasification due to the intervention of the microorganism to convert the components of the organic matter (OM) to methane (CH_4) and carbon dioxide (CO_2). The most accepted model on how the reactions take place in the anaerobic digester in the absence of oxygen describes 4 different stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 1.2) The limiting step is the hydrolysis, whilst the methanogenesis is quick therefore, preventing the accumulation of the volatile fatty acids (VFAs) in the system. In this way, the concentration of VFAs in the anaerobic digestester could be used as an indicator of the correct stationary operation of the bioreactor (Madsen *et al.*, 2011).

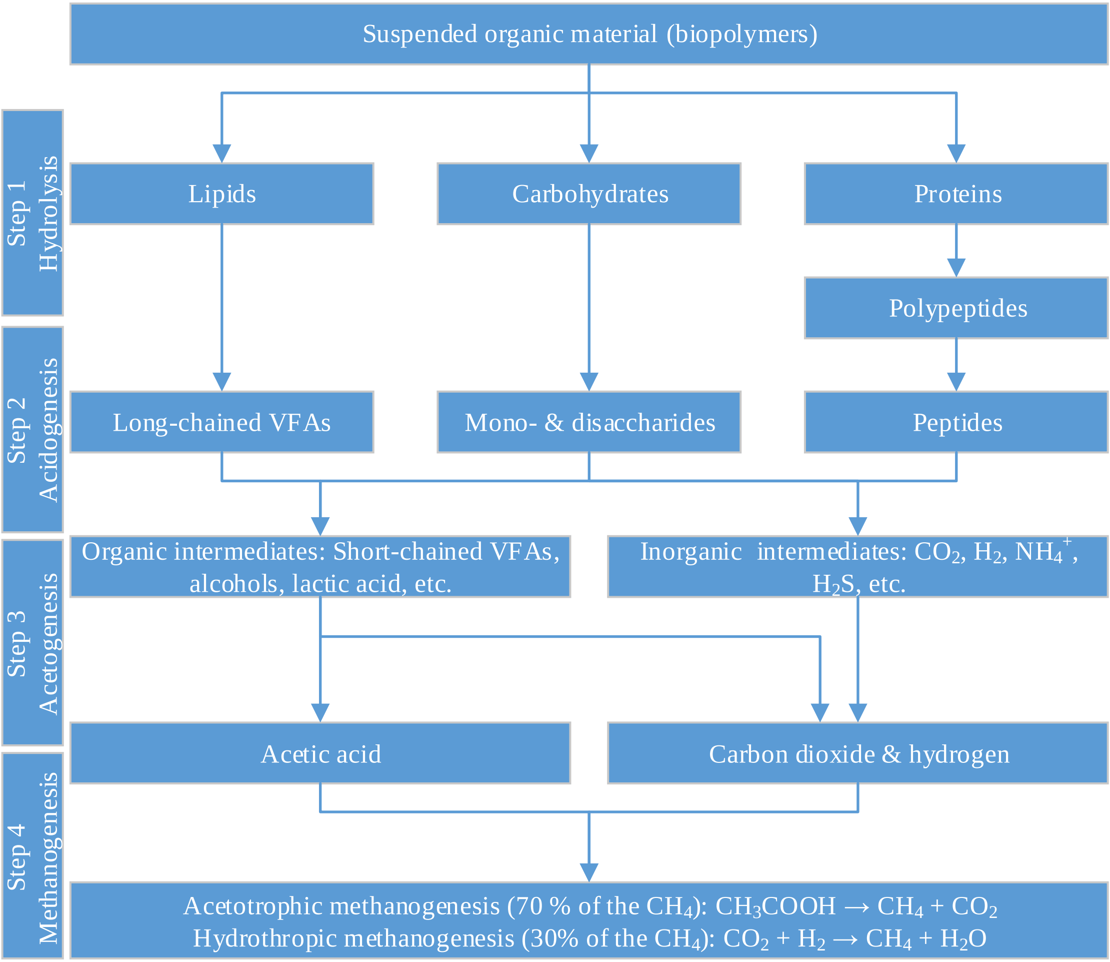


Figure 1.2. Breakdown of the AD process. Modified from Madsen *et al.* (2011).

1.3.Utilisation of anaerobic digestate as fertiliser in the UK

AD is a waste recovery operation; therefore, it must comply with the waste management controls and the environmental regulations. The Waste and Resources Action Programme (WRAP), in collaboration with the UK Government, has produced the quality protocol of anaerobic digestate (QPAD) to rule the utilisation of this material and the products obtained after simple processing (*i.e.* separated liquor and separated fibre) as soil amendments (WRAP, 2014b). The specifications of the products obtained *via* advanced processing and supplementation of the anaerobic digestate are out of the scope of the QPAD. According to the QPAD (WRAP, 2014b):

> "*1.3.4. If digestate which is compliant with this Quality Protocol is mixed with non-waste materials the blend will not, as a result of that, be waste.*
>
> *1.3.5. If digestate, which is compliant with this Quality Protocol, is mixed with a waste, the resulting blend will all be waste.*"

Thereby, if the quality digestate is mixed with a waste material (*e.g.* wood ash) to improve the nutrient profile, it would be required to conduct a self-assessment of the blend as specified by the Environment Agency (2021) before the utilisation of these materials as soil conditioners. The detailed specifications for a certified anaerobic digestate were published by the WRAP (2014b) and is regarded as the British Standards Institution's Publicly Available Specification 110 (BSI PAS 110:2014). The QPAD sets the framework for the application of the BSI PAS 110:2014 (Figure 1.3), which states the upper limit of the parameters that needs to be measured in the digestate. According to the BSI PAS 110:2014, a pasteurisation or equivalent treatment (able to reduce plant pathogen indicator species) is required for the anaerobic digestate to be regarded as fertiliser. The pasteurisation step requires to heat all the material to at least 70 °C for one hour. The pasteurised material might contain beneficial or harmless microorganisms (WRAP, 2014a). The protocol for conducting the residual biogas potential (RBP) test to characterise the stability of the anaerobic digestate needs to be found elsewhere (Banks *et al.*, 2013). The term stability refers to amount of biogas that remains in the AD. The BSI PAS 110:2014 states an upper limit of 0.45 L biogas/g volatile solid (VS) and any anaerobic digestate releasing a greater amount of biogas should undergo further anaerobic fermentation before being applied to land. The reason is that the biogas contains approximately 60 % in volume (vol.%) CH_4 and 40 vol.% CO_2 (Herout *et al.*, 2011), which are both greenhouse gases (GHGs).

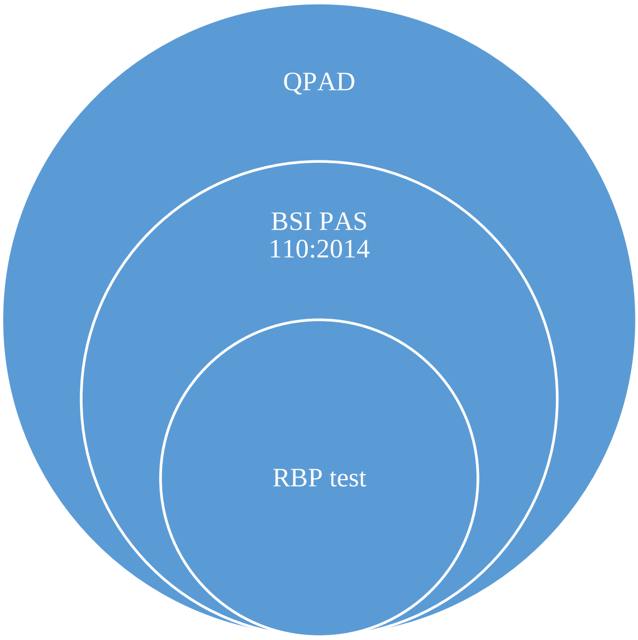


Figure 1.3. EoW criteria for digestate in the UK. Elaborated from WRAP (2014b).

1.4.GHGs emissions associated with agriculture

The agriculture contributes to approximately 30 % of the GHG total emissions (Lal, 2021). In addition to CH_4 and CO_2, the nitrous oxide (N_2O) is considered another big contributor to climate change. Ammonia (NH_3,) is an atmospheric pollutant and it is considered that 1 % of the emissions of ammonical nitrogen (NH_4^+-N) and nitrogen oxides (NO_x-N) are converted to N_2O after dry and wet depositions (IPCC, 2019). It should be noted that the N_2O is a GHG with 298 times greater global warming potential than the CO_2 (Kavanagh *et al.*, 2019).

The Clean Air Strategy that was established in 2019 in the UK identified the agriculture sector as the main source of NH_3 (UK Government, 2019): 88 % of the total emission of NH_3 are associated with storage and land-spreading of manures, slurries and anaerobic digestates in 2016 (UK DEFRA, 2018). For this reason, there is a requirement of full implementation of low-emission spreading equipment (*i.e.* trailing shoe, trailing hose or soil injection) by 2025 and covering the slurry and digestate stores by 2027 (UK Government, 2019). In line with this strategy is the Slurry Investment Scheme that offers subsidies to enable the implementation and compliance with the Agricultural Transition Plan (UK DEFRA, 2020a, 2020b).

The AD is able to degrade approximately the 20 – 95 % of the OM, depending on the composition of the feedstock. This biological transformation technology stabilises the anaerobic digestate, since less GHGs remain to be lost during the subsequent stages of storage and land application of the organic soil amendment. It should be noted that the less than 1 %

of the NH_4^+-N is volatilised in the biogas stream during the AD (Möller & Müller, 2012). Thereby, the emissions of NH_3 still need to be tackled using the measurements proposed by the UK Government (UK DEFRA, 2020a, 2020b) or the additives investigated by Teagasc (Agriculture and Food Development Authority of Ireland, 2021; Brennan *et al.*, 2015; Kavanagh *et al.*, 2019, 2021).

The degradability of the AD feedstock determines the extent of the mineralisation of complex organic nitrogen (N_{org}) compounds, thus the increase in the share of ammoniacal nitrogen NH_4^+-N and the decrease of the carbon (C) content. There is no clear evidence that the increase in NH_4^+-N content in anaerobic digestate, compared to the feedstock, would ensure higher nitrogen (N) uptake efficiency and greater savings in mineral fertiliser (Möller & Müller, 2012). An excess of application of organic manures, such as anaerobic digestate, to reach the targeted crop yields leads contamination of surface and underground waters due to phosphate and nitrate leaching (European Commission, 2020; Sogn *et al.*, 2018). Efforts are being made to improve the performance of the anaerobic digestate as fertiliser by supplementing this material with nitrification inhibitors (Pereira *et al.*, 2010) and biomass ash to improve the availability of P (Richards *et al.*, 2021).

1.5. Context of this PhD project for developing a suite of novel land conditioners and plant fertilisers from the waste streams of biomass energy generation

This PhD project is in line with the activities that were conducted as part of the Adding Value to Ash and Digestate (AVAnD) project (Lancaster University, 2020). The aim of the AVAnD project was to produce fertilisers, by means of blending bioenergy waste streams, that provides similar crop yields to that of the mineral fertilisers whilst inducing neutral or positive effects in the plant-soil system (Richards *et al.*, 2021). This would be a way of enhancing the circular economy and minimising the consumption of resources (Lag-Brotons *et al.*, 2020; Marshall *et al.*, 2020). The participants of the AVAnD project were the Lancaster Environment Centre, the School of Engineering of Lancaster University, the James Hutton Institute, AquaEnviro Ltd and Stopford Projects Ltd as industrial partners. This project received financial support (Reference: NE/L014122/1) from the UK Natural Environment Research Council (NERC, 2021) and the Resource Recovery from Waste programme (Lancaster University, 2017).

The AVAnD project focused on screening anaerobic digestates derived from source-segregated organic waste (mainly food) and biomass ash fractions (mainly derived from wood). It made a preliminary screening of six different types of ash, including fly and bottom ash fractions collected in each site, and six different types of anaerobic digestates. The deliverables of the AVAnD project were divided into three work packages (WP) going from characterisation of the samples in the laboratory and formulation of the blends (WP1) to subsequent testing laboratory/greenhouse scale (WP2) and mesocosms under field conditions (WP3). In this way, one of the main outcomes derived from AVAnD WP1 was the selection of those samples with better characteristics to produce a blended fertiliser. The samples selection criteria primarily implied presence of desired components (plant nutrients; total N-P content) and absence or low content of pollutants (*e.g.* heavy metals). During the three years of the project, the tests focused primarily on the role of the blends as potential fertilisers/soil conditioners, yet did also consider potential undesired effects (*e.g.* leaching potential). The blended fertilisers of anaerobic digestates and wood ashes intended to have a nutrient ratio N/P/K of 3/1/1, but only 2 nutrients out of 3 were able to be controlled in the preparation of the blends. The attained N/P of 3/1 was in agreement with the commonly reported wheat fertilisation practice (N-P ratios) informed by wheat nutritional requirements (UK AHDB, 2021a), which was convenient for the cultivation of winter wheat (*Triticum aestivum* sp.) in the UK. The ratio was based on total N and total P available in the wood ashes and the anaerobic digestates, thus not only the water-soluble (WS) readily available forms (*e.g.* NH_4^+-N and PO_4^{3-}-P) were taken into account. In this thesis, the term availability is used to refer to how likely is for a nutrient to be absorbed by plants. This means that the most available nutrients are those that are more reactive and more susceptible to be lost *via* leaching and volatilisation. Due to time constraints, a simple mixing approach was taken in the AVAnD WP2 & WP3, which led to limitations in the scope of the study. For example, this simplification of the experimental design implied uncertainty surrounding N-P dynamics because the losses during the preparation of the blended fertilisers and the stability within ash-digestate mixtures were not properly characterised.

The AVAnD project contributed to a policy briefing to inform the regulators and local authorities on the benefits of recycling the wood ash and the anaerobic digestate (UK Government, 2017). The divulgation of the results of the investigation was important because of the general concern about the use of the biomass ash (Vassilev *et al.*, 2013, 2014) and the suitability of the anaerobic digestate as a fertiliser (García-Sánchez *et al.*, 2015). The re-introduction of these elements into the natural cycle is part of the last element of the waste management system (Figure 1.1). The anaerobic digestates selected in the AVAnD project were certified by the BSI PAS 110:2014, thus could be applied to land as soil amendment. However, reaching the EoW status of the wood ashes (fly and bottom fractions) was a more challenging task since there was no straightforward Quality Protocol available for type of waste and the QPPLA was not directly applicable (WRAP, 2012a). An individual self-assessment of the wood ashes according to the Environmental Agency (2021) would be more tedious and time-consuming. The lengthy bureaucratic procedures limit the interest of the combined heat and power (CHP) plants, where the wood ashes are produced, the agroindustry and other stakeholders involved in the valorisation of wood ash, for the utilisation of these materials as fertilisers and liming agents. The utilisation of wood ash and anaerobic digestate as valuable resources in agriculture reduces the ecological impact and the regulatory burden of the industries where these residues are produced and reinforce the green credentials of agriculture (Fivelman, 2013). Otherwise, it could be expected high demand for synthetic inorganic fertilisers and ullage in the renewable energy production resulting from the combustion of biomass and the biogasification (Laohaprapanon *et al.*, 2010).

In addition to this PhD scholarship, the outcomes of the AVAnD project were included in the following funding proposals: (1) Global Challenges Research Fund (GCRF) – Economic and Social Research Council (Reference: ES/P010857/1, 2017-22): Growing Research Capability to Meet the Challenges Faced by Developing Countries. Driving Eco-Innovation in Africa: capacity building for a safe circular water economy. (2) International Opportunities Fund (Reference: NE/R005230/1; 2018-20). Bioenergy waste residues as alternatives to conventional inorganic fertilisers for sustainable food production in sub-Saharan Africa (including partners from Nigeria, Ghana, Kenya and Malawi). (3) GCRF Global Research Translation Award (Reference: EP/T015608/1; 2019-2021). Accelerating the adoption of circular sanitation demonstration systems for improved health outcomes (ACTUATE), with partners in Nigeria and Ghana.

1.6.Novelties of this PhD thesis

Before this PhD thesis, the preparation of a blend of organic manure and ash to enhance the circular economy has been addressed in the literature from several points of view:

- To enhance the AD process (Guerrero *et al.*, 2019).
- To improve the properties of the soil (Fernández-Delgado Juárez *et al.*, 2013).
- To promote the crop growth (Ibeto *et al.*, 2020, 2022).
- To control the release of the nutrients (Fenton, 2011).
- To prevent gaseous emissions and leaching during storage and land application (Brennan *et al.*, 2015).

- To achieve a better dewatering of the digestate (Zheng *et al.*, 2016).
- To promote the self-hardening and granulation of the digestate (Pesonen *et al.*, 2016).

In addition, the previous AVAnD project intended to formulate a blend of digestate and ash to commercialise a novel fertiliser, based on crop yield results obtained from field and pot experiments (Richards *et al.*, 2021).

This PhD thesis was inspired by the AVAnD project concept and outcomes but, especially, by the uncertainties and research directions derived from WP1: Improving the nutrient profile of the digestate might be a way of increasing its value and decrease the cost of transportation. The contribution to the knowledge of this PhD scholarship, which was funded by the Engineering and Physical Sciences Research Council (EPSRC; Reference: EP/N509504/1) for 3.5 years (*i.e.* from October 2016 to April 2020), was the elucidation of the underlying chemistry of blends of wood fly ash (WFA) and wood bottom ash (WBA) with food waste digestate (FWD) and post-harvest vegetable waste digestate (PVWD). The conditions of the wood ash-based treatment of the anaerobic digestate were optimised to reduce the cost and consumption of reagents, improve the stability of the soil organic amendment, enhance the nutrients use efficiency and reduce the contamination of the environment. The concept of pH of zero-point of charge (pH_{zpc}) was applied for first time to the preparation of a blend of wood ash and anaerobic digestate. The experimental and analytical setup of the static chamber with a sulphuric acid trap (H_2SO_4 trap) was modified to allow the better characterisation of the blending process, particularly in terms of reaction kinetic and mass transfer models of NH_3 (Chapter 6). This thesis directly addresses the findings of the primary and secondary market research, which highlights the importance of the organic manures to the farm economy (Moure Abelenda & Amaechi, 2022) and the urgent challenge of mitigating the pollution associated with the handling of nitrogenous materials (Wood *et al.*, 2020).

1.7.Research aim and objectives

As a continuation of the AVAnD project, the research aim of this thesis was to explore the efficacy of wood ash as a treatment for anaerobic digestate with the purposes of stabilisation, to minimise the release of GHGs, and preparation of a slow-released fertiliser for an effective management of the nutrients to prevent the eutrophication of underground waters. In order to achieve this aim, the following experiments of increasing complexity and difficulty were defined as primary and secondary objectives:

1) Characterise the two samples of wood ash and the two samples of anaerobic digestate selected in the AVAnD project, in terms of C, N, P and trace elements.
    - With regard to organic carbon (C_{org}) and N_{org} are essential nutrients for microbes and plant.
    - In relation to P, it is important to evaluate the fate of this element because there is an increasing concern about its sustainable supply for the manufacturing of the fertilisers.
2) Evaluate the combination of the raw (*i.e.* untreated) samples to meet the targeted nutrient ratio in terms of the speciation of C, N and P. This implies to:
    - Characterise the WS extract to assess the availability of the nutrients and the potential losses *via* leaching of the two blends of three samples.
    - Select the best samples for the preparation of two blends of two components, which and lead to the correct availability of the nutrients to minimise pollution during storage and land application, hence maximise the crop growth.
3) Titrate each sample of anaerobic digestate and wood ash to determine the amount of acid that is required for conditioning before the preparation of the two blends at the desired pH. In order to expand the understanding of the acidification process, it was necessary to:
    - Employ the most widely used commercial acids in the agroindustry to decrease the pH of the samples of anaerobic digestates and wood ashes: sulphuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and lactic acid ($CH_3CH(OH)COOH$).
4) Characterise the interaction of the acidification agents with the samples of anaerobic digestate and wood ash by means of performing computer simulation and modelling of the titrations of the samples with various acids.
    - The software Visual MINTEQ will allow elucidating the role of the anions provided by the acids. Determine the best acidification agent to prepare two blends of wood ash and anaerobic digestate at the targeted pH.
5) Evaluate the speciation of C, N and P in the best blend of wood ash and anaerobic digestate, prepared with several acidification agents at the target pH. This evaluation will require to:
    - Establish the mass balances of C, N and P considering the analyses of the WS fraction and the water-insoluble (WI) fraction of the acidified blend.

6) Use a closed chamber with a H_2SO_4 trap to account directly the ammonia volatilisation during the preparation of the acidified and the unacidified blends. This will allow to:
    - Compare the wood ash treatment against other nutrient management technologies, such as nitrification.
    - Determine the kinetics of ammonia volatilisation and the feasibility of recovery of the NH_4^+-N *via* reactive stripping with the H_2SO_4 trap.
    - Establish the mass balance of N considering amount of this element in the WS and WI fraction and in the H_2SO_4 trap.

1.8.Structure of the thesis

This thesis is presented in the classic structure with the following chapters:

- Chapter 1 introduces the motivation for the research, novelty, aim and objectives, and outline of the thesis.
- Chapter 2 is a literature review section that is focused on relevant processes, physico-chemical phenomena and reactions involving wood ash, anaerobic digestate and/or any of the components of these materials to achieve the stabilisation, reduce the gas emissions and the leaching of nutrients. This literature review justifies the novelty and the experiments that were conducted to achieve the objectives of this PhD thesis.
- Chapter 3 assesses two blends of anaerobic digestate and wood ash without acidification (two samples of each type). This chapter includes the characterisation of the samples that were employed in this PhD project, particularly focussing on the WS species.
- Chapter 4 determines the optimum pH for the preparation of the blends of anaerobic digestates and wood ashes: severe acidification and pH_{zpc}.
- Chapter 5 evaluates a blend of anaerobic digestate and wood ash with acidification (a sample of each type). This chapter introduces the analysis of the WI phase of the blended fertiliser.
- Chapter 6 evaluates a blend of anaerobic digestate and wood ash in a closed chamber. This setup with a H_2SO_4 trap allows to measure the NH_4^+-N in the gaseous fraction of the blended fertiliser. Furthermore, the comparison of the nutrient profile is done with respect to the first point of each measured in the incubation rather than initial characterisation containing parameters determined by the external laboratory.

- Chapter 7 is a kinetic study on the release of ammonia from a blend of anaerobic digestate and wood ash in a closed chamber. The low dose of WFA allows to reach the pH_{zpc}.
- Chapter 8 assesses the feasibility of the recovery of the ammonia release from a blend of anaerobic digestate and wood ash in a closed chamber.
- Chapter 9 includes concluding remarks from each of the previous chapters of the thesis and recommendations for future work.
- Appendix contains supplementary material cited in the chapters of this thesis.

1.9.Statement of authorship

The results presented in this thesis correspond with excerpts from the following articles:

- Chapter 2 is based on the published article: **Moure Abelenda, A.** and Aiouache, F. (2022) Wood Ash Based Treatment of Anaerobic Digestate: State-of-the-Art and Possibilities, *Processes*, *10*(1), 147. https://doi.org/10.3390/pr10010147.
- Chapter 3 is based on the published article: **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021). Effects of wood ash-based alkaline treatment on N, C and P availability in food waste and agro-industrial waste digestates. *Waste and Biomass Valorization*, *12*(6), pp. 3355–3370. https://doi.org/10.1007/s12649-020-01211-1.
- Chapter 4 is based on the article published: **Moure Abelenda, A.**, Semple, K. T., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2022). Strategies for the production of a stable blended fertiliser of anaerobic digestates and wood ashes. *Nature-Based Solutions*, 100014. https://doi.org/10.1016/j.nbsj.2022.100014.
- Chapter 5 is based on the published article: **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021). 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. *Journal of Environmental Chemical Engineering*, *9*(1), 105021. https://doi.org/10.1016/j.jece.2020.105021.
- Chapter 6 is based on the article published: **Moure Abelenda, A.**, Semple, K. T., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2022). Valorization of agrowaste digestate *via* addition of wood ash, acidification, and nitrification. *Environmental Technology & Innovation. 28*, 102632. https://doi.org/10.1016/j.eti.2022.102632.

- Chapter 7 is based on the published aarticle: **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021). Kinetic study of the stabilization of an agro-industrial digestate by adding wood fly ash. *Chemical Engineering Journal Advances*, *7*, 100127. https://doi.org/10.1016/j.ceja.2021.100127.
- Chapter 8 has been published as **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M., Aggidis, G., & Aiouache, F. (2021). Alkaline wood ash, turbulence, and traps with excess of sulphuric acid do not strip completely the ammonia off an agro-waste digestate. *Edelweiss Chemical Science Journal*, *4*(1), 19–24. https://doi.org/10.33805/2641-7383.127.

1.10. Publication history

The studies for developing the wood ash-based treatment of the anaerobic digestate, to achieve the chemical stabilisation (Figure 2.4), were carried out following an increasing level of complexity. This was considered to be the best methodology for elucidating the underlying chemistry of the blend of wood ash and anaerobic digestate and design a holistic process for the preparation of the stable soil organic amendment that minimised the capital and operating costs. Each study, which helped to improve the conceptualisation and design of the process, was made available to the public domain as described in Table 1.1. The same batches of WFA and WBA, which were sampled at the CHP plant of a sawmill, were used to conduct all the experiments. The wood ash samples were stored at room temperature to minimise the contact with the open atmosphere. On the other hand, fresh samples of the anaerobic digestate were procured to conduct the experiments of Chapter 6 onwards. The anaerobic digestates were stored in jerry can at 3 ºC to prevent the volatilisation of NH_3. In compliance with the research ethics, the confidential information of the suppliers of the samples was not disclosed in any of the articles in the public domain. The Chapter 2 of literature review was the last article to be prepared, once all the possibilities for the wood ash-based treatment of the anaerobic digestate were understood, since a short literature review was included in each of the previous articles.

Table 1.1. The publication history of the seven articles included in this PhD thesis

Chapter	Title	Journal	Published
4	Effects of wood ash-based alkaline treatment on nitrogen, carbon, and phosphorus availability in food waste and agro-industrial waste digestates	Waste and Biomass Valorization (Springer)	27/08/20
6	Impact of sulphuric, hydrochloric, nitric, and lactic acids in the preparation of a blend of	Journal of Environmental Chemical	31/12/20

Chapter	Title	Journal	Published
	agro-industrial digestate and wood ash to produce a novel fertiliser	Engineering (Elsevier)	
8	Kinetic study of the stabilization of an agro-industrial digestate by adding wood fly ash	Chemical Engineering Journal Advances (Elsevier)	05/05/21
9	Alkaline wood ash, turbulence, and traps with excess of sulfuric acid do not strip completely the ammonia off an agro-waste digestate	Edelweiss Chemical Science Journal (Edelweiss)	28/08/21
2	Wood ash based treatment of anaerobic digestate: State-of-the-art and possibilities	Processes (MDPI)	11/01/22
5	Strategies for the production of a stable blended fertiliser of anaerobic digestates and wood ashes	Nature-Based Solutions (Elsevier)	03/03/22
7	Valorization of agrowaste digestate *via* addition of wood ash, acidification, and nitrification	Environmental Technology & Innovation (Elsevier)	16/05/22

1.11. Other outputs of this PhD

1.11.1. Other related articles published during this period

- **Moure Abelenda, A.**, Semple, K. T., Aggidis, G., & Aiouache, F. (under review). Dataset on the solid-liquid separation of anaerobic digestate by means of wood ash-based treatment. *Data in Brief.* Retrieved July 8, 2022, https://track.authorhub.elsevier.com/?uuid=8a4802ca-82d4-4140-8175-cb76ee707fe8
- **Moure Abelenda, A.**, & Amaechi, C. V. (2022). Manufacturing of a Granular Fertilizer Based on Organic Slurry and Hardening Agent. *Inventions*, *7*(1), 26. https://doi.org/10.3390/inventions7010026
- **Moure Abelenda, A.**, Semple, K. T., Aggidis, G., & Aiouache, F. (2022). Circularity of Bioenergy Residues : Acidification of Anaerobic Digestate Prior to Addition of Wood Ash. *Sustainability*, *14*(5), 3127. https://doi.org/10.3390/su14053127
- Amaechi, C. V., Amaechi, E. C., Amechi, S. C., Oyetunji, A. K., Kgosiemang, I. M., Mgbeoji, O. J., Ojo, A. S., **Moure Abelenda, A.**, Milad, M., Adelusi, I., & Coker, A. O. (2022). Management of Biohazards and Pandemics: COVID-19 and Its Implications in the Construction Sector. *Computational Water, Energy, and Environmental Engineering*, *11*(01), 34–63. https://doi.org/10.4236/cweee.2022.111003

1.11.2. Featured articles

- Government website: **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021). *Effects of Wood Ash-Based Alkaline Treatment on Nitrogen, Carbon, and Phosphorus Availability in Food Waste and Agro-Industrial Waste Digestates*. U.S.A Department of Agriculture. Retrieved January 21, 2022, https://pubag.nal.usda.gov/catalog/7372720
- Citation in a review article: Venkateswarlu, K. (2021). Ashes from organic waste as reagents in synthetic chemistry: a review. *Environmental Chemistry Letters*, *19*(5), 3887–3950. https://doi.org/10.1007/s10311-021-01253-4
- **Moure Abelenda, A.** (2022). *Wood Ash Based Treatment of Anaerobic Digestate*. Scholarly Community Encyclopedia. Retrieved January 21, 2022, https://encyclopedia.pub/19875
- **Moure Abelenda, A.**, Semple, K. T., Aggidis, G., & Aiouache, F. (2022). *Circularity of Bioenergy Residues: Acidification of Anaerobic Digestate Prior to Addition of Wood Ash*. Ideas. Retrieved May 16, 2022 https://ideas.repec.org/a/gam/jsusta/v14y2022i5p3127-d766025.html
- Citation of 1 article in primary research article: Yu, L., Wen, Y., Luo, X., Xiang, Y., Yuan, X., Pang, S., Ma, X., & Li, X. (2022). Effects of Biogas Residues on Dissipation of Difenoconazole in Paddy Sediment System Under Field Conditions. *Frontiers in Environmental Science*, *10*, 1–8. https://doi.org/10.3389/fenvs.2022.814438
- Citation of 2 articles in primary research article: Centorcelli, J. C., Luyben, W. L., Romero, C. E., & Baltrusaitis, J. (2022). Dynamic Control of Liquid Biomass Digestate Distillation Combined with an Integrated Solar Concentrator Cycle for Sustainable Nitrogen Fertilizer Production. *ACS Sustainable Chemistry & Engineering*, *10*(22), 7409–7417. https://doi.org/10.1021/acssuschemeng.2c02019
- Direct citation in a primary research article: Gómez-Muñoz, B., Müller-Stöver, D., Hansen, V., Stoumann Jensen, L., & Magid, J. (2022). Nutrient interactions and salinity effects on plant uptake of phosphorus from waste-based fertilisers. *Geoderma*, *422*, 115939. https://doi.org/10.1016/j.geoderma.2022.115939

1.11.3. Conference oral presentation

- **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2017). *Design and modelling of the production of waste derived fertilisers from digestates and ashes*. Conference of the School of Engineering of

Lancaster University. In person presentation. **Second prize award to the best presentation**. https://doi.org/10.13140/RG.2.2.25158.40001

- **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2018). *Study of the acidification of the digestate before adding ashes to produce a blended fertiliser*. Conference of the School of Engineering of Lancaster University. In person presentation. https://doi.org/10.13140/RG.2.2.31869.28649
- **Moure Abelenda, A.**, Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2019). *Blend of digestate and ash as soil organic amendment*. Conference of the School of Engineering of Lancaster University. In person presentation. https://doi.org/10.13140/RG.2.2.21802.95685
- **Moure Abelenda, A.** (2021). *Stabilisation of anaerobic digestate by adding wood ash*. COP26 early careers presentation event organised by the Lancaster Environment Centre of Lancaster University. Online presentation. https://doi.org/10.13140/RG.2.2.10897.76648

1.11.4. Policy briefing

- **Moure Abelenda, A.** (2019). *Achega para a Lei do sistema integrado para a xestión de dexeccións gandeiras xeradas nas explotacións da Comunidade Autónoma de Galicia*. https://doi.org/10.13140/RG.2.2.35632.84483/1
- **Moure Abelenda, A.** (2020). Highlighting the importance of the chemical amendmentsto tackle greenhouse gas (GHG) emissions from manure and slurry. *Environmental Land Management and the agricultural transition - Committees - UK Parliament*. Retrieved June 9, 2022, https://committees.parliament.uk/writtenevidence/21876/html/?msclkid=f221205cbda011ec83b6b0420accb9a0

1.11.5. Research proposal

- **Moure Abelenda, A.**, Coca, M., Rubio García, R. (2020). *OWAS (Organic Waste Adsorption Stabilisation) project*. Unpublished. Retrieved January 9, 2022, https://euraxess.ec.europa.eu/jobs/hosting/msca-if-2020-%E2%80%93-chemical-and-biochemical-processes-group-chembiopro-%E2%80%93-expressions

- **Moure Abelenda, A.** (2021). *OWAS (Organic Waste Adsorption Stabilisation) project*. Unpublished. Retrieved February 4, 2022, https://rse.org.uk/funding-collaboration/award/enterprise-fellowships/
- **Moure Abelenda, A.** (2022). *OWAS (Organic Waste Adsorption Stabilisation) project*. Unpublished. Retrieved February 4, 2022, https://conceptionx.org/overview/

1.11.6. Presentation in outreach events

- **Moure Abelenda, A.**, Holden, C., Reeves, K. (2020). *Pint of Science: Scientific outreach during COVID-19*. Retrieved January 9, 2022, https://www.lancaster.ac.uk/lec/about-us/blogs/pint-of-science-scientific-outreach-during-c-19
- **Moure Abelenda, A.** (2021). *Presentation for public engagement at the Swindon Science Festival 2021 (Festival of Tomorrow)*. Retrieved January 9, 2022, https://whova.com/embedded/speaker/festi1_202102/14107187/
- **Moure Abelenda, A.**, Sarkar, B. (2021). *Air Quality briefing for COP26 of Lancaster University*. COP26 international outreach event at Lancaster University. https://doi.org/10.13140/RG.2.2.34385.86883
- **Moure Abelenda, A.** (2022). *Presentation for public engagement at the Swindon Science Festival 202 (Festival of Tomorrow)*. Retrieved February 7, 2022, https://www.festivaloftomorrow.com/about

1.11.7. Multimedia material outputs

- **Moure Abelenda, A.** (2020). *Video about the business idea of commercialisation of the technology*. Kickstarter Challenge 2020 organised by the enterprise Team of Lancaster University (Work In Progress). Retrieved January 9, 2022, https://www.youtube.com/watch?v=oDIJVlm5rks&t=8s
- **Moure Abelenda, A.** (2021). *Video about the prototype for stabilisation of organic manures. UK Pint of Science*. Retrieved January 9, 2022, https://www.youtube.com/watch?v=6bM9fVIaOow&t=1s
- **Moure Abelenda, A.**, López García, I. (2021). *Video on air quality for COP26 of Lancaster University. COP26 international outreach event at Lancaster University*. Retrieved January 9, 2022, https://www.youtube.com/watch?v=VfILqFYaLnI

1.11.8. Volunteering

- **Moure Abelenda, A.** (2020). *Presentation of the OWAS (Organic Waste Adsorption Stabilisation) project*. PowerPoint party organised by the Buddy Programme of the Graduate College of Lancaster University. https://doi.org/10.13140/RG.2.2.22222.38726

1.11.9. Awards

- Second best oral presentation among the first year PhD students of the School of Engineering of Lancaster University. Engineering PGR Conference 2017. Retrieved January 9, 2022, https://www.linkedin.com/in/alejandromoureabelenda/detail/overlay-view/urn:li:fsd_profileTreasuryMedia:(ACoAAA3KkkQBY5GrJDpZHJfsh8PqtptEu8Uz8Ow,1635479253641)/
- Awarded with 10,000-euro funding for the support of a business mentor to conduct the primary research market and a financial viability study as part of the EU project SPIN UP. Retrieved January 9, 2022, https://spinup-project.eu/
- Certificate of achieving the status of associate fellow (AFHEA) awarded by Advanced Higher Education Institution of the United Kingdom in 2021. Retrieved January 9, 2022, https://www.linkedin.com/in/alejandromoureabelenda/detail/overlay-view/urn:li:fsd_profileTreasuryMedia:(ACoAAA3KkkQBY5GrJDpZHJfsh8PqtptEu8Uz8Ow,1635479257180)/
- Gold Lancaster Award (2021). Retrieved January 9, 2022, https://www.linkedin.com/in/alejandromoureabelenda/detail/overlay-view/urn:li:fsd_profileTreasuryMedia:(ACoAAA3KkkQBY5GrJDpZHJfsh8PqtptEu8Uz8Ow,1635479253654)/

1.11.10. Primary market research

- **Moure Abelenda, A.**, (2020). *Online survey for stakeholders of the agro-industry participating in the Northern Real Farming Conference 2020*. Retrieved January 9, 2022, https://forms.gle/B9GCNbVbBk8r7h926
- **Moure Abelenda, A.**, Turnes Abelenda, A., Meana, S. (2020). *Application to the C-Voucher circular economy open call. Project Acronym OWAS (Organic Waste Adsorption Stabilisation) project*. https://doi.org/10.13140/RG.2.2.22222.38726.

1.11.11. Other conferences attended

- Lancaster Environment Centre winter conference (online). Retrieved January 21, 2022, https://www.lancaster.ac.uk/lec/about-us/events/next-steps-in-research-lec-winter-conference-2022
- Jornadas Latinoamericanas en Digestión Anaerobia. Uruguay 22nd October 2020, Brazil 29th October 2020, Chile 5th November 2020 and Mexico 12th November 2020. Online conference. Retrieved January 9, 2022, https://www.youtube.com/channel/UC7u1LNfdpMsMKVn316b-4cA
- Ramiran. 15th September 2020 Cambridge (UK). Online conference hosted by ADAS Ltd. Retrieved January 9, 2022, https://www.ramiran2020.org/
- Engineering PGR conference. 29th and 30th June 2021. MS teams online conference. Retrieved January 9, 2022, https://web.microsoftstream.com/video/cb660033-dda9-4b7d-9232-928d42665522
- Nothern Real farming Conference. 28th September to 10th October 2020.MS Teams online conference. Retrieved January 9, 2022, https://www.northernrealfarming.org/schedule/
- Faculty of Science and Technology of Lancaster University annual conference. 2016, 2017, 2018, 2019, 2020 and 2021. Retrieved January 9, 2022, https://www.lancaster.ac.uk/events/fst-annual-conference

1.11.12. Participation in workshops

- Postgraduate research training workshops of the Faculty of Science and Technology of Lancaster University (in person and online). Retrieved January 21, 2022, https://lancaster-uk.libcal.com/calendar/PGResearchTraining?cid=6200&t=d&d=0000-00-00&cal=6200&inc=0

2. Literature review on stabilisation of anaerobic digestate *via* the addition of wood ash

This literature review is presented in an organised manner that includes (a) the role of the wood ashes to enhance the biogas production in the AD, (b) the use of wood ashes in the downstream processing of anaerobic digestate (*e.g.* nutrient recovery and dewatering) and (c) the impact of the wood ashes in the performance of the anaerobic digestate as soil organic amendment. The results of both fractions of the wood ashes (fly and bottom) were considered to design a synergistic process that makes the most of the wood ash as alkaline agent and sorbent, to isolate the nutrients and improve the properties of the anaerobic digestate as slow-release fertiliser. The downstream processing also includes the destruction of pathogenic microorganism and the inoculation of biofertilisers that enhance the availability of the nutrients, once the blended fertiliser is applied to land. The literature review focussed primarily on the fate of C, N and P because these are the key elements that boost the microbial growth. Furthermore, the fate of these elements is associated (a) to the GHGs (CH_4, CO_2, N_2O) and ammonia (NH_3) emissions that contaminate the atmosphere and (b) to the leachates (NO_3^- and PO_4^{3-}) responsible of the eutrophication of surface and underground waters. Despite the C_{org} is not widely employed by plants, in this thesis, C is regarded as a nutrient because it is the substrate of the microbes in the AD and in the soil. Due to the limited literature found on the use of additives for stabilisation of anaerobic digestate, the studies involving other type of soil organic amendments (*e.g.* animal manure, slurry, MSW, SS, urine, wastewater and compost) were assessed to further build the knowledge of the underlying chemistry of the stabilisation. This chapter also includes the review of other additives different from the wood ashes and commercial acids (*e.g.* H_2SO_4 and HCl) that are used with the same purpose of stabilising the soil organic amendments, including anaerobic digestate. This literature review includes coal fly ash (CFA), MSW ash, SS ash and other type of biomass ash, biochar or charcoal (Brennan *et al.*, 2015), activated carbon (AC), lime (*i.e.* mixture of CaO, $Ca(OH)_2$ and $CaCO_3$), dolomite ($CaMg(CO_3)_2$) and waste magnesite dust.

2.1.State-of-the-art of AD

The AD process consists in the controlled fermentation of the OM. There is no agreement in the biochemical mechanisms taking place and there are models going from two to nine steps (García-Ochoa *et al.*, 1999). The widest accepted mechanism consist of four steps (Figure 1.2): hydrolysis, acidogenesis, acetogenesis and methanogenesis (Madsen *et al.*, 2011). Since the

AD is carried out by microorganisms, the fermentation is done at atmospheric pressure in an airtight reactor. Depending on the type of microbial consortium used, the AD can take place in psychrophilic (between 0 and 20 °C; (Madani-Hosseini *et al.*, 2015)) mesophilic (35 °C; (M. Kim *et al.*, 2002)) or thermophilic (55 °C; (M. Kim *et al.*, 2002)) conditions. Both the mesophilic and the thermophilic temperatures are the conditions most widely used to carry out the AD (Ward *et al.*, 2008). Despite the psychrophilic temperatures can be used for the main digestion (Madani-Hosseini *et al.*, 2015), these conditions are preferred for the storage of the digestate because of the low cost of keeping the storage tank at ambient temperature without insulation, heating, or cooling (Nohra *et al.*, 2003). In this way, the storage is also an important part of the stabilisation of the organic waste (UK Government, 2016).

A step-wise process (Figure 2.1) is the most efficient way of performing the anaerobic fermentation (Boe *et al.*, 2009; Fang *et al.*, 2011; Lemmer & Krümpel, 2017). Figure 2.1 shows the typical block flow diagram of a biogas plant. Not all the steps involve the anaerobic degradation of the OM. This is the case of the first step, which is the pre-treatment or conditioning of the feedstock. The operations included in this step can go from the simple removal of any indigestible material (Dumitru, 2014), such as stones and other impurities, to complex hydrolysis treatments. There are available biological, thermal, mechanical and chemical methods (Carrère *et al.*, 2010) to hydrolyse the non-fermentable compounds of the feedstock and to improve the yield of the remaining steps of the digestion system (Shah *et al.*, 2015). For example, the alkaline pre-treatment with wood ash can ease the fermentation of the substrates. It should be noted that the alkaline pre-treatment is less inhibitory for fermentation than the acid pre-treatment (J. S. Kim *et al.*, 2016; Miyafuji *et al.*, 2003).

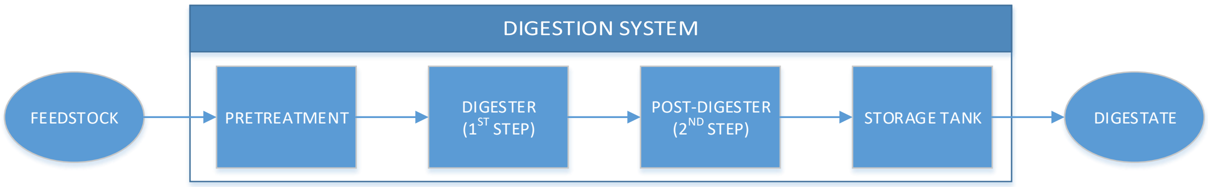


Figure 2.1. Stages of a digestion system. Elaborated based on the descriptions provided by J. S. Kim *et al.* (2016), Boe *et al.* (2009) and Madani-Hosseini *et al.* (2010).

The remaining three steps involve the use of anaerobes. These microbes are mostly active in the main digestion and the post-digestion. This is how they are called the first 2 steps of AD in the case of using continuous stirred tank reactors (CSTRs) in series (Tambone *et al.*, 2009). The most important parameter for the design and operation of the anaerobic digester (Linke, 2006; Nathalie Bachmann, 2013) is the organic loading rate (OLR; Equation 2.1). The Equation 2.1 was adapted from Bachmann (2013):

$$OLR\left(kg\,\frac{VS}{m^3 day}\right) = \frac{Input\left(\frac{kg\ substrate}{day}\right) \times Labile\ matter\ (\frac{kg\ VS}{kg\ substrate})}{Net\ digester\ volume\ (m^3)} \quad \textbf{Equation 2.1}$$

OLR, organic loading rate expressed as VS fed to each m^3 of anaerobic digester per day.
Input, could be expressed as mass or volume of substrate fed to the anaerobic digester each day.
Labile matter, expressed as share of VS in the feedstock of AD.

The last stage of the digestion system is the storage of the digestate in psychrophilic conditions at room temperature (Madani-Hosseini *et al.*, 2015; Nohra *et al.*, 2003). The tank is covered by an air-tight membrane or lid to collect the biogas release. The aim of this stage is to continue with the maturation (Figure 2.9) of the digestate although the biogas released is often not recovered (Gioelli *et al.*, 2011). The length of the stages of the digestion system follows the order: pre-treatment < digestion & post-digestion < storage (Table 2.1).

Table 2.1. Duration of the stages of the digestion system.

Stage	Length	Reference
Pre-treatment	From 1.5 seconds (ultrasounds) To 7 days	(Carrère *et al.*, 2010; Gavala *et al.*, 2003; Xie *et al.*, 2007)
[a]Primary digestion	Minimum of 10 days to avoid the washout of microbes To 30 – 40 days	(Eder & Schulz, 2012; Tambone *et al.*, 2009)
[a]Post-digestion	From 5.3 days To 50 days	(Boe *et al.*, 2009; Tambone *et al.*, 2009)
[a]Storage	From 4 months (UK) to 10 months (Sweden)	(Hermann & Hermann, 2019; Holm-Nielsen *et al.*, 2009; Lukehurst *et al.*, 2010; Nordberg, 1999)

[a]In the case of using manure or wastewater as feedstock of AD, the three last stages of the digestion process (*i.e.* primary digestion, post-digestion and storage) can be combined in a process so-called in-storage-psychrophilic-anaerobic-digestion with a duration ranging from 100 to 300 days (Madani-Hosseini *et al.*, 2015; Nohra *et al.*, 2003).

Reducing the storage capacity is important to lower the cost of handling the anaerobic digestate (Nohra *et al.*, 2003). This can be achieved by developing processing technologies to obtain novel fertilisers (*e.g.* granular) derived from the digestate (Fivelman, 2013). The length of the storage of the digestate is determined by:

1. The degree of stability of the digestate leaving the post-digestion: This parameter can be determined by a biochemical methane potential (BMP) test. In the UK, the BSI PAS 110:2014 establishes that the RBP test should be applied for this purpose (Saveyn &

Eder, 2014). The upper limit of the total amount of gas release under the conditions of the test and the threshold value for the preliminary screening were set as described in Table 2.2:

Table 2.2. Different threshold values to measure the stability of the anaerobic digestate available in the BSI PAS 110:2014 (WRAP, 2014a) and the RBP test (Banks *et al.*, 2013; Walker *et al.*, 2010).

[a]Upper limit RBP test	[b]Upper limit screening	Reference
0.45 L biogas/g volatile solids (VS)	0.774 g chemical oxygen demand (COD)/g VS	PAS 110 (WRAP, 2014a)
0.25 L biogas/g VS	0.43 g COD/g VS	RBP test (Banks *et al.*, 2013; Walker *et al.*, 2010)

[a] Upper limit for the total amount of gas release by the end of the RBP test (28 days).
[b] Upper limit for the preliminary screening of the samples before doing the test.

As described in Table 2.2, the anaerobic digestate should have a content lower than 0.774 g COD/g VS to perform the RBP test successfully. Figure 2.2 shows typical profiles of biogas release from healthy (blue line) and inhibited (red line) RBP tests (Walker et al., 2010). A healthy RBP test shows the total release of biogas within the 28 days that lasts the RBP test. An inhibited RBP test can lead to regard a sample as stable using a 28-day test, even when it can release more gas than the established upper limit (Figure 2.2). According to Walker *et al.* (2010), "*some of the results showed a long lag phase where, after deduction of the gas produced by the inoculum, the net biogas production from the tests is negative*". Walker *et al.* (2010) further explained the biochemical reason for which the red line in Figure 2.2 goes below zero:

> Negative net biogas production is generally associated with some inhibition of the inoculum by the substrate (digestate), either because of a component already present in the substrate or due to rapid fermentation of a readily degradable material producing acidic conditions (Walker et al., 2010, p. 26).

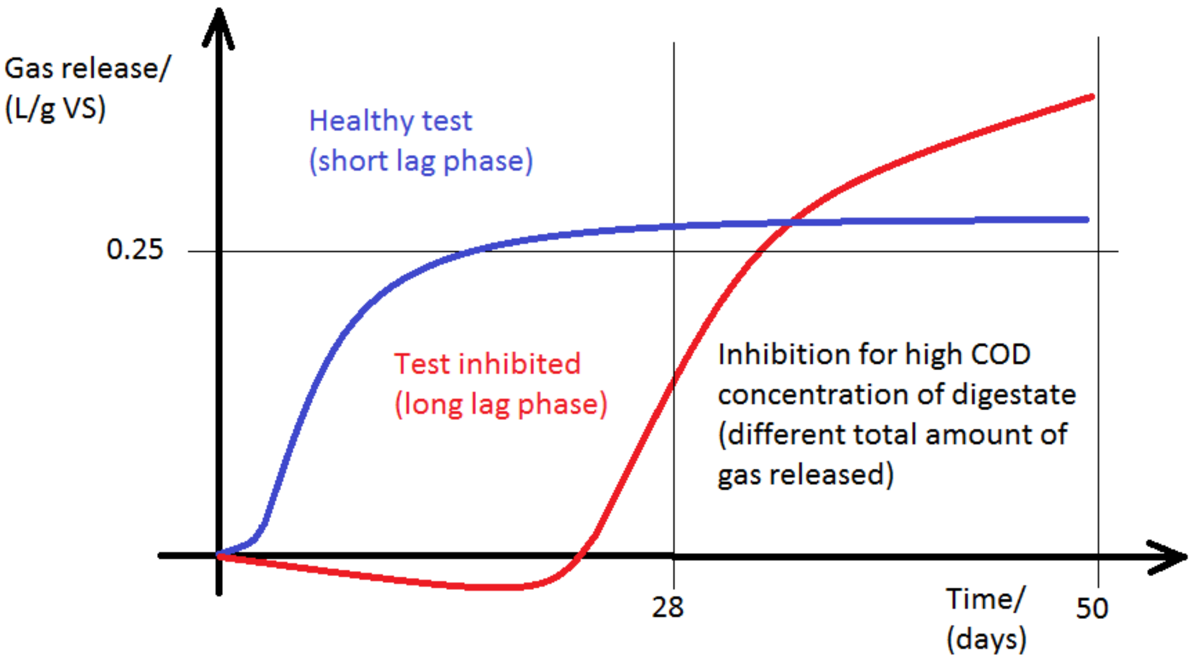


Figure 2.2. Heatlhy RBP test (blue line) released all the biogas during the first 28 days of the incubation. Inhibited RBP test (red line) by high COD concentration can lead to regard samples as stable when they are still releasing more gas than the established upper limit. This example is a modification of Figure 17 of the RBP test methodology (Banks *et al.*, 2013; Walker *et al.*, 2010).

2. Nutrient quotas: The utilisation of soil organic amendments (*e.g.* anaerobic digestate, animal manure and slurry) is only allowed during certain periods of the year (Hermann & Hermann, 2019). In countries like Sweden, it is compulsory to have a storage capacity for the digestate between 6 and 10 months (Holm-Nielsen *et al.*, 2009; Lukehurst *et al.*, 2010). On the other hand, in Italy, because of the warmer climate with fewer precipitations (resulting in higher crop growth, better nutrient uptake and less nutrient runoff), the required storage capacity for the digestate is between 3 and 6 months. During the growing season of the crops, the plant is ready to uptake the nutrients and there is less leaching and runoff to underground waters (Lukehurst *et al.*, 2010). The time of maximum crop growth is from late winter (*i.e.* February) through spring and summer. The application during autumn leads to large amounts of N being lost, unless the crop (*e.g.* oilseed rape) requires N at this time (WRAP, 2012b). The load of N onto the fields has been regulated since 1991 in Europe and in the UK by The Nitrates Directive 91/676/EEC (European Commission, 2020). This directive aims to decrease water pollution due to the leaching of the agricultural fertilisers. The

maximum allowed application rate of organic manures (*e.g.* anaerobic digestate) is 170 kg N/ha/year, although this depends on the type of crop and the location. After the 31st December 2020 (*i.e.* end of transition period for Brexit), the UK has established different nitrogen quotas for the Nitrate Vulnerable Zones in its territory (UK Government, 2021a) and a rate of application of organic manure up to 250 kg N/ha/year can be acceptable. In warmer countries, such as Ghana, that requires less amount of N to promote the crop growth, the recommended rate of application of organic manures is lower and around 60 kg N/ha/year (Essel *et al.*, 2020).

2.2. Use of wood ash as an additive for enhancing the AD

The addition of wood ash to the feedstock of AD can be understood as a way of promoting the stabilisation of the anaerobic digestate: the more the biogas is released during the AD, the lesser the emissions of CH_4 and CO_2 during storage and land application of the soil organic amendments (Appels *et al.*, 2011). It is also important to mention that the OM could be used as stabilising agent by enhancing the degradability of substrates during the AD, hence less GHG could be expected after land application of these recalcitrant wastes (Raman *et al.*, 2017). For example, Acosta *et al.* (2021) explained that cow manure can be used to promote the degradation of cocoa waste in an anaerobic co-digestion process. To authors’ knowledge 6 studies have been reported on the topic of anerobic co-digestion involving wood ash. Alavi-Borazjani *et al.* (2020) provided an insight into the feasibility of the utilisation of biomass ashes in AD and biogas upgrading. According to Alavi-Borazjani *et al.* (2020), biomass ashes are a cheap source of alkali suitable to control the excessive acidification of anaerobic digesters. The metal oxides present in the ashes could react with moisture and CO_2 of the biogas, leading to a decrease of alkalinity due to formation of hydroxides and carbonates (CO_3^{2-}), respectively (Demeyer *et al.*, 2001). These types of absorption reactions (*e.g.* neutralisation, carbonation, etc.) are widely used for cleaning the biogas (Mulu *et al.*, 2021; Papurello *et al.*, 2022) and even flue gases (Ahmaruzzaman, 2010). In addition to attain the upgrading of the biogas with a content of CH_4 from 60 vol.% to ≥ 90 vol.% (ie. biomethane grade), the neutralised ashes would be more suitable as a source of nutrients because avoid the pH shock (Bachmaier *et al.*, 2021; Belviso, 2018; Huotari *et al.*, 2015; Voshell *et al.*, 2018) of the microbial consortium in the anaerobic digester. Biomethane (~ 98 vol.% CH_4) can be used in the same infrastructure of natural gas (Da Costa Gomez, 2013; Ryckebosch *et al.*, 2011).

Biogas production is enhanced also due to the supplementation with the macro and micronutrient present in biomass ashes, which are required for the anaerobic microbes. The first experiments on the enhancement of AD *via* addition of wood ash were conducted by Adeyanju (2008) and Onwosi & Okereke (2009). Whilst Adeyanju (2008) used pig waste and cassava peel as substrate, Onwosi & Okereke (2009) prepared the brewery spent grains with rumen liquor as inoculum. Adeyanju (2008) combined organic material (25 %) with distilled water (75 %) as feedstock and Onwosi & Okereke (2009) confirmed that greater dilution of the organic material would reduce the biogas production. Adeyanju (2008) found that seeding the anaerobic digester with ash of *Bauhina monandrina* plant increase more than twice the biogas production during the 45-day incubation. Interestingly, Adeyanju (2008) reported that the pH of the digester sown with wood ash was 4.40 but the methanogen archaea were able to adapt to the acidic conditions of the digester media. According to Adeyanju (2008), the biodigester containing 25 % of pig waste and 75 % distilled water with a pH of 7.91 produced less amount of biogas because the methanogens in these experiments thrive better in non-alkaline conditions (Adeyanju, 2008). Onwosi & Okereke (2009) obtained the greatest release of biogas when the digestate was amended with wood ash than when poultry litter or urea were used as additives. High quality manure resulted from the AD process since the N content of the stabilised biowaste increase by the end of the fermentation (Onwosi & Okereke, 2009).

The most widely cited articles on the enhancement of the AD are compared in Table 2.4, from the points of view of the wood ash type and dose, the impact of the ash addition on the microbes, the biogas production and the final composition of the amended anaerobic digestate before land application of this material. Podmirseg *et al.* (2013) conducted a full study on the use of WBA as amendment to AD of cattle slurry. The authors considered the previous work of Lo *et al.* (2009) on the use of MSW ash to build their understanding of the impact of ash on AD. A similar stabilisation process can be considered for MSW landfilling (Lo *et al.*, 2009) and in this case, the gas and the leachate are collected *via* pipelines at the top of the landfill and at the bottom liner, respectively. Bauer *et al.* (2022) highlighted that their study was the first work on the co-digestion of WFA with thickened WWTP sludge and subsequent land application of the amended digestate. Cimon *et al.* (2020) tested wood ash and biochar as additives to temperature-phased AD of wastewater sludge and they acknowledge the previous work of Podmirseg *et al.* (2013).

Table 2.4. Summary of the most cited articles related to the use of wood ash in the AD.

Study	**Type of ash and incinerator.** **Type of substrate.** **Type of anaerobic digester.** **Ash dose.**	**Impact on the biogas production. Effect on the composition of the anaerobic digestate.**
Lo *et al.* (2009). This article was cited by the 3 articles below employing wood ash in AD.	MSW fly ash from an industrial incinerator, 850 – 1050 ºC. The flue gases were treated with semi-dry scrubber using $Ca(OH)_2$ as flushing agent, powdered C and filter bag. Synthetic MSW substrate and anaerobic sludge seeding 35 ºC leaching/percolate (100 mL/day) bed reactor. 0, 10 and 20 g MSW fly ash/L MSW (equivalent to 0.2 and 0.4 g/g VS or 0.17 and 0.33 g/g TS, respectively). Lo *et al.* (2010) tested 100 g MSW bottom ash/L MSW, 2 g MSW bottom ash/g VS or 1.67 g MSW bottom ash/g TS.	Drop in the pH due enhancement of the hydrolytic and acidogenic processes. After the 84 days of operation, decrease of VS and accumulation of the VFAs due to decrease of methanogenic activity. Biogas production rate in ash-added digesters was higher than in control experiment (*i.e.* unamended BMP) but total yield followed the trend: 20 g/L > 0 g/L > 10 g/L > 100 g/L (Lo *et al.*, 2010).
Podmirseg *et al.* (2013).	Wood bottom ash WBA (2-mm sieved and 105 ºC dried). 2-mm sieved cattle slurry (5 weeks AD). 1 L; 37 ºC; 50 revolutions per minute (rpm); 20-day retention time. 0 and 0.5 g ash/g TS, which is equivalent to 0.96 g wood ash/g VS or 9.65 g bottom ash/L digested cattle slurry.	Biogas stopped after the addition of ash and higher rates of production were found when the doe of ash decreased down to 0.25 g/g TS (0.48 g/g VS or 4.83 g/L digested cattle slurry). The biogas increased the content of CH_4. The NH_4^+-N was not affected by the ash amendment but VS increased. With excessive ash dose, C/N increase due to accumulation of VFAs.
Bauer *et al.* (2022).	WFA from CHP plant using wood residues as fuel of a fluidised bed incinerator. Thickened WWTP sludge. 37 ºC for 4 weeks. 0, 0.4, 0.7 and 1 g ash/g VS or 0, 0.28, 0.49 and 0.70 g ash/g TS or 0, 0.008, 0.015 and 0.022 g ash/L, respectively.	The elevated pH at the beginning of the AD was the responsible of the longer lag phase when adding the wood ash to the digester. After 3 to 5 days the production of biogas is comparable to the control experiment because the accumulation of VFAs decreases the pH.
Cimon *et al.* (2020).	Boiler ash granular (0.85 – 4.75 mm) and powdered (< 0.075 mm): Conventional fixed grate biomass combustion system fueled by pine, spruce and fir bark and some dry wood shavings. Fermented WWTP sludge.	Wood ash increase the lag phase of AD and decreased the total biogas produced. Wood ash accelerated the biodegradation of propionic and butyric acids. Even at a rate of 2.2 g ash/g $VS_{substrate}$ the wood ash poorly contributed to the total alkalinity, thus the authors recommend the use

Study	**Type of ash and incinerator.** **Type of substrate.** **Type of anaerobic digester.** **Ash dose.**	**Impact on the biogas production. Effect on the composition of the anaerobic digestate.**
	Wood ash doses ranging from 0.16 to 3.7 g/g VS fermented WWTP sludge, which is equivalent to 0.14 and 3.2 g ash/g TS or 5.72 and 133.94 g ash/L, respectively.	of a buffer (*e.g.* 20 mmol/L Na_2CO_3 & $KHCO_3$ even when adding the ash). The authors found that the granular wood ash was able to remove NH_4^+-N from the liquid phase due to adsorption *via* cation exchange.

2.3.Downstream processing of the anaerobic digestate *via* the addition of wood ash

The wood ash can be added to the anaerobic digestate after the biodigester, to ease the management of this material by developing a process complying with the green chemistry principles, with the minimum input of energy and resources due to all the synergies involved. The role of the wood ash as sorbent is essential to produce a controlled-release fertiliser derived from the anaerobic digestate (Moure Abelenda & Aiouache, 2022; Szymula *et al.*, 2021). The sorption (adsorption and/or absorption; (Laohaprapanon *et al.*, 2010)) will take place since the moment in which the ash gets in touch with the anaerobic digestate, hence this phenomenon is implicitly involved in each step of the process of Figure 2.3.

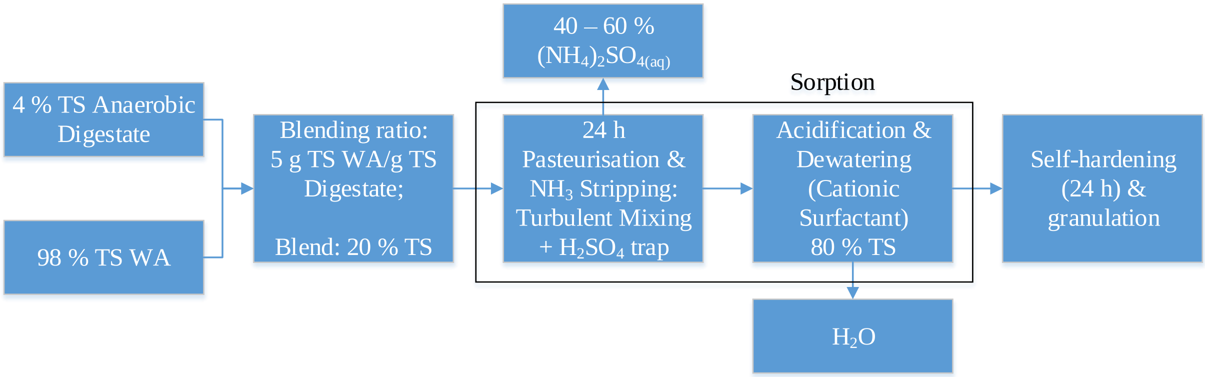


Figure 2.3. Block flow diagram of the proposed downstream processing of the anaerobic digestate with wood ash to produce a granular organic fertiliser (% TS = percentage of total solids). Elaborated considering the different treatments, synergies and technologies that can be implemented with a blend of wood ash and anaerobic digestate (Bauer *et al.*, 2022; Cimon *et al.*, 2020; Limoli *et al.*, 2016; Lo *et al.*, 2009; Pesonen *et al.*, 2016; Podmirseg *et al.*, 2013; Vaneeckhaute *et al.*, 2017; Zheng *et al.*, 2016).

The dose of wood ash depends on the intended properties of the fertiliser to be manufactured. The following are some of the considerations that were taken into account to establish the optimum blending ratio of 5 g TS wood ash/g TS anaerobic digestate (Figure 2.3):

(a) Enhancement of AD could be achieved by preparing the feedstock with up to 2.0 % CFA (Abbas *et al.*, 2021).

(b) Precipitation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) and adsorption of phosphate achieved by preparing a suspension with up to 2.8 % ash in swine wastewater (Huang *et al.*, 2017).

(c) Application to land of both raw materials following a blending of up to 7.2 % of wood ash (Bougnom *et al.*, 2012).

(d) Mitigation of CH_4, CO_2, NH_3, N_2O associated with the storage of cattle slurry with 4.6 % TS content by adding charcoal or biochar at a rate of 4.3 % (Miranda *et al.*, 2021) and around 10.7 vol.% (Brennan *et al.*, 2015).

(e) Adjustment of the pH to 5.5 of untreated pig slurry and co-digested pig slurry by adding 2.0 and 3.4 % of powdered aluminium sulphate ($Al_2(SO_4)_3$), respectively (Regueiro, Coutinho, & Fangueiro, 2016; Regueiro, Coutinho, Gioelli, *et al.*, 2016).

(f) Supplementation of the anaerobic digestate by means of wood ash dose up to 10.0 % or 3.1 g TS ash/ g TS digestate to improve the nutrient ratio (C/N/P), the availability of P and the microbial activity in the soil (Richards *et al.*, 2021).

(g) Agreement with the regulations in terms of the maximum content of heavy metals present in the anaerobic digestate (WRAP, 2012a, 2014a). The share of wood ash should not be greater 13.4 % in the blend with the anaerobic digestate or 1.5 g TS PLA/g TS AD. These values were obtained by considering the content of zinc as limiting factor. See more assumptions for these calculations in the section A.1.

(h) Prevention of a large volume of dewatered digestate obtained *via* filtration by using as much CFA as the TS of the digestate (*i.e.* 1 g TS CFA/g TS digestate) to assist the dewatering process (Zheng *et al.*, 2016).

(i) Alkaline stabilisation of SS *via* liming with a dose of CaO as high as 28.6 % or 8 g TS CaO/g TS SS to decrease the pathogens (Méndez *et al.*, 2002). A dose of 3.82 g TS CaO/g TS digestate or 224.5 g CaO/L digestate (5.5 % dry matter, DM) was required for reaching a pH 12 and removing the 51.2 % of the NH_4^+-N due to NH_3 volatilisation (Limoli *et al.*, 2016). Limoli *et al.* (2016) reported that a low dose of 45 g/L increased 42.7 % the TS content of the manure digestate. If the organic material have higher DM content (*e.g.* 25.4 %), a dose of 50 g CaO/kg SS represent an increase in the TS content of approximately 30 % and just 2 units of pH, but still might be enough to produce a liming effect and the availability of heavy metals (Jamali *et al.*, 2008).

(j) The reduction of phosphate availability by adding 5.6 kg of CFA to each kg of dairy slurry (Brennan *et al.*, 2011) could present a dose of greater 110 g TS CFA/g TS slurry, if the moisture content of the organic manure is 95 %.

(k) Preparation of granules with 100 % biomass ash showed the best mechanical properties. Decreasing the content to 80 % bio-ash and 20 % dewatered SS (45 % moisture), significantly affected the compressive strength of the pellets (Pesonen *et al.*, 2016). The lowest dose of bio-ash and $Ca(OH)_2$ that Pesonen *et al.* (2016) tested was corresponded to a 5.19 g TS bio-ash+$Ca(OH)_2$/g TS hygienised SS.

Ideally the dose of wood ash would be optimum to achieve of the the different levels of stability (Figure 2.4), as defined below:

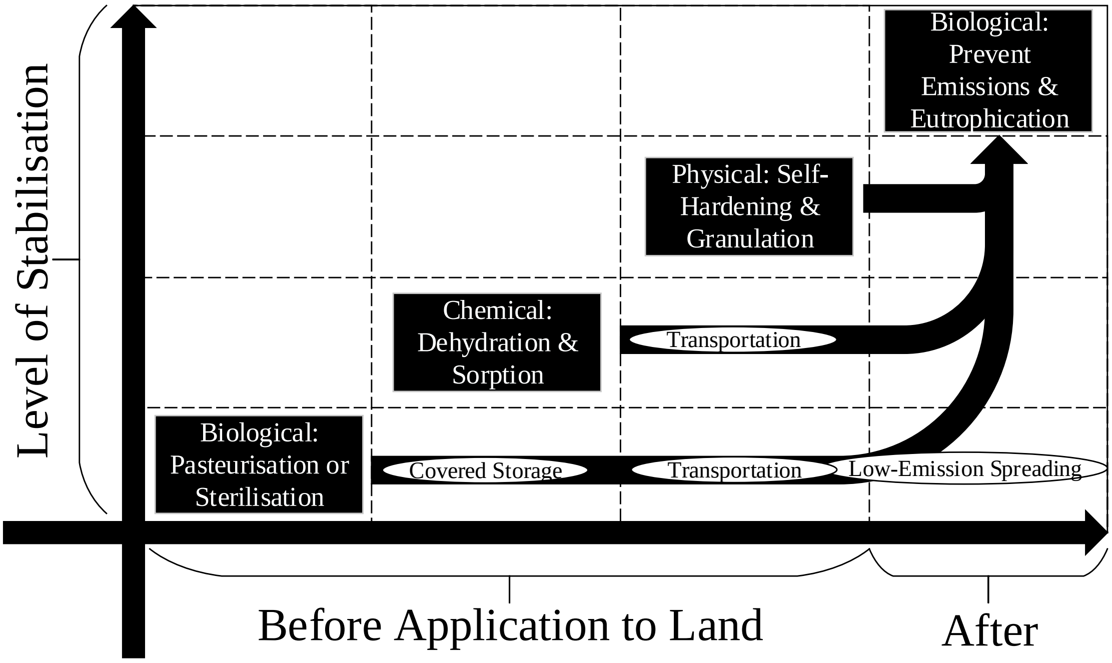


Figure 2.4. Different levels of stabilization of organic slurry with 95 % moisture (Moure Abelenda & Amaechi, 2022).

2.3.1. Pasteurisation and sterilisation

According to the animal by-product regulations for biogas plants in the UK (UK Government, 2020), unless the AD is done in the conditions of Table 2.5, pasteurisation (70 ºC for 1 hour) of the digestate is required before using the digestate for any application (WRAP, 2014a). A considerable reduction in the amount of pathogens can be achieved during the fermentation, especially if it is done in thermophilic conditions (Madsen *et al.*, 2011). Also, the best control of the digester was obtained in the one-stage non-mixing thermophilic reactor (M. Kim *et al.*, 2002).

Table 2.5. Conditions to produce a sanitised digestate when using ABP as feedstock in AD (UK Government, 2020).

Minimum temperature	Minimum time	Maximum particle size
57 °C	5 hours	50 mm

Greater doses of wood ash than that used to improve the performance of the AD (Table 2.4) need to be employed with pasteurisation and sterilisation purposes. While the sterilisation implies the destruction of all life forms in the anaerobic digestate, the pasteurised material might contain beneficial or harmless microorganisms (WRAP, 2014a). The aim is to keep the pH of the organic manure above 12 for at least 2 hours (Tchobanoglous *et al.*, 2014, pp. 1501-1502; UK Government, 2018). This is often achieved using a rate of application of wood ash to organic material of 0.1 g $Ca(OH)_2$ per g TS (J. S. Kim *et al.*, 2016; Tchobanoglous *et al.*, 2014, p. 1501). It should be noted that calcium (Ca) represent approximately the 18 % of the total weight of the wood ash (Demeyer *et al.*, 2001), thus this element is one of the main components of this material (Ribbing, 2007). This alkaline treatment, like the use of lime, reduces the time of storage of organic manures by 3 months while still preventing the contamination of the crops by pathogens (Nag *et al.*, 2021; UK Government, 2016). The shares of the calcium as oxide, hydroxide and CO_3^{2-} in the wood ashes are mainly determined by the temperature of incineration and storage conditions. Under 500 ºC CO_3^{2-} and bicarbonates predominate, while oxides require temperatures around 1,000 ºC (Demeyer *et al.*, 2001). Also, during storage the reaction with the moisture and the CO_2 in the atmosphere lead to the formation of hydroxides and CO_3^{2-} although the conversion to CaO is possible *via* calcination of the ashes at temperatures over 500 ºC (Al-Mallahi *et al.*, 2020; Sakthivel *et al.*, 2012).

2.3.2. N recovery processes

This subsection only describes processes of NH_3 stripping, struvite precipitation and sorption of the N in the soil organic amendments, for the exploitation of this element as fertiliser. The aforementioned technologies are the most convenient for the implementation with the wood ashes. Biological N removal processes, such as nitrification/denitrification, were not considered despite these technologies are suitable for the anaerobic digestate with low COD/NH_4^+-N (L. Liu *et al.*, 2015), before the addition of the wood ash. Traditional nitrification/denitrification technology, as expressed in Equation 2.4, is expensive due to high cost of oxygen supply (Equation 2.7) and external C_{org} source addition (Scaglione *et al.*, 2013;

Tian & Yu, 2020) as donor of electrons (Equation 2.12). The nitrification of the reduced N is a two-step process which can be done by several type of bacteria (Prosser, 2005). With regard to the first step (Equation 2.5), most of the oxidation of NH_4^+ (or NH_3) to nitrite is done by *Nitrosomonas*. Similarly, the final oxidation of nitrite to nitrate (Equation 2.6) is mainly carried out by Nitrobacter (International Plant Nutrition Institute of Canada, 2017b). The nitrification can be employed for the better preservation of N in the anaerobic digestate during the wood ash-based treatment, in the same way is applied before drying (Botheju *et al.*, 2010). However, this might affect the quality of the fertiliser due to the source of N, although none of this forms of N is very stable after land application (Cowan *et al.*, 2019).

$$\begin{array}{cl}
NH_4^+{}_{(aq)} + 3/2O_{2(g)} \rightarrow NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} + 4e^- & \textbf{Equation 2.2} \\
NO_3^-{}_{(aq)} + 6H^+{}_{(aq)} + 5e^- \rightarrow 1/2\,N_{2(g)} + 3H_2O_{(l)} & \textbf{Equation 2.3} \\
\hline
NH_4^+{}_{(aq)} + 3/2\,O_{2(g)} + 2H^+{}_{(aq)} + e^- \rightarrow 1/2\,N_{2(g)} + 3H_2O_{(l)} & \textbf{Equation 2.4}
\end{array}$$

$$\begin{array}{cl}
NH_4^+{}_{(aq)} + O_{2(g)} \rightarrow NO_2^-{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- & \textbf{Equation 2.5} \\
NO_2^-{}_{(aq)} + H_2O_{(l)} \rightarrow NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + 2e^- & \textbf{Equation 2.6} \\
\hline
NH_4^+{}_{(aq)} + 3/2\,O_{2(g)} \rightarrow NO_3^- + 4H^+{}_{(aq)} + 4e^- & \textbf{Equation 2.7}
\end{array}$$

$$\begin{array}{cl}
NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + 2e^- \rightarrow NO_2^-{}_{(aq)} + H_2O_{(l)} & \textbf{Equation 2.8} \\
NO_2^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightarrow NO_{(aq)} + H_2O_{(l)} & \textbf{Equation 2.9} \\
NO_{(aq)} + H^+{}_{(aq)} + e^- \rightarrow 1/2\,N_2O_{(g)} + 1/2\,H_2O_{(l)} & \textbf{Equation 2.10} \\
1/2\,N_2O_{(g)} + H^+{}_{(aq)} + e^- \rightarrow 1/2\,N_2 + 1/2\,H_2O_{(l)} & \textbf{Equation 2.11} \\
\hline
NO_3^-{}_{(aq)} + 6H^+{}_{(aq)} + 5e^- \rightarrow 1/2\,N_{2(g)} + 3H_2O_{(l)} & \textbf{Equation 2.12}
\end{array}$$

Pseudomonas aeruginosa is capable of perform complete denitrification (Arat *et al.*, 2015; International Plant Nutrition Institute of Canada, 2017a), hence this bacteria is able to provide the enzymes: nitrate reductase (Equation 2.8), nitrite reductase (Equation 2.9), nitric oxide reductase (Equation 2.10) and nitrous oxide reductase (Equation 2.11).

The autotrophic N removal process involving partial nitrification (Equation 2.13) and anammox (*i.e.* anaerobic ammonium oxidation; Equation 2.17) with 85 – 90 % N removal efficiency are still applicable to the anaerobic digestate with low COD/NH_4^+-N (Scaglione *et al.*, 2015). Nevertheless, this technology in not interesting for this section of the literature review about N recovery processes. In a wastewater treatment plant, the anammox process reduces SS production and energy consumption but high capital investment is required due to the control and automation equipment. Several bacteria of the *phylum Planctomycetes*, like Brocadia, are able to assist the anammox process. The SS is traditionally employed as a feedstock of AD, hence reducing the production of this material could be regarded as a strategy for improving the management of the anaerobic digestate and the nutrients.

$$NH_4^+{}_{(aq)} + O_{2(g)} \rightarrow NO_2^-{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \quad \textbf{Equation 2.13}$$

$$2NO_2^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightarrow NO_{(aq)} + H_2O_{(l)} \quad \textbf{Equation 2.14}$$

$$NO_{(aq)} + H^+{}_{(aq)} + e^- \rightarrow 1/2\, N_2O_{(g)} + 1/2\, H_2O_{(l)} \quad \textbf{Equation 2.15}$$

$$1/2\, N_2O_{(g)} + H^+{}_{(aq)} + e^- \rightarrow 1/2\, N_{2(g)} + 1/2\, H_2O_{(l)} \quad \textbf{Equation 2.16}$$

$$NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)} \quad \textbf{Equation 2.17}$$

2.3.2.1. NH$_3$ stripping processes from the anaerobic digestate enhanced with the use of wood ash

Limoli *et al.* (2016) tested the addition of the CaO to the anaerobic digestate to increase the pH and promote the volatilisation of NH$_3$. These authors described a stepwise mechanism involving the ammonium dissociation ($NH_4^+ \rightarrow NH_3 + H^+$) and the mass transfer in the water-air interface. Since the wood ash primarily consists of Ca and other alkaline elements (Demeyer *et al.*, 2001), this material can be used to increase the pH of the anaerobic digestate and promote the volatilisation of NH$_3$. The reason of the costly amount of alkali required is the fact that there are 3 buffer equilibriums responsible of the pH in the anaerobic digestate: $NH_4^+ \leftrightarrow NH_3$; $CO_2 \leftrightarrow HCO_3^- \leftrightarrow CO_3^{2-}$; $CH_3COOH \leftrightarrow CH_3COO^-$ (Möller & Müller, 2012). It is noteworthy to highlight that 2 of these equilibria are connected by the precipitation of $(NH_4)_2CO_3$ and NH_4HCO_3 which naturally increases the pH of the anaerobic digestate (Georgacakis *et al.*, 1982). Drapanauskaite (2021) designed a process for the manufacturing of the NH_4HCO_3 from the liquid digestate. Unlike the open-loop strategy of the ammonia stripping, which requires H_2SO_4 for the manufacturing of the $(NH_4)_2SO_4$, the reagents for the preparation of the $(NH_4)_2CO_3$ and NH_4HCO_3 are components of the anaerobic digestate (Drapanauskaite *et al.*, 2021). Less than 1 % of the NH_4^+-N is volatilised as part of the biogas release during the AD (Möller & Müller, 2012). It is important to consider the cost of the alkaline agent when designing the process for stripping the NH$_3$ off the anaerobic digestate (Limoli *et al.*, 2016; L. Liu *et al.*, 2015). Basic cations (*e.g.* Ca^{2+} and K^+) increase the pH because the electric charge of the liquid digestate needs to be neutral, thus the concentration of H^+ is lower (Möller & Müller, 2012). Mu *et al.* (2018) also considered the role of sulphide (S^{2-}) and phosphate in the control of the pH of the anaerobic digestate. The addition of iron removes the sulphide and the phosphate and acidifies the medium (Möller & Müller, 2012), according to Equation 2.18 and Equation 2.19. This increases the amount of wood ash that needs to be added to the anaerobic digestate, since this element might be present in trace amounts in this waste stream (Demeyer *et al.*, 2001).

$$H_2S_{(aq)} + 2Fe^{3+}{}_{(aq)} \rightarrow S_{(s)} + 2Fe^{2+}{}_{(aq)} + 2H^{+}{}_{(aq)} \qquad \textbf{Equation 2.18}$$

$$H_nPO_4^{n-3}{}_{(aq)} + Fe^{3+}{}_{(aq)} \rightarrow FePO_{4(s)} + nH^{+}{}_{(aq)} \qquad \textbf{Equation 2.19}$$

Limoli *et al.* (2016) highlighted that the CaO required 40 minutes to reach the target pH while the NaOH has instantaneous impact on the pH, owe to the hydration reaction leading to the formation of $Ca(OH)_2$. Moreover, a higher dose of CaO than that of NaOH is required to reach the target pH. On the other hand, the increase of the temperature in the anaerobic digestate upon the addition of CaO due to the exothermic reactions was greater than the NaOH amendment. Limoli *et al.* (2016) proposed that this was due to the heat absorbed by the solids, thus less heat was lost to the surrounding environment. It should be noted that the volatilisation of NH_3 is enhanced at higher temperature (Drosg *et al.*, 2015). The $Ca(OH)_2$ subsequently reacted with the residual CO_2 present in the digestate leading to the formation of insoluble CO_3^{2-} salts (Limoli *et al.*, 2016). This could be the reason for which the addition of CaO was directly related to the increase of the TS content in the anaerobic digestate. A way of minimising the increase of the TS and the amount of CaO necessary would be by removing the residual CO_2 *via* extensive aeration. For this purpose, L. Liu *et al.* (2015) employed a closed system including the air recirculation to avoid discharging any gas to the atmosphere. Their batch system operated in 2 stages: firstly, the depletion of the CO_2 is done by bubbling air in the anaerobic digestate; secondly, the CaO is added to the anaerobic digestate to promote the volatilisation of NH_3. In both stages the air goes through 2 traps: one containing an alkaline solution and the second with H_2SO_4 (L. Liu *et al.*, 2015). The removal of the CO_2 can be done by adding HCl to the anaerobic digestate (Podmirseg *et al.*, 2013) but in this case an increase in the pH of the anaerobic digestate will not be observed. The aeration of the anaerobic digestate amended with CaO would promote the removal of Ca *via* precipitation of $CaCO_3$ (Malinowski *et al.*, 2021).

The traditional air-stripping systems can be categorised as packing columns, bubble-aeration setups and water-sparged reactors (L. Liu *et al.*, 2015). Limoli *et al.* (2016) reported that, unlike the addition of NaOH to the anaerobic digestate, the addition of the CaO leads to an increase in the TS of the anaerobic digestate. The authors concluded that the CaO needs to be used in combination with a turbulent mixing because the conventional gas-liquid contacting systems are not able to handle anaerobic digestates with high TS content, low degree of fluency and tendency to foul the equipment. Limoli *et al.* (2016) claim that the turbulent mixing procedure is easy to implement in farms due to the low capital investment and low cost of maintenance (Hou *et al.*, 2018). Limoli *et al.* (2016) obtained similar NH_4^+-N removal efficiencies (around 90 %) with the turbulent mixer as the data available in the literature concerning the performance of air diffusers. However, Limoli *et al.* (2016) did not consider how much of this N ends up in a trap containing a sulphuric acid. The resulting 40 – 60 % ammonium sulphate ($(NH_4)_2SO_4$) solution used can be as commercial-grade fertiliser (Equation 2.20), although this will depend on the organic contamination of the liquid fertiliser (Cavalli *et al.*, 2017; Limoli *et al.*, 2016).

$$2NH_{3(g)} + H_2SO_{4(aq)} \rightarrow 2NH^{+}_{4(aq)} + SO^{2-}_{4(aq)} \rightarrow (NH_4)_2SO_{4(s)} \qquad \textbf{Equation 2.20}$$

Considering the limitation of the volume of air to be employed for the stripping process, the use of a hydrodynamic cavitation reactor can enhance the amount of NH_3 volatilised (Taşdemir *et al.*, 2020). Another way of minimising the amount of air that goes through the H_2SO_4 trap is with a thermal vacuum stripping system using temperatures between 50 and 100 ºC, thus only the vapours released from the anaerobic digestate need to be in touch the with H_2SO_4 trap (Ukwuani & Tao, 2016). The combination of the thermal vacuum with a hollow fibre membrane to recirculate the H_2SO_4 solution in the trap has also been tested to avoid the use of air as vector to enhance the transfer phenomena of the NH_3 (Chen *et al.*, 2021). In line with avoiding both increase the pH of the digestate and blowing air during the stripping is the electrochemical system developed by Lee *et al.* (2021), which is able to accumulate the NH_3 neutral species in the cathode. The systems of Ukwuani & Tao (2016), Chen *et al.* (2021) and Lee *et al.* (2021) can be implemented as part of two-stage AD process, to avoid the NH_3 inhibition in the second stage of AD and to recover more biogas from the substrate, hence achieving very low C/N ratio. Even Limoli *et al.* (2016) proposed that the stripping could operate at pH 10 to prevent sodium concentrations greater than 5 g/L in the anaerobic digester that might inhibit the second stage AD (L. Zhang *et al.*, 2012; L. Zhang & Jahng, 2010) and still achieve removals of NH_4^+-N greater than 40 %. Limoli *et al.* (2019) explain the 25 % drop in the soluble COD during the stripping process was due to the volatilisation of organic compounds (*e.g.* VFAs) at pH greater than 9. As per the results of Ukwuani & Tao (2016), the H_2SO_4 trap can absorb volatile organic compounds like cyclohexene, although they reported that the crystals of $(NH_4)_2SO_4$ were free of this compound (Equation 2.20). According to Limoli *et al.* (2016), the NH_3-depleted organic amendment is used in agriculture after neutralisation with H_2SO_4.

2.3.2.2. Struvite ($MgNH_4PO_4{\cdot}6H_2O$) isolation using the wood ash a source of magnesium (Mg)

Another strategy to remove the excess of NH_4^+-N from the anaerobic digestate using the wood ash is *via* isolation of struvite (Drosg *et al.*, 2015). However, the production of this slow-release fertiliser is expensive due to the cost of the source of Mg and the alkaline agent that is needed to reach the target pH for the crystallisation of this material (Al-Mallahi *et al.*, 2020; Huang *et al.*, 2017; Sakthivel *et al.*, 2012). Huang *et al.* (2017) reported that 0.31 USA Dollar/kg PO_4^{3-}-P can be saved if straw ash is employed instead of NaOH to regulate the pH. Both Sakthivel *et al.* (2012) and Huang *et al.* (2017) recovered more than the 96 % of the phosphate in the ureolysed urine and swine wastewater, respectively, by means of using different doses of wood ash. While Sakthivel *et al.* (2012) employed 2.7 mol Mg/mol P, Huang *et al.* (2017) used 1.2 mol Mg/mol P. This might be related to the fact that only the 50 % of Mg in the wood ash of Sakthivel *et al.* (2012) was water-soluble (WS), thus only this amount was available for the formation of struvite. It would be possible to increase the availability of the Mg *via* calcination of the wood ash at temperatures higher than 600 ºC (Sakthivel *et al.*, 2012). Other option would be to perform aeration at the time of adding the wood ash to the anaerobic digestate to remove the carbonic carbon (CO_3^{2-}-C), following the same procedure developed by Huang *et al.* (2017). Drosg *et al.* (2015) explained that the Mg should be added in excess, according to the molar ratio 1.3:1:0.9 for Mg:N:P. This also agrees with the dose of Mg proposed by Miles & Ellis (2001) 1.25:1:1 and both nutrient ratios recommended for the precipitation of struvite are slightly different from the stoichiometry of the chemical reaction (Equation 2.21). It should be noted that Equation 2.21 implies the release of H^+ (Campos *et al.*, 2019; Möller & Müller, 2012) but there are other authors that prefer to represent the drop of the pH as consumption of OH^- (Drosg *et al.*, 2015). According to Drosg *et al.* (2015), materials such as anaerobic digestate contain more amount of NH_4^+-N hence the addition of orthophosphoric acid (H_3PO_4) to reach the target nutrient ratio (Drosg *et al.*, 2015). Escudero *et al.* (2015) studied how the removal of water-soluble ammonium (WS NH_4^+) from anaerobically treated effluents was affected by the source of water-soluble orthophosphate (WS PO_4^{3-}) and Mg^{2+} and the nutrient ratio. The found a WS NH_4^+ removal of 95 % in 30 seconds when using a molar ration Mg:N:P of 1:1:1 (Escudero *et al.*, 2015).

$$NH_4^+{}_{(aq)} + Mg^{2+}{}_{(aq)} + H_nPO_4^{n-3}{}_{(aq)} + 6H_2O_{(l)} \rightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + nH^+{}_{(aq)} \qquad \textbf{Equation 2.21}$$

Source of Equation : (Campos *et al.*, 2019)

Sakthivel *et al.* (2012) reported that their solid precipitate was not pure struvite due to the high content of $CaCO_3$ in the wood ash. They found a P content of 3 % in the precipitate that is lower than the one of the struvite (13 %) or the diammonium phosphate (46 %). Although the P content in the precipitate was greater than in the initial wood ash, the estimated value of the precipitate was lower than the wood ash because 60 % of the potassium (K) initially present in the wood ash remained in dissolved in the phosphate-depleted ureolysed urine (Sakthivel *et al.*, 2012). Huang *et al.* (2017) reported the competition reaction between struvite (Figure 2.5) and K-struvite ($MgKPO_4{\cdot}6H_2O$). These authors reported the greater share of K-struvite at pH 10, which is higher than pH 7.5 to 9 for the optimum for the precipitation of struvite (Campos *et al.*, 2019). According to Huang *et al.* (2017), at a pH 9.5 and with a dose of plant ash of 6 mol K/mol NH_4^+-N, the amounts of struvite and K-struvite are the same. Sakthivel *et al.* (2012) informed that the content of heavy metal in the precipitate should be determined by the initial composition of the wood ash. Thereby, the use of wood ash as P-enhanced conditioner for acidic soils should be based on the threshold values of the fertiliser regulations. According to the X-ray diffraction (XRD) measurements of Sakthivel *et al.* (2012), the struvite was the main phosphate compound produced during some of their experiments. Calcium phosphate compounds such as hydroxylapatite ($Ca_5(PO_4)_3OH$) or octacalcium phosphate ($Ca_8H_2(PO_4)_6{\cdot}5H_2O$) were regarded as transient compounds that were formed due to the CaO dissolution since they were not found in the precipitate (Sakthivel *et al.*, 2012). According to W. Shi *et al.* (2021), the CaO in the wood ash might interfere in struvite crystallisation and lead to the formation of calcium phosphates.

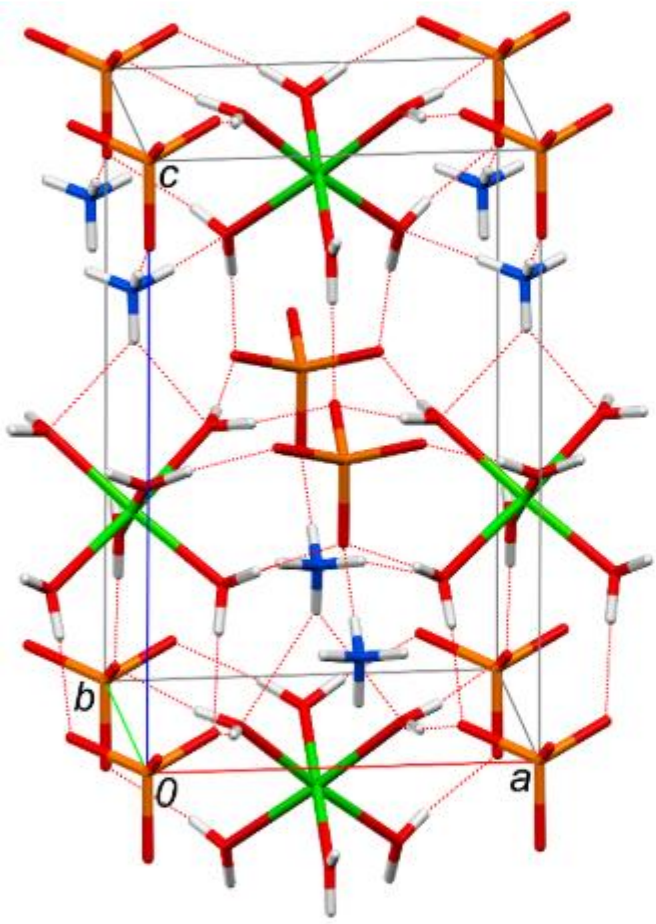


Figure 2.5. Structure of the struvite represented by Prywer *et al.* (2019): the Mg (green) is surrounded by 6 molecules of water (oxygen in red and hydrogen in white) and the N (blue) and the P (yellow). Using the coordinate system adopted by Prywer *et al.* (2019) and the hydrogen-bond network marked with dotted lines. Reproduced with the permission of Crystals (MDPI).

2.3.3. Use the wood ash as a sorbent to improve the properties of the anaerobic digestate as slow-release fertiliser

According to Laohaprapanon *et al.* (2010), sorption is a method with high capacity to isolate nutrients. Laohaprapanon *et al.* (2010) investigated WFA as low-cost sorbent to remove organic pollutants from wastewaster. The wastewater resulting from cleaning the machinery of the wood floor industry contains a lot of pollutants that impair the municipal wastewater treatment. For this reason, Laohaprapanon *et al.* (2010) proposed a simple on-site pre-treatment before discharging into a sewerage system. In order to pursue the simplest, cheapest and most practical method to be implemented under normal working conditions, the experiment was performed initially without applying any pre-treatment to the WFA. The authors explained that there are more than 1,000 different organic compounds in wastewater. Rather than identify each individual unknown organic compounds, lumping is required to ease the characterisation of the wastewater while ensuring an effective removal of pollutants. COD, biological oxygen demand (BOD) and total organic carbon (TOC) are well-known conventional parameters and non-specific (proxy) indicators used to detect the presence of organic compounds in wastewater (Laohaprapanon *et al.*, 2010). Laohaprapanon *et al.* (2010) recommended the investigation with an adsorption column before large scale implementation. The equipment has simple design and is easy to operate and maintain at large scale. Although there are 10 to 15 % losses of sorbent during its regeneration, this is only a problem when employing costly materials such as the AC (Leechart *et al.*, 2009). Depending on the C content of the wood ash, the physicochemical properties of this material could be like the ones of the commercial AC, hence the wood ash can be safely used as alternative.

According to Laohaprapanon *et al.* (2010), the impurities in the unwashed WFA are likely to compete later on with the pollutants for the sorption sites (Kaczala *et al.*, 2009), resulting in lower removal of pollutants from the wastewater. Washing could be also employed as conditioning of the wood ashes to remove heavy metals (Liodakis *et al.*, 2009). A similar procedure was employed by Bauer *et al.* (2022), using five times more water than WFA to obtain the leachate. The main difference was that they neutralised the leachate with H_2SO_4 before adding it to the blend of SS and digested sludge to improve the AD process. Furthermore, Laohaprapanon *et al.* (2010) used a much higher dose (up to 75 % of washing water was mixed with 25 % of wastewater), compared to the 100 µL of neutralised leached per litre of sludge employed by Bauer *et al.* (2022) to undergo AD. According to Mall *et al.* (2006), the sorption rate is dependent on the pH and the number of sorption sites available. Laohaprapanon *et al.* (2010) did not neutralise the washing waters because they aimed the reaction between the dissolved oxides and the organic load and the subsequent increase the pH to values around 5 to 8 in which the $Al_2(SO_4)_3$ present in the wastewater would coagulate and remove the pollutants. M. Fan *et al.* (2005) prepared a complex coagulant containing $Al_2(SO_4)_3$ (Equation 2.22) and $Fe_2(SO_4)_3$ (Equation 2.23) from the CFA and reported a reduction in turbidity, arsenic and COD concentrations in water treated with the CFA-derived coagulant.

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$ **Equation 2.22**

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$ **Equation 2.23**

In order to assess the EoW status of the WFA, Laohaprapanon *et al.* (2010) analysed 12 trace metals in the treated wastewater and they only found concentrations greater than < 0.0005 mg/L in chromium, zinc, barium and lead. Usually cadmium is one of the main heavy metals leaching from the wood ashes (Narodoslawsky & Obernberger, 1996) but Laohaprapanon *et al.* (2010) reported a concentration < 0.0005 mg/L. The highest concentration of 3 mg/L corresponded to chromium despite this element is often a minor constituent in the wood. Laohaprapanon *et al.* (2010) suggested that its high concentration might be due to the treatment of the wood with preservatives containing chromates (*e.g.* painted wood) or the co-combustion with coal. Generally, chromium is oxidised in the combustion to produce the hexavalent form (Cr-VI) that can be dissolved in the leachate. The disposal of wood ash in an inert landfill is only allowed if the leachate does not exceed 0.05 mg/L of this element (Pohlandt-Schwandt *et al.*, 2002). The tolerance is greater for non-hazardous waste (1 mg/L) and for hazardous waste (7 mg/L) but also the cost of disposal (James *et al.*, 2012; Pöykiö *et al.*, 2011). In addition to promote the sorption properties, the washing can also be conceived as a treatment to decrease the heavy metal content of the WFA, before its use as fertiliser. Liodakis *et al.* (2009) revealed that more metals can be removed by washing with acidic aqueous solutions of pH 1 than when using an extractant with a pH 6, but they still found that even with a pH-6-wash, the 95 % of the Cr was removed from the wood ash. Pohlandt-Schwandt *et al.* (2002) developed a method to remove the Cr-VI from the WBA using aqueous formaldehyde solutions. The wastewater treated by Laohaprapanon *et al.* (2010) contained formaldehyde and this might be the reason for which they detected high extraction of Cr-VI. According to Pohlandt-Schwandt *et al.* (2002), the alkaline conditions promoted by the wood ash could promote the decomposition *via* disproportionation of the formaldehyde (Equation 2.24).

$$HCHO_{(aq)} + HCHO_{(aq)} + H_2O_{(l)} \rightarrow CH_3OH_{(aq)} + HCOOH_{(aq)} \qquad \textbf{Equation 2.24}$$

Source of this reaction taking place under strong alkaline conditions: (Akgül & Kruse, 2013)

Fomenko & Sokolov (2015) removed the phosphates in the wastewater using a mixture of the fraction of wood ash with granular sizes ranging from 0.08 to 2 mm and with a composition of 38.68 % CaO, 12.85 % MgO, 9.93 % SiO_2, 7.44 % SO_3, 3.75 % Fe_2O_3, 2.58 % K_2O, 2.31 % Al_2O_3, 0.45 % Na_2O, 0.44 % TiO_2, 0.40 % P_2O_5 and 17.11 % calcination loss (*e.g.* H_2O and C). It should be noted the low content of P was expressed as anhydrous orthophosphoric acid ($P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$) initially present in the wood ashes (Fomenko & Sokolov, 2015). Compared to the composition of the WFA reported by Laohaprapanon *et al.* (2010) with approximately 50 % unburned C, the wood ash employed by Fomenko & Sokolov should be less efficient adsorbent due to its lower C content (Leechart *et al.*, 2009). Pyrolysed biomass with a C content higher than 50 % is recognised as biochar, otherwise it is called pyrochar (W. Shi *et al.*, 2021). The differentiation of the adsorbent materials could also be made from the point of view of the manufacturing process. For example, the hydrochar produced *via* hydrothermal carbonisation presents lower porosity and surface specific area than the biochar (usually > 400 m^2 per gram of biochar). Furthermore, biochar presents greater content of condensed polyaromatic structures, which makes this material a good adsorbent for various contaminants. Nevertheless, due to the presence of oxygen-rich functional groups on the surface of hydrochar, its adsorption capacity is also high (W. Shi *et al.*, 2021). All these technologies to improve the management of the nutrients of the organic soil amendments are grouped as STRUBIAS (STRUvite, BIochar and ASh).

The silica particles in water can interact with the impurities to bear both negative and positive charges on the basal faces and on the lateral faces, respectively (Grekov *et al.*, 2021). Awad *et al.* (2019) reported the influence of the pH on the charge of the surfaces of the silicates. It should be noted that Fomenko & Sokolov (2015) did not adjust the pH to conduct the sorption kinetic and equilibrium experiments, and the pH was approximately 11.6. The extraction of negatively charged phosphate anions in sols and solutions was also possible as result of their interaction with metal cations to give aluminium phosphate and calcium and magnesium hydroxyapatites (Equation 2.25, Equation 2.26 and Equation 2.27). Furthermore, cations of trivalent iron can also extract phosphates from solutions by forming poorly soluble $FePO_4$ (Fomenko & Sokolov, 2015). In fact, it is possible to enhance the efficiency of phosphate precipitation with Ca and Mg by combining any of these elements with iron (H. Liu *et al.*, 2021; D. Wu *et al.*, 2021).

$$Al_2(SO_4)_{3_{(s)}} + 2PO_4^{3-}{}_{(aq)} \rightarrow 2AlPO_{4_{(s)}} + 3SO_4^{2-}{}_{(aq)} \qquad \textbf{Equation 2.25}$$

$$5Ca^{2+}{}_{(aq)} + 4OH^-{}_{(aq)} + 3HPO_4^{2-}{}_{(aq)} \rightarrow Ca_5(OH)(PO_4)_{3_{(s)}} + 3H_2O_{(l)} \qquad \textbf{Equation 2.26}$$

$$\begin{aligned} &5Mg^{2+}{}_{(aq)} + 4OH^-{}_{(aq)} + 3HPO_4^{2-}{}_{(aq)} \\ &\qquad \rightarrow Mg_5(OH)(PO_4)_{3_{(s)}} + 3H_2O_{(l)} \end{aligned} \qquad \textbf{Equation 2.27}$$

Fomenko & Sokolov (2015) reported phosphates removal of 77.8 % after 5 minutes, 87.99 % after 30 minutes and greater than 97.1 % after 3 hours in synthetic wastewater of initial concentrations of 100 – 600 mg K_2HPO_4/L. According to Fomenko & Sokolov (2015), the high rate of adsorption indicates a possible mechanism of physical adsorption (*i.e.* physisorption) caused by the van der Waals intermolecular interaction forces. The profile of the kinetics of removal of phosphate ions was like that found by Laohaprapanon *et al.* (2010) for the COD removal. The results of Fomenko & Sokolov (2015) proved the good equilibrium-kinetic properties of the wood ash as sorbent and the authors suggested that this material could be used without any additional processing for purification of water (> 80 % removal of phosphate ions). On the other hand, Laohaprapanon *et al.* (2010) found around 35 % removal of COD. The measurement of the concentration of adsorbate in equilibrium with the saturate sorbent is done after the solid liquid separation. In the case of Fomenko & Sokolov (2015), Laohaprapanon et al (2010) and Leechart *et al.* (2009) the saturated sorbent was separated from the solution *via* filtration. Fomenko & Sokolov (2015) acknowledged that aluminium or iron salts and lime are often used as coagulant for the chemical precipitation of the phosphates. The problems of these chemicals are their costs and the fact that the precipitates formed are highly humid with a limited application. Fomenko & Sokolov (2015) claimed that it is possible to utilise the spent adsorbent as a phosphate-saturated component of soils at green farms. According to W. Shi *et al.* (2021), the calcium phosphates have better fertilising properties than the phosphate compounds including aluminium and/or iron that completely reduce the availability of phosphate. In fact, both aluminium and iron are employed to prevent the eutrophication of underground waters due to the expressing of soil organic amendments, such as animal manure and slurry (Kavanagh *et al.*, 2021; Regueiro, Coutinho, Gioelli, *et al.*, 2016). The $Al_2(SO_4)_3$ and the iron chloride ($FeCl_2$ and $FeCl_3$; Equation 2.28) are among the best acidifying additives for the stabilisation of animal slurry anaerobic digestate (Drosg *et al.*, 2015; Kavanagh *et al.*, 2019, 2021). Furthermore, considering that the acidification also promotes the solid-liquid separation of the anaerobic digestate (Limoli *et al.*, 2016), the acid treatment should also improve the stability of the solid and the liquid fractions resulting from the separation (Zeshan & Visvanathan, 2014), hence avoiding the pollution swapping (Fangueiro *et al.*, 2015; Mohankumar Sajeev *et al.*, 2018).

$$Fe_3O_{4(s)} + 8HCl_{(aq)} \rightarrow FeCl_{2(s)} + 2FeCl_{3(s)} + 4H_2O_{(l)} \qquad \textbf{Equation 2.28}$$

2.3.4. Acidification of the anaerobic digestate and activation of the wood ash

The most common approach for the solid and the liquid fractions obtained after the separation is their use as fertiliser. There is particular concern about the emission form the resulting solid fraction (Dinuccio *et al.*, 2012, 2019; Dinuccio, Balsari, *et al.*, 2008; Dinuccio, Berg, *et al.*, 2008; Gioelli *et al.*, 2011, 2016), due to the higher area for gas exchange compared to the liquid fraction (Figure 2.6). While the gaseous emitting area of the slurry is the horizontal cross-section of the storage tank, the shape of the pile of dried organic manure was described by

Dinuccio *et al.* (2012), Dinuccio, Balsari, *et al.* (2008) and Dinuccio, Berg, *et al.* (2008) as truncated cone heap with greater area to volume ratio.


(a) (b)

Figure 2.6. (a) The surface area of the liquid slurry (3.9 % TS) in an open storage pond (Balsari *et al.*, 2007). Reprinted with the permission of Biosystems Engineering (Elsevier). (b) Surface area of dewatered pig slurry (65.4 % TS after composting without a bulking agent) (Pampuro *et al.*, 2017). Reprinted with the permission of Powder Technology (Elsevier).

Regueiro, Coutinho, Gioelli, *et al.* (2016) concluded that the $Al_2(SO_4)_3$ was able to reduce the gaseous emissions (NH_3, CO_2, CH_4 and N_2O) even after the solid-liquid separation (*i.e.* dewatering of the solid fraction) of raw and co-digested pig slurries. The $Al_2(SO_4)_3$ increases the TS in the liquid fraction but has the opposite effect in the solid fraction, obtained after the solid-liquid separation. Regueiro, Coutinho, & Fangueiro *et al.* (2016) attributed this fact to the role of the sulfate (Gioelli *et al.*, 2016) and explained that the increase of the TS in the liquid fraction *via* formation of low molecular weight carbohydrates derived from the acid hydrolysis of cellulose or hemicellulose. The acid pH provided by the $Al_2(SO_4)_3$ enhances the retention of nutrients in the liquid fraction, minimising the gaseous emissions from the solid fraction. It should be noted that the nutrients are more stable in the liquid fraction than in the solid fraction, due to the high moisture content (*i.e.* lower concentration) and lower surface area. Kavanagh *et al.* (2019) explained that a slurry with 4 % TS is more stable than the undiluted slurry with 7 % TS. Thereby, the lower amount of TS in the solid fraction, the lesser the gaseous emissions. Regueiro, Coutinho, Gioelli, *et al.* (2016) found that the gaseous emissions were also minimised in the liquid fraction, due to its lower pH compared to the liquid fraction obtained from the solid-liquid separation without acidification. It should be noted that the content of N, expressed in grams of N per gram of TS, decreased in the solid and in the liquid fractions due to the increase of the TS, which resulted from the addition of $Al_2(SO_4)_3$ (Regueiro, Coutinho, Gioelli, *et al.*, 2016).

The commercial acids, such as H_2SO_4, HCl, HNO_3 and H_3PO_4, or easily fermentable compounds which ultimately lead to the formation of organic acids due to the microbial metabolism, such as the lactic acid ($C_6H_{12}O_6 \rightarrow 2\ CH_3CH(OH)COOH$) or acetic acid ($C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$), represent the most obvious choice to reduce the pH of the organic manures (Anukam *et al.*, 2019; Fangueiro *et al.*, 2015; Mao *et al.*, 2015). However, better stabilisations have been reported with the use of salts such as $Al_2(SO_4)_3$ (Regueiro, Coutinho, Gioelli, *et al.*, 2016), $FeCl_2$ (Brennan *et al.*, 2015) and $FeCl_3$ (Hjorth *et al.*, 2009) and $CaCl_2$ (Y. Shi *et al.*, 2001; Vandré & Clemens, 1996). Miranda *et al.* (2021) found that the direct addition of H_2SO_4 to a 4.3 % blend of biochar and cattle slurry mitigated less the NH_3 emissions than just applying the 0.3 mL H_2SO_4 (98 %) to 50 g of cattle slurry to reach a pH 5.5. These acid salts can be produced by neutralising ores or ashes with commercial acids (Equation 2.22, Equation 2.23, Equation 2.28 and Equation 2.29). These salts are widely employed in the wastewater treatment for coagulation and precipitation of compounds (Drosg *et al.*, 2015; Regueiro, Coutinho, Gioelli, *et al.*, 2016). This use is in line with the properties of wood ash as sorbent (Fomenko & Sokolov, 2015; Hamidi *et al.*, 2021; Mosoarca *et al.*, 2020; Rosenfeld & Henry, 2001). The activation of the raw materials (*e.g.* ores and ashes) for the manufacturing of the salts might be the reason for which they are able to decrease the pH of the organic manures. The calcium chloride ($CaCl_2$) does not necessarily need to be produced with quicklime (CaO; Equation 2.29) but with slaked lime ($Ca(OH)_2$), limestone ($CaCO_3$) or a mixture of these compounds that might be present in the wood ash.

$$CaO_{(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2\,(s)} + H_2O_{(l)} \qquad \textbf{Equation 2.29}$$

The $CaCl_2$ is one of the key components of the specially formulated products to stabilise the organic manures (Kavanagh *et al.*, 2021) and this compounds is also widely used as extracting agent for soil analysis. A solution of 0.01 M of $CaCl_2$ provides with the same ionic strength (Houba *et al.*, 2000) as the average salt concentration in many soil solutions (*i.e.* the medium in which surface and aqueous solution reactions occur in the soil). The rationale of solubilising the elements to minimise the gaseous emissions agrees with the higher of the stability of the organic manures with higher moisture content. On the other hand, when manures are diluted with water, most of the H^+ ions tend to remain attracted to the solid particles and are not released to the aqueous fraction. The simple dilution of a manure with water reduces the emissions (Kavanagh *et al.*, 2019) but does not acidify the medium.

Leechart *et al.* (2009) developed the properties (*i.e.* greater surface area, the porosity and the surface charge of the carbon-based adsorbent) of the WBA by means of 2 different treatments. Each treatment consisted in suspending 100 g of WBA in 1 L of deionised water (WBA/H_2O) or 1L of 0.1 N H_2SO_4 (WBA/H_2SO_4) and stirring for 1 hour. Subsequently, the WBA was washed with an excess of double distilled water until the pH of the washing solutions reached constant values of ~ 11 and ~ 10 for the WBA/H_2O and the WBA/H_2SO_4 treatments, respectively. The WBA contained initially 4 % moisture, 29 % ash and it had pHs 12.3 and 11.6 in when soaking in 10 % suspensions with H_2O and 0.1 N H_2SO_4, respectively. These treatments were compared against the untreated WBA and the AC of coconut shells in terms of efficiency of adsorption of the azo reactive dye red 141 from synthetic and industrial wastewater. It should be noted that the use of H_2O as extracting agent resulted in a more alkaline pH because the dissolved alkali and alkaline metals of the WBA were not neutralised as in the case of using 0.1 N H_2SO_4 as extractant. According to Leechart *et al.* (2009), the reason for the alkaline pH when soaking the WBA in H_2O are the following reactions (Equation 2.30, Equation 2.31 and Equation 2.32):

$$2K_{(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_{2\,(g)}$$ **Equation 2.30**

$$2Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} + H_{2\,(g)}$$ **Equation 2.31**

$$2Mg_{(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_{2\,(g)}$$ **Equation 2.32**

Based on the Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDX) results, Leechart *et al.* (2009) recognised the presence of oxides in the surface of WBA. The redox reactions (Equation 2.30, Equation 2.31 and Equation 2.32) are unlikely upon adding the WBA to an aqueous solution because the alkali and alkaline earth metals are very good reducers. These elements would have donated their valence electrons to form the corresponding oxides during the combustion or during the storage the oxygen available in the atmosphere. Moisture (H_2O) and CO_2 in the atmosphere will further promote the formation of hydroxides and CO_3^{2-} in the wood ash. Since oxides, hydroxides and CO_3^{2-} are the most common forms of the metals in the wood ashes (Demeyer *et al.*, 2001), the reactions of the WBA in water, involving the alkali and alkaline metals, should be (Equation 2.33 to Equation 2.38):

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2K^+_{(aq)} + O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2K^+_{(aq)} + 2OH^-_{(aq)}$$ **Equation 2.33**

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$ **Equation 2.34**

$$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg^{2+}_{(aq)} + O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$ **Equation 2.35**

After the dissociation of the alkaline oxide, the oxide anion (O^{2-}) rapidly react with water (Barrett, 2007, pp. 98–123; Zumdahl, 2018), leading to the formation of hydroxide anion (OH^{-}).

$$K_2CO_{3(s)} + H_2O_{(l)} \rightarrow 2K^{+}_{(aq)} + CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow \\ \rightarrow 2K^{+}_{(aq)} + CO_{2\,(g)} + 2OH^{-}_{(aq)}$$ **Equation 2.36**

$$CaCO_{3(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow \\ \rightarrow Ca^{2+}_{(aq)} + CO_{2\,(g)} + 2OH^{-}_{(aq)}$$ **Equation 2.37**

$$MgCO_{3(s)} + H_2O_{(l)} \rightarrow Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow \\ \rightarrow Mg^{2+}_{(aq)} + CO_{2\,(g)} + 2OH^{-}_{(aq)}$$ **Equation 2.38**

It is important to mention that the shift of the reversible equilibrium of the carbonate ion Equation 2.39) is promoted *via* aeration and CO_2 stripping under acid conditions (Podmirseg *et al.*, 2013).

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow HCO_3^{-}{}_{(aq)} + H^{+}{}_{(aq)} \leftrightarrow CO_3^{2-}{}_{(aq)} + 2H^{+}{}_{(aq)}$$ **Equation 2.39**

Another way of promoting the CO_2 release and the increase of the pH of the aqueous suspension of the WBA is by increasing the temperature, since the gases are less soluble in the liquids at higher temperatures. The increase of the temperature can be also used to promote the decomposition of the CO_3^{2-} and the formation of more soluble and reactive oxides (Equation 2.40, Equation 2.41 and Equation 2.42). The CO_3^{2-} salts have lower solubility and reactivity that the oxides.

$$K_2CO_{3(s)} \overset{\Delta}{\rightarrow} K_2O_{(s)} + CO_{2\,(g)}$$ **Equation 2.40**

$$CaCO_{3\,(s)} \overset{\Delta}{\rightarrow} CaO_{(s)} + CO_{2\,(g)}$$ **Equation 2.41**

$$MgCO_{3\,(s)} \overset{\Delta}{\rightarrow} MgO_{(s)} + CO_{2\,(g)}$$ **Equation 2.42**

Calcination at temperature greater than 600 ºC would be required for the decomposition of the CO_3^{2-} (Galan *et al.*, 2013). It is noteworthy to mention that the opposite process, the carbonation, could be regarded as an activation treatment of the adsorbents, since this technology increases the C content and decreases the basicity of this material. Unlike acidification, the carbonation uses CO_2 rather than commercial acids to decrease the pH of the adsorbent. In addition to the reagents, the suitability of each activation treatment depends on the origin of the adsorbent and the primarily mechanism for capturing the nutrients (Table 2.6). Laohaprapanon *et al.* (2010) reported that the sieving the WFA just below 1 mm, rather than below 2 mm, increased the removal of BOD and TOC from 24.5 and 0 % to 33.3 and 15.9 %, respectively (Laohaprapanon *et al.*, 2010). The authors reported that no increase in the removal efficiencies of COD and TOC after reducing the particle size from < 1 mm to < 0.5 mm because the fraction < 1 mm also contains < 0.5 mm particles. The removal efficiencies were lower than the ones obtained with the AC but the WFA still represent a low-cost material alternative for wastewater treatment due to its availability.

Table 2.6. Implications of the activation treatments that affect the suitability for a particular application (*e.g.* preparation of a slow-release fertiliser, liming agent, recovery of nutrients from wastewater, etc.). Elaborated by considering the descriptions provided by Al-Mallahi *et al.* (2020), Janiszewska *et al.* (2021), Leechart *et al.* (2009), Yagi & Fukushi (2012), Latham *et al.* (2021) and Lü *et al.* (2022).

Activation procedure	**C content**	**pH**	**Reactivity**
Carbonisation	Increase, due to loss of volatile compounds containing H, O, S and N	Slightly increase, due to the accumulation of ash with alkali and alkaline elements	Decrease. Mainly charred materials and recalcitrant compounds
Carbonation	Increase, in the form of inorganic carbon	Decrease, due to the neutralisation of the alkaline element with carbonic acid	Decrease, because CO_3^{2-} are less soluble than oxides.
Calcination	Decrease, since all volatile compounds have already been lost in the carbonisation	Increase, due to the release of CO_2	Increase, due to the formation of oxides
Acidification	Decrease, due to the dissociation of the CO_3^{2-}-C and subsequent CO_2 emissions	Decrease, due to the dissociation of the commercial acids	[a]Slightly increase
Wash	Slightly decrease, due to the removal of impurities	Slightly decrease, due to the solubilisation of alkalis	Slightly decrease, due to extraction of oxides

Activation procedure	**C content**	**pH**	**Reactivity**
Milling and sieving	Slightly increase. Might enhance carbonation reactions during storage	Slightly increase. Might enhance the reaction for acidic and alkaline salts	Increase, due to greater availability of the elements

[a]The oxides of the alkaline elements are more soluble and reactive than the CO_3^{2-}. It is considered that the acidification of the alkaline oxides (*e.g.* CaO) with commercial acids, rather than with CO_2, surpasses the preparation of adsorbents (*e.g.* $CaCO_3$) and lead to the formation of coagulants and flocculants (*e.g.* $CaCl_2$; Equation 2.29).

Leechart *et al.* (2009) used the Brunauer, Emmett and Teller (BET) isotherm to determine the sorptive surface area. It should be noted that the BET isotherm considers the possibility that the monolayer in the Langmuir adsorption isotherm could act as a substrate for further adsorption. The N adsorption-desorption isotherm employed for the BET study of these adsorbents was characterised by clear hysteresis loops due to the capillary condensation occurring in the mesopore range (Leechart *et al.*, 2009). The H_2O treatment removed some tars and led to a higher development of porosity and surface area than the treatment with 0.1 N H_2SO_4. The WBA/H_2O still had lower surface area than AC. The average pore diameter of WBA, WBA/H_2O and WBA/H_2SO_4 was of mesoporous size (*i.e.* 20 – 500 Å) whilst the AC had micropores. All adsorbents (WBA, WBA/H_2O, WBA/H_2SO_4 and AC) were ground and sieved to the size of 0.75 µm before drying at 105 °C for 4 hours (Leechart *et al.*, 2009). WBA, WBA/H_2O, WBA/H_2SO_4 and AC removed 57, 73, 87 and 97 % of a recalcitrant azo dye with sulfonate groups (D-SO_3Na) from a solution with an initial concentration of 400 mg/L wastewater, when these adsorbents were applied at a dose of 2 %. It is important to mention that the WBA/H_2SO_4 removed more reactive dye than the WBA/H_2O despite the WBA/H_2SO_4 had less BET surface area and its pore size was greater. In the aqueous solution, the sulphonate groups are dissociated and converted to the anionic dye ion (Mall *et al.*, 2005): $\text{D-SO}_3\text{Na} \rightarrow \text{D-SO}_3^- + \text{Na}^+$. The precipitation of aggregation complexes needed an abundant Ca^{2+} ion surrounding. Divalent Ca^{2+} ions can reduce the negative zeta potential on molecules more than monovalent Na^+ ions, at a fixed ionic strength (Awad *et al.*, 2019). Leechart *et al.* (2009) reported that only ~ 14 % of the dyes were removed despite the Ca^{2+} ion in solution was not entirely consumed and its concentration decreased from ~ 80 mg/L to ~ 45 mg/L. Removal of the D-SO_3Na was attributed to a combination of dye aggregation and adsorption. Leechart *et al.* (2009) reported that in addition to reduce the colour of the wastewater, the WBA based adsorbent was able to reduce the high level of COD. The adsorption of the D-SO_3Na increased by increasing the temperature. Leechart *et al.* (2009) explained that this might be due to the greater mobility of large dye ions at higher temperature. The endothermic process involved both chemical adsorption and precipitation with Ca.

The effect of the initial pH on the D-SO_3Na removal was explained by the amphoteric character of WBA/H_2O and WBA/H_2SO_4. Depending on the system pH, the surfaces of the adsorbents might be positively or negatively charged and this would have direct influence on electrostatic interactions. Leechart (2009) estimated the charge on the surface of the adsorbent particles (Q; Equation 2.43) by means of a titration method, which unlike the measurement of the zeta potential does not require specialised equipment and both parameters can be used interchangeably (Schwarz *et al.*, 2000). The zeta potential is the electrical voltage at the interface that separates mobile fluid from the fluid that remains attached to the particle surface. The pH of zero-point charge (pH_{zpc}) is defined as the pH that neutralises the surface charge of sorbents. The pH_{zpc} could be identified by plotting Q versus the pH and determining the minimum value of the quadratic regression (Figure 2.7).

$$Q = \frac{1}{W}(C_a - C_b - [H^+] + [OH^-])$$ **Equation 2.43**

Q (mol/L/g sorbent), surface charge.
W (g/L), mass of WBA based adsorbent in the aqueous system (*i.e.* analyte).
C_a (mol/L), concentration of the acid titrant in the aqueous system.
C_b (mol/L), concentration of the basic titrant in the aqueous system. In the case of the wood ashes, the addition of alkali is not required to determine the pH_{zpc} and this parameter is equal to zero.
$[H^+]$ & $[OH^-]$, concentration of H^+ and OH^- resulting from the direct measurement of the pH in the aqueous system ($pH=-\log([H^+])$; $[H^+]\cdot[OH^-]=10^{-14}$).

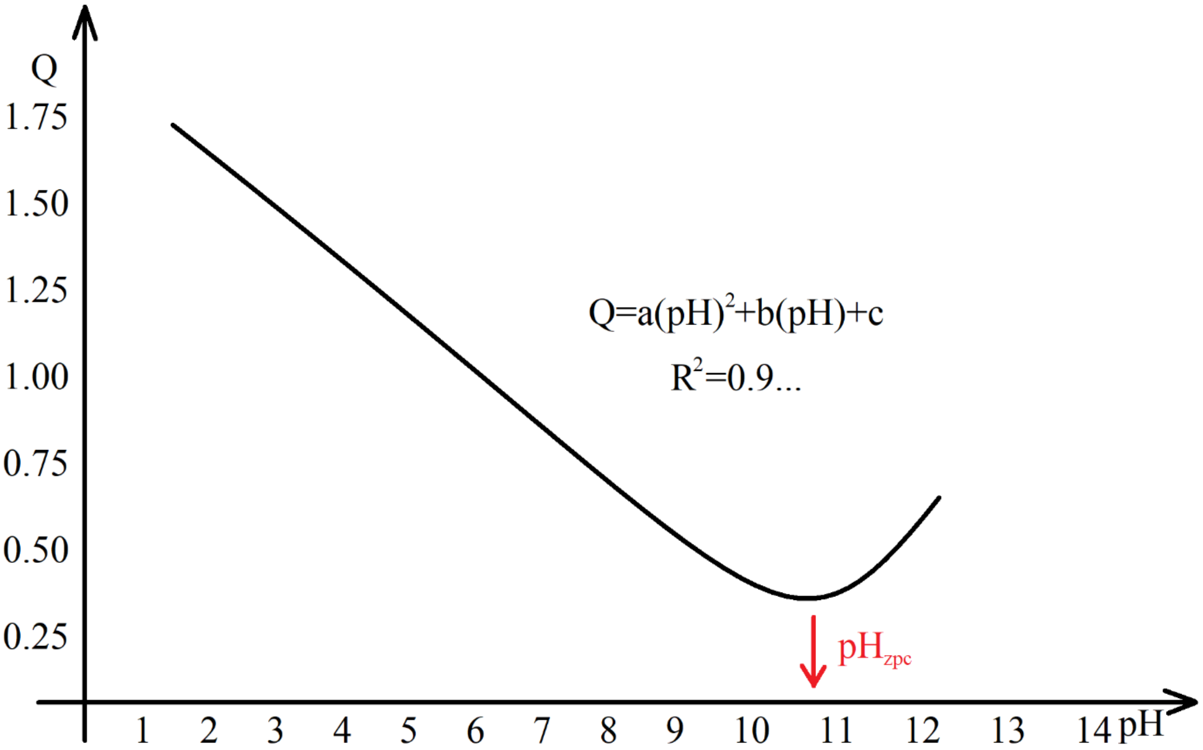


Figure 2.7. Determination of the pH_{zpc} of the WBA representing the surface charge of the WBA adsorbent, Q, as a function of the titrate aqueous solution (Moure Abelenda & Aiouache, 2022). Elaborated from the description provided by Leechart *et al.* (2009) and Shah *et al.* (2015).

In the case of the WBA, WBA/H_2O, WBA/H_2SO_4 and AC the pH_{zpc}s were 10.8, 10.9, 10.9 and 9.5, respectively (Leechart *et al.*, 2009). While the systems had a lower pH than the pH_{zpc} the surface of the WBA-based adsorbents becomes positively charged (Equation 2.44), favouring the adsorption of anionic species. Furthermore, since the pH of minimum solubility of CaO and MgO are 11.0 and 12.4, the surface of CaO and MgO could support the adsorption of the dye when the pH of the system was greater than pH_{zpc}. The adsorption of the D-SO_3Na increased by increasing the temperature. Leechart *et al.* (2009) explained that this might be due to the greater mobility of large dye ions at higher temperature. The endothermic process involved both chemical adsorption and precipitation with Ca.

$$Surface^{+}_{(n-1)} \underset{+H^{+}}{\overset{+OH^{-}}{\longleftrightarrow}} \underbrace{Surface^{0}_{n}(s)}_{pH_{zpc}} \underset{+H^{+}}{\overset{+OH^{-}}{\longleftrightarrow}} Surface^{-}_{(n+1)} \qquad \textbf{Equation 2.44}$$

The plus (+), zero (0) and minus (-) represent the oxidation state of the surface.
The “n” represents whether the surface is available: (n+1) corresponds 2 surfaces attached and (n-1) represents 1 sorptive site available

Leechart *et al.* (2009) concluded that the WBA/H_2O used more heterogeneous surface than the WBA/H_2SO_4 for the adsorption of the D-SO_3Na. The adsorption behaviour of WBA/H_2O was less favourable than WBA/H_2SO_4 and AC. Both WBA/H_2SO_4 and AC could be regarded as weakly irreversible adsorbents with very low desorption rates of the D-SO_3Na. According to the dye loading experiments and subsequent elution studies, dyes adsorbed to WBA/H_2O and WBA/H_2SO_4 were very difficult to desorb, hence these dye-loaded adsorbent could be safely disposed. This implies that the WBA might be suitable to produce a controlled-release fertiliser in combination with the anaerobic digestate.

2.3.5. Use of wood ash to enhance the dewatering of the anaerobic digestate

The dewatering of the anaerobic digestate is required to reduce the cost of storage, transportation and land application (Victor, 2020; Wood *et al.*, 2020). Although the AD plants are located in strategic site, usually with several farms around and with plenty of nearby areas to apply the anaerobic digestate to land, the transportation of this material to remote locations is still required once the nutrient quotas is reached in the fields around the plants (Drapanauskaite *et al.*, 2021; Ronga *et al.*, 2020). A costly membrane treatment with a final step of reverse osmosis is able to produce an effluent that meets the specification to be discharge to the local rivers. The greater the efficiency of the solid-liquid separation applied to the anaerobic digestate, the more expensive is the treatment (Drosg *et al.*, 2015). The sorption and precipitation processes are investigated as a way of reducing the cost of the purification of the water and prevent the eutrophication of underground water. Yagi & Fukushi (2012) studied the mechanisms of adsorption and precipitation of calcium phosphate onto monohydrocalcite ($CaCO_3 \cdot H_2O$). The clean effluent obtained by of Yagi & Fukushi (2012) could be coupled with air or CO_2 bubbling to remove any trace of Ca^{2+} ion *via* precipitation of $CaCO_3$ (Courtney *et al.*, 2021). Similarly, Brennan *et al.* (2015) tested whether the addition of lime to the cattle slurry minimised the emission of NH_3, N_2O, CH_4 and CO_2 and the leaching of WS PO_4^{3-}.

Commercial acids are also employed to activate the ash and the preparation of a cheap and sustainable sorbent (Equation 2.22, Equation 2.23, Equation 2.28 and Equation 2.29). For example, as described by Mor *et al.* (2016), who used the calcination at 500 ºC and HCl to activate the rice husk ash. Mor *et al.* (2016) reported an increase in the adsorption of the WS PO_4^{3-} with a maximum removal (91.7 %) of WS PO_4^{3-} at pH 2 and the lowest removal at pH 10. According to Mor *et al.* (2016), this is because at high pH there are more OH^- interacting with the surface, thus decreasing the WS PO_4^{3-} adsorption. Ma *et al.* (2011) described a more complicated activation procedure for producing an adsorbent based on wheat straw. They reported how the pH and the level of hydration affect to the adsorption of WS NH_4^+ and WS PO_4^{3-} (Ma *et al.*, 2011). According to the results of Ma *et al.* (2011), the optimum pH for the adsorption of these ions is between 4 and 8. The explanation that Ma *et al.* (2011) provided for the trend of the WS NH_4^+ is that at acidic pH, the H^+ ions will compete with the WS NH_4^+ for the anionic groups in the wheat straw derived adsorbent. On the other hand, at alkaline pH the more NH_4^+ will be in the form of NH_3 that will escape from the aqueous solution. According to Ma *et al.* (2011), the adsorption of WS PO_4^{3-} showed less dependence on the pH. Ma *et al.* (2011) described the impact of the pH and the swelling capacity (*i.e.* hydration) of the performance of the wheat straw derived adsorbent. The high swelling of the wheat straw derived adsorbent obtained at pH 3 and above was associated with high diffusion of the water and ions into the pores and through the internal skeleton of the adsorbent. The highest swelling was obtained at a pH 7 because in acidic and alkaline solutions, the higher concentration of H^+ and OH^- ions reduce the difference of ion concentration between inside and outside the porous network structure of the wheat straw derived adsorbent (Ma *et al.*, 2011). As described by Awad et al (2019), the swelling phenomenon is often associated with an increase in the adsorption of the organic materials in the WS phase. This can also be seen in the structure of the struvite (Figure 2.5), in which the nutrients NH_4^+ and PO_4^{3-} remain attached to the magnesium hexaaqua ($Mg^{2+}(H_2O)_6$).

The studies of Ma *et al.* (2011) and Mor *et al.* (2016) provided opposite results in terms of how the pH and the level of swelling/hydration affect the adsorption. The dehydration without acidification was tested by Zheng *et al.* (2016). They used a cationic surfactant (cetyltrimethylammonium bromide; CTAB) together with CFA to ease the filtration of the anaerobic digestate. The CTAB neutralised the negative charges on the surface of the flocs of the anaerobic digestates, reduced the electrostatic repulsion between the flocs and promoted the coagulation-flocculation. Moreover, the neutralisation of the charges allowed the release of the extracellular polymeric substances (EPS) of the cells and fibre of the digestates and bound water molecules. The proteins and polysaccharides are components of the EPS that largely contributed to enhance the binding ability of water to the flocs of the digestate. Award *et al.* (2019) divided the EPS in subgroups of mains source of C, N and P. An example of EPS containing P fraction would be the nucleic acids (Awad *et al.*, 2019). After the release of the hydrated EPS from the flocs surface, the bound water that was coordinated with the EPS became free water (Zheng *et al.*, 2016). On the top of that, the CFA acted as a rigid lattice to reduce the filter cake compressibility and to provide drainage pathways for water to exit the filter cake (Figure 2.8).

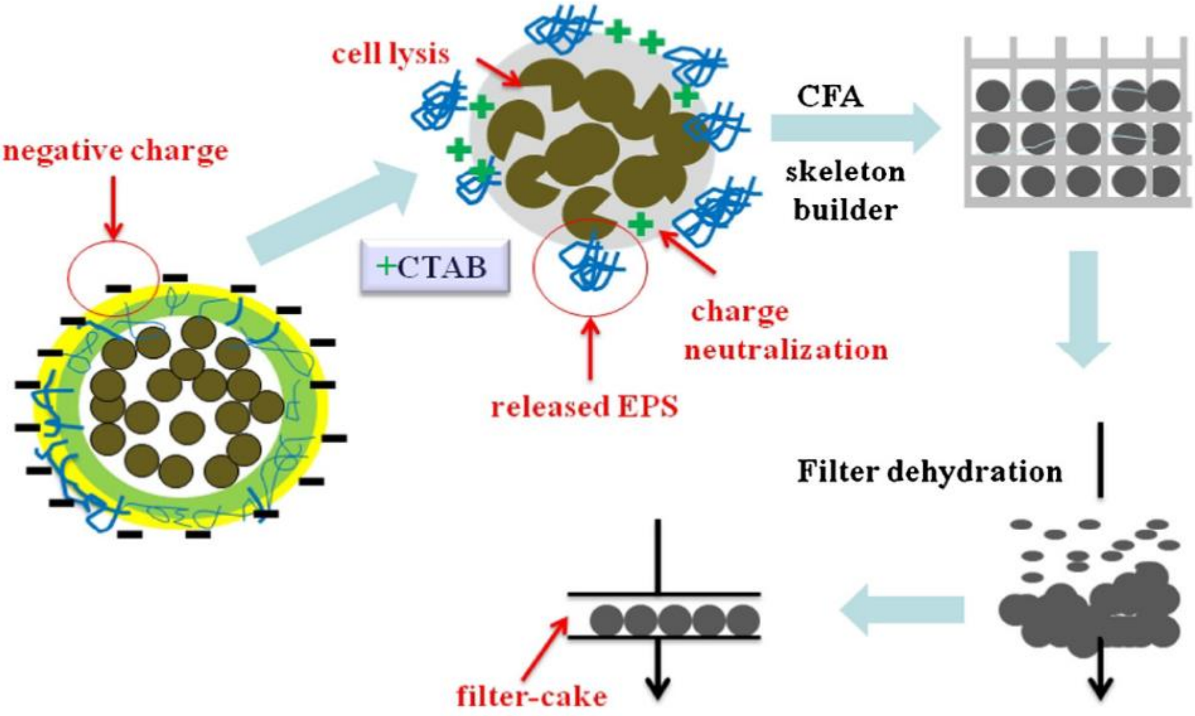


Figure 2.8. The mechanism proposed by Zheng *et al.* (2016) for the flocculation of the anaerobic digestate by adding a cationic surfactant (CTAB) and subsequent filtration using coal fly ash (CFA) to improve the drainage of the filter cake to achieve the dewatering. The CTAB neutralised the surface charges of the flocs of the anaerobic digestate and enable the release of the hydrated extracellular polymeric substances (EPS). The CFA acted as a physical conditioner and skeleton builder of the filter cake and enhanced the mechanical solid-liquid separation by decreasing the compressibility of the filter cake. Reprinted with the permission of Separation and Purification Technology (Elsevier).

The improvement in the filterability and the solid-liquid separation of the anaerobic digestate can be also attained by neutralising the anaerobic digestate with H_2SO_4 after the addition of NaOH to perform the NH_3 stripping (Limoli *et al.*, 2016). Based on the results of the capillary suction time and the specific resistance to filtration, Limoli *et al.* (2016) concluded that the increase in the sludge dewaterability was due to change in the structure of the flocs and microbes and variation of the properties of the particle surface. A more suitable technique for determining the changes it the surface of the particles is the zeta potential because is a measure of the surface charge (Zheng *et al.*, 2016). As consequence of improving the filterability the overall amount of EPS in the filtrate/supernatant was greater (Zheng *et al.*, 2016), unless the

EPS were retained in the filter cake. In addition to contaminate the supernatant with CTAB, it should be noted that the EPS increased the COD of the filtrate. Their approach was different from enhancing the adsorption but Zheng *et al.* (2016) recognised that the surface of the CFA was coarse and porous, which could aid particle adsorption. It could be expected that enhancing the filtration by means of vacuum leads to NH_3 volatilisation during this mechanical separation step that needs to be recovered (Ukwuani & Tao, 2016). The efficiency of the solid-liquid separation was not as high as if pure water was obtained after the filtration and the effluent cannot be directly discharged to the local river. Thereby, wastewater treatment is still required for this liquid fraction of the anaerobic digestate (Drapanauskaite *et al.*, 2021; Drosg *et al.*, 2015). It is important to remark that the solid-liquid separation needs to be done in a way (*e.g.* using the appropriate additives) that it does not affect negatively the stability of the resulting solid and liquid fractions in order to holistically improve the management of the anaerobic digestate (Zeshan & Visvanathan, 2014).

The maximum dose of CFA recommended by Zheng *et al.* (2016) is as much TS provided by the anaerobic digestate, otherwise a very large mass of filter cake will be obtained. Limoli *et al.* (2016) reported that after filtration, the solid fraction was 20 – 25 % TS and that those solids were able to trap NH_3 in their surface, reducing the volatilisation of this compound. In terms of the mass of CTAB used to prepare the blend before the filtration, Zheng *et al.* (2016) recommended not to exceed half of the amount of dry matter (DM; Equation 2.45) in the digestates. According to Zheng *et al.* (2016), CTAB was mixed with the digestates for 20 minutes at 200 rpm after which the ash was added and the stirring at 300 rpm continues for 10 minutes. Although they tested higher doses of ash, for practical reasons they recommended to use as much ash as the DM of the digestate, since using greater dose of ash would generate an excessive amount of dewatered material. Laohaprapanon *et al.* (2010) also proposed to use the wood ash as a sorption media/filter.

$$DM(\%) = \frac{TS(\,g/L)}{10} \qquad \textbf{Equation 2.45}$$

DM, dry matter
TS, total solids

The technology developed by Zheng *et al.* (2016) is not limited to filtration and it could be applicable to any system of mechanical solid-liquid separation (*e.g.* screw press) since the role of the ash is to provide drainage pathways for water to exit. The acidification promote the dehydration of the solids (Limoli *et al.*, 2016) but there is no clear evidence in literature whether this is always associated with an increase in the adsorption (Ma *et al.*, 2011; Mor *et al.*, 2016) and the optimum conditions might depend on the type of adsorbent. In the structure of the struvite (Figure 2.5), the Mg^{2+} is able to coordinate with the WS PO_4^{3-} and the WS NH_4^+ despite being surrounded by six water molecules arranged according to an octahedral geometry. Nevertheless, the removal of PO_4^{3-} (N. Park *et al.*, 2021) and the NH_4^+ (Escudero *et al.*, 2015) from the WS phase *via* struvite crystallisation is not promoted at acidic pH. The dose of acid needs to be as much as is required to reach the pH_{zpc} without further decrease (Leechart *et al.*, 2009).

It might be possible to apply the mechanism of formation of struvite for the activation of the wood ash as sorbent. Due to the complexity of the composition of the bulk wood ash and the presence of carbonaceous compounds, this sorbent material could be more versatile than if only the available Mg were provided by the wood ash. The rate of dehydration of the wood ash loaded with organic compounds (*e.g.* urea; $CO(NH_2)_2$) is a key factor to minimise the amount of NH_3 that might be lost (Simha *et al.*, 2020). The thermal drying of the anaerobic digestate is well-known for the NH_3 emissions, particularly if the alkaline pH is generated by the wood ash (Simha *et al.*, 2018) to enhance the evaporation process (Ukwuani & Tao, 2016). There are options available to proceed with the dewatering of the anaerobic digestate by means of this energy-intensive technology, such as the acidification before drying to pH 5.5 (Pantelopoulos *et al.*, 2016) or the use of a H_2SO_4 scrubber to recover the NH_3 from the exhaust (Awiszus *et al.*, 2018). It would be also possible to perform the nitrification before providing the conditions for the evaporation of water (Botheju *et al.*, 2010). Alkaline conditions at low temperature (< 40 ºC) prevent the volatilisation of NH_3 and can be provided with $Ca(OH)_2$ or wood ash at a total cost of 0.03 to 0.04 Euros/L urea (Riechmann *et al.*, 2021).

2.3.6. Production of granular fertiliser with wood ash and anaerobic digestate

The features of the process of Limoli *et al.* (2016) employing CaO and H_2SO_4 and the process of Zheng *et al.* (2016) using CFA and CTAB were compared against processes implementing the granulation, as this step could improve the aesthetic properties of the blended fertiliser of wood ash and anaerobic digestate to be retailed (Table 2.7). There is a lack of holistic approach in the processes described above as none of them complies with the entire of the following objectives:

- Using of the most cost-efficient way of achieving the solid-liquid separation.

- Finding the optimum nutrient profile of the main stream coming out of the process, intended to be used as organic amendment.
- Self-hardening to provide this material with the best mechanical properties before and after the granulation.
- Minimising any waste streams with valuable nutrients or other pollutants that need to be removed before disposal.

Table 2.7. Identification of the synergies and possibilities in processes involving the mixture of anaerobic digestate or SS with wood ash or alike materials.

Process	Raw Materials	Blending Ratio	Advantages	Disadvantages
Limoli *et al.* (2016).	Anaerobic digestate, CaO and H_2SO_4.	> 95 % moisture of anaerobic digestate. Dose of CaO to operate the stripping at pH 10.	Recovery of the NH_3 volatilised. Enable the self-hardening and granulation of the NH_3-depleted organic amendment.	Low fluency to be employed in a traditional stripping column (*i.e.* packed tower). High COD content of the filtrate.
Zhengh *et al.* (2016).	Anaerobic digestate, CFA and CTAB.	> 93 % moisture of anaerobic digestate. Mass of CTAB up to half of the TS of the digestate. Mass of CFA up to the TS of the digestate.	Reduce the energy consumption of the filtration of anaerobic digestate. Possible to enhance the mechanical separation with adsorption.	Presence of CTAB and heavy metals of the CFA in the filtrate. High COD content in the filtrate.
RecoPhos (Weigand *et al.*, 2013).	SS and H_3PO_4.	Incineration to produce SS ash. Reaction of the SS ash with the H_3PO_4 using P molar ratio 1:12 of SS ash:H_3PO_4.	Marketable granular product with similar properties to the triple superphosphate.	The NH_3 volatilised during the drying is not recovered. Emission of NO_x during incineration.
ADFerTech (Fivelman, 2013).	Anaerobic digestate, dolomite ($CaMg(CO_3)_2$),	Solid-liquid separation of the anaerobic digestate. Dolomite was added to the liquid fraction (> 91 %	Improve the aesthetic properties of the liquid fraction of anaerobic digestate. Decrease the cost of transportation and storage.	Additives of the liquid fraction of the anaerobic digestate might not be suitable for land application.

Process	**Raw Materials**	**Blending Ratio**	**Advantages**	**Disadvantages**
	organic binders and coating.	moisture) in a dose ranging from 10 to 200 g/L.		
Pesonen *et al.* (2016).	SS, wood-peat ash and $Ca(OH)_2$.	Up to 40 % of SS (45 % moisture) and up to 30 % $Ca(OH)_2$. The dose of ash can go up to 100%.	No need to including $Ca(OH)_2$ to have a high compressive strength. Low presence of heavy metals.	Dewatering and sanitation The NH_3 released is not captured.
Jewiarz *et al.* (2018).	Anaerobic digestate and woody biomass.	18 – 20 % moisture of the anaerobic digestate. Up to 75 % wood ash.	Save in energy for drying the anaerobic digestate by thermal drying in fueling the drum drier with the biomass to produce the ash.	The NH_3 released is not captured. Not possible to include the biofertiliser together with the ash due to the high pH.

2.3.7. Inoculation of biofertilisers in the blended fertiliser prepared with anaerobic digestate and wood ash

The composition of the digestate also depends mainly on the composition of the feedstock used for AD. The content of primary macronutrients (N, P, K), secondary macronutrients (Ca, Mg, Na and S), micronutrients (B, Co, Cu, Cl, Fe, Mn, Mo, Ni, Se and Zn) and heavy metals (Pb, Cr, Cd and Hg) remains the same (European Parliament, 2003, 2019; Lukehurst *et al.*, 2010). This is because, despite the mass of the feedstock reduces up to 15 % during AD due to the C release in the form of biogas, the volume is approximately the same (Pell Frischmann Consultants Ltd, 2012). Frost & Gilkinson (2010) reported a concentration of 3.5 g of N per kg of feedstock (dairy cow slurry) and 3.6 g of N per kg of anaerobic digestate. The slightly increase in the concentration could be explained by the fact that the biogas contains trace amounts of N so most of it remains in the digestate. It is worth to mention that, in their study (Frost & Gilkinson, 2010), the concentration of NH_3 increased significantly from 2.0 g NH_4-N/kg in the feedstock (dairy cow slurry) to 2.4 g NH_4-N/kg in the digestate. The mineralisation of N containing organic compounds, *e.g.* proteins, is well known to happen during AD (Möller & Müller, 2012). The changes of the organic molecules that occur during AD, enhance the bioavailability of nutrients to crops (Lukehurst *et al.*, 2010).

After the removal of the pathogens by processing the anaerobic digestate with wood ash (USA EPA, 2000), it is possible to inoculate microbial species (Rajendran & Devaraj, 2004) which enhance the fertilising effect of the blended fertiliser (Jewiarz *et al.*, 2018). In the UK, the laboratory test for the determination of the microorganism present in the digestate should be done in accordance to the Biofertiliser Certification Scheme (Renewable Energy Assurance Ltd, 2015) and the appointed laboratories (Renewable Energy Assurance Ltd, 2017). These microbes regarded as biofertilisers are divided in four categories (S. C. Wu *et al.*, 2005). The following are some examples of microbial species that can improve the fertilisation in the rhizosphere:

1. Vascular Arbuscular Mycorrhiza fungus.
    - *Glomus mosseae* (Aseri *et al.*, 2008; S. C. Wu *et al.*, 2005).
    - *Glomus intraradices* (S. C. Wu *et al.*, 2005).
    - *Glomus fasciculatum* (Aseri *et al.*, 2008).
2. N-fixer bacterias can be symbiotic and non-symbiotic.
    - *Azotobacter chroococcum* (Aseri et al., 2008; Mahfouz & Shamf-Eldin, 2007; S. C. Wu *et al.*, 2005).

  - *Azospirillum lipoferum* (Mahfouz & Shamf-Eldin, 2007).
  - *Azospirillum brasilense* (Aseri *et al.*, 2008; Mahfouz & Shamf-Eldin, 2007).
3. PO_4^{3-}-solubilising bacteria.
  - *Bacillus megatherium* (Mahfouz & Shamf-Eldin, 2007; S. C. Wu *et al.*, 2005).
4. K-solubilising bacteria.
  - *Bacillus mucilaginous* (S. C. Wu *et al.*, 2005).

Mahfouz & Shamf-Eldin (2007) concluded that the growth of the plant Fennel (*Foeniculum vulgare* Mill.) was greater when using half of the recommended dose of the NPK mineral fertiliser (*i.e.* synthetic material containing N, P and K) and a mixture of *Azotobacter chroococcum*, *Azospirillum lipoferum* and *Bacillus megatherium*, compared to the full NPK dose. The total carbohydrates in the dry plant material were impacted by the use of the mixture of biofertilisers. Similarly, the biofertilisers also increase the yield of essential oil in the plant (Mahfouz & Shamf-Eldin, 2007). According to Brar *et al.* (2015), the best physical properties of the soil (*e.g.* water infiltration) and highest crop yield in maize-wheat rotation were obtained by means of a balanced application of NPK fertilisers and organic farmyard manure (Singh Brar *et al.*, 2015).

In addition to greater crop growth, better fertilisation is also associated with less GHG emissions, since the nutrients are employed more efficiently once the organic material is applied to the soil. Johansen *et al.* (2013) evaluated compared the raw and digested animal slurry and a green manure (*e.g.* grass-clover) in terms of their impact in the soil microbiota and fertility because organic farmers are concerned about the lower C/N of the anaerobic digestates. Johansen *et al.* (2013) found that anaerobic digestates increased 30 40 % the amount of NO_3^- in the soil, compared to when raw slurry was applied. On the other hand, the green manure provided 4 times more degradable C_{org} than the digested and undigested slurries. The green manure caused an increase in the microbial population in the soil and led to the depletion of the oxygen associated to any type of eutrophication. Therefore, the green manure increased approximately 10 times the emissions of CO_2 and N_2O during the 9 days of the incubation (Johansen *et al.*, 2013). The study of Johansen *et al.* (2013) confirmed the AD as a climate mitigation technique upon land application of the organic amendments.

2.4.Land application of a combination of anaerobic digestate and wood ash

Usually, the studies about the performance of the organic amendments in the soil evaluate the transformation of C, N and P. The K does not become part of structural components in the crops and remains dissolved in the plants' cell sap. In fact, this is the reason for which this element is found in manures and digestates (Möller & Müller, 2012). The higher NH_4^+-N content of digested slurries, compared to the undigested ones, does not guarantee an improvement in the uptake efficiency of the slurry-N and better savings in fertiliser-N. Contradictory results regarding the phytotoxicity of the anaerobic digestate can be found in literature, particularly associated to the NH_4^+-N and acid concentrations (Möller & Müller, 2012). Organic farmers are concerned about how this organic manure with a greater share of ready available N and lower content of C_{org} might affect the soil microbiota, fertility and contamination of the environment *via* lixiviation and gaseous emissions (Johansen *et al.*, 2013). According to Möller & Müller (2012), negative phytotoxic effects of any kind will decrease shortly after land application of the anaerobic digestate.

There are a number of processes that are triggered by the application of anaerobic digestate to the soil, such as priming effects and inorganic-N immobilisation. A significant negative correlation between the net N mineralisation and the mineralised C has been reported (Möller & Müller, 2012). The carbon use efficiency (CUE) or the metabolic quotient (qCO_2) can be used to account the priming effect upon application of an organomineral amendment to land (Dijkstra *et al.*, 2015; Fernández-Delgado Juárez *et al.*, 2015). The CUE measures the fraction of C employed for microbial growth (*i.e.* g biomass-C synthesised/g substrate-C consumed (Dijkstra *et al.*, 2015)) and which is not lost as part of the microbial respiration (*i.e.* C mineralisation). On the other hand, the qCO_2 is focussed on the basal respiration and it is calculated by dividing the mineralised C by the microbial C, which is usually determined as TOC in the extract of a soil sample with a 0.5 M K_2SO_4 solution after fumigation with chloroform.

The interactions with the elements present in the soil should be considered at the time of preparing the blend. Nevertheless, the assessment of the enhancement of the microbial activity and the C fate needs to be done in field experiments. Bougnom *et al.* (2012) employed three different rates of wood ash (0, 1 and 3 t/ha) together with manure digestate (67 t/ha) as fertiliser for pastures. The corresponding dose of wood ash relative to the anaerobic digestate would be lower than 5 %. They did not find significant difference in terms of C 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 Juárez *et al.* (2013) concluded that the C assimilation was not affected by the dose of wood ash (0, 1 and 3 t/ha), but in their study lower losses of C 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). These would correspond to dose of wood ash was roughly 5 and 7 % for the anaerobic digestate and the undigested cattle manure, respectively.

The characterisation of the WS extract of the blend before land application (*i.e.* without dilution with the elements of the soil), represents a more conservative scenario to assess the readily available nutrients, since more leaching and volatilisation are expected due to higher concentration of nutrients. Insam *et al.* (2009) 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 fertilisation of a 350 kg/ha mixture of seeds (85% grass and 15% legume). The dose of wood ash, relative to the anaerobic digestate, employed by Insam *et al.* (2009) was around 21 %. From the point of view of logistics to be managed in place, the characterisation of the blend alone could clarify how long before the land application the mixture should be prepared, the type of storage and whether advance processing (*e.g.* removal of heavy metals) would be required to achieve the end-of-waste status.

2.4.1. Biological stability and maturity of the soil organic amendment

In some of the UK and European regulations, the term stability and maturity are used indistinctly to describe the properties of a soil organic amendment (Saveyn & Eder, 2014; UK Government, 2012; WRAP, 2011). The biological stability is related to the reactions affecting the fate of C, which is the most abundant element in the organic materials, and the maturity focuses on all the other elements (Figure 2.9). Some of them are nutrients necessary for the plant growth (*e.g.* N, P, K, etc.), while others are phytotoxic compounds (*e.g.* Cd, Hg, Pb, etc.) that limit seed germination and root development. It is important to mention that the excess of any type of nutrients has detrimental effect on the soil biota. Because the N is the most abundant of these nutrients, its mineralised form, the NH_4^+-N, could be a measurement of the maturity (Alburquerque *et al.*, 2012; Astals *et al.*, 2013; Bernal *et al.*, 2009).

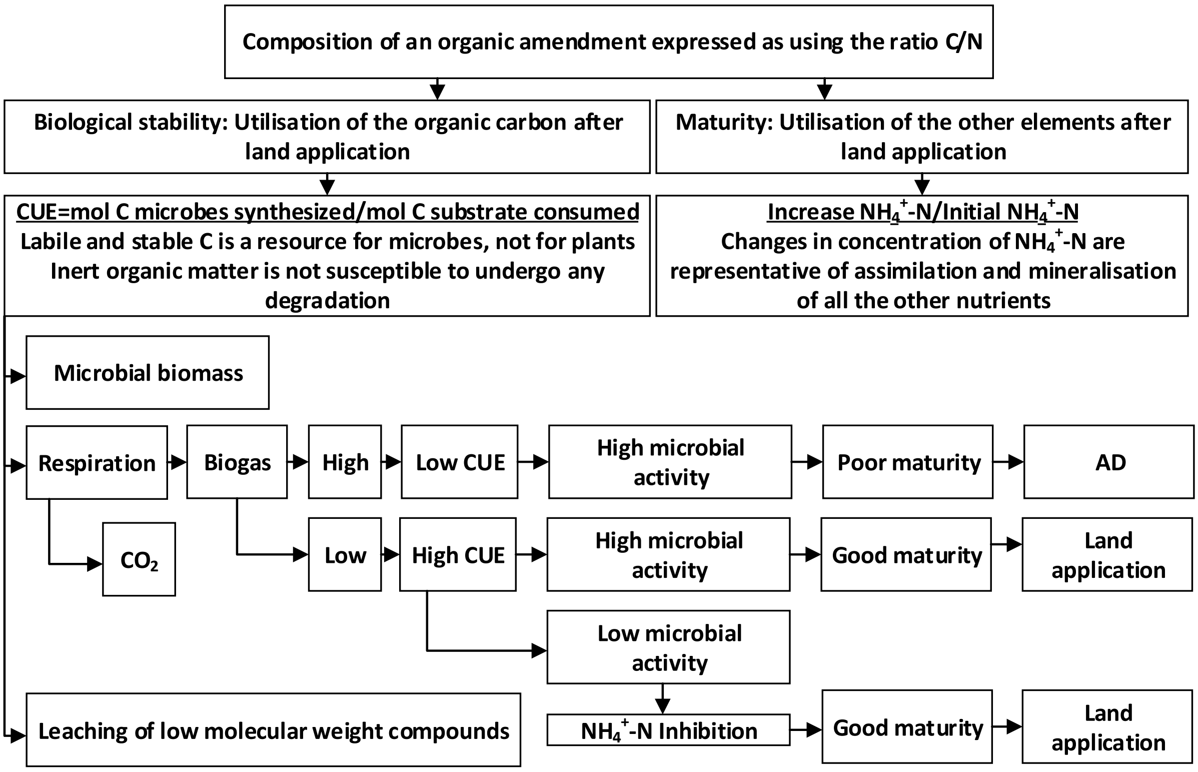


Figure 2.9. Evaluation of the quality of an organic amendment in terms of biological stability and maturity. Elaborated based on the information provided by Alburquerque et al. (2012), Astals et al. (2012), Dijkstra et al. (2015), Geyer et al. (2016), Manzoni et al. (2012) and Sinsabaugh et al. (2013).

The aim of the determining the stability is to find out what is the fate of the C present in the labile and stable OM, since the inert OM will not suffer any degradation (Strosser, 2011). As displayed in the Figure 2.9, the C could be (a) assimilated by the microorganisms for their growth, (b) lost *via* respiration, also known as C mineralisation, and in less extent (c) lost due to leaching of the low organic molecular weight compounds. The CUE only accounts the C used for the microbial growth, hence this parameter, could be a direct measurement of the stability of an organic amendment for a more efficient management of nutrients. However, the most common way of determining the stability is by measuring the losses *via* respiration (Banks *et al.*, 2013; Saveyn & Eder, 2014; WRAP, 2014a) although the test is not carried out in similar conditions to the land application but in AD conditions as per the BMP protocol.

In a BMP test of an organic amendment (Figure 2.10), the release of biogas due to microbial activity depends on the composition expressed as the carbon to nitrogen ratio (C/N) and the relative amount of this material with respect to the microbial biomass (*i.e.* substrate-to-inoculum ratio, S/I), expressed as organic loading rate (OLR) in a continuous reactor. The highest CUE, and therefore the highest stability of the organic amendment, were obtained at the lowest C/N (Figure 2.10), because the microbes have all the nutrients that they need to build their cell structures and do not need to get rid of the excess of C (Cimon *et al.*, 2020; Sinsabaugh *et al.*, 2013). Similarly, with low amounts of organic waste (OLR < 6), the microbes would be in starvation mode processing more efficiently the C for their growth, compared to higher OLRs in which more C is lost in microbial respiration due to the excessive microbial activity (Figure 2.10). Since less C ends up in the microbial biomass, which is measured as part of the VS, the CUE decreases. Despite the different physiology of the terrestrial microorganisms from the consortium of the AD, the trend of CUE measured in an aerobic environment is useful to explain the fate of C during batch and continuous AD operations (Figure 2.10). There are similar processes involved in the nutrient turnover in the AD and once the soil organic amendment is applied to land.

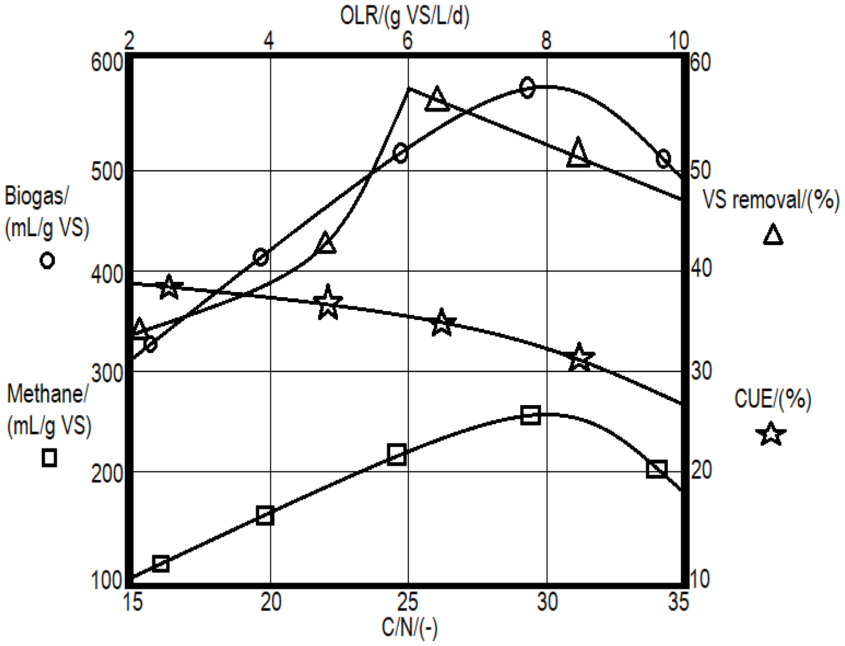


Figure 2.10. Application of the concept of CUE from soil science to the AD process. The relation between the CUE and the C/N for terrestrial decomposers was taken from Figure 1a by Sinsabaugh *et al.* (2013). The relation between the biogas yield, the methane yield and the VS removal with the C/N for the operation of a discontinuous reactor was taken from Figure 3 by X. Wang *et al.* (2012), who carried out 30-day AD experiments with a S/I of 0.5 (expressed in terms of VS). The scale of the OLR for the operation of a continuous reactor, equivalent of the S/I in a batch reactor, was taken from Figures 4 and 5 by Rincón *et al.* (2008), who reported

similar trends of biogas release and VS removal. In their article, the OLR was expressed in COD basis, however it is recommended to use the VS instead (Angelidaki *et al.*, 2009).

Microbes get rid of any nutrient in excess available in the medium, hence the composition of the organic amendment should be as similar as possible to the composition of the microbes. If C is in excess ($C/N \geq 35$), the microbes get rid of it *via* respiration or EPS segregation (Mannina *et al.*, 2020). That is the reason for which supplementing the AD feedstock with ashes (Romero-Güiza *et al.*, 2016a). The composition of the AD feedstock has been traditionally measured using the ratio C/N and this parameter has been employed for other types of fermentations, such as composting and land application of the organic soil amendment (Richards *et al.*, 2021). Möller & Müller (2012) emphasised that a more representative ratio to express the composition of the organic soil amendment would be the C_{org} to N_{org} ratio. Some researchers reported C as the main component of the wood ashes (Laohaprapanon *et al.*, 2010; Leechart *et al.*, 2009). According to Forbes *et al.* (2006), the continuum of combustion products such as char, ash and charcoal are referred to as black carbon (BC). This feature makes the properties of the wood ashes more suitable to be employed as land amendment, to restore the soil as C sink, maintain an adequate microbial activity in the soil, appropriate management of the nutrients to boost crop growth and prevent the pollution *via* leaching and gaseous emissions. The addition of wood ash to the feedstock of AD initially leads to an increase in C content, due to the accumulation of the VFAs (Bauer *et al.*, 2022; Cimon *et al.*, 2020; Lo *et al.*, 2009; Onwosi & Okereke, 2009; Podmirseg *et al.*, 2013). Once the methanogenesis reaches a stationary state, the C/N decreases and lead to the formation of an organic manure with better fertilising properties that the initial feedstock of AD.

According to the BSI PAS 110:2014 (WRAP, 2014a), the upper limit for a stable organic amendment in the 28-day test is 450 mL biogas/g VS (Table 2.2), which is in agreement with Figure 2.10. It should be noted that this threshold value was established in the conditions of no inhibition of the test (*e.g.* Figure 2.2), which could be related to an inappropriate S/I (*i.e.* OLR>10 g VS/L/d) and/or low nutrient content (*i.e.* $C/N > 35$). It is important to highlight that N plays a role in enhancing the biogas production but supplementing the organic amendment with other nutrients is advised (Menon *et al.*, 2017). Equation 2.46 represents how the heterotrophic microbial biomass ($C_5H_7NO_2$) is built from $C_6H_{12}O_6$, as a source of C_{org}, and NH_3, as a source of N. In this way, the maximum theoretical CUE is 55 % in an aerobic fermentation (Tchobanoglous *et al.*, 2014, p. 576), in agreement with Figure 2.10. The reason because in AD technology the stability is measured as release of biogas is because there is no accurate quantification of the microbial biomass available in the biodigester as this is measured as suspended VS. Less common is the measurement the ATP or phospholipids to quantify only the active cells in the anaerobic digester. The CUE measured in soil science is a more straightforward technique that relies in the in the extraction of the microbial C with a solution 0.5 M K_2SO_4 after fumigation with chloroform.

$$3C_6H_{12}O_{6(s)} + 8O_{2(g)} + 2NH_{3(g)} \rightarrow 2C_5H_7NO_{2(s)} + 8CO_{2(g)} + 14H_2O_{(l)}$$

Equation 2.46

Source: Tchobanoglous *et al.* (2014, p. 576); $C_6H_{12}O_6$ is the molecular formula of glucose and $C_5H_7NO_2$ is the empirical molecular formula of the SS microbes (Hoover & Porges, 1952).

For a high protein feedstock (C/N ≤ 20) containing N_{org}, as the AD progresses, the labile fraction of C in the system decreases, because of microbial growth and biogas release, and the excess of N_{org} is converted to NH_4^+-N. It should be noted that the co-digestion of substrates with high N_{org} could be understood as supplementation of the main feedstock of AD to produce a more stable digestate. In a deficit of C, the CUE increases as most of C_{org} is employed in creating cell structures. At the time of the preparation of the blended fertiliser, any increase in stability cannot be at the expense of excessive maturity (Figure 2.9). Otherwise, toxic effect on soil biota, lower fertility (Johansen *et al.*, 2013), losses *via* volatilisation and leaching during storage and after land application could be expected due to the high availability of the nutrients. Figure 2.11 shows that only when X. Wang *et al.* (2012) used a feedstock with a composition of C/N 20 or 35, correct maturity was obtained, at a C/N 15, there would be an excess of NH_4^+-N in the anaerobic digestate. On the other hand, at C/N of 25 and 30 the microbes assimilated and immobilised all the NH_4^+-N in the microbial biomass, hence there would be a lack of supply of this preferred source of N for the crops.

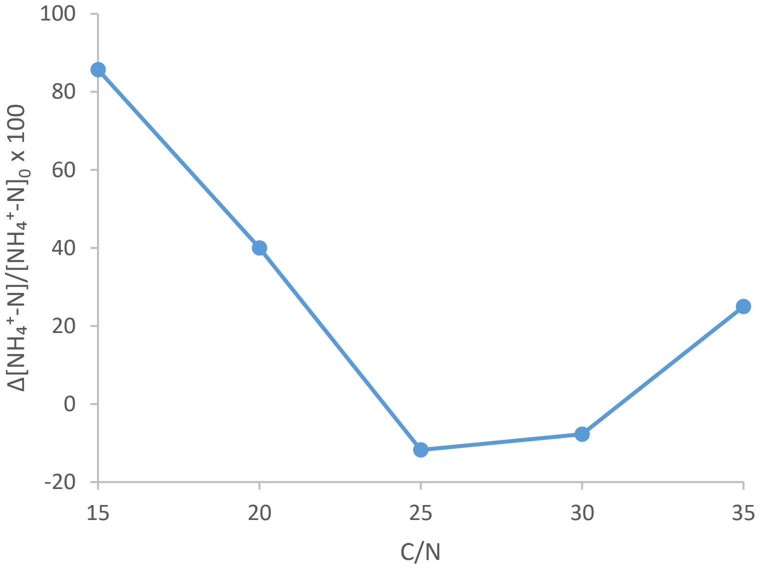


Figure 2.11. Experimental values of maturity based on the work of X. Wang *et al.* (2012) about trying to optimising the feedstock composition for a greater methane production during the anaerobic co-digestion of dairy manure, chicken manure and wheat straw (Moure Abelenda & Aiouache, 2022).

Bhogal *et al.* (2018) reported the relevance of the stable fraction of the OM that remains in the biologically stabilised organic wastes, *via* AD or composting, to restore the soil as a natural C 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 C_{org} as much as the application of farmyard manure for 20 years. However, when looking at the C speciation in the soil, the C immobilised in microbial biomass was more than twice in the case of manure. Thus, the stable OM prevented the excessive growth of microbes in the soil. It is important to mention that in the study of Bhogal *et al.* (2018), the food waste digestate offered similar results to the compost when these soil organic amendments were applied for 3 years. The land spreading of livestock slurry for 20 years provided with a lower increase in soil C_{org} 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 (Hou *et al.*, 2018), the procedures for combating antibiotic resistance are regulated and demanded by governments (UK Government, 2016).

Since agricultural soils have been identified as one of the major sources of the GHG, N_2O (Butterbach-Bahl *et al.*, 2013; Murphy *et al.*, 2022), 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 (Northern Ireland Department of Agriculture Environment and Rural Affairs, 2019), aims to limit the rate of application to 170 kg N/ha/y. The development of nitrification inhibitors aims to address this environmental (Recio *et al.*, 2018) as well as economic problems, since crops generally prefer NH_4^+-N to grow (Kiba & Krapp, 2016). Advocates for organic agriculture claim that the excess of N is also responsible of health issues as the high crop yields lead to food containing less nutrients in the human diet (Coelho *et al.*, 2007).

The wood ash-based technology enables the easier handling (*i.e.* store, transport and spread to land) of organic waste. This technological solution is in agreement with the perception of farmers and other stakeholders such as public authorities, agricultural advisors and consultants (Hou *et al.*, 2018). At both sides of the supply and demand of organic 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. The CATNAP (cheapest available technology narrowly avoiding prosecution) approach aims to bridge the gaps, preventing the efficient recycling of 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 and agricultural transition plan (UK DEFRA, 2020b, 2020a; UK Government, 2019), respectively.

2.5.Conclusions

The valorisation of the anaerobic digestate *via* wood ash treatment offer many possibilities. The challenge relies on choosing the appropriate blending ratio to maximise the number of synergies that can be attained by combining these 2 waste streams during the manufacturing of novel fertilisers. The reduction of the cost of processing these 2 raw materials, in terms of requirements for additional resources (*e.g.* commercial acids and surfactants) and energy (*e.g.* dewatering *via* mechanical solid-liquid separation) is key for encouraging the energy industries to take advantage of these materials. Furthermore, from the point of view of the properties of the slow-release soil organic amendment, the optimum blending ratio should enhance the nutrient use efficiency, thus minimising the pollution and demand of the agroindustry for chemical fertilisers.

3. Stability of the blends of anaerobic digestates and wood ashes under alkaline conditions

3.1. 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 (UK Government, 2019). 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 N quota (Northern Ireland Department of Agriculture Environment and Rural Affairs, 2019). 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 fertilisers are known for having low nutrient availability, which is typically enough for the utilisation by the soil biota while preventing important losses due to runoff waters and gas exchange (Rop *et al.*, 2018).

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 (WRAP, 2012a), 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 K comparable to the K-chemical fertilisers (Demeyer *et al.*, 2001). Digestates and ashes could be combined to improve the handling of these wastes and to enhance their properties as fertilisers (*e.g.* nutrient profile).

The term stability is applied in literature indistinctly to several parameters which provide completely different information about waste materials. In this thesis, the differences between biological, chemical and physical stabilities have been established as follows (Figure 2.4). The biological stability (Tambone *et al.*, 2019) 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 C mineralised as biogas or CO_2 release due to microbial respiration, depending on the methodology used (Walker *et al.*, 2010; WRAP, 2011). Steenari and Lindqvist (1997) employed the term chemical stabilisation 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 thesis it is regarded as physical stabilisation (Figure 2.4). The term chemical stability is employed in this thesis to refer to changes in composition of the waste streams overtime, due to volatilisation and solubilisation of nutrients (*i.e.* N, C and P). 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. Below, a discussion is offered on how ashes can be employed to maximise the stabilisation of digestates to produce a novel fertiliser.

First of all, there is evidence that the use of ash as source of nutrients affects the C utilisation during the AD of organic waste (Romero-Güiza *et al.*, 2016b). Guerrero *et al.* (2019) tested doses up to 200 mg of thermoelectric fly ash per litre of digester prepared with 2 g of COD of secondary sludge and 2.5 g of volatile suspended solids of inoculum. Similarly, Huiliñir *et al.* (2017) studied how concentrations of CFA up to 500 mg/L would enhance the digestion of SS 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 SS, 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.* (2009) employed up to 20 g of MSW fly ash per kg of MSW (94 % moisture) to enhance the biogas production (Table 2.4).

The biological stabilisation in not limited to improve the C utilisation 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 stabilisation of liquid sludge is described to occur at pH above 12 when it is operated for at least two hours (UK Government, 2018), for which is required a dose of 3.9 g $Ca(OH)_2$ per kg of SS (1.3 % TS) (Tchobanoglous *et al.*, 2014, p. 1501). Jamali *et al.* (2008) reported a ratio of 50 g CaO per kg SS, although they only reached a pH 9.1 due to the 25 % TS. It should be noted the moderate (*i.e.* ~ 18 %; although this depends on the amount of bark containing most minerals used as fuel) Ca content of biomass ashes (Demeyer *et al.*, 2001; Steenari & Lindqvist, 1997), at the time of proposing the amounts of these materials to be added to the organic wastes. Ca and Mg are not very soluble (Table A.5) that is why the sorption of the OM takes place onto these elements. Thereby the chemical stability also increases because of the lower availability of nutrients (Figure 2.4).

Fivelman (2013) employed the adsorption technology to enhance the solid-liquid separation of the liquid fraction (*i.e.* liquor) of the digestate (ADFerTech; Table 2.7). The main powder adsorbent that they added was dolomite ($CaMg(CO_3)_2$) in doses ranging from 10 to 200 g/L (mixed for 5 min at 20 ºC), which was able to retain around 250 mg N and 300 mg P per gram of dolomite. Biomass ashes are a source of Mg which can be used to decrease the availability of nutrients like N and P in the digestate due to the formation of $MgNH_4PO_4 \cdot 6H_2O$ (Figure 2.5). 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 (Yagi & Fukushi, 2012). Similarly, the concentration of adsorbent also determines the predominant phenomenon. Mor *et al.* (2016) found the greatest adsorption in a 10 mg PO_4^{3-}/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 PO_4^{3-} 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.* (2011), 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 immobilise the nutrients which further reduce the leaching and enhance the chemical stability (Figure 2.4). The characterisation of the WS extract of the blends digestates and ashes before land application represents a more conservative approach to assess the potential losses of nutrients, since more leaching and volatilisation are expected in the blended fertiliser due to the higher concentration of nutrients than that in the amended soil. Furthermore, the characterisation of the blend, is less subjective to decrease the availability of the elements due to microbial assimilation. The assessment of the availability of nutrients in the blend could provide with key information to optimise the processing towards minimisation of resources and better properties of the waste-derived fertiliser. 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 (Ma *et al.*, 2011; Mor *et al.*, 2016; Yagi & Fukushi, 2012).

The doses of ash added to organic waste that results in a pH beyond 13, also lead to chemical hydrolysis (Randall *et al.*, 2016), which has a negative impact on the chemical stability to the liquid blend (Figure 2.4). This effect is desired for purposes that are different from the production of a fertiliser. Concentrations between 50 and 150 g $Ca(OH)_2$ per kg biomass (5 to 20 % TS) are usually employed as caustic pre-treatment of the bioconversion of lignocellulosic biomass in the ethanol production (J. S. Kim *et al.*, 2016). The solubilisation of C_{org} (Tavakkoli *et al.*, 2015) enhances the subsequent fermentation (Huiliñir *et al.*, 2017), although it is necessary the previous neutralisation with an acid agent to reach an appropriate pH for microbial activity. The physical stabilisation (Figure 2.4) of the organic wastes to produce a granular fertiliser is achieved even with higher doses of ashes (Mudryk *et al.*, 2018; Pesonen *et al.*, 2016), but the moisture level of the final pellets should be less than around 3 % (Fivelman, 2013; Pesonen *et al.*, 2016), which reduces the extent of the hydrolysis of the OM.

Steenari and Lindqvist (1997) explained that the self-hardening of 1 g of wood ash when adding between 0.3 and 0.5 g of water as binder depends on a number of on-going reactions which can last from days to months. The hydration of CaO to produce $Ca(OH)_2$ is the main responsible of the curing since the subsequent formation of $CaCO_3$ is a much slower reaction due to the mass transfer resistance, which limits diffusion of CO_2 from the atmosphere. In addition to the solidification, Steenari and Lindqvist (1997) 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 burn crop tissues). Moilanen *et al.* (2013) 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 solubilisation rates of the self-hardened ash and the granulated ash with regard to the untreated powder ash. Thereby, advanced manufacturing (*e.g.* pelletisation) 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 (2016) reported the smell of ammonia during the granulation of a fertiliser based on biomass ash and dewatered sludge. Although they included $Ca(OH)_2$ in the blends, the compressive strength of the granules did not increase. Mudryk *et al.* (2018) 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.* (2018), Jewiarz *et al.* (2018) proposed the entire process for the production of this granular fertiliser. 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. This is an example 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 fertiliser (Figure 2.3).

This chapter evaluates how high doses of biomass ashes of wood origin affect the availability of N, C and P 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 fertiliser. 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 fertiliser 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 minimise the cost of isolating nutrients to produce an organic fertiliser.

3.2.Materials and methods

3.2.1. 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 3.1. The FWD was produced in compliance with the BSI PAS 110:2014, thus fulfilled the criteria towards the end-of-waste status according to the UK regulations (WRAP, 2014a). 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 for this chapter took place on September 2016.

Each digestate sample consisted in 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 ºC) 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 (N, P and trace elements).

Each ash sample received consisted in 10 kg of material, which was sent by the producer in a sealed plastic box to minimise 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.

Table 3.1. Description of the samples used in this thesis (Moure Abelenda *et al.*, 2021c).

Sample	**Plant production and feedstock composition**
FWD	17600 t/year source segregated food waste (mainly household).
PVWD	Maize Silage (10,000 t/year), vegetables waste (5,000 t/year), sweet-corn waste (15,000 t/year), aerobically treated food waste (10,000 t/year) and biodegradable sludge (2,000 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.

The samples were blended in order to achieve ashes-to-digestates ratios of 1/4.6 and 1/2.3 (Table 3.2). Usually, alkaline stabilisation requires a ratio of g $Ca(OH)_2$/g solid of 1/10 (J. S. Kim *et al.*, 2016). It should be noted the significant amount (~ 10 %) of Ca presented in the wood ashes (Table A.3) and the low DM of the digestates (Table 3.3) when comparing the blending ratios. The blends of these samples (Table 3.2) have a nutrient profile around C/N/P 10/1/1 (Table 3.4), hence low C mineralisation would be expected after land application. The ashes were used directly without any prior treatment/activation (*e.g.* Table 2.6) to enhance the sorption process.

Table 3.2. Mass percentage of each fresh sample for the preparation of approximately 3 g of each blend (Moure Abelenda *et al.*, 2021c). The procedure for the calculation of the error propagation is described in the section A.2 and section A.3.

Share	**Blend 1**		**Blend 2**	
Sample	**Average**	**St. deviation**	**Average**	**St. deviation**
FWD/(%)	65.03	3.03	-	-
PVWD/(%)	17.13	3.23	67.49	3.14
WFA/(%)	17.84	1.89	16.03	1.97
WBA/(%)	-	-	16.48	2.87
Digestates:Ashes/(-)	4.60	0.60	2.08	0.30
Total/(g)	3.28	0.17	3.27	0.24
g TS Ash/g TS Dig.	2.99	0.59	6.01	1.00

3.2.1. Methods

The preparation of the 3 g of each mixture was done in 50-mL Corning® flasks (Figure 3.1) by following the mass percentages shown in Table 3.2. 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 3.2) and (b) the length of the incubation at 22 °C (0, 0.5, 1, 3, 6 and 10 hours). 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 physicochemical 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 physicochemical transformation would be reflected in this phase and also because was the phase where risks (*e.g.* nutrients leaching) could be better understood (Schwab, 2011). The parameters measured were the pH, EC, WS NH_4^+-N (*i.e.* N in the form of $NH_4^+{}_{(aq)}$ or $NH_{3(aq)}$), WS NO_3^--N (includes N in the form of $NO_3^-{}_{(aq)}$ or $NO_2^-{}_{(aq)}$), WS PO_4^{3-}-P, WS N and WS C. Two steps were required for the isolation of the WS extract (Figure 3.1).

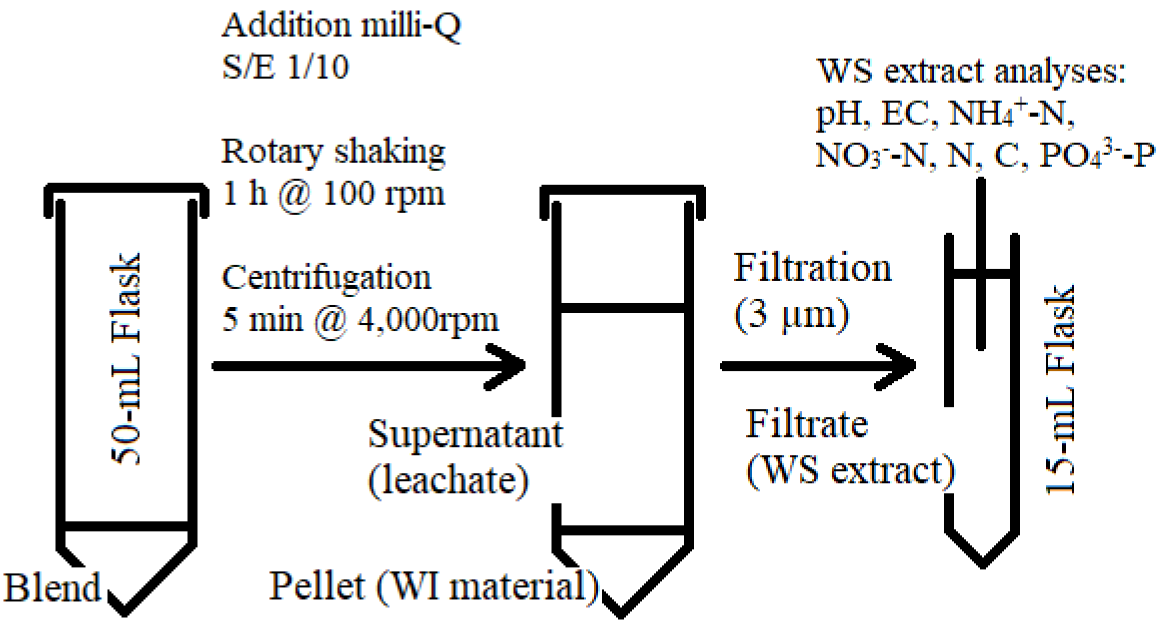


Figure 3.1. Stepwise methodology for the characterisation of the WS extract of the blends after the 10-h incubation at 100 rpm and 22 ºC (Moure Abelenda *et al.*, 2021c). The WS extract was prepared following a sample-to-extractant ratio (S/E) of 1 part of sample and 10 parts of ultrapure [milli-Q] water (1/10).

The procedures available in the literature for the determination of pH and electric conductivity (EC) mainly differ in the dilution ratio used (Table A.4). 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 (Alburquerque *et al.*, 2012) but it was performed to match the procedure employed for the characterisation of the ashes. In agreement with the procedure used by NRM laboratory, the WS extract was prepared following a sample-to-extractant ratio (S/E) of 1 part of sample and 10 parts of ultrapure [milli-Q] water (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 hour at 100 rpm. Finally, the lixiviation was achieved *via* centrifugation for 5 min at 4,000 rpm and subsequently filtered down to pass 3 µm.

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^+-N (methods DIN 38406 and ISO/DIN 11732), WS NO_3^--N (methods DIN 38405 and ISO/DIS 13395) and WS PO_4^{3-}-P (methods DIN/EN/ISO 15681-2) 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 N and WS C were measured with the TOC-L Shimadzu® *via* combustion of the sample and detection of CO_2 and NO gases. The C of all the samples and the N of the ashes (Table 3.3 and Table A.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 C during the drying at 105 ºC. The N of the digestates together with the P 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 of N, the initial N of the blends at time zero (Table 3.4) was divided into the actual N that remains in the blend (N_{blend}), ammonia nitrogen gas lost (NH_3-N; N in the form of $NH_{3(g)}$) and nitrous oxide nitrogen gas lost (N_2O-N; Equation 2.10). Furthermore, the N_{blend} was divided into WI N and WS N. It is important to highlight that although the WI N_{org} of the digestates presented different availability (*i.e.* different solubilisation rates) than the WI N of the ashes, this distinction was not considered in this chapter. With regard to the WS N, the following fractions were considered as the fate of N in the WS extract: WS N_{org}, WS NH_4^+-N and WS NO_3^--N. The WS N_{org} was calculated as the difference between the WS N and the sum of WS NH_4^+-N and WS NO_3^--N (Urgun-Demirtas *et al.*, 2008). A widely used procedure is the calculation of the $NH_{3(g)}$ volatilisation based on the decrease of the concentration of NH_4^+-N in the digestates (Ndegwa *et al.*, 2009; Whelan *et al.*, 2010). In the chapter, the increase in the formation of $NH_{3(g)}$ was accounted for the decrease in all the other forms of N, with the exception of WS NO_3^--N, for which the decrease was expressed as an increase of the $N_2O_{(g)}$. In this way, the rate of formation of NH_3-N during the incubation of the samples was calculated based on reduction of the N_{blend} for both blends, since the variation in the concentration of the WS NH_4^+-N was not representative of N lost because of the pool of both WS N_{org} and WI N_{org}, for example due to reactions such as Equation 3.1 or abiotic mineralisation. The approach of Ukwuani & Tao (2016) to this problem was to begin the calculation of the NH_3-N volatilised 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 operating temperature for the next 4 hours which lasted the ammonia stripping.

$$N_{org(aq)} \xrightarrow{Ammonification\,\&\,Mineralisation} NH_4^+ - N_{(aq)} \qquad \textbf{Equation 3.1}$$

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^+-N, WS NO_3^--N, WS PO_4^{3-}-P, WS N or WS C 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 Equation A.11. The single-factor analysis of variance (ANOVA) was performed with MS excel ($p < 0.05$) to decide whether the measured parameters remained constant during the incubation period. For this purpose, it was necessary to assume that the data obtained for each blend during the 10-h incubation followed a normal distribution. The determination of the outlier values was done following the procedures of interquartile range and z-score.

3.3.Results and discussions

3.3.1. Initial characterisation

The characterisation of the samples, in terms of the parameters concerning this thesis, is shown in Table 3.3. While the values for the samples were determined empirically, the characterisation of the blends at time zero (Table 3.4) was estimated based on the data of each sample and their share in each blend (Table 3.2). The low reproducibility of the results (*i.e.* standard deviations greater than the 10 % of the average value) was related to the heterogeneity of the samples.

The digestates were the main source of N 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 EC (Shcherbakov *et al.*, 2009), together with other elements (Table A.5), 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 (Equation 3.2).

$$NH_{4(aq)}^{+} \xrightarrow{Neutralisation} NH_{3(aq)} + H_{(aq)}^{+}$$ **Equation 3.2**

The ashes were the main source of WI P and they were also loaded with alkali and alkaline earth metals (Table A.3), which confered them high pH. It should be noted that less than 1 % of the P contained in the ashes was soluble (Table 3.3) because it was in the form of insoluble calcium compounds, such as hydroxyapatite ($Ca_5(PO_4)_3OH$) (Steenari & Lindqvist, 1997). The fate of most of the phytotoxic elements, such as heavy metals (*e.g.* As, Cd, Pb and Zn (Steenari & Lindqvist, 1997)), usually are the finer fractions of ashes. The reason could be that the fly ash account for most ashes (~ 80 %) generated during combustion, although the exact mass distribution depends on the type of incinerator. 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.) of the flue gas treatment system, depending on the particle size (Dahl *et al.*, 2010, 2009; Pöykiö *et al.*, 2011, 2009; Strand *et al.*, 2002). The ashes employed were generated in a grate combustion chamber, thereby the bottom ash represented the main fraction (Table 3.1) 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 (Chindaprasirt *et al.*, 2009) 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 DM and TS; Equation 2.44) than the WBA. Similarly, the neutralisation and carbonation, that took place during storage, were enhanced in the WFA, leading to a greater C and lower pH of the WFA compared to the WBA (Table 3.3). Values with an uncertainty greater than 10 %, such as the C 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 3.1), and it 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 CO_3^{2-} (Steenari & Lindqvist, 1997). Thirdly, the drying at high temperature decreased the moisture content, restored the alkalinity, due to the decomposition of CO_3^{2-} and even hydroxides (Demeyer *et al.*, 2001), 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 3.3). The higher content of K^+ explained the higher conductivity of the WBA in spite of its lower moisture content (Table A.3). Generally, the EC of the ashes increases with the moisture content but beyond the water sorption saturation level, which corresponds to a S/E 1/0.4 (Sakai *et al.*, 2005; Wei & Li, 2005), the EC decreases because of the dilution effect and the lack compaction. It is important to mention that Maresca *et al.* (2019) reported a decrease in the EC during the first 20 days of the self-hardening of the WFA and the WBA, using a S/E 1/5. Under the conditons of this experiment (*i.e.* S/E 1/10 and 10-h incubation), the level of self-hardening of the ashes did not impacted on the measurement of the EC, which was determined by the amount of mobile ions. According to Karoline (2012),

SO_4^{2-}, 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 this thesis (Table 3.3) was associated with the low solubility of Ca^{2+} and Mg^{2+} (Table A.5), the SO_4^{2-} and the Cl^- were the counter ions associated with the K. K-salts are very soluble and are rarely related to the hardening phenomenon, with the exception of $K_2Ca(SO_4)_2 \cdot H_2O$ (Steenari & Lindqvist, 1997).

Table 3.3. Characterisation of the four samples in terms of the relevant parameters for this thesis (Figure 3.1). The average and standard deviation (n=3) for all the measurements are expressed in fresh weight (Moure Abelenda *et al.*, 2021c).

Sample		**FWD**		**PVWD**		**WFA**		**WBA**	
Parameters	**Units**	**Average**	**St. dev.**	**Average**	**St. dev.**	**Average**	**St. dev.**	**Average**	**St. dev.**
pH	-	8.80	0.01	8.84	0.01	12.89	0.02	13.38	0.01
EC	dS/m	8.59	0.08	2.37	0.04	20.60	0.56	57.90	0.96
DM	%	6.27	0.50	7.57	0.32	90.01	0.45	98.90	0.58
C	mg/kg	21,332.30	805.14	31,959.34	43.60	41,398.70	575.23	22,069.71	1,145.77
WS C	mg/kg	4,073.55	251.97	2,041.50	87.73	3,773.59	515.97	1,824.97	113.57
[a]N	mg/kg	8,500.00	850.00	3,800.00	380.00	1,061.23	152.58	831.58	191.62
WS N	mg/kg	8,799.54	246.61	2,062.70	18.89	61.07	3.34	46.58	13.88
WS NH_4^+-N	mg/kg	3,402.85	117.58	689.74	86.78	4.12	0.21	4.29	0.77
WS NO_3^--N	mg/kg	1.70	0.23	18.94	0.65	6.78	0.12	1.30	0.02
[a]P	mg/kg	1,004.00	100.40	1,119.00	111.90	23,848.16	2,384.82	11,123.10	1,112.31
WS PO_4^{3-}-P	mg/kg	54.87	3.71	38.99	2.74	22.49	0.22	22.25	1.51

[a]Parameters measured by NRM: the estimated expanded uncertainty calculated as per the NORTEST 537 method was 10 %.

Table 3.4. Characterisation of the two types of blends (Table 3.2) in terms of the relevant parameters for this chapter (Table 3.3). The average and standard deviation (n=3) for all the measurements are expressed in fresh weight (Moure Abelenda *et al.*, 2021c). A description of the calculation of the error propagation is offered in the section A.4.

Sample		Blend 1		Blend 2	
Parameters	Units	Average	St. dev.	Average	St. dev.
pH	-	8.89	0.00	9.01	0.00
EC	dS/m	9.67	0.49	14.44	1.72
DM	%	21.43	1.77	35.83	3.36
C	mg/kg	26,733.11	1,543.14	31,843.05	1,454.60
WS C	mg/kg	3,671.89	245.40	2,283.48	151.82
N	mg/kg	6,367.59	626.27	2,871.90	287.47
WS N	mg/kg	6,086.28	318.12	1,409.67	66.12
WS NH_4^+-N	mg/kg	2.331.65	131.09	466.90	62.45
WS NO_3^--N	mg/kg	5.55	0.65	14.08	0.75
P	mg/kg	5,120.81	629.13	6,633.57	737.20
WS PO_4^{3-}-P	mg/kg	46.37	3.25	33.59	2.36

Figure 3.2 represents all the possible blends fulfilling the above criteria employed to define the Blend 1 and the Blend 2 (Table 3.2). Similar representations have been employed to describe the biomass ash composition (Ribbing, 2007; Vassilev et al., 2010, 2021). The evaluation of the chemical stabilities of Blend 1 (65.03 ± 3.02 % FWD, 17.13 ± 3.23 % PVWD and 17.84 ± 1.89 % WFA) and Blend 2 (67.49 ± 3.14 % PVWD, 16.03 ± 1.97 % WFA and 16.48 ± 2.87 % WBA) provides important information to understand the underlying chemistry and to optimise of the blended fertiliser. Mixture 1 and 2 represent the edges of the system in which was studied the interaction between the share of ash in the blend and the volatilization of ammonia, which is mainly provided by the FWD.

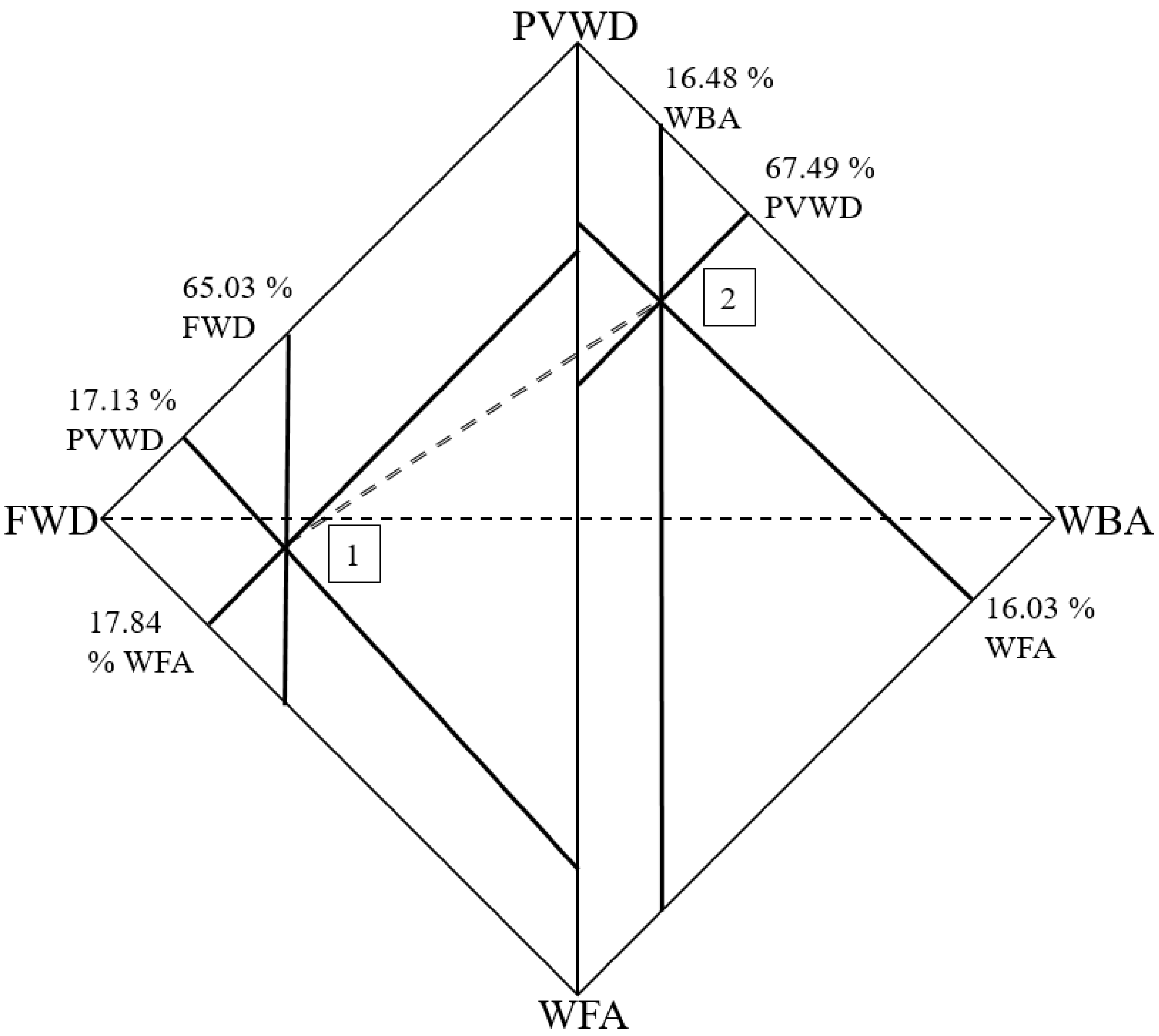


Figure 3.2. Quaternary diagram (*i.e.* triangular pyramid with 100 % of one component in each vertex) representing all the blends (*i.e.* dashed line between 1 and 2; Table 3.2) that were expected to fulfil the criteria of biological, chemical and physical stability (Figure 2.4) (Moure Abelenda, Semple, Aggidis, *et al.*, 2022).

3.3.2. pH and EC profiles

As illustrated in Figure 3.3, 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 NH_4^+-N (Table 3.4) with buffer effect, which prevented a drastic increase of the pH. These two characteristics (*i.e.* content of ashes and NH_4^+-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 that for the Blend 2. In fact, the one-way ANOVA test ($p < 0.05$) 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 (Figure 3.3b) could be related to the greater particle size of the WBA that made this sample more susceptible to be affected by sampling errors and, therefore, less homogenous than the WFA. Moreover, as the EC of the WBA was higher than the one of WFA (Table 3.3), 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 3.2).

The mobility of H^+ ions, explained by the Grotthuss mechanism, is almost twice as those of OH^- ions (Agmon, 1995). Thereby, strongly acidic solutions have more EC than the highly basic ones. At the pH of the blends (Figure 3.3a), 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 (Fangueiro *et al.*, 2015), such as NH_4^+, Na^+ and K^+, but greater basicity could even promote the solubilisation of OM (López Torres & Espinosa Lloréns, 2008). The EC of both blends matched > 4 dS/m of saline soils (Conklin, 2014, p. 188; Daliakopoulos et al., 2016), 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 stabilisation 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 (Randall *et al.*, 2016).

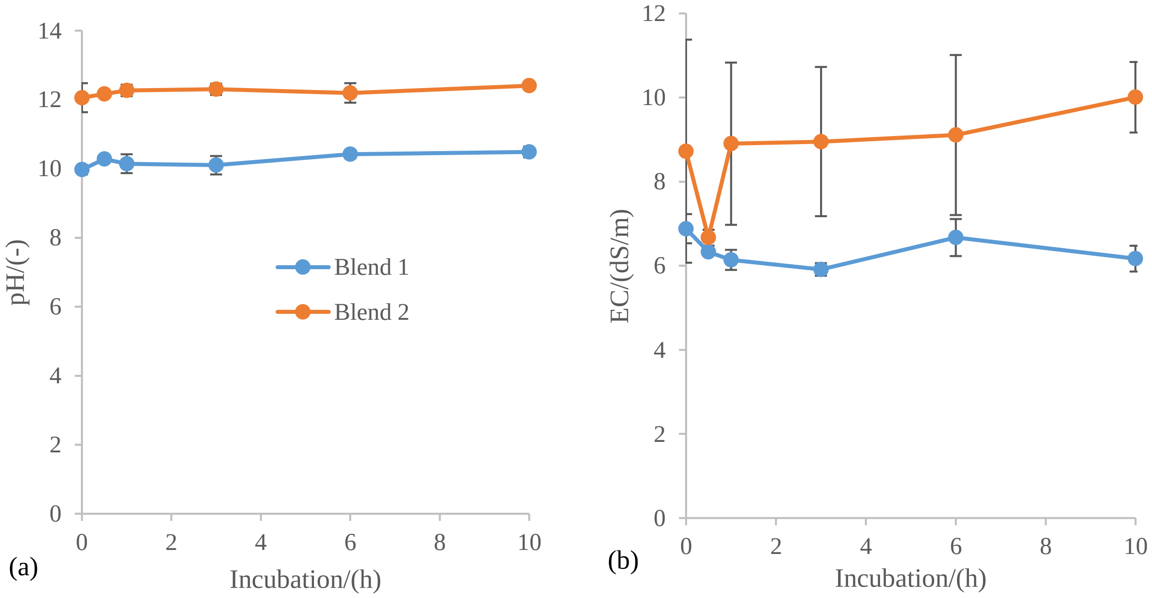


Figure 3.3. Changes of the pH (a) and the EC (b) of the ~ 30 mL WS extracts (S/E 1/10) of each of the blends (Table 3.2) obtained after the incubation at 100 rpm and 22 ºC (Moure Abelenda *et al.*, 2021c).

The straightforward comparison of the pH and EC values obtained for the WS extracts of the incubated blends (Figure 3.3) with the pH and EC values of the initial characterisation (Table 3.4) was not possible because different S/Es were used for the preparation of the WS extract. The increase of the EC of the digestates when the ashes were added, was less significant than the increase of the pH, considering the wider range for the variation of EC. Garfí *et al.* (2011) reported a value of EC as low as 6.88 10^{-3} dS/m for digested guinea pig manure determined with a standard method for the characterisation of wastewater (Table A.4). On the other hand, Walker *et al.* (2010), using a standard method for the characterisation 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 used to produce the WS extract (Karoline, 2012). The pH was less affected by the dilution (*i.e.* 1/5 to 1/10) because the decrease of the concentration of $H^+_{(aq)}$ 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.

3.3.3. WS NH_4^+-N profiles

The amount of WS NH_4^+-N in Blend 1 was greater than in the Blend 2 (Figure 3.4a) in agreement with the higher share of digestates (Table 3.2) and the large concentration of these species in the FWD (Table 3.3). The results of the single-factor ANOVA for both blends were that $F > F_{crit} = 2.36$. Thereby, it was possible to claim with a 95 % of certainty ($p < 0.05$) that, during the 10 hours of incubation at 22 ºC, the concentration of WS NH_4^+-N in both blends was not constant.

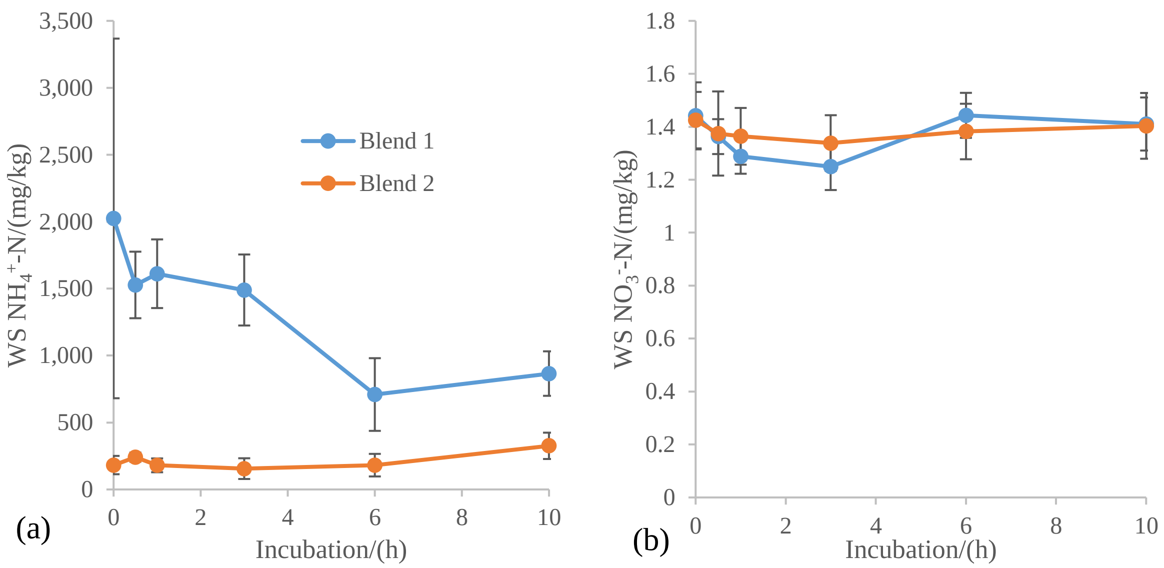


Figure 3.4. Concentration of WS NH_4^+-N (a) and WS NO_3^- & WS NO_2^- (b) in 3 g of each of the blends (Table 3.2) measured after the incubation at 100 rpm and 22 ºC (Moure Abelenda *et al.*, 2021c).

The large error bars of the first time-point of WS NH_4^+-N, at the zero hours of incubation of the Blend 1 (Figure 3.4a), was due to the fact that data from 2 different set of experiments was considered to present more generalised trends. It is important to mention that this was applied to all the other time-points and all the other parameters measured in the blends. The subsequent fluctuations of the concentration of WS NH_4^+-N in both blends in the remaining time-points (Figure 3.4a) could be related to the mineralisation of the N_{org} due to abiotic factors (Equation 3.1). Given the high concentration of Ca in the ash samples (Table A.3), the hydrolysis with the exchangeable calcium was possible (Jones *et al.*, 2007). Subsequently, the NH_4^+ would be released and then neutralised into $NH_{3(aq)}$ owing to the high pH of the medium as per the reaction pathway (Equation 3.2). 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 (Figure 3.3a), since the FWD had more WS NH_4^+-N, together with the lower share of ashes compared to the Blend 2 (Table 3.2). Furthermore, the FWD had a greater pool of $NH_4^+{}_{(aq)}$ than the PVWD, in agreement with the higher concentration of WS NH_4^+-N in the Blend 1 during the incubation (Figure 3.4a), confirming a the greater protein content of the materials used as feedstock for AD. The WS NH_4^+-N could build up at the first hour of incubation because the rate of hydrolysis of the N_{org} was faster than the volatilisation of $NH_{3(g)}$. At a pH value of 11, all WS NH_4^+-N in the blends would be in the form of $NH_{3(aq)}$ (Fangueiro *et al.*, 2015). Thereby, it was considered that what limited the flux of $NH_{3(aq)}$ from the blends to the air was the mass transfer step Equation 3.3.

$$NH_{3(aq)} + H^{+}_{(aq)} \xrightarrow{Mass\ transfer} NH_{3(g)} + H^{+}_{(aq)}$$ **Equation 3.3**

The theoretical content of WS NH_4^+-N in the blends (Table 3.4) was higher than the content of WS NH_4^+-N measured at time zero (Figure 3.4a). Blend 1 and Blend 2 lost 37.26 ± 9.13 % (Figure 3.6a) and 10.36 ± 3.82 % (Figure 3.6b) of the N content at the time of blending the samples. It was considered that a minimum amount of N was lost during the storage of the digestates at (< 4 ºC). 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 (Verdouw *et al.*, 1978), which is a modification of the Berthelot's reaction. This pH was meant to be achieved after the WS extract (S/E 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 ammines could react like $NH_{3(aq)}$, resulting in an overestimation of the concentration of WS NH_4^+-N (SEAL Analytical, 2012).

Méndez *et al.* (2002) reported a 4.99 % loss of NH_4^+-N when adding 600 g of quicklime (81.5 % CaO) to 2 kg municipal wastewater sludge after 2 hours of incubation at 300 rpm and 20 ºC in an open system. They did not provide information on how the measurement was performed, which would be required to understand how much of the WS NH_4^+-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-gram blends of this chapter, the concentration of WS NH_4^+ & WS NH_3 in their wastewater sludge was 1,000 times lower (*i.e.* 0.12 mg NH_4^+-N/kg sludge) than the ones of the blends in this chapter (Table 3.4). Whelan *et al.* (2010) reported a loss of 1,500 mg WS NH_4^+-N in 120 g of digestate (mixture of ruminant slurry and food waste) during three weeks of incubation at 25 ºC. The initial WS NH_4^+-N content was 4,490 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 $NH_{3(g)}$. The amount of $NH_{3(aq)}$ volatilised in their system with the H_2SO_4 trap for more than 3 weeks, was like the loss of $NH_{3(aq)}$ in the Blend 1 at time zero (2348 mg $NH_{3(aq)}$/kg blend; Figure 3.6a). On the other hand, in this chapter their model has been used to predict that ~ 6 % of the initial WS NH_4^+-N 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 $NH_{3(aq)}$ volatilisation given by the addition of the ashes to the digestates. The $NH_{3(aq)}$ volatilisation was also estimated using the values of the vapour pressure tables available for the aqua ammonia (NH_4OH) solutions

(Eggeman, 1992). For the calculation, it was considered that the concentration of $NH_{3(aq)}$ in the blend was 10 % (*i.e.* approximately 10 times higher compared to the initial composition of the blends; Table 3.3), to take into account the enhancement in the volatilisation 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^+-N in the Blend 1 and Blend 2, respectively.

Other possible routes for the decrease of concentration of WS NH_4^+-N would be adsorption and precipitation. This would be reflected by a translocation of a share of the N from the WS phase to the WI phase. However, it was expected that only Blend 2 increases the WI N at the time of the preparation (Figure 3.6). Ma *et al.* (2011) studied the removal of NH_4^+-N and PO_4^{3-}-P from water with concentrations up to 200 and 250 mg/L, respectively. In their study, the optimum pH required for adsorption in a 40 mg NH_4^+-N/L solution was between 3 and 9, and higher pH could lead to losses *via* $NH_{3(aq)}$ volatilisation. With regard to the precipitation, the formation of struvite could explain a share of the decrease in the concentration of WS NH_4^+-N. Changes in the concentration of NH_4^+-N lower than 15 % have been reported by Sakthivel *et al.* (2012), during the incubation at 25 ºC of 11.4 g of wood ash with 1 litre of ureolysed urine with an initial content of 2,720 mg NH_4^+-N per litre. Similarly, Huang *et al.* (2017) tested the dose of plant ash up to 28.5 g per litre of swine wastewater with 410 mg NH_4^+-N per litre. Although the precipitation of the 97 % of the 105 mg PO_4^{3-}-P/L in a 500 mL swine wastewater was found after 1 hour using a dose of plant ash of 12.5 g/L, they did not report which share of PO_4^{3-}-P 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 Ca, as hydroxyapatite, and with the K, as K-struvite.

3.3.4. WS NO_3^--N profiles

In both blends, the same levels of WS NO_3^--N were constant (1.36 ± 0.11 mg/kg Blend 1 and 1.37 ± 0.11 mg/kg Blend 2) during the incubation (Figure 3.4b). The low values of WS NO_3^--N could be associated with the low reactivity of these species at low concentrations (Fanning, 2000). Other explanation for the constant levels of WS NO_3^--N 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^--N shown in the Figure 3.4b is expressed in terms of fresh base of the blend (Table A.5), and the concentration in the WS extract (S/E 1/10) was 0.13 ± 0.03 mg WS NO_3^--N/L. This concentration is much greater than the detection limit of the method used, which is 0.23 µg WS NO_3^--N/L (SEAL Analytical, 2012).

Similarly to WS NH_4^+-N, there was a loss of the WS NO_3^--N at the time of blending. It was not very likely that the nitrate remained in the system adsorbed in the ashes (Öztürk & Bektaş, 2004) or in the digestates fibres (Stjepanović *et al.*, 2019), since these materials have not been activated for that purpose, for example, with the procedures described in Table 2.6. Also, the biological desnitrification (Johansen *et al.*, 2013) should not be possible in the blends due to the high pH and short incubation (Figure 3.3a). However, the $N_2O_{(g)}$ has been reported as the main product of abiotic reduction of WS NO_3^- (Y. Wang *et al.*, 2017) and WS NO_2^- (Buchwald *et al.*, 2016) under 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 (Table A.3), which were set by the temperature of incineration and the conditions of storage. In the Chapter 5, the WBA was combined with HNO_3 before addition to the acidified PVWD and an increase in the NH_4^+-N of the WBA was observed due to the abiotic denitrification (Figure 5.5a).

3.3.5. WS N and WS C profiles

The blends had opposite trends both for the WS N and the WS C (Figure 3.5). The Blend 2 had a more constant WS N during the whole incubation period (883.88 ± 147.16 mg/kg), while its WS C significantly increased (4,917.95 ± 1,380.46 mg/kg). On the other hand, the Blend 1 had a decrease in the WS N during the first 3 hours of incubation (2,857.75 ± 594.73 mg/kg) and the WS C increased less than the Blend 2 (4,742.81 ± 931.26 mg/kg). 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^+-N via abiotic mineralisation in the conditions of chemical alkaline stabilisation that were tested. The N_{org} could be an important component of both, the WI N and the WS N, and it was taken into account to explain the changes in the concentrations of WS NH_4^+-N and WS N, in both blends (Figure 3.6).

The content of WS NH_4^+-N in the blends was between one and two orders of magnitude greater than the WS NO_3^--N (Table 3.4). Therefore, the loss of WS N at the time of blending was mainly given by the reduction of the concentration of WS NH_4^+-N in both blends (Figure 3.6). In an open system (*e.g.* after applying the blended fertiliser to land), the leaching of WS N_{org} could be the main way of losing N (Perakis & Hedin, 2002). Because of the high concentration of WS NH_4^+-N in the Blend 1, resulting from the conversion of the N_{org}, it took longer to reach a stable level (Figure 3.4a).

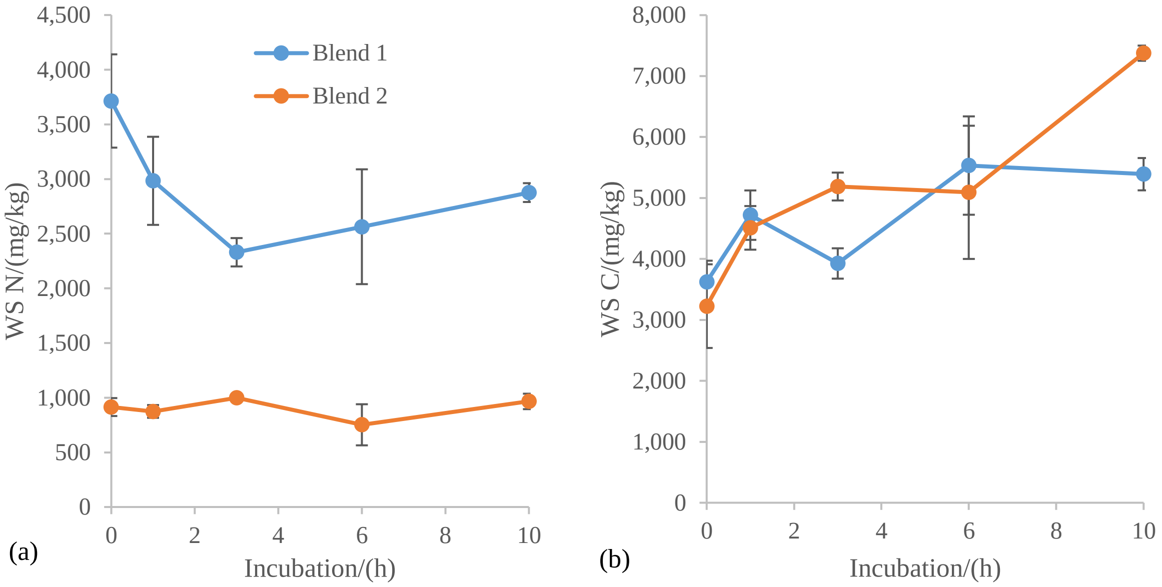


Figure 3.5. Concentration of WS N (a) and WS C (b) in 3 g of each blend (Table 3.2) measured after the incubation at 100 rpm and 22 ºC (Moure Abelenda *et al.*, 2021c).

C 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 C 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 1/10) was assumed to be negligible considering the high amount of C presented in the blends (Table 3.4).

The trends found for the WS C of both blends (Figure 3.5b) could be explained based on the type of C containing compounds in each sample and the blending ratio. While the FWD contained more easily degradable labile OM, the stable fraction of OM abounded in the PVWD (Ahmed *et al.*, 2016). The initial WS C of Blend 1 was therefore higher than the initial WS C of the Blend 2 in spite of the lower C content of the Blend 1 (Table 3.4). The BC provided by the ashes was less reactive (*i.e.* less soluble) and can be regarded as the inert fraction of the OM (Strosser, 2011). Furthermore, since both blends had similar share of the WFA, the increase of the WS C because of the CO_3^{2-} is similar for both blends. Only the Blend 2 further included the WBA to promote the hydrolysis of the stable OM of the PVWD (Tambone *et al.*, 2019), leading to a greater increase of the WS C. Under the conditions of chemical alkaline stabilisation attained in the Blend 1, the Ca^{2+} could promote the neutralisation and sorption of OM (Tavakkoli *et al.*, 2015). In this way, the organic acids could undergo saponification reactions (Handojo *et al.*, 2018) which increased the yield of the WI material. These organic salts were expected to remain in the WI material due to the low solubility of Ca and Mg (Table A.5). The slight increase in the WS C of Blend 1 (Figure 3.5b) with respect to the initial (Table

3.3) 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.

3.3.6. N profile

Based on the empirical results obtained for N, the speciation of Blend 1 and Blend 2 were represented in Figure 3.6. A detailed description of the assumptions made for this simulation is offered in the methodology section of this chapter. Based on the empirical data (Figure 3.4 and Figure 3.5), it was only possible to include a mechanism of N translocation from the WS phase to the WI phase when preparing the Blend 2 of the incubation of the blend (Figure 3.6b). This could be related to sorption or precipitation processes, although the wood ashes have not been activated. In the case of the Blend 1, the poor retention of N in the WI phase (Figure 3.6b) could be due to an underestimation of the WI N. The higher concentration of WI N in the Blend 2 (Figure 3.6b) compared to the Blend 1 (Figure 3.6a), was in agreement with the lower NH_3-N losses in the Blend 2. The $N_2O_{(g)}$ emissions were higher in the Blend 2 than in the Blend 1, but any of these losses were negligible compared to the $NH_{3(aq)}$ volatilisation. In this way, $NH_{3(g)}$ was the main form in which the N was lost, with the highest volatilisation rate of $NH_{3(aq)}$ at the time of blending the samples (Figure 3.7a). However, the determination of the rate of volatilisation of $NH_{3(aq)}$ at time zero was not possible because of the negligible time interval. It took 6 hours to have similar rates of NH_3-N volatilisation in both blends (81.55 ± 0.93 mg/kg/hour), which will continue to decrease after the 10 hours of incubation until reaching a minimum $NH_{3(aq)}$ concentration (it is not shown in the Figure 3.6). Ukwuani and Tao (2016) found similar volatilisation rates, ranging from 151 to 1,284 mg NH_3-N/kg digestate/hour, in 15 L municipal sludge digestate and 10 L retrentate of landfill leachate, respectively. In their experiment, the incubation of each waste took place for 2 hours at 65–70 ºC and 25.3–34.7 kPa of absolute pressure. Other $NH_{3(aq)}$ volatilisation rates available in the literature were lower than the values found for the two blends (Figure 3.7a). Whelan *et al.* (2010) found a rate of volatilisation of 2.6 mg NH_3-N/kg digestate/hour during the first two weeks of incubation. Besides, it was possible to calculate a rate of volatilisation of 2.3 µg NH_3-N/kg sludge/hour with the results of Méndez *et al.* (2002).

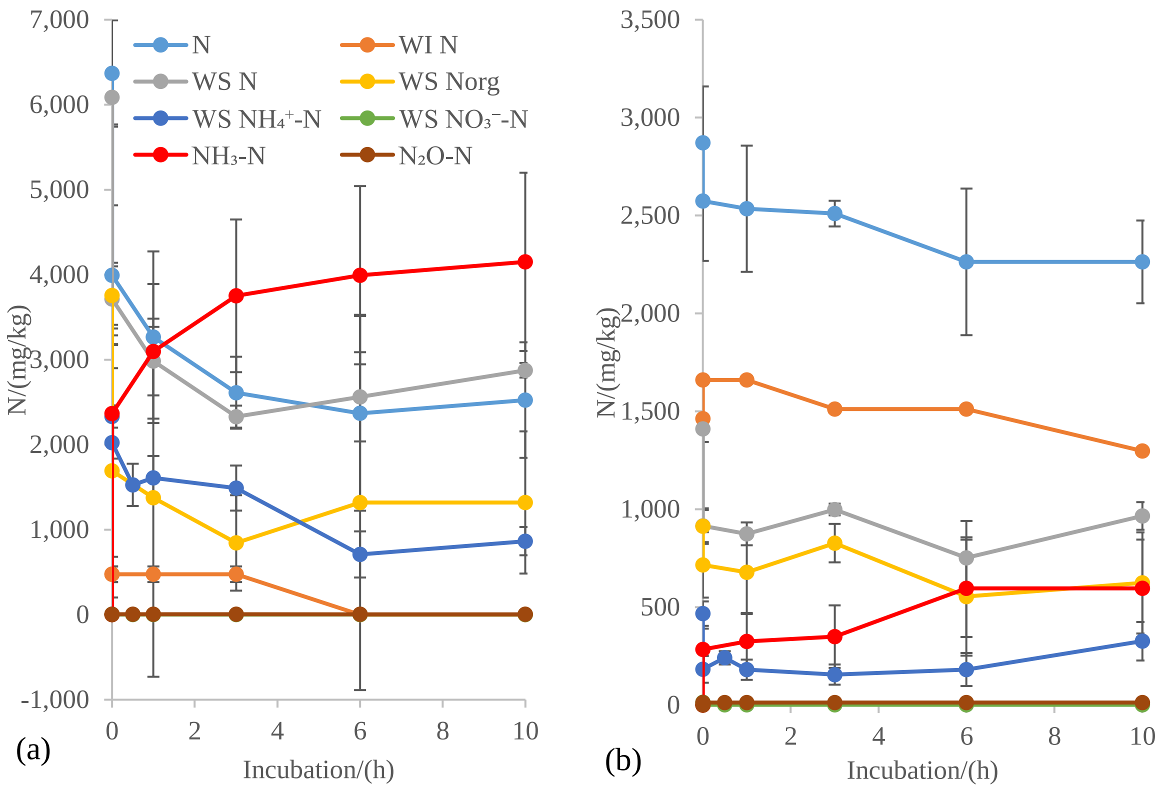


Figure 3.6. Calculated profiles of N species in 3 g of Blend 1 (a) and 3 g of Blend 2 (b) during the incubation at 100 rpm and 22 ºC (Table 3.2) (Moure Abelenda *et al.*, 2021c).

3.3.7. WS PO_4^{3-}-P profile

The result of the single-factor ANOVA for Blend 1 was that $F = 8.03 > F_{crit} = 2.35$. Thereby, it was possible to claim with a 95 % of certainty ($p < 0.05$) that, during the 10 hours of incubation at 22 ºC, the concentration of WS PO_4^{3-}-P of Blend 1 increased (Figure 3.7b). The reason for the lower concentration of WS PO_4^{3-}-P in both blends, compared to their initial characterisation (Table 3.3), would be the gradual process of adsorption and precipitation, as described by Yagi & Fukushi (2012). The kinetic of adsorption was faster than precipitation, therefore the continuous 100 rpm shaking prevented the formation of new crystals. Millero *et al.* (2001) found that the optimum pH for the adsorption of WS PO_4^{3-}-P onto aragonite (*i.e.* a form of $CaCO_3$) was 8.6 at 25 ºC. Considering the high content of Ca of both types of ash (Table A.3), similar pH would be desired in both blends to promote the adsorption. Unlike the increase of the content of WS NH_4^+-N (Figure 3.4a), the raise of WS PO_4^{3-}-P in Blend 1 (Figure 3.7b) was due to desorption rather than chemical hydrolysis. The kinetic control of the desorption was only seen in the solubilisation of PO_4^{3-}-P in Blend 1 (Figure 3.7b), which had a pH slightly higher than 10 but lower than the Blend 2 (Figure 3.3a). Therefore, the greater decrease in the WS PO_4^{3-}-P found in the Blend 2 (Figure 3.7b) because of the twice more content of ashes compared to Blend 1 (Table 3.2), in spite of its higher pH and its higher ionic strength of the solution (*i.e.* greater salinity due to higher content of ashes). These are factors that affect negatively the adsorption process but still precipitation of calcium phosphate species was possible (Cerozi & Fitzsimmons, 2016). This conclusion is in agreement with the results of Pesonen *et al.* (2016), who obtained the greatest WS P when the lowest amount of ash (40 %) was used to prepare the blend with dewatered SS (30 %) and $Ca(OH)_2$ (30 %).

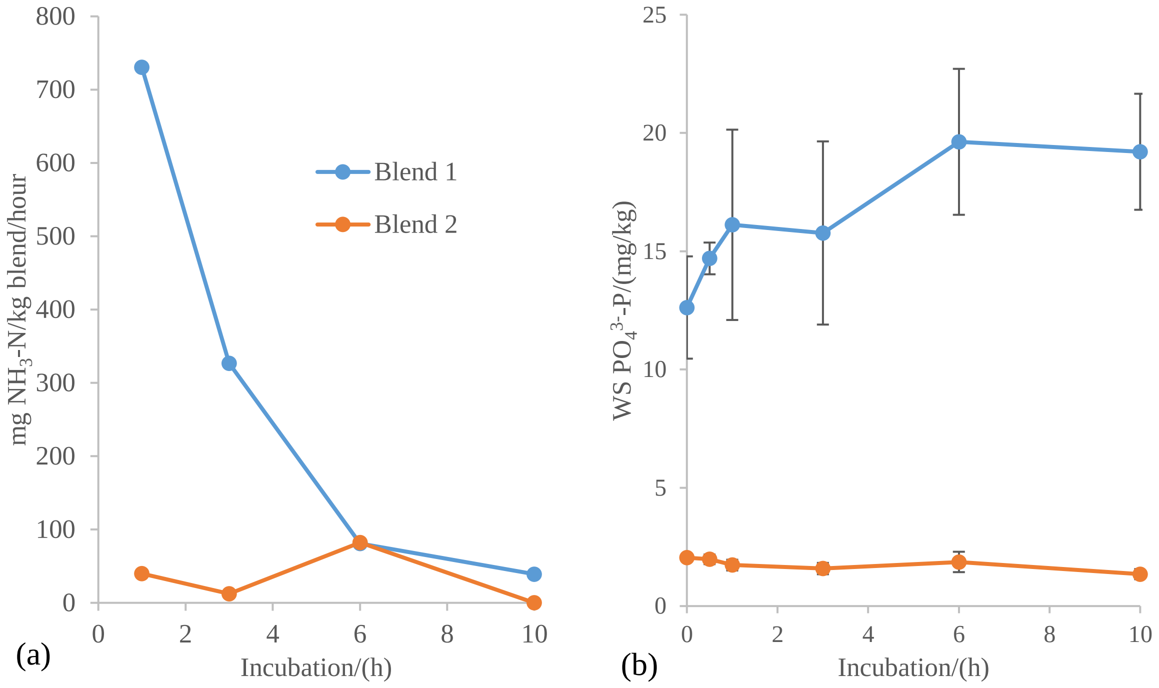


Figure 3.7. (a) Calculated rate of NH_3-N volatilised in each blend. (b) Concentration of WS PO_4^{3-}-P in 3 g of each blend (Table 3.2) measured after the incubation at 100 rpm and 22 ºC (Moure Abelenda *et al.*, 2021c).

Mor *et al*. (2016) had the greatest adsorption of WS PO_4^{3-}-P at pH 2. On the other hand, Ma *et al.* (2011) found that the pH required for the adsorption in a 10 mg PO_4^{3-}-P/L solution was between 4 and 11. In the study of Huang *et al.* (2017), the pH of the 500 mL swine wastewater rose from 7.1 to > 9 after they added 14.25 g of plant ash followed by 30-minute mixing and 30-minute precipitation. Sakthivel *et al.* (2012) 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-}-P of 225 mg/L after 15 minutes of mixing and 4 hours of settling. They used an ash-to-urine ratio of 1/88, which is lower than the dose of wood ashes used in this chapter (Table 3.2), in spite of the higher concentration of PO_4^{3-}-P in their urine solution compared to the digestates used for the experiments of this thesis (Table 3.3). 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 ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$), without taking into account the excess of WS NH_4^+-N in the urine. The 53 % of the Mg in their wood ash was soluble. According to Drosg *et al.* (2015), a nutrient ratio of Mg/N/P 1.3/1/0.9 is necessary to maximise 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 (Drosg *et al.*, 2015). The Mg/N/P total nutrient ratios 1.92 ± 0.47/1/0.80 ± 0.13 and 4.50 ± 1.01/1/2.31 ± 0.35 correspond to the Blend 1 and Blend 2, respectively. The low solubility of the Mg (Table A.5) justifies the excess of this element to attain the precipitation of struvite in the Blend 2.

By comparing the values of Figure 3.7 (b) with the initial characterisation (Table 3.3), it was possible to conclude that both doses of ashes used in this chapter (Table 3.2) decreased the availability of P. The amounts of WS PO_4^{3-}-P sorbed were 29.84 ± 5.09 and 31.85 ± 2.39 mg/kg for Blend 1 and Blend 2, respectively. As per the reversible solubilisation of PO_4^{3-}-P that can be seen in Figure 3.7b, indicating a physisorption mechanism rather than chemisorption (Mor *et al.*, 2016). On the other hand, 307.28 ± 1,349.55 and 284.73 ± 92.59 mg WS NH_4^+-N/kg Blend 1 and the Blend 2, respectively (Figure 3.4a), were discounted at the time of preparation of the blend. It is important to mention that the reason for the large error bars for the average value of the WS NH_4^+-N of Blend 1 at time zero (Figure 3.4a) was that the data was obtained from 2 different set of experiments, which were considered to provide more overarching results. Although approximately the 77 % of the K of the ashes was soluble, the formation of either struvite or K-struvite in the blends was unlikely because less than 1 % of Mg provided by the ashes was soluble (Table A.5). Moreover, given the high content of Ca 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 (Tunesi *et al.*, 1999). However, since less than 1 % of the Ca of the ashes was soluble, the precipitation of a calcium phosphate compound was less feasible. Sakthivel *et al.* (2012) 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 (2012), calcium phosphates with lower concentrations than 1 % could not be detected from the XRD patterns. Yagi & Fukushi (2012) studied the adsorption and precipitation by adding 100 mg monohydrocalcite ($CaCO_3 \cdot H_2O$) to 50 mL solutions ranging from 0.37 to 7.83 mg PO_4^{3-}-P/L under continuous stirring for 6 to 216 hours. The higher sulibility and reactivity of the $CaCO_3 \cdot H_2O$ 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 hours 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 hours. Sakthivel *et al.* (2012) reported a decrease of WS PO_4^{3-}-P in less time (*i.e.* 87 % removal after 0.5 hours, 97 % removal after 1.5 hours and 99.5 % removal after 4 hours of adding the ash). In this chapter, reductions of the concentration of the WS PO_4^{3-}-P of 64.34 ± 11.86 % and 94.81 ± 9.75 % were achieved at the time of preparing the Blend 1 and the Blend 2, respectively (Figure 3.7b).

In the study of Yagi & Fukushi (2012), 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 the precipitation of calcium phophates, they used a concentration of WS PO_4^{3-}-P higher than 4.10 mg/L and a soluble sorptive agent, such as $CaCO_3{\cdot}H_2O$. Other process parameter that could reduce the availability of the WS PO_4^{3-} is the operating temperature. Yagi and Fukushi (2012) found the greatest removal of the WS PO_4^{3-} at the highest temperature that they tested (15, 25 and 35 ºC). On the other hand, Mor et al (2016) found that the removal of WS PO_4^{3-} was better at 30 ºC than at any of the other temperature that they tested (25, 35 and 40 ºC). Moreover, it is necessary to take into account that the increase of the temperature of the blends could lead to higher $NH_{3(aq)}$ volatilisation (Ukwuani & Tao, 2016).

P was not expected to be lost *via* gas exchange under the conditions of incubation of this chapter (*i.e.* 10 hours at 100 rpm and 22 ºC) and the total initial amount would thereby be expected to remain split into the WS phase and the WI phase of each blend. P in the ashes was in the form of PO_4^{3-} (Maresca *et al.*, 2017), whether it was part of the WS P or the WI P. On the other hand, the P 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 P) in organic amendments (Sharpley & Moyer, 2000). In this way, the determination of the dissolved reactive P, which is the WS PO_4^{3-}-P that responds to the molybdate colorimetric test without previous hydrolysis (Pote & Daniel, 2000), could give a good idea of the WS P in the blends. It should be noted that some of the particulate P and WS P_{org} were anticipated to be hydrolysed easily (Tiecher *et al.*, 2012), even with the reagents of the improved colorimetric method of Murphy and Riley (Pote & Daniel, 2000), which was used in this thesis.

3.4.Conclusions

The changes in the availabilities of N, C and P in food waste and agrowaste digestates due to the addition of wood ashes, were monitored for 10 hours of incubation. It was proposed that the NO_3^--N was lost as $N_2O_{(g)}$ due to the reducing effect of the alkali and alkaline earth metals contained in the ashes. This was confirmed in the Chapter 5 of this thesis, which reports the decrease in N after the addition of HNO_3 directly to the WBA (Figure 5.5 and Figure A.18). The high pH of the blends (> 10) promoted the volatilisation of NH_4^+-N and the solubilisation of C. A ratio around 3 g TS wood ash/g TS digestate was considered the most convenient for the subsequent chapters of the thesis. The extents of the physicochemical phenomena were also related to the composition of the digestates and the ashes. The greatest loss of N 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 C *via* CO_2 release was regarded as negligible at the high pH of the blends. In terms of P 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 fertiliser. Digestates with high content of NH_4^+-N or other easily converted forms, such as FWD, were anticipated to have greater losses *via* $NH_{3(aq)}$ volatilisation. In this way, the PVWD was the most suitable digestate for the production of a controlled-release fertiliser. 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 Ca and Mg; Table A.3 and Table A.5). 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, since the utilisation of this resource is more urgent than that of WFA. Furthermore, the higher pH of WBA could be used to enhance the $NH_{3(aq)}$ stripping from the digestates which would be recovered with a H_2SO_4 trap. Although the pH of WFA is lower, still required the use of acid to prevent the loss of N and the C solubilisation. Finally, since ashes are an important source of nutrients (*i.e.* the WFA was richer in P while WBA was richer in K), 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 fertilisers nor on the self-hardening to improve the granulation process.

4. Determination of the optimum pH for the preparation of the blends of anaerobic digestates and wood ashes

4.1.Introduction

The use of biologically stabilised organic waste as soil amendment is a common practice in the agroindustry. The mineralisation involved in biological treatments (*e.g.* AD and composting) increases the nutrients availability, hence these processes could lead to pollution of the environment. There is a range of additives that have been tested to improve the management of organic soil amendments, by means of minimising the losses of nutrients during storage and land application. The nature of these materials goes from special formulated cocktails of microorganisms (Bastami *et al.*, 2016; Van der Stelt *et al.*, 2007) to commercial acidifiers (Kavanagh *et al.*, 2019; Regueiro, Coutinho, & Fangueiro, 2016). Materials widely handled in farms, such as lime (Brennan *et al.*, 2015) or agricultural residues (Kavanagh *et al.*, 2021), have been investigated for the same purpose, in order to minimise the cost of handling the organic manures. Even CFA has been tested to minimise the losses of P *via* leaching (Brennan *et al.*, 2011; Zhou *et al.*, 2020). However, the nature of these additives needs to be taken into account as they might be a source of toxic elements (*e.g.* heavy metals) for crops. Biomass ashes are regarded as a clean waste stream and have been used to improve the performance of anaerobic digestates as fertiliser by providing additional nutrients (Fernández-Delgado Juárez *et al.*, 2013; Insam *et al.*, 2009). In terms of chemical stabilisation (Figure 2.4), the wood ash has been employed as a source of Mg for precipitation of struvite in urine (Sakthivel *et al.*, 2012) and swine wastewater (Huang *et al.*, 2017). The struvite ($NH_4^+Mg^{2+}(H_2O)_6PO_4^{3-}$) is a well-known controlled-release fertiliser in which Mg^{2+} is surrounded by six molecules of water (Prywer *et al.*, 2019) arranged in an octahedral geometry (Figure 2.5). In the literature, there is evidence about how the acidification promotes the dehydration (Limoli *et al.*, 2016; Ma *et al.*, 2011) because the H^+ ions act as a cationic surfactant (Zheng *et al.*, 2016). According to Leechart *et al.* (2019), the surfaces of the adsorbents might be positively or negatively charged depending on the system pH and this would have direct influence on electrostatic interactions. The pH of zero-point of charge (pH_{zpc}) is defined as the pH that neutralises the charge of the sorbents (Equation 2.44).

The activation of ashes as sorbents *via* acidification (Table 2.6) aims to reduce the availability of all elements (Kocatürk-Schumacher *et al.*, 2017) in the soil organic amendments, which increases the properties of these materials as slow-release fertilisers. When the blend has a lower pH than the pH_{zpc}, the surface of the ash-based adsorbents becomes positively charged (Equation 2.44), favoring the adsorption of anionic species. The removal of PO_4^{3-} (N. Park *et al.*, 2021) and the NH_4^+ (Escudero *et al.*, 2015) from the water-soluble (WS) phase *via* struvite crystallisation is not promoted by working at acidic pH and the dose of acid or alkali reagents need to be as much as it is required to reach the pH_{zpc} (Leechart *et al.*, 2009). In the previous Chapter 3, the WFA and WBA were employed to achieve the alkaline stabilisation of FWD and PVWD. The acidification is regarded among the best available techniques to reduce ammonia emissions (European Commission, 2017) and including the wood ash in the treatment aims to further improve the chemical stability of the organic manure (Figure 2.4). Acidification of organic slurries alone (*i.e.* without the addition of wood ashes) increases the losses of nutrients in runoff waters (Fangueiro *et al.*, 2015) whilst the ash-based treatment could prevent them (Richards *et al.*, 2021). In addition to sorption processes, several other mechanisms are involved in the chemical stabilisation of organic manures. The precipitation of calcium phosphate can be used in combination with sorption processes to improve the stability of the organic manure (Leechart *et al.*, 2009; W. Shi *et al.*, 2021). The main component of the wood ashes is Ca (Ribbing, 2007; Vassilev *et al.*, 2017), which is in the form of oxide, hydroxide or CO_3^{2-}, depending on combustion temperature and storage conditions (Demeyer *et al.*, 2001). Particularly, the WFA sampples that have been used in the experiments of this thesis have a content of Ca around 27 % (Table A.5).

This chapter optimises the wood ash-based treatment of anaerobic digestate and offers insights into the possibilities of this technology. This processing of organic manures is in agreement with the existing infrastructure in the agroindustry and requires low capital investment, hence it might be easily adopted by farmers (Hou *et al.*, 2018). This chapter contains the results corresponding to the evaluation of 3 different studies that aimed the preparation of blends of anaerobic digestates and wood ashes. These outcomes represent the first step for understanding the techno-economic viability of achieving the chemical stabilisation of the anaerobic digestate by means of adding wood ash at appropriate pH.

4.2.Materials and methods

The characterisation of WFA, WBA, PVWD and FWD can be found in the previous chapter (Table 3.3). Only a subsample of WFA was sent to the external NRM laboratory for determination of the content of trace elements (Table A.5), due to the concern about high content of heavy metals and impurities (Dahl *et al.*, 2010, 2009; Pöykiö *et al.*, 2011, 2009) and how they impact in the sorption capacity of the finer fraction of the ashes. The pH was monitored, as proxy of other parameters (*i.e.* nutrient speciation), to follow up the underlying chemistry of the samples. The measurement was performed with the same equipment described in the methodology section of Chapter 3. The WS fraction was generated using an approximate sample to solvent ratio of 1/10 in the case of the anaerobic digestate and 1/40 in the case of the wood ash. This was achieved by mixing approximately 20 mL of fluidising agent with 2 g of anaerobic digestate and 0.5 g of wood ash in 50-mL Corning® flasks. For the incubation at 21 ºC and 100 rpm, the 50-mL closed tubes were placed horizontally in an orbital shaker. The acidifying agents were prepared with ultrapure milli-Q® water and analytical grade H_2SO_4, HCl, HNO_3 and $CH_3CH(OH)COOH$. These acids were selected because they are widely used to decrease the pH of animal slurry (Fangueiro *et al.*, 2015). Following the methodology of Regueiro, Coutinho, & Fagueiro (2016), the doses were expressed as milliequivalents of acid per gram of waste sample (mEq/g). The procedures for the three studies are slightly different as described below.

4.2.1. First strategy: Characterisation of the acid neutralising capacity of the ash and digestate samples

The titrations of WFA, WBA, PVWD and FWD were performed to determine the pH_{zpc} and the OH (H_2CO_3), P (HCO_3^-) and M (CO_3^{2-}) alkalinities of each sample. The OH alkalinity is also known as caustic alkalinity, the P alkalinity or partial alkalinity is a measurement of the bicarbonate concentration and the M alkalinity or total alkalinity corresponds to the dissociation of VFA and CO_3^{2-} (Jantsch & Mattiasson, 2003). In this way, the amount of acid that would need to be added to each sample before the mixing to achieve a pH 5.5 in the blends was determined. A pH 5.5 ensures that all the NH_4^+-N is in the form of ammonium (Fangueiro *et al.*, 2015). Moreover, the low pH prevents microbial degradation of the OM before application to land of the manure (Regueiro, Coutinho, Gioelli, *et al.*, 2016). The analytes were prepared by adding 20 mL of milli-Q® water to approximately 2 g of digestate or approximately 0.5 g of ash for measuring the initial pH after 1 hour shaking at 100 rpm. The four titrants employed were: 18.29 M H_2SO_4, 11.81 M HCl, 15.21 M HNO_3 and 11.99 M $CH_3CH(OH)COOH$. These concentrated acids were used in steps of 10 µL to avoid a change in the size of the analytes and to determine the minimum amount of acid that is required to meet the desired pH. The addition of titrant was followed by incubation at 21 ºC and 100 rpm before measuring the pH. The acid was only added when the pH of the sample was constant for 30 minutes. It took 530 hours to reach the endpoint of the titrations ($pH < 2$) after consuming all the alkalinities (*i.e.* OH, P and M) of the samples. The pH_{zpc}s of the sorbents were estimated following a modification of the procedure described by Leechart *et al.* (2019) and Shah *et al.* (2015), as described in the section of acidification of Chapter 2. The pH_{zpc} was determined by (1) plotting the charge of the sorbents (Q; Equation 2.43) versus the pH, (2) selecting the best second order fittings (generic form $Q=a(pH)^2+b(pH)+c$) among the 4 acid titrants and (3) identifying the pH associated with the minimum empirical values of Q (Figure 2.7). The calculation of the error propagation was conducted with the Equation A.8, Equation A.9 and Equation A.10.

Simulations of the titrations were performed with the software Visual MINTEQ (version 3.1) by using the compositions of the samples determined in-house (Table A.3) and reported in NRM (Table A.5). Tuning the composition of the analytes (*i.e.* testing different shares of CO_3^{2-}, bicarbonate and C_{org} of the samples) was done to reach the closest similarities between the predicted and empirical titration curves. In this way, the pH profiles of the simulations were compared against the experimental results to confirm the trends found for the 4 acids and to elucidate the underlying chemistry. The profiles of the anion concentrations of the acids (SO_4^{2-}, Cl^-, NO_3^- and $CH_3CH(OH)COO^-$) in the WS phase of the analytes were used to elucidate the interaction of the acids with the samples.

4.2.2. Second strategy: Addition of the ashes to the acidified digestates

Given the low amount of acid required to reach the pH_{zpc} (determined in during the characterisation of the first strategy), the second study assessed whether the doses employed in the agroindustry (Eriksen *et al.*, 2012; Sørensen & Eriksen, 2009) would be suitable to attain the pH_{zpc} upon addition of wood ashes to the acidified digestates, to obtain an stable blended fertiliser. The acidification conditions 0.00, 0.08, 0.16, 0.24, 0.32 and 0.40 mmol H^+/g digestate are widely used to decrease the pH of the animal slurry and manure (Table A.6). These nominal conditions (Table A.7) were monitored for up to 2 weeks before the addition of the ash, which according to Regueiro, Coutinho, & Fangueiro (2016) is the minimum time to ensure a constant pH has been reached in animal slurry. Moreover, after the addition of the ash, the pH was measured for more than 4 weeks. The blends consisted of 80 % of one digestate type and 20 % of one ash type. The PVWD was grouped with the WBA (*i.e.* PVWD+WBA) because these were the less reactive samples with the best properties for the intended slow-release fertiliser. On the other hand, the blend of the FWD with the WFA (*i.e.* FWD+WFA) was also studied because more stabilisation processes were expected from the interaction of these samples. The WFA had smaller particle size and greater surface area that the WBA, hence more sorption processes were anticipated (Laohaprapanon *et al.*, 2010). The FWD had approximately 5 times more NH_4^+-N than the PVWD (Table 3.3). In this way, the 3 factors investigated in the second strategy were (a) the components of the blend, (b) the acidification dose and (c) the time of incubation. The first factor had two levels, which were the 2 blends that were tested (*i.e.* WBA + PVWD and WFA + FWD). The second factor had 21 levels, corresponding to 5 doses of each of the 4 acids employed and the 1 experimental blank (*i.e.* no acidification). The third factor had 11 levels, as the pH was measured 7 times in the acidified digestates and 4 times after the addition of the ashes. To ensure the reproducibility of the results, three replicates (n = 3) per condition were made. The average values and the standard deviations were plotted in scatter charts to assess trends and behaviors using descriptive statistics. Furthermore, the two-way ANOVA test ($p < 0.001$) was used to identify significantly differences among the dose-response curves.

4.2.3. Third strategy: Wash the ashes with water to reduce their basifying power

The wood ashes were washed 7 times with ultrapure milli-Q® water to reduce the acid required to reach the pH_{zpc} in the blends with the anaerobic digestates. By washing the ashes before adding them to the digestates, most impurities and alkali metals (*e.g.* Na and K; (El-Nahas *et al.*, 2021)) would be removed while leaving the less soluble elements (*e.g.* Ca, Mg and C; Table A.5 and Table 3.3), which could act as sorbents, upon addition to the anaerobic digestates. The pH was measured at the time of adding the 20 mL of ultrapure milli-Q® water to approximately 0.5 g of ash and after 24-h incubation at 21 ºC under 100 rpm continuous shaking. Subsequently, the 4,000 rpm centrifugation allowed to discard the WS extract *via* decantation and fresh 20 mL of milli-Q® water were mixed with the depleted ash for the next iteration. The seventh extraction was followed by a 264-h of incubation to evaluate whether the reduction in the pH of the ashes was maintained. The two-way ANOVA test ($p < 0.001$) was used to compare the kinetics of pH reduction in the WFA (n = 3) and the WBA (n = 3).

4.3. Results and discussion

4.3.1. First strategy: Acidification of the samples separately before the blending

4.3.1.1. Experimental results of the titrations

Figure 4.1 shows the experimental results and simulation of the titrations of the samples with H_2SO_4, HCl, HNO_3 and $CH_3CH(OH)COOH$. The titration curves of the digestates (Figure 4.1a,b) were smoother than the ones of the ashes (Figure 4.1c,d). In the case of the wood ashes (Figure 4.1c,d), the variable kinetics of neutralisation made difficult to predict when the equilibria of the on-going neutralisation reactions were going to be achieved, before adding the next dose of acid to the samples. The reasons for the fluctuations in the curves obtained for the ashes (Figure 4.1c,d) were the high complexity (*i.e.* speciation of metal oxides, hydroxides and CO_3^{2-}) and high buffer capacity of these materials compared to the ones of the digestates (Figure 4.1a,b). Despite the fluctuations in the titration curves of WFA (Figure 4.1c) and WBA (Figure 4.1d), it was possible to identify the OH, P and M alkalinities, corresponding to the three equivalence points found at pH ranges of 13 – 11, 10 – 8 and 7 – 2. Some of the chemical species that provided acid neutralising capacity to the digestates were different from the components which play that role in the ashes. First of all, there was no OH alkalinity because of the initial pH of the FWD (8.45 ± 0.02; Figure 4.1a) and PVWD (7.85 ± 0.12; Figure 4.1b). The M alkalinity was greater in the FWD than in the PVWD, in agreement with the higher content of NH_4^+-N (Table 3.3). The doses of H_2SO_4, HCl and HNO_3 to finish the P alkalinities of the FWD and the PVWD were around 0.75 and 0.25 mEq/g, respectively (Figure 4.1a,b). Vandré & Clemens (1996) needed around 0.25 mEq HCl/g cattle slurry to consume the P alkalinity and reach the endpoint of the titration at a pH value of 2. It should be noted the exception of the $CH_3CH(OH)COOH$ to neutralise the M alkalinity of all the samples, due to the pKa 3.86 of this acid (Regueiro, Coutinho, & Fangueiro, 2016). The plateau observed in the titration curves using the $CH_3CH(OH)COOH$ as titrant was the result of the dissociation equilibrium of this molecule that allow the sorption of $CH_3CH(OH)COO^-$ and release of H^+ ions. The amount of H^+ provided by the lactic acid was up to 30 times lower than the protons provided by the nitric acid to reach a pH below 2 in the WFA (Figure A.1). The use of lactic acid was regarded as the most expensive procedure to decrease the pH of the samples. The 3 strong acids (H_2SO_4, HCl and HNO_3) concur in the doses for the OH, P and M alkalinities around 2.5 mEq/g WFA, 7.5 mEq/g WFA and 20 mEq/WFA (Figure 4.1c). The dose-response curves which resembled the most, were the ones of the HCl and the HNO_3, thus similar doses of these acids were required to acidify the samples. Etiégni and Cambel (1991) found that around 8, 16 and 22 mEq HCl/g were required to finish the alkalinities of wood ash and reach a pH below 2. It should be noted that the valence of H_2SO_4 is 2 (Regueiro, Coutinho, & Fangueiro, 2016), hence less moles of this acid than that of HCl or HNO_3 are required to provide the same level of H^+ to the samples (Table A.7).

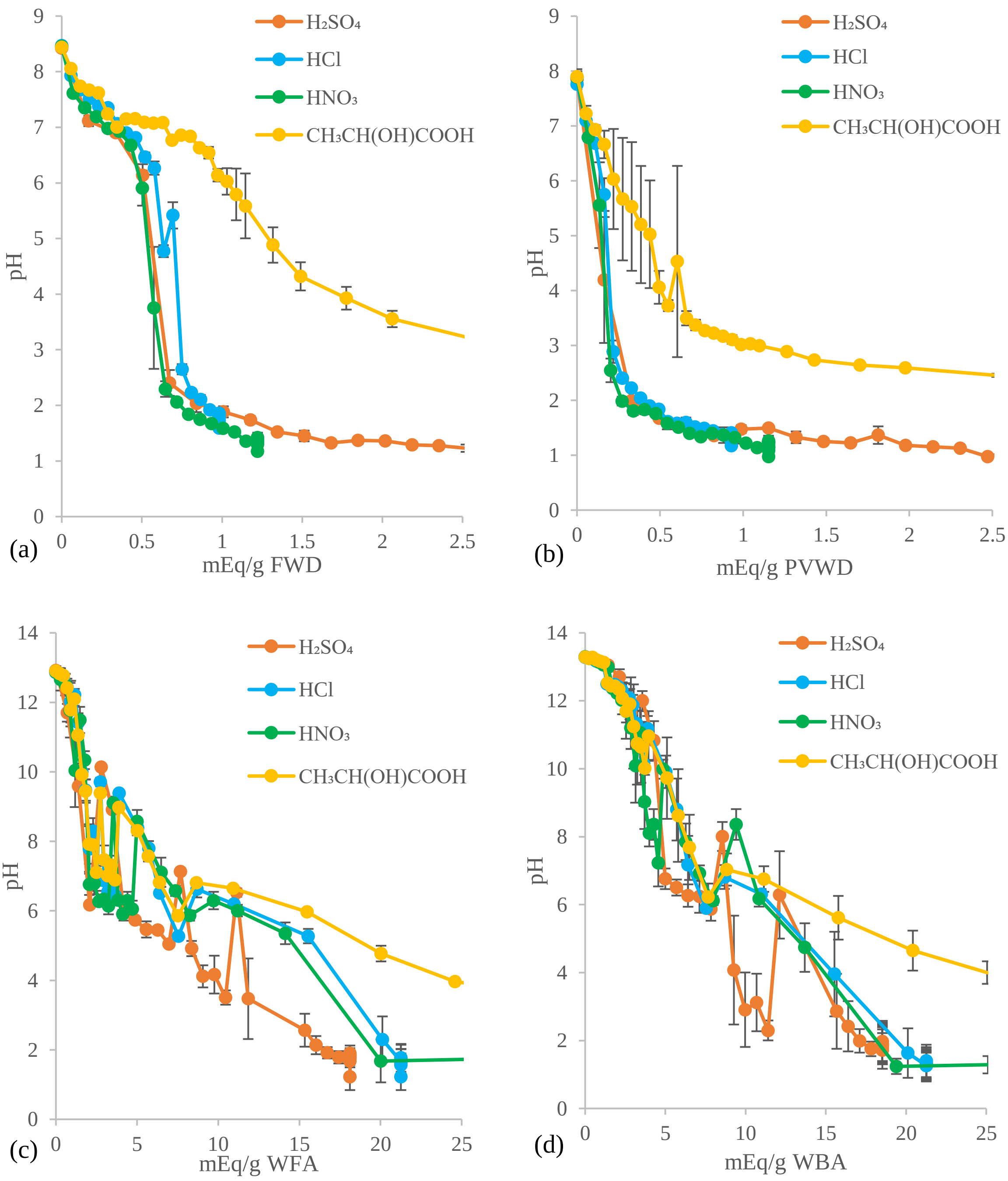


Figure 4.1. Experimental results (n = 3) of the titration of analytes prepared by mixing 20 mL of milli-Q® water with (a) 2.11 ± 0.09 g of FWD, or (b) 2.20 ± 0.10 g of PVWD, or (c) 0.52 ± 0.02 g of WFA, or (d) 0.52 ± 0.02 g of WBA (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022). The titrants (18.29 mol H_2SO_4/L, 11.81 mol HCl/L, 15.21 mol HNO_3/L and 11.99 mol $CH_3CH(OH)COOH$/L) were employed in volumes ≤ 200 µL per dose-point, with the exception of $CH_3CH(OH)COOH$ that required volumes up to 10 times higher per dose-point to reach the titration end-point (pH < 2).

The reaction of wood ash with HCl could be used to produce $CaCl_2$ (Equation 2.29), which is a widely used chemical stabiliser of animal slurry (Kavanagh *et al.*, 2021; Y. Shi *et al.*, 2001; Vandré & Clemens, 1996). The chemical stabilisation with $CaCl_2$ relies on the solubilisation of nutrients, which are more stable in the WS fraction of the organic manures. For example, Kavanagh *et al.* (2019) concluded that cattle slurry with a 7 % DM releases more atmospheric pollutants (NH_3, N_2O, CH_4 and CO_2) during storage than a cattle slurry with 4 % DM. The DM of the cattle slurry is directly related to the content of OM and nutrients. In addition to the higher nutrient concentration, the chemical instability of (dewatered) solid manures could be explained by the large surface area (Figure 2.6), which enhances the mass transfer (*e.g.* volatilisation of ammonia) compared to the liquid slurry (Dinuccio *et al.*, 2012). The use of alum ($Al_2(SO_4)_3$) as acidifying agent can reduce the gaseous emissions even after the solid-liquid separation of the pig slurry (Regueiro, Coutinho, Gioelli, *et al.*, 2016). The aluminum is present in the wood ashes (Table A.3), hence the alum could be manufactured as described by Equation 2.22 (M. Fan *et al.*, 2005). Moreover, the presence of BC (Forbes *et al.*, 2006; Liang *et al.*, 2010) in the wood ashes (Table 3.3) could serve as a lattice structure that enhances the sorbent properties of Ca (Kocatürk-Schumacher *et al.*, 2017; Yagi & Fukushi, 2012).

4.3.1.2. Visual MINTEQ results of the titrations

The software Visual MINTEQ assumes instantaneous thermodynamic equilibrium free of chemical kinetic limitations (Gustafsson, 2014), hence there were no fluctuations in the titration curves and it was possible to clearly identify the OH, P and M alkalinities (Figure 4.2). The theoretical titrations of the anaerobic digestates (Figure 4.2a,b) confirmed that the greater M alkalinity measured experimentally in the FWD (Figure 4.1a) was due to the greater NH_4^+-N content, compared to the PVWD (Figure 4.1b). The acetic acid (pKa of 4.75 at 25 ºC), which is often the main VFA in anaerobic systems (Mao *et al.*, 2015), was not considered to be responsible of the inflexion point corresponding to the M alkalinity in the pH range 4.75 to 4.25 (Mu *et al.*, 2018). Despite the chemistry of the acetic acid was not implemented in the simulation model, approximately 10 times higher doses of the 3 strong acids were required in the simulations to finish the M alkalinity of the FWD and the PVWD (Figure 4.2a,b) than in the real titrations of the digestates (Figure 4.1a,b). The initial pHs of the FWD and the PVWD in the Visual MINTEQ simulations (Figure A.4a,b) are in accordance with the empirical data (Figure 4.1a,b) and with the results of Vandré & Clemens (1996), who needed to add NaOH to cattle slurry to observe the P alkalinity.

According to the simulation carried out with the in-house characterisation of the wood ashes (Table A.3), the WFA (Figure 4.2c) had more alkalinity than the WBA (Figure 4.2d). This fact cannot be appreciated in the experimental results (Figure 4.1c,d). The simulations did not account factors such as the greater particle size of the WBA, which decreased its reactivity compared to the WFA (Laohaprapanon *et al.*, 2010; Leechart *et al.*, 2009). These simulations significantly ($p < 0.001$) underestimated the dose of the strong acids to consume the M alkalinity in the WFA (~ 12.5 mEq/g; Figure 4.2c), with respect the empirical titrations of WFA (~ 20 mEq/g; Figure 4.1c). On the other hand, the values for the OH and P alkalinities were found to be roughly 2.5 mEq/g WFA and 7.5 mEq/g WFA, respectively, both in the experimental (Figure 4.1c) and the theoretical (Figure 4.2c) results. The results of the simulations considering the characterisation of WFA provided by an external laboratory (Table A.5) better matched the empirical data depicted in the Figure 4.1c, in terms of the dose required to reach the titration end-point (~ 20 mEq/g; Figure A.2a). However, this better correlation of the empirical (Figure 4.1c) and theoretical (Figure A.2a) total alkalinity of WFA, affected negatively the OH and the P alkalinities, which were found to be approximately 10 mEq/g and 15 mEq/g, respectively.

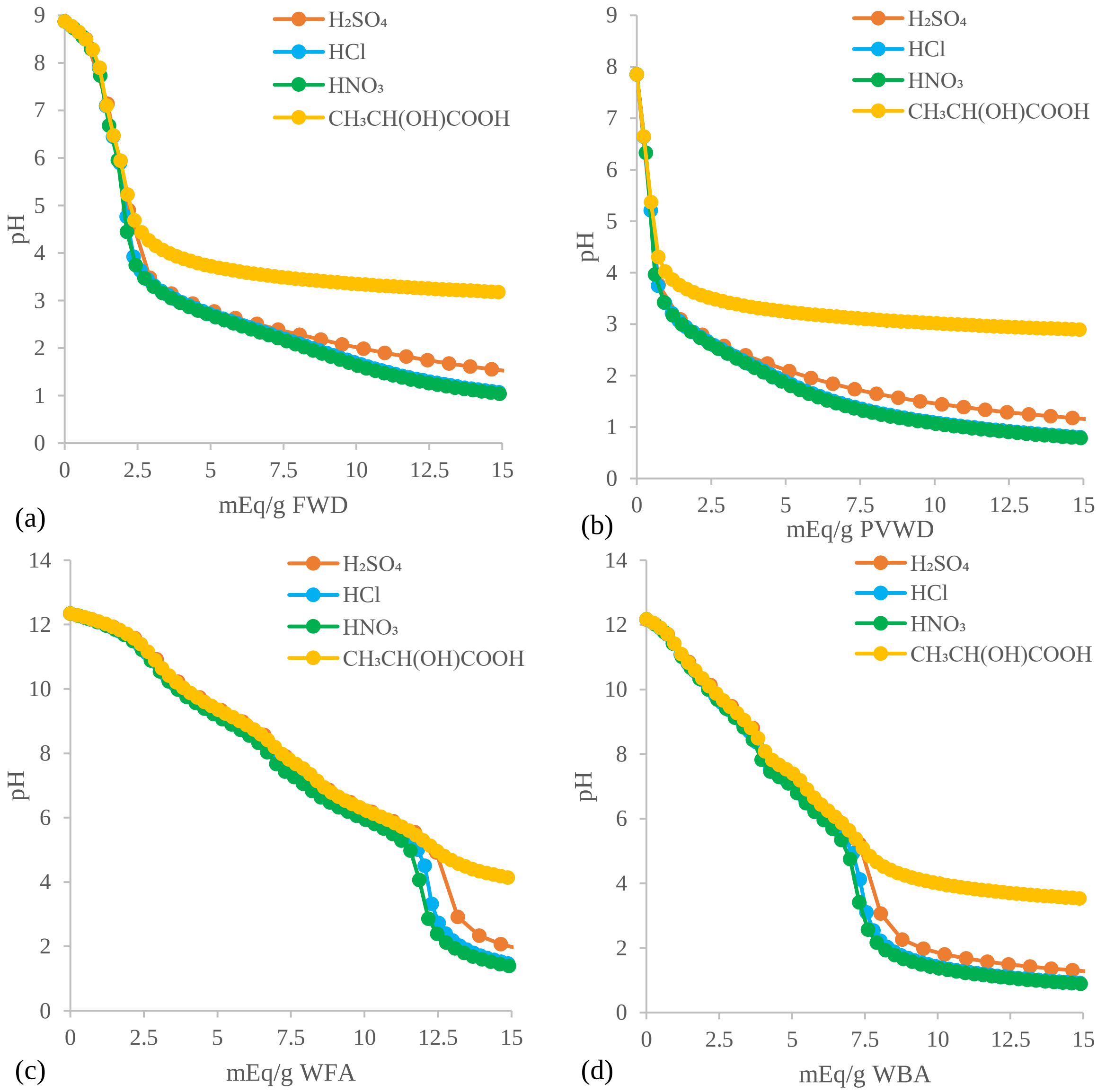


Figure 4.2. Theoretical results (n = 3) of the titration of analytes prepared by mixing 20 mL of milli-Q® water with (a) 0.52 ± 0.02 g of WFA, or (b) 0.52 ± 0.02 g of WBA, or (c) 2.11 ± 0.09 g of FWD, or (d) 2.20 ± 0.10 g of PVWD. Up to 1 mL of titrants (18.29 mol H_2SO_4/L, 11.81 mol HCl/L, 15.21 mol HNO_3/L and 11.99 mol $CH_3CH(OH)COOH$/L) employed were in volumes of 10 µL per dose-point. The simulations were conducted using the composition of the samples determined in-house (Table A.3). The Dissolved Inorganic Carbon model was used for the wood ashes. Molecules of glycine and glyphosate were used to represent the C_{org}, N_{org} and P_{org} of the anaerobic digestates (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

Other deviation between the empirical results (Figure 4.1) and the modelling (Figure 4.2) was found in the dose of H_2SO_4 required to reach the titration endpoint (pH < 2). The actual impact of the sorption of SO_4^{3-} (Figure A.3) on the reduction of the pH (Figure 4.1) was greater than that in the predictions (Figure 4.2). The number of moles of SO_4^{2-} that remained in solution by the end of the titration was less than a fifth of the number of moles of either Cl^- or NO_3^- (Figure A.3), due to dissociation equilibrium of the second proton and the sorption of the SO_4^{3-}. The same phenomena was involved in the acidification with lactic acid, as per the similar profile of $CH_3CH(OH)COO^-$ and SO_2^- in the Figure A.3, due to the dissociation equilibria of these acids and the formation of chemical species such as calcium lactate and calcium sulfate (Figure A.4) in the form of gypsum and anhydrite. This could be an indication that the SO_4^{2-} and the $CH_3CH(OH)COO^-$ limit the sorption processes due to complexation and attachment to active sites that hinder the interaction between the nutrients of the wood ashes and the anaerobic digestates. The increase of the WI fraction when using sulphuric and lactic acids to acidify the samples, particularly the wood ashes, was observed in the next chapter (Figure A.13d). The lower amount of exogenous H^+ that needed to be provided by the H_2SO_4 and $CH_3CH(OH)COOH$ to decrease the pH of the samples could be related to the sorption of their anions. The concentration of the Cl^- and NO_3^- ions increased progressively in the WS fraction of the titrate without reaching saturation (Figure A.3 and Figure A.4). The concentration of SO_4^{2-} and $CH_3CH(OH)COO^-$ did not increase beyond a certain level and even decreased upon addition of more acid (Figure A.3). The N_{org}, C_{org} and P_{org} were taken into account in the simulations of the titrations of the anaerobic digestates in the form of glycine and glyphosate. These organic molecules affected negatively the sorption of SO_4^{2-} and $CH_3CH(OH)COO^-$, as can be seen in Figure A.3. This fact and the pKa_2 1.99 could explain why the H_2SO_4 did not finish the titration of the anaerobic digestates sooner than all the other acids (Figure 4.1a,b), as it happened with the wood ashes (Figure 4.1c,d). Unlike the results of the ashes, the trends (*i.e.* order in which the acids reached a $pH < 2$) in the titration curves of the digestates found experimentally (Figure 4.1a,b) agree with the simulations (Figure 4.2a,b).

4.3.1.3. Calculation of the pH_{zpc}

Considering the role of the wood ashes as sorbents and the negative impact that severe acidification could have on the role of the wood ashes to prepare a slow-release fertiliser, mild acidification conditions were thought to be optimal for this purpose. In addition to enhance the sorption of the WS nutrients of the anaerobic digestates onto the wood ashes, mild acidification implies a saving in acid reagents in the preparation of the blended fertilisers. The best fitted quadratic correlations of Q and the pH were obtained with the HCl and the HNO_3 (Figure 4.3). According to Figure 4.3, the pH_{zpc} of the WFA (11.90 ± 0.50) was lower than the one of the WBA (12.43 ± 0.06). The R^2 of the Q profiles obtained with H_2SO_4 and the $CH_3CH(OH)COOH$ were below 0.9 (Figure A.5). Leechart *et al.* (2009) reported a pH_{zpc} of 10.8 for the WBA and

10.9 after soaking this material with H_2SO_4 or deionised water and subsequent washing with double-distilled water.

The same methodology was applied to the digestate but the profile of Q (Equation 2.43) consistently increased with the acidification (Figure A.6 and Figure A.7). This means that the addition of any amount of acid increases the surface changes in the anaerobic digestates (Equation 4.1; (Leechart *et al.*, 2009)). It would be necessary to test the alkalinisation of the anaerobic digestates to enhance sorption of WS nutrients onto the fiber, although the neutralisation of the charge of the ammonium (Equation 3.2) might lead to losses of the aqueous ammonia *via* mass transfer to the gaseous phase (Equation 3.3). The addition of the wood ash to the anaerobic digestate would avoid the requirement for basic titrants.

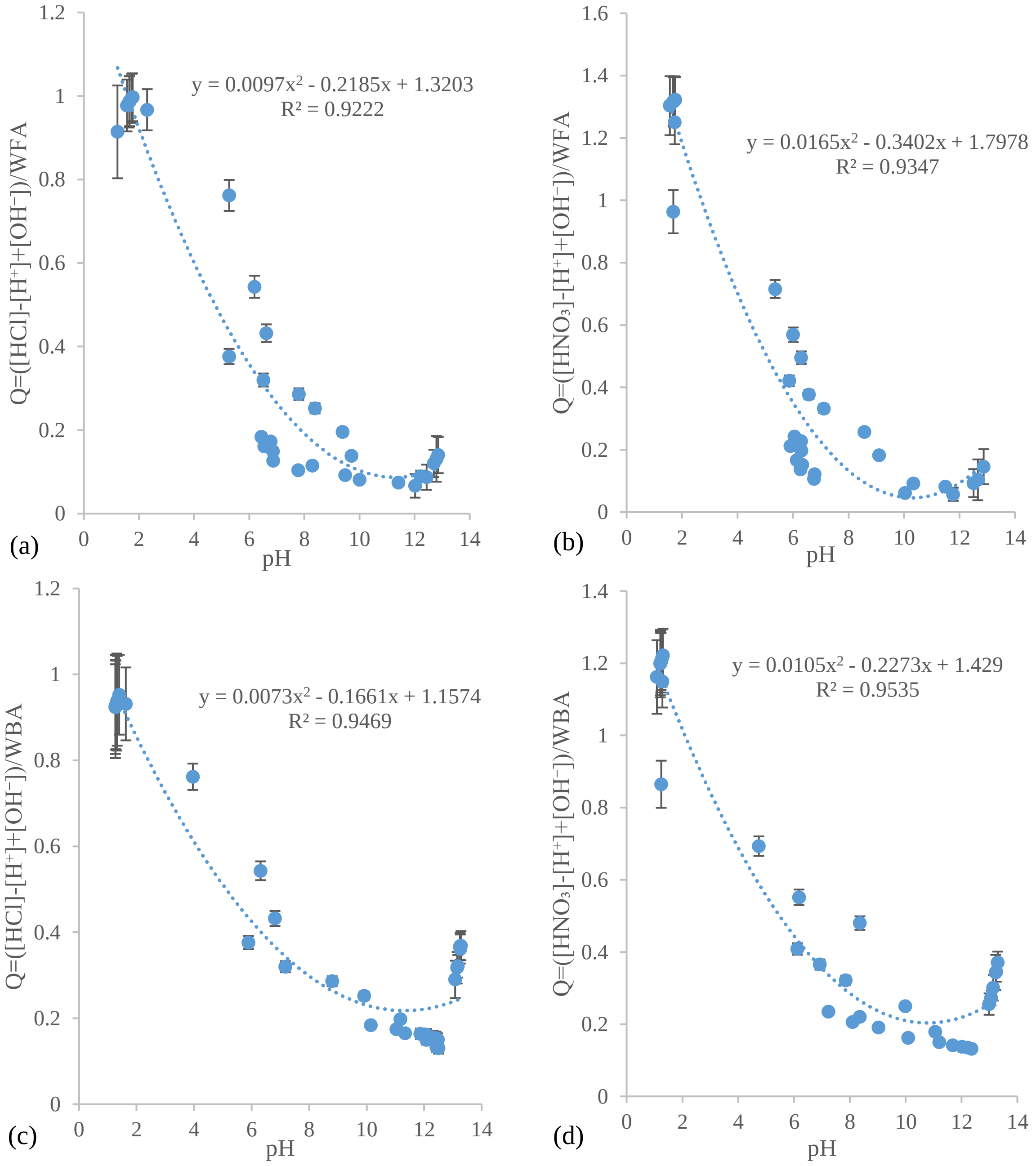


Figure 4.3. Calculation of the pH_{zpc} of the WFA using as titrants (a) 11.81 mol HCl/L or (b) 15.21 mol HNO_3/L. Calculation of the pH_{zpc} of the WBA using as titrants (c) 11.81 mol HCl/L or (d) 15.21 mol HNO_3/L (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

4.3.2. Second strategy: Addition of the ashes to the acidified digestates

The conditions of mild acidification to enhance the adsorption capacity of the wood ashes were attained by applying commercial doses of the acids to the anaerobic digestates before the addition of the wood ashes. The preparation of the blends PVWD+WBA and FWD+WFA were evaluated. The formulation of these blends was based on the content of NH_4^+-N and fiber in the anaerobic digestates and the pH and particle size of the wood ashes. In these kinetic studies, the buffer capacity of PVWD and FWD can be observed in Figure 4.4 and Figure 4.5, respectively, during the first 200 hours of incubation before the addition of the ashes. Different responses were found for all the acids in spite of being applied at the same rates (*i.e.* 0.00, 0.08, 0.16, 0.24, 0.32 and 0.40 mmol H^+/g digestate). Large volumes of concentrated $CH_3CH(OH)COOH$ were required to meet the target acidification doses, expressed as mEq/g (Table A.7). This explains the low levels of pH achieved with this acidifying agent in spite of being considered a weak organic acid. Unlike the high acidification with oxidising agents such as HNO_3 and H_2SO_4, the severe acidification with the $CH_3CH(OH)COOH$ was not a problem because this is an acid already present in anaerobic digestates (Mao *et al.*, 2015) and it does not damage the OM of the soil amendment (Regueiro, Coutinho, Gioelli, *et al.*, 2016). The dose-response curves of the H_2SO_4 were used as reference to establish the buffer capacity of the digestates, for being the strongest acid and the most widely employed in the agroindustry (Regueiro, Coutinho, Gioelli, *et al.*, 2016). In agreement with the results of the first strategy (Figure 4.1b), the PVWD (< 0.16 mEq H_2SO_4/g; Figure 4.4a) had lower buffer capacity than the FWD (0.49 mEq H_2SO_4/g; Figure 4.5a) due to the lower content of NH_4^+-N (Table 3.3). It should be noted the self-acidification of the experimental blanks of PVWD and FWD before the addition of the WBA (Figure 4.4) and WFA (Figure 4.5) at the 240 hours and the 330 hours of incubation, respectively. This was due to the fermentation carried out by the endogenous microbes of the anaerobic digestate under the incubation conditions (Clemens *et al.*, 2002). In both blends, the heat released at the time of mixing the samples of wood ash and anaerobic digestate resulted in increasing the temperature of the mixtures by approximately 1 ºC. A clear pattern of flocculation, settling and dewaterability (Figure A.8) was not identified but excessive formation of foam was only found when the ashes were added to the digestates acidified with $CH_3CH(OH)COOH$ (Figure A.9).

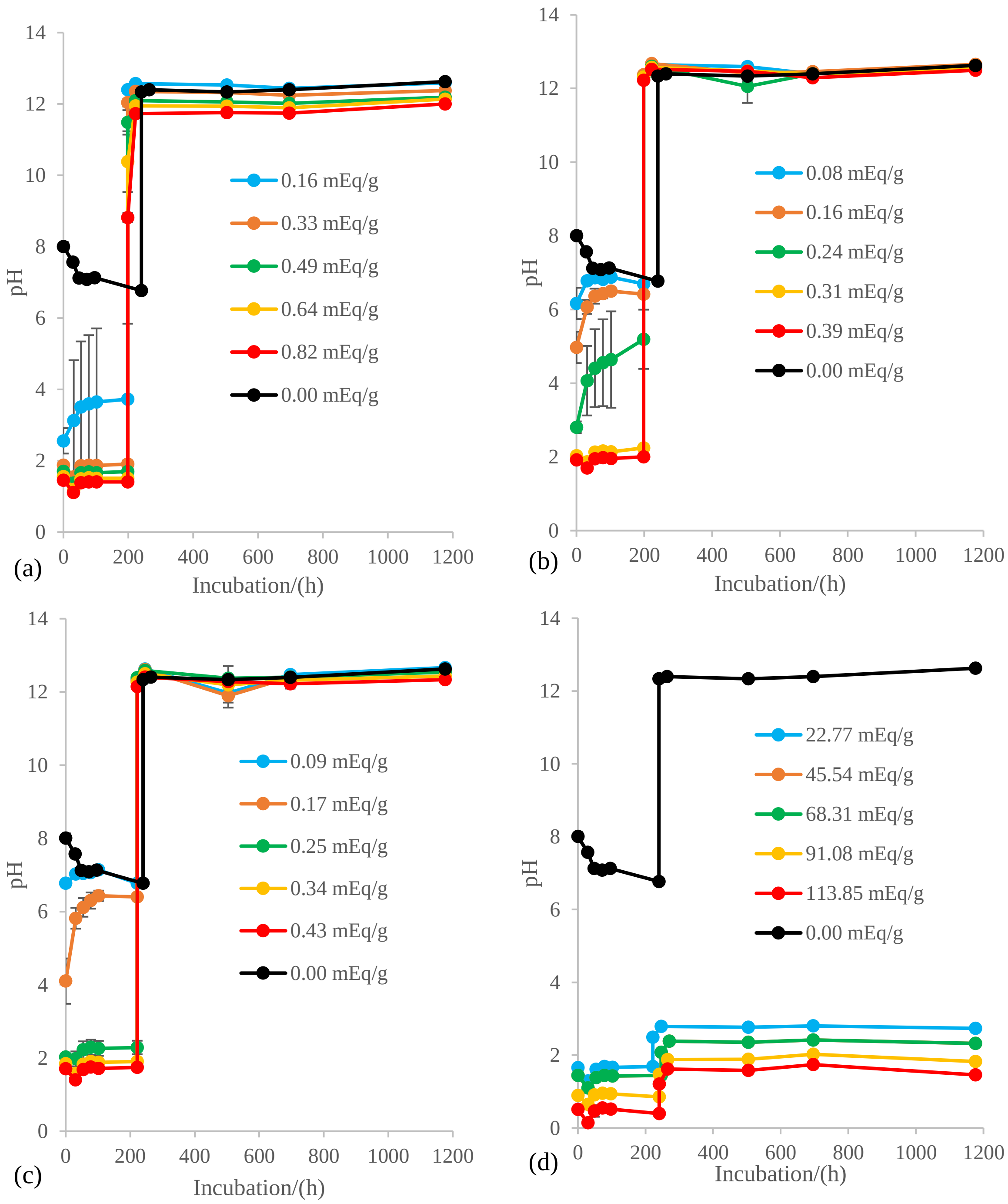


Figure 4.4. Acidification of 2.18 ± 0.09 g of PVWD (n = 3) with 20.56 mL of titrants (Table A.7) which were prepared with (a) H_2SO_4, (b) HCl, (c) HNO_3 and (d) $CH_3CH(OH)COOH$ in 6 different doses and subsequent addition of 0.55 ± 0.04 g of WBA (n = 3) after 200 hours of incubation (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

The pH of the blend PVWD+WBA was 12.25 ± 0.54 (Figure 4.4), despite the acidification with H_2SO_4, HCl and HNO_3. It was not possible to appreciate any buffer effect due to the volatilisation of ammonia but the concentration of WS NH_4^+-N was reduced by 500 mg/kg PVWD+WBA (Figure 5.3a). According to the two-way ANOVA ($p < 0.001$), the 6 doses tested for each acid provided the blend PVWD+WBA with a different pH. This could be seen clearly in the case of the H_2SO_4 (Figure 4.4a) and $CH_3CH(OH)COOH$ (Figure 4.4d), where the pH level was in agreement with the severity of the acidification. Although these differences of pH cannot be fully appreciated in the treatments with HCl (Figure 4.4b) and HNO_3 (Figure 4.4c), the same trends were found at the end of the incubations.

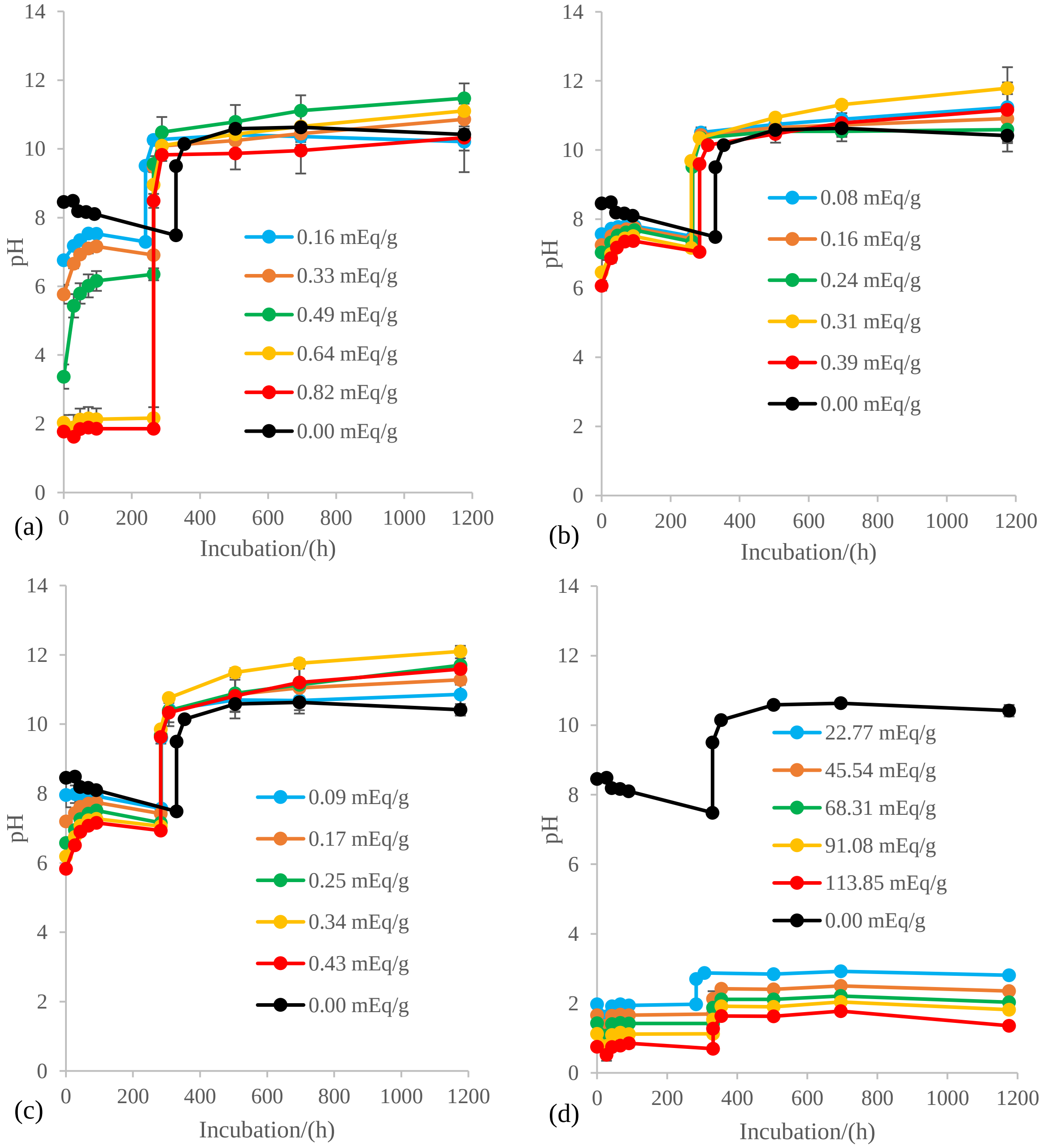


Figure 4.5. Acidification of 2.15 ± 0.08 g of FWD (n = 3) with 20.56 mL of titrants (Table A.7) which were prepared with (a) H_2SO_4, (b) HCl, (c) HNO_3 and (d) $CH_3CH(OH)COOH$ in 6 different doses and subsequent addition of 0.55 ± 0.04 g of WFA (n = 3) after 200 hours of incubation (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

The pH of the blend FWD+WFA was 10.49 ± 0.76 (Figure 4.5), despite the acidification with H_2SO_4, HCl and HNO_3. The pH profile corresponding to the preparation of FWD+WFA without acidification (Figure 4.5) was the result of the mass transfer resistance that limited the $NH_{3(aq)}$ volatilisation (Palakodeti *et al.*, 2021). At a pH above 10 (Fangueiro *et al.*, 2015), most of the NH_4^+-N is in the form of NH_3, hence the volatilisation of ammonia decreased the pH of the blend FWD+WFA because the H^+ remained in the WS fraction. The reason for the higher pH at the 500 and 700 hours of incubation of the blend was that the volatilisation of ammonia was limited, due to the liquid-gas mass transfer resistance (Equation 3.3 and Figure 3.4a). As more NH_3 was lost by the end of the incubation, the dissociation of NH_4^+ was greater (*i.e.* Le Chatelier's principle) and the pH decreased. On the contrary, the sorption of the WS NH_4^+ onto the WFA aided the rising of the pH over a value of 11, because the H^+ ions were removed from the WS fraction of the blend FWD+WFA. This was the only possible explanation for obtaining a higher pH when acidifying the FWD before the addition of the WFA, apart from the scenario evaluating the use of $CH_3CH(OH)COOH$ (Figure 4.5d). The greatest increase in pH was achieved when HCl or HNO_3 were used at a rate of 0.31 (Figure 4.5b) and 0.34 mEq/g FWD (Figure 4.5c), respectively. In the case of the H_2SO_4, the extent of this phenomenon was lesser and the greatest sorption of NH_4^+ onto the WFA was achieved at a higher dose (0.49 mEq/g FWD; Figure 4.5a) than in the case of using HCl and HNO_3. This can be explained by complexation and attachment of the ion SO_4^{2-} to some of the active sites of the ash (Figure A.13d), in agreement with the Equation 2.44. Leechart *et al.* (2009) described the formation of ternary sulfate complexes of surface-sulfate-cations (Ca^{2+}, Mg^{2+}) when the WBA is treated with 0.1 N H_2SO_4.

The acid dose had a role in the sorption of the WS NH_4^+ onto the WFA but this phenomenon mainly took place at a pH_{zpc}, which was above 10 (Figure 4.5). The optimum pH of the precipitation of struvite is between 7.5 and 9 (Campos *et al.*, 2019), although the Mg^{2+} hexaaqua is stable up to pH 11.4 (Barrett, 2007, pp. 124–159). The dose of acid needs to be as much as is required to reach the pH_{zpc} without further decrease (Leechart *et al.*, 2009). However, since the pH of minimum solubility of CaO and MgO are 11.0 and 12.4, the surface of CaO and MgO could support the adsorption when the pH of the system was greater than pH_{zpc} (Leechart *et al.*, 2009). The acidification of the FWD prevented the volatilisation of ammonia and the primary mechanism of removal of the NH_4^+ from the WS fraction, after the addition of the WFA, was sorption. This procedure for the preparation of the blended fertiliser minimises the loss of N. The more sorptive sites available in the WFA agree with the greater sorption of NH_4^+-N when preparing the blend FWD+WFA with HCl or HNO_3 (Figure 4.5b,c). This technology is in line with the investigation of Simha *et al.* (2018, 2020, 2021), who tested several alkaline materials, including wood ash, as substrates for preventing the volatilisation of NH_3 during the dehydration of urine.

4.3.3. Third strategy: Wash the ashes with water to reduce their basifying power

In order to maximise the sorptive sites available and reduce the consumption of acid reagents, the washing of the wood ashes with ultrapure milli-Q® water was evaluated. Figure 4.6 shows that the greatest decrease of the pH of both ashes took place in the first WS extraction and the subsequent washes were less effective in reducing the pH. This could be related to the depletion of the most WS elements and the impurities present in the wood ashes. The greater pH of the WBA, compared to the one of the WFA, could be justified by the greater content of K of the coarser fraction of the ashes. Although the content of sodium was higher in the WFA than in the WBA, this element was in lesser amount than other alkali and alkaline earth metals in the wood ashes (Table A.3 and Table A.5). It should be noted that the pH of WFA reached a plateau with less extractions than the WBA (Figure 4.6). This could be related to the greater particle size of the WBA that limited the mass transfer (Laohaprapanon *et al.*, 2010; Leechart *et al.*, 2009). According to the two-way ANOVA test ($p < 0.001$), the kinetics of reduction of the pH in WFA and WBA differ significantly. More number of 24-h extractions (*i.e.* more volume of water) were required to remove the alkali elements from the WBA, compared to the WS extraction of these elements from the WFA. Since the pH increased after the seventh extraction, the savings in acid were not expected to be great, in order to have a pH 5.5 in the blend of anaerobic digestate and wood ash. The overall pH decrease after 432 hours of washing were 4.69 ± 0.29 % and 5.30 ± 0.66 % for the WFA and the WBA, respectively (Figure 4.6).

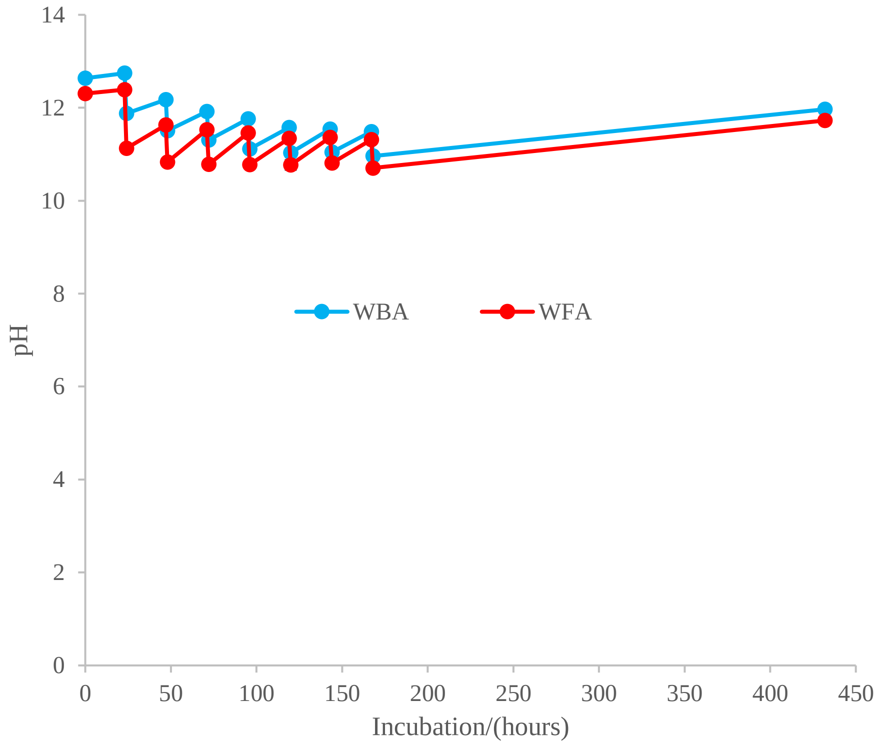


Figure 4.6. Seven washes of approximately 0.5 g of WFA and the WBA with 20 mL of milli-Q® water (n = 3). The pH was measured straight after adding the extractant and after 24 hours of incubation at 21 ºC and 100 rpm. The last measurement which was made after 264 hours of incubation (Moure Abelenda, Semple, Lag-Brotons, et al., 2022).

As washing is a common step in the synthesis of adsorbents (Zhou *et al.*, 2020), it would be interesting to test the impact of this pretreatment of the ashes on the sorption of the WS elements of the commercially acidified digestates. Unless the washing is performed, the impurities of the wood ashes are likely to compete with the WS nutrients for the active sites (Laohaprapanon *et al.*, 2010). The extraction of impurities could be improved by boiling the ashes and water at 95 ºC for 1 hour (Laohaprapanon *et al.*, 2010). The ionic product of water increase as the temperature increase, while in the subcritical region (Loppinet-Serani & Aymonier, 2014), hence the dissolution of impurities in the eluate. The washing could be used to remove the pollutants such as heavy metals; for example, Liodakis *et al.* (2005) reported the removal of 95 % of the chromium of the wood ash by using a solution of pH 6. On the other hand, Leechart *et al.* (2009) explained the importance of the basic solution that is generated due to the dissolution of the alkali element of the wood ashes. According to them (Leechart *et al.*, 2009), the high pH enabled the removal of tar and improved and surface area more than soaking the WBA in a solution of 0.1 N H_2SO_4. The dissolution of the metal oxides embedded in the frame, which was made primarily of C and oxygen, increased the porosity because these elements had a weak attachment to the carbonaceous structure. It should be noted that the C was the fourth most important element in the WFA and the WBA employed in this thesis (Table A.3), after Ca, Mg and K. After the washing and before adding the clean ash to the commercially acidified digestate, the procedure described by Leechart *et al.* (2009) of drying the wood ashes at 105 ºC and sieving (< 0.75 µm) should be implemented. Although this ash pre-treatment is simple, implementation at pilot plant level is required to appraise its economic viability (Laohaprapanon *et al.*, 2010).

4.4.Conclusions

The deep acidification was more convenient for the stabilisation of the PVWD with the WBA, since these waste streams required less amount of acid to reach the target pH of 5.5 in the blend. The determination of the pH_{zpc} allowed to reduce the consumption of acid reagent for the preparation of PVWD+WBA and FWD+WFA at pHs 12.25 ± 0.54 and 10.49 ± 0.76, while maximising sorption processes that increased the stability and the properties of the soil organic amendment as controlled-release fertiliser. The acidification of the anaerobic digestates with commercial doses before the addition of the wood ashes was found particularly promising for the preparation of the blend of FWD with WFA. The HCl and HNO_3 offered better performance than H_2SO_4 and $CH_3CH(OH)COOH$. As one of the purposes of stabilisation is to improve the holistic management of N, the HCl was deemed as more suitable, since the excess of the ion NO_3^- would lead to leaching and potentially N_2O emissions. The extent of the sorption of the WS NH_4^+-N onto the WFA needs to be characterised by determining the increase in N content in the WI fraction of the blend FWD+WFA. The washing of the ashes was not sufficient to reduce significantly the demand of reagents for deep acidification (pH ~ 5), as part of the wood ash-based treatment of the organic manures. However, the washing might be enough to reach the pH_{zpc} and enhance the sorption capacity of the ashes and their suitability as chemical stabiliser. Thereby, the impact of adding the depleted ashes to the raw digestates or commercially acidified digestates should be evaluated. Also, acid wash may improve the extraction of alkali metals and the sorption capacity of the wood ashes.

5. Preparation of the blend PVWD+WBA under acid conditions, employing sulphuric, hydrochloric, nitric and lactic acids

5.1.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* 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 (Khalid *et al.*, 2020). Moreover, the resulting anaerobic digestate potentially has a significant role to play in recycling key plant nutrients (*e.g.* N and P) back to land (Lag-Brotons *et al.*, 2020; Marshall *et al.*, 2020). The use of this organic amendment with low pathogen content offers opportunities to restore the soil as a natural C sink as well as promoting soil health and fertility for greater crop yield (Bhogal *et al.*, 2018). However, the high moisture content of digestate poses problems of high capital investment and operational costs (*i.e.* storage and haulage) due to the large volume of this material (Fuchs & Drosg, 2013). 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 SS), and the performances of several technologies have been evaluated (Fuchs & Drosg, 2013). 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 (Dinuccio *et al.*, 2012; Popovic *et al.*, 2017) 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 (Fuchs & Drosg, 2013). In the case of the agroindustrial digestate, the fibres can be employed as bedding material for animals while the liquor requires expensive low emission spreading techniques, such as soil injection (Lanigan *et al.*, 2018).

Additives, such as $Al_2(SO_4)_3$, $FeCl_3$, CH_3COOH and H_2SO_4, can be used to minimise the release of atmospheric contaminants during storage (Kavanagh *et al.*, 2019) and application (Brennan *et al.*, 2015) of animal manure and slurry to soil. This technology aims to ease the handling of agroindustrial residues and might improve their performance in terms of crop growth, but farmers continue to rely on NPK chemical fertilisers (Tur-Cardona *et al.*, 2018).

For this reason biomass ashes have been used to supplement the nutrients of digestate (Lag-Brotons *et al.*, 2020; Marshall *et al.*, 2020). 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 (Figure 2.8). Zheng et al (2016) found that the effectiveness of the filtration was higher when a cationic surfactant was included in the blend of agroindustrial digestate and CFA, as this resulted in a release of the water which was bounded to the fibre of digestate. Instead of using chemicals of questionable suitability for land application, commercial acids can be employed as cationic surfactants to enhance the dewatering of the anaerobic digestate (Limoli *et al.*, 2016) and prevent the NH_3 volatilisation.

The granulation processes proposed so far (Table 2.7) for SS (Pesonen *et al.*, 2016) and digestate (Mudryk *et al.*, 2018) together with biomass ashes have been investigated with the purpose of obtaining an user-friendly product with superior aesthetic properties. 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. This chapter is in line with the development of a manufacturing and synergistic process to achieve the three levels of stabilisation (Figure 2.4): (a) chemical stabilisation based on the adsorption of 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 nutrient losses due to excessive mineralisation (*e.g.* N_2O emissions and NO_3^- leaching).

Particularly, this chapter contains two studies about the chemical stabilisation of the PVWD by means of blending it with the WBA 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.* P) 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 (Szymula *et al.*, 2021). 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 P, C and N were monitored before and after blending the two waste streams, under different acidification conditions.

5.2.Materials and methods

5.2.1.1.Materials

The WBA was selected because it represented the main share of the ashes generated in the grate combustion chamber of the sawmill cogeneration plant (Table 3.1). 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 (Pöykiö *et al.*, 2011). 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 (N. D. Park *et al.*, 2012). The PVWD was selected based on its moderate amount of NH_4^+-N (Table 3.3) resulting from the limited degradation undergone by fibrous vegetable material during the AD (Chojnacka *et al.*, 2020). Table 5.1 contains the initial characterisation of the blend PVWD+WBA calculated using the experimental composition (Table 3.3) of the samples in the blend (2.59 ± 0.55 g PVWD and 0.87 ± 0.40 g WBA; n=3). A detailed description of the procedure for the estimation of the propagation of uncertainty in the calculation of the parameters of a bi-component blend is shown in the section A.7.

Table 5.1. Initial characterisation was expressed in a fresh basis of the blend PVWD+WBA employed in Chapter 5 (Moure Abelenda *et al.*, 2021b), which was calculated using the experimental composition (Table 3.3) of the samples in the blend (2.59 ± 0.55 g PVWD and 0.87 ± 0.40 g WBA; n=3).

Sample		**PVWD+WBA**	
Parameter	**Units**	**Average**	**St. deviation**
pH	-	8.97	0.06
EC	dS/m	16.28	5.49
DM	%	30.45	9.40
C	mg/kg	29,482.21	3,687.73
WS C	mg/kg	1,987.27	260.86
N	mg/kg	3,058.58	369.11
WS N	mg/kg	1,557.71	195.37
WS NH_4^+-N	mg/kg	518.05	65.66
WS NO_3^--N	mg/kg	14.52	1.90
P	mg/kg	3,624.80	1,094.33
WS PO_4^{3-}-P	mg/kg	34.80	4.44

The WS fraction of P, N and C were measured using S/E 1/10. A detailed explanation of the calculations to express the concentration of the WS species in fresh basis is presented in the section A.4, section A.9 and section A.10. As in Chapter 3, the characterisation of the samples during their incubation at 100 rpm and 20 ºC, and their blending at the 96 hours, were compared to the initial characterisation (Table 5.1). This made possible to elucidate any undergoing phenomena which might have affected the masses of the WS and WI fractions of the blend or the availability the P, N and C.

The samples were blended in order to achieve an approximate C/N/P of 10:1:1 (Table 5.1). The PVWD was the main source of N (93.18 ± 29.21 %) and C (81.25 ± 25.61 %) in the blend (Table 3.3). On the other hand, the WBA was the main source of P (76.86 ± 32.14 %), alkali and alkaline-earth metals (Table A.3). The EC of WBA was higher because of the greater content of Na^+ and K^+, since both Ca and Mg had lower effect on the EC due to their low solubility (Table A.5).

5.2.1.2.Methodology

In order to develop the technology of stabilisation of the PVWD with the WBA a series of increasingly complexity studies were to carry out, in favour of minimising the cost of the processing and expand the knowledge on the underlying chemistry. This would allow (a) to find the cheapest technologies to reduce the 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; (b) to reach a more efficient solid-liquid separation using cheap technologies (*e.g.* sedimentation), as part of the first manufacturing operation. Chapter 3 has already evaluated the scenario of dispensing with the acid medium.

In the present two studies, several acidification conditions were tested 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 sorption capacity of WBA but would also lead to a more energy and resource intensive process (Table 2.6).

5.2.1.2.1. Factorial design of each study of this chapter

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 5.2). 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 of this chapter, the acid doses for PVWD (Table 5.2) were based on information taken from the literature relating to the treatment of manure and slurry (Table A.6) since digestates have been traditionally treated in the same way (Sommer & Husted, 1995). 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 of this chapter, the dose of each acid (Table 5.2) was based on preliminary titrations of the PVWD and the WBA (Figure 4.1b,d), to ensure that the target pH value around 5.5 (Miranda *et al.*, 2021; Pantelopoulos *et al.*, 2016; Regueiro, Coutinho, & Fangueiro, 2016) 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.

Table 5.2. Blends were characterised during the incubation at 100 rpm shaking and 20 ºC in the two studies (Moure Abelenda *et al.*, 2021a).

Study	WBA	Extractant WBA	PVWD	Extractant PVWD
First/(g)	0.51 ± 0.05	[a]5	2.24 ± 0.09	[a]20.5
Solutions/ (mmol H^+/g WBA)	H_2SO_4	0	(mmol H^+/ g PVWD)	0.08
		0		0.24
	HCl	0		0.08
		0		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 (mmol H^+/g WBA)	H_2SO_4	6.29	(mmol H^+/ g PVWD)	0.12
	HCl	15.21		0.19
	HNO_3	11.97		0.14
	$CH_3CH(OH)COOH$	[b]0.16		[b]0.03
	-	0		0

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

[b] It should be noted the large volume of commercial (~ 90 %) $CH_3CH(OH)COOH$ required to reach these proton concentrations of the extractant solutions (Table A.7).

Two-factor ANOVA with replication was performed with Microsoft® Excel 2013 ($p < 0.05$) 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 P, N and C. Furthermore, this statistical analysis enabled the rigorous selection of the best acidifying agent and optimum concentration to be used. The data obtained in the two studies was considered to follow a normal distribution, in order to apply the ANOVA test.

5.2.1.2.2. 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 Figure A.8, Figure A.11 and Figure A.12. The volume of the extractant (*i.e.* acidifying agent) that was added to each sample before blending, followed an approximate S/E 1/10 (Table 5.2). Chapter 3 has proven that adding the extractant before the incubation did not significantly affect the composition of 2.5 g blend undergoing 10-h incubations at 100 rpm and 20 ºC in closed 50-mL Corning® tubes. The acid solutions prepared with ultrapure milli-Q water and reagent grade H_2SO_4, HCl, HNO_3 and $CH_3CH(OH)COOH$ 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 the pH and (d) extract nutrients for fractionation of the samples and the blend. The term fractionation refers to the analytical solid-liquid separation with higher performance that what would be expected for farm processing equipment. The fluidised samples and blends were incubated (*i.e.* extraction) at 100 rpm and 20 ºC in closed 50-mL Corning® tubes with stopper (Figure 5.1). It is important to highlight that in the first study of this chapter, 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 4,000 rpm and filtration of the supernatant using Whatman® No 44 filter paper (3-µm pore size). The gravity was the driving force of the filtration rather than vacuum to minimise the release of the gases (*e.g.* NH_3) solubilised in the WS extract, since the gaseous fraction of the samples after the incubation was not characterised in the experiments of this chapter. For the isolation of the WI material, both the pellet and the cake that remained in the filter paper were dried at 105 ºC for 24 hours (Figure 5.1).

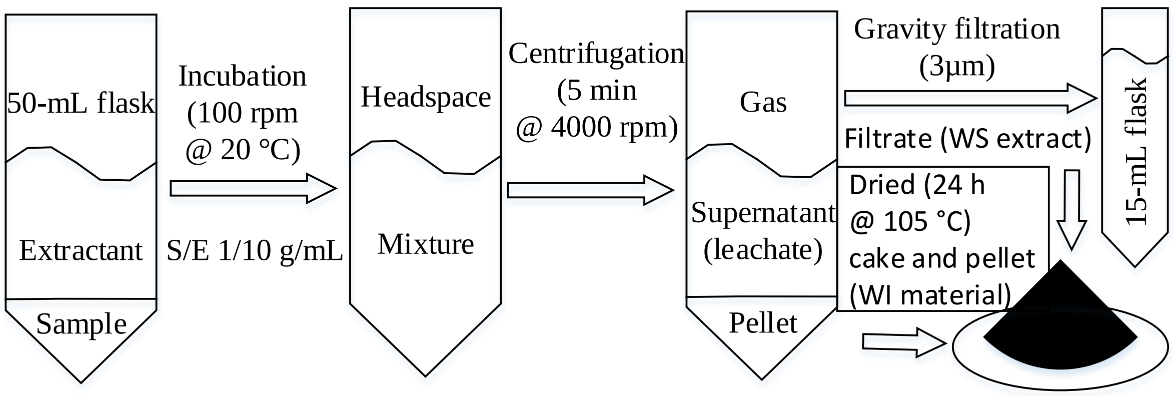


Figure 5.1. Stepwise methodology for the characterisation of the WS extract and the WI material of the samples and their blend after the incubation at 100 rpm and 20 ºC (Moure Abelenda *et al.*, 2021b).

In the first study of this chapter, the initial volumes of the WS extracts of the blends were determined considering the moisture of each sample and the blend (Table 3.3 and Table 5.1), in addition to the volume of extractant used to prepare the blends (Table 5.2). For this calculation, it was considered a density of 1 g/mL for both the moisture of the samples and the extractant. The initial masses of WI materials were assumed to be the DM of the blend (Table 5.1). For the second study of this chapter, the final WI material recovered after the incubation was weighed. The experimental WS extract was calculated by substracting the empirical WI material from the initial mass of the sample and adding the amount of extractant used as fluidising agent. The comparisons between the initial and the final masses of WS extracts and WI materials of the second study are shown in Figure A.13.

5.2.1.2.3. Characterisation of the fractions of the samples and the blend

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

The parameters measured in the WS extract were mass, pH, NH_4^+-N, NO_3^--N, PO_4^{3-}-P, N and C. Measurement of WS extract pH was performed with a Mettler Toledo® Seven Compact^{TM} S220 pH/Ion meter. Determination of concentrations of WS NH_4^+ & NH_3 and WS NO_3^- & 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 Autoanalyzer^{TM} (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 N and WS C were measured with the TOC-L Shimadzu® *via* combustion of the sample and detection of CO_2 and NO gases. Thus, the WS N_{org} could be calculated as the difference between the WS N and the WS NH_4^+-N + WS NO_3^--N (Urgun-Demirtas *et al.*, 2008). Although digestates could contain significant amounts of bicarbonate buffer (Lin *et al.*, 2013), most of the C of the PVWD was present as C_{org}. On the other hand, a greater proportion of CO_3^{2-}-C was expected in the WBA with regard to the BC.

The characterisation of WI material was made in terms of mass WI P, WI C and WI N. The calculation procedure of the WS and the WI species is offered in the section A.9 and section A.10. The samples of WI material were milled before doing any analysis. Measurement of WI N and WI C was done in elemental analyser (Elemental vario EL cube) using acetanilide as standard. Sulphuric-peroxide digestion of the WI material at 400 ºC for 2 hours was done following the method described by Grimshaw (Grimshaw, 1987) to obtain the phosphate-rich extract which was measured in the Autoanalyzer™ to determine the WI P.

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

Whether the experimental results were referred to the WS extract (S/E 1/10) without units for pH, or were expressed in terms of fresh base (mg of WS PO_4^{3-}-P, WS NH_4^+-N, WS NO_3^--N, WS N, WS C, WI P, WI N and WI C, per kg fresh samples), 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 P, C and N WS and WI species were calculated to represent the mass balances of these elements in the Appendix (Figure A.9, Figure A.10, Figure A.15, Figure A.17 and Figure A.19). The calculation of concentrations and masses of the chemical species in the first study was based on the initial masses of the WS extracts and WI materials; for this reason, they are regarded as theoretical concentrations and mass balances. On the other hand, the results of the second study rely on the final WS extracts and WI materials recovered for each blend after the incubation; hence they are regarded as empirical concentrations and mass balances. 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 final masses of the WS extracts and WI materials obtained after the analytical solid-liquid separation. 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 P, C and N recovered for each blend over the incubation period against the initial amount of each element (Table 3.3 and Table 5.1) Particularly, the average recovery effectiveness, which was expressed as mass percentage for each acidification condition and sample type, was calculated as the final amount of an element divided by the initial one.

5.3.Results and discussion

5.3.1. First study

5.3.1.1.pH, WS PO_4^{3-}-P and C speciation

The decrease of the pH in the PVWD due to acidification (Figure 5.2a) promoted processes such as the solubilisation of P before the addition of the WBA (Figure 5.2b) and the depletion of the C from the WS phase (Figure 5.2d). The different doses of acidification did not affected significantly ($p < 0.05$) to the WI C of the PVWD (Figure 5.2e), therefore it was not possible to claim that the acidification promoted the sorption of some of the WS C onto the solid fraction (*i.e.* fibre). On the other hand, the different doses of acidification reduced significantly ($p < 0.05$) the amount of C retained in the WS phase. The CO_3^{2-}-C was lost as CO_2 and the N_{org} was not solubilised due to the lack of alkaline conditions (Ohno *et al.*, 2019). It should be noted that the excessive solubilisation of P would lead to eutrophication of inland and coastal waters (Fangueiro *et al.*, 2015; Leip *et al.*, 2015).

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 (Figure 5.2a). This agrees with the results of the second strategy tested in the previous chapter (Figure 4.4). Moreover, these results are in line with the description provided by Wróbel *et al.* (2018), who informed 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, Wróbel *et al.* (2018) employed dewatered digestate in order to have a final blend with a moisture content of 18 %. The stabilisation that Wróbel *et al.* (2018) referred to in their study was regarded in this thesis as physical stabilisation (Figure 2.4), which is mainly the result of the hydration of oxides to hydroxides and, to a lesser extent, later the subsequent formation of CO_3^{2-}. 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 Ca content (Steenari & Lindqvist, 1997).

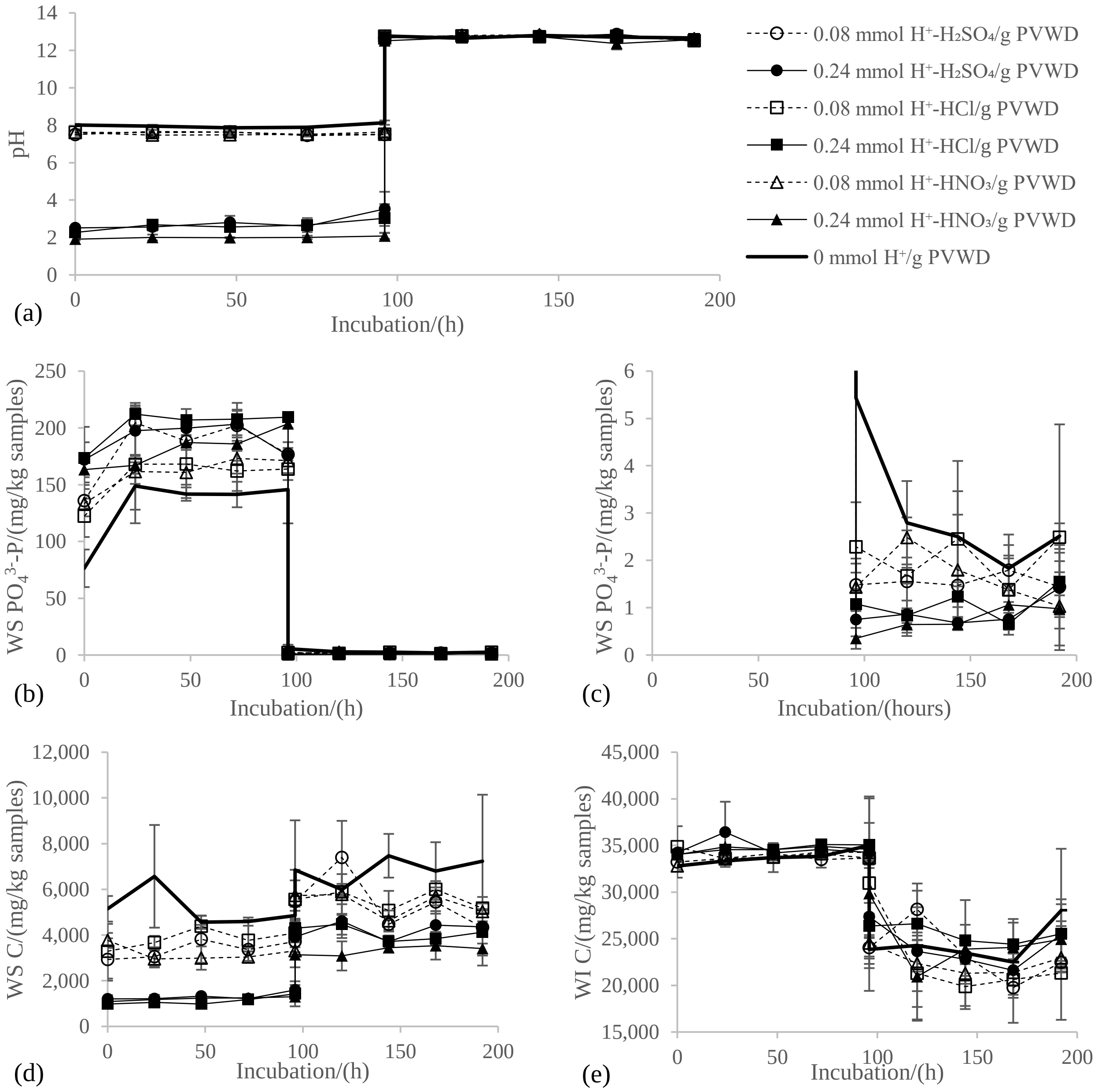


Figure 5.2. Characterisation in terms of (a) pH, (b) WS PO_4^{3-}-P, (c) zoom in WS PO_4^{3-}-P, (d) WS C and (e) WI C, 2.24 ± 0.09 g of PVWD acidified with 2 dose (0.08 and 0.24 mmol H^+/g PVWD) of 3 acids (H_2SO_4, HCl and HNO_3) and without acidification, followed by the addition of 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-h incubation (Moure Abelenda *et al.*, 2021b).

Ca also plays a key role in the chemical stabilisation as it precipitates the P effectively while the blend remains at pH above 8.5 (Cerozi & Fitzsimmons, 2016; Leechart *et al.*, 2009; W. Shi *et al.*, 2021). In the blend PVWD+WBA of the first study of this chapter, most of the P was in the WI fraction, remaining only 1.56 ± 1.22 mg WS PO_4^{3-}-P/kg blend. Figure 5.2c illustrates how acidification promoted the sorption of WS PO_4^{3-}-P onto the WBA. Similarly, the effect of acidification on the WS C could be seen even after the addition of the WBA. As per the alkaline solubilisation, increases in pH resulted in greater amounts of C in the WS fraction of the blend. Although there was significant difference ($p < 0.05$) in terms of WI C of the blend due to the doses of acid, no clear trend was identified that could be explained by sorption processes. It should be noted that the decrease in the amount of C in the WI fraction was due to the lower content of C of the WBA, which was the main contributor to the DM of the blend (Table 5.1).

As can be seen in the theoretical C balances (Figure A.9) the average recovery effectiveness of C for all the acidification conditions was 105.47 ± 16.01 %. The reason was that the WI C was the main form of C in the samples and the blend, thus the losses WS C in the form of CO_2 were regarded as negligible. This could be related to the weak acidification or to the fact that the C was predominantly in forms different from CO_3^{2-}-C (Strosser, 2011; Tambone *et al.*, 2019), such as C_{org} and BC in PVWD and WBA, respectively. Both these forms of C are important to maintain a healthy soil and maximise crop productivity (Amoah-Antwi *et al.*, 2020; Liang *et al.*, 2010).

5.3.1.2. N speciation

The content of WS NH_4^+-N progressively increased ($p < 0.05$) during the first 96 hours of incubation (a), especially with the acidification. The reason could be the abiotic mineralisation (Equation 3.1) *via* hydrolysis of N_{org} under the acid conditions or ammonification due to microbial activity (Cossu *et al.*, 2018; Romillac, 2019; Strock, 2008). Abiotic mineralisation processes such as the photolysis (Y. Zhang *et al.*, 2021) were not considered significant under the conditions of the incubation. It should be noted that these levels of WS NH_4^+-N in the PVWD were slightly overestimated because the samples would require further dilution to fit in the calibration range of the Autoanalyzer™. This explains why that the concentrations of WS NH_4^+-N in Figure 5.3a were like the WS N in Figure 5.3c, since the WS N should include as well other forms of N, such as the WS N_{org}.

High levels of WS NO_3^--N (246.63 ± 28.75 mg/kg PVWD) were only found when using HNO_3 for acidification (Figure 5.3b). A lower concentration of WS NO_3^--N (4.75 ± 2.31 mg/kg PVWD) was found for all the other conditions. The measurement of the concentration of WS NO_3^--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 Autoanalyzer^{TM} (Broughton, 1984). It should be noted that the best conditions for nitrification include a neutral pH (Wong-Chong & Loehr, 1975), therefore it was unlikely that the progressive increase in the concentration of WS NO_3^--N for the H_2SO_4 and HCl acidifications was due to this biological process. Only the HNO_3 acidification affected significantly WS N of PVWD (Figure 5.3c) but the impact on the WI N of the PVWD was less significant (Figure 5.3d).

The addition of the WBA at the 96 hours of incubation significantly decreased the concentration of all forms of N in the blend. Only the dose 0.24 mmol H^+-HNO_3/g PVWD did not show significant decrease in the level of WS NO_3^--N, because the concentration was out of the calibration range of the Autoanalyzer^{TM}. This also explains why a greater difference of the concentration of WS N was found for the doses 0.08 and 0.24 mmol H^+-HNO_3/g PVWD in Figure 5.3c. The values of WS N provided by the TOC-L Shimadzu® were used to establish the N mass balances (Figure A.10). The average recovery effectiveness found was 68.62 ± 36.67 % because of the decrease of the N 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 N due to N_2O release need to be considered as well. The N_2O is product of the denitrification (Equation 2.10; (Velthof & Oenema, 1993)), although this compound coul be generated due to the abiotic reduction of WS NO_3^- & NO_2^- (Buchwald *et al.*, 2016), given the reducing effect of the alkaline metals contained in the WBA (Leechart *et al.*, 2009). It could be considered as well that the denitrification yielded N_2 as well, since the reduction potentials for the NO_3^-/NO_2^-, NO_2^-/NO, NO/N_2O and N_2O/N_2 are 0.94, 1.00, 1.59 and 1.77 V (Harvey, 2021). 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 (Flowers *et al.*, 2019).

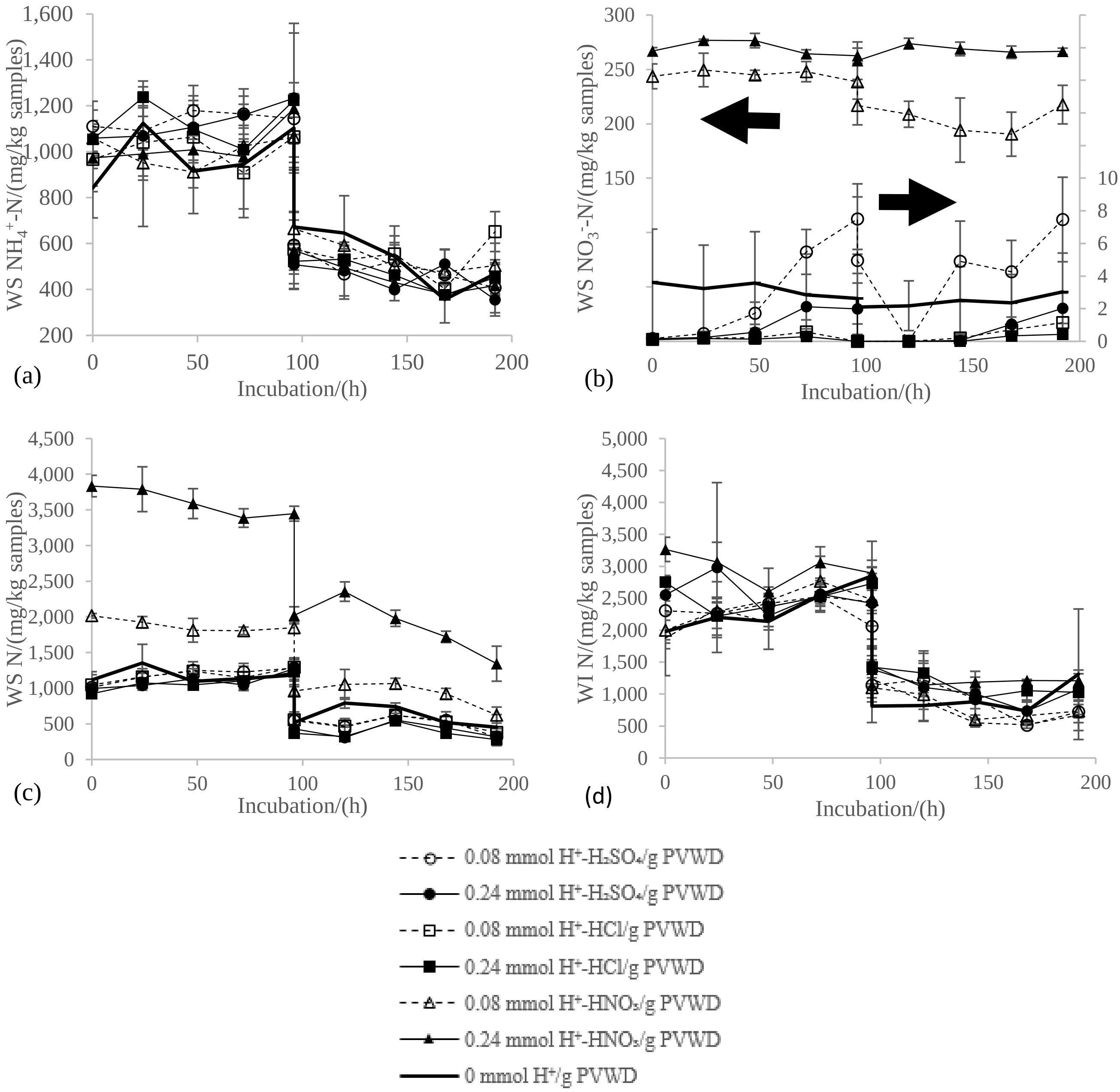


Figure 5.3. Characterisation in terms of (a) WS NH_4^+-N, (b) WS NO_3^--N, (c) WS N and (d) WI N, 2.24 ± 0.09 g of PVWD acidified with 2 dose (0.08 and 0.24 mmol H^+/g PVWD) of 3 acids (H_2SO_4, HCl and HNO_3) and without acidification, followed by the addition of 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-h incubation (Moure Abelenda *et al.*, 2021b).

In terms of N management, biomass ash should act as sorbent of NH_4^+-N (Szymula *et al.*, 2021) 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 N. 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.* (2016). 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 Ca which prevent the crystallisation of the zeolite structure during the cooling stage of the hydrothermal synthesis (Elliot & Zhang, 2005). Although the levels of toxic elements (*e.g.* heavy metals) in the coal ash might limit the application as fertiliser.

5.3.2. Second study

5.3.2.1. pH, P and C speciation

The acidification of the WBA before its addition to the PVWD prevented the increase in the pH above a value of 8 (Figure 5.4a). 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 A.3). This resulted in a decrease of WS PO_4^{3-}-P (Figure A.14), which had been solubilised due to the severe acidification of the WBA (Figure 5.4b). After the blending at the 96 hours of incubation, 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 PO_4^{3-}-P in the blends at the 144 hours of incubation was 74.53 ± 52.43 mg/kg blend (Figure 5.4a). This concentration was higher than what was found in the first study of this chapter (1.56 ± 1.22 mg WS PO_4^{3-}-P/kg blend; Figure 5.2c), due to the lower pH of the blends at the end of incubation. This level of P availability would provide the crops with enough PO_4^{3-}-P while preventing the excessive leaching. In fact, most P in the blend was in the form of WI P (Figure 5.4c), since the WBA was the main source of P and the main contributor to the WI fraction (Table 5.1). The mass balances (Figure A.15), show that only 38.76 ± 11.67 % and 22.20 ± 10.20 % of the P initially present in the WBA and the PVWD, respectively, were measured in all conditions (*i.e.* with and without acidification). The low average recovery effectiveness could be related to other forms of WS P different from PO_4^{3-}-P (*e.g.* P_{org}) which were not determined. Furthermore, similarly to the mass balances of C and N, the losses of WI material and WS extract during the fractionation of the samples and the blend would affect the recovery effectiveness of P. Nevertheless, only the WBA acidified with H_2SO_4 and $CH_3CH(OH)COOH$ showed significant deviations from the ideal behaviour (Figure A.13). 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 $CH_3CH(OH)COOH$.

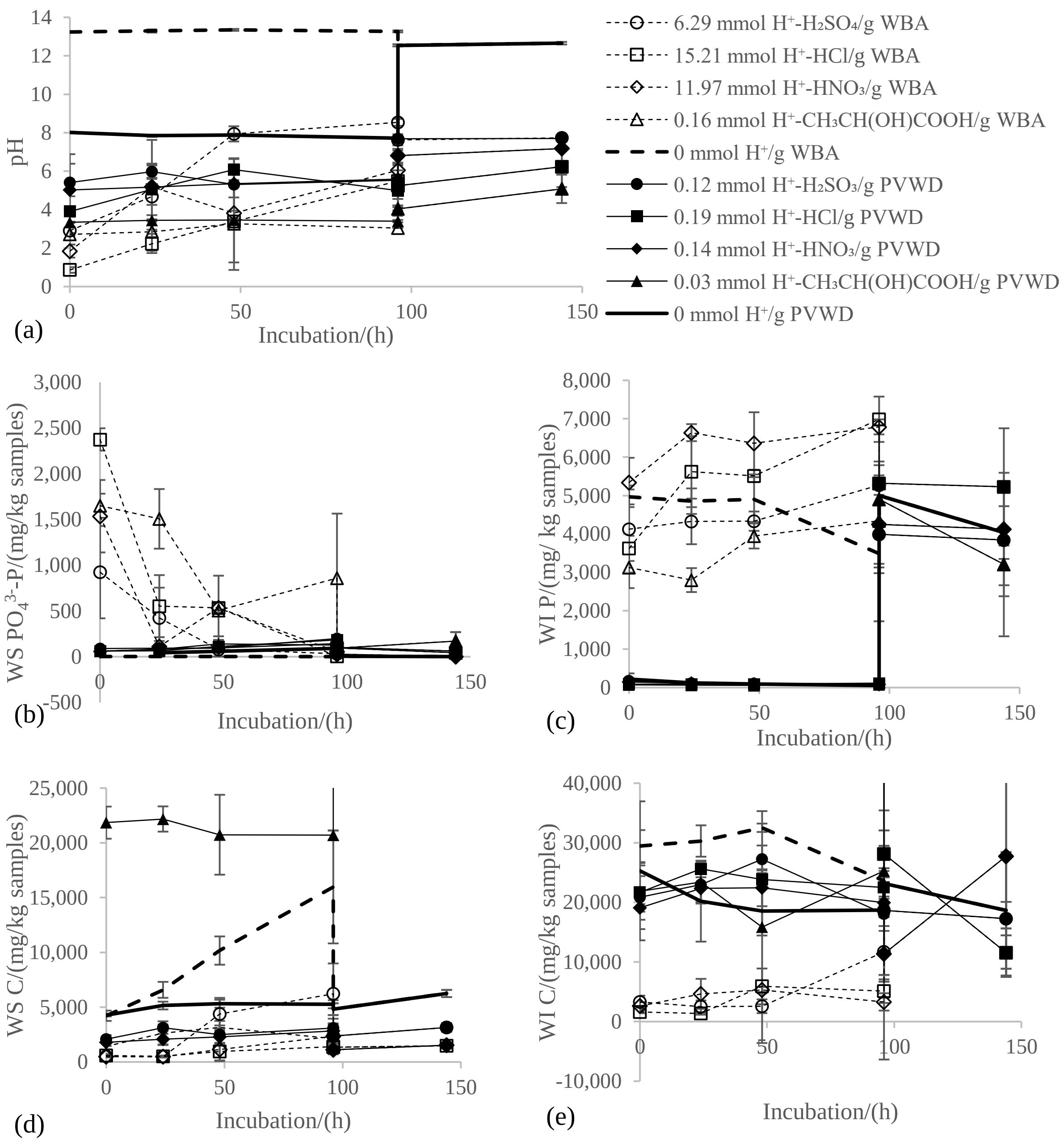


Figure 5.4. Characterisation in terms of (a) pH, (b) WS PO_4^{3-}-P, (c) WI P, (d) WS C and (e) WI C of 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD acidified with 4 acids (*i.e.* H_2SO_4, HCl, HNO_3 and $CH_3CHCOOH$) and without acidification before and after blending (at the 96 hours) during the 144-h incubation (Moure Abelenda *et al.*, 2021b).

The high concentration of the WS C due to the acidification of the ash with $CH_3CH(OH)COOH$ (259,917 ± 94,320 mg/kg WBA; Figure A.16a) 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 H_2SO_4 (Figure 5.4d). It should be noted that this type of analytical error is less likely to happen in the TOC-L Shimadzu® than in the Autoanalyzer^{TM} because of the type of determination (*i.e.* combustion rather than colorimetry) and because the washing of the probe between the samples is done for longer time. The base line and the analytical blanks of the TOC-L Shimadzu® were less affected by the high concentration of analyte, given by the severe acidification with $CH_3CH(OH)COOH$. Of all acidifications, the H_2SO_4 gave to the WBA and the PVWD the highest pH. Similarly to the samples that were not acidified (*i.e.* experimental blank), this could explain the greater content of WS C, since less C would not be lost as CO_2 due to the limited dissociation of the carbonic acid in water at low pH (Equation 2.39).

The results of WI C obtained in the second study (Figure 5.4d) agree with the data of the first study (Figure 5.2c). The WI C found for the WBA without any acidification during the first 96 hour of incubation (28,965 ± 6,320.1 mg WI C/kg WBA; (Figure 5.4e) was significantly higher than the value of the initial characterisation (20,245 ± 1,032 mg WI C/kg WBA; Table 5.1). There is not possible carry-over error in the measurements of the WI C with the elemental Anayser (Elementar Vario EL cube®), despite the high amount of C which ended up in the WI fraction of the WBA acidified with $CH_3CH(OH)COOH$ (679,467 ± 253,462 mg/kg; Figure A.16b) due to adsorption. Both the moderate acidification of the PVWD and the severe acidification of the WBA significantly decreased the C content in the WI fraction due to the release of of CO_2. The trends of WS C in the PVWD and WI C in the WBA could be used for the estimation of the share of CO_3^{2-}-C in these samples (Huang *et al.*, 2017; Podmirseg *et al.*, 2013). According to Figure 5.4d, PVWD lost the 48.49 ± 16.20 % of the WS C in the PVWD due to the acidification with H_2SO_4, HCl and HNO_3. It is important also to mention the 120.53 ± 69.82 % increase in the WI C of the PVWD under that acidification conditions (Figure 5.4e). With regard to the WBA, the data of Figure 5.4d needs to be used cautiously due to the carry over of the $CH_3CH(OH)COOH$ affecting the increase of WS C of the control PVWD and the H_2SO_4-WBA. Although the quatification is not possible, it can be clearly seen that the WS C in the case of the control WBA is always greater than that of the acidified (H_2SO_4, HCl and HNO_3). Since the WI C of the WBA also decreased due to the acidification (Figure 5.4e), the share of the C in the WBA is CO_3^{2-}-C should be at least 85.64 ± 12.48 %.

After the blending at the 96 hours, the level of WI C raised (Figure 5.4e) to a similar level as in the first study of this chapter (Figure 5.2d), despite the final pH of the blends of the second study was lower than 8 (Figure 5.4a). Nevertheless, these lower levels of the WI C in the WBA acidified with H_2SO_4, HCl and HNO_3 were reflected in their mass balance for C (Figure A.17) with an average recovery effectiveness (40.41 ± 41.50 %), which was lower than the 114.02 ± 24.57 % recovery of C in the WBA that was not acidified. It should be noted that there was not significant difference ($p < 0.05$) in the concentration of WI C in each blend by the end of the

144-h incubation, with the exception of the blend acidified with $CH_3CH(OH)COOH$. The average value of 18,810 ± 11,468 mg WI C/kg blend (Figure 5.4e) found in the second study was like the one found in the first study (24,380 ± 3,821 mg WI C/kg blend; (Figure 5.4d).

The cheapest option for restoring the levels of C in the soil is *via* restoration with vegetation. This strategy can be applied in remote areas which are not subjected to intensive agricultural practices (Bai *et al.*, 2020). Even on farm land, the use of cover crops is considered as a valuable resource, although reduced tillage is not widely applied in the agroindustry (Powlson *et al.*, 2012). Primary market research carried out by Hou *et al.* (2018) 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 GHG during application to land (Figure 2.4). The wood ash-based additive can improve the utilisation of the whole anaerobic 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 GHGs due to the broadcast spreading (Brennan *et al.*, 2015) and open storage of manure and slurry (Kavanagh *et al.*, 2019). An analysis made by the Teagasc Greenhouse Gas Working Group (Lanigan *et al.*, 2018) on the strategies for the abatement of this problem, highlighted that the low emission spreading techniques (*e.g.* soil injection) coming into force (UK DEFRA, 2020b; UK Government, 2019) are the most expensive technologies. The farmers need to hire these equipment due to the lack of capital investment (Hou *et al.*, 2018). Furthermore, the use of these machineries is economically inefficient since their operation cost are more expensive than reasonable C prices (Lanigan *et al.*, 2018).

Wróbel *et al.* (2018) proposed an economical way of achieving the granulation of the organic wastes treated with wood ashes by means of creating a mobile granulation unit (*i.e.* decentralised plant). In order to reduce the use of energy and resources, it is necessary to reinforce the synergies between the underlying phenomena responsible of the chemical and the physical stabilisation (Figure 2.4) in the process of production of a granular organic amendment (Table 2.7). 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 CO_2. On the other hand, the CO_2 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 NH_3. Even if the solid-liquid separation of the digestate is done prior to the blending with biomass ash, acidification would be required to prevent NH_3 volatilisation (Pantelopoulos *et al.*, 2016).

5.3.2.2. N speciation

In the second study, the levels of WS NH_4^+-N in the PVWD (Figure 5.5a) were in agreement with the initial characterisation (689.74 ± 86.78 mg/kg; Table 5.1), because appropriate dilution of the samples was done for the measurement in the Autoanalyzer^{TM}. The acidification of the PVWD made a clear difference in preserving the WS NH_4^+-N with regard to the control PVWD. The effect of acidification could not be seen in the WS N (Figure 5.5c) due to the impact of the samples acidified with HNO_3 in the measurements (Figure A.18c). While it was confirmed that the carry-over error occurred in the first study using the Autoanalyzer^{TM}, the values of the WS N in the second study are less likely to be affected by the carry over.

The concentrations of WS NO_3^--N in the PVWD before and after the blending found in the second study (1.60 ± 2.46 mg/kg; Figure 5.5b), with the exception of the blend prepared with HNO_3, agree with the values found in Chapter 3 (1.11 ± 0.05 mg WS NO_3^--N /kg blend; Figure 3.4b) and in the first study of this chapter (1.49 ± 2.34 mg/kg sample; Figure 5.3b). The characterisation of the WBA in terms of WS NO_3^--N was not possible due to interactions with the reagents of the colorimetric procedure employed by the Autoanalyzer^{TM}. The undesired reactions also affected the PVWD and reduced the replicates of some conditions. Therefore, the two-way ANOVA test for balanced design experiments could not be applied to know whether the concentration of WS NO_3^--N in the $CH_3CH(OH)COOH$ extract was significantly different form the other conditions used to prepare the blend of the WBA with the PVWD (Figure 5.5b).

The amount of WI N in the PVWD was greater than in the WBA (Figure 5.5d), except when the acidification was done with HNO_3, because of the adsorption of the WS NO_3^--N onto the WBA (Figure A.18c). This phenomenon could not be seen significantly ($p < 0.05$) in the first study (Figure 5.3d) and the losses as N_2O were the main effect observed (Figure 5.3c). 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 N. This explains the greater N recovery effectiveness found for the blend prepared with HNO_3 in the second study (Figure A.19c). It should be noted that the N_2O release due to abiotic mineralisation (Equation 2.8, Equation 2.9 Equation 2.10) could be also present in the second study, as per the progressive decrease in the WS N shown in Figure A.18b for the WBA acidified with HNO_3. On the other hand, the WBA acidified with the HNO_3 showed a significant concentration of WS NH_4^+-N (Figure 5.5a). The reason would be the reducing effect of the WBA and the high oxidation capacity of the WS NO_3^--N. Furthermore, the approximate decrease of 30,000 mg WS N/kg WBA Figure A.18b) could be related to the respective increase in the WI N (Figure A.18c). The greater levels of WI N obtained when acidifying the WBA with H_2SO_4 or $CH_3CH(OH)COOH$ are not considered to be related to an enhancement in the sorption of the WS N but due to the greater yield of the WI material (Figure A.13d), which affected the calculation of the concentration of WI N (section A.9).

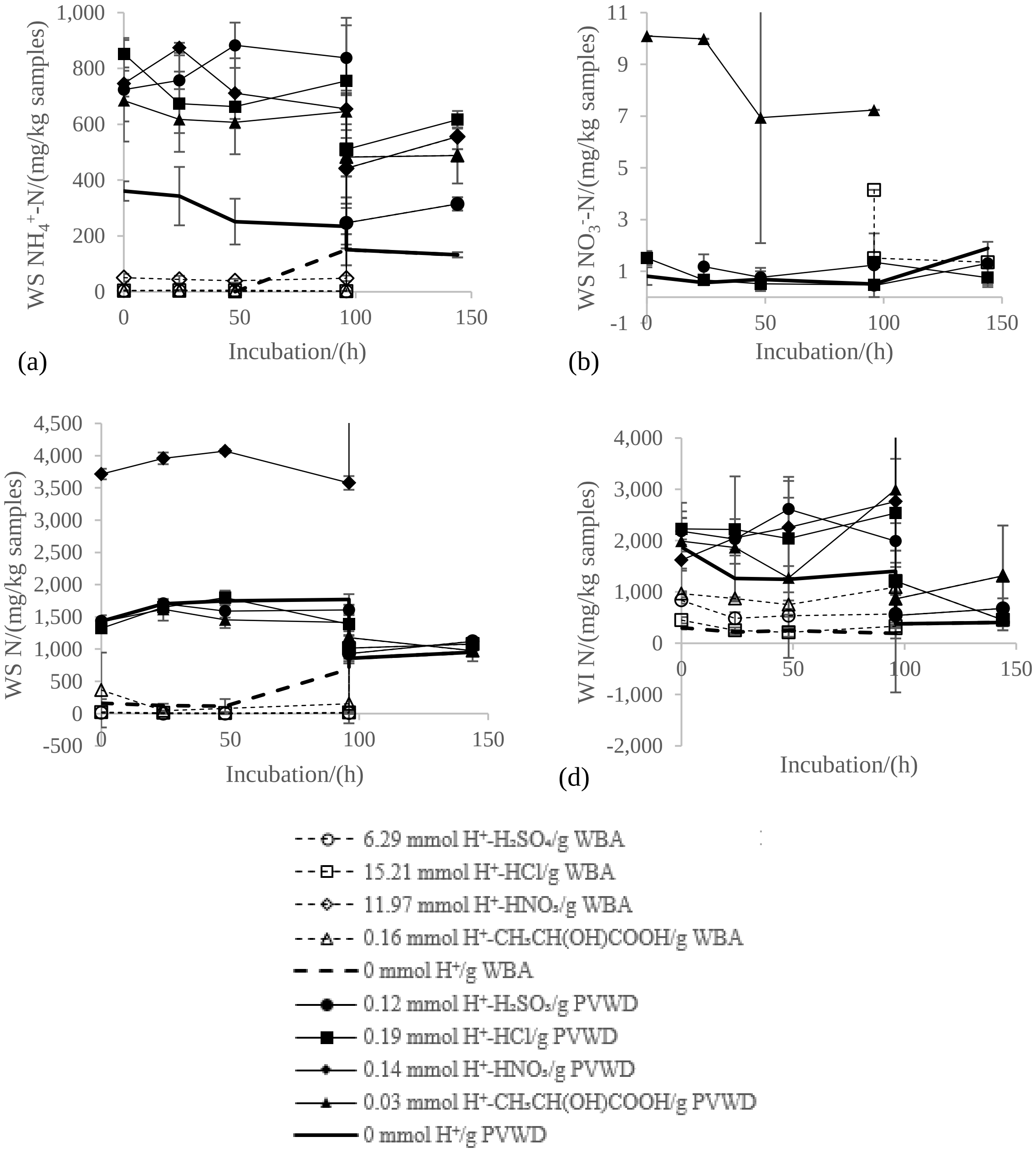


Figure 5.5. Characterisation in terms of (a) WS NH_4^+-N, (b) WS NO_3^--N, (c) WS N and (d) WI N of the 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 of PVWD before and after blending (at the 96 hours), under 4 acidification conditions (*i.e.* H_2SO_4, HCl, HNO_3 and $CH_3CHCOOH$) and no acidification, during the 144-h incubation (Moure Abelenda *et al.*, 2021b).

The mass balances of the 3 elements (Figure A.15, Figure A.17 and Figure A.19) show that only for the N, the WS fraction was 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 N is the most available element) was found in the mass balances of the first study for C and N (Figure A.9 and Figure A.10; respectively). Therefore, the treatment of the PVWD with the acids and the WBA needs to be improved to reduce the availability of N as much as all the other elements, in order to reduce losses of N before and after land application. The sorption capacity of the WBA was not enhanced significantly *via* treatment with HCl before being added to the PVWD, in a similar way the $Ca(OH)_2$ is prepared with HCl to produce $CaCl_2$ (Equation 2.29). The activation with HNO_3 would result in the formation of $Ca(NO_3)_2$, which may increase the denitrification to produce N_2O after land application, due to the excessive content of N in the blended fertiliser (Vandré & Clemens, 1996). In addition to Ca, the WBA contained other elements such as Mg and BC (Table A.3) that might be responsible of sorption processes as well. The treatment of the WBA and the PVWD with H_2SO_4 and $CH_3CH(OH)COOH$ might have not prevented the sorption of WS N significantly ($p < 0.05$). The higher amounts of WI N found when the WBA was acidified with H_2SO_4 and $CH_3CH(OH)COOH$ (Figure 5.5d) could be explained by the greater amount of WI material obtained with these 2 acids (Figure A.13d) and the procedure for the calculation of the concentration of WI N (section A.10).

According to this project agricultural advisors (*i.e.* primary and secondary market research), even in high clay soils where the adsorption of NH_4^+-N is common, the organic slurry 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 palletisation (Figure 2.4) can improve the control of excess of N in the soil because of the easier and more accurate spreading (Wróbel *et al.*, 2017). The study of Hou *et al.* (2018) suggested the willingness of the farmers in using processed organic fertiliser due to the increasing cost of industrial fertilisers and the need to facilitate the export of manure from farms.

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). In fact, Jewiarz *et al.* (2018) could not include a biofertiliser (fungal strains of *Trichoderma spieces*) in the blend agricultural waste digestate and biomass ash because the microbes would not thrive. Ideally the blend would be pasteurised rather than sterilised, to allow the presence of unharmful microorganism (WRAP, 2014a). 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 C and N use efficiency have been investigated when applying simultaneously digestate and wood ash (Bougnom et al., 2012; Fernández-Delgado Juárez et al., 2013, 2015; Insam et al., 2009). 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 fertilisers.

The AD is regarded as a technology to achieve the biological stabilisation of organic waste (UK Government, 2018; WRAP, 2014a). 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 miscibility with the ashes because the AD is able to eliminate the small particles (Lindner *et al.*, 2015; Möller & Müller, 2012). This organic amendment would be less likely to decay and putrefy in the soil. For these reasons, the processing of the organic wastes firstly *via* AD and secondly with the ash treatment, whether these materials are sourced from somewhere else or produced onsite, could be regarded as a good ecological practice. The maturation of organic manures (Figure 2.9) involves the mineralisation of the organic nutrients. The inorganic forms of the nutrient to be more suitable for sorption by interacting with the components of the ashes and the preparation of a slow-release fertiliser (*i.e.* chemical stabilisation; Figure 2.4).

5.4.Conclusions

In terms of time required for the chemical stabilisation, in the first study of this chapter the composition of the blend remained constant straight after the mixing. The reason for the low P recovery effectiveness was the initial characterisation provided by the external laboratory of this element (Table 3.3), as the in-house analysis was able to measure four times less P. Thereby, the targeted nutrient ratio was redefined as C/N/P 40/4/1 for the subsequent chapters.

The severe acidification of the WBA, which was employed in the second study of this chapter, prevented the increase of the pH of the blend above the initial value of the digestate, thus minimising the losses of NH_3. Both H_2SO_4 and $CH_3CH(OH)COOH$ decreased the sorption capacity of the WBA and minimised the potential decrease in the availability of the P, C and N of the PVWD. It is important to mention that both H_2SO_4 and HNO_3 are able to oxidise the OM, enhancing the losses of CO_2. Although the incubation with HNO_3 as extractant did not increase the mass of the WI fraction of the WBA, the excessive content of N in the organic amendment would boost the losses of this nutrient before and after land application. Therefore, the HCl 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 HCl enhances sorption processes, it would be necessary to determine the content of the chloride ion 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 Cl^- attached to the surface of the WBA. In this way, the acid wash would be performed after milling, sieving and calcinating 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 (Figure 2.4).

The results obtained proved 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 anaerobic digestate and wood 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 addition to the techno-economical assessment, a primary market research is required to ensure the wood ash-based treatment addresses the problems of the stakeholders of the agroindustry 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.* capital investment, 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).

6. Comparison of the wood ash-based treatment of the anaerobic digestate to acidification and nitrification

6.1.Introduction

The uneven distribution of worldwide resources, such as crude oil and phosphate rock, creates conflicts between countries and is a matter of concern for a sustainable supply of energy and chemical fertilisers (Elser & Bennett, 2011). Extensive research activities have targeted the processing, with positive energy balance (Da Costa Gomez, 2013), of clean and source segregated wastes (Demirbas, 2011). The energy recovery from biomass can be carried out *via* thermo-chemical degradation (*e.g.* combustion, gasification, hydrothermal liquefaction and pyrolysis) or biological fermentation (*e.g.* AD and alcoholic fermentation) (X. Yang *et al.*, 2015). The selection of the biomass conversion technology is important because it affects the availability of the nutrients in the energy-depleted byproduct resulting from the process (Sarvi *et al.*, 2021).

Materials with level of contaminants lower than the threshold values established in the environmental legislation in force, such as the biomass ashes (Bougnom *et al.*, 2012; Fernández-Delgado Juárez *et al.*, 2013; Insam *et al.*, 2009; Richards et al., 2021), could be used directly as soil amendments (Owamah *et al.*, 2014; Silva *et al.*, 2019). Some obstacles that need to be solved are the fate of the trace elements of ashes (Voshell *et al.*, 2018) and the suitability of anaerobic digestates as fertilisers (García-Sánchez *et al.*, 2015; Owamah *et al.*, 2014). The utilisation of wood ash and anaerobic digestate as valuable resources in agriculture reduces the ecological impact and the regulatory burden of the industries where these residues are produced and reinforce the green credentials of agriculture (Fivelman, 2013).

The anaerobic digestate is well known for having greater availability of the nutrients than the initial feedstock used for the production of biogas (Dahlin *et al.*, 2015). Due to the high investment of the AD processing facilities (Hou *et al.*, 2018), the only compulsory treatment is to store the organic manures for a minimum of six months before land application to undergo a similar type of fermentation (Janni & Cortus, 2020). Organic wastes that have undergone maturation until reaching a C/N (*i.e.* < 20; Figure 2.10) can be used as soil amendments (Bernal *et al.*, 2009). During this process, the mineralisation of the N_{org} leads to the formation of NH_4^+-N (Equation 3.1), which is the preferred source of N by plants but is an atmospheric pollutant (Chojnacka *et al.*, 2020). While the C is released as CH_4 or CO_2, most of the ammonia remains in the liquid slurry, as ammonium (Möller & Müller, 2012). Szymula *et al.* (2021) described the hydrolytic reaction of the biotic ammonification for urea as Equation 6.1:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad \textbf{Equation 6.1}$$

Nitrification and acidification are widely used techniques to minimise NH_3 losses from digestate and other of organic manures (Botheju *et al.*, 2010; Kavanagh *et al.*, 2019; Regueiro, Coutinho, & Fangueiro, 2016). Biomass ash, in addition to be a source of P (Tan & Lagerkvist, 2011), contains elements such as Ca, Mg and BC which can promote adsorption processes and the formation of precipitates in the digestate (Daifullah *et al.*, 2003; James *et al.*, 2012; Sakthivel *et al.*, 2012). This chemical stabilisation (Figure 2.4) is intended to minimise the losses of nutrients due to gaseous emissions and leaching during storage and after land application of organic manures (Brennan *et al.*, 2015; Miranda *et al.*, 2021). According to Chapter 4 and Chapter 5 of this thesis, the HCl gives the best results for preparing an ash-based additive for the anaerobic digestate. This chapter assesses the changes in the availability of N, C and P in a digestate treated *via* (a) addition of wood ash under different acidification conditions and (b) nitrification.

6.2.Materials and methods

6.2.1. Materials

The selection of the pristine WFA and the PVWD for the experiments of this chapter was based on their capacity to retain nutrients and to remain chemically stable, as per the results of Chapter 4 and Chapter 3, respectively. Furthermore, the previous investigation involving the WBA (Chapter 5) did not show a clear enhancement of the sorption of nutrients when the blend with PVWD was prepared using 4 different acids. The present chapter investigates the effect of the best adsorbent found in the Chapter 4 (HCl-WFA) on the composition of the PVWD. To compare the WFA-based treatment with the nitrification and the acidification alone, the two-factor ANOVA with replication was performed with Microsoft® Excel ($p < 0.05$). Table 6.1 summarises the treatments investigated: HCl-WFA+PVWD, the WFA was conditioned with a 1.82 M aqueous solution of HCl before being added to the PVWD; HCl-WFA+HCl-PVWD, the PVWD was acidified with a 0.06 M solution of HCl before the blending with the HCl-WFA; and PVWD, no acidification was applied to allow the nitrification. Chapter 4 contains the preliminary titrations of the samples with HCl were performed to determine the amount of acid required to maintain the pH around 5.5 (Figure 4.1). Approximately 10 mL of HCl aqueous solution were added to each gram of WFA and PVWD (Figure A.20). The two factors assessed were the type of treatment or blend composition (HCl-WFA+PVWD, HCl-WFA+HCl-PVW, PVWD and HCl-PVWD) and the time of incubation (0, 1, 3, 6, 12, 24, 48, 72, 96, 120 and 144 hours). Because of the destructive sampling procedure used to carry out the experiment, 176 experimental units (*i.e.* 4 treatments or blends, each with 4 repetitions, measured at 11 incubations times) were prepared.

Table 6.1. Blends were characterised during the incubation in a closed chamber at 100 rpm shaking and 20 ºC (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

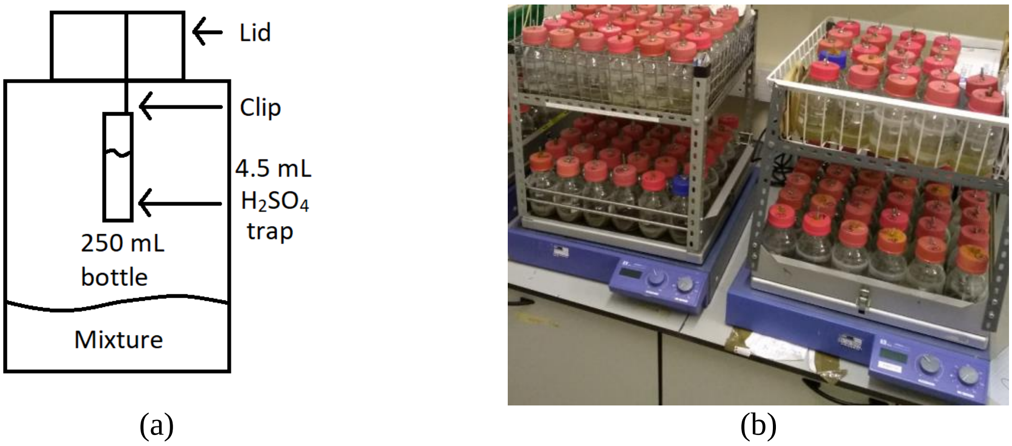
Sample	**WFA**			**PVWD**			**Incubation**	**Trap for NH_3**
Treatment	**Sample**	**Extractant**	**[a]HCl/(M)**	**Sample**	**Extractant**	**[a]HCl/(M)**	**/(h)**	**[a]H_2SO_4/(M)**
HCl-WFA+PVWD	0.49 ± 0.05	4.45 ± 0.04	1.82	2.88 ± 0.99	20.02 ± 0.13	0.00	0, 1, 3, 6, 12, 24, 48, 72, 96, 120, 144	0.11
HCl-WFA+HCl-PVWD	0.46 ± 0.06	4.50 ± 0.03	1.82	2.75 ± 1.24	20.16 ± 0.34	0.06		
PVWD	0.00	0.00	0.00	2.60 ± 0.85	20.09 ± 0.11	0.00		
HCl-PVWD	0.00	0.00	0.00	2.48 ± 0.77	20.11 ± 0.12	0.06		

[a] Analytical grade HCl and H_2SO_4 were used to prepare acid solutions together with ultrapure milli-Q® water.

6.2.2. Methods

6.2.2.1. Absorption of the NH_3 volatilised

The 144-h incubations took place in a closed chamber (Figure 6.1a), which consisted in a 250-mL Schott Duran® bottle with a stopper from which a vial was held, containing 4.43 ± 0.12 mL of a 0.11 M H_2SO_4 aqueous solution to capture the $NH_{3(g)}$ in the headspace. To ensure the equilibrium between the blend and the acid trap, the whole system was shaken at 100 rpm and 20 °C during the incubation up to 144 hours (Figure 6.1b). This setup was a modification of the procedure developed by Velthof *et al.* (2005), which has been widely used for determination of N losses due to volatilisation of NH_3. The purpose of the H_2SO_4 trap was to determine the amount of $NH_{3(g)}$ that can be recovered as part of the treatments of the digestate, from the headspace of the closed chamber.



(a) (b)

Figure 6.1. (a) Schematic of the closed chamber used for the incubation of blends (Table 6.1) up to 144 hours at 20 °C and 100 rpm. (b) Closed chambers in the rotary shakers placed in the climate-controlled room (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

A review of the different type of chambers employing H_2SO_4 to measure the emissions of NH_3 is offered in Table A.8. The amount of H_2SO_4 in the trap exceed the stoichiometric requirements (Equation 6.2), which were calculated considering that all the N in the samples would volatilise as NH_3. The H_2SO_4 solution in the trap was regarded as one of the fractions isolated after the treatment of the PVWD (Figure A.22): sulphuric ([H_2SO_4]) fraction.

$$NH_{3_{(g)}} + H_2SO_{4_{(aq)}} \rightarrow (NH_4)_2SO_{4_{(s)}} \qquad \textbf{Equation 6.2}$$

6.2.2.2. Fractionation of the treated PVWD

After completing the incubation of each destructive sample, the closed chamber was disassembled and the concentration of ammoniacal and nitric nitrogen in the sulphuric fraction ([H_2SO_4] NH_4^+-N and [H_2SO_4] NO_3^--N, respectively) was determined using segmented flow analysis (Autoanalyzer^{TM}, SEAL analytical). The treated PVWD was transferred to a 50-mL Corning® tube to conduct the solid-liquid separation, by means of a 5-minute centrifugation at 4,000 rpm and subsequent 3-µm filtration of the supernatant. The WS phase was characterised in terms of pH, NH_4^+-N, NO_3^--N, N, C and PO_4^{3-}-P. The content of N, C and P was determined as previous described (Chapter 5) in WI material (*i.e.* solid pellet and filter cake) obtained after dying at 105 ºC. The distribution of each element among the [H_2SO_4], WS and WI fractions, cited in decreasing order of availability, was taken into account for the analysis of the results. Particularly, for the analysis of the speciation of the P, the availability was defined as the WS PO_4^{3-}-P to WI P ratio. The amounts of N, C and P in the fractions of the blends (Figure A.22) were used to establish the mass balances of these elements (Regueiro, Coutinho, Gioelli, *et al.*, 2016). Differently from the analytical procedure followed in Chapter 3 and Chapter 5, the profiles observed were not compared to the initial characterisation of the sample (Table 3.3), which includes some of the analyses of NRM (*i.e.* content of N and P)], but to the first point measured at the time zero of the incubation. The average recovery effectiveness of each element was calculated as the final amount of a nutrient divided by its initial amount.

6.2.2.3. Calculation of the concentration of [H_2SO_4] NH_4^+-N and [H_2SO_4] NO_3^--N in fresh basis

Similar procedure for the calculation of the WS species (section A.4), with the difference that the concentration (X; Equation 6.3) provided by the Autoanalyzer^{TM} is multiplied by the final volume (V; Equation 6.3) of the [H_2SO_4] fraction (Figure A.22b), instead of the one of the WS extract (Figure A.22d). This is the volume determined after the incubation by weighing the trap and assuming a density of 1 g/mL for the H_2SO_4 solution.

$$[H_2SO_4]\,N = X\,\frac{mg\,N}{L} \times dilution\ factor \times \frac{1\,L}{10^3 mL} \times \times V\,mL\,H_2SO_4 \times \frac{1}{Y\,g\,fresh\,blend} \times \frac{10^3 g}{1\,kg}$$

Equation 6.3

For the calculation of the mass of any of the species that ended up in the H_2SO_4 solution of the trap, it would not be necessary to divide by the mass of the fresh blend (Y) in the Equation 6.3.

6.3.Results and discussion

6.3.1. Fractionation of the blends after the incubation

The mass losses of the H_2SO_4 solution in the 4.43 ± 0.12 mL traps were negligible (Figure 6.2a) since the isolation of this phase did not imply transferring the content of the trap vial to a flask for solid-liquid separation. Approximately 10 mL of WS extract were lost during incubation and subsequent filtration of the blends (Figure A.20 and Figure 6.2b). Similarly, around 0.2 g of WI material were lost (Figure A.20 and Figure 6.2c). The initial volumes of the WS fraction of the blends were determined considering the moisture of samples (Table 3.3), in addition to the volume of extractant used to prepare the blends (Table 6.1). The DM of the samples (Table 3.3) was assumed to be the initial masses of the WI fraction.

The hydrolytic and dehydration effects of the acidification could be seen in the mass of WS and WI fractions of the blend. In this way, the acidified digestate had more WS fraction than the PVWD alone (Figure 6.2b). On the other hand, a greater drop in the amount of WI material recovered could be seen in the blend HCl-WFA+HCl-PVWD (Figure 6.2c), which was more severely acidified than the blend HCl-WFA+PVWD (Figure 6.2b).

The losses during incubation and subsequent processing (*i.e.* isolation of the fractions) of the blends affected mass balance of each nutrient and even the concentrations of the chemical species in [H_2SO_4], WS and WI forms. Since the values of the pH refer to the WS extracts and they were not expressed in fresh basis, this parameter was not affected by the losses of the fractions of the blends during the incubation and subsequent solid-liquid separation.

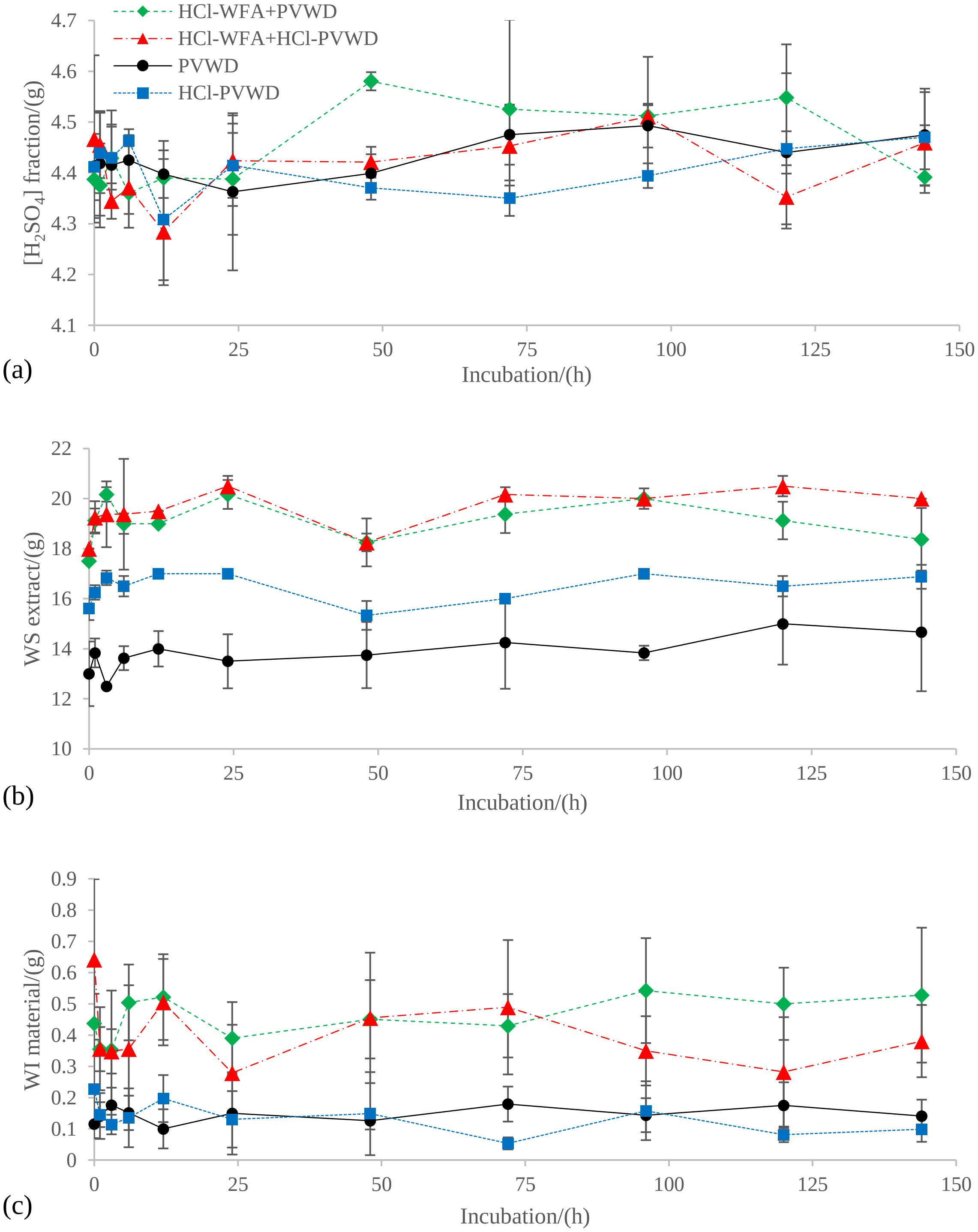


Figure 6.2. Masses of (a) [H_2SO_4], (b) WS and (c) WI fractions recovered after the incubation of the destructive samples of HCl-WFA+PVWD, HCl-WFA+HCl-PVWD, PVWD and HCl-PVWD (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

6.3.2. pH of the [H_2SO_4] and the WS fractions

The acid traps had similar pH (Figure 6.3a) because they were filled before starting the incubation with 4.43 ± 0.12 mL of the same 0.11 M H_2SO_4 solution, which had a pH of 0.92

measured at 17.9 ºC. According to the Figure 6.3a, the blend HCl-WFA+PVWD had the lowest [H_2SO_4] NH_4^+-N. In order to confirm these trends, the measurement of the pH was repeated after diluting eleven times (1/10) the [H_2SO_4] extract. This ensured a better contact with the probe and prevented the values of the pH to be affected by the detection limit of the pH-meter. The pH in the undiluted traps was calculated based on the concentration of the H^+ species measured in the eleven times diluted (1/10) [H_2SO_4] fraction (Figure 6.3b).

The differences in pH of the WS extracts of the treatments were greater (Figure 6.3c) because of the amount of HCl used to prepare them (Table 6.1). According to the two-way ANOVA test ($p < 0.05$), even for the blends HCl-WFA+HCl-PVWD and HCl-PVWD there was significant difference in terms of pH (Figure 6.3c).

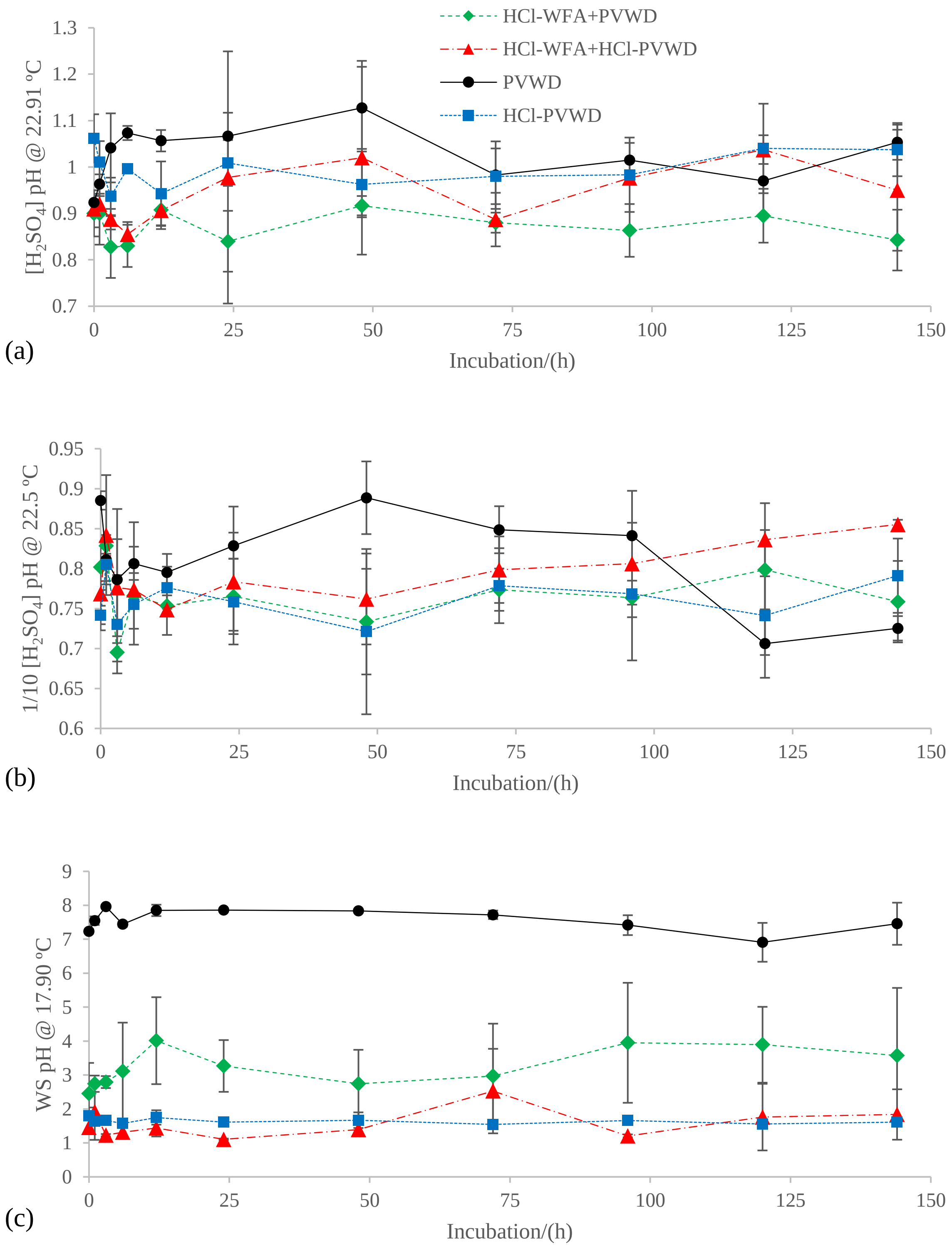


Figure 6.3. Changes in the pH of the 4.42 ± 0.10 mL 0.11 M H_2SO_4 traps: (a) values directly measured at 22.91 ± 2.05 ºC and (b) values calculated from the measurements at 22.49 ± 0.74 ºC of the eleven-time diluted (1/10) [H_2SO_4] extract. (c) Changes in the pH of the 17.17 ± 2.56 mL WS extract of the HCl-WFA+PVWD, HCl-WFA+HCl-PVWD, PVWD and HCl-PVWD during the 144-h incubation (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

6.3.3. N speciation

The highest concentration of [H_2SO_4] NH_4^+-N (Figure 6.4a) and the lowest concentration of WS NH_4^+-N (Figure 6.4c) were found in the PVWD, followed by the HCl-WFA+PVWD. The reason was that the greater level of acidification achieved in the HCl-WFA+HCl-PVWD and the HCl-PVWD treatments (Figure 6.3c). It took 48 hours of incubation to reach the maximum concentration of [H_2SO_4] NH_4^+-N (Figure 6.4a) in the PVWD. Both WS NO_3^--N (Figure 6.4d) and WS N (Figure 6.4e) increased significantly ($p < 0.05$) between 48 and 120 hours of incubation of the PVWD. At the 120 hours of incubation, the levels of WS NO_3^--N (Figure 6.4d) and WS N (Figure 6.4e) in the PVWD decreased.

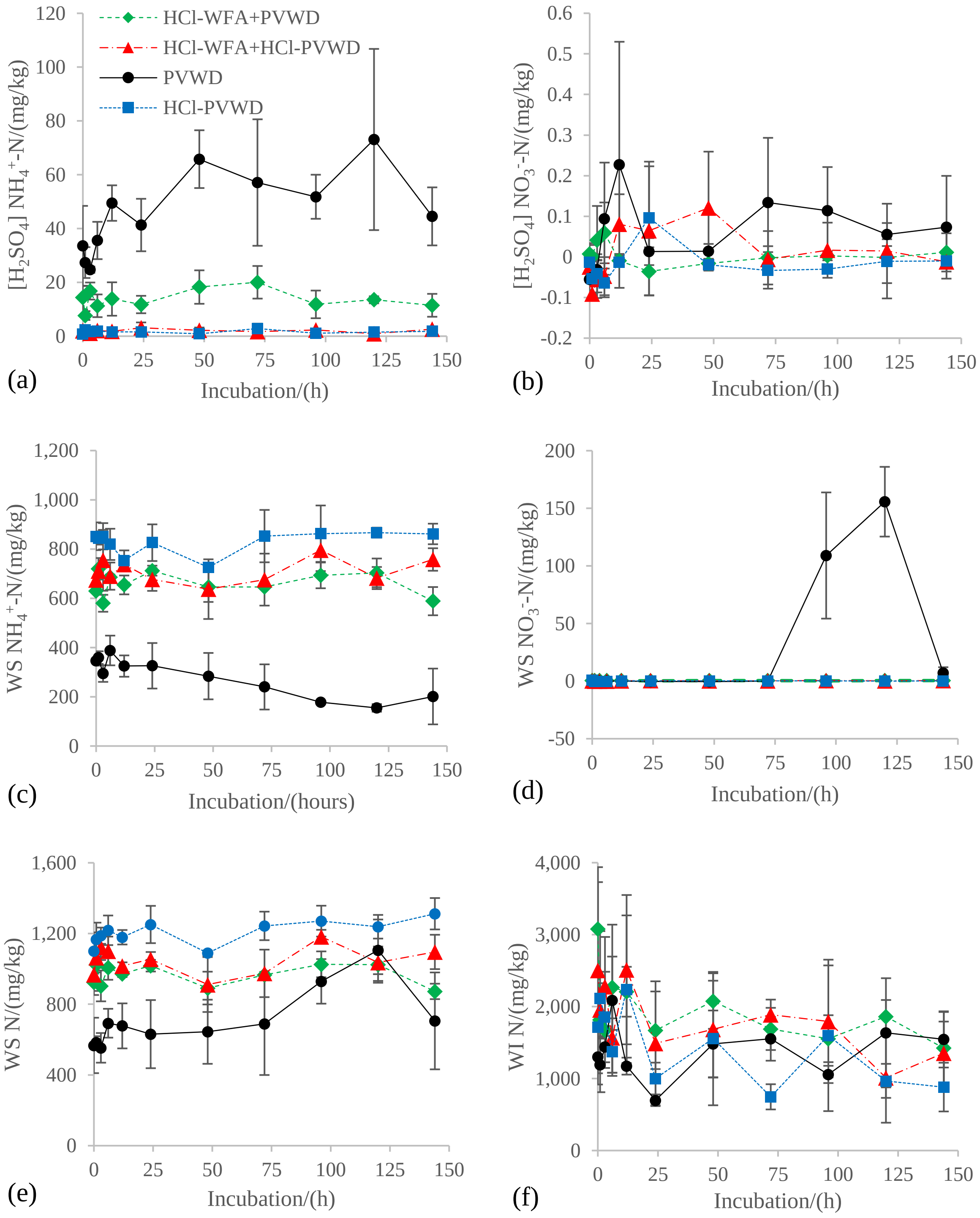


Figure 6.4. Concentrations of (a) [H_2SO_4] NH_4^+-N, (b) [H_2SO_4] NO_3^--N, (c) WS NH_4^+-N, (d) WS NO_3^--N, (e) WS N and (f) WI N in the blends HCl-WFA+PVWD, HCl-WFA+HCl-PVWD, PVWD and HCl-PVWD during the 144-h incubation at 100 rpm and 20 ºC (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

A stepwise mechanism was proposed to explain the change of the N species in the PVWD (Figure 6.4). During the first 48 hours, took place the volatilisation of NH_3 from the PVWD until reaching a pseudo-equilibrium. The saturation level was 58.47 ± 20.50 mg [H_2SO_4] NH_4^+-N/kg PVWD, due to the mass transfer resistance of NH_3 from the WS fraction to the air and from the air to the [H_2SO_4] fraction. During the next 72 hours (*i.e.* until the 120 hours of incubation), nitrification took place until reaching a new pseudo-equilibrium in the WS fraction (Figure 6.4d). Adams (1986) reported a similar profile of NO_3^--N for PVWD (Figure 6.4d) associated to ammonification (Figure 6.4), but the latter process could not be confirmed since the WS NH_4^+-N of the PVWD consistently decreased during the incubation (Figure 6.4c). As the profile of WS NH_4^+-N of PVWD reached a minimum, instead of having a bell shape (Romillac, 2019; Wong-Chong & Loehr, 1975), there was no formation of WS NH_4^+-N and the decrease of this chemical species was primarily due to the NH_3 volatilisation and the nitrification. The faster kinetics of the dissociation of NH_4^+ and subsequent NH_3 volatilisation, compared to that of the nitrification, was the reason for which the biochemical process took place after reaching the top level of [H_2SO_4] NH_4^+-N. The apparent nitrification that took place in the control PVWD of the first study of Chapter 5 (Figure 5.3b) was not regarded as such because, according to the 2 way ANOVA test, there was not significant difference ($p < 0.05$) between the trend of the control PVWD and the PVWD acidified with a low dose of H_2SO_4 (0.08 mol H^+-H_2SO_4/g PVWD).

In this chapter, the neutral pH in the PVWD (7.55 ± 0.40; Figure 6.3c) allowed firstly the NH_3 release and secondly the microbial nitrification (Jeschke *et al.*, 2013). The WS NH_4^+-N decreased (148.18 ± 92.67 mg/kg PVWD; Figure 6.4c) as much the WS NO_3^--N increased (155.73 ± 30.26 mg/kg PVWD; Figure 6.4d). However, there was an overall increase of approximately 475.95 ± 230.80 mg WS N per kg PVWD (Figure 6.4e) without reducing the WI N (Figure 6.4f). The increase of the WS N (Figure 6.4e) while the WS NH_4^+-N decreased (Figure 6.4c) could be related to the microbial growth of *Nitrosomonas* (Papp *et al.*, 2016), which would follow the same trend as the WS NO_3^--N formation (Figure 6.4d). The overall conversion reaction of autotrophic nitrification (Equation 2.7) is shown in Equation 6.4 (Botheju *et al.*, 2010).

$$NH_4^+ + 1.863O_2 + 0.098CO_2 \rightarrow 0.0196C_5H_7NO_2 + 0.98\,NO_3^- + 0.0941H_2O + 1.98H^+$$

Equation 6.4

During the incubation of the PVWD, the microbial biomass (represented as $C_5H_7NO_2$) would have been able to use for their growth some of the NH_4^+ that remained in the WS fraction. This interpretation was not confirmed experimentally since the quantification of these microorganisms is usually done through absorbance measurement or counting the DNA molecules after polymerase chain reaction (Qiao *et al.*, 2020), rather than by determining the WS N. The reason for which some of these microbes ended up in the WS fraction rather than in the WI material was the low effectiveness of the solid-liquid separation as part of the analytical procedure. It would be necessary centrifugation at 8,500 rpm for at least 10 min and/or 0.2 µm filtration to completely remove the particulate matter from the WS extract (Burrell *et al.*, 2001).

After the 120 hours of incubation the PVWD, the denitrification occurred to give N_2O and/or N_2 (Figure 6.4d,e). The reason for the denitrification could be that the high levels of WS NO_3^--N were not stable under the incubation conditions. Both in the acidified blends and all the H_2SO_4 traps, the levels of the NO_3^--N were low (Figure 6.4d,b) because the acid pH (Figure 6.3a) prevented the nitrification (Papp *et al.*, 2016). The low levels of NO_3^--N in equilibrium with the NH_4^+-N could be related to the abiotic nitrification (Figure 6.4b). The oxidative power of H_2SO_4 was not considered to be related to this process since the redox potential of the NO_3^- to NO_2^- (0.94 V; (Harvey, 2021)) is greater than the SO_4^{2-} to SO_3^{2-} (0.17 V; (Harvey, 2021)) (Pulford, 2007). A more logical explanation is that this could be related to background noise due to the detection limit of the Autoanalyzer™. Approximately ten times higher concentration of NO_3^--N was found in the WS extract of HCl-WFA+PVWD, HCl-WFA+HCl-PVWD and HCl-PVWD (0.24 ± 0.25 mg WS NO_3^--N/kg; Figure 6.4d) than in the [H_2SO_4] extract of all the blends (0.01 ± 0.10 mg [H_2SO_4] NO_3^--N/kg; Figure 6.4b).

Despite the treatments HCl-WFA+HCl-PVWD and HCl-PVWD had similar pH (Figure 6.3c), the WI N (Figure 6.4f) was greater in the HCl-WFA treatment of the PVWD. The role of the WFA as sorbetn was enhanced under the acid conditions that promoted the dehydration (*i.e.* release of the attached water molecules to the EPS; Figure 6.2b,c) (Astals *et al.*, 2021; Mor *et al.*, 2016). It should be noted that the addition of the WFA to the PVWD is not supposed to decrease the concentration of WI N as much as with the WBA (*i.e.* drop of 1,494.86 ± 555.96 (Figure 5.3d) and 1,269.94 ± 1,147.17 mg WI N/kg blend (Figure 5.5d) in the first and second studies of Chapter 5, respectively, due to the higher content of N in the WFA (Table 3.3). Therefore, besides preventing the volatilisation of NH_3 during storage, the HCl-WFA treatment of the PVWD has the potential to reduce the losses of N *via* leaching after land application compared to the acidification alone. Nevertheless, in the closed chamber, the nitrification was the best management strategy for the N of the PVWD, as can be seen in the N mass balances (Figure 6.5).

6.3.4. Mass balances and recovery effectiveness of N

Most N was in the form of WI N (4.83 ± 2.81 mg; Figure 6.5) and lower fluctuation were found in the WS N (2.85 ± 1.10 mg). It should be noted that swapped trends of WI N and WS N were found in the treatment HCl-PVWD (Figure 6.5d), since the acidification led to the solubilisation of nutrients. The amount of [H_2SO_4] N was negligible (0.04 ± 0.05 mg NH_4^+-N + NO_3^--N) compared to the other forms of N and the highest amount of this N species was found in the PVWD alone (Figure 6.5).

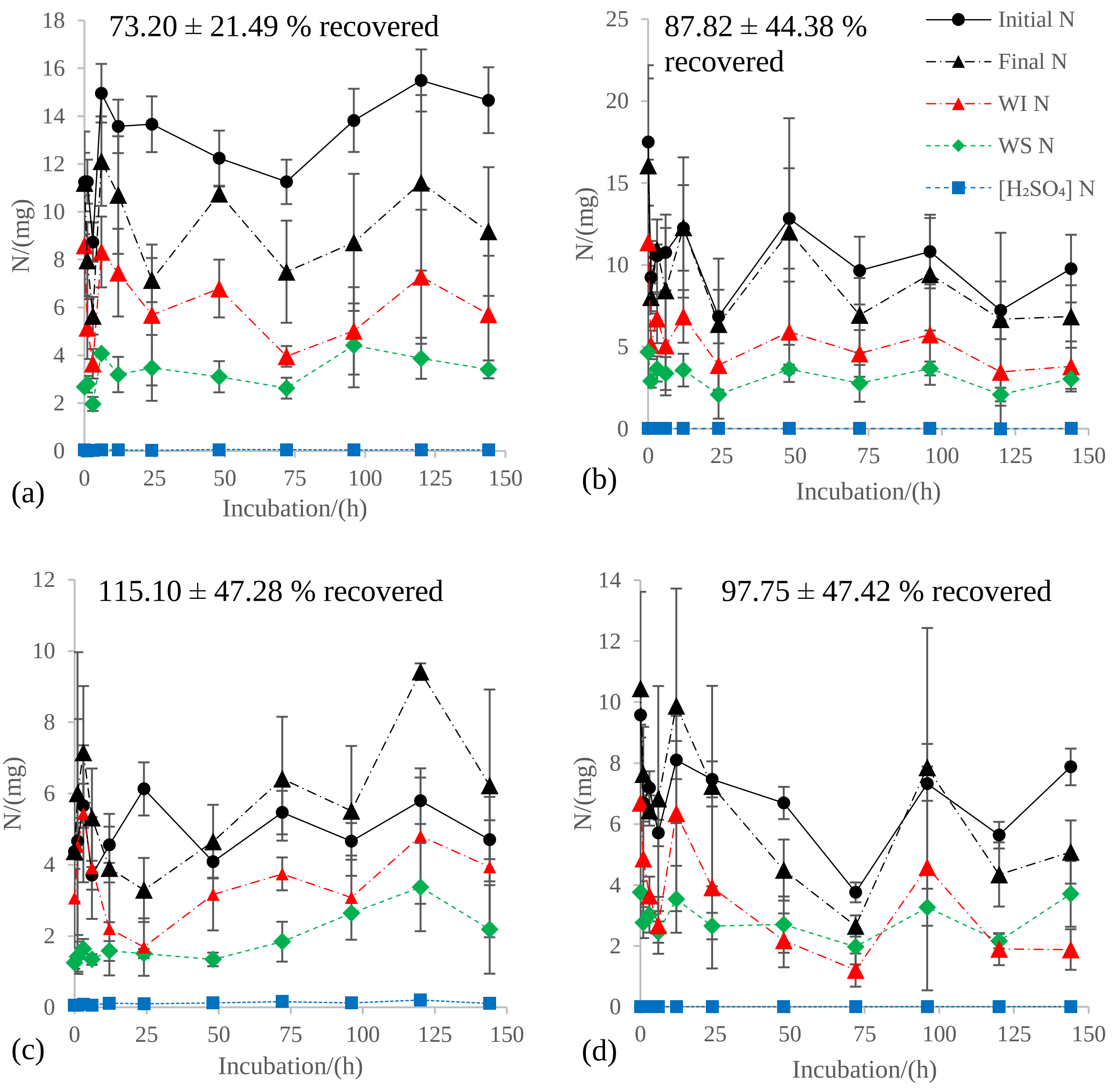


Figure 6.5. N mass balance for (a) HCl-WFA+PVWD, (b) HCl-WFA+HCl-PVWD, (c) PVWD and (d) HCl-PVWD blends (Table 6.1) during the 144 hours of incubation at 100 rpm for 20 ºC in the presence of a 0.11 M H_2SO_4 trap. Initial N stands for the calculated N introduced in the system (Figure 6.1a) at the beginning of the incubation, which depended on the mass of each blend (Figure A.20). Final N is the sum of the masses of WS N, WI N and

[H_2SO_4] N. The average values of N recovery effectiveness over the whole of incubation period is stated in each graph (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

The greatest amount of N was recovered with the WFA treatments (9.47 ± 3.88 mg N; Figure 6.5a,b) because of the additional N provided by the WFA (Table 3.3) but the recovery effectiveness decreased overtime. The greater acidification of the HCl-WFA+HCl-PVWD prevented N losses over the first 72 hours (Figure 6.5b), while the HCl-WFA+PVWD started to have significant ($p < 0.05$) losses of N at the 12 hours (Figure 6.5a). Similarly, the HCl-PVWD started to have significant ($p < 0.05$) losses of N at the 12 hours (Figure 6.5d). It should be noted the opposite trend found in the PVWD, which underwent nitrification (Figure 6.5c). Since the N recovery effectiveness increased towards the end of the incubation, leading to the greatest recovery of N during the 144-h incubation (115.10 ± 47.28 %; Figure 6.5c). The nitrification started at the 48 hours of incubation, at which time the trap reached the top concentration of [H_2SO_4] NH_4^+-N (Figure 6.4a). Therefore, the nitrification was prevented by the flux of NH_3 towards the [H_2SO_4] fraction, which was a way of acidifying the WS fraction without adding acid nor decreasing the pH of the digestate. This explanation is in agreement with the Le Chatelier's principle and the Equation 6.4. As soon as there was no NH_3 flux towards the H_2SO_4 solution, because the trap was NH_3-saturated due to mass transfer resistance, the nitrification started. After the 120 hours of incubation, the system kept transitioning towards a more stable state leading to formation of N_2O and N_2 gases due to the denitrification (Ahn *et al.*, 2011; Gao *et al.*, 2010). Therefore, the acidification conditions are able to preserve the NH_4^+-N in the PVWD while an airtight storage prevents the losses of N but allows the change of N speciation (*i.e.* nitrification and denitrification).

6.3.5. C speciation

The treatments of the PVWD involving the WFA reduced the concentration of WS C (Figure 6.6a) and increased the content of WI C (Figure 6.6b). Towards the end of the incubation, after the 48 hours, the WI C of the PVWD was higher than what was found in the HCl-PVWD and the opposite trend was found in the WS C. The same dependence of the availability of C on the acidification was found for the WFA-based treatments, after the 96 hours of incubation. The large error bars were the results of dealing with non-homogeneous samples of digestate and ash.

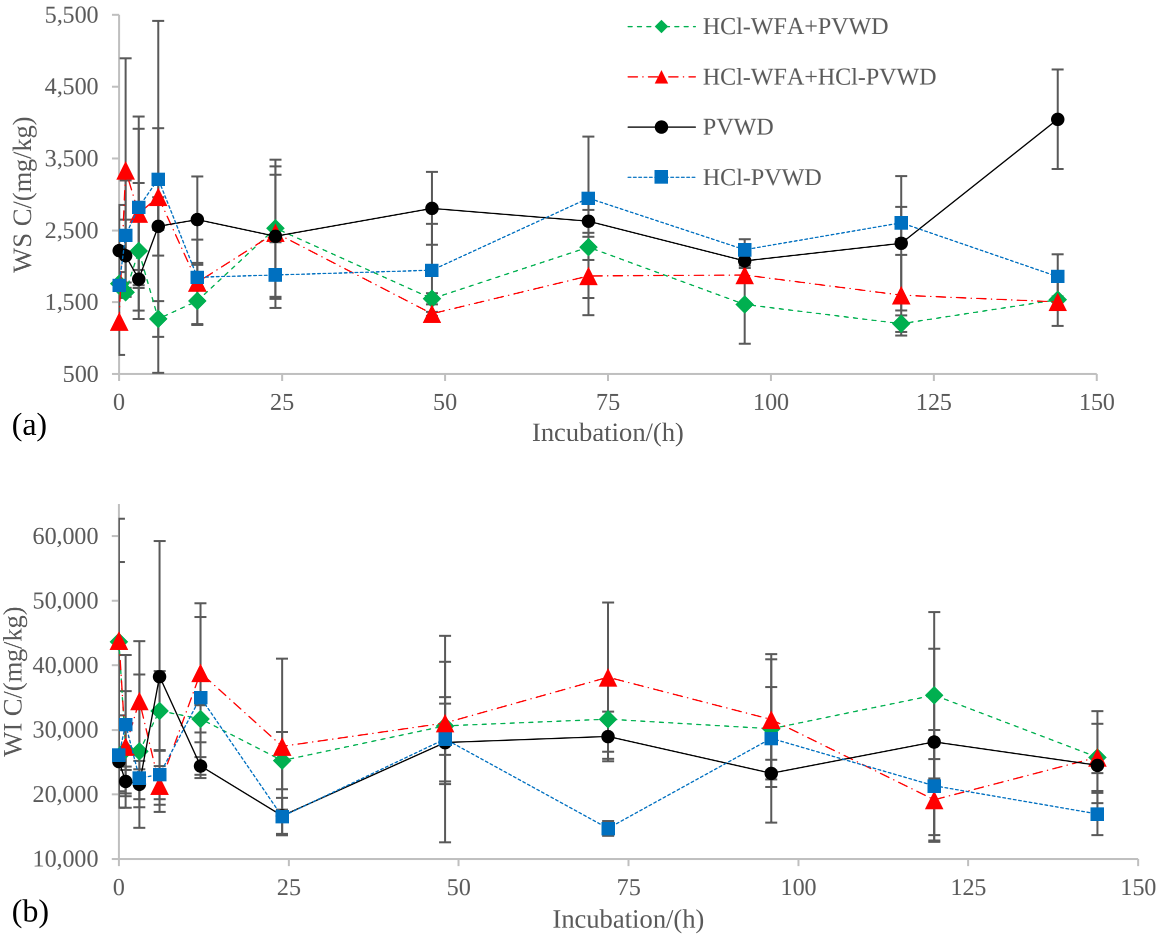


Figure 6.6. Concentrations of (a) WS C and (b) WI C in the HCl-WFA+PVWD, HCl-WFA+HCl-PVWD, PVWD and HCl-PVWD during the incubation at 100 rpm and 20 ºC in the presence of a 0.11 M H_2SO_4 solution in the trap (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

The changes in the C speciation were primarily explained by the hydrolysis of the C_{org} of the PVWD and the high biological stability (*i.e.* reluctance to undergo hydrolysis and microbial degradation) of the BC of the WFA. The BC is also known as unburnt carbon and it has similar composition to the biochar and AC (Forbes *et al.*, 2006; Hale *et al.*, 2013; James *et al.*, 2012; Strosser, 2011). The lower pH of HCl-WFA+HCl-PVWD (1.59 ± 0.68; Figure 6.3c) compared to the one of HCl-WFA+PVWD (3.24 ± 1.22; Figure 6.3c), enhanced the solubilisation of C_{org} for which the WS C increased and WI C decreased after the 96 hours of incubation (Figure 6.6). Similarly, after the 48 hours of incubation, the WS C of the HCl-PVWD was greater than the one of the PVWD and the opposite occurred with the WI C (Figure 6.6a). This agrees with the low share of CO_3^{2-} in the PVWD, compared to the content of C_{org}, which was previously seen in the Figure 5.4e. The higher WI C in the PVWD that was treated with HCl-WFA can be explained by the fact that most C in the WFA was in the form of BC and the low share of CO_3^{2-}

-C present in this waste stream was lost as CO_2. The role of HCl-WFA as sorbent (Laohaprapanon *et al.*, 2010) could be one of the reasons behind the lower content of WS C of the blends including this material (Figure 6.6a), since the pH of the HCl-WFA+HCl-PVWD was like the one of the HCl-PVWD (1.62 ± 0.49; Figure 6.3c). The C content of the WFA was higher than the one of the PVWD and the WFA was the main contributor to the WI fraction (Table 3.3). In this way, the WI C of the blends containing the WFA was higher than the one of the PVWD alone (Figure 6.6b). The autotrophic/heterotrophic nitrification/denitrification (Bhattacharya & Mazumder, 2021) that took place in the PVWD (Figure 6.4d) could explain the similar trends of the WI N (Figure 6.4f) and WI C (Figure 6.6b). It should be noted that the concentration of WI C in the blends was 10 times higher than the content of WI N, thus the reaction kinetics (*e.g.* physicochemical sorption and microbial assimilation) of C were 10 times faster than the ones of N. The treatments involving acidification loss more C than the nitrification of the PVWD (Figure 6.7).

6.3.6. Mass balances and recovery effectiveness of C

The qualitative comparison of the mass balances of C (Figure 6.7) provided information for understanding the underlying chemistry of the blends. All the treatments which involved acidification decreased the C content after the 25 hours of incubation. The C provided by the WFA explain the greater amount recovered in these treatments. The adsorption of WS C_{org} onto the WFA could not be identified in the mass balances (Figure 6.7a,b). The WI C was the main form of C in all treatments, hence all conditions minimise the C losses *via* leaching after land application. The greatest recovery of C during the 144-h incubation was obtained for the PVWD alone (103.54 ± 43.49 %). The solubilisation of CO_3^{2-} and the release of CO_2 was considered the reason for the lower recovery of C when acid conditions were used to treat the PVWD. The trend of the PVWD found for C (Figure 6.7c) was like the trend found for N (Figure 6.5c). Therefore, the nitrification that took place after 48 hours of incubation of the PVWD (Figure 6.4d) enhanced the C recovery (Q. Wang *et al.*, 2014; J. Zhang *et al.*, 2015). It should be noted that more destructive samples were prepared for the beginning of the incubation and therefore, the characterisation of the treatments before the 48 hours of incubation has more weight in the calculation of the average recovery effectiveness.

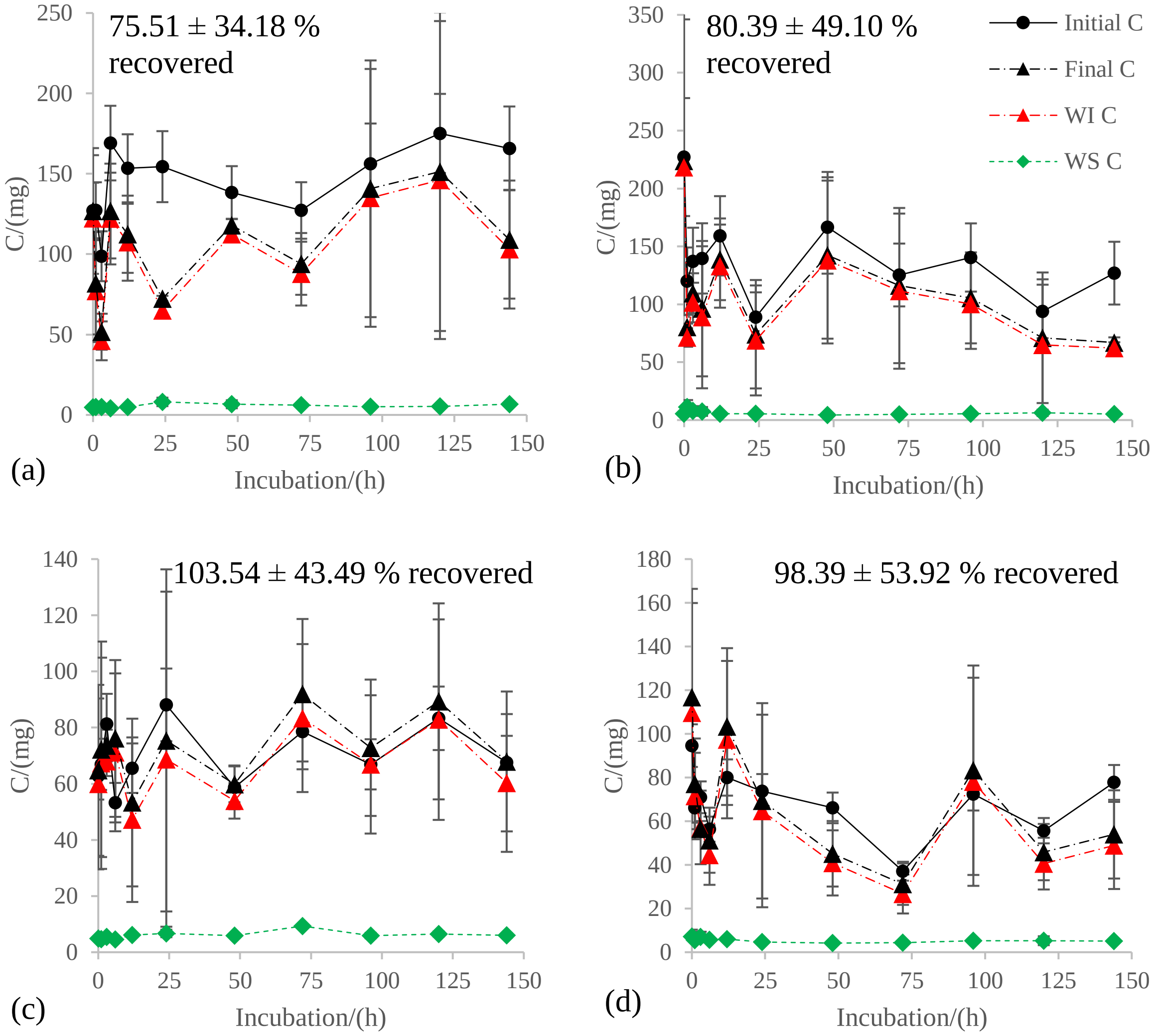


Figure 6.7. C mass balance for (a) HCl-WFA+PVWD, (b) HCl-WFA+HCl-PVWD, (c) PVWD and (d) HCl-PVWD blends (Table 6.1) during the 144 hours of incubation at 100 rpm for 20 ºC in the presence of a 0.11 M H_2SO_4 trap. Initial C stands for the calculated C introduced in the system (Figure 6.1a) at the beginning of the incubation, which depended on the mass of each blend (Figure A.20). Final C is the sum of the masses of WS C and WI C. The average values of the C recovery effectiveness over the whole incubation period is stated in each graph (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

6.3.7. P speciation

Figure 6.8 shows that the acidification significantly ($p < 0.05$) enhanced the solubility of P and decreased the concentration of WI P. This means that the quotient WS PO_4^{3-}-P/WI P for the HCl-PVWD (705.35 ± 486.70; Figure 6.8) was greater than for the PVWD alone (118.06 ± 104.24; Figure 6.8). The leaching problems associated with the acidification treatment of soil organic amendments are well-known because this is a common practice in farms (Fangueiro *et* *al.*, 2015). Generally, there are no losses of P during the storage of the organic amendments but a low availability of P at the time of land application would reduce contamination of surface and underground waters (Brennan *et al.*, 2012). The HCl-WFA treatment of the PVWD prevented the increase in P availability. The WS PO_4^{3-}-P/WI P found for the HCl-WFA+PVWD (119.53 ± 180.69; Figure 6.8) and the HCl-WFA+HCl-PVWD (179.47 ± 176.60; Figure 6.8) was like the one of the PVWD which underwent nitrification. Furthermore, the acidification of the PVWD without adding the WFA would lead to the acidification of the soil, if this material is used as fertiliser. It is expected an alkaline pH in the soil even after applying the blends of the PVWD and the HCl-WFA, due to the high content of basic elements in this material. The low pH of the HCl-WFA treatments enhances the absorption of the components of the blend into the soil. Thereby, the HCl-WFA treatment is a promising technology for improving the management of the nutrients in the PVWD because it safely increases the content of P (Figure 6.9) while preserving the NH_4^+-N.

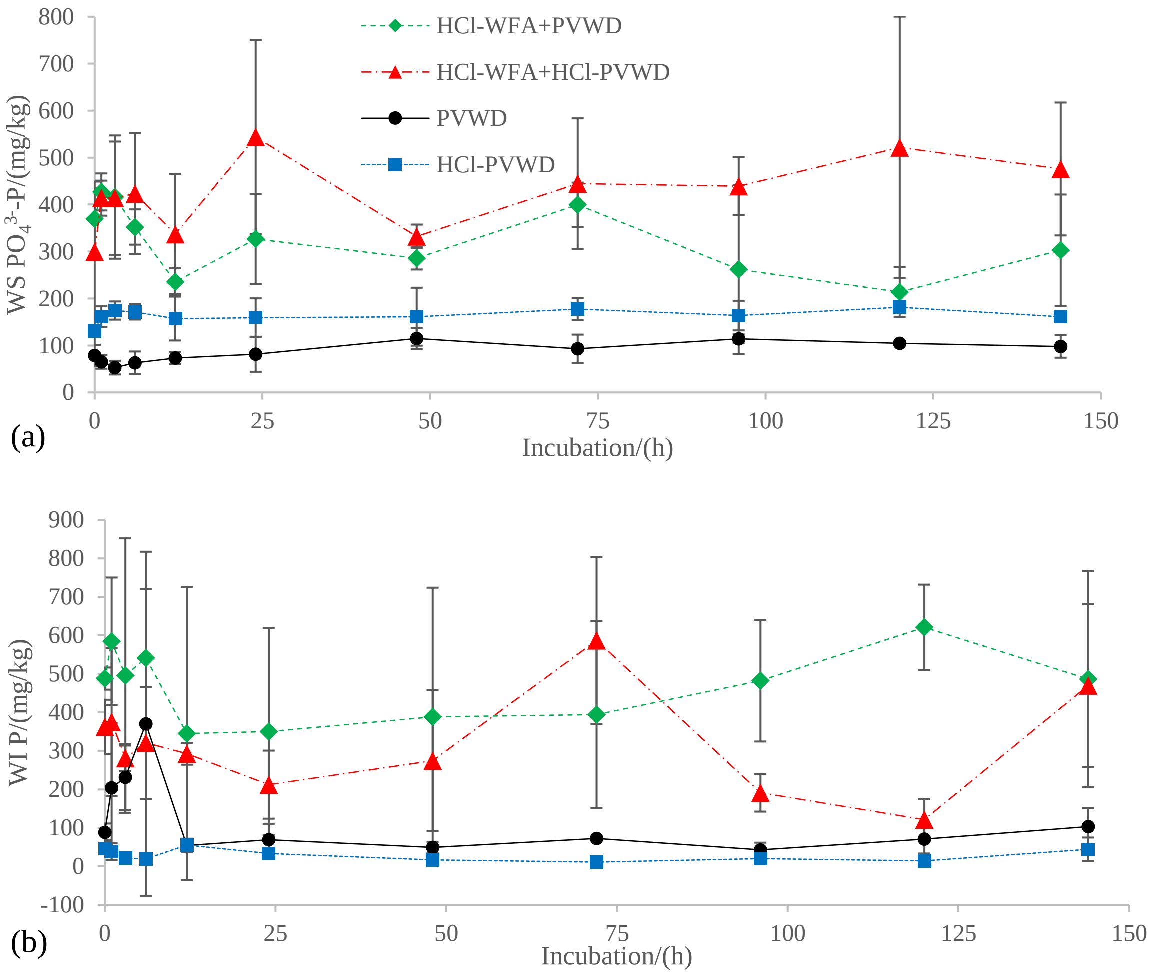


Figure 6.8. (a) WS PO_4^{3-}-P and (b) WI P in the HCl-WFA+PVWD, HCl-WFA+HCl-PVWD, PVWD and HCl-PVWD during the incubation at 100 rpm and 20 ºC in the presence of a 0.11 M H_2SO_4 solution in the trap (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

6.3.8. Mass balances and recovery effectiveness of P

Similar WS PO_4^{3-}-P to WI P ratios were found for the HCl-WFA+PVWD (1.20 ± 1.81 mg WS PO_4^{3-}-P/mg WI P; Figure 6.9a), the HCl-WFA+HCl-PVWD (1.79 ± 1.77 mg WS PO_4^{3-}-P/mg WI P; Figure 6.9b) and the PVWD (1.18 ± 1.04 mg WS PO_4^{3-}-P/mg WI P; Figure 6.9c). Therefore, the addition of the HCl-WFA to the PVWD and to the HCl-PVWD did not increase the availability of P. In fact, the blend HCl-WFA+PVWD had a significant ($p < 0.05$) decrease in P availability after the 72 hours of incubations (Figure 6.9a). The greatest enhancement in P availability was achieved in the HCl-PVWD (7.05 ± 4.87 mg WS PO_4^{3-}-P/mg WI P; Figure 6.9d). It was considered that the HCl-WFA treatments were the best way of improving the properties or the PVWD as controlled-release fertiliser.

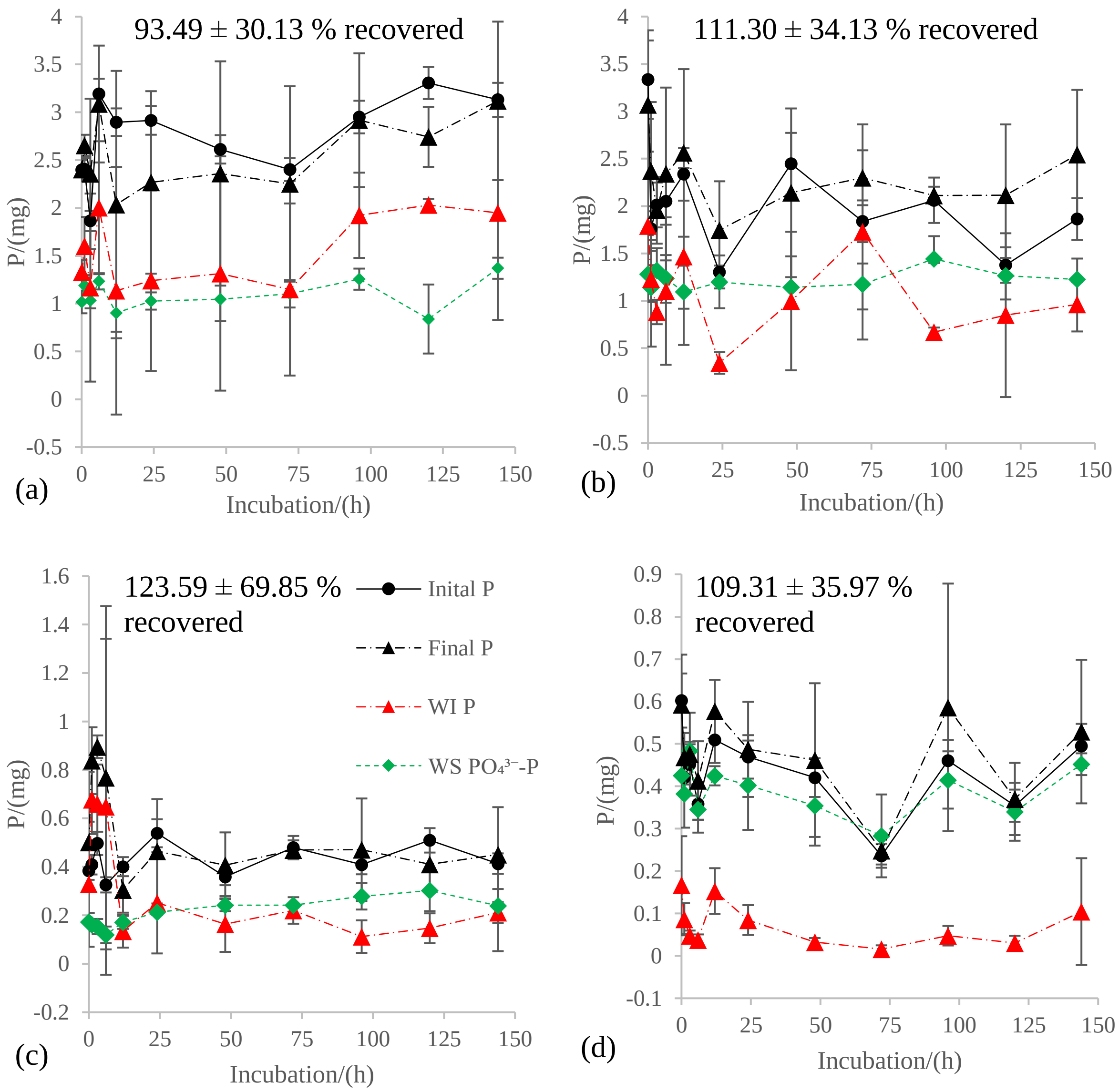


Figure 6.9. P mass balance for (a) HCl-WFA+PVWD, (b) HCl-WFA+HCl-PVWD, (c) PVWD and (d) HCl-PVWD (Table 6.1) during the 144 hours of incubation at 100 rpm for 20 ºC in the presence of a 0.11 M H_2SO_4 trap. Initial P stands for the calculated P introduced in the system (Figure 6.1a) at the beginning of the incubation and it depends on the mass of each blend (Figure A.20). Final P is the sum of the masses of WS PO_4^{3-}-P and WI P. The average values of P recovery effectiveness over the whole incubation period is stated in each graph (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

No gaseous losses of P were expected during the incubation at 20 ºC, since the volatilisation of phosphine (PH_3) was not feasible under any of those conditions (F. Yang *et al.*, 2019). Even during the AD, only trace levels of PH_3 are released (Y. Fan *et al.*, 2020). On the other hand, the losses of the P of the ash *via* gas exchange would be only possible during the incineration, when highly turbulent flue gases with particles, go through the gas treatment and ash collection systems (James *et al.*, 2012).

6.3.9. Nutrient ratio of each treatment

Among the 4 treatments investigated (Table 6.2), the greatest share of C was obtained for the PVWD alone because the nitrification preserved the C (103.54 ± 43.49 % accounted after the 144-h incubation; Figure 6.7c) and the N (115.10 ± 47.28 % accounted; Figure 6.5c) more than the treatments with hydrochloric acid. In this way, the PVWD which underwent nitrification had the greatest C/P because of the lack of CO_2 emissions and P supplementation. Although given the fact that most C of the PVWD was in the organic form rather than as CO_3^{2-}, the release of CO_2 because of the acidification did not represent a huge loss of C. For this reason, the C/N and the C/P of the HCl-PVWD were slightly lower than the ones of the PVWD.

Table 6.2. Nutrient ratios obtained in each treatment (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

Treatment	C/N	C/P
HCl-WFA+PVWD	10.99 ± 1.69	46.10 ± 26.30
HCl-WFA+HCl-PVWD	11.32 ± 1.70	46.79 ± 18.04
PVWD (nitrification)	12.91 ± 2.04	155.17 ± 54.71
HCl-PVWD	9.65 ± 1.28	138.57 ± 52.81

The HCl-WFA treatments reduced significantly ($p < 0.05$) the C/P of the PVWD, leading to a more balanced nutrient ratio that should minimise the requirements for mineral fertilisers. The HCl-WFA treatments were considered to be the most appropriate procedures for reducing the losses of the nutrients during storage and after land application of the treated PVWD. The assessment of different procedures for the activation of the WFA as sorbent before blending with the PVWD is required to minimise the need for acidification and reduce the cost of the wood ash-based treatment. For example, thermal activation of the ashes by means of calcination at 500 °C (Al-Mallahi *et al.*, 2020), followed by mild acidification (Astals *et al.*, 2021), would allow to prepare a controlled-release fertiliser with an appropriate pH for the targeted soil (Brennan *et al.*, 2012). In order to obtain more realistic results, it would be required the evaluation of the chemical stability of greater volumes of treated organic waste (*e.g.* 1,000

L) during larger incubation periods (*e.g.* 6 months), which resembles the conditions employed in the industry for the storage of these materials.

6.4.Conclusions

The treatment of the PVWD with the HCl-WFA was found to be the best technology to maintain the NH_4^+-N in the digestate, while preventing the increase in P availability. The ammonium is the preferred form of N for plants, hence using nitrification to treat the PVWD should lead to lower crop yields. The conventional treatment of the PVWD *via* HCl acidification increased P availability and leaching potential and the combination with the WFA is required. Due to the high content of BC in the WFA, this technology contributes to restore the soil as a natural C sink, upon application of the treated organic amendment to land. Alternative routes for the activation of the wood ash as sorbent, different from acidification (*e.g.* washing, calcination, milling and sieving; Table 2.6), need to be investigated to reduce the cost of the treatment of the anaerobic digestate.

7. Kinetic study of the stabilisation of an agroindustrial digestate by adding wood bottom ash

7.1. Introduction

Regardless of the apparent economic and environmental benefits of using anaerobic digestate as organic soil amendments, farmers continue to rely on mineral fertilisers for cultivation of crops and they consider digestate exclusively for grassland and pastures (Bougnom *et al.*, 2012; Insam *et al.*, 2009; Tur-Cardona *et al.*, 2018). Excessive use of inorganic fertilisers deteriorates soil health because the nutrients are only provided in a mineralised form (*i.e.* extremely mobile and bioavailable) ready for plant uptake, which leads to an increase in the salinity of the soil (Fernández-Delgado *et al.*, 2020). Using digestate as organic amendment was investigated as a solution to this problem (Hupfauf *et al.*, 2016; Sapp *et al.*, 2015). As previous works have demonstrated (Singh Brar *et al.*, 2015), the way to produce a digestate-based fertiliser, which is competitive with conventional inorganic fertilisers, would be to supplement the nutrients already present in digestate (de França *et al.*, 2021; Erraji *et al.*, 2021). Given the large production and chemical composition of ashes, including some type of these materials in a blended fertiliser with digestate could be an appropriate solution (Huotari *et al.*, 2015; Voshell *et al.*, 2018). Thereby, it is important to select the right type of ash as this determines the concentration of pollutants in the blend (Maresca *et al.*, 2017). In this respect, the use of biomass ash is widely accepted as could be liming agent for land reclamation (Fernández-Delgado Juárez *et al.*, 2020) because it generally presents lower pollutants levels than other ash streams (*e.g.* from coal burning). Richards *et al.* (2021) used wood ash was as a source of P, to decrease the C/N/P of an anaerobic digestate, which was rich in C and N. They found that the preparation of the mixture of wood ash and anaerobic digestate following a C/N/P of 23/3/1 improved utilisation of these elements by the microbial biomass, after applying the blend to the soil. Pristine wood ashes contain elements that might play a role on reducing the availability of the nutrients of the digestate, *via* sorption, thus improving the properties of the blend as slow-release fertiliser (Moure Abelenda & Aiouache, 2022). It was anticipated that this blended fertiliser would minimise the losses of nutrients *via* gaseous emissions and leaching. These improvements of the organic amendment intend to decrease the cost of handling the digestate, for example, minimising the requirements of covered storage facilities and low emission spreading equipment for application to land. A reduction of the pollution associated with the management of organic manures also implies that less chemical fertilisers to maintain high crop yield, as the fertilisation of the crops is done more efficiently.

In this chapter, the PVWD was treated by means of addition of the WFA. Considering the nutrient ratios found in the previous Chapter 6 (Table 6.2), the purpose of this treatment was to achieve a C/N/P < 40/4/1 in the blend WFA+PVWD. Moreover, the composition of the blend WFA+PVWD should be constant to meet this specification at all times in the supply & demand chain and to enable the commercialisation of the novel fertiliser. To assess the level of chemical stabilisation attained (Figure 2.4), the availabilities of N, C and P were monitored in the blend WFA+PVWD and the untreated PVWD. The incubations were carried out for 7 hours, straight after the blending of the WFA and the PVWD, in a closed chamber containing a H_2SO_4 trap, which aimed to account for the ammonia volatilisation.

7.2.Materials and methods

The two factors assessed in this chapter were the type of treatment (WFA+PVWD and PVWD) and the time of incubation (0, 1, 2, 3, 4, 5, 6 and 7 h). The PVWD alone was used as reference (*i.e.* experimental blank) to evaluate the effect of the WFA treatment. The two-factor ANOVA with replication was performed with Microsoft® Excel ($p < 0.05$) to decide whether the trends found for the blend WFA+PVWD and the PVWD were significantly different and to identify any significant change over the incubation time in the measured variables. The destructive sampling methodology led to the preparation of 64 experimental units (*i.e.* 2 treatments, each with 4 repetitions, to be measured over 8 incubations times) for this chapter. The WFA was used directly without any further treatment or activation, to enhance the sorption processes. The lower dose of WFA and low buffer capacity of the PVWD (Figure 4.1a,b), compared to experiments of Chapter 4 with FWD (Figure 4.5), aims to achieve a pH close to the pH_{zpc} of the WFA (Figure 4.3a,b) without the need for acidification. 10 g of ultrapure milli-Q® water was added to each gram of WFA and PVWD as fluidising agent and extractant to ease the preparation of the blend and to enable the analytical procedure after the incubation of each destructive sample (Table 7.1). The same procedure was followed for the preparation of the untreated PVWD before the incubation. The fluidised samples (39.86 ± 0.94 g of WFA +PVWD and 33.51 ± 0.84 g of PVWD; Table 7.1) were incubated under continuous 100 rpm shaking at 20 ºC. The closed chamber (Figure 6.1a) contained 4.38 ± 0.02 mL of a 0.11 M H_2SO_4 solution. A stoichiometric excess of H_2SO_4 was used to ensure all NH_3 released to the headspace could be captured. In addition, the continuous shaking aimed to minimise the mass transfer resistance and to enable the equilibrium between the 3 fractions of each treatment (*i.e.* [H_2SO_4], WS and WI fractions). A detailed description of the component of each treatment can be found in the Figure A.27.

Table 7.1. Treatments were characterised during the incubation at 100 rpm shaking and 20 ºC (Moure Abelenda *et al.*, 2021d).

Treatment	WFA/(g)				PVWD/(g)			
	Sample		Extractant		Sample		Extractant	
	µ	σ	µ	σ	µ	σ	µ	σ
WFA+PVWD	0.48	0.08	5.59	0.04	3.38	0.92	30.66	1.42
PVWD					3.10	0.85	30.41	0.07

µ = average value (n = 4); σ = standard deviation (n = 4)

After the incubation, the 7-mL vial containing the H_2SO_4 solution was easily removed and the [H_2SO_4] was isolated without any major loss. In addition to the determination of the [H_2SO_4] NH_4^+-N, the characterisation of the treatments was done in terms of WS and WI species. The solid-liquid separation of the destructive samples was done *via* 5 minutes centrifugation at 4,000 rpm and 3-µm filtration. The volume of the WS extract recovered after the incubation was measured in a 50-mL graduated cylinder. The parameters measured in the WS extract were WS NH_4^+-N, WS NO_3^--N, WS N, WS C and WS PO_4^{3-}-P. The WS N_{org} was estimated as the difference between the WS N and the sum of WS NH_4^+-N and WS NO_3^--N. The parameters measured in the WI material were WI N, WI C, WI P. The contents of C_{org} and P_{org} were estimated based on the nature of the samples. For example, a large fraction in organic molecules was expected in the PVWD while the WFA contain CO_3^{2-}-C or BC (Forbes *et al.*, 2006). The share of CO_3^{2-}-C in the PVWD and the WFA were estimated considering the results of Chapter 6 (Figure 6.6). High content of P_{org} was expected in the PVWD, as this is the main form of P in manures (McDowell *et al.*, 2021), but the PO_4^{3-}-P was the most abundant species in the WFA. As in the previous chapter, the availability was defined as the ratio of the WS form of an element to the WI form of that element. It is important to remark that the [H_2SO_4] NH_4^+-N was regarded as the most available form of N as this is the most prone to be lost in an open system, due to NH_3 volatilisation (Equation 3.3). The mass balances of N, C and P were established to determine the average recovery effectiveness of each element during the 7-h incubation. The percentage recovered was based on the initial amount of each element fed to the closed chamber at the beginning of the incubation (*i.e.* zero hours).

7.3.Results and discussion

7.3.1. Fractionation of the destructive samples of each treatment after the incubation

The destructive samples of each treatment were prepared with the components described in the Figure 7.1. The fractions of WFA+PVWD and PVWD recovered after the incubation are shown in Figure 7.1a,b. Most losses were due to the isolation of the fractions of WFA+PVWD and PVWD after the incubation (*i.e.* 3-μm filtration of the WS extract and 105 ºC drying of the WI material). Assuming that these losses were constant for all the destructive samples, greater evaporation occurred towards the end of the incubation. In this way, the longer the incubation at 20 ºC and 100 rpm, the greater the expected losses of moisture. Figure 7.1c and Figure 7.1d show that the losses of [H_2SO_4] increased after the 2 hours of incubation. Unlike the variation of the WS extract and the WI material, the changes in the [H_2SO_4] were expressed as losses with respect to the amount charge in the trap at the beginning of the incubation. Besides NH_4^+-N and moisture, none of the components of WFA+PVWD or PVWD could affect the mass of the [H_2SO_4]. The reason for the very low losses of [H_2SO_4] (0.02 ± 0.01 mg; Figure 7.1c,d) was the lack of filtration or drying to achieve the isolation and also the low pH of this fraction (0.78 ± 0.07; Figure 7.2a). According to the results of Ukwuani & Tao (2016), the boiling point decreases as the pH of the digestate increases. This could explain the greater losses of moisture of the WFA+PVWD blend (Figure 7.1a), which had a pH of 10.18 ± 0.34 (Figure 7.2b), compared to the evaporation of the PVWD (Figure 7.1b), which had a pH of 8.32 ± 0.12 (Figure 7.2b). Since the WFA has not received any activation treatment, it was unlikely that the decrease in the recovered volume of the WS extract (Figure 7.1e) was related to the adsorption of water (*i.e.* hydration) into the ashes.

A closer look to the WS extract (Figure 7.2e,f), revoke the hypothesis of greater losses of moisture at higher pH. Figure 7.2e shows that the significant (p-value 0.25) losses started at the 6 hours of incubation of the WFA+PVWD. On the other hand, the significant (p-value 0.10) losses of the WS extract of PVWD started at the second hour of incubation. The lower losses of the WS extract of the WFA+PVWD could be explained by the colligative properties of the aqueous solutions. Hence, the greater solute concentration in the WFA+PVWD, decreased the vapor pressure of the blend compared to the untreated PVWD. It should be noted that the reason for which the overall values of WS extract/sample are lower for the WFA+PVWD is because of the size of the sample (3.86 ± 0.94 mg) was greater than the PVWD alone (3.09 ± 0.85 mg), while the amount of milli-Q® water added as extractant was the same in both cases (30.42 ± 0.92 mg). Since there was lower moisture in the headspace of the WFA+PVWD, the loss of the [H_2SO_4] of the blend was more significant (p-value 0.07; Figure 7.2c) than the one of the untreated PVWD (p-value 0.88; Figure 7.2d).

The above explanations for the resulting masses of the [H_2SO_4] and WS fractions are based on different underlying phenomena (*i.e.* the pH of each treatment and the level nonvolatile of solute particles). Nevertheless, none of these explanations was essential to explain the distribution of the chemical species of N, C and P among the 3 fractions. In order to explain the outcomes of the mass balances of these elements (Figure 7.5), the most important explanation to the changes in the WI material (Figure 7.1g,h). Furthermore, greater drop in the amount of WS extract were found in the PVWD (Figure 7.1f). The reason is that, despite being the smallest fraction (Figure 7.1a,b), the WI material contained most of the nutrients (Figure 7.3 and Figure 7.4) and its variation had a greater impact in the overall fate of N, C and P. While the WI material of the WFA+PVWD remained constant (p-value 0.8783; Figure 7.1g), the WI material of the PVWD increased progressively (p-value 0.3138; Figure 7.1h).

The reason for the slight increase of the WI material recovered after the incubation (Figure 7.1f) could be that the DM of the PVWD changed because the first samples contained less fiber than the latter ones. The solid fraction rapidly settled to the flask in which the digestate was stored. Despite of the shaking, which was done every time before sampling, the DM of the PVWD would have built up in the flask in which the PVWD was stored. The constant amount of WI material in the WFA+PVWD (0.14 ± 0.03 mg; Figure 7.1g) could be related to the fact that the WFA was the main source of the WI material (95.88 ± 34.51 %), which hid the small increase of the WI material due to the heterogeneity of the PVWD (1.93 ± 0.81 %). As the WFA is 95.88 ± 34.51 % WI material and PVWD is only 1.93 ± 0.81 % WI material, the blend WFA+PVWD had 10 times more WI material than the PVWD alone (Figure 7.1g,h).

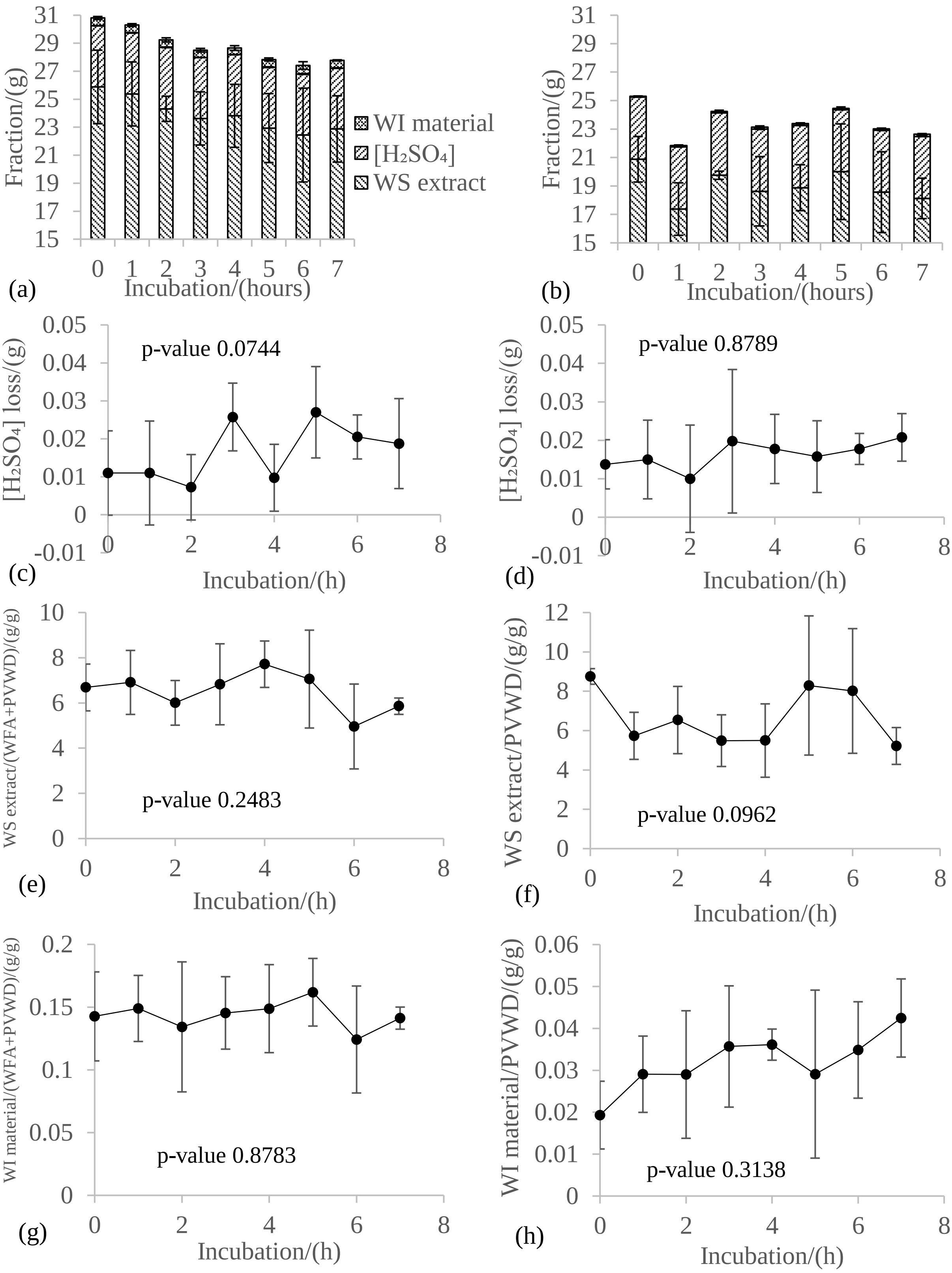


Figure 7.1. Fractions isolated after the incubation of (a) WFA+PVWD and (b) PVWD. Losses of the 0.11 M H_2SO_4 solution in the trap of the closed chamber used to incubate (c) WFA+PVWD and (d) PVWD. Changes in the amount of WS extract of (c) WFA+PVWD and

(d) PVWD. Changes in the mass of the WI material of (e) WFA+PVWD and (f) PVWD. P-values were calculated with the one-way ANOVA test (Moure Abelenda *et al.*, 2021d).

7.3.2. pH of the WS extract and the H_2SO_4 trap

Despite the clear difference in the pH of the blend WFA+PVWD and the PVWD (1.87 ± 0.22 difference expressed as units of pH; Figure 7.2a), the pH of the [H_2SO_4] fractions were similar (0.03 ± 0.01 difference in unit of pH; Figure 7.2b).

The initial pH of the H_2SO_4 solution used in the traps before incubation was 1.10 (n = 1) measured at 23.6 ºC. Since a 0.11 M H_2SO_4 solution is supposed to have a pH of 0.94, the dilution of the H_2SO_4 solutions would be required to prevent the underestimation of the pH, due to the upper detection limit of the Mettler Toledo® Seven Compact^{TM} S220 pH/Ion meter.

In fact, lower pH was found in the [H_2SO_4] (Figure 7.2b) in spite of the absorption of NH_3 (Figure 7.1a). The [H_2SO_4] was diluted eleven times (*i.e.* 10 mL of milli-Q® water were added to each mL of the H_2SO_4 solutions) to ensure a good contact of the liquid with the probe of the pH-meter. The pH in the undiluted [H_2SO_4] was calculated based on the concentration of the H^+ species in the 1/10 diluted H_2SO_4 solutions.

Only when the measurement was done directly in a reduced number of undiluted samples (*i.e.* only those that left with enough H_2SO_4 solution), an increase of the pH was noticed (Figure 7.2c) with respect to the initial pH of 1.10 (n = 1) determined at 23.6 ºC.

It was considered that the more accurate values were obtained when the H_2SO_4 solutions were diluted eleven times prior to the measurement of the pH. Thereby, to follow the absorption of NH_3 in the [H_2SO_4], the dilution of the H_2SO_4 solutions is required prior to carry out the measurement of the pH.

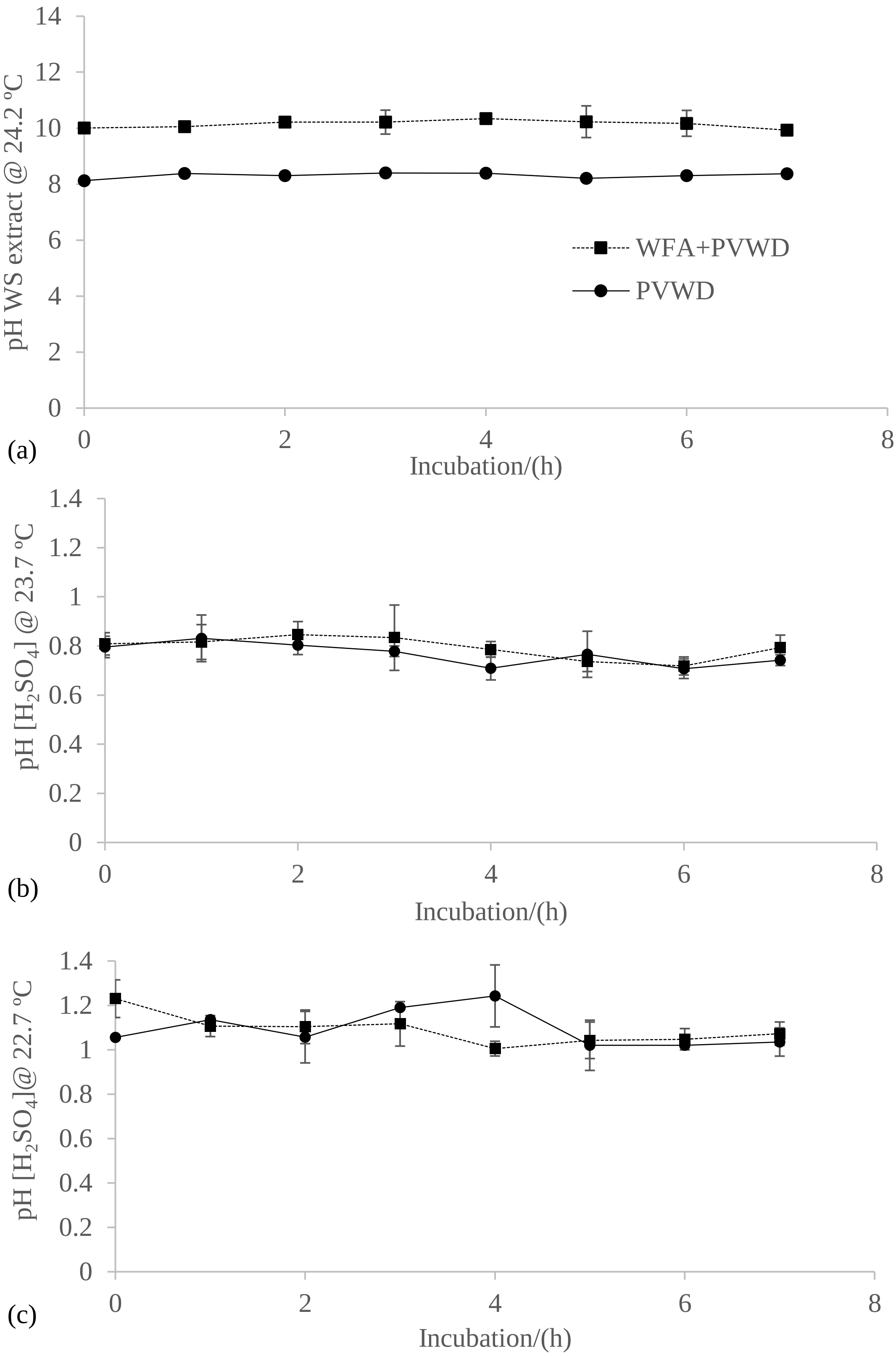


Figure 7.2. (a) pH of the WS extract of the blend WFA+PVWD and PVWD measured at 24.19 ± 0.11 ºC. pH of the [H_2SO_4] measured (a) at 22.71 ± 0.21 ºC after 11 times dilution with milli-Q water and (b) at 22.68 ± 0.26 ºC without prior dilution (Moure Abelenda *et al.*, 2021d).

7.3.3. N speciation

The greater volatilisation of NH_3 was found in the WFA+PVWD (Figure 7.3a), because the blend had higher pH (10.18 ± 0.34; Figure 7.2a) the PVWD alone (8.32 ± 0.12; Figure 7.2a). The low pH of the [H_2SO_4] (0.78 ± 0.07; Figure 7.2b) allowed the absorption of the NH_3 which was released to the headspace (*i.e.* reactive stripping). This process took place continuously during the 7 hours of incubation and the [H_2SO_4] did not reach the saturation (Figure 7.3a). By the 7th hour of incubation, the levels found were 33.84 ± 3.79 mg [H_2SO_4] NH_4^+-N/kg WFA+PVWD and 3.78 ± 0.82 mg [H_2SO_4] NH_4^+-N/kg PVWD. In Chapter 6, the 0.11 M H_2SO_4 trap reached the saturation at the 48 hours with a level of 65.79 ± 10.73 mg [H_2SO_4] NH_4^+-N/kg PVWD (Figure 6.1). Although the concentration of NH_4^+-N increased progressively in the [H_2SO_4], the drop in the concentrations of WS NH_4^+-N in the blend WPA+PVWD (95.35 ± 21.00 mg/kg; Figure 7.3b) and the PVWD (357.64 ± 54.10 mg/kg; Figure 7.3b) occurred at time zero. It could be possible to increase the rate of mass transfer of NH_3 towards the 0.11 M H_2SO_4 solution in the trap, by means of using a bubbling system to increase the surface area between the gas and liquid phases (L. Liu *et al.*, 2015; L. Zhang *et al.*, 2012). This would allow to completely achieve the equilibrium between the 3 phases of the blend.

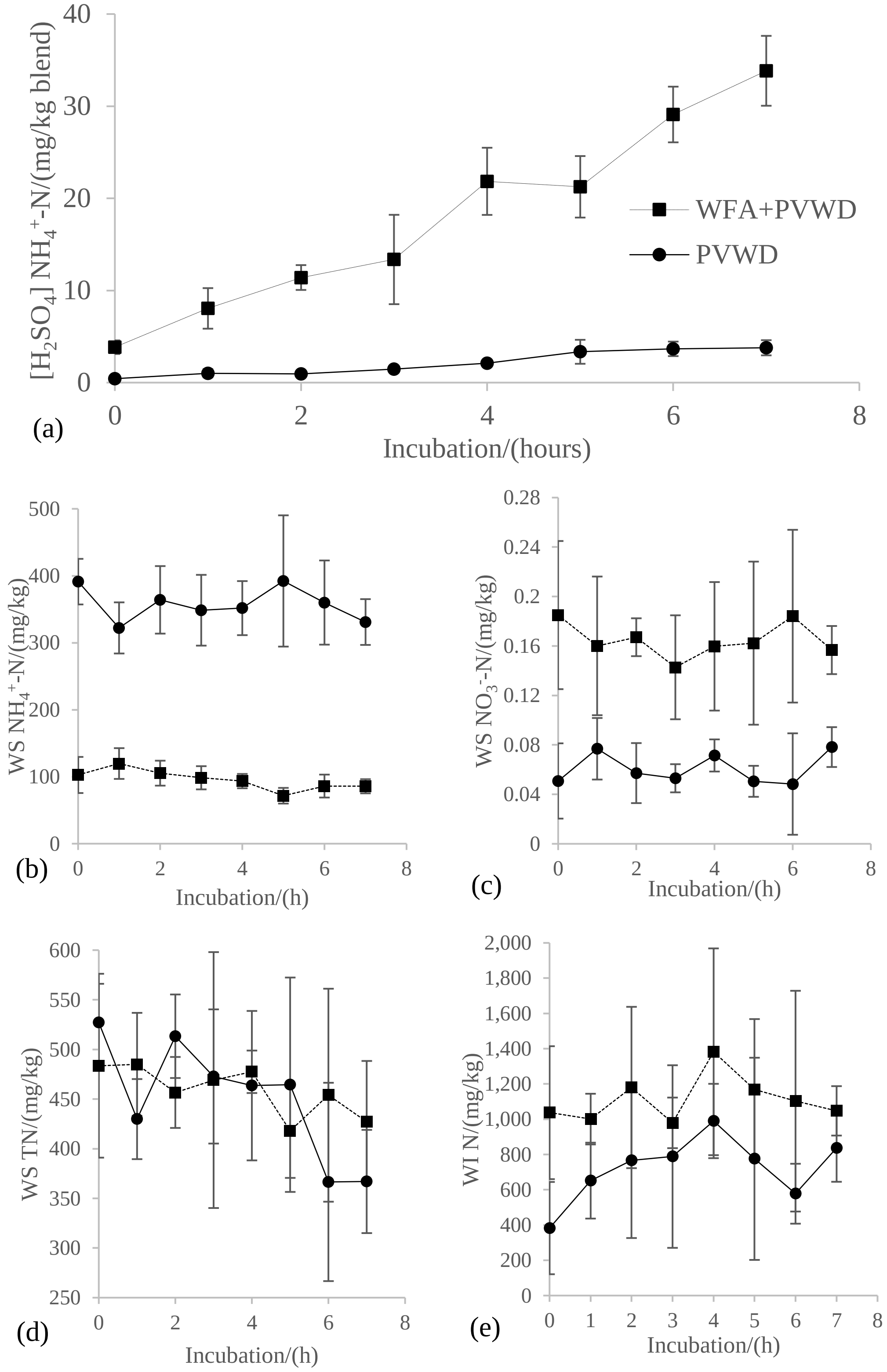


Figure 7.3. (a) [H_2SO_4] NH_4^+-N, (b) WS NH_4^+-N, (c) WS NO_3^--N, (d) WS N and (e) WI N in the blend WFA+PVWD and the PVWD during the 7-h incubation at 100 rpm and 20 ºC in the presence of 0.11 M H_2SO_4 trap (Moure Abelenda *et al.*, 2021d).

The [H_2SO_4] NO_3^--N concentration of the blend WFA+PVWD and the PVWD were below the detection limit of the Autoanalyzer^{TM}. The levels of WS NO_3^--N were significantly higher in the blend WFA+PVWD (0.16 ± 0.05 mg/kg; Figure 7.3c) than in the PVWD alone (0.06 ± 0.02 mg/kg; Figure 7.3c). The reason is that, although most N was lost as NO_x during the incineration of wood, what remained in the WFA was mainly in the form of NO_3^-. It should be noted that the concentration of WS NO_3^--N, was around 100 times lower than the concentration of [H_2SO_4] NH_4^+-N, which was the second less abundant N species in the blend. Therefore, the variations of WS NO_3^--N, and the potential emissions of N_2O *via* abiotic denitrification, were regarded as less relevant than the changes of WS NH_4^+-N and WS N_{org} during the assessment of the WFA-based treatment.

With the exception of the [H_2SO_4] NH_4^+-N, lower concentrations of all N species were expected in the blend WFA+PVWD compared to the PVWD. This assumption was based on the fact that the ash was not the main source of N in the blend (Table 3.3). Thereby, any addition of ash to the PVWD would result in a dilution of the N. The greater drop in the concentration of the WS NH_4^+-N in the blend WFA+PVWD, than in the untreated PVWD, could be associated as well with the adsorption onto the WFA. This phenomenon would be in agreement with the higher level of WI N found in the blend WFA+PVWD and the untreated PVWD (p-value 0.38; Figure 7.3e). The reason for the same levels of WS N in the WFA+PVWD and the PVWD (Figure 7.3d) could be that some of the particulate N was present in the WS fraction. This included the WS NH_4^+-N that was adsorbed onto the WFA and therefore was part of the WI TN, but it was also accounted as WS TN. The 3-µm filtration, which was performed to achieve the separation of the liquid from the solid fraction of the blend WFA+PVWD, did not completely remove the suspended solids from the WS extract. In this way, the colloidal particles with adsorbed NH_4^+-N remained suspended in the WS extract. This N was accounted as WS N by the TOC-L Shimadzu®, but the salicylate method of the Autoanalyzer^{TM} for the determination of WS NH_4^+-N was not able to measure the adsorbed NH_4^+-N.

Unless the WFA promoted the adsorption of the WS N, this raw material should contain 5,369.62 ± 3,555.03 mg WI N/kg for the blend of 13.12 ± 2.87 % of WFA and 86.88 ± 2.87 % PVWD (Table 7.1) to have initially 1,037.02 ± 376.97 mg WI/kg (Figure 7.3e). As per the decreasing WS N (Figure 7.3d) and the increasing WI N (Figure 7.3e) of WFA+PVWD, the adsorption might have continued during the 7 hours of incubation. Although the same profiles were found in the untreated PVWD, these were derived from the sampling error as it is explained in the section 7.3.5 about the mass balances of N, C and P.

7.3.4. Speciation of C and P

The blend WFA+PVWD had higher content of WS C than the PVWD (p-value 0.12; Figure 7.4a). This is because the WS C of the WFA was higher than the one of the PVWD (Table 3.3) and the blend WFA+PVWD should retain more C than the PVWD alone. Despite the greater concentration of WS C in the alkaline treatment (3,315.71 ± 557.08 mg/kg WFA+PVWD; Figure 7.4a) than that of the HCl-WFA+HCl-PVWD (2,111.48 ± 1,189.70 mg WS C/kg; Figure 6.6a), the amount of WI C (24,412.25 ± 8,991.15 mg/kg WFA+PVWD; Figure 7.4b) in the WFA+PVWD was lower than that in the HCl-WFA+HCl-PVWD (31,061.43 ± 11,616.77 mg WS C/kg; Figure 6.6b). Furthermore, the C distribution among the WS and WI fractions of the blend WBA+PVWD depending on the pH can be explained by an increase of the WS C sorption under acic conditions and by a minium shate (~ 0 %) of CO_3^{2-}-C both in the WFA and the PVWD. The alkaline pH promoted the solubilisation of C (Leechart *et al.*, 2009; Q. Wang et al., 2016) and based on the previous comparison with the C speciation of the blend HCl-WFA+HCl-PVWD evaluated in the Chapter 6, it is not possible to claim that WFA+PVWD has absorbed of the CO_2 of the headspace of the closed chamber. Despite the higher content of WI C in the WFA+PVWD than that in the untreated PVWD (p-value 0.26; Figure 7.4b), the availability of C (*i.e.* WS C/WI C) was slightly higher in the blend WFA+PVWD (0.14 ± 0.05; Figure 7.4a,b) than in the PVWD (0.10 ± 0.05; Figure 7.4a,b). However, it should be noted the consistent decrease of the WS C (Figure 7.4a) in the WFA+PVWD indicates that the equilibrium conditions have not been reached during the 7-h incubation. The pH 10.14 ± 0.32 (Figure 7.4a) around the pH_{zpc} of WFA (Figure 4.3a,b) might still promote the sorption of WS C.

These on-going phenomena could be related to the H_2SO_4 non-intrusive acidification, which removed the NH_3 form the headspace and created a greater concentration gradient. The H^+ ion that remained in the blend after the dissociation of the WS NH_4^+ and subsequent volatilisation of the NH_3, enabled the dehydration of the WI fraction (Zheng *et al.*, 2016) and promote the adsorption of the of the WS elements (Mor *et al.*, 2016; Zazycki *et al.*, 2018). The acidification is widely used to improve the management of anaerobic digestates, particularly to achieve the dewatering (Limoli *et al.*, 2016). However, the excessive and invasive acidification (*e.g.* using any acids employed in the agroindustry to improve the management of manures (Fangueiro *et al.*, 2015)) might enhance the emissions of CO_2. In the conditions of the closed chamber, the release of CO_2 and CH_4 from the WFA+PVWD blend were expected to be lower than the ones resulting from the handling of the untreated PVWD.

The concentration of WS PO_4^{3-}-P increased overtime in the PVWD while it decreased in the blend WFA+PVWD (Figure 7.4c). The opposite trend was found in the concentration of the WI P (Figure 7.4d). The apparent solubilisation of the P of the PVWD (Figure 7.4c) was due to sampling error as it is explained in the next section (7.3.5) about the mass balances of N, C and P. The high pH of the blend WFA+PVWD promoted the precipitation of the WS PO_4^{3-}-P, likely in the form of struvite, K-struvite (Huang *et al.*, 2017) and calcium phosphate (Cerozi & Fitzsimmons, 2016; W. Shi *et al.*, 2021), given the high content of Ca of the WFA (Table A.3 and Table A.5). The WFA decreased the availability of P in the PVWD from 0.64 ± 0.61 to 0.01 ± 0.00 mg WS PO_4^{3-}-P/mg WI P. Richards *et al.* (2021) confirmed that the WFA-treatment prevent excessive losses *via* leaching after land application. They applied a dose of WFA to the PVWD almost 10 lower than the dose used in this chapter (Table 7.1), to fertilise winter wheat at a rate of 26 kg P/ha, in agreement with the UK Fertiliser Manual RB209 (UK AHDB, 2021b, 2021a).

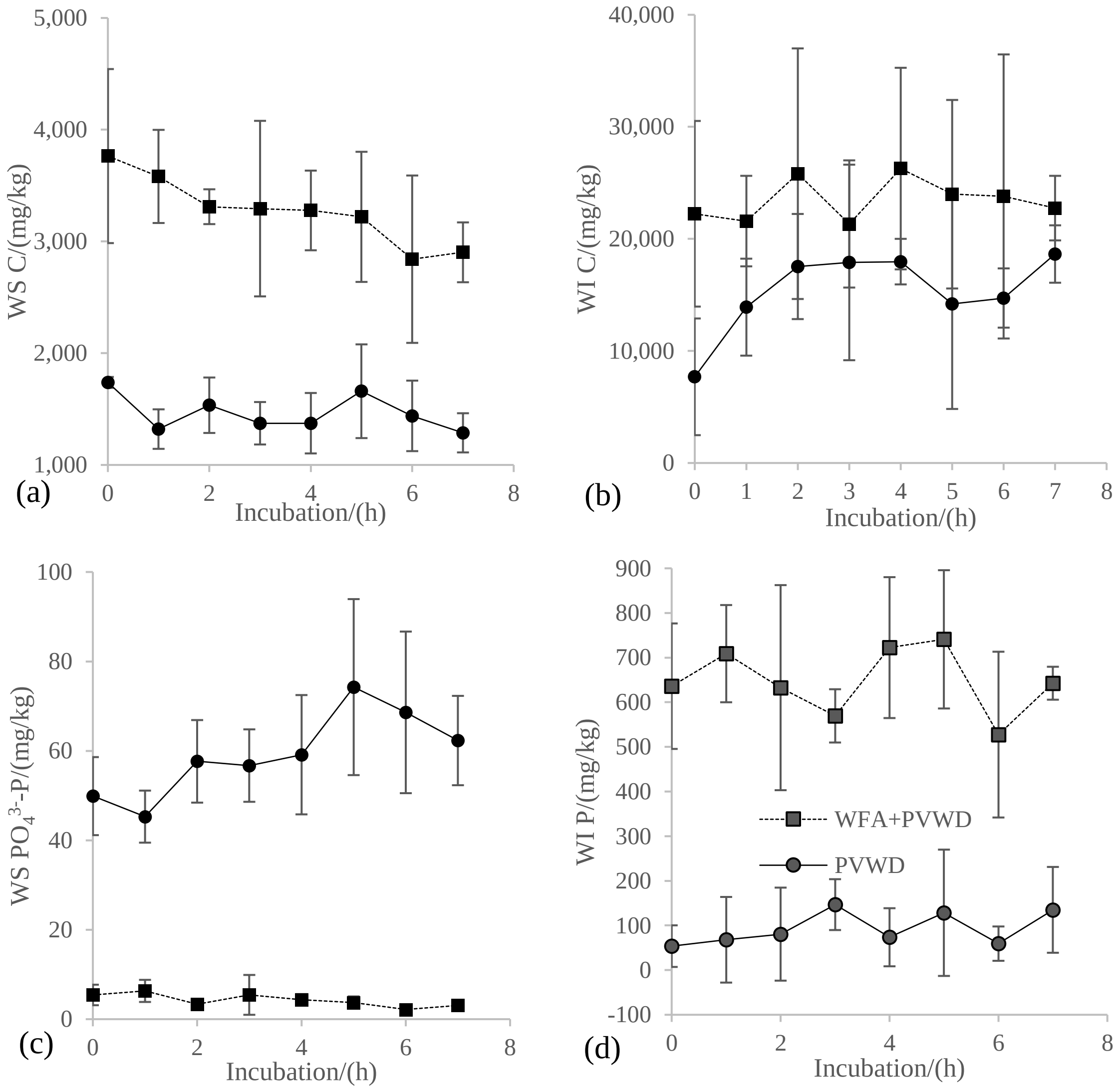


Figure 7.4. (a) WS C, (b) WI C, (c) WS PO_4^{3-}-P and (d) WI P of the destructive samples of the blend WFA+PVWD and the PVWD after the incubation at 100 rpm and 20 ºC (Moure Abelenda *et al.*, 2021d).

7.3.5. Mass balances of N, C and P

Both for the WFA+PVWD and the PVWD, most of N was in the form of WI N (4.07 ± 3.97 mg and 1.88 ± 1.16 mg; Figure 7.5a,b). Similar amount of WS N was found in the blend WFA+PVWD (1.74 ± 0.37 mg; Figure 7.5a) and the PVWD (1.37 ± 0.37 mg; Figure 7.5b). The amount of N trapped in the H_2SO_4 solution was negligible in both the incubation of WFA+PVWD (0.07 ± 0.05 mg; Figure 7.5a) and PVWD (0.01 ± 0.00 mg; Figure 7.5b) compared to the other N species. Since the closed chamber prevented the losses of N, the recovery effectiveness of this element during the incubation of the WFA+PVWD was 99.27 ± 0.29 % (Figure 7.5a). This means that almost all N initially fed to the closed chamber was accounted at the end of the incubation of each destructive sample of WFA+PVWD. The resistance of NH_3 transfer from the headspace to the [H_2SO_4] prevented the complete recovery due to low rate of absorption. Some NH_3 might have remained in the headspace at the end of the incubation.

The 112.84 ± 0.48 % (Figure 7.5b) N recovery effectiveness obtained during the incubation of the PVWD was due to the lower WI material of the destructive samples used to study the beginning of the incubation. The variation of the WI of PVWD can be seen in Figure 7.1h. The calculation of the N recovery effectiveness was based on the N initially fed to the closed chamber. If the final values were used instead, the N recovery effectiveness of the PVWD would be lower than 100 %. The homogenisation of the PVWD before sampling was done by means of stirring the 1-L container. However, the settling of the PVWD made that the destructive samples towards the end of the incubation had a greater WI material than at the destructive samples used to study the beginning of the 7-h incubation. Since the WI fraction contained most N, C and P (Figure 7.5), the changes in the DM affected significantly the nutritional value of the PVWD. This is a usual problem of sampling and emptying the lagoons where organic manures are stored (Boltianskyi *et al.*, 2016; McLaughlin *et al.*, 2014). It is important to highlight that even greater changes in the composition of the digestates would need to be taken into account when designing the process for handling this organic waste. The composition of the industrial digestates is affected not only by the seasonal feedstock of the AD plant but also by the storage, which can be up to 10 months according to the regulations of each country (Holm-Nielsen *et al.*, 2009). The use of the WFA enabled the production of a novel fertiliser with constant composition. The 95.88 ± 34.62 % WI matter of WFA was key to prevent the changes in the composition of the WFA+PVWD, due to sampling error affecting the 1.93 ± 0.81 % WI matter of the PVWD. Other benefit of using the WFA was that the total amount of N recovered was greater in the blend WFA +PVWD (5.84 ± 1.66 mg N; Figure 7.5a) than in the untreated PVWD (3.17 ± 1.34 mg N; Figure 7.5b).

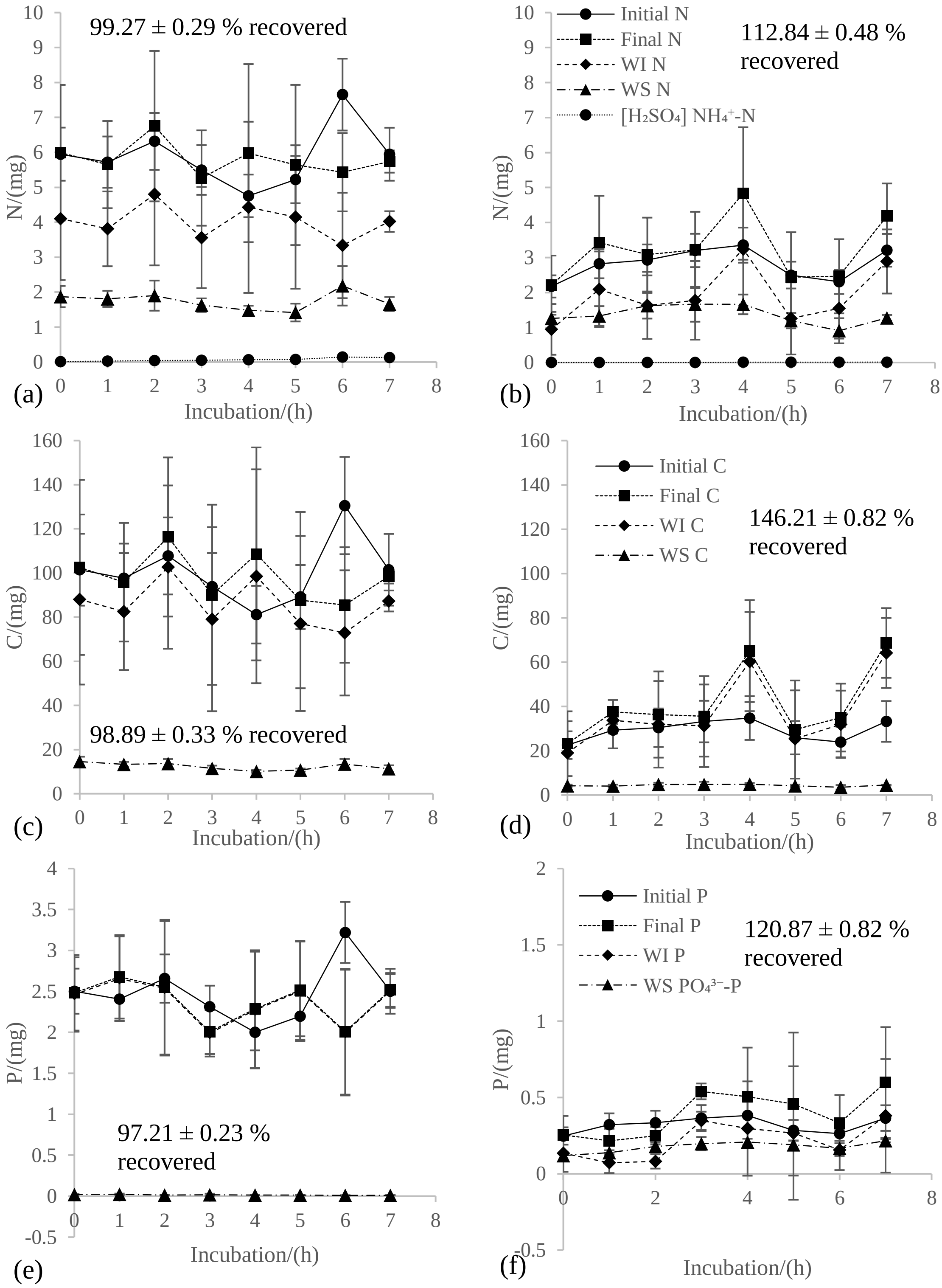


Figure 7.5. N mass balances of (a) WFA+PVWD and (b) PVWD. C mass balances of (c) WFA +PVWD and (d) PVWD. P mass balances of (e) WFA+PVWD and (f) PVWD during the 7-h incubation (Moure Abelenda *et al.*, 2021d).

The C recovery effectiveness during the incubation of the blend WFA +PVWD was 98.89 ± 0.33 % (Figure 7.5c). Therefore, the CO_2 from the atmosphere was not incorporated after the blending and there was not a progressive increase of C during the 7-h incubation. This should be the reason for which the C recovery effectiveness did not exceed 100 %, unlike in the case of the incubation of the untreated PVWD (Figure 7.5d). The excess of 46.21 ± 0.82 % of C measured during the incubation of the PVWD was related to the greater content of WI material of the destructive samples towards the end of the incubation (Figure 7.1h). Overall, the WFA provided the PVWD with 56.63 ± 40.04 mg C (Figure 7.5).

Almost the entire amount of P (97.21 ± 0.23 %; Figure 7.5e) initially fed to the closed chamber was accounted during the 7-h incubation of the blend WFA+PVWD. The recovery effectiveness during the incubation of the PVWD was 120.87 ± 0.82 % (Figure 7.5f) but 6.22 ± 4.42 times more P was present in the blend WFA+PVWD. The increase of the WI material towards the end of the incubation (Figure 7.1h) led to a change in the most abundant P species. It was unlikely that this effect was due to the adsorption of the WS PO_4^{3-}-P as the amount of this P species remained constant. As the profile of the WI P looks like the profile of the WI N and WI P, the possible adsorption of the WS P_{org} onto the digestate fibre was also discarded as a possible explanation. Contrary to what was expected, the amount of WS P_{org} in the PVWD should have been lower than the WS PO_4^{3-}-P, otherwise the WI material was not the richest P fraction (Figure 7.5f).

7.4.Conclusions

The preparation of the blend WFA+PVWD needs to be carried out in a system like the closed chamber, which allow to recover the NH_3 released. In this chapter, the limitation of scrubbing the NH_3 was found at the interface with the H_2SO_4 trap. This non-intrusive acidification, coupled with the composition of the WFA, might be responsible of some of the sorption processes and the chemical stabilisation of the PVWD. It was anticipated that the blend WFA+PVWD will behave as a controlled-release fertiliser after land application because the amount of N, C and P retained at the WI material was greater than in the untreated PVWD. The WFA-based treatment was successful in improving the composition of the PVWD to reach a C/N/P 40/4/1, which should favor a better performance in terms of enhancing the microbial activity in the soil. The C/N/P ratio of the blend WFA+PVWD and the untreated PVWD were 42.05 ± 9.88/2.48 ± 0.58/1 and 121.51 ± 57.18/9.94 ± 4.21/1. The more constant composition achieved with the addition of the WFA to the PVWD eases the commercialisation of the WFA+PVWD, as the same specifications of the blended fertiliser can be guarantee over different production batches. The conclusions of this chapter need to be applied cautiously when handling ashes and digestates of different nature. In the case of ash, its properties and composition does not only depend on the type of fuel but on the fraction (*e.g.* bottom, cyclone, electrostatic precipitator, filter bag, etc).

8. Evaluation of the physicochemical equilibrium of the blend of WFA with PVWD under different concentrations of H_2SO_4 in excess

8.1.Introduction

The commercialisation of waste-derived fertilisers is constrained by the level of contaminants (Huotari *et al.*, 2015). It might be easier to isolate the plant nutrients contained in the residues and sell them as conventional fertilisers (Bolzonella *et al.*, 2018). The addition of ashes to organic manures, such as anaerobic digestates, could be proposed for: (a) improving the properties of these organic amendments as fertilisers (Fernández-Delgado Juárez *et al.*, 2013); (b) reducing the greenhouse emission and P leaching associated to the management and use of these materials (Brennan *et al.*, 2015); (c) manufacturing of a granular fertilisers (Pesonen *et al.*, 2016); and (d) increasing the pH to promote the volatilisation of ammonia and subsequent capturing the NH_3 in a H_2SO_4 trap (Limoli *et al.*, 2016). The ammonium sulfate could be sold as liquid fertiliser (40 – 60 % $(NH_4)_2SO_4$ aqueous solution; (Cavalli *et al.*, 2017; Limoli *et al.*, 2016)) or as solid after crystallisation (Cavalli *et al.*, 2017; Ukwuani & Tao, 2016). On the other hand, the use of clean materials with low content of pollutants, such as biomass ash and agroindustrial digestate, enables the end-of-waste status and the marketability of the blend as bulk soil amendment (Johansson & Forsgren, 2020).

Mixing wood ash and agrowaste digestate to get an approximate C/N/P of 40/4/1 could enhance the use efficiency of these elements upon spreading the blend in the soil (Cattin *et al.*, 2021; Richards *et al.*, 2021). Given the high pH of the blend ash-digestate, this material could be used as liming agent (Voshell *et al.*, 2018), after the removal of the NH_4^+-N. This nutrient management strategy might offer better results than the preparation of the blend under acid conditions to promote the adsorption and to minimise the loss of NH_4^+-N (Figure A.19 and Figure 6.5a,b). In fact, Miranda el at. (2021) found that the direct addition of H_2SO_4 to a 4.5 % (w/v) blend of biochar and cattle slurry mitigated less the NH_3 emissions than just applying the 0.3 mL H_2SO_4 (98 %) to 50 g of cattle slurry to reach a pH 5.5. The stepwise mechanism of acidification, dehydration and adsorption or flocculation is widely used to improve the management of anaerobic digestates (Limoli *et al.*, 2016; Zheng *et al.*, 2016). This chapter analyses how the H_2SO_4 non-invasive acidification affects the alkaline stabilisation of a blend of WFA and PVWD in terms of: (a) NH_4^+-N recovery, (b) N, C and P availability and, (c) overall C/N/P. The severe H_2SO_4 non-invasive acidification was meant to decrease the amount of NH_3 in the gas phase and create a greater gradient of concentration, which would be enough to overcome the mass transfer resistance at the layer between the blend WFA+PVWD and the headspace. The H^+ that remains in the blend WFA+PVWD due to the dissociation of WS NH_4^+ (Equation 3.2) and subsequent volatilisation of NH_3 (Equation 3.3) might promote dehydration and adsorption processes affecting the availability of N, C and P, as might indicated the results of Chapter 7 (Figure 7.2a).

8.2.Materials and methods

For the preparation of the blend WFA+PVWD, the 10 mL of ultrapure milli-Q® water was added to each gram of sample before blending. A detailed description of the components of the blend WFA+PVWD is shown in the Figure 8.1.

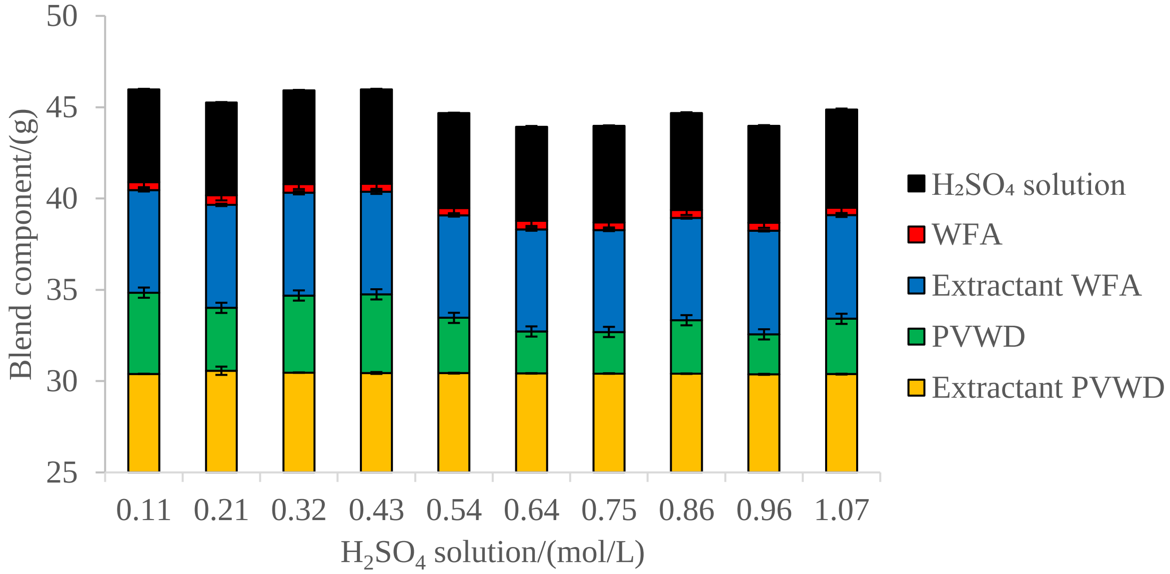


Figure 8.1. Detailed amounts of samples and extractant (ultrapure milli-Q® water) used for the preparation of the blend WFA+PVWD (Table 8.1) incubated in a closed chamber with different concentrations of H_2SO_4 in the trap Figure 8.2) (Moure Abelenda *et al.*, 2021a).

The 60-h incubation of the 39.71 ± 1.44 g fluidised blend WFA+PVWD was carried out under 100 rpm continuous shaking at 20 °C in a 250-mL (Schott Duran® bottle) closed chamber with a 5.21 ± 0.10 g H_2SO_4 solution to capture the NH_3 released, containing an aqueous solution of H_2SO_4 (Figure 8.2). To evaluate the effect of the non-intrusive acidification on the alkaline stabilisation of the blend WFA+PVWD, the following concentrations of H_2SO_4 were tested: 0.11, 0.21, 0.32, 0.43, 0.54, 0.64, 0.75, 0.86, 0.96 and 1.07 mol/L. The setup employed was a modification of the procedure developed by Velthof *et al.* (2005), who performed 90-day incubation of manures. At every sampling point, they refreshed the H_2SO_4 solution and flushed the bottle containing the manure with N_2 gas for 10 minutes, to avoid any interference of the previous NH_3 release in the next measurement. A similar procedure was followed by Van der Stelt *et al.* (2007) for a 223-day incubation of a dairy farm slurry. Destructive sampling was more convenient for this thesis due to the shorter incubation. In this way, 40 experimental units (*i.e.* 4 repetitions for each of the 10 H_2SO_4 non-intrusive acidifications) were prepared. This methodology also offered more realistic results about the potential of the H_2SO_4 non-invasive acidification to affect the composition of the blend WFA+PVWD. The way of conducting this experiment was based on a previous Chapter 7 and aimed that, by the end of the treatment, all the fractions of the blend were in equilibrium, including the H_2SO_4 fraction. It is important to mention that the stoichiometric amount required to capture all the N of the blend WFA+PVWD (Table 8.1) would correspond to a 3.43-mL solution of 0.11 mol/L H_2SO_4.

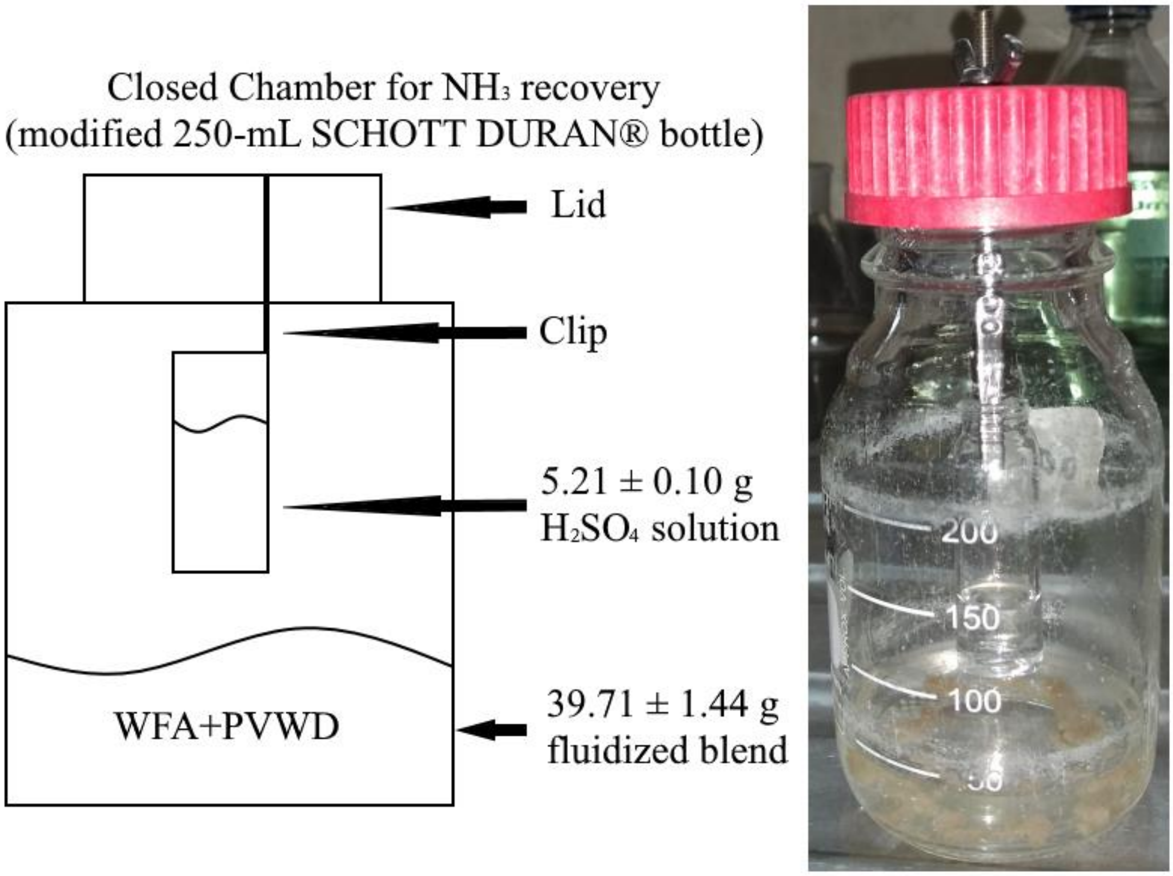


Figure 8.2. Experimental setup: Closed chamber for isolation of NH_4^+-N of the blend WFA+PVWD (Moure Abelenda *et al.*, 2021a).

Table 8.1 describes the first time-point of the blend WFA+PVWD assessed in Chapter 7. The composition of the blend WFA+PVWD is expressed in terms of the concentration of [H_2SO_4] NH_4^+-N, WS and WI species of N, C and P in fresh basis. In this chapter the trap effectiveness of stripping the NH_3 off the headspace was calculated as the ratio of [H_2SO_4] NH_4^+-N to N which could not be found in any of the WS and WI fractions. The one-way ANOVA was performed with Microsoft® Excel ($p < 0.05$) to decide whether the H_2SO_4 non-invasive acidification affected significantly the composition of the blend WFA+PVWD.

Table 8.1. Initial characterisation (first time-points of the blend WFA+PVWD of Chapter 7), expressed in a fresh basis, of a blend (n=4) of 0.51 ± 0.07 g WFA and 3.40 ± 0.41 g PVWD prepared in a closed chamber with a 4.39 ± 0.02 g trap of 0.11 mol/L H_2SO_4 aqueous solution. The amounts of milli-Q® water added to WFA and the PVWD were 5.58 ± 0.02 g and 30.43 ± 0.05 g, respectively (Moure Abelenda *et al.*, 2021a).

Parameter	Unit	Average	Standard deviation
DM	%	14.26	3.55
[H_2SO_4] NH_4^+-N	mg/kg	3.84	0.74
WS NH_4^+-N	mg/kg	102.59	26.96
WS NO_3^--N	mg/kg	0.18	0.06
WS N_{org}	mg/kg	380.83	96.43
WS N	mg/kg	483.60	92.59
WI N	mg/kg	1,037.01	376.97
WS C	mg/kg	3,763.92	778.70
WI C	mg/kg	22,243.23	8,283.15
WS PO_4^{3-}-P	mg/kg	5.42	2.30
WI P	mg/kg	636.01	140.53

8.3.Results and discussion

8.3.1. Fractionation of the blend after the incubation

The mass of the 5 mL acid solutions in the traps increased in agreement with the content in H_2SO_4 (Figure 8.3a). The 5 mL H_2SO_4 solutions of 0.64 and 0.96 mol/L had lower density than expected. The reason could be that in non-ideal solutions, the volumes are not strictly additive. However, the data reported by Hovey & Hepler (1990) did not agree with the excess partial molar volume in that range of concentrations for the mixtures of H_2SO_4 and water. On the other hand, it was unlikely that less volume or less concentrated H_2SO_4 solutions were used instead because these trends have not been seen in any of the other results of this chapter.

A volume of 17.11 ± 3.45 mL of WS extract was lost during the 60 hours incubation at 100 rpm and 20 ºC and subsequent filtration of the blends (Figure 8.3b). According to the ANOVA test ($p < 0.05$), there was not significant increase in the amount of WS fraction recovered when using H_2SO_4 solutions in the trap with greater concentration than 0.43 M. This effect would be explained by the neutralisation of the surface negative charges of the colloids of the PVWD by adding a cationic surfactant (Zheng *et al.*, 2016) or *via* intrusive acidification (Figure 6.2b), which make feasible their dehydration and flocculation. Similarly, the losses of WI material were 0.13 ± 0.05 g and did not show dependence on the concentration of the H_2SO_4 solution in the trap (Figure 8.3c). The explanation for the constant losses could be the procedure followed to achieve the solid-liquid separation. Some of the WI material would have remained stuck to the walls of the closed chamber and any weight gain due to the hydration of the ashes would have been lost during the drying at 105 ºC, before weighting the mass of the WI fraction recovered.

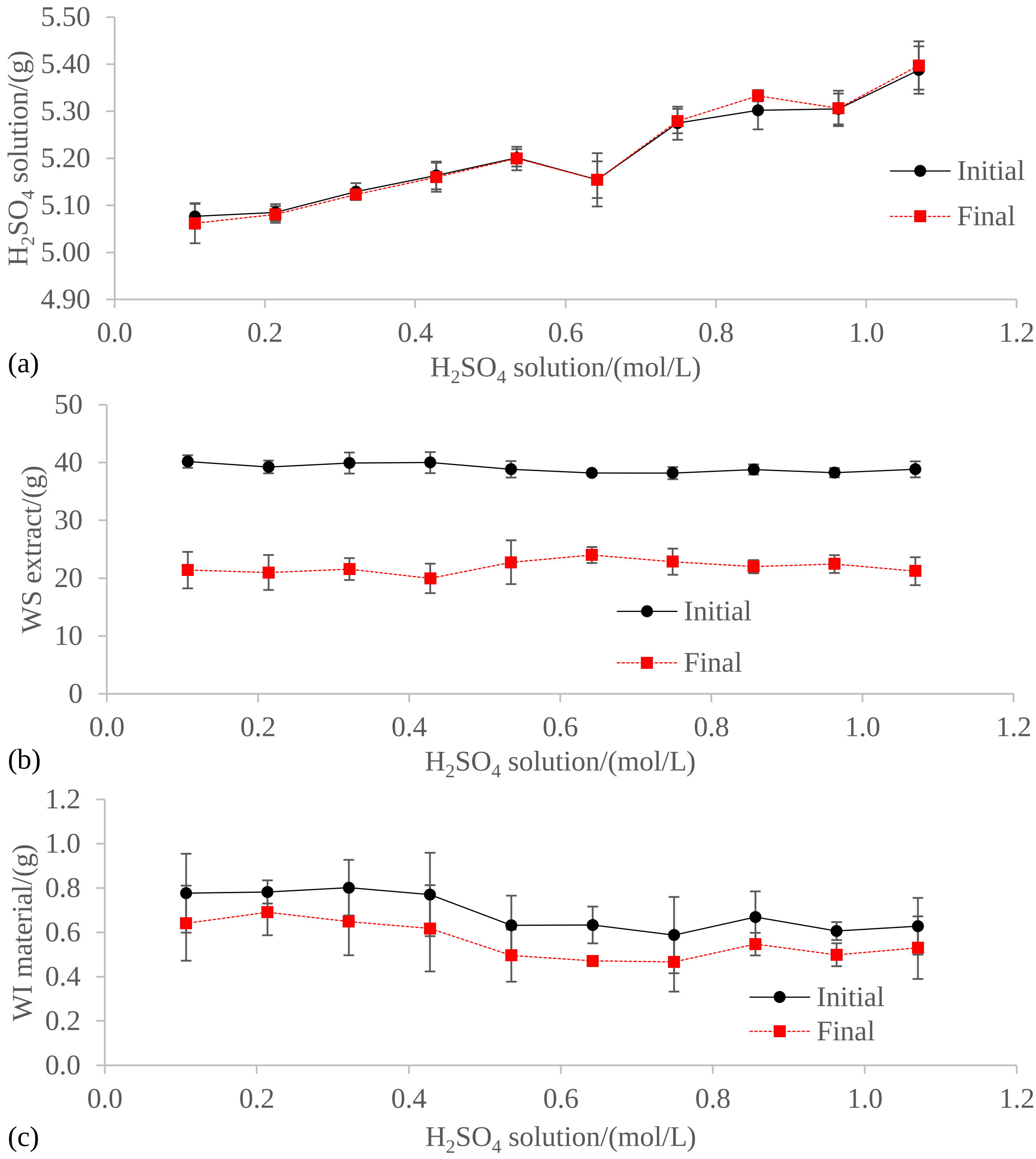


Figure 8.3. Initial (*i.e.* before the incubation) and final (*i.e.* isolated after 60 hours of incubation at 100 rpm and 20 ºC) masses of the fractions of the blend WFA+PVWD: (a) H_2SO_4 solution, (b) WS extract and (c) WI material (Moure Abelenda *et al.*, 2021a). The initial volume of the WS fraction was determined considering the moisture of WFA+PVWD (Table 8.1) and the milli-Q® water used to prepare the blend (Figure 8.1). The initial mass of WI material was assumed the DM of the blend (Table 8.1).

8.3.2. pH of H_2SO_4 trap and the blend WFA+PVWD

Since the volume of the traps were 5.21 ± 0.10 mL (Figure 8.3a), the pH of the H_2SO_4 solutions were measured directly (at 23.38 ± 0.36 ºC) and also after eleven times dilution, to ensure a better contact with the probe of the Mettler Toledo® Seven Compact^{TM} S220 pH/Ion meter.

For the second set of measurements, the pH in the undiluted traps was calculated by increasing an order of magnitude on the concentration of the H^+ species determined in the eleven times diluted H_2SO_4 solutions. The first thing that needs to be highlighted is that the pH decreased during the incubation. This is opposite to what was expected since the absorption of NH_3 should increase the pH of the H_2SO_4 solutions. Understanding why the pH of the trap decreased is important to enhance the absorption and recovery of the NH_3 in the headspace. It could be possible that the pH of the trap decreased because of the evaporation of the water and subsequent increase in the concentration of H^+ ions. However, the losses of the mass of the traps were negligible. It should be noted that, even when the pH decreased during the incubation, greater values than the initial ones were obtained. For example, the 1.07 M H_2SO_4 solution should have a pH lower than zero (*i.e.* -0.03) before the incubation and the value measured was 0.74 ± 0.02. After the incubation, the calculated value of pH from the measurements in the eleven times diluted (1/10) H_2SO_4 solutions (0.03 ± 0.06; Figure 8.4a) was lower than the values measured in the undiluted traps (0.45 ± 0.05; Figure 8.4a). Thereby, these calculated values of the pH could be considered more accurate than the values of the pH obtained from the direct measurements of the H_2SO_4 solutions after the incubation. Therefore, the H_2SO_4 solutions needed to be diluted for the measurement of the variations in the concentrations of the H^+ species due to the upper detection limit of the pH-meter.

The pH of the blend WFA+PVWD was not affected by the level of non-invasive acidification (10.40 ± 0.46; Figure 8.4b).

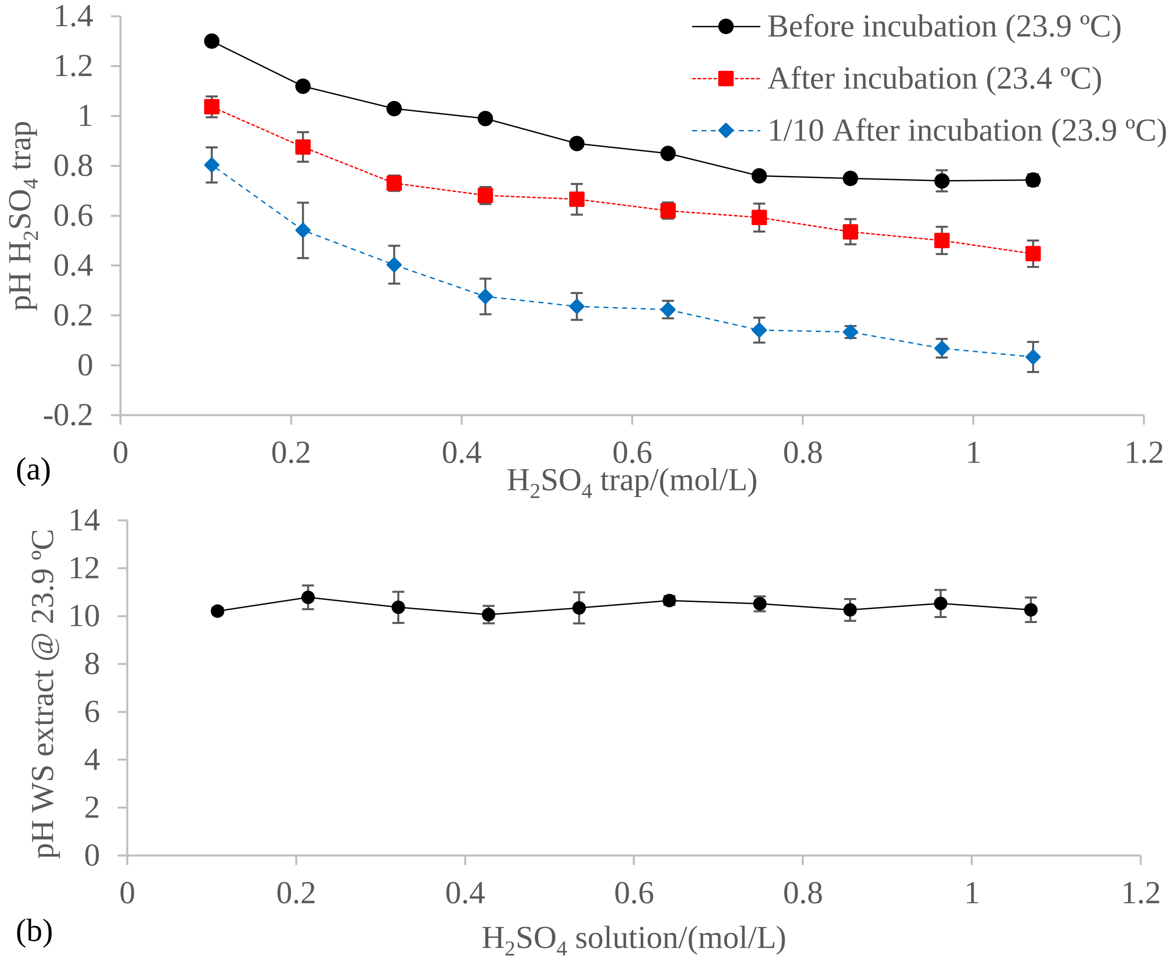


Figure 8.4. (a) pH of the 5.21 ± 0.10 mL H_2SO_4 traps (Figure 8.3a) measured before the incubation at 23.93 ± 0.18 ºC, eleven times diluted (1/10) with milli-Q® after the incubation at 23.90 ± 0.16 ºC and without dilution after the incubation at 23.38 ± 0.36 ºC. (b) pH of the 21.92 ± 0.15 mL (Figure 8.3b) extract of the blend WFA+PVWD measured at 23.91 ± 0.15 ºC (Moure Abelenda *et al.*, 2021a).

8.3.3. N speciation

The [H_2SO_4] NH_4^+-N was the only N species that increased significantly ($p < 0.05$) with respect to the initial characterisation (Table 8.1). The concentrations of WS NH_4^+-N (83.45 ± 56.99 mg/kg; Figure 8.5a), WS NO_3^--N (0.18 ± 0.06 mg/kg; Figure 8.5b), WS N (463.91 ± 87.99 mg/kg; Figure 8.6a) and WI N (1,030.87 ± 185.20 mg/kg; Figure 8.6a) did not change significantly regarding the initial characterisation (102.59 ± 26.96 mg WS NH_4^+-N/kg, 0.18 ± 0.06 mg WS NO_3^--N/kg, 483.60 ± 92.59 mg WS/kg and 1,037.01 ± 376.97 mg WI N/kg; Table 8.1). High [H_2SO_4] NH_4^+-N was expected because of the low pH of the H_2SO_4 solutions in the trap (0.29 ± 0.24; Figure 8.4a) were able to absorb the NH_3 available in the headspace. The effect of the non-intrusive acidification can be seen in Figure 8.5a, which shows increase (23.69 ± 5.72 %) in [H_2SO_4] NH_4^+-N and decrease (41.08 ± 17.46 %) of WS NH_4^+-N when the concentration of the H_2SO_4 solution in the trap was increased from 0.11 mol/L to 1.07 mol/L. Furthermore, Figure 8.3b shows the increase in the amount of WS fraction due to the presence of a H_2SO_4 trap with a concentration greater than 0.43 M. This significant dehydration of the WI fraction has a p-value of 0.16. In Chapter 6, in which the WFA was acidified with a 1.82 mol/L aqueous solution of hydrochloric acid before mixing it with the PVWD, a level of 1,968.90 ± 588.36 mg WI N/kg blend (HCl-WFA+PVWD) was reached (Figure 6.4f). Since lower concentration of WI N was found in the blend WFA+PVWD of this chapter, the H_2SO_4 non-invasive acidification did not promote the adsorption of WS N as much as the HCl intrusive acidification.

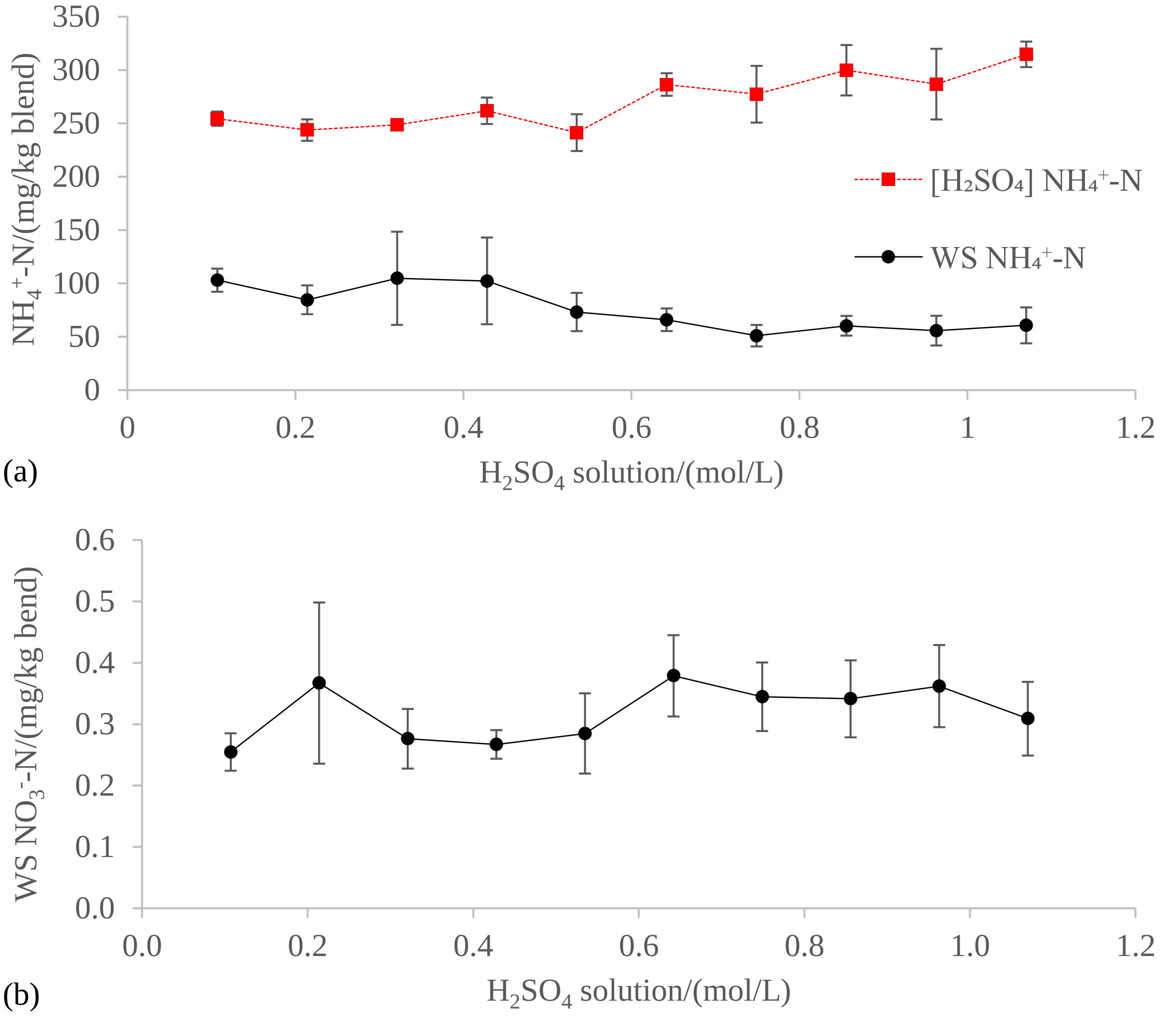


Figure 8.5. (a) [H_2SO_4] NH_4^+-N and WS NH_4^+-N and (b) WS NO_3^--N in the blend WFA+PVWD after a 60-h incubation at 100 rpm and 20 °C with different concentrations of H_2SO_4 in the trap of the closed chamber for scrubbing the NH_3 off the headspace (Moure Abelenda *et al.*, 2021a).

A calibration procedure is typically required for measuring the concentration of NH_3 in the air using H_2SO_4 solutions (Ndegwa *et al.*, 2009). Nevertheless, in this chapter, the trap effectiveness in all the conditions evaluated was 100 % (*i.e.* all the NH_3 released to the headspace was absorbed in the H_2SO_4 solutions in the trap) and what limited the depletion of the WS NH_4^+-N, was the mass transfer resistance at the film between the fluidised blend and the gaseous phase. This constant value of trap effectiveness was calculated without considering the amount of H_2SO_4 used, which ranged from 0.05 ± 0.00 g to 0.54 ± 0.01 g of H_2SO_4. Otherwise, there would be a difference of one order of magnitude between the effectiveness of the less concentrated and the most concentrated traps.

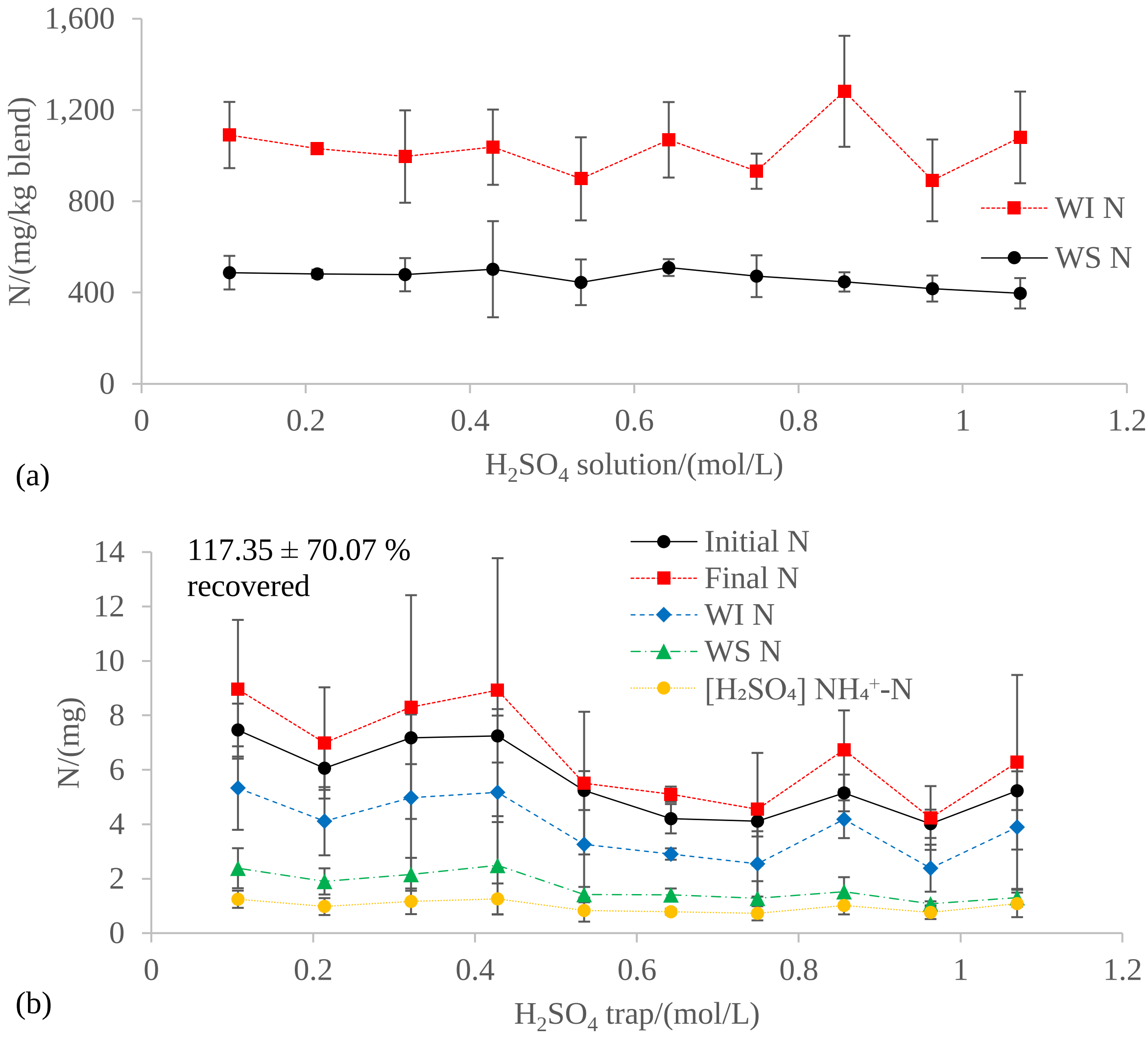


Figure 8.6. (a) WS N and WI N in the blend WFA+PVWD and (b) mass balance of N after a 60-h incubation at 100 rpm and 20 °C with different concentrations of H_2SO_4 in the trap of the closed chamber for scrubbing the NH_3 off the headspace. The overall recovery effectiveness of N is shown in the graph b (Moure Abelenda *et al.*, 2021a).

The concentration of the H_2SO_4 trap did not affect the volatilisation of NH_3 from the blend WFA+PVWD. Similar amounts of [H_2SO_4] NH_4^+-N were found in all the conditions evaluated (0.99 ± 0.38 mg; Figure 8.6b). Most of N recovered was in the form of WI N and only the 15.52 ± 2.13 % of N accounted after the incubation was in the form of [H_2SO_4] NH_4^+-N. The overall recovery effectiveness of N was 117.35 ± 70.07 % (Figure 8.6b), as more N was accounted after the incubation than in the initial characterisation. Most of the volatilisation of NH_3 took place immediately after the blending (Figure 3.4) and the absorption in the H_2SO_4 trap continued progressively during the course of the incubation, due to the mass transfer resistance (Figure 7.3a). Thereby, in processes with short contact time between the gas and the H_2SO_4 solution, it might be convenient to use bubbling systems to increase surface area between the two phases and thus the rate of transfer of NH_3.

As the WFA+PVWD blend had a pH of 10.40 ± 0.46 (Figure 8.4b), the 90 % of the WS NH_4^+-N was in the form of NH_3 (Fangueiro *et al.*, 2015). The closed chamber continuously shaken at 100 rpm was not enough to enable the equilibrium between the three fractions of the blend WFA+PVWD. This setup was chosen for its low capital and operating cost but the use of an excess of H_2SO_4 in the trap could not be justified technically and economically. It might be possible to attain the depletion of the WS NH_4^+-N in the blend WFA+PVWD using advanced equipment, which allow to operate at higher temperatures under vacuum conditions (*e.g.* 65 ºC and 25.1 kPa; (Ukwuani & Tao, 2016)) or perform hydraulic cavitation (Taşdemir *et al.*, 2020). Another processing option would be to reduce the moisture content of the blend, for the production of the granular fertiliser. As the surface area of the dewatered material is greater than the fluidised blend WFA+PVWD (Figure 2.6), the emissions of ammonia increase (Dinuccio *et al.*, 2012; Kavanagh *et al.*, 2019; Pesonen *et al.*, 2016).

8.3.4. C speciation

Similarly to N, most of the C was in the WI form (Figure 8.7a). Despite the variability of the results of WI C obtained with H_2SO_4 traps with concentrations greater than 0.54 M, there was clear difference between the concentration of the WI and the WS species of C. The level of WS C (4,022.26 ± 883.39 mg/kg blend; Figure 8.7a) and WI C (25,350.70 ± 185.20 mg/kg blend; Figure 8.7a) after the incubation was the same as in the initial characterisation (3,763.92 ± 778.70 mg WS C/kg blend and 22,243.23 ± 8,283.15 mg WI C/kg blend; Table 8.1). Therefore, the H_2SO_4 non-intrusive acidification did not promote the adsorption of the WS C_{org} onto the WFA, the release of CO_2 or emission of volatile organic molecules. It is important to mention that Ukwuani & Tao (2016) reported the flux of other compounds different from NH_3, such as cyclohexene, towards the H_2SO_4 trap. In this chapter, the concentration of the H_2SO_4 solution in the trap was not responsible of any phenomena which affected the distribution of C between the fractions of the blend WFA+PVWD and did not affect the C recovery effectiveness after the incubation. The alkaline pH (Figure 8.4b) of the blend prevented C losses and the recovery effectiveness after the incubation was 114.53 ± 50.68 % (Figure 8.7b), which could be related to the fact that the blend was a sink of carbon. It should be noted that the distribution of the C_{org} among the WS and WI fraction of the WBA+PVWD was better (*i.e.* greater WI C/WS C) when the blend was prepared under acid conditions (*i.e.* HCl-WFA+HCl-PVWD). In order to apply acid conditions in the preparation of the blend of wood ash and anaerobic digestate, it is necessary to select samples with low CO_3^{2-}-C, such as WFA and PVWD, otherwise large CO_2 emissions can be expected. This explains the lower C recovery effectivess of the HCl-WFA+HCl-PVWD (80.39 ± 49.10; Figure 6.7b) compared to the WBA+PVWD (114.53 ± 50.68; Figure 8.7b).

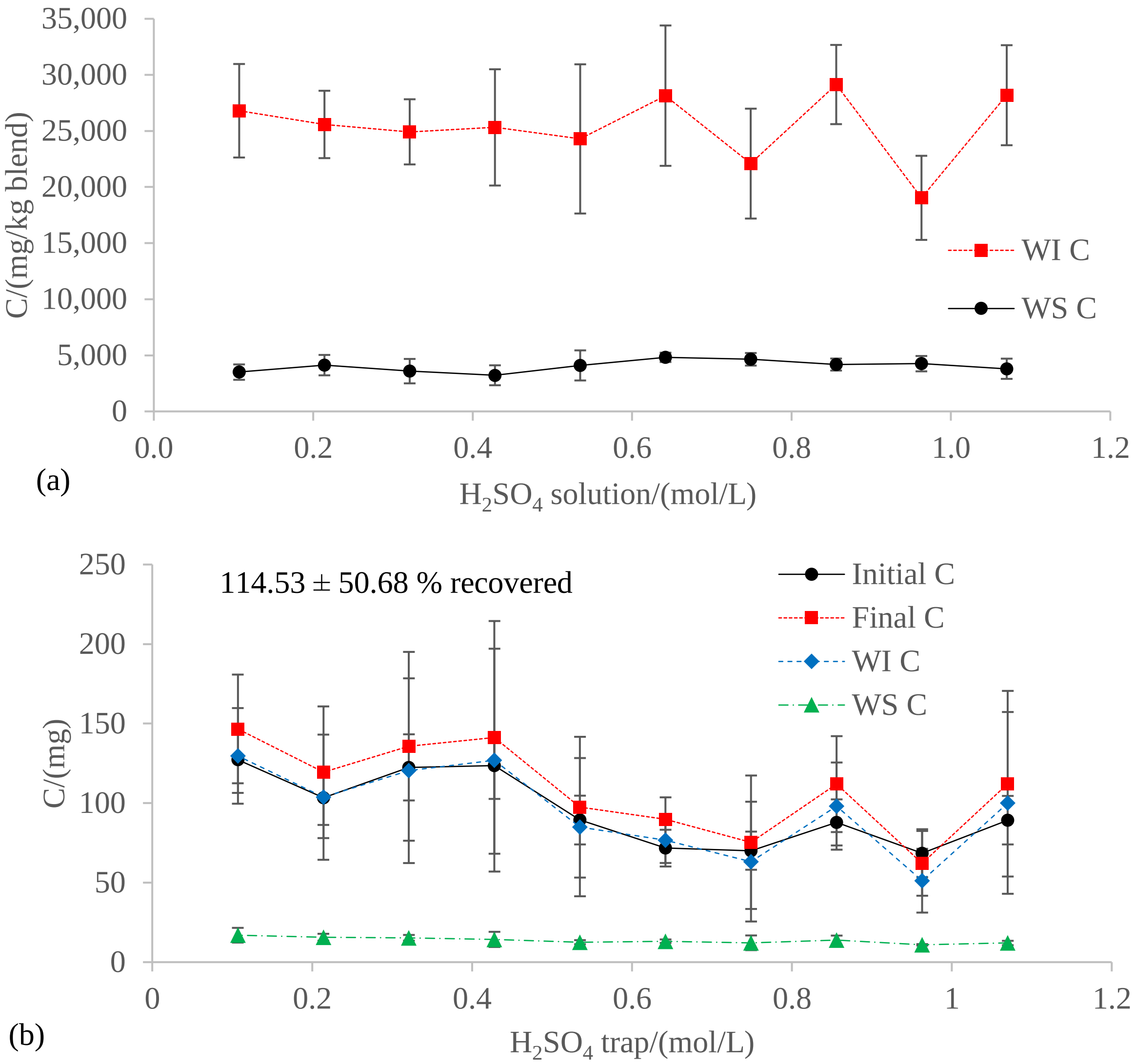


Figure 8.7. (a)WS C and WI C in the blend WFA+PVWD and (b) C mass balance after the 60-h incubation at 100 rpm and 20 ºC with different concentrations of H_2SO_4 in the trap of the closed chamber for capturing the NH_3 in the headspace. The overall C recovery effectiveness is shown in the graph b (Moure Abelenda *et al.*, 2021a).

8.3.5. P speciation

The concentration of WS PO_4^{3-}-P (3.75 ± 1.45 mg/kg; Figure 8.8a) and WI P (792.88 ± 218.92 mg/kg; Figure 8.8a) after the incubation was the same as before the incubation (5.42 ± 3.84 mg WS PO_4^{3-}-P/kg and 636.01 ± 140.53 mg WI P /kg; Table 8.1). Thus, most of the P was in the form of WI P, regardless the concentration of the H_2SO_4 solution in the trap. Both the fact that there were no losses of P *via* gaseous emissions in the studied conditions and the adsorption of the WS P_{org} could explain the 114.60 ± 27.94 % of average recovery effectiveness (Figure 8.8b). Any change in the amount of adsorbed WS P_{org} would be accounted by the colorimetric analytical method (*i.e.* molybdenum blue reaction) followed. The reason is that the sulphuric-peroxide digestion of the WI fraction led to the formation of WS PO_4^{3-}-P, which was measured with the segmented flow analysis. The availability of P went from 0.0083 ± 0.0021 mg WS PO_4^{3-}-P/mg WI P at the beginning of the incubation to 0.0048 ± 0.0015 mg WS PO_4^{3-}-P/mg WI P at the end. This tiny difference in the availability could prevent losses *via* leaching in an open system, for example, when applying P to land at a rate of 26 kg/ha (Richards *et al.*, 2021).

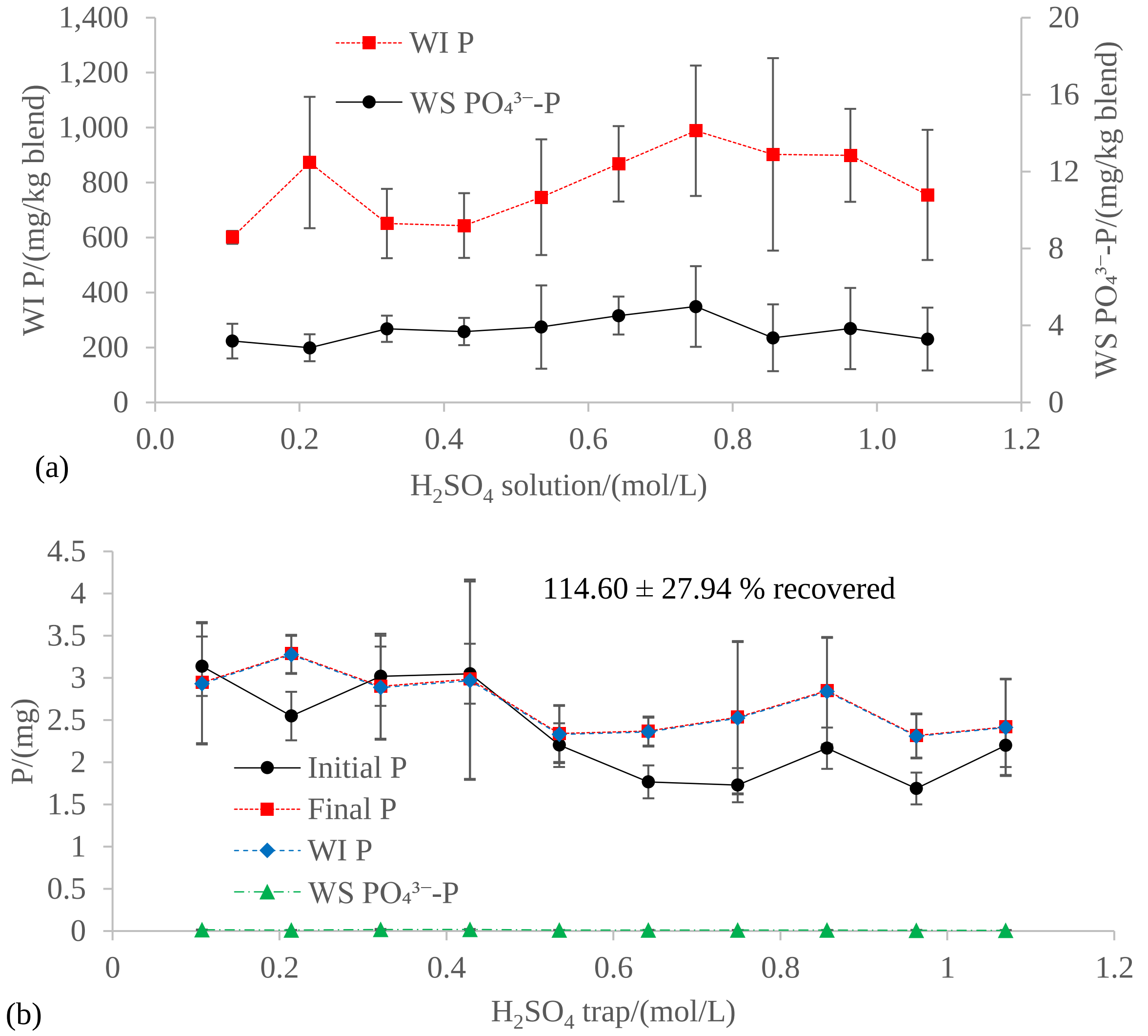


Figure 8.8. (a) WS PO_4^{3-}-P and WI P of the blend WFA+PVWD and (b) P mass balance after the 60-h incubation at 100 rpm and 20 ºC with different concentrations of H_2SO_4 in the trap of the closed chamber for stripping the NH_3 in the headspace. The overall recovery effectiveness of P is shown in the graph b (Moure Abelenda *et al.*, 2021a).

The fluctuations of the amount of WI N (Figure 8.6b), WI C (Figure 8.7b) and WI P (Figure 8.8b) were related to the size of the system (Figure 8.1) and the losses during the incubation and subsequent isolation of this fraction (Figure 8.3c). The relatively small variations seen in the WS N, [H_2SO_4] NH_4^+-N, WS C and WS PO_4^{3-}-P could be explained by the fact that less amount of N, C and PO_4^{3-}-P ended up in the WS extract.

8.4.Conclusions

Exceeding the H_2SO_4 non-intrusive acidification beyond the stoichiometric limit was not an efficient way of stripping the WS NH_4^+-N off the blend WFA+PVWD. The depletion of the NH_3 in the headspace of the closed chamber and the turbulence created with the 100 rpm rotary mixing did not sort out the bottleneck of NH_3 transfer from the WFA+PVWD blend to the gas phase. Advanced processing conditions (*e.g.* vacuum thermal stripping and hydraulic cavitation) or dewatering of the blend are required to increase the rate of NH_3 volatilisation. Although a 10-time increase of the concentration of the solution in the trap resulted in 23.69 ± 5.72 % more [H_2SO_4] NH_4^+-N, this only represented an increase of 3.57 ± 2.05 % in the overall fate of N in this fraction. The C/N/P 38.74 ± 17.56/2.38 ± 0.69/1 found after the incubation was the same as the intended C/N/P 40.55 ± 15.72/2.38 ± 0.80/1 (Table 8.1), as there was no losses during the treatment. The greatest share of these elements was found in the WI fraction and the WS P_{org} was more susceptible to be adsorbed under the studied conditions than the WS N_{org} and WS C_{org}. This controlled-release fertiliser should minimise the GHG emissions, eutrophication of underground waters upon land application and pollution swapping. Activating the WFA as adsorbent, for example *via* calcination at temperatures greater than 500 ^oC, could improve the valorisation of PVWD by enhancing the retention of nutrients in the WI fraction of the blend.

9. Conclusions and recommendations for future work

This PhD project has been able to test and to optimise the conditions for wood ash-based treatment of the anaerobic digestate to attain the chemical stabilisation (Figure 2.4) and prepare slow-release fertilisers with balanced nutrient ratio (C/N/P 40/4/1). Based on the literature review provided in Chapter 2, the optimum dose of wood ash that maximises the synergies in the upstream (i.e. pretreatment and conditions of the feedstock to enhance the biogas production) and the downstream (e.g. nutrient recovery and dewatering) processes of an AD plant was considered to be up to 5 g TS wood ash/g TS digestate. The features of wood ash that promote the best sorptive properties were identified: (a) source of Mg as oxide rather than hydroxide or CO_3^{2-} and (b) C content. Among the simple activation procedures available (*i.e.* carbonisation, carbonation, calcination, acidification, wash, milling and sieving), the acidification was reagarded as the best route for the valorization of wood ash.

The cheapest and simplest approach of combining the 4 raw samples (FWD, PVWD, WFA and WBA) to prepare 2 different blends was tested in the Chapter 3. The key parameters were found to be the NH_4^+-N of the anaerobic digestate and the share of wood ash in the blends. The greater maturity of the FWD made this material less chemically stable than the PVWD and more proned to lose NH_4^+-N *via* volatilisation of NH_3. This phenomenon also had a direct relation with the content of wood ash in the blends, which was responsible of the alkalinisation and immobilisation of the WS PO_4^{3-}-P. The smaller particle size and greater BC content of the WFA, compared to the WBA, also determined the speciation of C, N and P. The optimum pHs, which were found in the Chapter 4, to enhance the role of WFA and WBA as sorbents were 11.90 ± 0.50 (Figure 4.3a,b) and 12.43 ± 0.06 (Figure 4.3c,d). The pH_{zpc} was found to be the most economically viable blending conditions to promote sorption processes becasue it can be attained by mild acidification of the anaerobic digestate with commercial doses of H_2SO_4, HCl and HNO_3, before the addition of the wood ash. The pH trends observed in the preparation of blend of 80% FWD and 20 % WFA could only be explained by the sorption of the NH_4^+-N, wich imply good management of N. The washing of the wood ashes with ultrapure milli-Q water was evaluated as a cheap strategy to reach the pH_{zpc} upon blending with the anaerobic digestates and the overall pH decrease after 432 hours of washing were 4.69 ± 0.29 % and 5.30 ± 0.66 % for the WFA and the WBA, respectively (Figure 4.6).

Chapter 5 contains the detailed analysis of the 2 strategies proposed in the previous Chapter 4: (a) the addition of the WBA to the acidified PVWD; (b) acidification of the WBA and the

PVWD separately before the blending. As elucidated in the Chapter 3, the greatest drop of N due to NH_3 release took place when adding the WBA to the PVWD. The drop of NH_4^+-N was minimised by acid conditioning of the WBA (i.e. severe acidfication) before mixing this material with the acidified PVWD. However, the severe acidification of the WBA led to CO_2 release with more 80 % of C being lost, although normal levels of CO_3^{2-}-C were restored after the blending with the acidified PVWD (Figure 5.4d). In the case of P, the greater sorption of WS PO_4^{3-}-P (Figure 5.2c) was found at the pH_{zpc}. The HCl was regarded as the best acidification agent because it did not increase the content of WI material of the wood ash during the conditioning stage and it was not a source of N_2O emissions.

Unlike in the previous studies (Chapter 3 to Chapter 5), Chapter 6 relied on a closed chamber at 20 ºC and 100 rpm to evaluate the impact of the HCl-WFA based treatment on the composition of PVWD and directly determine the NH_4^+-N in the gaseous phase ($[H_2SO_4]$) of the blend. Based on the profiles of the N species in the different fractions, a stepwise mechanism for the untreated PVWD was proposed: Once the maximum level of $[H_2SO_4]$ N was reached in the trap (*i.e.* 58.47 ± 20.50 mg $[H_2SO_4]$ NH_4^+-N/kg PVWD; Figure 6.4a) at the 48 hours, the nitrification started until reaching the maximum level of (155.73 ± 30.26 mg/kg PVWD; Figure 6.4d) at the 96 hours and subsequently denitrification took place. The lowest levels of $[H_2SO_4]$ N were found for the HCl-WFA+HCl-PVWD and the HCl-PVWD, thus these treatments minimised the volatilisation of NH_3. The HCl-WFA treatment performed better in terms of management of C and P, compared to the HCl-PVWD. The HCl-PVWD promoted CO_2 release but high content of BC in the WFA increased the WI C upon addition to the PVWD. On the top, the HCl-WFA treatment of the PVWD did not increase the availability of the P, hence it did not promete the leaching, as it occurred in the HCl-PVWD. The WS PO_4^{3-}-P/WI P found for the HCl-WFA+PVWD (119.53 ± 180.69; Figure 6.8) and the HCl-WFA+HCl-PVWD (179.47 ± 176.60; Figure 6.8) was like that of the untreated PVWD.

In the Chapter 7, the pH_{zpc} was reached with the non-invasive acidification (i.e. NH_3 volatilisation) and with a lower dose of the WFA (1.69 ± 0.54 g TS WFA/g TS PVWD). The rate of increase of $[H_2SO_4]$ NH_4^+-N was approximately 8 times higher in the case of WFA+PVWD, compared to the untreated PVWD. The H_2SO_4 trap did not reach saturation during the incubation for 7 hours, despite the higher rate of release of ammonia from the blend PVWD+WFA. In Chapter 8, a 60-h incubation of the blend WBA+PVWD was performed in closed chambers using concentration of H_2SO_4 up to 10 times higher than in the two previous studies (Chapter 6 and Chapter 7). Chapter 8 shows levels as high as 0.99 ± 0.38 mg $[H_2SO_4]$

NH_4^+-N, comparable to the WS N. Most N was in the WI phase and the recovery effectiveness of the N was improved, compared to the values found in Chapter 7. The WFA provided the BC but the WI C in the blend WFA+PVWD was lower than in the HCl-WFA+HCl-PVWD, which was tested in Chapter 6, because the alkaline pH promoted the solubilisation of C. Unlike the WS PO_4^{3-}-P of the untreated PVWD, which increased during the incubation (Figure 6.8a and Figure 7.4c), the treatement with WFA was able to maintain a reduced availability of P during the whole 60-h incubation (Figure 8.8).

Based on these outcomes, it was proposed the following concepts as future work to design more sustainable processes, complying with the green chemistry principles of minimum input of energy and resources, to produce recyclable products:

- Addition of minimum amount of wood ash in the anaerobic digester to enhance the biogas production and subsequent increase the share of the stabilising agent once the anaerobic digestate leaves the fementor.
- Assessment of the impact of a greater dose of ash on the content of pathogens of the granular fertiliser and the mechanical properties of the pellets (*e.g.* durability).
- Assessment of doses of wood ashes to optimise all the steps of the process, in order to link the chemical and the physical stabilisations for the production of a granular fertiliser (Figure 2.4).
- Systematic approach for testing different activation techniques of the wood ashes as sorbents (Table 2.7).
- Combination of the anaerobic digestion with hydrothermal technologies (e.g. hydrothermal carbonization and hydrothermal liquefaction) to increase the yiled of biofuel and take advantage of the use of wood ash-alike materials (e.g. hydrochar) for the processing of the anaerobic digestate.
- Direct comparison between the effects of the pH_{zpc} obtained with mild acidification of the anaerobic digestate before the addition of the wood ash and the use of a lower amount of wood ash to treat the unacidified digestate.
- Characterisation of the quality of the other products obtained during the processing of anaerobic digestate and wood ash. For example, the crystals of $(NH_4)_2SO_4$ that can be isolated due to non-invasive acidification of the anaerobic digestate with a low dose of wood ash.
- Confirmation of the nutrient use efficiency after land application: Stablishment of a relation between the speciation of C, N and P among the 3 fractions of the blends of

anaerobic digestate and wood ash and the behaviour of the novel soil organic amendment as slow-release fertiliser once applied to land.

- Comparison of the effect upon land application (e.g. crop yield measurement) of the wood ash-based treatment and the nitrification of the anaerobic digestate. This approach would be particularly suitable for plants that prefer NH_4^+-N rather than NO_3^--N.

List of bibliographic references

Abbas, Y., Yun, S., Wang, K., Ali Shah, F., Xing, T., & Li, B. (2021). Static-magnetic-field coupled with fly-ash accelerant: A powerful strategy to significantly enhance the mesophilic anaerobic-co-digestion. *Bioresource Technology, 327,* 124793. https://doi.org/10.1016/j.biortech.2021.124793

Acosta, N., Duh Kang, I., Rabaey, K., & De Vrieze, J. (2021). Cow manure stabilizes anaerobic digestion of cocoa waste. *Waste Management,* 126, 508–516. https://doi.org/10.1016/j.wasman.2021.02.010

Adams, J. A. (1986). Nitrification and ammonification in acid forest litter and humus as affected by peptone and ammonium-n amendment. *Soil Biology and Biochemistry*, 18(1), 45–51. https://doi.org/10.1016/0038-0717(86)90102-1

Adeyanju, A. A. (2008). Effect of seeding of wood-ash on biogas production using pig waste and cassava peels. *Journal of Engineering and Applied Sciences*, *3*(3), 242–245. Retrieved February 4, 2022, https://medwelljournals.com/abstract/?doi=jeasci.2008.242.24

Agmon, N. (1995). The Grotthuss mechanism. *Chemical Physics Letter*, *244*(5–6), 456462. https://doi.org/10.1016/0009-2614(95)00905-J

Agriculture and Food Development Authority of Ireland. (2021). *New Ammonia MACC – outlook to 2030*. Retrieved February 4, 2022, https://www.teagasc.ie/about/research--innovation/teagasc-research-insights-webinars/new-macc-outlook-to-2030/

Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science*, *36*(3), 327–363. https://doi.org/10.1016/j.pecs.2009.11.003

Ahmed, S., Einfalt, D., & Kazda, M. (2016). Co-Digestion of Sugar Beet Silage Increases Biogas Yield from Fibrous Substrates. *BioMed Research International*, *2016*. https://doi.org/10.1155/2016/2147513

Ahn, J. H., Kwan, T., & Chandran, K. (2011). Comparison of Partial and Full Nitrification Processes Applied for Treating High-Strength Nitrogen Wastewaters: Microbial Ecology through Nitrous Oxide Production. *ACS Environmental Science and Technology*, *45*(7), 2734–2740. https://doi.org/10.1021/es103534g

Akgül, G., & Kruse, A. (2013). Hydrothermal disproportionation of formaldehyde at subcritical conditions. *Journal of Supercritical Fluids, 73,* 43–50.

https://doi.org/10.1016/j.supflu.2012.11.007

Al-Mallahi, J., Sürmeli, R. Ö., & Çalli, B. (2020). Recovery of phosphorus from liquid digestate using waste magnesite dust. *Journal of Cleaner Production*, *272*. https://doi.org/10.1016/j.jclepro.2020.122616

Alburquerque, J. A., de la Fuente, C., & Bernal, M. P. (2012). Chemical properties of anaerobic digestates affecting C and N dynamics in amended soils. *Agriculture, Ecosystems and Environment*, *160*, 15–22. https://doi.org/10.1016/j.agee.2011.03.007

AMEC Environment & Infrastructure UK limited. (2014). *Collection and Analysis of Data for the Control of Emissions from the Spreading of Manure*. European Commission Directorate-General for Environment. Retrieved January 6, 2014, https://ec.europa.eu/environment/air/pdf/Final Report.pdf

Amoah-Antwi, C., Kwiatkowska-Malina, J., Thornton, S. F., Fenton, O., Malina, G., & Szara, E. (2020). Restoration of soil quality using biochar and brown coal waste: A review. *Science of the Total Environment*, *722*, 137852. https://doi.org/10.1016/j.scitotenv.2020.137852

Andersson, L. (2007). *Regular Recycling of Wood Ash To Prevent Waste Production. RecAsh*. Retrieved February 4, 2022, https://www.osti.gov/etdeweb/servlets/purl/20886561

Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J. L., Guwy, A. J., Kalyuzhnyi, S., Jenicek, P., & Van Lier, J. B. (2009). Defining the biomethane potential (BMP) of solid organic wastes and energy crops: A proposed protocol for batch assays. *Water Science and Technology*, *59*(5), 927–934. https://doi.org/10.2166/wst.2009.040

Anukam, A., Mohammadi, A., Naqvi, M., & Granström, K. (2019). A Review of the Chemistry of Anaerobic Digestion: Methods of Accelerating and Optimizing Process Efficiency. *Processes*, *7*(8), 504. https://doi.org/10.3390/pr7080504

Appels, L., Lauwers, J., Degrve, J., Helsen, L., Lievens, B., Willems, K., Van Impe, J., & Dewil, R. (2011). Anaerobic digestion in global bio-energy production: Potential and research challenges. *Renewable and Sustainable Energy Reviews*, *15*(9), 4295–4301. https://doi.org/10.1016/j.rser.2011.07.121

Arat, S., Bullerjahn, G. S., & Laubenbacher, R. (2015). A network biology approach to denitrification in *Pseudomonas aeruginosa*. *PLoS ONE*, *10*(2), 1–12.

https://doi.org/10.1371/journal.pone.0118235

Aseri, G. K., Jain, N., Panwar, J., Rao, A. V., & Meghwal, P. R. (2008). Biofertilizers improve plant growth, fruit yield, nutrition, metabolism and rhizosphere enzyme activities of Pomegranate (*Punica granatum L.*) in Indian Thar Desert. *Scientia Horticulturae*, *117*(2), 130–135. https://doi.org/10.1016/j.scienta.2008.03.014

Astals, S., Martínez-Martorell, M., Huete-Hernández, S., Aguilar-Pozo, V. B., Dosta, J., & Chimenos, J. M. (2021). Nitrogen recovery from pig slurry by struvite precipitation using a low-cost magnesium oxide. *Science of the Total Environment*, *768,* 144284. https://doi.org/10.1016/j.scitotenv.2020.144284

Astals, S., Nolla-Ardèvol, V., & Mata-Alvarez, J. (2012). Anaerobic co-digestion of pig manure and crude glycerol at mesophilic conditions: Biogas and digestate. *Bioresource Technology*, *110*, 63–70. https://doi.org/10.1016/j.biortech.2012.01.080

Astals, S., Nolla-Ardèvol, V., & Mata-Alvarez, J. (2013). Thermophilic co-digestion of pig manure and crude glycerol: Process performance and digestate stability. *Journal of Biotechnology*, *166*(3), 97–104. https://doi.org/10.1016/j.jbiotec.2013.05.004

Awad, A. M., Shaikh, S. M. R., Jalab, R., Gulied, M. H., Nasser, M. S., Benamor, A., & Adham, S. (2019). Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *Separation and Purification Technology*, *228*, 115719. https://doi.org/10.1016/j.seppur.2019.115719

Awiszus, S., Meissner, K., Reyer, S., & Müller, J. (2018). Ammonia and methane emissions during drying of dewatered biogas digestate in a two-belt conveyor dryer. *Bioresource Technology*, *247*, 419–425. https://doi.org/10.1016/j.biortech.2017.09.099

Bachmaier, H., Kuptz, D., & Hartmann, H. (2021). Wood ashes from grate-fired heat and power plants: Evaluation of nutrient and heavy metal contents. *Sustainability*, *13*(10). https://doi.org/10.3390/su13105482

Bai, Y., Ma, L., Degen, A. A., Rafiq, M. K., Kuzyakov, Y., Zhao, J., Zhang, R., Zhang, T., Wang, W., Li, X., Long, R., & Shang, Z. (2020). Long-term active restoration of extremely degraded alpine grassland accelerated turnover and increased stability of soil carbon. *Global Change Biology*, *September*, 1–12. https://doi.org/10.1111/gcb.15361

Balsari, P., Airoldi, G., Dinuccio, E., & Gioelli, F. (2007). Ammonia emissions from farmyard manure heaps and slurry stores—Effect of environmental conditions and measuring methods. *Biosystems Engineering*, *97*(4), 456–463. https://doi.org/10.1016/j.biosystemseng.2007.03.033

Banks, C. J., Haeven, S., Zhang, Y., & Sapp, M. (2013). *Review of the application of the Residual Biogas Potential test*. Retrieved February 4, 2022, http://www.organics-recycling.org.uk/uploads/article2652/PAS110 digestate stability review.pdf

Banwart, S. (2011). Save our soils. *Nature*, *474*(7350), 151–152. https://doi.org/10.1038/474151a

Barrett, J. (2007). *Inorganic Chemistry in Aqueous Solution*. Royal Society of Chemistry. https://doi.org/10.1039/9781847551139

Bastami, M. S. B., Jones, D. L., & Chadwick, D. R. (2016). Reduction of Methane Emission during Slurry Storage by the Addition of Effective Microorganisms and Excessive Carbon Source from Brewing Sugar. *Journal of Environmental Quality*, *45*(6), 2016–2022. https://doi.org/10.2134/jeq2015.11.0568

Bauer, T., Pelkonen, M., & Lagerkvist, A. (2022). Co-digestion of sewage sludge and wood fly ash. *Environmental Technology*, *43*(12), 1853–1859. https://doi.org/10.1080/09593330.2020.1856937

Belviso, C. (2018). State-of-the-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. *Progress in Energy and Combustion Science*, *65*, 109–135. https://doi.org/10.1016/j.pecs.2017.10.004

Berg, W., Brunsch, R., & Pazsiczki, I. (2006). Greenhouse gas emissions from covered slurry compared with uncovered during storage. *Agriculture, Ecosystems and Environment*, *112*(2–3), 129–134. https://doi.org/10.1016/j.agee.2005.08.031

Bernal, M. P., Alburquerque, J. A., & Moral, R. (2009). Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresource Technology*, *100*(22), 5444–5453. https://doi.org/10.1016/j.biortech.2008.11.027

Bhattacharya, R., & Mazumder, D. (2021). Simultaneous nitrification and denitrification in moving bed bioreactor and other biological systems. *Bioprocess and Biosystems Engineering*, *44*(4), 635–652. https://doi.org/10.1007/s00449-020-02475-6

Bhogal, A., Nicholson, F. A., Rollett, A., Taylor, M., Litterick, A., Whittingham, M. J., &

Williams, J. R. (2018). Improvements in the Quality of Agricultural Soils Following Organic Material Additions Depend on Both the Quantity and Quality of the Materials Applied. *Frontiers in Sustainable Food Systems*, *2,* 1–13. https://doi.org/10.3389/fsufs.2018.00009

Blanes-Vidal, V., Guàrdia, M., Dai, X. R., & Nadimi, E. S. (2012). Emissions of NH 3, CO 2 and H 2S during swine wastewater management: Characterization of transient emissions after air-liquid interface disturbances. *Atmospheric Environment*, *54*, 408–418. https://doi.org/10.1016/j.atmosenv.2012.02.046

Blumenthal, K. (2014). *Generation and treatment of municipal waste*. Eurostat. https://ec.europa.eu/eurostat/documents/3433488/5579064/KS-SF-11-031-EN.PDF/00c0b3fe-db08-4076-b39a-e92015ce99e0

Boe, K., Karakashev, D., Trably, E., & Angelidaki, I. (2009). Effect of post-digestion temperature on serial CSTR biogas reactor performance. *Water Research*, *43*(3), 669–676. https://doi.org/10.1016/j.watres.2008.11.037

Boltianskyi, O., Boltianskyi, B., Boltyanska, N., & Sosnowski, S. (2016). Analysis of major errors in the design of pumping stations and manure storage on pig farms. *Teka. commission of motorization and energetics in agriculture*, *16*(2), 49–54. Retrieved February 4, 2022, https://amse.czasopisma.pan.pl/Content/108363/PDF/8_Boltianskyi.pdf?handler=pdf

Bolzonella, D., Fatone, F., Gottardo, M., & Frison, N. (2018). Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full scale applications. *Journal of Environmental Management*, *216*, 111–119. https://doi.org/10.1016/j.jenvman.2017.08.026

Bond, T., & Templeton, M. R. (2011). History and future of domestic biogas plants in the developing world. *Energy for Sustainable Development*, *15*(4), 347–354. https://doi.org/10.1016/j.esd.2011.09.003

Botheju, D., Svalheim, O., & Bakke, R. (2010). Digestate Nitrification for Nutrient Recovery. *The Open Waste Management Journal*, *3*(1), 1–12. https://doi.org/10.2174/1876400201003010001

Bougnom, B. P., Niederkofler, C., Knapp, B. A., Stimpfl, E., & Insam, H. (2012). Residues from renewable energy production: Their value for fertilizing pastures. *Biomass and Bioenergy*, *39*, 290–295. https://doi.org/10.1016/j.biombioe.2012.01.017

Brennan, R. B., Fenton, O., Rodgers, M., & Healy, M. G. (2011). Evaluation of chemical amendments to control phosphorus losses from dairy slurry. *Soil Use and Management*, *27*(2), 238–246. https://doi.org/10.1111/j.1475-2743.2011.00326.x

Brennan, R. B., Healy, M. G., Fenton, O., & Lanigan, G. J. (2015). The effect of chemical amendments used for phosphorus abatement on greenhouse gas and ammonia emissions from dairy cattle slurry: Synergies and pollution swapping. *PLoS ONE*, *10*(6), e0111965. https://doi.org/10.1371/journal.pone.0111965

Brennan, R. B., Healy, M. G., Grant, J., Ibrahim, T. G., & Fenton, O. (2012). Incidental phosphorus and nitrogen loss from grassland plots receiving chemically amended dairy cattle slurry. *Science of the Total Environment*, *441*, 132–140. https://doi.org/10.1016/j.scitotenv.2012.09.078

Broughton, P. M. G. (1984). Carry-over in automatic analysers. *Journal of Automatic Chemistry*, *6*(2), 94–95. https://doi.org/10.1155/S1463924684000201

Buchwald, C., Grabb, K., Hansel, C. M., & Wankel, S. D. (2016). Constraining the role of iron in environmental nitrogen transformations: Dual stable isotope systematics of abiotic NO_2^- reduction by Fe(II) and its production of N_2O. *Geochimica et Cosmochimica Acta*, *186*, 1–12. https://doi.org/10.1016/j.gca.2016.04.041

Burrell, P. C., Phalen, C. M., & Hovanec, T. A. (2001). Identification of Bacteria Responsible for Ammonia Oxidation in Freshwater Aquaria. *Applied and Environmental Microbiology*, *67*(12), 5791–5800. https://doi.org/10.1128/AEM.67.12.5791

Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., & Zechmeister-Boltenstern, S. (2013). Nitrous oxide emissions from soils: How well do we understand the processes and their controls? *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, *368*(1621), 20130122. https://doi.org/10.1098/rstb.2013.0122

Campos, J. L., Crutchik, D., Franchi, Ó., Pavissich, J. P., Belmonte, M., Pedrouso, A., Mosquera-Corral, A., & Val del Río, Á. (2019). Nitrogen and Phosphorus Recovery From Anaerobically Pretreated Agro-Food Wastes: A Review. *Frontiers in Sustainable Food Systems*, *2*(91), 1–11. https://doi.org/10.3389/fsufs.2018.00091

Carrère, H., Dumas, C., Battimelli, A., Batstone, D. J., Delgenès, J. P., Steyer, J. P., & Ferrer, I. (2010). Pretreatment methods to improve sludge anaerobic degradability: A review. *Journal of Hazardous Materials*, *183*(1–3), 1–15. https://doi.org/10.1016/j.jhazmat.2010.06.129

Cattin, M., Semple, K. T., Stutter, M., Romano, G., Lag-Brotons, A. J., Parry, C., & Surridge, B. W. J. (2021). Changes in microbial utilization and fate of soil carbon following the addition of different fractions of anaerobic digestate to soils. *European Journal of Soil Science*, *August 2020*, 1–16. https://doi.org/10.1111/ejss.13091

Cavalli, D., Corti, M., Baronchelli, D., Bechini, L., & Marino Gallina, P. (2017). CO_2 emissions and mineral nitrogen dynamics following application to soil of undigested liquid cattle manure and digestates. *Geoderma*, *308*, 26–35. https://doi.org/10.1016/j.geoderma.2017.08.027

Cerozi, B. da S., & Fitzsimmons, K. (2016). The effect of pH on phosphorus availability and speciation in an aquaponics nutrient solution. *Bioresource Technology*, *219*, 778–781. https://doi.org/10.1016/j.biortech.2016.08.079

Chen, B., Shao, Y., Shi, M., Ji, L., He, Q., & Yan, S. (2021). Anaerobic digestion of chicken manure coupled with ammonia recovery by vacuum-assisted gas-permeable membrane process. *Biochemical Engineering Journal*, *175*, 108135. https://doi.org/10.1016/j.bej.2021.108135

Chertow, M. R. (2000). Industrial Symbiosis: Literature and Taxonomy. *Annual Review of Energy and the Environment*, *25*(1), 313–337. https://doi.org/10.1146/annurev.energy.25.1.313

Chindaprasirt, P., Jaturapitakkul, C., Chalee, W., & Rattanasak, U. (2009). Comparative study on the characteristics of fly ash and bottom ash geopolymers. *Waste Management*, *29*(2), 539–543. https://doi.org/10.1016/j.wasman.2008.06.023

Chojnacka, K., Moustakas, K., & Witek-Krowiak, A. (2020). Bio-based fertilizers: A practical approach towards circular economy. *Bioresource Technology*, *295*, 122223. https://doi.org/10.1016/j.biortech.2019.122223

Cimon, C., Kadota, P., & Eskicioglu, C. (2020). Effect of biochar and wood ash amendment on biochemical methane production of wastewater sludge from a temperature phase anaerobic digestion process. *Bioresource Technology*, *297*, 122440. https://doi.org/10.1016/j.biortech.2019.122440

Clemens, J., Bergmann, S., & Vandré, R. (2002). Reduced ammonia emissions from slurry after self-acidification with organic supplements. *Environmental Technology*, *23*(4), 429–435. https://doi.org/10.1080/09593332508618400

Codling, E. E., Chaney, R. L., & Sherwell, J. (2017). Poultry Litter Ash as a Potential Phosphorus Source for Agricultural Crops. *Journal of Environment Quality*, *31*(3), 954. https://doi.org/10.2134/jeq2002.9540

Coelho, C. M. M., Bellato, C. de M., Santos, J. C. P., Ortega, E. M. M., & Tsai, S. M. (2007). Quality of plant products from organic agriculture. *Journal of the Science of Food and Agriculture*, *1243*(October 2006), 1237–1243. https://doi.org/10.1002/jsfa

Conklin, A. R. (2014). *Introduction to Soil Chemistry: Analysis and Instrumentation*. John Wiley & Sons, Inc. https://doi.org/10.1002/9781118773383

Cordell, D., Drangert, J. O., & White, S. (2009). The story of phosphorus: Global food security and food for thought. *Global Environmental Change*, *19*(2), 292–305. https://doi.org/10.1016/j.gloenvcha.2008.10.009

Corden, C., Bougas, K., Cunningham, E., Tyrer, D., Kreißig, J., Zetti, E., Gamero, E., Wildey, R., & Crookes, M. (2019). *Digestate and compost as fertilisers: Risk assessment and risk management options*. Retrieved February 4, 2022, https://ec.europa.eu/environment/chemicals/reach/pdf/40039 Digestate and Compost RMOA - Final report i2_20190208.pdf

Cossu, R., Morello, L., & Stegmann, R. (2018). Biochemical Processes in Landfill. In *Solid Waste Landfilling* (pp. 91–115). Elsevier. https://doi.org/10.1016/B978-0-12-407721-8.00006-1

Courtney, C., Brison, A., & Randall, D. G. (2021). Calcium removal from stabilized human urine by air and CO2 bubbling. *Water Research*, *202*(December 2020), 117467. https://doi.org/10.1016/j.watres.2021.117467

Cowan, N., Levy, P., Moring, A., Simmons, I., Bache, C., Stephens, A., Marinheiro, J., Brichet, J., Song, L., Pickard, A., McNeill, C., McDonald, R., Maire, J., Loubet, B., Voylokov, P., Sutton, M., & Skiba, U. (2019). Nitrogen use efficiency and N_2O and NH_3 losses attributed to three fertiliser types applied to an intensively managed silage crop. *Biogeosciences*, *16*(23), 4731–4745. https://doi.org/10.5194/bg-16-4731-2019

Da Costa Gomez, C. (2013). Biogas as an energy option: an overview. In A. Wellinger, J. D. Murphy, & D. Baxter (Eds.), *The Biogas Handbook* (1st ed., pp. 1–16). Elsevier. https://doi.org/10.1533/9780857097415.1

Dagnall, S. (1995). UK strategy for centralised anaerobic digestion. *Bioresource Technology*, *52*(3), 275–280. https://doi.org/10.1016/0960-8524(95)00039-H

Dahl, O., Nurmesniemi, H., Pöykiö, R., & Watkins, G. (2009). Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. *Fuel Processing Technology*, *90*(7–8), 871–878. https://doi.org/10.1016/j.fuproc.2009.04.013

Dahl, O., Nurmesniemi, H., Pöykiö, R., & Watkins, G. (2010). Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Processing Technology*, *91*(11), 1634–1639. https://doi.org/10.1016/j.fuproc.2010.06.012

Dahlin, J., Herbes, C., & Nelles, M. (2015). Biogas digestate marketing: Qualitative insights into the supply side. *Resources, Conservation and Recycling*, *104*, 152–161. https://doi.org/10.1016/j.resconrec.2015.08.013

Daifullah, A. A. M., Girgis, B. S., & Gad, H. M. H. (2003). Utilization of agro-residues (rice husk) in small waste water treatment plans. *Materials Letters*, *57*(11), 1723–1731. https://doi.org/10.1016/S0167-577X(02)01058-3

Daliakopoulos, I. N., Tsanis, I. K., Koutroulis, A., Kourgialas, N. N., Varouchakis, A. E., Karatzas, G. P., & Ritsema, C. J. (2016). The threat of soil salinity: A European scale review. *Science of the Total Environment*, *573*, 727–739. https://doi.org/10.1016/j.scitotenv.2016.08.177

de França, A. A., von Tucher, S., & Schmidhalter, U. (2021). Effects of combined application of acidified biogas slurry and chemical fertilizer on crop production and N soil fertility. *European Journal of Agronomy*, *123*, 126224. https://doi.org/10.1016/j.eja.2020.126224

Dela Piccolla, C., Hesterberg, D., Muraoka, T., & Novotny, E. H. (2021). Optimizing pyrolysis conditions for recycling pig bones into phosphate fertilizer. *Waste Management*, *131*, 249–257. https://doi.org/10.1016/j.wasman.2021.06.012

Demeyer, A., Voundi Nkana, J. C., & Verloo, M. G. (2001). Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview. *Bioresource Technology*, *77*(3), 287–295. https://doi.org/10.1016/S0960-8524(00)00043-2

Demirbas, A. (2011). Waste management, waste resource facilities and waste conversion processes. *Energy Conversion and Management*, *52*(2), 1280–1287. https://doi.org/10.1016/j.enconman.2010.09.025

Dijkstra, P., Salpas, E., Fairbanks, D., Miller, E. B., Hagerty, S. B., van Groenigen, K. J., Hungate, B. A., Marks, J. C., Koch, G. W., & Schwartz, E. (2015). High carbon use efficiency in soil microbial communities is related to balanced growth, not storage compound synthesis. *Soil Biology and Biochemistry*, *89*, 35–43. https://doi.org/10.1016/j.soilbio.2015.06.021

Dinuccio, E., Balsari, P., & Berg, W. (2008). GHG emissions during the storage of rough pig slurry and the fractions obtained by mechanical separation. *Australian Journal of Experimental Agriculture*, *48*, 93–95. https://doi.org/10.1071/EA07239

Dinuccio, E., Berg, W., & Balsari, P. (2008). Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. *Atmospheric Environment*, *42*(10), 2448–2459. https://doi.org/10.1016/j.atmosenv.2007.12.022

Dinuccio, Elio, Biagini, D., Rosato, R., Balsari, P., & Lazzaroni, C. (2019). Organic matter and nitrogen balance in rabbit fattening and gaseous emissions during manure storage and simulated land application. *Agriculture, Ecosystems and Environment*, *269*, 30–38. https://doi.org/10.1016/j.agee.2018.09.018

Dinuccio, E., Gioelli, F., Balsari, P., & Dorno, N. (2012). Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry. *Agriculture, Ecosystems and Environment*, *153*(2), 16–23. https://doi.org/10.1016/j.agee.2012.02.015

Drapanauskaite, D., Handler, R. M., Fox, N., & Baltrusaitis, J. (2021). Transformation of Liquid Digestate from the Solid-Separated Biogas Digestion Reactor Effluent into a Solid NH 4 HCO 3 Fertilizer: Sustainable Process Engineering and Life Cycle Assessment. *ACS Sustainable Chemistry & Engineering*, *9*(1), 580–588. https://doi.org/10.1021/acssuschemeng.0c08374

Drosg, B., Fuchs, W., Al Seadi, T., Madsen, M., & Linke, B. (2015). *Nutrient Recovery by Biogas Digestate Processing*. Retrieved February 4, 2022, http://www.iea-biogas.net/files/daten-redaktion/download/Technical Brochures/NUTRIENT_RECOVERY_RZ_web2.pdf

Dumitru, M. (2014). Considerations over a biogas plant components. *Scientific Papers Series Management , Economic Engineering in Agriculture and Rural Development*, *14*(1), 121–126. Retrieved February 4, 2022, http://managementjournal.usamv.ro/pdf/vol4_1/Art19.pdf

Eder, B., & Schulz, H. (2012). *Biogas-Praxis: Grundlagen, Planung, Anlagenbau, Beispiele, Wirtschaftlichkeit*. Oekobuch Verlag. Retrieved February 4, 2022, https://oekobuch.de/buecher/biogas-praxis/

Eggeman, T. (1992). Ammonia. In *Kirk-Othmer Encyclopedia of Chemical Technology* (Fourth edi, pp. 461–642). John Wiley & Sons, Inc. https://doi.org/10.1002/0471238961

El-Nahas, S., Arafat, A. S., Din, H. S. El, Alhamzani, A. G., Abou-Krisha, M. M., & Alsoghier, H. M. (2021). A novel alternative methods for decalcification of water resources using green agro-ashes. *Molecules*, *26*(22). https://doi.org/10.3390/molecules26226777

Elliot, A. D., & Zhang, D. (2005). *Controlled Release Zeolite Fertilisers : A Value Added Product Produced from Fly Ash*. 2005 World of Coal Ash. Retrieved June 8, 2022, https://p2infohouse.org/ref/45/44846.pdf

Elser, J., & Bennett, E. (2011). A broken biogeochemical cycle. *Nature*, *478*, 29–31. https://doi.org/10.1038/478029a

Environment Agency. (2021). *Check if your material is waste*. Guidance. Retrieved February 4, 2022, https://www.gov.uk/guidance/check-if-your-material-is-waste

Eriksen, J., Andersen, A. J., Poulsen, H. V., Adamsen, A. P. S., & Petersen, S. O. (2012). Sulfur Turnover and Emissions during Storage of Cattle Slurry: Effects of Acidification and Sulfur Addition. *Journal of Environment Quality*, *41*(5), 1633–1641. https://doi.org/10.2134/jeq2012.0012

Erraji, H., Afilal, M. E., Asehraou, A., & Azim, K. (2021). Biogas and digestate production from food waste: a case study of dome digester in Morocco. *Biomass Conversion and Biorefinery, 0123456789*. https://doi.org/10.1007/s13399-021-01999-5

Escudero, A., Blanco, F., Lacalle, A., & Pinto, M. (2015). Struvite precipitation for ammonium removal from anaerobically treated effluents. *Journal of Environmental Chemical Engineering*, *3*(1), 413–419. https://doi.org/10.1016/j.jece.2015.01.004

Essel, B., Abaidoo, R. C., Opoku, A., & Ewusi-Mensah, N. (2020). Economically Optimal Rate for Nutrient Application to Maize in the Semi-deciduous Forest Zone of Ghana. *Journal of Soil Science and Plant Nutrition*, *20*(4), 1703–1713. https://doi.org/10.1007/s42729-020-00240-y

Etiégni, L., & Campbell, A. G. (1991). Physical and chemical characteristics of wood ash. Bioresource Technology, 37(2), 173–178. https://doi.org/10.1016/0960-8524(91)90207-Z

European Commission. (2017). *BAT conclusions for the intensive rearing of poultry or pigs*. Official Journal of the European Union. Retrieved February 4, 2022, https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32017D0302&from=ES

European Commission. (2020). *The Nitrates Directive*. Environment. Retrieved February 4, 2022, https://ec.europa.eu/environment/water/water-nitrates/index_en.html

European Parliament. (2003). *Regulation EC 2003/2003 relating to fertilizers*. Official Journal of the European Union. Retrieved February 4, 2022, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32003R2003

European Parliament. (2018). *Directive 2018/851 amending Directive 2008/98/EC on waste Framework*. Official Journal of the European Union. Retrieved February 4, 2022, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.150.01.0109.01.ENG

European Parliament. (2019). *Regulation (EU) 2019/1009 Fertilizer Products*. Official Journal of the European Union. Retrieved February 4, 2022, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32019R1009

Fahimi, A., Bilo, F., Assi, A., Dalipi, R., Federici, S., Guedes, A., Valentim, B., Olgun, H., Ye, G., Bialecka, B., Fiameni, L., Borgese, L., Cathelineau, M., Boiron, M. C., Predeanu, G., & Bontempi, E. (2020). Poultry litter ash characterisation and recovery. *Waste Management*, *111*, 10–21. https://doi.org/10.1016/j.wasman.2020.05.010

Fan, M., Brown, R. C., Wheelock, T. D., Cooper, A. T., Nomura, M., & Zhuang, Y. (2005).

Production of a complex coagulant from fly ash. *Chemical Engineering Journal*, *106*(3), 269–277. https://doi.org/10.1016/j.cej.2004.12.044

Fan, Y., Lv, M., Niu, X., Ma, J., & Zhang, D. (2020). The key step of gaseous phosphorus release in anaerobic digestion. *Process Safety and Environmental Protection*, *137*, 238–245. https://doi.org/10.1016/j.psep.2020.02.035

Fang, C., O-Thong, S., Boe, K., & Angelidaki, I. (2011). Comparison of UASB and EGSB reactors performance, for treatment of raw and deoiled palm oil mill effluent (POME). *Journal of Hazardous Materials*, *189*(1–2), 229–234. https://doi.org/10.1016/j.jhazmat.2011.02.025

Fangueiro, D., Hjorth, M., & Gioelli, F. (2015). Acidification of animal slurry - A review. *Journal of Environmental Management*, *149*, 46–56. https://doi.org/10.1016/j.jenvman.2014.10.001

Fanning, J. C. (2000). The chemical reduction of nitrate in aqueous solution. *Coordination Chemistry Reviews*, *199*(1), 159–179. https://doi.org/10.1016/s0010-8545(99)00143-5

Fenton, O. (2011). *Chemical amendment of slurry to control phosphorus losses in runoff*. Teagasc. Retrieved February 4, 2022, https://www.teagasc.ie/media/website/publications/2011/5669-Chemical-Amendment-of-Slurry.pdf

Fernández-Delgado Juárez, M., Fabiani, G., Mazzier, T., Schönegger, D., Pietramellara, G., Gómez-Brandón, M., & Insam, H. (2020). Reclamation of Acid Soils with Biomass Ashes from Pyrolytic Wood Liquefaction. *Waste and Biomass Valorization*, *11*(9), 5067–5078. https://doi.org/10.1007/s12649-019-00789-5

Fernández-Delgado Juárez, M., Gómez-Brandón, M., Knapp, A., Stöhr, D., & Insam, H. (2015). Chemical and microbiological properties of alpine forest soils: Effects of pelletized ashes in a short-term trial. *Forest Ecology and Management*, *357*, 42–49. https://doi.org/10.1016/j.foreco.2015.08.014

Fernández-Delgado Juárez, M., Waldhuber, S., Knapp, A., Partl, C., Gómez-Brandón, M., & Insam, H. (2013). Wood ash effects on chemical and microbiological properties of digestate- and manure-amended soils. *Biology and Fertility of Soils*, *49*(5), 575–585. https://doi.org/10.1007/s00374-012-0747-5

Fernández-Delgado, M., Amo-Mateos, E. del, Lucas, S., García-Cubero, M. T., & Coca, M. (2020). Recovery of organic carbon from municipal mixed waste compost for the production of fertilizers. *Journal of Cleaner Production*, *265*. https://doi.org/10.1016/j.jclepro.2020.121805

Fivelman, Q. (2013). *Granular Fertiliser from Anaerobic Digestate Liquor*. WRAP. Retrieved February 4, 2022, https://pdfslide.net/documents/feasibility-study-granular-fertiliser-from-anaerobic-digestate-diad-2-2019-05-09.html

Flowers, P., Theopold, K., Langley, R., & Robinson, W. R. (2019). Electrochemistry. In *Chemistry* (2nd ed.). OpenStax. Retrieved February 4, 2022, https://openstax.org/books/chemistry-2e/pages/17-3-electrode-and-cell-potentials

Fomenko, A. I., & Sokolov, L. I. (2015). A study of sorption of phosphate ions from aqueous solutions by wood ash. *Russian Journal of Applied Chemistry*, *88*(4), 652–656. https://doi.org/10.1134/S1070427215040175

Forbes, M. S., Raison, R. J., & Skjemstad, J. O. (2006). Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Science of the Total Environment*, *370*(1), 190–206. https://doi.org/10.1016/j.scitotenv.2006.06.007

Foth, H. D. (1990). Soil Chemistry. In H. D. Foth (Ed.), *Fundamentals of soil science* (8th ed., pp. 164–185). John Wiley & Sons, Inc.

Frost, J. P., & Gilkinson, S. R. (2010). *First Year Performance Summary for Anaerobic Digestion of Dairy Cow Slurry at AFBI Hillsborough*. Retrieved June 8, 2022, https://www.afbini.gov.uk/sites/afbini.gov.uk/files/publications/%5Bcurrent-domain%3Amachine-name%5D/Anaerobic%20Digestion%20Performance%20Summary%2012%20months.pdf#:~:text=SUMMARY%20of%20AFBI%20DIGESTER%20PERFORMANCE%20Following%20intensive%20monitoring,cubic%20meters%20ofbiogas%20with%2079%20kWh%20of%20energy

Fuchs, W., & Drosg, B. (2013). Assessment of the state of the art of technologies for the processing of digestate residue from anaerobic digesters. *Waster Science & Technology*, *67*(9), 1984–1993. https://doi.org/10.2166/wst.2013.075

Galan, I., Glasser, F. P., & Andrade, C. (2013). Calcium carbonate decomposition. *Journal of*

Thermal Analysis and Calorimetry, *111*(2), 1197–1202. https://doi.org/10.1007/s10973-012-2290-x

Gao, D., Peng, Y., & Wu, W.-M. (2010). Kinetic Model for Biological Nitrogen Removal Using Shortcut Nitrification-Denitrification Process in Sequencing Batch Reactor. *ACS Environmental Science and Technology*, *44*(13), 5015–5021. https://doi.org/10.1021/es100514x

García-Ochoa, F., Santos, V. E., Naval, L., Guardiola, E., & López, B. (1999). Kinetic model for anaerobic digestion of livestock manure. *Enzyme and Microbial Technology*, *25*(1–2), 55–60. https://doi.org/10.1016/S0141-0229(99)00014-9

García-Sánchez, M., Siles, J. A., Cajthaml, T., García-Romera, I., Tlustoš, P., & Száková, J. (2015). Effect of digestate and fly ash applications on soil functional properties and microbial communities. *European Journal of Soil Biology*, *71*, 1–12. https://doi.org/10.1016/j.ejsobi.2015.08.004

Garfí, M., Gelman, P., Comas, J., Carrasco, W., & Ferrer, I. (2011). Agricultural reuse of the digestate from low-cost tubular digesters in rural Andean communities. *Waste Management*, *31*(12), 2584–2589. https://doi.org/10.1016/j.wasman.2011.08.007

Gavala, H. N., Yenal, U., Skiadas, I. V., Westermann, P., & Ahring, B. K. (2003). Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature. *Water Research*, *37*(19), 4561–4572. https://doi.org/10.1016/S0043-1354(03)00401-9

Georgacakis, D., Sievers, D. M., & Iannotti, E. L. (1982). Buffer stability in manure digesters. *Agricultural Wastes*, *4*(6), 427–441. https://doi.org/10.1016/0141-4607(82)90038-5

Geyer, K. M., Kyker-Snowman, E., Grandy, A. S., & Frey, S. D. (2016). Microbial carbon use efficiency: accounting for population, community, and ecosystem-scale controls over the fate of metabolized organic matter. *Biogeochemistry*, *127*(2–3), 173–188. https://doi.org/10.1007/s10533-016-0191-y

Gioelli, F., Dinuccio, E., & Balsari, P. (2011). Residual biogas potential from the storage tanks of non-separated digestate and digested liquid fraction. *Bioresource Technology*, *102*(22), 10248–10251. https://doi.org/10.1016/j.biortech.2011.08.076

Gioelli, F., Dinuccio, E., Cuk, D., Rollè, L., & Balsari, P. (2016). Acidification with sulfur of the separated solid fraction of raw and co-digested pig slurry: Effect on greenhouse gas and ammonia emissions during storage. *Animal Production Science*, *56*(3), 343–349. https://doi.org/10.1071/AN15618

Grekov, D. I., Kalinichev, A. G., Suzuki-Muresan, T., Pré, P., & Grambow, B. (2021). Direct Experimental Evidence of the Effects of Clay Particles' Basal-to-Lateral Surface Ratio on Methane and Carbon Dioxide Adsorption. *Journal of Physical Chemistry C*, *125*(21), 11499–11507. https://doi.org/10.1021/acs.jpcc.1c00039

Grimshaw, H. M. (1987). The determination of total phosphorus in soils by acid digestion. In A. P. Rowland (Ed.), *Chemical analysis in environmental research* (pp. 92–95). NERC Open Research Archive. Retrieved February 4, 2022, http://nora.nerc.ac.uk/id/eprint/5224/

Guerrero, L., Da Silva, C., Barahona, A., Montalvo, S., Huiliñir, C., Borja, R., Peirano, C., Toledo, M., & Carvajal, A. (2019). Fly ash as stimulant for anaerobic digestion: effect over hydrolytic stage and methane generation rate. *Water Science and Technology*, *80*(7), 1384–1391. https://doi.org/10.2166/ws.2016.055

Gustafsson, J. P. (2014). *Visual MINTEQ 3.1 user guide*. Retrieved February 4, 2022, https://vminteq.lwr.kth.se/

Hale, S. E., Alling, V., Martinsen, V., Mulder, J., Breedveld, G. D., & Cornelissen, G. (2013). The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. *Chemosphere*, *91*(11), 1612–1619. https://doi.org/10.1016/j.chemosphere.2012.12.057

Hamidi, N. H., Ahmed, O. H., Omar, L., & Ch'ng, H. Y. (2021). Soil Nitrogen Sorption Using Charcoal and Wood Ash. *Agronomy*, *11*(9), 1801. https://doi.org/10.3390/agronomy11091801

Handojo, L. A., Indarto, A., Shofinita, D., Saadi, M. R., Yulistia, D., & Hasyyati, F. I. (2018). Calcium Soap from Palm Fatty Acid Distillate for Ruminant Feed: The Influence of Initial Mixing Temperature. *IOP Conference Series: Materials Science and Engineering*, *543*(1). https://doi.org/10.1088/1757-899X/543/1/012017

Harvey, D. T. (2021). *Standard Reduction Potentials by Value*. Chemistry Libretext. Retrieved February 4, 2022, https://chem.libretexts.org/@go/page/2190

Hermann, L., & Hermann, R. (2019). Report on regulations governing anaerobic digesters and nutrient recovery and reuse in EU member states. *Wageningen University & Research*. https://doi.org/10.18174/476673

Herout, M., Malaták, J., Kucera, L., & Dlabaja, T. (2011). Biogas composition depending on the type of plant biomass used. *Research in Agricultural Engineering*, *57*(4), 137–143. https://doi.org/10.17221/41/2010-RAE

Hjorth, M., Christensen, K. V., Christensen, M. L., & Sommer, S. G. (2009). Solid-liquid separation of animal slurry in theory and practice. *Sustainable Agriculture*, *2*, 953–986. https://doi.org/10.1007/978-94-007-0394-0_43

Holm-Nielsen, J. B., Al Seadi, T., & Oleskowicz-Popiel, P. (2009). The future of anaerobic digestion and biogas utilization. *Bioresource Technology*, *100*(22), 5478–5484. https://doi.org/10.1016/j.biortech.2008.12.046

Hoover, S. R., & Porges, N. (1952). Assimilation of Dairy Wastes by Activated Sludge : II . The Equation of Synthesis and Rate of Oxygen Utilization. *Sewage and Industrial Wastes*, *24*(3), 306–312. Retrieved February 8, 2022, http://www.jstor.org/stable/25031525

Hovey, J. K., & Hepler, L. G. (1990). Thermodynamics of sulphuric acid: apparent and partial molar heat capacities and volumes of aqueous HSO –4 from 10–55 °C and calculation of the second dissociation constant to 350 °C. *Journal of the Chemical Society, Faraday Transactions*, 86(16), 2831–2839. https://doi.org/10.1039/FT9908602831

Hou, Y., Velthof, G. L., Case, S. D. C., Oelofse, M., Grignani, C., Balsari, P., Zavattaro, L., Gioelli, F., Bernal, M. P., Fangueiro, D., Trindade, H., Jensen, L. S., & Oenema, O. (2018). Stakeholder perceptions of manure treatment technologies in Denmark, Italy, the Netherlands and Spain. *Journal of Cleaner Production, 172*, 1620–1630. https://doi.org/10.1016/j.jclepro.2016.10.162

Houba, V. J. G., Temminghoff, E. J. M., Gaikhorst, G. A., & van Vark, W. (2000). Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Communications in Soil Science and Plant Analysis*, *31*(9–10), 1299–1396. https://doi.org/10.1080/00103620009370514

Hsu, E. (2021). Cost-benefit analysis for recycling of agricultural wastes in Taiwan. *Waste Management*, *120,* 424–432. https://doi.org/10.1016/j.wasman.2020.09.051

Huang, H., Zhang, D. D., Li, J., Guo, G., & Tang, S. (2017). Phosphate recovery from swine wastewater using plant ash in chemical crystallization. *Journal of Cleaner Production*, *168*, 338–345. https://doi.org/10.1016/j.jclepro.2017.09.042

Huiliñir, C., Pinto-Villegas, P., Castillo, A., Montalvo, S., & Guerrero, L. (2017). Biochemical methane potential from sewage sludge: Effect of an aerobic pretreatment and fly ash addition as source of trace elements. *Waste Management*, *64*, 140–148. https://doi.org/10.1016/j.wasman.2017.03.023

Huotari, N., Tillman-Sutela, E., Moilanen, M., & Laiho, R. (2015). Recycling of ash - For the good of the environment? *Forest Ecology and Management*, *348*, 226–240. https://doi.org/10.1016/j.foreco.2015.03.008

Hupfauf, S., Bachmann, S., Fernández-Delgado Juárez, M., Insam, H., & Eichler-Löbermann, B. (2016). Biogas digestates affect crop P uptake and soil microbial community composition. *Science of the Total Environment*, *542*, 1144–1154. https://doi.org/10.1016/j.scitotenv.2015.09.025

Ibeto, C. N., Lag-Brotons, A. J., Marshall, R., & Semple, K. T. (2020). The Nutritional Effects of Digested and Undigested Organic Wastes Combined with Wood Ash Amendments on Carrot Plants. *Journal of Soil Science and Plant Nutrition*, *20*(2), 460–472. https://doi.org/10.1007/s42729-019-00131-x

Ibeto, C. N., Lag-Brotons, A. J., Marshall, R., & Semple, K. T. (2022). Wood ash effects on soil properties and *Lactuca sativa* growth in soils amended with digestate and poultry litter. *Journal of Plant Nutrition*, 1–15. https://doi.org/10.1080/01904167.2022.2067065

Insam, H., Franke-Whittle, I. H., Knapp, B. A., & Plank, R. (2009). Use of wood ash and anaerobic sludge for grassland fertilization: Effects on plants and microbes. *Die Bodenkultur*, *60*(2), 39–51. Retrieved February 4, 2022 https://diebodenkultur.boku.ac.at/volltexte/band-60/heft-2/insam.pdf

International Plant Nutrition Institute of Canada. (2017a). *Nitrogen Notes: Denitrification*. Retrieved February 4, 2022. http://www.ipni.net/publication/nitrogen-en.nsf/0/668099AE825517CB85257DD600054B8C/$FILE/NitrogenNotes-EN-5.pdf

International Plant Nutrition Institute of Canada. (2017b). *Nitrogen Notes: Nitrification*. Retrieved February 4, 2022 http://www.ipni.net/publication/nitrogen-en.nsf/0/7F7F448C4D064A5985257C13004C83A3/$FILE/NitrogenNotes-EN-04.pdf

IPCC. (2019). Chapter 11: N_2O Emissions From Managed Soils, and CO_2 Emissions From Lime and Urea Application. In *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Volume 4: Agriculture, Forestry and Other Land Use*. Retrieved February 4, 2022, https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/4_Volume4/19R_V4_Ch11_Soils_N2O_CO2.pdf

Jamali, M. K., Kazi, T. G., Arain, M. B., Afridi, H. I., Memon, A. R., Jalbani, N., & SHAH, A. (2008). Use of Sewage Sludge After Liming as Fertilizer for Maize Growth. *Pedosphere*, *18*(2), 203–213. https://doi.org/10.1016/S1002-0160(08)60008-9

James, A. K., Thring, R. W., Helle, S., & Ghuman, H. S. (2012). Ash management review-applications of biomass bottom ash. *Energies*, *5*(10), 3856–3873. https://doi.org/10.3390/en5103856

Janiszewska, D., Olchowski, R., Nowicka, A., Zborowska, M., Marszałkiewicz, K., Shams, M., Giannakoudakis, D. A., Anastopoulos, I., & Barczak, M. (2021). Activated biochars derived from wood biomass liquefaction residues for effective removal of hazardous hexavalent chromium from aquatic environments. *GCB Bioenergy*, *13*(8), 1247–1259. https://doi.org/10.1111/gcbb.12839

Janni, K., & Cortus, E. (2020). Common Animal Production Systems and Manure Storage Methods. In H. M. Waldrip, P. H. Pagliari, & Z. He (Eds.), *Animal Manure: Production, Characteristics, Environmental Concerns, and Management, Volume 67* (pp. 27–44). American Society of Agronomy, Inc. Soil Science Society of America, Inc. https://doi.org/10.2134/asaspecpub67.c3

Jantsch, T. G., & Mattiasson, B. (2003). A simple spectrophotometric method based on ph-indicators for monitoring partial and total alkalinity in anaerobic processes. *Environmental Technology*, *24*(9), 1061–1067. https://doi.org/10.1080/09593330309385646

Jeschke, C., Falagán, C., Knöller, K., Schultze, M., & Koschorreck, M. (2013). No Nitrification in Lakes Below pH 3. *ACS Environmental Science and Technology*, *47*(27), 14018–14023. https://doi.org/10.1021/es402179v

Jewiarz, M., Wróbel, M., Fraczek, J., Mudryk, K., & Dziedzic, K. (2018). Digestate, ash and

Trichoderm based fertilizer-production line concept design. *MATEC Web of Conferences*, *168*, 1–6. https://doi.org/10.1051/matecconf/201816804004

Johansen, A., Carter, M. S., Jensen, E. S., Hauggard-Nielsen, H., & Ambus, P. (2013). Effects of digestate from anaerobically digested cattle slurry and plant materials on soil microbial community and emission of CO_2 and N_2O. *Applied Soil Ecology*, *63*, 36–44. https://doi.org/10.1016/j.apsoil.2012.09.003

Johansson, N., & Forsgren, C. (2020). Is this the end of end-of-waste? Uncovering the space between waste and products. *Resources, Conservation and Recycling*, *155*, 104656. https://doi.org/10.1016/j.resconrec.2019.104656

Jones, C. A., Koenig, R. T., Ellsworth, J. W., Brown, B. D., & Jackson, G. D. (2007). *Extension Soil Fertility Specialist Management of Urea Fertilizer to Minimize Volatilization*. Retrieved February 4, 2022, http://www.extension.uidaho.edu/Nutrient/pdf/smallgrain/New/Management of Urea fertilizer to minimize volatilization.pdf

Kaczala, F., Marques, M., & Hogland, W. (2009). Lead and vanadium removal from a real industrial wastewater by gravitational settling/sedimentation and sorption onto Pinus sylvestris sawdust. *Bioresource Technology*, *100*(1), 235–243. https://doi.org/10.1016/j.biortech.2008.05.055

Karoline, K. (2012). *Chemistry of wood ash leachates and the filter effect of soil columns on leachate composition* [master thesis]. University of Natural Resources and Life Sciences, Vienna. Retrieved February 4, 2022, http://epub.boku.ac.at/urn:nbn:at:at-ubbw:1-4762

Kavanagh, I., Burchill, W., Healy, M. G., Fenton, O., Krol, D. J., & Lanigan, G. J. (2019). Mitigation of ammonia and greenhouse gas emissions from stored cattle slurry using acidifiers and chemical amendments. *Journal of Cleaner Production*, *237*(3), 117822. https://doi.org/10.1016/j.jclepro.2019.117822

Kavanagh, I., Fenton, O., Healy, M. G., Burchill, W., Lanigan, G. J., & Krol, D. J. (2021). Mitigating ammonia and greenhouse gas emissions from stored cattle slurry using agricultural waste, commercially available products and a chemical acidifier. *Journal of Cleaner Production*, *294*, 126251. https://doi.org/10.1016/j.jclepro.2021.126251

Khalid, H., Zhang, H., Liu, C., Li, W., Abuzar, M. K., Amin, F. R., Liu, G., & Chen, C. (2020).

PEST (political, environmental, social & technical) analysis of the development of the waste-to-energy anaerobic digestion industry in China as a representative for developing countries. *Sustainable Energy and Fuels*, *4*(3), 1048–1062. https://doi.org/10.1039/c9se00692c

Kiba, T., & Krapp, A. (2016). Plant nitrogen acquisition under low availability: Regulation of uptake and root architecture. *Plant and Cell Physiology*, *57*(4), 707–714. https://doi.org/10.1093/pcp/pcw052

Kim, J. S., Lee, Y. Y., & Kim, T. H. (2016). A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. *Bioresource Technology*, *199*, 42–48. https://doi.org/10.1016/j.biortech.2015.08.085

Kim, M., Ahn, Y. H., & Speece, R. E. (2002). Comparative process stability and efficiency of anaerobic digestion; mesophilic *vs.* thermophilic. *Water Research*, *36*(17), 4369–4385. https://doi.org/10.1016/S0043-1354(02)00147-1

Kocatürk-Schumacher, N. P., Zwart, K., Bruun, S., Brussaard, L., & Jensen, L. S. (2017). Does the combination of biochar and clinoptilolite enhance nutrient recovery from the liquid fraction of biogas digestate? *Environmental Technology*, *38*(10), 1313–1323. https://doi.org/10.1080/09593330.2016.1226959

Korczynski, M. (2005). The Point of Selling: Capitalism, Consumption and Contradictions. *Organization*, *12*(1), 69–88. https://doi.org/10.1177/1350508405048577

Lag-Brotons, A. J., Marshall, R., Herbert, B. M. J., Hurst, L., Inam, E. J., & Semple, K. T. (2020). Adding Value to Ash and Digestate (AVAnD Project): Elucidating the Role and Value of Alternative Fertilisers on the Soil-Plant System. In L. E. Macaskie, D. J. Sapsford, & W. M. Mayes (Eds.), *Resource Recovery from Wastes: Towards a Circular Economy* (pp. 113–139). Royal Society of Chemistry. https://doi.org/10.1039/9781788016353-00113

Lal, R. (2021). Climate change and agriculture. In T. M. Letcher (Ed.), *Climate Change, Observed Impacts on Planet Earth* (3rd ed., pp. 661–686). Elsevier B.V. https://doi.org/10.1016/b978-0-12-821575-3.00031-1

Lancaster University. (2017). *AVAnD Project*. Resource Recovery from Waste. Retrieved February 4, 2022, https://rrfw.org.uk/projects/avand/

Lancaster University. (2020). *Developing a suite of novel land conditioners and plant fertilizers from the waste streams of biomass energy generation*. UK Research and Innovation. Retrieved February 4, 2022, https://gtr.ukri.org/projects?ref=NE/L014122/1

Lanigan, G. J., Donnellan, T., Lanigan, G. J., Hanrahan, K., Paul, C., Shalloo, L., Krol, D., Forrestal, P., Farrelly, N., O'brien, D., Ryan, M., Murphy, P., Caslin, B., Spink, J., Finnan, J., Boland, A., Upton, J., & Richards, K. (2018). *An Analysis of Abatement Potential of Greenhouse Gas Emissions in Irish Agriculture 2021-2030*. Retrieved February 4, 2022 https://www.teagasc.ie/media/website/publications/2018/An-Analysis-of-Abatement-Potential-of-Greenhouse-Gas-Emissions-in-Irish-Agriculture-2021-2030.pdf

Laohaprapanon, S., Marques, M., & Hogland, W. (2010). Removal of organic pollutants from wastewater using wood fly ash as a low-cost sorbent. *Clean - Soil, Air, Water*, *38*(11), 1055–1061. https://doi.org/10.1002/clen.201000105

Latham, K. G., Kozyatnyk, I., Figueira, J., Carlborg, M., Rosenbaum, E., & Jansson, S. (2021). Self-generation of low ash carbon microspheres from the hydrothermal supernatant of anaerobic digestate: Formation insights and supercapacitor performance. *Chemical Engineering Journal Advances*, *6*, 100097. https://doi.org/10.1016/j.ceja.2021.100097

Lee, G., Kim, K., Chung, J., & Han, J. I. (2021). Electrochemical ammonia accumulation and recovery from ammonia-rich livestock wastewater. *Chemosphere*, 270, 128631. https://doi.org/10.1016/j.chemosphere.2020.128631

Leechart, P., Nakbanpote, W., & Thiravetyan, P. (2009). Application of "waste" wood-shaving bottom ash for adsorption of azo reactive dye. *Journal of Environmental Management*, *90*(2), 912–920. https://doi.org/10.1016/j.jenvman.2008.02.005

Leip, A., Billen, G., Garnier, J., Grizzetti, B., Lassaletta, L., Reis, S., Simpson, D., Sutton, M. A., De Vries, W., Weiss, F., & Westhoek, H. (2015). Impacts of European livestock production: Nitrogen, sulphur, phosphorus and greenhouse gas emissions, land-use, water eutrophication and biodiversity. *Environmental Research Letters*, *10*(11). https://doi.org/10.1088/1748-9326/10/11/115004

Lemmer, A., & Krümpel, J. (2017). Demand-driven biogas production in anaerobic filters. *Applied Energy*, *185*, 885–894. https://doi.org/10.1016/j.apenergy.2016.10.073

Lencioni, G., Imperiale, D., Cavirani, N., Marmiroli, N., & Marmiroli, M. (2016).

Environmental application and phytotoxicity of anaerobic digestate from pig farming by in vitro and in vivo trials. *International Journal of Environmental Science and Technology*, *13*(11), 2549–2560. https://doi.org/10.1007/s13762-016-1088-y

Leuning, R., Freney, J. R., Denmead, O. T., & Simpson, J. R. (1985). A sampler for measuring atmospheric ammonia flux. *Atmospheric Environment*, *19*(7), 1117–1124. https://doi.org/10.1016/0004-6981(85)90196-9

Liang, B., Lehmann, J., Sohi, S. P., Thies, J. E., O'Neill, B., Trujillo, L., Gaunt, J., Solomon, D., Grossman, J., Neves, E. G., & Luizão, F. J. (2010). Black carbon affects the cycling of non-black carbon in soil. *Organic Geochemistry*, *41*(2), 206–213. https://doi.org/10.1016/j.orggeochem.2009.09.007

Limoli, A., Langone, M., & Andreottola, G. (2016). Ammonia removal from raw manure digestate by means of a turbulent mixing stripping process. *Journal of Environmental Management*, *176*, 1–10. https://doi.org/10.1016/j.jenvman.2016.03.007

Lin, Y., Lü, F., Shao, L., & He, P. (2013). Influence of bicarbonate buffer on the methanogenetic pathway during thermophilic anaerobic digestion. *Bioresource Technology*, *137*, 245–253. https://doi.org/10.1016/j.biortech.2013.03.093

Lindner, J., Zielonka, S., Oechsner, H., & Lemmer, A. (2015). Effects of mechanical treatment of digestate after anaerobic digestion on the degree of degradation. *Bioresource Technology*, *178*, 194–200. https://doi.org/10.1016/j.biortech.2014.09.117

Linke, B. (2006). Kinetic study of thermophilic anaerobic digestion of solid wastes from potato processing. *Biomass and Bioenergy*, *30*(10), 892–896. https://doi.org/10.1016/j.biombioe.2006.02.001

Liodakis, S., Tsoukala, M., & Katsigiannis, G. (2009). Laboratory Study of Leaching Properties of Mediterranean Forest Species Ashes. *Water, Air, and Soil Pollution*, *203*(1–4), 99–107. https://doi.org/10.1007/s11270-009-9994-y

Liu, H., Shan, J., Chen, Z., & Lichtfouse, E. (2021). Efficient recovery of phosphate from simulated urine by Mg/Fe bimetallic oxide modified biochar as a potential resource. *Science of the Total Environment*, *784*, 147546. https://doi.org/10.1016/j.scitotenv.2021.147546

Liu, L., Pang, C., Wu, S., & Dong, R. (2015). Optimization and evaluation of an air-recirculated stripping for ammonia removal from the anaerobic digestate of pig manure. *Process Safety and Environmental Protection*, *94*, 350–357. https://doi.org/10.1016/j.psep.2014.08.006

Lo, H. M., Kurniawan, T. A., Sillanpää, M. E. T., Pai, T. Y., Chiang, C. F., Chao, K. P., Liu, M. H., Chuang, S. H., Banks, C. J., & Wang, S. C. (2010). Modeling biogas production from organic fraction of MSW co-digested with MSWI ashes in anaerobic bioreactors. *Bioresource Technology*, *101*(16), 6329–6335. https://doi.org/10.1016/j.biortech.2010.03.048

Lo, H. M., Liu, M. H., Pai, T. Y., Liu, W. F., Lin, C. Y., Wang, S. C., Banks, C. J., Hung, C. H., Chiang, C. F., Lin, K. C., Chen, P. H., Chen, J. K., Chiu, H. Y., Su, M. H., Kurniawan, T. A., Wu, K. C., Hsieh, C. Y., & Hsu, H. S. (2009). Biostabilization assessment of MSW co-disposed with MSWI fly ash in anaerobic bioreactors. *Journal of Hazardous Materials*, *162*(2–3), 1233–1242. https://doi.org/10.1016/j.jhazmat.2008.06.028

López Torres, M., & Espinosa Lloréns, M. del C. (2008). Effect of alkaline pretreatment on anaerobic digestion of solid wastes. *Waste Management*, *28*(11), 2229–2234. https://doi.org/10.1016/j.wasman.2007.10.006

Loppinet-Serani, A., & Aymonier, C. (2014). Hydrolysis in Near- and Supercritical Water for Biomass Conversion and Material Recycling. In *Supercritical Fluid Technology for Energy and Environmental Applications* (pp. 140–142). Elsevier. https://doi.org/10.1016/B978-0-444-62696-7.00007-1

Lukehurst, C., Frost, P., & Seadi, T. Al. (2010). *Utilisation of digestate from biogas plants as biofertiliser*. IEA Bioenergy. Retrieved February 4, 2022, https://www.ieabioenergy.com/publications/utilisation-of-digestate-from-biogas-plants-as-biofertiliser/

Lü, F., Lu, X., Li, S., Zhang, H., Shao, L., & He, P. (2022). Dozens-fold improvement of biochar redox properties by KOH activation. *Chemical Engineering Journal*, *429,* 132203. https://doi.org/10.1016/j.cej.2021.132203

Ma, Z., Li, Q., Yue, Q., Gao, B., Li, W., Xu, X., & Zhong, Q. (2011). Adsorption removal of ammonium and phosphate from water by fertilizer controlled release agent prepared from wheat straw. *Chemical Engineering Journal, 171*(3), 1209–1217. https://doi.org/10.1016/j.cej.2011.05.027

Madani-Hosseini, M., Mulligan, C. N., & Barrington, S. (2015). Acidification of In-Storage-Psychrophilic-Anaerobic-Digestion (ISPAD) process to reduce ammonia volatilization: Model development and validation. *Waste Management*, *52*, 104–111. https://doi.org/10.1016/j.wasman.2016.03.043

Madsen, M., Holm-Nielsen, J. B., & Esbensen, K. H. (2011). Monitoring of anaerobic digestion processes: A review perspective. *Renewable and Sustainable Energy Reviews*, *15*(6), 3141–3155. https://doi.org/10.1016/j.rser.2011.04.026

Mahfouz, S. a, & Shamf-Eldin, M. a. (2007). Effect of mineral *vs*. biofertilizer on growth, yield, and essential oil content of fennel (Foeniculum vulgare Mill.). *International Agrophysics*, *21*(1991), 361–366. https://doi.org/10.1055/s-2007-987419

Malinowski, M., Famielec, S., Wolny-Koładka, K., Sikora, J., Gliniak, M., Baran, D., Sobol, Z., & Salamon, J. (2021). Impact of digestate addition on the biostabilization of undersized fraction from municipal solid waste. *Science of the Total Environment*, *770*. https://doi.org/10.1016/j.scitotenv.2021.145375

Mall, I. D., Srivastava, V. C., Agarwal, N. K., & Mishra, I. M. (2005). Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses. *Chemosphere*, *61*(4), 492–501. https://doi.org/10.1016/j.chemosphere.2005.03.065

Mannina, G., Presti, D., Montiel-Jarillo, G., Carrera, J., & Suárez-Ojeda, M. E. (2020). Recovery of polyhydroxyalkanoates (PHAs) from wastewater: A review. *Bioresource Technology*, *297*, 122478. https://doi.org/10.1016/j.biortech.2019.122478

Manzoni, S., Taylor, P., Richter, A., Porporato, A., & Ågren, G. I. (2012). Environmental and stoichiometric controls on microbial carbon-use efficiency in soils. *New Phytologist*, *196*(1), 79–91. https://doi.org/10.1111/j.1469-8137.2012.04225.x

Mao, C., Feng, Y., Wang, X., & Ren, G. (2015). Review on research achievements of biogas from anaerobic digestion. *Renewable and Sustainable Energy Reviews*, *45*, 540–555. https://doi.org/10.1016/j.rser.2015.02.032

Maresca, A., Hyks, J., & Astrup, T. F. (2017). Recirculation of biomass ashes onto forest soils: ash composition, mineralogy and leaching properties. *Waste Management*, *70*, 127–138. https://doi.org/10.1016/j.wasman.2017.09.008

Maresca, A., Krüger, O., Herzel, H., Adam, C., Kalbe, U., & Astrup, T. F. (2019). Influence of wood ash pre-treatment on leaching behaviour, liming and fertilising potential. *Waste Management*, *83*, 113–122. https://doi.org/10.1016/j.wasman.2018.11.003

Marshall, R., Lag-Brotons, A. J., Inam, E. J., Herbert, B. M. J., Hurst, L., & Semple, K. T. (2020). From Bioenergy By-products to Alternative Fertilisers: Pursuing a Circular Economy. In L. E. Macaskie, D. J. Sapsford, & W. M. Mayes (Eds.), *Resource Recovery from Wastes: Towards a Circular Economy* (pp. 298–314). https://doi.org/10.1039/9781788016353-00287

McDowell, R. W., Worth, W., & Carrick, S. (2021). Evidence for the leaching of dissolved organic phosphorus to depth. *Science of the Total Environment*, *755*, 142392. https://doi.org/10.1016/j.scitotenv.2020.142392

McLaughlin, M. R., Brooks, J. P., & Adeli, A. (2014). A new sampler for stratified lagoon chemical and microbiological assessments. *Environmental Monitoring and Assessment*, *186*(7), 4097–4110. https://doi.org/10.1007/s10661-014-3683-z

Méndez, J. M., Jiménez, B. E., & Barrios, J. A. (2002). Improved alkaline stabilization of municipal wastewater sludge. *Water Science and Technology*, *46*(10), 139–146. https://doi.org/10.2166/wst.2002.0312

Menon, A., Wang, J. Y., & Giannis, A. (2017). Optimization of micronutrient supplement for enhancing biogas production from food waste in two-phase thermophilic anaerobic digestion. *Waste Management*, *59*, 465–475. https://doi.org/10.1016/j.wasman.2016.10.017

Tchobanoglous, G., Stensel, H. D., Tsuchihashi, R., & Burton, F. (2014). *Wastewater Engineering: Treatment and Resource Recovery* (5th ed.). Mc Graw Hill.

Miles, A., & Ellis, T. G. (2001). Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Water Science & Technology*, 43(11), 259–266. https://doi.org/https://doi.org/10.2166/wst.2001.0690

Millero, F., Huang, F., Zhu, X., Liu, X., & Zhang, J. Z. (2001). Adsorption and desorption of phosphate on calcite and aragonite in seawater. *Aquatic Geochemistry*, 7(1), 33–56. https://doi.org/10.1023/A:1011344117092

Miranda, C., Soares, A. S., Coelho, A. C., Trindade, H., & Teixeira, C. A. (2021).

Environmental implications of stored cattle slurry treatment with sulphuric acid and biochar: A life cycle assessment approach. *Environmental Research*, *194*, 110640. https://doi.org/10.1016/j.envres.2020.110640

Miyafuji, H., Danner, H., Neureiter, M., Thomasser, C., & Braun, R. (2003). Effect of wood ash treatment on improving the fermentability of wood hydrolysate. *Biotechnology and Bioengineering*, *84*(3), 390–393. https://doi.org/10.1002/bit.10672

Mohankumar Sajeev, E. P., Winiwarter, W., & Amon, B. (2018). Greenhouse Gas and Ammonia Emissions from Different Stages of Liquid Manure Management Chains: Abatement Options and Emission Interactions. *Journal of Environmental Quality*, *47*(1), 30–41. https://doi.org/10.2134/jeq2017.05.0199

Moilanen, M., Saarsalmi, A., Kukkola, M., & Issakainen, J. (2013). Effects of stabilized wood ash on nutrient status and growth of Scots pine – Comparison between uplands and peatlands. *Forest Ecology and Management*, 295, 136–144. https://doi.org/10.1016/j.foreco.2013.01.021

Möller, K., & Müller, T. (2012). Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review. *Engineering in Life Sciences*, *12*(3), 242–257. https://doi.org/10.1002/elsc.201100085

Mor, S., Chhoden, K., & Ravindra, K. (2016). Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. *Journal of Cleaner Production*, *129*, 673–680. https://doi.org/10.1016/j.jclepro.2016.03.088

Mosoarca, G., Vancea, C., Popa, S., Boran, S., & Tanasie, C. (2020). A green approach for treatment of wastewater with manganese using wood ash. *Journal of Chemical Technology and Biotechnology*, *95*(6), 1781–1789. https://doi.org/10.1002/jctb.6376

Moure Abelenda, A., & Aiouache, F. (2022). Wood Ash Based Treatment of Anaerobic Digestate: State-of-the-Art and Possibilities. *Processes*, *10*(1), 147. https://doi.org/10.3390/pr10010147

Moure Abelenda, A., & Amaechi, C. V. (2022). Manufacturing of a Granular Fertilizer Based on Organic Slurry and Hardening Agent. *Inventions*, *7*(1), 26. https://doi.org/10.3390/inventions7010026

Moure Abelenda, A., Semple, K. T., Aggidis, G., & Aiouache, F. (2022). Circularity of

Bioenergy Residues: Acidification of Anaerobic Digestate Prior to Addition of Wood Ash. *Sustainability*, *14*(5), 3127. https://doi.org/10.3390/su14053127

Moure Abelenda, A., Semple, K. T., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2022). Valorization of agrowaste digestate via addition of wood ash, acidification, and nitrification. *Environmental Technology & Innovation*, *28*, 102632. https://doi.org/10.1016/j.eti.2022.102632

Moure Abelenda, A., Semple, K. T., Lag-Brotons, A. J., Herbert, B. M., Aggidis, G., & Aiouache, F. (2021a). Alkaline Wood Ash, Turbulence, and Traps with Excess of Sulfuric Acid Do Not Strip Completely the Ammonia off an Agro-waste Digestate. *Edelweiss Chemical Science Journal*, *4*(1), 19–24. https://doi.org/10.33805/2641-7383.127

Moure Abelenda, A., Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021b). 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. *Journal of Environmental Chemical Engineering*, *9*(1), 105021. https://doi.org/10.1016/j.jece.2020.105021

Moure Abelenda, A., Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021c). Effects of Wood Ash-Based Alkaline Treatment on Nitrogen, Carbon, and Phosphorus Availability in Food Waste and Agro-Industrial Waste Digestates. *Waste and Biomass Valorization*, *12*(6), 3355–3370. https://doi.org/10.1007/s12649-020-01211-1

Moure Abelenda, A., Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2021d). Kinetic study of the stabilization of an agro-industrial digestate by adding wood fly ash. *Chemical Engineering Journal Advances*, *7*, 100127. https://doi.org/10.1016/j.ceja.2021.100127

Moure Abelenda, A., Semple, K. T., Lag-Brotons, A. J., Herbert, B. M. J., Aggidis, G., & Aiouache, F. (2022). Strategies for the production of a stable blended fertilizer of anaerobic digestates and wood ashes. *Nature-Based Solutions, 2,* 100014. https://doi.org/10.1016/j.nbsj.2022.100014

Mu, Z. X., He, C. S., Jiang, J. K., Zhang, J., Yang, H. Y., & Mu, Y. (2018). A modified two-point titration method for the determination of volatile fatty acids in anaerobic systems. *Chemosphere, 204,* 251–256. https://doi.org/10.1016/j.chemosphere.2018.04.038

Mudryk, K., Frączek, J., Wróbel, M., Jewiarz, M., & Dziedzic, K. (2018). Agglomeration of Ash-Based Fertilizer Mixtures from Biomass Combustion and Digestate. In M. Krzysztof & W. Sebastian (Eds.), *Renewable Energy Sources: Engineering, Technology, Innovation, Springer* (Issue January, pp. 823–834). Springer. https://doi.org/10.1007/978-3-319-72371-6_80

Mulu, E., M’Arimi, M. M., Ramkat, R. C., & Mecha, A. C. (2021). Potential of wood ash in purification of biogas. *Energy for Sustainable Development*, *65*, 45–52. https://doi.org/10.1016/j.esd.2021.09.009

Murphy, R. M., Richards, K. G., Krol, D. J., Gebremichael, A. W., Lopez-sangil, L., Rambaud, J., Cowan, N., Lanigan, G. J., & Saunders, M. (2022). Agricultural and Forest Meteorology Assessing nitrous oxide emissions in time and space with minimal uncertainty using static chambers and eddy covariance from a temperate grassland. *Agricultural and Forest Meteorology*, *313*, 108743. https://doi.org/10.1016/j.agrformet.2021.108743

Nag, R., Auer, A., Nolan, S., Russell, L., Markey, B. K., Whyte, P., O’Flaherty, V., Bolton, D., Fenton, O., Richards, K. G., & Cummins, E. (2021). Evaluation of pathogen concentration in anaerobic digestate using a predictive modelling approach (ADRISK). *Science of the Total Environment*, *800*, 149574. https://doi.org/10.1016/j.scitotenv.2021.149574

Narodoslawsky, M., & Obernberger, I. (1996). From waste to raw material - The route from biomass to wood ash for cadmium and other heavy metals. *Journal of Hazardous Materials*, *50*(2–3), 157–168. https://doi.org/10.1016/0304-3894(96)01785-2

Nathalie Bachmann, E. S. A. (2013). Design and engineering of biogas plants. In A. Wellinger, J. Murphy, & D. Baxter (Eds.), *The Biogas Handbook* (1st ed., pp. 191–211). Elsevier. https://doi.org/10.1533/9780857097415.2.191

Ndegwa, P. M., Vaddella, V. K., Hristov, A. N., & Joo, H. S. (2009). Measuring Concentrations of Ammonia in Ambient Air or Exhaust Air Stream using Acid Traps. *Journal of Environmental Quality*, *38*(2), 647–653. https://doi.org/10.2134/jeq2008.0211

NERC. (2021). *Developing a suite of novel land conditioners and plant fertilizers from the waste streams of biomass energy generation*. Details Award Reference NE/L014122/1. Retrieved February 4, 2022, http://gotw.nerc.ac.uk/list_full.asp?pcode=NE%2FL014122%2F1&cookieConsent=A

Nohra, J. A., Barrington, S., Frigon, J. C., & Guiot, S. R. (2003). In storage psychrophilic anaerobic digestion of swine slurry. *Resources, Conservation and Recycling*, *38*(1), 23–37. https://doi.org/10.1016/S0921-3449(02)00092-7

Nordberg, Å. (1999). *Legislation in different European countries regarding implementation of anaerobic digestion*. Retrieved February 4, 2022, https://www.semanticscholar.org/paper/Legislation-in-different-European-countries-of-Nordberg/c512c6756a44f78fe768346ce47a9493e9dcba29

Northern Ireland Department of Agriculture Environment and Rural Affairs. (2019). *Nitrate Directive partial derogation*. Retrieved February 4, 2022, https://www.daera-ni.gov.uk/articles/nitrates-directive

Ohno, T., Hess, N. J., & Qafoku, N. P. (2019). Current Understanding of the Use of Alkaline Extractions of Soils to Investigate Soil Organic Matter and Environmental Processes. *Journal of Environmental Quality*, *48*(6), 1561–1564. https://doi.org/10.2134/jeq2019.08.0292

Onwosi, C. O., & Okereke, G. U. (2009). Effect of water dilution and nutrient supplements (wood ash, urea and poultry droppings) on biogas production from brewers spent grain. In A. Mendez-Vilas (Ed.), *Current Research Topics in Applied Microbiology and Microbial Biotechnology* (pp. 232–235). WORLD SCIENTIFIC. https://doi.org/10.1142/9789812837554_0048

Owamah, H. I., Dahunsi, S. O., Oranusi, U. S., & Alfa, M. I. (2014). Fertilizer and sanitary quality of digestate biofertilizer from the co-digestion of food waste and human excreta. *Waste Management*, *34*(4), 747–752. https://doi.org/10.1016/j.wasman.2014.01.017

Öztürk, N., & Bektaş, T. E. (2004). Nitrate removal from aqueous solution by adsorption onto various materials. *Journal of Hazardous Materials*, *112*(1–2), 155–162. https://doi.org/10.1016/j.jhazmat.2004.05.001

Palakodeti, A., Azman, S., Rossi, B., Dewil, R., & Appels, L. (2021). A critical review of ammonia recovery from anaerobic digestate of organic wastes *via* stripping. *Renewable and Sustainable Energy Reviews, 143*(July 2020), 110903. https://doi.org/10.1016/j.rser.2021.110903

Pampuro, N., Bagagiolo, G., Priarone, P. C., & Cavallo, E. (2017). Effects of pelletizing pressure and the addition of woody bulking agents on the physical and mechanical properties of pellets made from composted pig solid fraction. *Powder Technology*, *311*, 112–119. https://doi.org/10.1016/j.powtec.2017.01.092

Pantelopoulos, A., Magid, J., & Jensen, L. S. (2016). Thermal drying of the solid fraction from biogas digestate: Effects of acidification, temperature and ventilation on nitrogen content. *Waste Management*, *48*, 218–226. https://doi.org/10.1016/j.wasman.2015.10.008

Papp, B., Török, T., Sándor, E., Fekete, E., Flipphi, M., & Karaffa, L. (2016). High cell density cultivation of the chemolithoautotrophic bacterium Nitrosomonas europaea. *Folia Microbiologica*, *61*(3), 191–198. https://doi.org/10.1007/s12223-015-0425-8

Papurello, D., Silvestri, S., Biasioli, F., & Lombardi, L. (2022). Wood ash biomethane upgrading system: A case study. *Renewable Energy*, *182*, 702–712. https://doi.org/10.1016/j.renene.2021.10.037

Park, N., Chang, H., Jang, Y., Lim, H., Jung, J., & Kim, W. (2021). Prediction of adequate pH and Mg^{2+} dosage using an empirical MgO solubility model for struvite crystallization. *Environmental Technology and Innovation*, *21*, 101347. https://doi.org/10.1016/j.eti.2020.101347

Park, N. D., Michael Rutherford, P., Thring, R. W., & Helle, S. S. (2012). Wood pellet fly ash and bottom ash as an effective liming agent and nutrient source for rye grass (Lolium perenne L.) and oats (Avena sativa). *Chemosphere*, *86*(4), 427–432. https://doi.org/10.1016/j.chemosphere.2011.10.052

Pelissetti, S., & Balsari, P. (2021). Testing the Efficiency of a Passive Sampler for Ammonia Monitoring and Comparison with Alpha- Samplers. *International Workshop on Metrology for Agriculture and Forestry*, 157–161. Retrieved June 8, 2022, https://ieeexplore.ieee.org/document/9628774

Maffia, J., Pelissetti, S., Balsari, P., Dinuccio, E., & Sacco, D. (2021). Testing the Efficiency of a Passive Sampler for Ammonia Monitoring and Comparison with Alpha-Samplers. *2021 IEEE International Workshop on Metrology for Agriculture and Forestry (MetroAgriFor)*, 157–161. https://doi.org/10.1109/MetroAgriFor52389.2021.9628774

Pell Frischmann Consultants Ltd. (2012). *Enhancement and treatment of digestates from* *anaerobic digestion*. Retrieved February 4, 2022, https://archive.wrap.org.uk/content/enhancement-and-treatment-digestates-anaerobic-digestion

Perakis, S. S., & Hedin, L. O. (2002). Nitrogen loss from unpolluted South American forests mainly *via* dissolved organic compounds. *Nature*, *415*(6870), 416–419. https://doi.org/10.1038/415416a

Perazzolo, F., Mattachini, G., Tambone, F., Misselbrook, T., & Provolo, G. (2015). Effect of mechanical separation on emissions during storage of two anaerobically codigested animal slurries. *Agriculture, Ecosystems and Environment*, *207*, 1–9. https://doi.org/10.1016/j.agee.2015.03.023

Pereira, J., Fangueiro, D., Chadwick, D. R., Misselbrook, T. H., Coutinho, J., & Trindade, H. (2010). Effect of cattle slurry pre-treatment by separation and addition of nitrification inhibitors on gaseous emissions and N dynamics: A laboratory study. *Chemosphere*, *79*(6), 620–627. https://doi.org/10.1016/j.chemosphere.2010.02.029

Pesonen, J., Kuokkanen, V., Kuokkanen, T., & Illikainen, M. (2016). Co-granulation of bio-ash with sewage sludge and lime for fertilizer use. *Journal of Environmental Chemical Engineering*, *4*(4), 4817–4821. https://doi.org/10.1016/j.jece.2015.12.035

Pitman, R. M. (2006). Wood ash use in forestry - A review of the environmental impacts. *Forestry*, *79*(5), 563–588. https://doi.org/10.1093/forestry/cpl041

Podmirseg, S. M., Seewald, M. S. A., Knapp, B. A., Bouzid, O., Biderre-Petit, C., Peyret, P., & Insam, H. (2013). Wood ash amendment to biogas reactors as an alternative to landfilling? A preliminary study on changes in process chemistry and biology. *Waste Management and Research*, *31*(8), 829–842. https://doi.org/10.1177/0734242X13497077

Pohlandt-Schwandt, K., Salthammer, T., & Marutzky, R. (2002). Reduction of soluble chromate in wood ash by formaldehyde. *Biomass and Bioenergy*, *22*(2), 139–143. https://doi.org/10.1016/S0961-9534(01)00053-8

Popovic, O., Gioelli, F., Dinuccio, E., Rollè, L., & Balsari, P. (2017). Centrifugation of digestate: The effect of chitosan on separation efficiency. *Sustainability*, *9*(12), 1–9. https://doi.org/10.3390/su9122302

Pote, D. H., & Daniel, T. C. (2000). Analyzing for dissolved reactive phophorus in water samples. In G. M. Pierzynski & S. C. Hodges (Eds.), *Methods of phosphorus analysis for soils, sediments, residuals, and waters* (pp. 91–97). Retrieved February 4, 2022, https://www.ars.usda.gov/research/publications/publication/?seqNo115=120921

Powlson, D. S., Bhogal, A., Chambers, B. J., Coleman, K., Macdonald, A. J., Goulding, K. W. T., & Whitmore, A. P. (2012). The potential to increase soil carbon stocks through reduced tillage or organic material additions in England and Wales: A case study. *Agriculture, Ecosystems and Environment*, *146*(1), 23–33. https://doi.org/10.1016/j.agee.2011.10.004

Pöykiö, R., Rönkkömäki, H., Nurmesniemi, H., Perämäki, P., Popov, K., Välimäki, I., & Tuomi, T. (2009). Chemical and physical properties of cyclone fly ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW). *Journal of Hazardous Materials*, *162*(2–3), 1059–1064. https://doi.org/10.1016/j.jhazmat.2008.05.140

Pöykiö, R., Manskinen, K., Nurmesniemi, H., & Dahl, O. (2011). Comparison of trace elements in bottom ash and fly ash from a large-sized (77 MW) multi-fuel boiler at the power plant of a fluting board mill, Finland. *Energy Exploration and Exploitation*, *29*(3), 217–234. https://doi.org/10.1260/0144-5987.29.3.217

Prywer, J., Sieroń, L., & Czylkowska, A. (2019). Struvite Grown in Gel, Its Crystal Structure at 90 K and Thermoanalytical Study. *Crystals*, *9*(2), 89. https://doi.org/10.3390/cryst9020089

Pulford, I. D. (2007). Chapter 5. The Chemistry of the Solid Earth. In R. M. Harrison (Ed.), *Principles of Environmental Chemistry* (PCR Publishing, p. 262). Royal Society of Chemistry. https://doi.org/10.1039/9781847557780-00234

Qiao, Z., Sun, R., Wu, Y., Hu, S., Liu, X., Chan, J., & Mi, X. (2020). Characteristics and metabolic pathway of the bacteria for heterotrophic nitrification and aerobic denitrification in aquatic ecosystems. *Environmental Research, 191*, 110069. https://doi.org/10.1016/j.envres.2020.110069

Rajendran, K., & Devaraj, P. (2004). Biomass and nutrient distribution and their return of Casuarina equisetifolia inoculated with biofertilizers in farm land. *Biomass and Bioenergy*, *26*(3), 235–249. https://doi.org/10.1016/j.biombioe.2003.07.001

Raman, A. A. A., Asghar, A., Buthiyappan, A., & Daud, W. M. A. W. (2017). Treatment of

Recalcitrant Waste. In *Current Developments in Biotechnology and Bioengineering* (pp. 409–442). Elsevier. https://doi.org/10.1016/B978-0-444-63665-2.00016-3

Randall, D. G., Krähenbühl, M., Köpping, I., Larsen, T. A., & Udert, K. M. (2016). A novel approach for stabilizing fresh urine by calcium hydroxide addition. *Water Research*, *95*, 361–369. https://doi.org/10.1016/j.watres.2016.03.007

Recio, J., Vallejo, A., Le-Noë, J., Garnier, J., García-Marco, S., Álvarez, J. M., & Sanz-Cobena, A. (2018). The effect of nitrification inhibitors on NH_3 and N_2O emissions in highly N fertilized irrigated Mediterranean cropping systems. *Science of the Total Environment*, *636*, 427–436. https://doi.org/10.1016/j.scitotenv.2018.04.294

Regueiro, I., Coutinho, J., & Fangueiro, D. (2016). Alternatives to sulfuric acid for slurry acidification: Impact on slurry composition and ammonia emissions during storage. *Journal of Cleaner Production*, *131*, 296–307. https://doi.org/10.1016/j.jclepro.2016.05.032

Regueiro, I., Coutinho, J., Gioelli, F., Balsari, P., Dinuccio, E., & Fangueiro, D. (2016). Acidification of raw and co-digested pig slurries with alum before mechanical separation reduces gaseous emission during storage of solid and liquid fractions. *Agriculture, Ecosystems & Environment*, *227*, 42–51. https://doi.org/10.1016/j.agee.2016.04.016

Renewable Energy Assurance Ltd. (2015). Rules for England , Scotland , Wales & Northern Ireland. *Biofertiliser Certification Scheme*. Retrieved February 4, 2022, http://www.biofertiliser.org.uk/pdf/scheme-rules-4-0.pdf

Renewable Energy Assurance Ltd. (2017). Laboratory Tests. *Biofertiliser Certification Scheme*. Retrieved February 4, 2022, http://www.biofertiliser.org.uk/certification/laboratory-tests

Ribbing, C. (2007). Environmentally friendly use of non-coal ashes in Sweden. *Waste Management*, *27*(10), 1428–1435. https://doi.org/10.1016/j.wasman.2007.03.012

Richards, S., Marshall, R., Lag-brotons, A. J., Semple, K. T., & Stutter, M. (2021). Phosphorus solubility changes following additions of bioenergy wastes to an agricultural soil : Implications for crop availability and environmental mobility. *Geoderma*, *401*(April), 115150. https://doi.org/10.1016/j.geoderma.2021.115150

Riechmann, M. E., Ndwandwe, B., Greenwood, E. E., Reynaert, E., Morgenroth, E., & Udert,

K. M. (2021). On-site urine treatment combining $Ca(OH)_2$ dissolution and dehydration with ambient air. *Water Research X*, 100124. https://doi.org/10.1016/j.wroa.2021.100124

Rincón, B., Borja, R., González, J. M., Portillo, M. C., & Sáiz-Jiménez, C. (2008). Influence of organic loading rate and hydraulic retention time on the performance, stability and microbial communities of one-stage anaerobic digestion of two-phase olive mill solid residue. *Biochemical Engineering Journal*, *40*(2), 253–261. https://doi.org/10.1016/j.bej.2007.12.019

Roberts, T. L., & Stewart, W. M. (2002). Inorganic Phosphorus and Potassium Production and Reserves. *International Plant Nutrition Institute*, *86*(2), 6–7. Retrieved February 4, 2022, http://www.ipni.net/publication/bettercrops.nsf/issue/BC-2002-2

Romero-Güiza, M. S., Vila, J., Mata-Alvarez, J., Chimenos, J. M., & Astals, S. (2016a). The role of additives on anaerobic digestion: A review. *Renewable and Sustainable Energy Reviews*, *58*, 1486–1499. https://doi.org/10.1016/j.rser.2015.12.094

Romero-Güiza, M. S., Vila, J., Mata-Alvarez, J., Chimenos, J. M., & Astals, S. (2016b). The role of additives on anaerobic digestion: A review. *Renewable and Sustainable Energy Reviews*, *58*, 1486–1499. https://doi.org/10.1016/j.rser.2015.12.094

Romillac, N. (2019). Ammonification. In *Encyclopedia of Ecology* (pp. 256–263). Elsevier. https://doi.org/10.1016/B978-0-12-409548-9.10889-9

Ronga, D., Mantovi, P., Pacchioli, M. T., Pulvirenti, A., Bigi, F., Allesina, G., Pedrazzi, S., Tava, A., & Dal Prà, A. (2020). Combined effects of dewatering, composting and pelleting to valorize and delocalize livestock manure, improving agricultural sustainability. *Agronomy*, *10*(5). https://doi.org/10.3390/agronomy10050661

Rop, K., Karuku, G. N., Mbui, D., Michira, I., & Njomo, N. (2018). Formulation of slow release NPK fertilizer (cellulose-graft-poly(acrylamide)/nano-hydroxyapatite/soluble fertilizer) composite and evaluating its N mineralization potential. *Annals of Agricultural Sciences*, *63*(2), 163–172. https://doi.org/10.1016/j.aoas.2018.11.001

Rosenfeld, P. E., & Henry, C. L. (2001). Activated Carbon and Wood Ash Sorption of Wastewater, Compost, and Biosolids Odorants. *Water Environment Research*, *73*(4), 388–393. https://doi.org/10.2175/106143001x139425

Ryckebosch, E., Drouillon, M., & Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, *35*(5), 1633–1645. https://doi.org/10.1016/j.biombioe.2011.02.033

Sakai, E., Miyahara, S., Ohsawa, S., Lee, S. H., & Daimon, M. (2005). Hydration of fly ash cement. *Cement and Concrete Research*, *35*(6), 1135–1140. https://doi.org/10.1016/j.cemconres.2004.09.008

Sakthivel, S. R., Tilley, E., & Udert, K. M. (2012). Wood ash as a magnesium source for phosphorus recovery from source-separated urine. *Science of the Total Environment*, *419*, 68–75. https://doi.org/10.1016/j.scitotenv.2011.12.065

Sapp, M., Harrison, M., Hany, U., Charlton, A., & Thwaites, R. (2015). Comparing the effect of digestate and chemical fertiliser on soil bacteria. *Applied Soil Ecology*, *86*, 1–9. https://doi.org/10.1016/j.apsoil.2014.10.004

Sarvi, M., Hagner, M., Velmala, S., Soinne, H., Uusitalo, R., Keskinen, R., Ylivainio, K., Kaseva, J., & Rasa, K. (2021). Bioavailability of phosphorus in granulated and pyrolyzed broiler manure. *Environmental Technology and Innovation*, *23*, 101584. https://doi.org/10.1016/j.eti.2021.101584

Saveyn, H., & Eder, P. (2014). *End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals*. Retrieved February 4, 2022, https://publications.jrc.ec.europa.eu/repository/handle/JRC87124

Scaglione, D., Ficara, E., Corbellini, V., Tornotti, G., Teli, A., Canziani, R., & Malpei, F. (2015). Autotrophic nitrogen removal by a two-step SBR process applied to mixed agro-digestate. *Bioresource Technology*, *176*, 98–105. https://doi.org/10.1016/j.biortech.2014.11.019

Scaglione, D., Tornotti, G., Teli, A., Lorenzoni, L., Ficara, E., Canziani, R., & Malpei, F. (2013). Nitrification denitrification *via* nitrite in a pilot-scale SBR treating the liquid fraction of co-digested piggery/poultry manure and agro-wastes. *Chemical Engineering Journal*, *228*, 935–943. https://doi.org/10.1016/j.cej.2013.05.075

Schmidt, D. R., & Bicudo, J. R. (2002). Using a Wind Tunnel to Determine Odor and Gas Fluxes from Manure Surfaces. *ASAE Meeting, Paper No. 024083*, 1–13. https://doi.org/10.13031/2013.10481

Schwab, P. (2011). Soil solution. In P. M. Huang, Y. Li, & M. E. Sumner (Eds.), *Handbook of* *soil sciences: properties and processes* (2^{nd} ed., pp. 353-376). CRC Press. https://doi.org/10.1201/b11267

Schwarz, S., Lunkwitz, K., Keßler, B., Spiegler, U., Killmann, E., & Jaeger, W. (2000). Adsorption and stability of colloidal silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *163*(1), 17–27. https://doi.org/10.1016/S0927-7757(99)00426-4

SEAL Analytical. (2012). AutoAnalyzer Method no. G-102-93 Rev. 8. In *Instructions manual* (pp. 1–10).

Shah, I., Adnan, R., Wan Ngah, W. S., & Mohamed, N. (2015). Iron Impregnated Activated Carbon as an Efficient Adsorbent for the Removal of Methylene Blue: Regeneration and Kinetics Studies. *PLOS ONE, 10*(4), e0122603. https://doi.org/10.1371/journal.pone.0122603

Shah, F. A., Mahmood, Q., Rashid, N., Pervez, A., Raja, I. A., & Shah, M. M. (2015). Co-digestion, pretreatment and digester design for enhanced methanogenesis. *Renewable and Sustainable Energy Reviews*, *42*, 627–642. https://doi.org/10.1016/j.rser.2014.10.053

Sharpley, A., & Moyer, B. (2000). Phosphorus forms in manure and compost and their release during simulated rainfall. *Journal of Environmental Quality*, *29*(5), 1462–1469. https://doi.org/10.2134/jeq2000.00472425002900050012x

Shcherbakov, V. V., Artemkina, Y. M., Ponomareva, T. N., & Kirillov, A. D. (2009). Electrical conductivity of the ammonia-water system. *Russian Journal of Inorganic Chemistry*, *54*(2), 277–279. https://doi.org/10.1134/S0036023609020193

Shi, W., Healy, M. G., Ashekuzzaman, S. M., Daly, K., Leahy, J. J., & Fenton, O. (2021). Dairy processing sludge and co-products: A review of present and future re-use pathways in agriculture. *Journal of Cleaner Production*, *314*, 128035. https://doi.org/10.1016/j.jclepro.2021.128035

Shi, Y., Parker, D. B., Cole, N. A., Auvermann, B. W., & Mehlhorn, J. E. (2001). Surface amendments to minimize ammonia emissions from beef cattle feedlots. *Transactions of the American Society of Agricultural Engineers*, *44*(3), 677–682. https://doi.org/10.13031/2013.6105

Silva, F. C., Cruz, N. C., Tarelho, L. A. C., & Rodrigues, S. M. (2019). Use of biomass ash-based materials as soil fertilisers: Critical review of the existing regulatory framework.

Journal of Cleaner Production, *214*, 112–124. https://doi.org/10.1016/j.jclepro.2018.12.268

Simha, P., Friedrich, C., Randall, D. G., & Vinnerås, B. (2021). Alkaline Dehydration of Human Urine Collected in Source-Separated Sanitation Systems Using Magnesium Oxide. *Frontiers in Environmental Science*, 8, 1–9. https://doi.org/10.3389/fenvs.2020.619901

Simha, P., Lalander, C., Nordin, A., & Vinnerås, B. (2020). Alkaline dehydration of source-separated fresh human urine: Preliminary insights into using different dehydration temperature and media. *Science of the Total Environment*, *733*, 139313. https://doi.org/10.1016/j.scitotenv.2020.139313

Simha, P., Senecal, J., Nordin, A., Lalander, C., & Vinnerås, B. (2018). Alkaline dehydration of anion–exchanged human urine: Volume reduction, nutrient recovery and process optimisation. *Water Research*, *142*, 325–336. https://doi.org/10.1016/j.watres.2018.06.001

Singh Brar, B., Singh, J., Singh, G., & Kaur, G. (2015). Effects of Long Term Application of Inorganic and Organic Fertilizers on Soil Organic Carbon and Physical Properties in Maize–Wheat Rotation. *Agronomy*, *5*(2), 220–238. https://doi.org/10.3390/agronomy5020220

Sinsabaugh, R. L., Manzoni, S., Moorhead, D. L., & Richter, A. (2013). Carbon use efficiency of microbial communities: stoichiometry, methodology and modelling. *Ecology Letters*, *16*(7), 930–939. https://doi.org/10.1111/ele.12113

Sogn, T. A., Dragicevic, I., Linjordet, R., Krogstad, T., Eijsink, V. G. H., & Eich-Greatorex, S. (2018). Recycling of biogas digestates in plant production: NPK fertilizer value and risk of leaching. *International Journal of Recycling of Organic Waste in Agriculture*, *7*(1), 49–58. https://doi.org/10.1007/s40093-017-0188-0

Sommer, S. G., & Husted, S. (1995). The chemical buffer system in raw and digested animal slurry. *The Journal of Agricultural Science*, *124*(1), 45–53. https://doi.org/10.1017/S0021859600071239

Sørensen, P., & Eriksen, J. (2009). Effects of slurry acidification with sulphuric acid combined with aeration on the turnover and plant availability of nitrogen. *Agriculture, Ecosystems* *and Environment*, *131*(3–4), 240–246. https://doi.org/10.1016/j.agee.2009.01.024

Steenari, B. M., & Lindqvist, O. (1997). Stabilisation of biofuel ashes for recycling to forest soil. *Biomass and Bioenergy*, *13*(1–2), 39–50. https://doi.org/10.1016/S0961-9534(97)00024-X

Stjepanović, M., Velić, N., Lončarić, A., Gašo-Sokač, D., Bušić, V., & Habuda-Stanić, M. (2019). Adsorptive removal of nitrate from wastewater using modified lignocellulosic waste material. *Journal of Molecular Liquids*, *285*, 535–544. https://doi.org/10.1016/j.molliq.2019.04.105

Strand, M., Pagels, J., Szpila, A., Gudmundsson, A., Swietlicki, E., Bohgard, M., & Sanati, M. (2002). Fly ash penetration through electrostatic precipitator and flue gas condenser in a 6 MW biomass fired boiler. *Energy and Fuels*, *16*(6), 1499–1506. https://doi.org/10.1021/ef020076b

Strock, J. S. (2008). Ammonification. In S. E. Jørgensen & B. D. Fath (Eds.), *Encyclopedia of Ecology* (pp. 162–165). Elsevier. https://doi.org/10.1016/B978-008045405-4.00256-1

Strosser, E. (2011). Methods for determination of labile soil organic matter: An overview. *Journal of Agrobiology*, *27*(2), 49–60. https://doi.org/10.2478/s10146-009-0008-x

Szymula, A., Wlazło, Ł., Sasáková, N., Wnuk, W., & Nowakowicz-Dębek, B. (2021). The Use of Natural Sorbents to Reduce Ammonia Emissions from Cattle Faeces. *Agronomy*, *11*(12), 2543. https://doi.org/10.3390/agronomy11122543

Tambone, F., Genevini, P., D’Imporzano, G., & Adani, F. (2009). Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW. *Bioresource Technology*, *100*(12), 3140–3142. https://doi.org/10.1016/j.biortech.2009.02.012

Tambone, F., Orzi, V., Zilio, M., & Adani, F. (2019). Measuring the organic amendment properties of the liquid fraction of digestate. *Waste Management*, *88*, 21–27. https://doi.org/10.1016/j.wasman.2019.03.024

Tan, Z., & Lagerkvist, A. (2011). Phosphorus recovery from the biomass ash: A review. *Renewable and Sustainable Energy Reviews*, *15*(8), 3588–3602. https://doi.org/10.1016/j.rser.2011.05.016

Taşdemir, A., Cengiz, İ., Yildiz, E., & Bayhan, Y. K. (2020). Investigation of ammonia stripping with a hydrodynamic cavitation reactor. *Ultrasonics Sonochemistry*, *60*, 104741. https://doi.org/10.1016/j.ultsonch.2019.104741

Tavakkoli, E., Rengasamy, P., Smith, E., & Mcdonald, G. K. (2015). The effect of cation-anion interactions on soil pH and solubility of organic carbon. *European Journal of Soil Science*, *66*(6), 1054–1062. https://doi.org/10.1111/ejss.12294

Tian, T., & Yu, H. Q. (2020). Denitrification with non-organic electron donor for treating low C/N ratio wastewaters. *Bioresource Technology*, *299*, 122686. https://doi.org/10.1016/j.biortech.2019.122686

Tiecher, T., dos Santos, D. R., & Calegari, A. (2012). Soil organic phosphorus forms under different soil management systems and winter crops, in a long term experiment. *Soil and Tillage Research*, *124*, 57–67. https://doi.org/10.1016/j.still.2012.05.001

Tunesi, S., Poggi, V., & Gessa, C. (1999). Phosphate adsorption and precipitation in calcareous soils: The role of calcium ions in solution and carbonate minerals. *Nutrient Cycling in Agroecosystems*, *53*(3), 219–227. https://doi.org/10.1023/A:1009709005147

Tur-Cardona, J., Bonnichsen, O., Speelman, S., Verspecht, A., Carpentier, L., Debruyne, L., Marchand, F., Jacobsen, B. H., & Buysse, J. (2018). Farmers' reasons to accept bio-based fertilizers: A choice experiment in seven different European countries. *Journal of Cleaner Production*, *197*, 406–416. https://doi.org/10.1016/j.jclepro.2018.06.172

UK AHDB. (2021a). Section 4 Arable Crops. *Nutrient Management Guide (RB209)*. Retrieved February 4, 2022, https://ahdb.org.uk/knowledge-library/rb209-section-4-arable-crops

UK AHDB. (2021b). Section 2 Organic Materials. *Nutrient Management Guide (RB209)*. Retrieved February 4, 2022, https://ahdb.org.uk/knowledge-library/rb209-section-2-organic-materials

UK DEFRA. (2018). *Emissions of air pollutants in the UK, 1970 to 2016*. Retrieved February 4, 2022, https://www.burnright.co.uk/wp-content/uploads/2019/02/Statistics-Defra-air-pollution-graph.pdf

UK DEFRA. (2020a). *Farming is Changing*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/future-farming-changes-to-farming-in-england

UK DEFRA. (2020b). *The Path to Sustainable Farming: An Agricultural Transition Plan 2021 to 2024*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/agricultural-transition-plan-2021-to-2024

UK Government. (2012). *Quality Protocol: Compost - End of waste criteria for the production and use of quality compost from source-segregated biodegradable waste*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/quality-protocol-for-the-production-and-use-of-compost-from-waste

UK Government. (2016). *Handling of manure and slurry to reduce antibiotic resistance*. Retrieved February 4, 2022, https://www.gov.uk/guidance/handling-of-manure-and-slurry-to-reduce-antibiotic-resistance

UK Government. (2017). *From waste to resource productivity*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/from-waste-to-resource-productivity

UK Government. (2018). *Sewage sludge in agriculture: code of practice for England, Wales and Northern Ireland*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/sewage-sludge-in-agriculture-code-of-practice/sewage-sludge-in-agriculture-code-of-practice-for-england-wales-and-northern-ireland

UK Government. (2019). Clean air strategy 2019. In *Department for Environment, Food & Rural Affairs*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/clean-air-strategy-2019

UK Government. (2020). *Using animal by-products at compost and biogas sites*. Retrieved February 4, 2022,. https://www.gov.uk/guidance/using-animal-by-products-at-compost-and-biogas-sites

UK Government. (2021a). *Nitrate vulnerable zones*. Retrieved February 4, 2022, https://www.gov.uk/guidance/nutrient-management-nitrate-vulnerable-zones

UK Government. (2021b). *Quality protocols: converting waste into non-waste products*. Retrieved February 4, 2022, https://www.gov.uk/government/collections/quality-protocols-end-of-waste-frameworks-for-waste-derived-products

UK Quality Ash Association. (2016). *UKQAA Ash Availability Report*. Retrieved February 4, 2022, http://www.ukqaa.org.uk/wp-content/uploads/information/statistics/UKQAA-Ash-

Availability-Report-Jan-2016.pdf

UK Quality Ash Association. (2021). *About us*. Retrieved February 4, 2022, http://www.ukqaa.org.uk/about/

Ukwuani, A. T., & Tao, W. (2016). Developing a vacuum thermal stripping – acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Research*, *106*, 108–115. https://doi.org/10.1016/j.watres.2016.09.054

Urgun-Demirtas, M., Sattayatewa, C., & Pagilla, K. R. (2008). Bioavailability of Dissolved Organic Nitrogen in Treated Effluents. *Water Environment Research*, *80*(5), 397–406. https://doi.org/10.2175/106143007x221454

USA EPA. (2000). *Biosolids Technology Fact Sheet: Alkaline Stabilization of Biosolids*. Retrieved June 8, 2022, https://www.epa.gov/biosolids/fact-sheet-alkaline-stabilization-biosolids

USA Geological Survey. (2021). *Mineral Commodity Summaries 2021*. https://doi.org/10.3133/mcs2021

Vaccari, D. A. (2009). Phosphorus: A Looming Crisis. *Scientific American*, *300*(6), 54–59. https://doi.org/10.1038/scientificamerican0609-54

Van der Stelt, B., Temminghoff, E. J. M., Van Vliet, P. C. J., & Van Riemsdijk, W. H. (2007). Volatilization of ammonia from manure as affected by manure additives, temperature and mixing. *Bioresource Technology*, *98*(18), 3449–3455. https://doi.org/10.1016/j.biortech.2006.11.004

Vandré, R., & Clemens, J. (1996). Studies on the relationship between slurry pH, volatilization processes and the influence of acidifying additives. *Nutrient Cycling in Agroecosystems*, *47*(2), 157–165. https://doi.org/10.1007/BF01991547

Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P. A., Tack, F. M. G., & Meers, E. (2017). Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste and Biomass Valorization*, *8*(1), 21–40. https://doi.org/10.1007/s12649-016-9642-x

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913–933. https://doi.org/10.1016/j.fuel.2009.10.022

Vassilev, S. V., Baxter, D., & Vassileva, C. G. (2013). An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel*, *112*, 391–449. https://doi.org/10.1016/j.fuel.2013.09.024

Vassilev, S. V., Baxter, D., & Vassileva, C. G. (2014). An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types. *Fuel*, *117*(PART A), 152–183. https://doi.org/10.1016/j.fuel.2013.09.024

Vassilev, S. V., Vassileva, C. G., Song, Y. C., Li, W. Y., & Feng, J. (2017). Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. *Fuel*, *208*, 377–409. https://doi.org/10.1016/j.fuel.2017.07.036

Vassilev, S. V., Vassileva, C. G., & Petrova, N. L. (2021). Mineral Carbonation of Biomass Ashes in Relation to Their CO2Capture and Storage Potential. *ACS Omega*, *6*(22), 14598–14611. https://doi.org/10.1021/acsomega.1c01730

Velthof, G. L., Nelemans, J. A., Oenema, O., & Kuikman, P. J. (2005). Gaseous Nitrogen and Carbon Losses from Pig Manure Derived from Different Diets. *Journal of Environmental Quality*, *34*(2), 698. https://doi.org/10.2134/jeq2005.0698

Velthof, G., & Oenema, O. (1993). Nitrous oxide flux from nitric-acid-treated cattle slurry applied to grassland under semi-controlled conditions. *Netherlands Journal of Agricultural Science*, *41*(2), 81–93. https://doi.org/10.18174/njas.v41i2.624

Verdouw, H., Van Echteld, C. J. A., & Dekkers, E. M. J. (1978). Ammonia determination based on indophenol formation with sodium salicylate. *Water Research*, *12*(6), 399–402. https://doi.org/10.1016/0043-1354(78)90107-0

Victor, L. (2020). *AD and Composting Industry Market Survey Report 2020*. Retrieved February 4, 2022, https://wrap.org.uk/resources/report/anaerobic-digestion-and-composting-latest-industry-survey-report-new-summaries

Visconti, F., J.M., & Rubio, J. L. (2010). An empirical equation to calculate soil solution electrical conductivity at 25 ºC from major ion concentrations. *European Journal of Soil Science*, *61*(6), 980–993. https://doi.org/10.1111/j.1365-2389.2010.01284.x

Voshell, S., Mäkelä, M., & Dahl, O. (2018). A review of biomass ash properties towards treatment and recycling. *Renewable and Sustainable Energy Reviews*, *96*, 479–486. https://doi.org/10.1016/j.rser.2018.07.025

Walker, M., Banks, C., Heaven, S., & Frederickson, J. (2010). *Residual biogas potential test for digestates*. Retrieved February 4, 2022, http://www.wrap.org.uk/sites/files/wrap/Residual Biogas Potential.pdf

Wang, Q., Jiang, G., Ye, L., Pijuan, M., & Yuan, Z. (2014). Heterotrophic denitrification plays an important role in N_2O production from nitritation reactors treating anaerobic sludge digestion liquor. *Water Research*, *62*, 202–210. https://doi.org/10.1016/j.watres.2014.06.003

Wang, Q., Zhou, X., Peng, L., Wang, D., Xie, G. J., & Yuan, Z. (2016). Enhancing post aerobic digestion of full-scale anaerobically digested sludge using free nitrous acid pretreatment. *Chemosphere*, *150*, 152–158. https://doi.org/10.1016/j.chemosphere.2016.02.035

Wang, X., Yang, G., Feng, Y., Ren, G., & Han, X. (2012). Optimizing feeding composition and carbon – nitrogen ratios for improved methane yield during anaerobic co-digestion of dairy, chicken manure and wheat straw. *Bioresource Technology*, *120*, 78–83. https://doi.org/10.1016/j.biortech.2012.06.058

Wang, Y., Cao, W., Zhang, X., & Guo, J. (2017). Abiotic nitrate loss and nitrogenous trace gas emission from Chinese acidic forest soils. *Environmental Science and Pollution Research*, *24*(28), 22679–22687. https://doi.org/10.1007/s11356-017-9797-4

Ward, A. J., Hobbs, P. J., Holliman, P. J., & Jones, D. L. (2008). Optimisation of the anaerobic digestion of agricultural resources. *Bioresource Technology*, *99*(17), 7928–7940. https://doi.org/10.1016/j.biortech.2008.02.044

Wei, X., & Li, Z. (2005). Study on hydration of Portland cement with fly ash using electrical measurement. *Materials and Structures/Materiaux et Constructions*, *38*(277), 411–417. https://doi.org/10.1617/14108

Weigand, H., Bertau, M., Hübner, W., Bohndick, F., & Bruckert, A. (2013). RecoPhos: Full-scale fertilizer production from sewage sludge ash. *Waste Management*, *33*(3), 540–544. https://doi.org/10.1016/j.wasman.2012.07.009

Whelan, M. J., Everitt, T., & Villa, R. (2010). A mass transfer model of ammonia volatilisation from anaerobic digestate. *Waste Management*, *30*(10), 1808–1812. https://doi.org/10.1016/j.wasman.2009.08.012

Wong-Chong, G. M., & Loehr, R. C. (1975). The kinetics of microbial nitrification. *Water*

Research, *9*(12), 1099–1106. https://doi.org/10.1016/0043-1354(75)90108-6

Wood, E., James, K., & Barker, E. (2020). *Comparison of the Environmental Impacts of Nitrogenous Materials*. Retrieved February 4, 2022, https://wrap.org.uk/resources/report/anaerobic-digestion-and-composting-latest-industry-survey-report-new-summaries

WRAP. (2011). PAS 100:2011 Specification for Composted Materials. In *British Standards Institution, London, UK*. Retrieved February 4, 2017, https://www.wrap.org.uk/sites/files/wrap/PAS 100_2011.pdf

WRAP. (2012a). *Quality Protocol Poultry Litter Ash. End of waste criteria for the production and use of treated ash from the incineration of poultry litter, feathers and straw*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/quality-protocol-poultry-litter-ash

WRAP. (2012b). *Using quality anaerobic digestate to benefit crops*. Retrieved February 4, 2022, https://www.nutrientmanagement.org/using-quality-digestate-to-benefit-crops/

WRAP. (2014a). *BSI PAS 110:2014 Specification for whole digestate, separated liquor and separated fibre derived from the anaerobic digestion of source-segregated biodegradable materials*. Retrieved February 4, 2022, http://www.wrap.org.uk/content/bsi-pas-110-specification-digestate

WRAP. (2014b). *Quality protocol of anaerobic digestate. End of waste criteria for the production and use of quality outputs from anaerobic digestion of source-segregated biodegradable waste*. Retrieved February 4, 2022, https://www.gov.uk/government/publications/quality-protocol-anaerobic-digestate

Wróbel, M., Frączek, J., Jewiarz, M., Mudryk, K., & Dziedzic, K. (2017). Impact of Selected Properties of Raw Material on Quality Features of Granular Fertilizers Obtained from Digestates and ASH Mixtures. *Agricultural Engineering*, *20*(4), 207–217. https://doi.org/10.1515/agriceng-2016-0078

Wróbel, M., Jewiarz, M., Mudryk, K., Frączek, J., & Dziedzic, K. (2018). Conceptual design of the mobile granulation line for production fertilizers from digestates and ash mixtures. *MATEC Web of Conferences*, *168*, 04003. https://doi.org/10.1051/matecconf/201816804003

Wu, D., Tian, S., Long, J., Peng, S., Xu, L., Sun, W., & Chu, H. (2021). Remarkable phosphate recovery from wastewater by a novel Ca/Fe composite: Synergistic effects of crystal structure and abundant oxygen-vacancies. *Chemosphere*, *266*, 129102. https://doi.org/10.1016/j.chemosphere.2020.129102

Wu, S. C., Cao, Z. H., Li, Z. G., Cheung, K. C., & Wong, M. H. (2005). Effects of biofertilizer containing N-fixer, P and K solubilizers and AM fungi on maize growth: A greenhouse trial. *Geoderma*, *125*(1–2), 155–166. https://doi.org/10.1016/j.geoderma.2004.07.003

Xie, R., Xing, Y., Ghani, Y. A., Ooi, K. E., & Ng, S. W. (2007). Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge. *Journal of Environmental Engineering and Science*, *6*(5), 533–541. https://doi.org/10.1139/S07-013

Yagi, S., & Fukushi, K. (2012). Removal of phosphate from solution by adsorption and precipitation of calcium phosphate onto monohydrocalcite. *Journal of Colloid and Interface Science*, *384*(1), 128–136. https://doi.org/10.1016/j.jcis.2012.06.063

Yang, F., Zhang, C., Rong, H., & Cao, Y. (2019). Research progress and application prospect of anaerobic biological phosphorus removal. *Applied Microbiology and Biotechnology*, *103*(5), 2133–2139. https://doi.org/10.1007/s00253-019-09634-0

Yang, X., Choi, H. S., Park, C., & Kim, S. W. (2015). Current states and prospects of organic waste utilization for biorefineries. *Renewable and Sustainable Energy Reviews, 49*, 335–349. https://doi.org/10.1016/j.rser.2015.04.114

Zazycki, M. A., Godinho, M., Perondi, D., Foletto, E. L., Collazzo, G. C., & Dotto, G. L. (2018). New biochar from pecan nutshells as an alternative adsorbent for removing reactive red 141 from aqueous solutions. *Journal of Cleaner Production*, *171*, 57–65. https://doi.org/10.1016/j.jclepro.2017.10.007

Zeshan, & Visvanathan, C. (2014). Evaluation of anaerobic digestate for greenhouse gas emissions at various stages of its management. *International Biodeterioration and Biodegradation*, *95*, 167–175. https://doi.org/10.1016/j.ibiod.2014.06.020

Zhang, J., Müller, C., & Cai, Z. (2015). Heterotrophic nitrification of organic N and its contribution to nitrous oxide emissions in soils. *Soil Biology and Biochemistry*, *84*, 199–209. https://doi.org/10.1016/j.soilbio.2015.02.028

Zhang, L., & Jahng, D. (2010). Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types. *Journal of Hazardous Materials*, *182*(1–3), 536–543. https://doi.org/10.1016/j.jhazmat.2010.06.065

Zhang, L., Lee, Y. W., & Jahng, D. (2012). Ammonia stripping for enhanced biomethanization of piggery wastewater. *Journal of Hazardous Materials*, *199–200*, 36–42. https://doi.org/10.1016/j.jhazmat.2011.10.049

Zhang, Y., Zhang, R., Li, S. L., Mostofa, K. M. G., Fu, X., Ji, H., Liu, W., & Sun, P. (2021). Photo-ammonification of low molecular weight dissolved organic nitrogen by direct and indirect photolysis. *Science of the Total Environment*, *764,* 142930. https://doi.org/10.1016/j.scitotenv.2020.142930

Zheng, Y., Ke, L., Xia, D., Zheng, Y., Wang, Y., Li, H., & Li, Q. (2016). Enhancement of digestates dewaterability by CTAB combined with CFA pretreatment. *Separation and Purification Technology*, *163,* 282–289. https://doi.org/10.1016/j.seppur.2016.01.052

Zhou, H., Margenot, A. J., Li, Y., Si, B., Wang, T., Zhang, Y., Li, S., & Bhattarai, R. (2020). Phosphorus pollution control using waste-based adsorbents: Material synthesis, modification, and sustainability. *Critical Reviews in Environmental Science and Technology*, *52*(12), 2023-2059. https://doi.org/10.1080/10643389.2020.1866414

Zhu, N. min, Qiang-Li, Guo, X. jing, Hui-Zhang, & Yu-Deng. (2014). Sequential extraction of anaerobic digestate sludge for the determination of partitioning of heavy metals. *Ecotoxicology and Environmental Safety*, *102*(1), 18–24. https://doi.org/10.1016/j.ecoenv.2013.12.033

Zumdahl, S. S. (2018). *Peroxide Ion. Oxides of Phosphorus*. Britannica. Retrieved February 4, 2022, https://www.britannica.com/science/peroxide-ion

Appendix

A.1. Calculation of the blending ratio of wood ash and anaerobic digestate based on the threshold values in the UK regulation

The following assumption were made for the calculation:

1. Consider the threshold value reported in the QPPLA for the wood ash. As described in the QPPLA, the incineration fuel can contain up to 10 % of forestry waste (*e.g.* woodchip) but it needs to have a minimum of 85 % of poultry litter (WRAP, 2012a).
2. Wood ash that meets the QPPLA is no longer regarded as a waste.
3. The blend of wood ash and anaerobic digestate is not regarded as a waste.
4. Consider a moisture content of 5 % for the PLA and 90 % for the anaerobic digestate.

The calculation was based on the specifications for the heavy metals that are defined both for the PLA and the anaerobic digestate (Table A.1).

Table A.1. Upper limits of heavy metals are reported in the EoW criteria of PLA and anaerobic digestate (WRAP, 2012a, 2014a).

Metal/(mg/kg fresh weight)	PLA[a]	Digestate (< 1 kg N/t)	Digestate (> 9 kg N/t)
As	17	0.12	1.2
Cd	3		
Co	11		
Cr	31	8	80
Cu	596	16	160
Hg	0.5	0.08	0.8
Mn	3,500		
Mo	45		
Ni	24	4	40
Pb	244	16	160
Se	11		
V	20		
Zn	2,063	32	320

[a] Reported in dry weight (WRAP, 2012a) but employed in fresh weight for the calculation considering the low moisture content of the ash (< 5 %).

The upper limit for the manganese is not reported for the anaerobic digestate in the BSI PAS 110:2014 (WRAP, 2014a). The reason might be that QPAD (WRAP, 2014b) specifies the biowaste types acceptable for the production of quality digestate, which general contain a low amount of this heavy metal. The second highest allowance in the PLA is for Zn and it was found that this is the limiting factor that determines the blending ratio of wood ash and anaerobic digestate (Table A.2).

Table A.2. Calculation of the blending ratio based on the content of Zn in the anaerobic digestate supplemented with wood ash (Moure Abelenda & Aiouache, 2022).

		< 1 kg N/t	**< 9 kg N/t**	**DOSE/(g TS wood ash/g TS digestate)**	**0.147345**		**1.473545**	
		MIN	**MAX**	**DOSE/(%)**	**1.53 %**		**13.43 %**	
mg/kg	**PLA**	**Digestate**	**Digestate**	**g wood ash/kg anaerobic digestate**	**15.51**	15.52	**155.11**	155.12
As	17				0.26367	0.26384	2.63687	2.63704
Cd	3	0.12	1.2		0.04653	0.04656	0.46533	0.46536
Co	11				0.17061	0.17072	1.70621	1.70632
Cr	31	8	80		0.48081	0.48112	4.80841	4.80872
Cu	596	16	160		9.24396	9.24992	92.44556	92.45152
Hg	0.5	0.08	0.8		0.007755	0.00776	0.077555	0.07756
Mn	3500				54.285	54.32	542.885	542.92
Mo	45				0.69795	0.6984	6.97995	6.9804
Ni	24	4	40		0.37224	0.37248	3.72264	3.72288
Pb	244	16	160		3.78444	3.78688	37.84684	37.84928
Se	11				0.17061	0.17072	1.70621	1.70632
V	20				0.3102	0.3104	3.1022	3.1024
Zn	2063	32	320		31.99713	32.01776	319.9919	320.0126

A.2. Description of error propagation associated with the calculation of the share of the samples FWD, PVWD and WFA in the Blend 1 tested in Chapter 3

The share of each sample in the tri-component Blend 1 of chapter 3 was determined with Equation A.1, Equation A.2 and Equation A.3. for FWD, PVWD and WFA, respectively. Since the standard deviations ($\sigma_{\overline{FWD}}$, $\sigma_{\overline{PVWD}}$ and $\sigma_{\overline{WFA}}$) represented less than 20 % of the average masses ($\overline{\text{FWD}}$, $\overline{\text{PVWD}}$, $\overline{\text{WFA}}$,), the calculation of the propagation of the uncertainty was done with Equation A.4, Equation A.5 and Equation A.6. Additionally, it should be noted that this approach can only be followed when the uncertainties are regarded as random and independent from each other (Batstone, 2013; Tellinghuisen, 2001).

$$FWD = \frac{\overline{FWD}}{\overline{FWD} + \overline{PVWD} + \overline{WFA}}$$

Equation A.1

$$PVWD = \frac{\overline{PVWD}}{\overline{FWD} + \overline{PVWD} + \overline{WFA}}$$

Equation A.2

$$WFA = \frac{\overline{WFA}}{\overline{FWD} + \overline{PVWD} + \overline{WFA}}$$

Equation A.3

$$\sigma_{FWD}^2 = \left(\frac{\delta FWD}{\delta \overline{FWD}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\delta FWD}{\delta \overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\delta FWD}{\delta \overline{WBA}}\right)^2 \cdot \sigma_{\overline{WBA}}^2$$

$$\sigma_{FWD} = \sqrt{\left(\frac{\overline{PVWD} + \overline{WFA}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{-\overline{FWD}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{-\overline{FWD}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{WFA}}^2}$$

Equation A.4

$$\sigma_{PVWD}^2 = \left(\frac{\delta PVWD}{\delta \overline{FWD}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\delta PVWD}{\delta \overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\delta PVWD}{\delta \overline{WFA}}\right)^2 \cdot \sigma_{\overline{WFA}}^2$$

$$\sigma_{PVWD} = \sqrt{\left(\frac{-\overline{PVWD}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\overline{FWD} + \overline{WFA}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{-\overline{PVWD}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{WFA}}^2}$$

Equation A.5

$$\sigma_{WFA}^2 = \left(\frac{\delta WFA}{\delta \overline{FWD}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\delta WFA}{\delta \overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\delta WFA}{\delta \overline{WFA}}\right)^2 \cdot \sigma_{\overline{WFA}}^2$$

$$\sigma_{WFA} = \sqrt{\left(\frac{-\overline{WFA}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{-\overline{WFA}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\overline{FWD} + \overline{PVWD}}{(\overline{FWD} + \overline{PVWD} + \overline{WFA})^2}\right)^2 \cdot \sigma_{\overline{WFA}}^2}$$

Equation A.6

A.3. Error propagation associated with the calculation of the ratio of anaerobic digestates to wood ashes, in the Blend 1 (B1) and the Blend 2 (B2) tested in Chapter 3

$$B1 = \frac{\overline{FWD} + \overline{PVWD}}{\overline{WFA}}$$

Equation A.7

$$\sigma_{B1}^2 = \left(\frac{\delta B1}{\delta\overline{FWD}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\delta B1}{\delta\overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\delta B1}{\delta\overline{WFA}}\right)^2 \cdot \sigma_{\overline{WFA}}^2$$

$$\sigma_{B1} = \sqrt{\left(\frac{1}{\overline{WFA}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{1}{\overline{WFA}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\overline{FWD} + \overline{PVWD}}{\overline{WFA}^2}\right)^2 \cdot \sigma_{\overline{FWD}}^2}$$

Equation A.8

$$B2 = \frac{\overline{PVWD}}{\overline{WFA} + \overline{WBA}}$$

Equation A.9

$$\sigma_{B2}^2 = \left(\frac{\delta B2}{\delta\overline{FWD}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{\delta B2}{\delta\overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\delta B2}{\delta\overline{WFA}}\right)^2 \cdot \sigma_{\overline{WFA}}^2$$

$$\sigma_{B2} = \sqrt{\left(\frac{1}{\overline{WFA}}\right)^2 \cdot \sigma_{\overline{FWD}}^2 + \left(\frac{1}{\overline{WFA}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2 + \left(\frac{\overline{FWD} + \overline{PVWD}}{\overline{WFA}^2}\right)^2 \cdot \sigma_{\overline{FWD}}^2}$$

Equation A.10

Table A.3. Parameters were determined in-house by Dr Alfonso Lag Brotóns and Dr Rachel Marshall, in collaboration with Stopford Projects Ltd. as part of the AVAnD project, using the method BS EN 13657. The average and the standard deviation (n=3) of the concentration of all the elements is expressed as mg/kg fresh sample (Moure Abelenda *et al.*, 2021c).

Element	**FWD**		**PVWD**		**WFA**		**WBA**	
mg/kg sample	**Average**	**St. Dev.**	**Average**	**St. Dev.**	**Average**	**St. Dev.**	**Average**	**St. Dev.**
Ca	893.22	130.14	987.99	14.51	112,686.35	22,169.69	82,846.38	9,370.46
Mg	38.53	3.33	157.21	4.52	68,094.13	13,684.32	11,513.72	1,570.79
K	2,787.19	150.98	2,128.45	138.55	18,837.07	3,738.85	40,189.39	5,771.37
Na	1,447.88	78.13	631.26	37.14	8,196.90	1,633.44	4,284.92	539.76
P	374.37	23.46	543.45	14.15	12,833.40	2,249.82	5,968.87	492.99
S	274.48	12.87	298.30	19.82	12,440.02	2,178.54	4,667.30	342.04
Al	1,298.37	109.68	1,945.27	63.32	6,317.10	1,068.97	8,988.84	796.42
Cu	38.36	1.03	34.87	0.52	135.09	23.60	106.2	10.44
Fe	4,581.08	78.98	3,265.22	84.85	7,081.67	438.76	16,050.89	2,279.87
Mn	172.28	5.92	123.98	3.64	9,962.25	1,632.06	5,586.48	465.68
Zn	215.41	5.79	155.99	2.49	1,097.76	188.54	409.27	56.67
Co	45.68	2.62	<DL	<DL	33.65	5.42	43.70	5.39
Ni	37.72	0.88	<DL	<DL	<DL	<DL	<DL	<DL
Cr	<DL	<DL	<DL	<DL	54.88	7.77	82.43	4.93
Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

Element	**FWD**		**PVWD**		**WFA**		**WBA**	
mg/kg sample	**Average**	**St. Dev.**	**Average**	**St. Dev.**	**Average**	**St. Dev.**	**Average**	**St. Dev.**
[a]N	1,274.81	281.89	1,900.74	49.70	662.62	75.79	962.94	96.48
[b]C	11,612.57	120.83	16,246.60	276.77	13,016.74	59.94	81,338.54	2,527.80
[c]P	29.01	3.47	53.03	5.05	2,281.01	621.20	2,035.04	554.25

<DL = below the detection limit.

[a] Determined following the method BS EN 16168.

[b] Determined following the method BS EN 13137.

[c] Determined following the method described by Grimshaw (1987).

Table A.4. Procedures for the determination of pH and EC in digestate and soil samples (Moure Abelenda *et al.*, 2021c).

References	pH/(-)	EC/(dS/m)	Method	Origen of the sample
(Alburquerque *et al.*, 2012)	5.64–8.20	8.7–30.3	Directly measurement of EC, after homogenisation of the samples	Co-digestion of different feedstock in different ratios: cattle slurry, cattle manure, glycerine, maize-oat silage, orange peel waste, wastewaters and pasteurised slaughterhouse water.
(Foth, 1990)	4–10		S/E ratio 1/3, 30 min mixing, no settling	Soil
(Lencioni *et al.*, 2016)	8.5	2.8–41	ISO Standard methods "ICS 65.080: Fertilisers and Soil Conditioners". Several dilutions ranging from S/E ratios 1/1 to 1/20	Digestion of swine manure
(Lencioni *et al.*, 2016)	5.5–8.76	[a]0.7–1.56	US EPA method 9045D "Soil and water pH" (S/E ratio 1/3.5, mixing and sedimentation before measuring) and method 9050A "Specific conductance" (S/E ratio 1/6, no settling).	Soil fertilised with digestate. Dilution ratios ranging from 1/1 to 1/1.43 (*i.e.* 1.43 g of the total mixture of digestate with soil contain 1 gram of soil).
(Zhu *et al.*, 2014)	7.38	12.32	Not reported	Digestion of pig slurry

References	**pH/(-)**	**EC/(dS/m)**	**Method**	**Origen of the sample**
(Astals *et al.*, 2013)	7.7–8.1	18.8–20.4	Not reported	Digestion of pig manure and co-digestion of pig manure and crude glycerol.
(Garfí *et al.*, 2011)	7.10	6.88 10^{-3}	APHA, 1998. Standard methods for the examination of water and wastewater	Digestion of guinea pig manure diluted in water (~ 6–8 % solid concentration).
(Walker *et al.*, 2010)	7.0–8.9	From 23.2 to 145	For pH the BS EN 12176:1998 For EC the BS EN 13370:2003	Co-digestion of food waste, agricultural waste, maize, cattle and pig slurry.

[a] To authors’ knowledge Lencioni *et al.* (2016) are the only authors who determined the EC of the undiluted samples (soil amended with digestate) using the data of EC of the diluted sample (S/E 1/6) and an empirical equation (Visconti *et al.*, 2010)**.**

A.4. Calculation of the concentration of the WS species in fresh blends and their total mass in the samples and the blend

The calculation of the concentration of the WS species (Equation A.11) was based on the value (V) given by the Autoanalyzer^{TM} and the TOC-L Shimadzu®. It was necessary to take into account any dilution of the WS extract required in order to have a concentration in the calibration range of the equipment. In the case of the TOC-L Shimadzu®, the results V provided by the machine already consider the dilution made to the extract.

Both the mass of the sample or blend (Y) and the volume of WS extract (W) were required to express the concentration of the WS species in fresh basis of the blend according to Equation A.11. Due to the heterogeneity of both samples (*i.e.* the digestates and the ashes), the intended 3 grams of blend were not always achieved. However, the Y was recorded and the S/E 1/10 was kept approximately constant by adding the corresponding volume of ultrapure milli-Q water (W). These details of Chapter 5 are presented in Figure A.8, Figure A.11 and Figure A.12. In Chapter 3, the W was considered to be equal to the volume of ultrapure milli-Q water added to carry out the WS extraction. This was a reasonable assumption because the water provided by the ~ 3 g of each blend (~ 90 % moisture) was negligible compared to the volume of ultrapure milli-Q water added (~ 30 mL). On the other hand, the losses of liquid during the WS extraction were regarded as minimal. In the first study of Chapter 5, the initial volume of the WS extract was calculated based on the volume of extractant (Table 5.2) and the moisture of the samples (Table 5.1). In the second study of Chapter 5, the empirical WS extract was calculated based on the experimental WI material recovered after the incubation (Table 5.1), the initial mass of the sample and the initial mass of extractant (Table 5.2). In all calculations, a density of 1 g/mL was assumed for both extractant solutions and moisture of the samples.

$$WS\ species\ \left(\frac{mg}{kg}\right) = V\frac{mg}{L} \times dilution\ factor \times \frac{1\ L}{10^3 mL} \times \times W\ mL\ WS\ extract \times \frac{1}{Y\ g\ fresh\ blend} \times \frac{10^3 g}{1\ kg} \quad \textbf{Equation A.11}$$

The coversion factors N/NH$_4^+$ = 0.78, N/NO$_3^-$ = 0.23 and P/PO$_4^{3-}$ = 0.33 were applied to determine the amount of N in the form of NH$_4^+$ & NH$_3$ and NO$_3^-$ & NO$_2^-$ and P in the form of PO$_4^{3-}$, respectively.

For the calculation of the total mass of any of the WS species in the samples or blends, it would not be necessary to divide by Y in Equation A.11.

Table A.5. Characterisation of the FWD, PVWD and WFA by NRM laboratory. For all the values, the estimated expanded uncertainty calculated as per the NORTEST 537 method was 10 % (Moure Abelenda *et al.*, 2021c).

Element	**FWD**		**PVWD**		**WFA**	
mg/kg sample	**Total**	**WS**	**Total**	**WS**	**Total**	**WS**
Na	3,734.00	3,269.00	323.00	289.00	7,931.15	4,260.59
K	3,127.00	2,643.00	3,675.00	3,149.00	113,099.66	87,208.77
Ca	4,609.00	18.10	705.00	38.80	266,156.53	76.81
Mg	213.00	2.46	518.00	14.40	35,012.06	<0.01
S	485.00	125.00	291.00	38.50	15,126.99	13,851.40
Cu	2.10		1.44		175.12	
Zn	12.40	0.14	6.52	0.10	1,627.82	
Mo	0.40	0.25	0.14	0.03	3.26	
Pb	<0.50	<0.01	<0.5	<0.01	19.80	
Cd	0.03	<0.01	0.01	<0.01	27.90	
Hg	<0.01	<0.01	<0.05	<0.05	<0.20	
Ni	1.69	0.58	0.95	0.13	30.15	
Cr	0.91	0.02	1.29	0.07	72.54	
F^-	<10.00		<10.00			
As	<0.50	0.03	<0.50	<0.01	4.01	
Se	0.33	<0.05	<0.02	<0.05	0.84	
Co					13.72	
Fe					12,974.80	
Mn					19,024.40	
V					15.72	
B					408.95	
N	8,500.00		3,800.00			
P	1,004.00	174.00	1,119.00	200.00	23,848.16	11.04

A.5. Propagation of uncertainty in the calculation of the initial composition of a tri-component blend (*e.g.* Blend 1; FWD+PVWD+WFA)

It is noteworthy to highlight that this approach can only be followed when the uncertainties are regarded as random and independent from each other (Batstone, 2013; Tellinghuisen, 2001). Furthermore, it is necessary to consider the nominal share of each sample in the tri-component blend Table 3.2 (FWD, PVWD and WFA) and that the standard deviations ($\sigma_{[FWD]}, \sigma_{[PVWD]}$ and $\sigma_{[WFA]}$) shown in the Table 3.3 of the initial characterisation represent less than 20 % of the average values ([FWD], [PVWD] and [WFA]). In this way, X represents the average value (Equation A.12) of a particular parameter in the blend (*e.g.* EC, DM, C, N, etc.) and σ_X the standard deviation (Equation A.13) at time zero.

$$X = FWD \cdot [FWD] + PVWD \cdot [PVWD] + WFA \cdot [WFA]$$

Equation A.12

$$\sigma_X^2 = \left(\frac{\delta X}{\delta [FWD]}\right)^2 \cdot \sigma_{[FWD]}^2 + \left(\frac{\delta X}{\delta [PVWD]}\right)^2 \cdot \sigma_{[PVWD]}^2 + \left(\frac{\delta X}{\delta [WFA]}\right)^2 \cdot \sigma_{[WFA]}^2$$

$$\sigma_X = \sqrt{FWD^2 \cdot \sigma_{[FWD]}^2 + PVWD^2 \cdot \sigma_{[PVWD]}^2 + WFA^2 \cdot \sigma_{[WFA]}^2}$$

Equation A.13

Only the average value and the uncertainty of the pH of the blend were determined differently, because of the logarithmic relation with the concentration of protons in the blend (Equation A.17).

$$pH = -\log[H^+] \rightarrow [H^+] = 10^{-pH}$$

Equation A.14

$$Y = FWD \cdot 10^{-[FWD]} + PVWD \cdot 10^{-[PVWD]} + WFA \cdot 10^{-[WFA]}$$

Equation A.15

$$\sigma_Y^2 = \left(\frac{\delta Y}{\delta [FWD]}\right)^2 \cdot \sigma_{[FWD]}^2 + \left(\frac{\delta Y}{\delta [PVWD]}\right)^2 \cdot \sigma_{[PVWD]}^2 + \left(\frac{\delta Y}{\delta [WFA]}\right)^2 \cdot \sigma_{[WFA]}^2$$

Equation A.16

$$\sigma_Y = \sqrt{\left(FWD \cdot \frac{ln10}{10^{[FWD]}}\right)^2 \cdot \sigma_{[FWD]}^2 + \left(PVWD \cdot \frac{ln10}{10^{[PVWD]}}\right)^2 \cdot \sigma_{[PVWD]}^2 + \left(WFA \cdot \frac{ln10}{10^{[WFA]}}\right)^2 \cdot \sigma_{[WFA]}^2}$$

$$Z = -\log Y\,;\; \sigma_Z^2 = \left(\frac{\delta Z}{\delta Y}\right)^2 \cdot \sigma_Y^2 \rightarrow \sigma_Z = \sqrt{\left(\frac{-1}{Y \cdot \ln 10}\right)^2 \cdot \sigma_Y^2}$$

Equation A.17

A.6. Error propagation in the calculation of the Q

$$pH = -log[H^{+}] \rightarrow [H^{+}] = 10^{-pH}$$

$$\sigma_{[H^{+}]} = \sqrt{\left(\frac{\partial([H^{+}])}{\partial(pH)}\right)^{2} \cdot \sigma_{pH}^{2}} \rightarrow \sigma_{[H^{+}]} = \sqrt{\left(\frac{ln10}{10^{pH}}\right)^{2} \cdot \sigma_{pH}^{2}}$$

Equation A.18

$$[H^{+}] \cdot [OH^{-}] = 10^{-14} \rightarrow [OH^{-}] = \frac{10^{-14}}{[H^{+}]}$$

$$\sigma_{[H^{+}]} = \sqrt{\left(\frac{\partial([OH^{-}])}{\partial([H^{+}])}\right)^{2} \cdot \sigma_{[H^{+}]}^{2}} \rightarrow \sigma_{[OH^{-}]} = \sqrt{\left(\frac{10^{-14}}{[H^{+}]^{2}}\right)^{2} \cdot \sigma_{[H^{+}]}^{2}}$$

Equation A.19

$$Q = \frac{1}{W}(C_{a} - [H^{+}] + [OH^{-}])$$

$$\sigma_{Q} = \sqrt{\left(\frac{1}{W}\right)^{2} \cdot \sigma_{H^{+}}^{2} + \left(\frac{1}{W}\right)^{2} \cdot \sigma_{H^{+}}^{2} + \left(\frac{-C_{a} + [H^{+}] - [OH^{-}]}{W^{2}}\right)^{2} \cdot \sigma_{W}^{2}}$$

Equation A.20

Table A.6. Target pH and doses of the acids used in the treatment of slurry and manure (Moure Abelenda *et al.*, 2021b).

Target pH	Acidifying agent	Dose	Dose equivalent/(mmol H^+/g slurry)	Reference
<5.5	H_2SO_4			(Jensen, 2002)
< 6.0	96 % H_2SO_4	0.5 kg/100 L slurry	0.0510	(Kai *et al.*, 2008)
5.9 – 6.7	H_2SO_4 (concentrated)	1.9 – 3.3 L/ton slurry	[a]0.0464	(Nyord *et al.*, 2013)
5.5 (increase to 6 after storage)	H_2SO_4	5.4 mL/kg pig slurry 2.85 mL/kg cattle slurry	0.0963 0.0508	(Sørensen and Eriksen, 2009)
6.0 – 7.3 (19 hours after acidification)	5 M H_2SO_4	Up to 2.2 % acid to slurry	[b]0.1102	(Frost and Laughlin, 1992)
5.5	K_2SO_4 + HCl	1.6 g sulphur/kg slurry	[c]0.0575	(Eriksen *et al.*, 2012)
5.3	4 M HCl	17 – 18 mL/L manure	[d]0.0700	(Panetta *et al.*, 2005)
7.0 – 6.0	0.5 M HCl	0 – 0.4 mol HCl/kg slurry	[e]0.2000	(Vandré and Clemens, 1996)
4.5 and 6.0	HNO_3			(Velthof and Oenema, 1993)

Target pH	Acidifying agent	Dose	Dose equivalent/(mmol H^+/g slurry)	Reference
> 8.0 - < 4.0	HNO_3	0.7 – 3.5 mg HNO_3-N/g slurry	[f]0.1500	(Laughlin and O'bric, 1995)
5.0	HNO_3 $CH_3CH(OH)COOH$		0.1587 0.0008	(Berg *et al.*, 2006)
5.5 – 7.5	80 % $CH_3CH(OH)COOH$ Sucrose	0.2 mL $CH_3CH(OH)COOH$ /cm^3 manure 0.12 g sucrose/cm^3 manure	0.0077 [g]0.0008	(Berg and Pazsiczki, 2006)

[a] Considering average value 2.6 L H_2SO_4 and density 1.84 g/mL according to the Material Safety Data Sheet (MSDS) of 95 % H_2SO_4.

[b] Assuming that the density of the 5 M H_2SO_4 is around 1 g/mL. According to the MSDS, the density of the 18.8 M (100 %) H_2SO_4 is 1.84 g/mL. Also, assuming that the density of the acidified slurry is around 1 g/mL.

[c] Assuming that the concentration of the HCl is equal to the proton concentration provided by the H_2SO_4.

[d] Taking average value 17.5 mL HCl/L manure and assuming density of manure 1 kg/L.

[e] Taking average value 0.2 mol HCl/Kg slurry.

[f] Taking average value 2.1 mg HNO_3-N/g slurry.

[g] Considering that all the sucrose (compound made of one molecule of glucose and one molecule of fructose) was converted to $CH_3CH(OH)COOH$ due to the anaerobic fermentation and assuming that there are no losses of COD due to the microbial metabolism.

Table A.7. Preparation of the acidifying agents for the evaluation of the first strategy (*i.e.* acidification of the anaerobic digestates with commercial doses before the addition of the wood ashes). The total volume of acidifying agent added to the digestates (20.557 mL) was determined by the amount of concentrated lactic acid required to meet the highest dose (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

Acid	**mol acid/L**	**^{a}[H$^+$]/(mol H$^+$/L)**	**Target dose/(mmol H$^+$/g digestate)**	**Volume acid/(mL)**	**Milli-Q/(mL)**	**mEq/g digestate**
H_2SO_4	18.293	18.304	0.08	0.009	20.548	0.156
			0.16	0.020	20.538	0.33
			0.24	0.029	20.528	0.486
			0.32	0.038	20.519	0.643
			0.40	0.048	20.509	0.816
HCl	11.813	11.813	0.08	0.014	20.543	0.079
			0.16	0.029	20.528	0.157
			0.24	0.043	20.514	0.236
			0.32	0.058	20.500	0.314
			0.40	0.072	20.485	0.393
HNO_3	15.212	15.212	0.08	0.012	20.545	0.087
			0.16	0.025	20.533	0.173
			0.24	0.036	20.521	0.253
			0.32	0.048	20.509	0.339
			0.40	0.061	20.497	0.426
$CH_3CHOHCOOH$	11.989	0.041	0.08	4.112	16.446	22.77
			0.16	8.223	12.334	45.54
			0.24	12.334	8.223	68.31

Acid	mol acid/L	[a]$[H^+]$/(mol H^+/L)	Target dose/(mmol H^+/g digestate)	Volume acid/(mL)	Milli-Q/(mL)	mEq/g digestate
			0.32	16.446	4.112	91.08
			0.40	20.557	0	113.85

[a] Calculated considering pKa_2 of 1.99 for the H_2SO_4 and a pKa_1 of 3.86 for the $CH_3CH(OH)COOH$ (Regueiro, Coutinho, & Fangueiro, 2016).

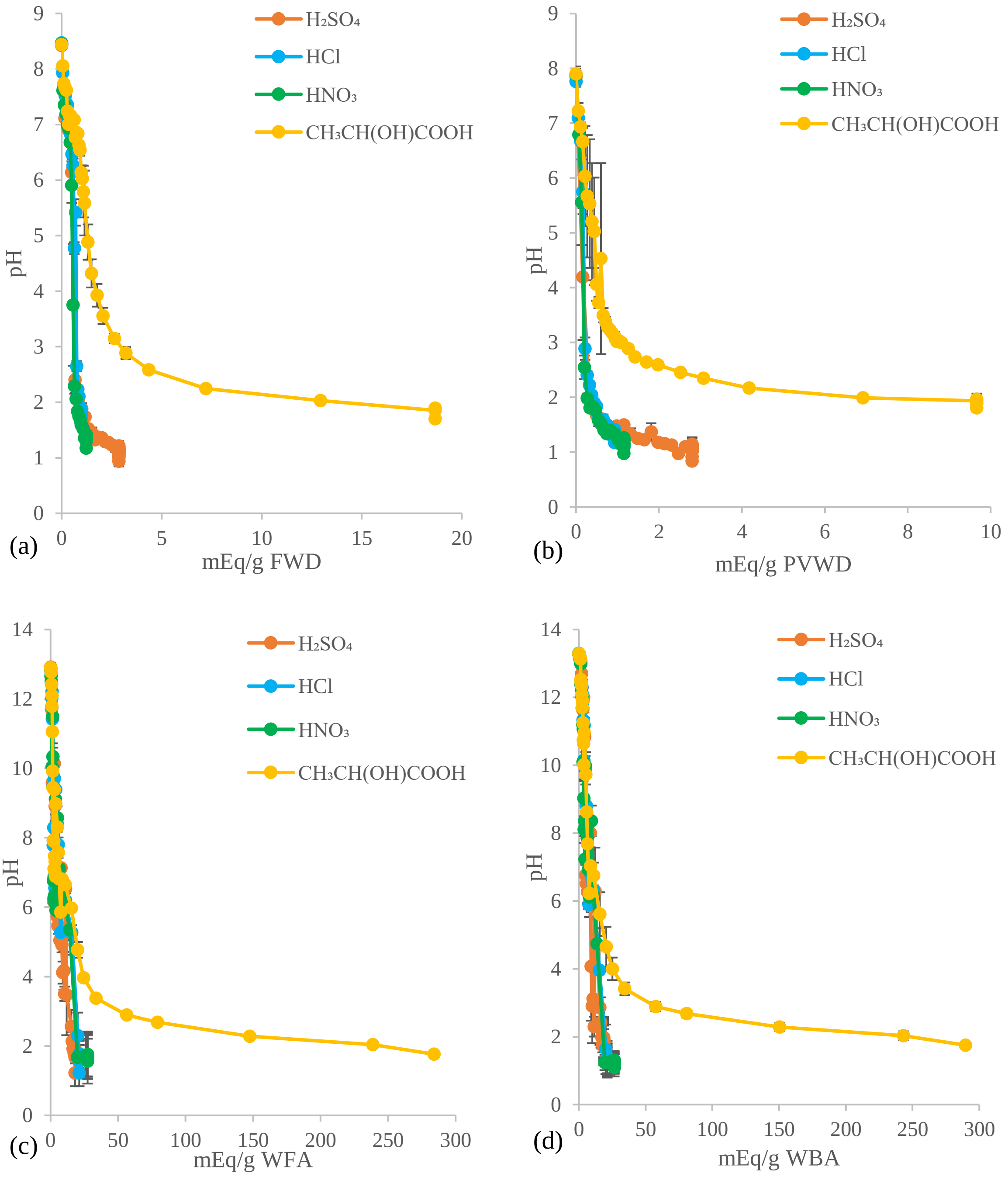


Figure A.1. Zooming out of the experimental results (n = 3) of the titration of analytes prepared by mixing 20 mL of milli-Q® water with (a) 2.11 ± 0.09 g of FWD, or (b) 2.20 ± 0.10 g of PVWD, or (c) 0.52 ± 0.02 g of WFA, or (d) 0.52 ± 0.02 g of WBA (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022). The titrants (18.29 mol H_2SO_4/L, 11.81 mol HCl/L, 15.21 mol HNO_3/L and 11.99 mol $CH_3CH(OH)COOH$/L) were employed in volumes ≤ 200 µL per dose-point, with the exception of $CH_3CH(OH)COOH$ that required volumes up to 10 times higher per dose-point to reach the titration end-point (pH < 2).

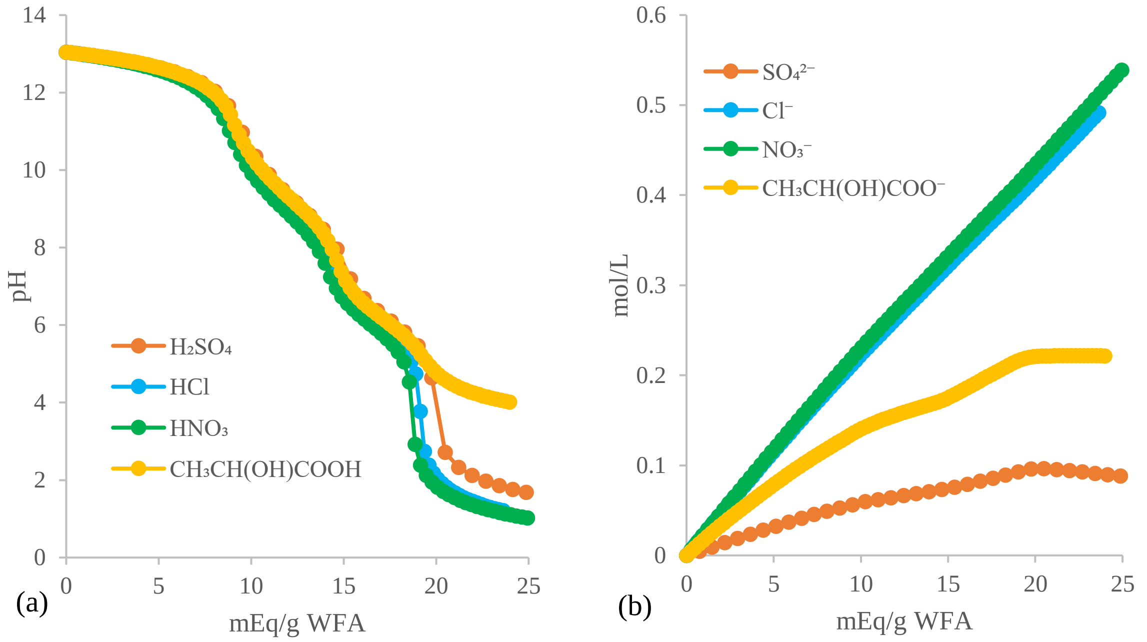


Figure A.2. (a)Visual MINTEQ simulation of the titration of a suspension of 20 mL milli-Q® water with 0.5 g of WFA (Table A.5) with four different acids: 17.82 mol H_2SO_4/L, 11.97 mol HCl/L, 15.78 mol HNO_3/L and 11.99 mol $CH_3CH(OH)COOH$/L. (b) Anion concentration in the water-soluble fraction of the analyte, in each titration (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

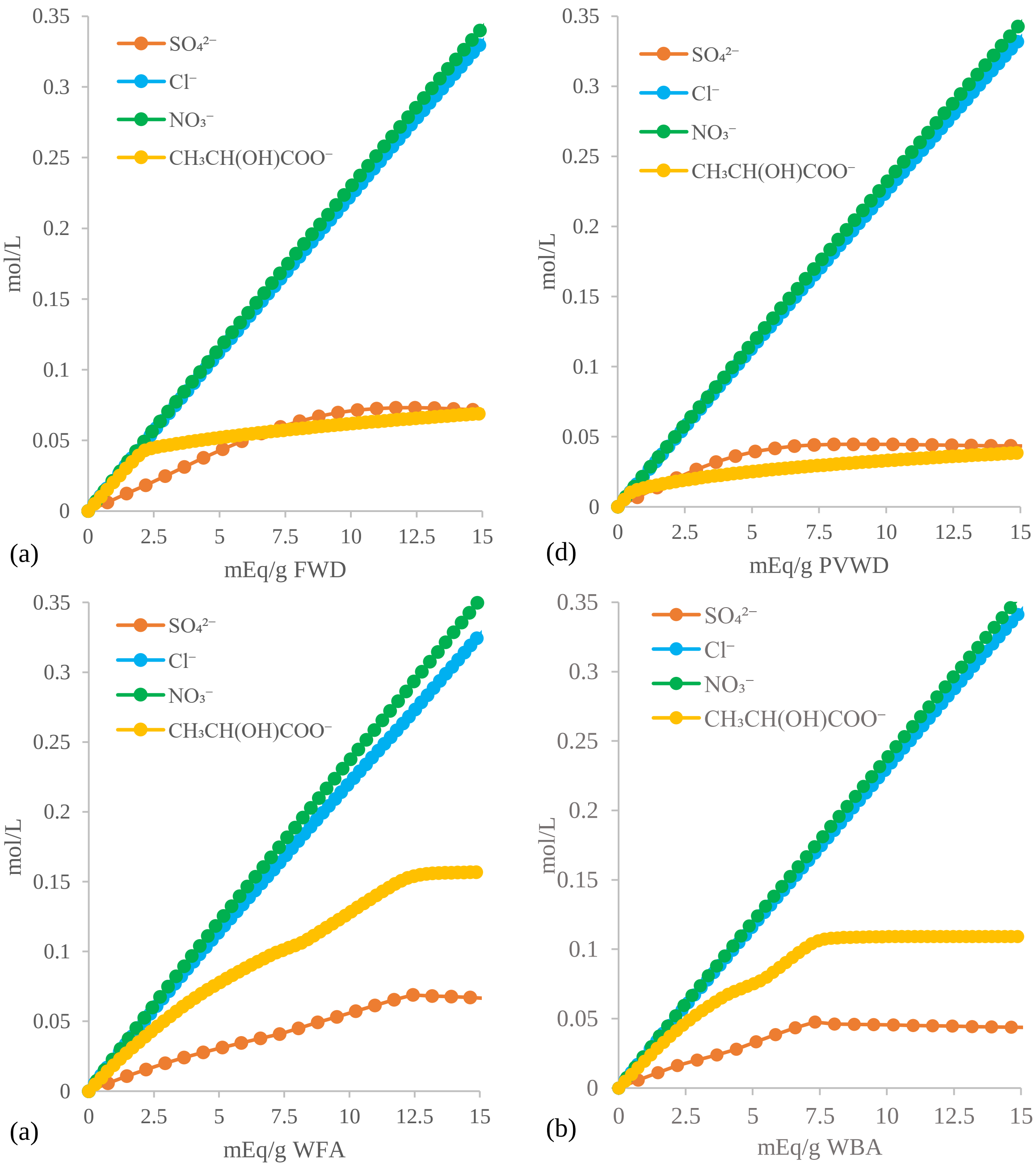


Figure A.3. Visual MINTEQ simulation of the concentration of the anions in the in the water-soluble fraction of the suspensions of 20 mL of milli-Q® water with (a) 2 g of FWD, (b) 2 g of PVWD, (c) 0.5 g of WFA, or (d) 0.5 g of WBA. The titrants employed were: 17.82 mol H_2SO_4/L, 11.97 mol HCl/L, 15.78 mol HNO_3/L and 11.99 mol $CH_3CH(OH)COOH$/L. The simulations were conducted using the composition of the samples reported in Table A.3. Molecules of glycine and glyphosate were used to represent the C_{org}, N_{org} and P_{org} of the anaerobic digestates. The Dissolved Inorganic Carbon model was used for the wood ashes (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

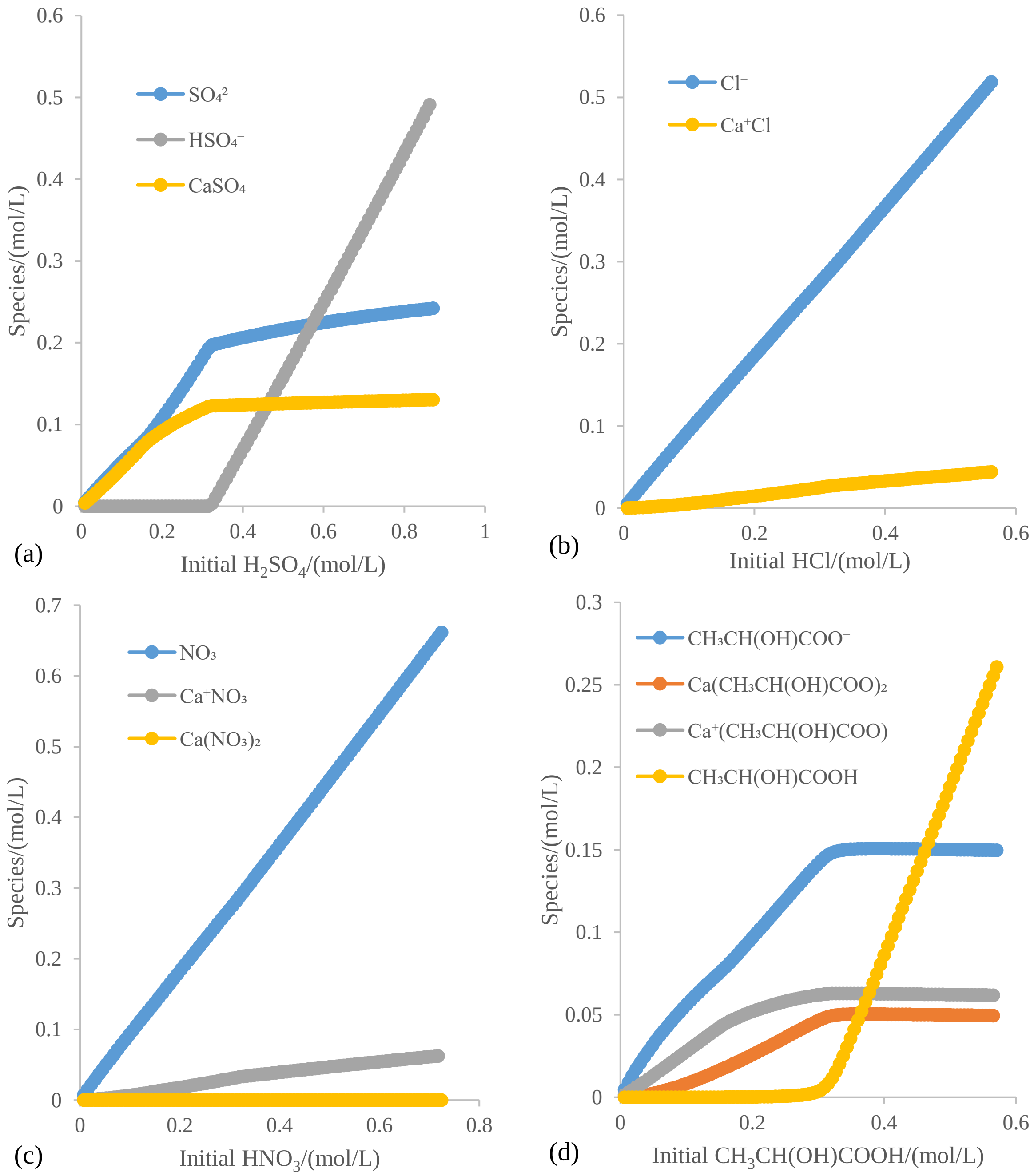


Figure A.4. Visual MINTEQ simulation of the fate of the cations of the acid titrants once added to the 20 mL analyte containing 162.79 mmol Ca^{2+}/L and 162.79 mmol CO_3^{2-}/L. Each step of the titration corresponds to the addition of 10 µL of the following concentrated acids: (a) 18.29 mol/L H_2SO_4; (b) 11.81 mol/L HCl; (c) 15.21 mL HNO_3; and (d) 11.99 mL $CH_3CH(OH)COOH$ (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

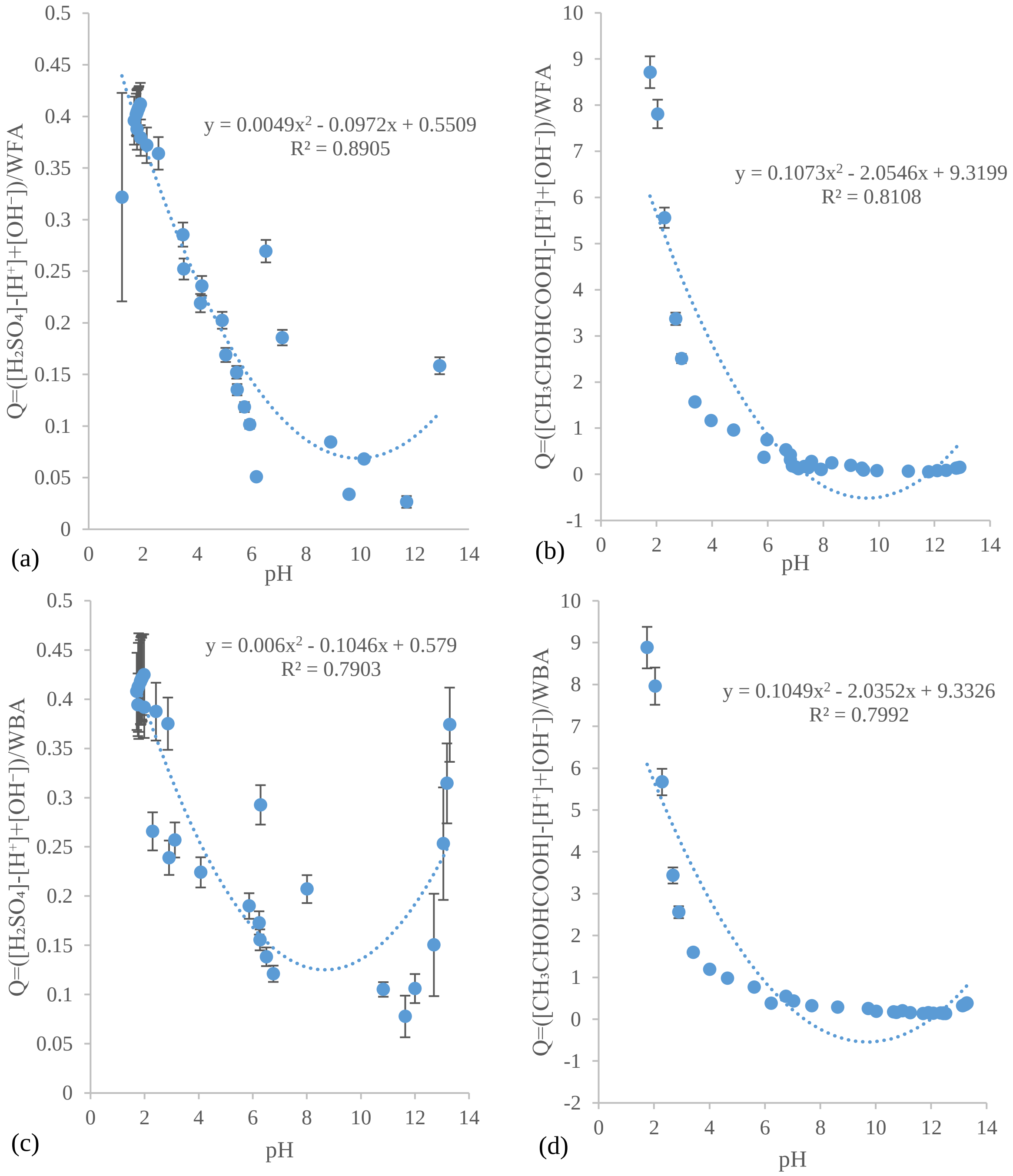


Figure A.5. Calculation of the pH_{zpc} of the WFA using as titrants (a) 17.82 mol H_2SO_4/L and (b) 11.99 mol $CH_3CH(OH)COOH$/L. Calculation of the pH_{zpc} of the WBA using as titrants (c) 17.82 mol H_2SO_4/L and (d) 11.99 mol $CH_3CH(OH)COOH$/L (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

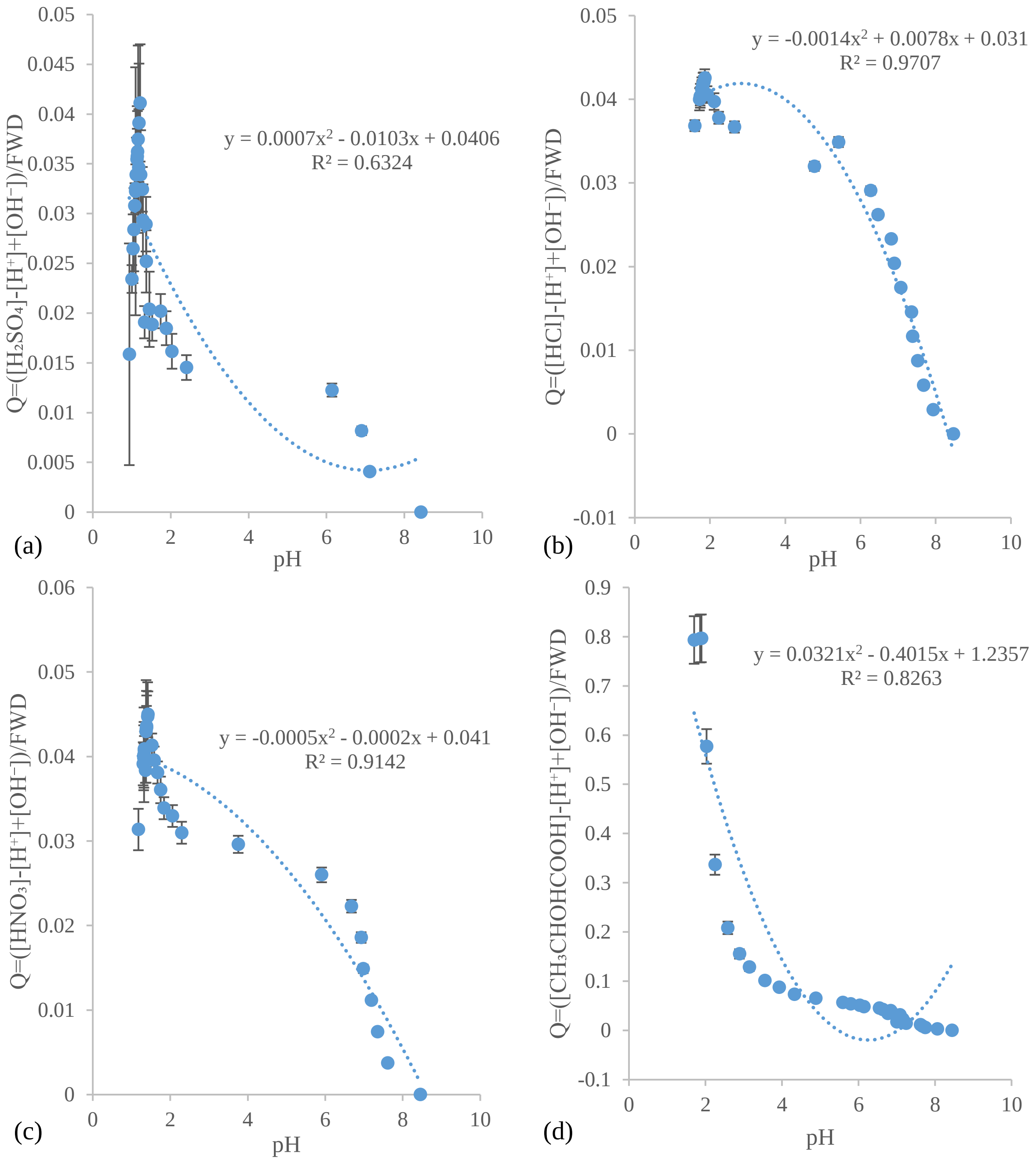


Figure A.6. Calculation of the pH$_{zpc}$ of the FWD using as titrants (a) 17.82 mol H_2SO_4/L, (b) 11.97 mol HCl/L, (c) 15.78 mol HNO_3/L and (d) 11.99 mol $CH_3CH(OH)COOH$/L (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

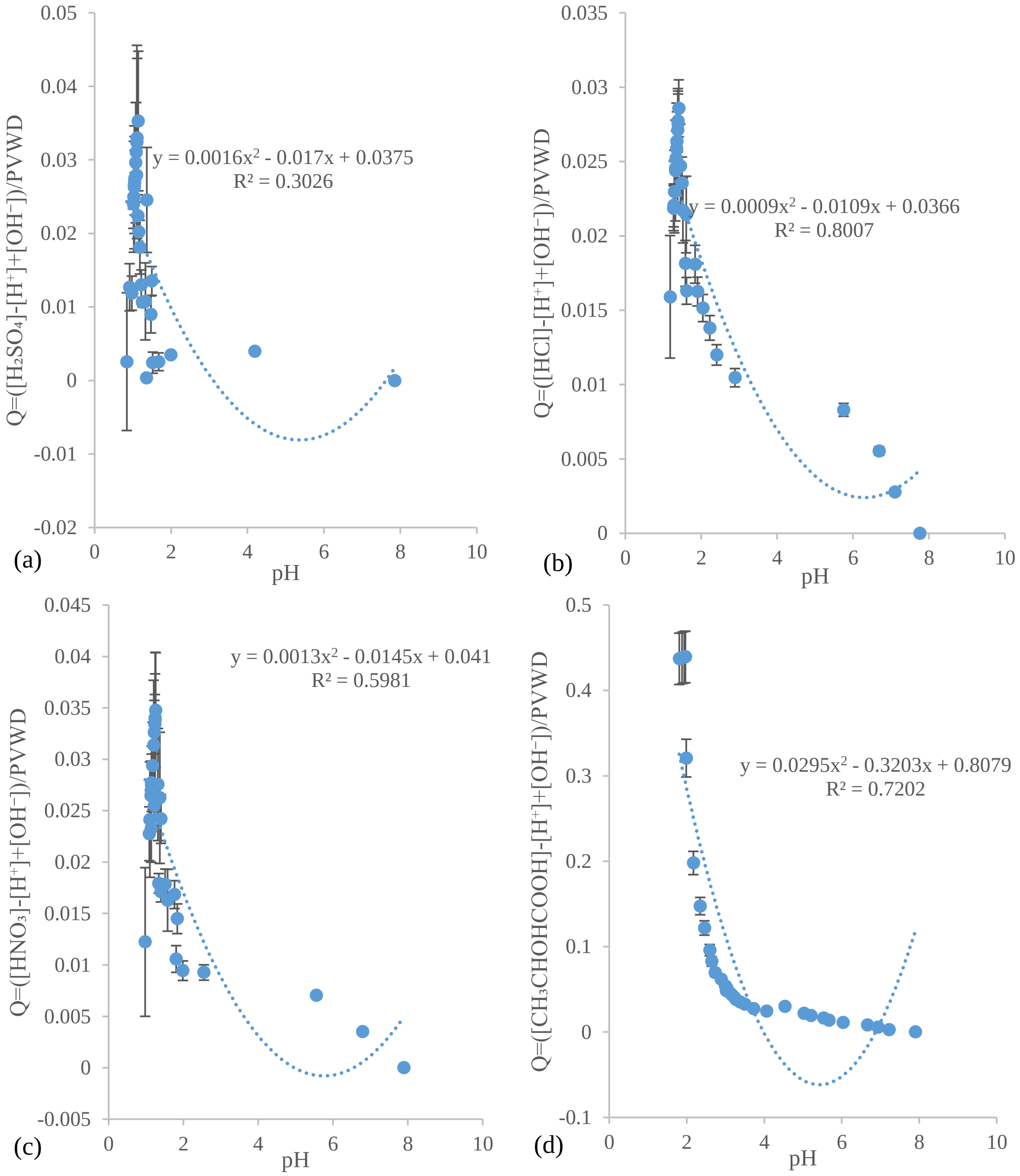


Figure A.7. Calculation of the pH_{zpc} of the PVWD using as titrants (a) 17.82 mol H_2SO_4/L, (b) 11.97 mol HCl/L, (c) 15.78 mol HNO_3/L and (d) 11.99 mol $CH_3CH(OH)COOH$/L (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

Figure A.8. Phase separation immediately after the addition WBA to the PVWD, which had been acidified at a rate of 0.16 mEq H_2SO_4/g (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

Figure A.9. Foam formation immediately after the addition WFA to the FWD, which had been acidified at a rate of 22.77 mEq $CH_3CH(OH)COOH$/g (Moure Abelenda, Semple, Lag-Brotons, *et al.*, 2022).

A.7. Propagation of uncertainty in the calculation of the initial composition of a bi-component blend (*e.g.* WBA mixed with PVWD)

Firstly, the share of each sample in the bi-component blend was determined with Equation A.21 and Equation A.22. Since all the standard deviations shown in the table of the initial characterisation (Table 3.3) represent less than 20 % of the average values, the calculation of the propagation of the uncertainty was done with Equation A.23 and Equation A.24. Additionally, it should be noted that this approach can only be followed when the uncertainties are regarded as random and independent from each other (Batstone, 2013; Tellinghuisen, 2001).

$$WBA = \frac{\overline{WBA}}{\overline{WBA} + \overline{PVWD}}$$

Equation A.21

$$PVWD = \frac{\overline{PVWD}}{\overline{WBA} + \overline{PVWD}}$$

Equation A.22

$$\sigma_{WBA}^2 = \left(\frac{\delta WBA}{\delta \overline{WBA}}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{\delta WBA}{\delta \overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2$$

$$\sigma_{WBA} = \sqrt{\left(\frac{\overline{PVWD}}{(\overline{WBA} + \overline{PVWD})^2}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{-\overline{WBA}}{(\overline{WBA} + \overline{PVWD})^2}\right)^2 \cdot \sigma_{\overline{PVWD}}^2}$$

Equation A.23

$$\sigma_{PVWD}^2 = \left(\frac{\delta PVWD}{\delta \overline{WBA}}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{\delta PVWD}{\delta \overline{PVWD}}\right)^2 \cdot \sigma_{\overline{PVWD}}^2$$

$$\sigma_{PVWD} = \sqrt{\left(\frac{-\overline{PVWD}}{(\overline{WBA} + \overline{PVWD})^2}\right)^2 \cdot \sigma_{\overline{WBA}}^2 + \left(\frac{\overline{WBA}}{(\overline{WBA} + \overline{PVWD})^2}\right)^2 \cdot \sigma_{\overline{PVWD}}^2}$$

Equation A.24

$\overline{\mathrm{WBA}}$, $\overline{\mathrm{PVWD}}$, $\sigma_{\overline{WBA}}$ and $\sigma_{\overline{PVWD}}$ represent the averages and the standard deviations (n=3) of the masses of each sample employed in the experiments. Therefore, WBA, PVWD, σ_{WBA} and σ_{PVWD} stand for the share of each sample in the blend. These values are necessary to determine the initial characterisation of the blend. In this way, X represents the average value (Equation A.25) of a particular parameter in the blend (*e.g.* EC, DM, C, N, etc.) and σ_{X} the standard deviation (Equation A.26).

$$X = WBA \cdot [WBA] + PVWD \cdot [PVWD]$$

Equation A.25

$$\sigma_X^2 = \left(\frac{\delta X}{\delta WBA}\right)^2 \cdot \sigma_{WBA}^2 + \left(\frac{\delta X}{\delta [WBA]}\right)^2 \cdot \sigma_{[WBA]}^2 + \left(\frac{\delta X}{\delta PVWD}\right)^2 \cdot \sigma_{PVWD}^2 + \left(\frac{\delta X}{\delta [PVWD]}\right)^2 \cdot \sigma_{[PVWD]}^2$$

$$\sigma_X = \sqrt{[WBA]^2 \cdot \sigma_{WBA}^2 + WBA^2 \cdot \sigma_{[WBA]}^2 + [PVWD]^2 \cdot \sigma_{PVWD}^2 + PVWD^2 \cdot \sigma_{[PVWD]}^2}$$

Equation A.26

Only the average value and the uncertainty of the pH of the blend (Equation A.28, respectively) were determined differently, because of the logarithmic relation with the concentration of protons in the blend.

$$pH = -\log[H^{+}] \rightarrow [H^{+}] = 10^{-pH}$$

$$Y = WBA \cdot 10^{-[WBA]} + PVWD \cdot 10^{-[PVWD]}$$

Equation A.27

$$\sigma_Y = \sqrt{10^{-2[WBA]} \cdot \sigma_{WBA}^{2} + \left(WBA \cdot \frac{ln10}{10^{[WBA]}}\right)^{2} \cdot \sigma_{[WBA]}^{2} + 10^{-2[PVWD]} \cdot \sigma_{PVWD}^{2} + \left(PVWD \cdot \frac{ln10}{10^{[PVWD]}}\right)^{2} \cdot \sigma_{[PVWD]}^{2}}$$

$$Z = -\log Y\,;\ \sigma_Z = \sqrt{\left(\frac{-1}{Y \cdot \ln 10}\right)^{2} \cdot \sigma_Y^{2}}$$

Equation A.28

A.8. Calculation of the empirical concentration of the WI P expressed in fresh basis and its empirical total mass in the blend

The calculation of the concentration of the WI P (Equation A.29) was based on the value given by the Autoanalyzer™ (X) which measured the concentration of PO_4^{3-} in the 50 mL acid extract obtained from the sulphuric-peroxide digestion of a subsample (W) of the total WI material (Z) recovered after the incubation of the blend (Y). The procedure establishes a dilution factor of 5 to produce an extract with up to 1 vol.% of acid that can be measured in the Autoanalyzer™.

$$\begin{aligned} WI\ P = X\frac{mg\ P}{L} \times dilution\ factor \times \frac{1\ L}{10^{3} mL} \times \\ \times 50\ mL\ acid\ extract \times \frac{1}{W\ g\ WI\ material\ digested} \times \\ \times \frac{Z\ g\ WI\ material\ recovered}{Y\ g\ fresh\ blend} \times \frac{10^{3} g}{1\ kg} \end{aligned}$$

Equation A.29

It should be noted that the factor $P/PO_4^{3-} = 0.33$ needs to be applied to determine the amount of P in the form of PO_4^{3-}.

For the empirical balance, the calculation of the total mass of the WI P in the blend, it would not be necessary to divide by mass of blend (Y) in the Equation A.29.

A.9. Calculation of the empirical concentration of the WI C and WI N, and their empirical and theoretical total mass in the blend

The calculation (Equation A.30) was based on the percentage values (X) provided by the elemental analyser Elementar Vario EL cube® which characterised a subsample of the total WI material (Z) recovered after the incubation of the blend (Y).

$$WI\ N = \frac{X(\%)}{100}\frac{mg\ TN}{mg\ WI\ material} \times \frac{Z\ mg\ WI\ material\ recovered}{Y\ g\ fresh\ blend} \times \frac{10^3 g}{1\ kg}$$

Equation A.30

For the calculation of the total mass of the WI C and WI N in the blend, it would not be necessary to divide to divide by mass of blend (Y) in the Equation A.30. For the theoretical balance, the initial masses (Z) of WI materials were assumed to be the DM of the blend (Table 5.1).

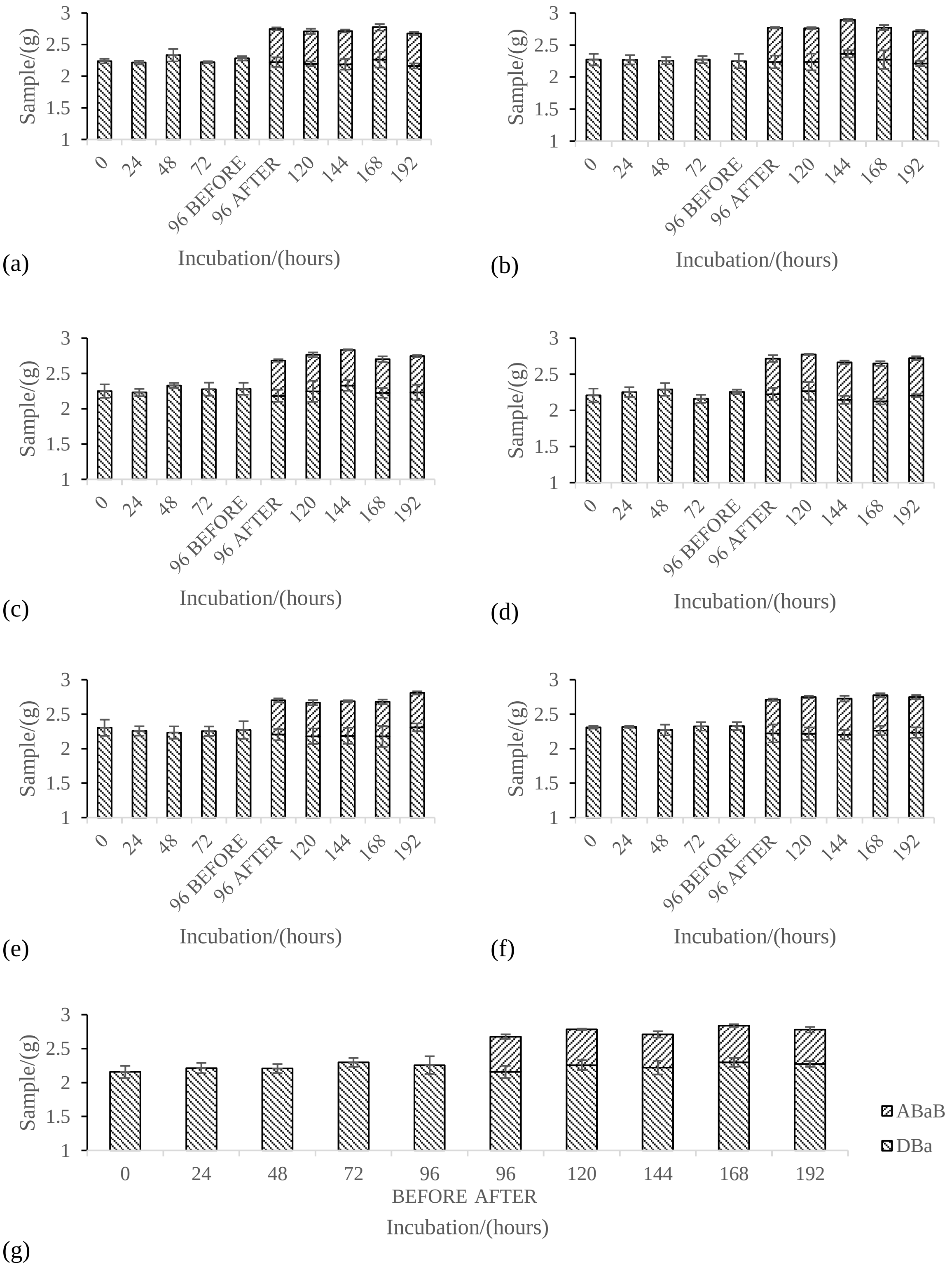


Figure A.8. Detailed amount of samples used for the preparation of the blend in the first study of Chapter 5, testing 7 acidification doses: (a) 0.08 mmol H^+-H_2SO_4/g PVWD, (b) 0.24 mmol H^+-H_2SO_4/g PVWD, (c) 0.08 mmol H^+-HCl/g PVWD, (d) 0.24 mmol H^+-HCl/g PVWD, (e) 0.08 mmol H^+-HNO_3/g PVWD, (f) 0.24 mmol H^+-HNO_3/g PVWD and (g) 0 mmol H^+/g PVWD (Moure Abelenda *et al.*, 2021b).

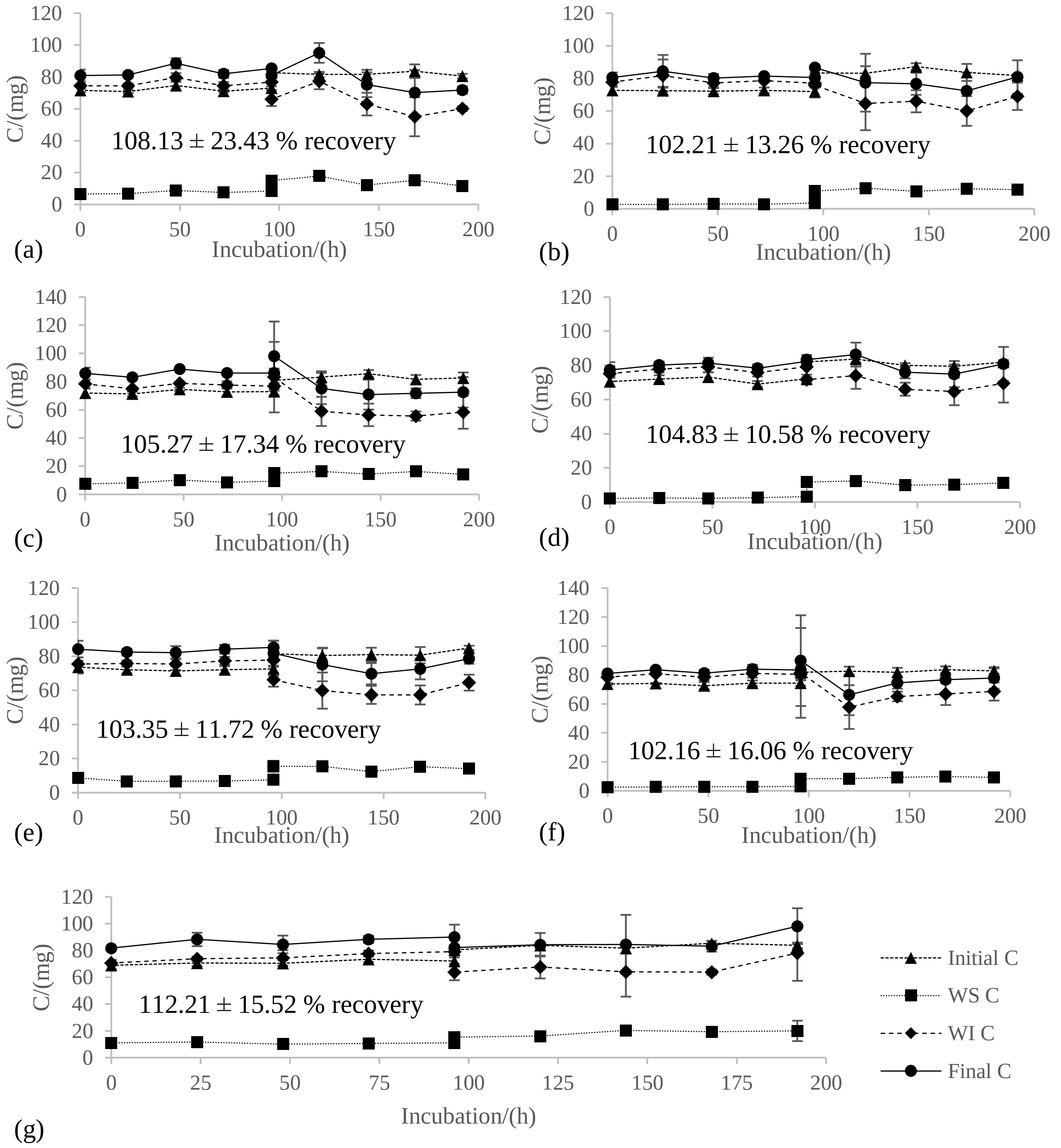


Figure A.9. Theoretical C balances in the first study of Chapter 5, about adding 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-h incubation of 2.24 ± 0.09 g of PVWD under 7 acidification conditions: (a) 0.08 mmol H^+-H_2SO_4/g PVWD, (b) 0.24 mmol H^+-H_2SO_4/g PVWD, (c) 0.08 mmol H^+-HCl/g PVWD, (d) 0.24 mmol H^+-HCl/g PVWD, (e) 0.08 mmol H^+-HNO_3/g PVWD, (f) 0.24 mmol H^+-HNO_3/g PVWD and (g) 0 mmol H^+/g PVWD. Initial C stands for the calculated C in the system based on the initial characterisation of the samples (Table 5.1). Final C was calculated as the addition of the empirical masses of WS C and WI C. The average values of the C recovery effectiveness over the 196 hours of incubation is stated in each graph (Moure Abelenda *et al.*, 2021b).

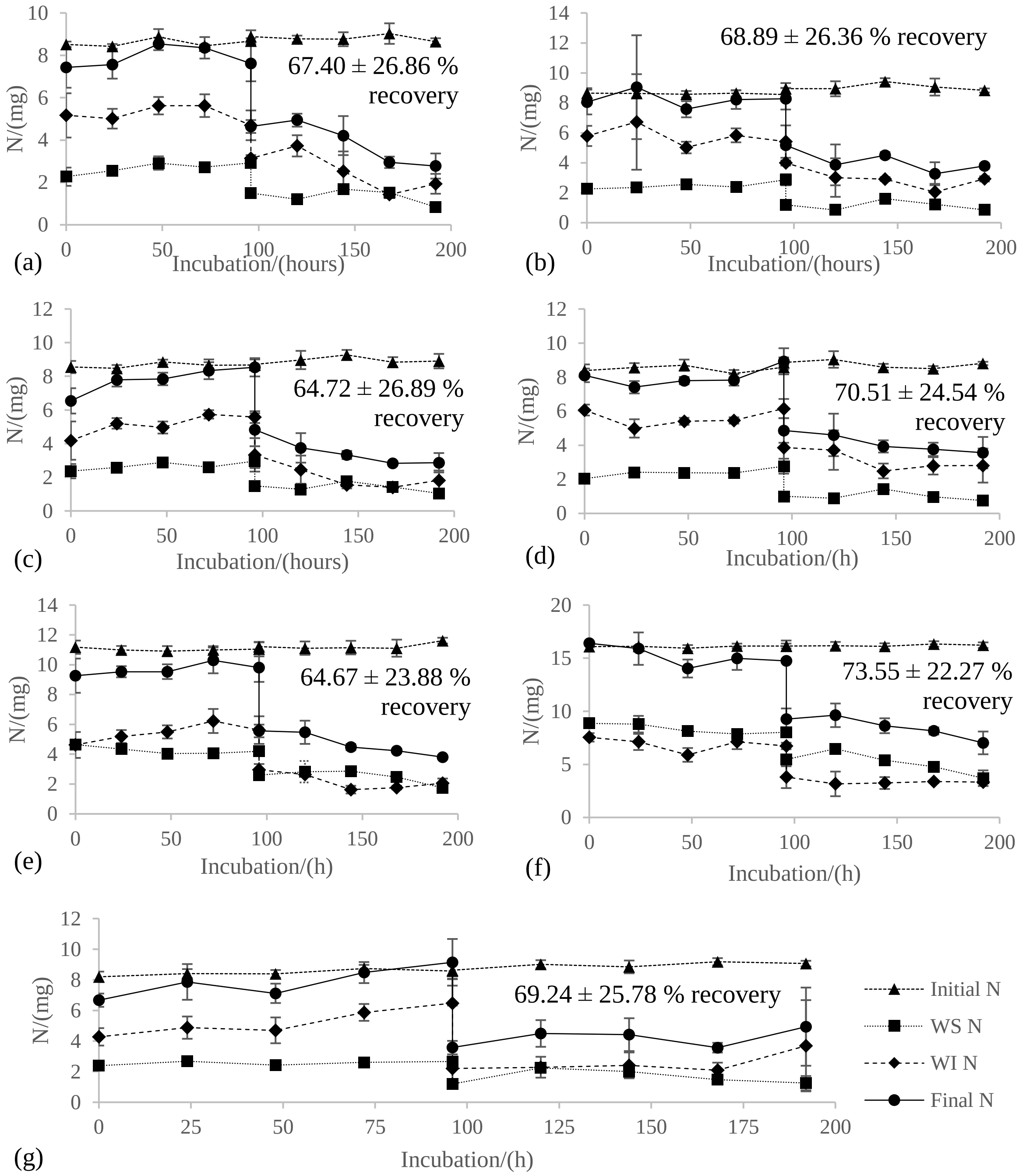


Figure A.10. Theoretical N balances in the first study of Chapter 5, about adding 0.51 ± 0.03 g of WBA in the middle (at the 96 hours) of the 192-h incubation of 2.24 ± 0.09 g of PVWD under 7 acidification conditions: (a) 0.08 mmol H^+-H_2SO_4/g PVWD, (b) 0.24 mmol H^+-H_2SO_4/g PVWD, (c) 0.08 mmol H^+-HCl/g PVWD, (d) 0.24 mmol H^+-HCl/g PVWD, (e) 0.08 mmol H^+-HNO_3/g PVWD, (f) 0.24 mmol H^+-HNO_3/g PVWD and (g) 0 mmol H^+/g PVWD. Initial N stands for the calculated N in the system based on the initial characterisation of the samples (Table 5.1). Final N was calculated as the addition of the empirical masses of WS N and WI N. The average values of the N recovery effectiveness over the 196 hours of incubation is stated in each graph (Moure Abelenda *et al.*, 2021b).

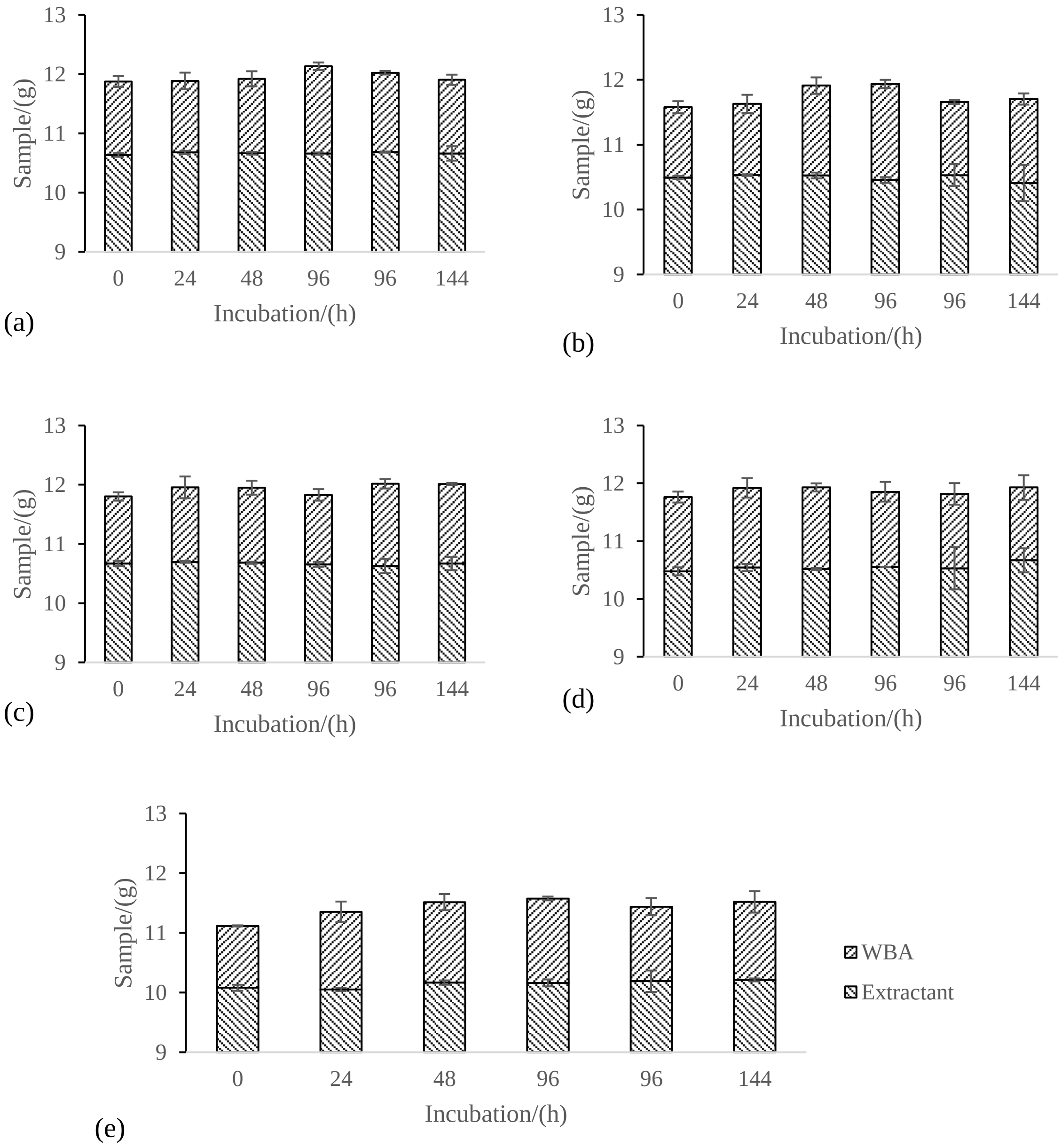


Figure A.11. Detailed amounts of WBA and extractant used for the preparation of the destructive samples before and after the blending with the PVWD at the 96 hours of incubation under 5 acidification conditions: (a) 6.29 mmol H^+-H_2SO_4/g WBA, (b) 15.21 mmol H^+-HCl/g WBA, (c) 11.97 mmol H^+-HNO_3/g WBA, (d) 0.16 mmol H^+-$CH_3CH(OH)COOH$/g WBA and (e) 0 mmol H^+/g WBA (Moure Abelenda *et al.*, 2021b).

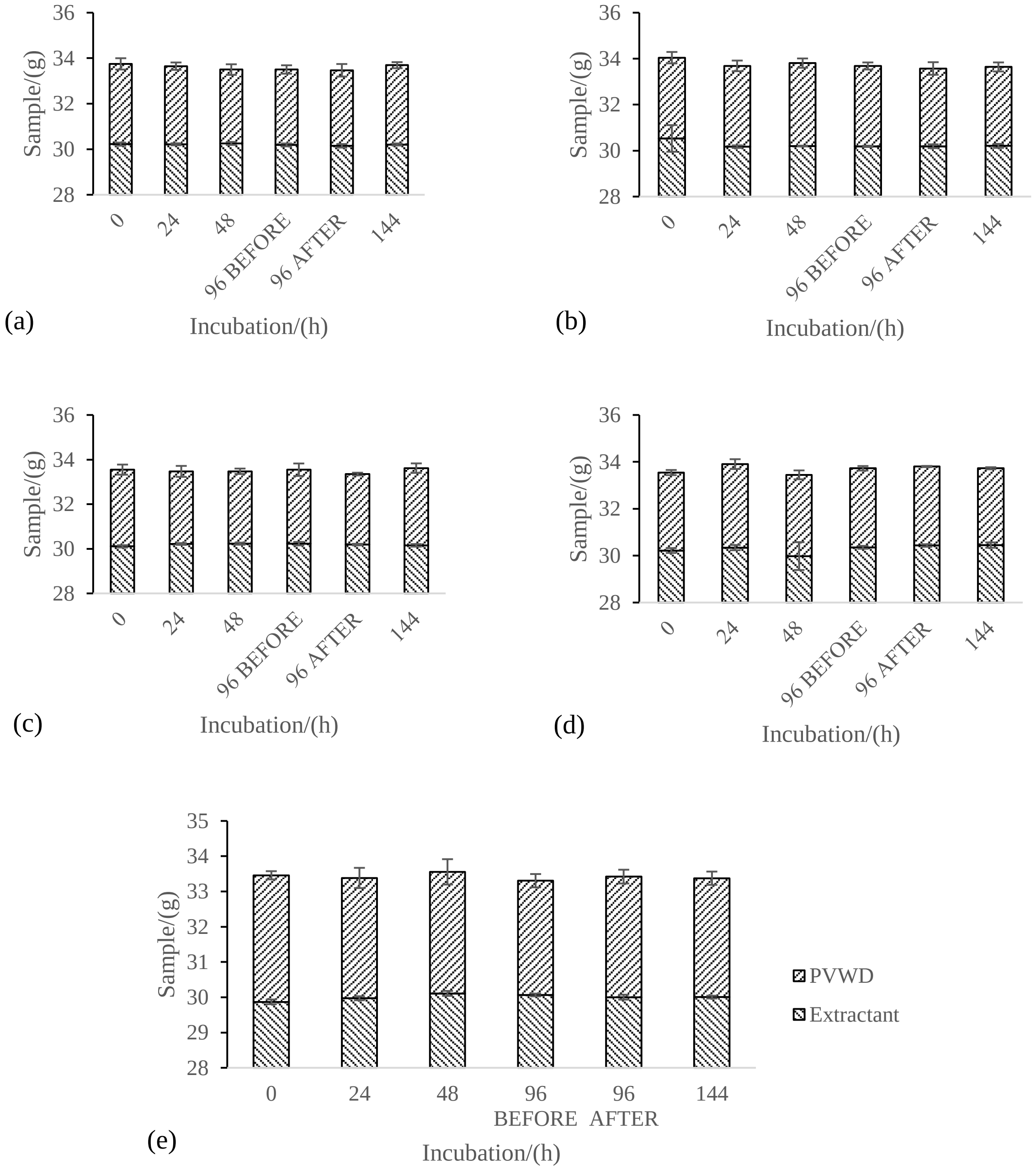


Figure A.12. Detailed amounts of PVWD and extractant used for the preparation of the destructive samples before and after the blending with the WBA at the 96 hours of incubation under 5 acidification conditions: (a) 6.29 mmol H^+-H_2SO_4/g PVWD, (b) 15.21 mmol H^+-HCl/g PVWD, (c) 11.97 mmol H^+-HNO_3/g PVWD, (d) 0.16 mmol H^+-$CH_3CH(OH)COOH$/g PVWD and (e) 0 mmol H^+/g PVWD (Moure Abelenda *et al.*, 2021b).

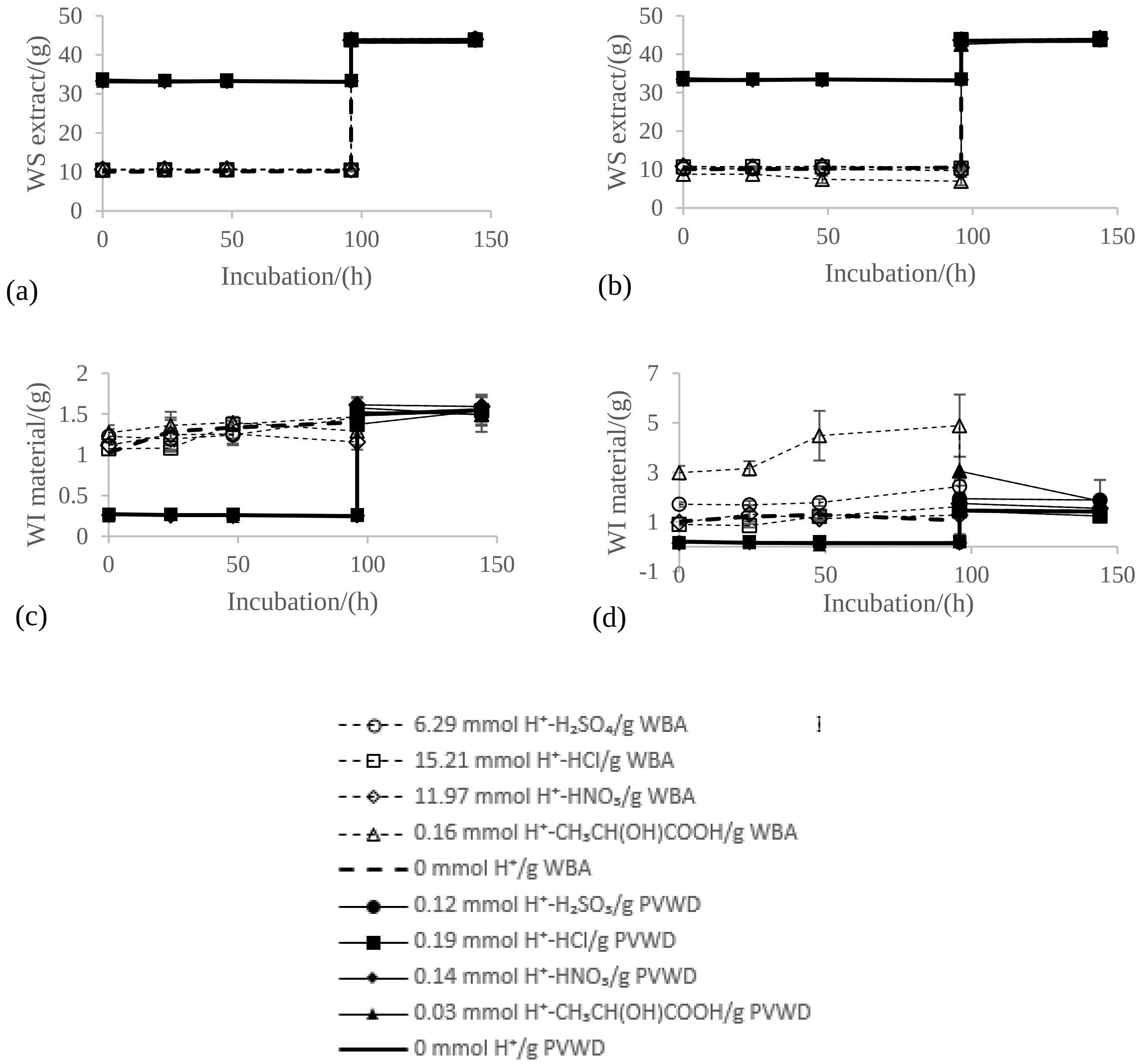


Figure A.13. Initial and final fractionation of 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours) under 5 acidification conditions: (a) initial WS extract, (b) final WS extract, (c) initial WI material and (d) final WI material (Moure Abelenda *et al.*, 2021b).

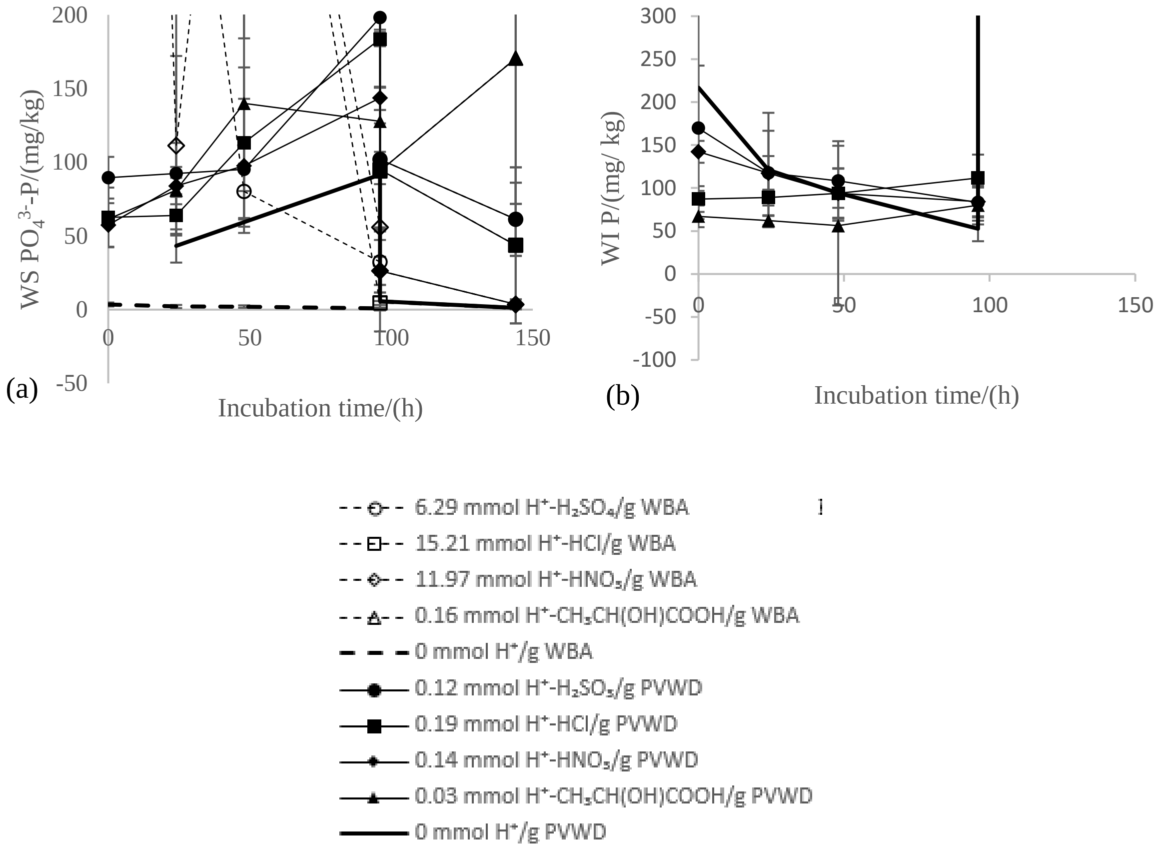


Figure A.14. Zoom in (a) the WS PO_4^{3-}-P and (b) the WI P of 1.27 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours), under 5 acidification conditions (*i.e.* H_2SO_4, HCl, HNO_3, $CH_3CHCOOH$ and no acidification), during the 144-h incubation (Moure Abelenda *et al.*, 2021b).

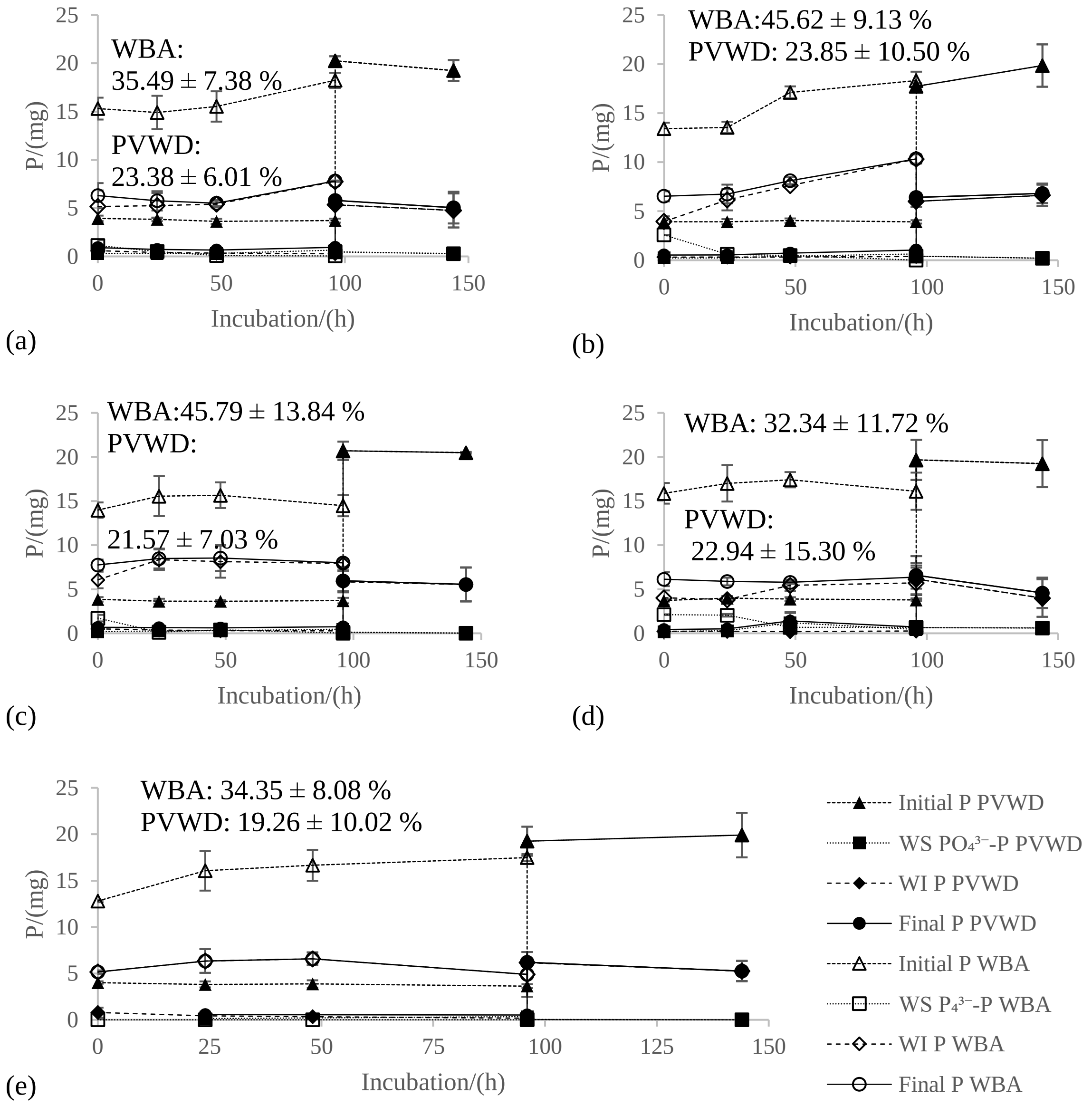


Figure A.15. Experimental P balances in the second study of Chapter 5, for1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours) under 5 acidification conditions: (a) 6.29 mmol H^+-H_2SO_4/g WBA and 0.12 mmol H^+-H_2SO_4/g PVWD, (b) 15.21 mmol H^+-HCl/g WBA and 0.24 mmol H^+-HCl/g PVWD, (c) 11.97 mmol H^+-HNO_3/g WBA and 0.14 mmol H^+-HNO_3/g PVWD, (d) 0.16 mmol H^+-$CH_3CH(OH)COOH$/g WBA and 0.03 mmol H^+-$CH_3CH(OH)COOH$/g PVWD, and (e) 0 mmol H^+/g WBA and 0 mmol H^+/g PVWD. Initial P stands for the calculated P in the system based on the initial characterisation of the samples (Table 5.1). Final P was calculated as the sum of the masses of WS PO_4^{3-}-P and WI P. The average values of the P recovery effectiveness over the 144 hours of incubation for each sample are stated in the graphs (Moure Abelenda *et al.*, 2021b).

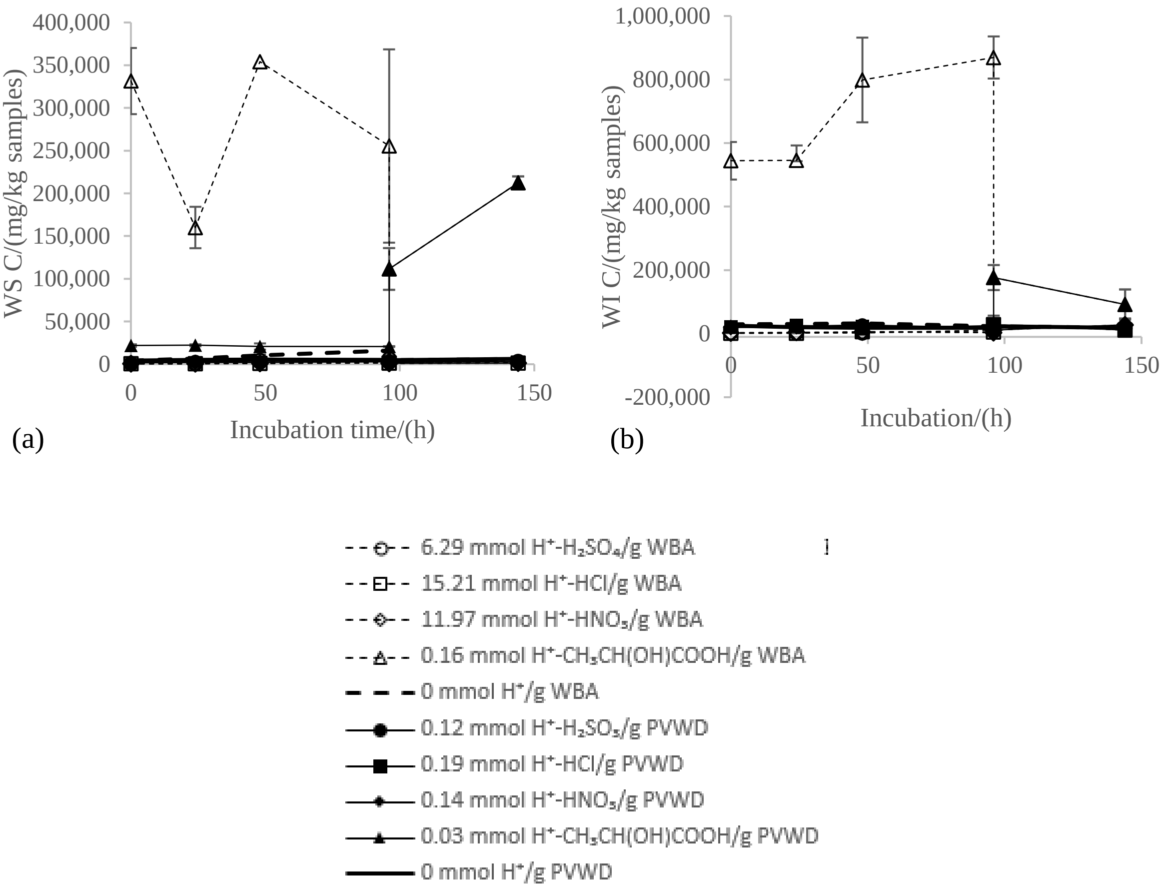


Figure A.16. Zoom out (a) the WS C and (b) the WI C of of 1.27 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours), under 5 acidification conditions (*i.e.* H_2SO_4, HCl, HNO_3, $CH_3CHCOOH$ and no acidification), during the 144-h incubation (Moure Abelenda *et al.*, 2021b).

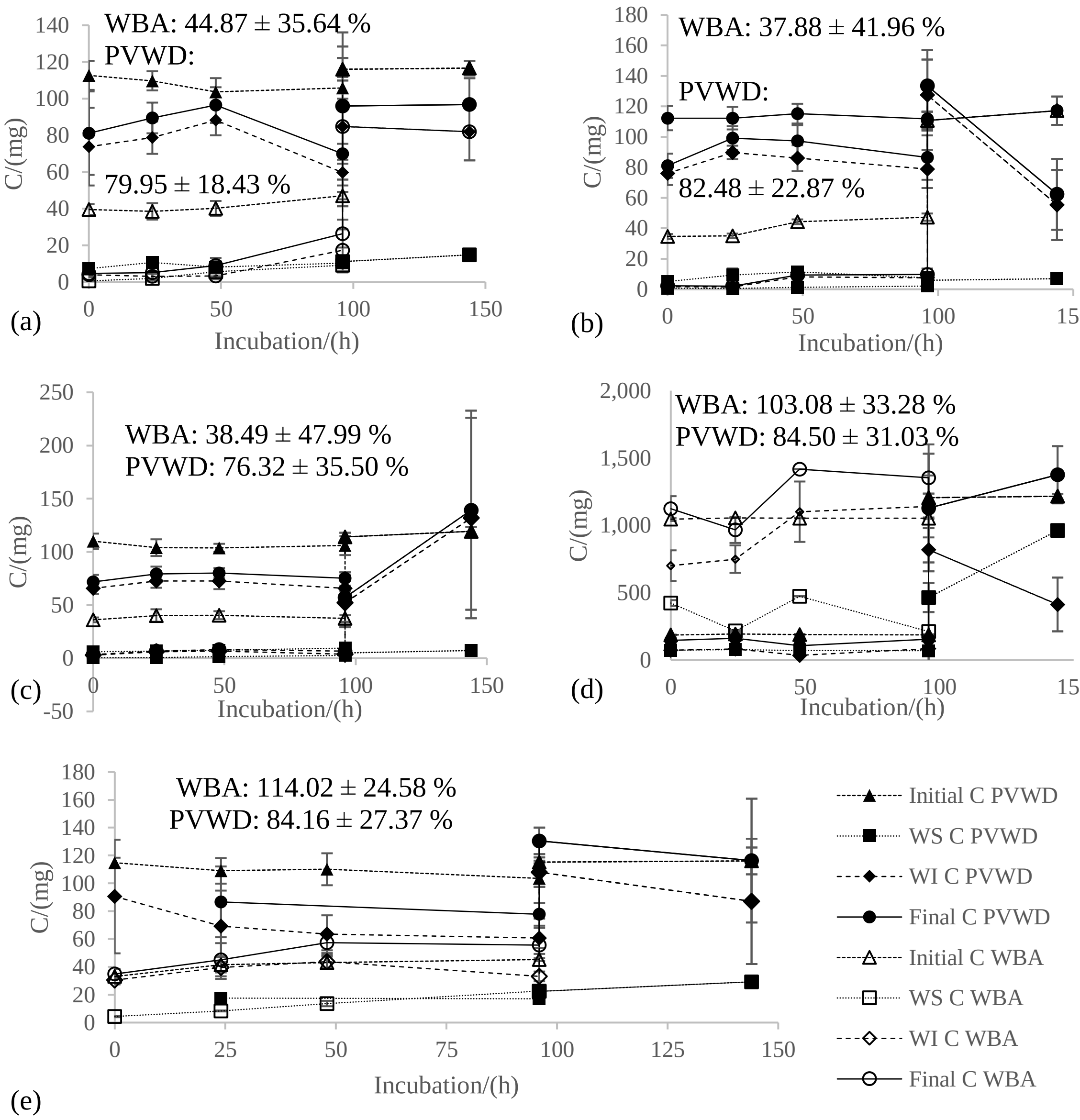


Figure A.17. Experimental C balances in the second study of Chapter 5, for 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours) under 5 acidification conditions: (a) 6.29 mmol H^+-H_2SO_4/g WBA and 0.12 mmol H^+-H_2SO_4/g PVWD, (b) 15.21 mmol H^+-HCl/g WBA and 0.24 mmol H^+-HCl/g PVWD, (c) 11.97 mmol H^+-HNO_3/g WBA and 0.14 mmol H^+-HNO_3/g PVWD, (d) 0.16 mmol H^+-$CH_3CH(OH)COOH$/g WBA and 0.03 mmol H^+-$CH_3CH(OH)COOH$/g PVWD and (e) 0 mmol H^+/g WBA and 0 mmol H^+/g PVWD. Initial C stands for the calculated C in the system based on the initial characterisation of the samples (Table 5.1). Final C was calculated as the sum of the empirical masses of WS C and WI C. The average values of the C recovery effectiveness over the 144 hours of incubation for each sample are stated in the graphs (Moure Abelenda *et al.*, 2021b).

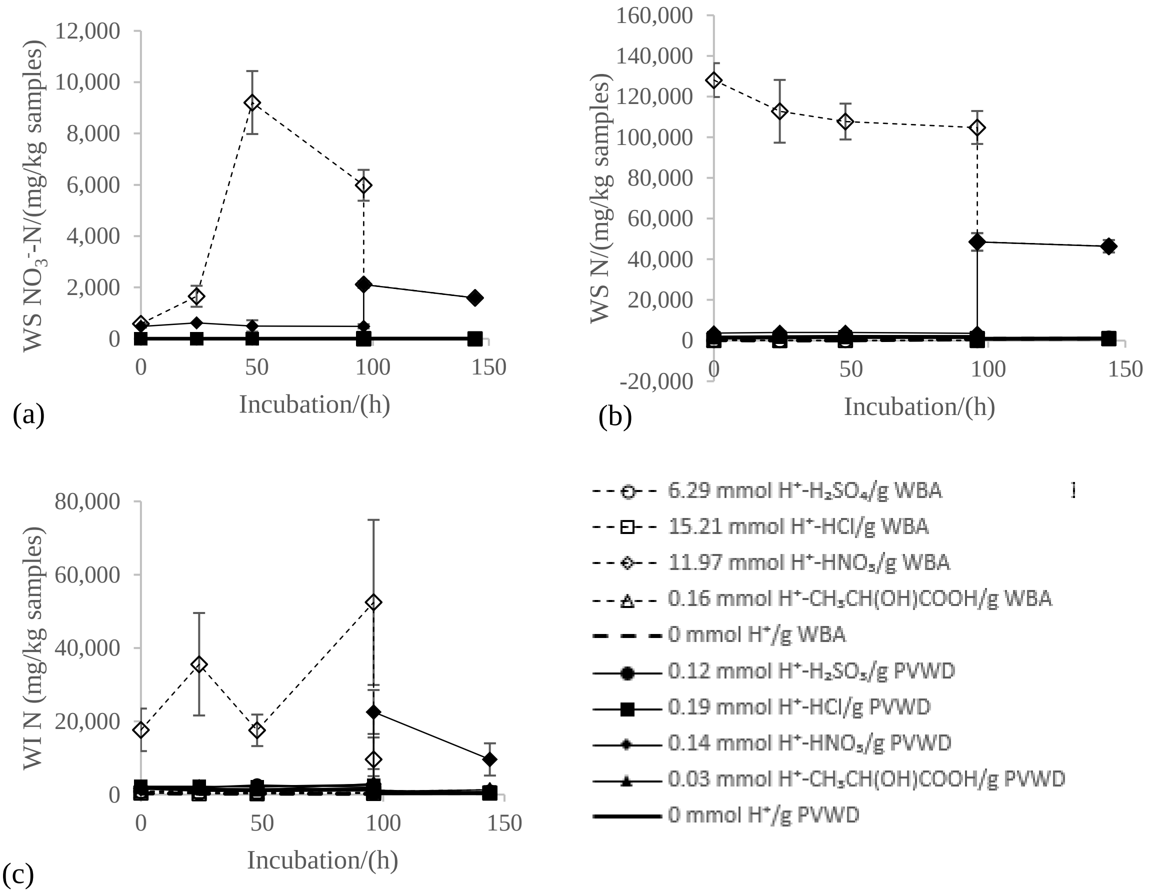


Figure A.18. Zoom out the (a) WS NO_3^--N, (b) WS N and (c) WI C of 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours), under 5 acidification conditions (*i.e.* H_2SO_4, HCl, HNO_3, $CH_3CHCOOH$ and no acidification), during the 144-h incubation (Moure Abelenda *et al.*, 2021b).

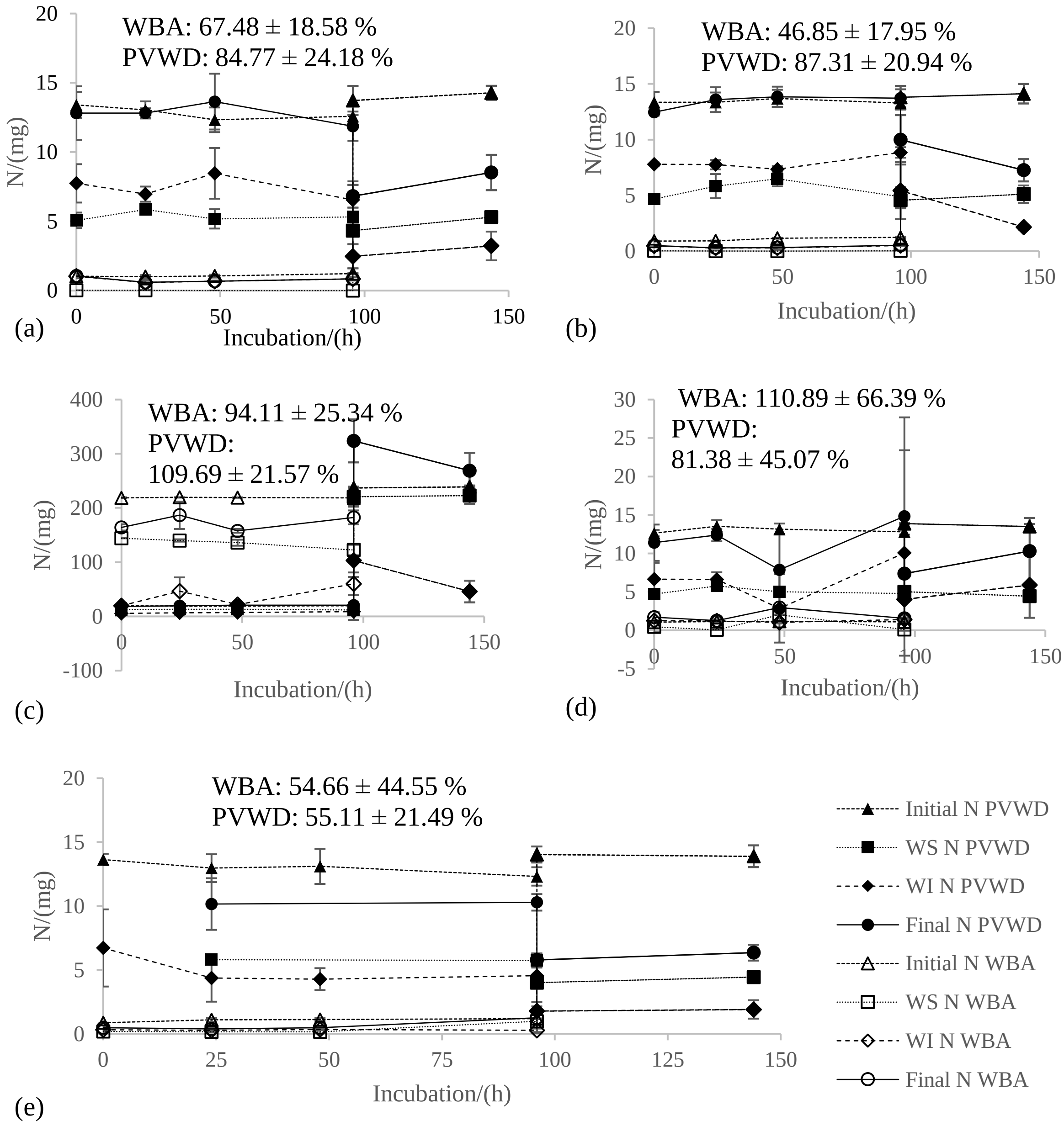


Figure A.19. Experimental N balances in the second study of Chapter 5, for 1.28 ± 0.27 g of WBA and 3.40 ± 0.20 g of PVWD before and after blending (at the 96 hours) under 5 acidification conditions: (a) 6.29 mmol H^+-H_2SO_4/g WBA and 0.12 mmol H^+-H_2SO_4/g PVWD, (b) 15.21 mmol H^+-HCl/g WBA and 0.24 mmol H^+-HCl/g PVWD, (c) 11.97 mmol H^+-HNO_3/g WBA and 0.14 mmol H^+-HNO_3/g PVWD, (d) 0.16 mmol H^+-$CH_3CH(OH)COOH$/g WBA and 0.03 mmol H^+-$CH_3CH(OH)COOH$/g PVWD and (e) 0 mmol H^+/g WBA and 0 mmol H^+/g PVWD. Initial N stands for the calculated N in the system based on the initial characterisation of the samples (Table 5.1). Final N was calculated as the sum of the empirical masses of WS N and WI N. The average values of the N recovery effectiveness over the 144 hours of incubation for each sample are stated in the graphs (Moure Abelenda *et al.*, 2021b).

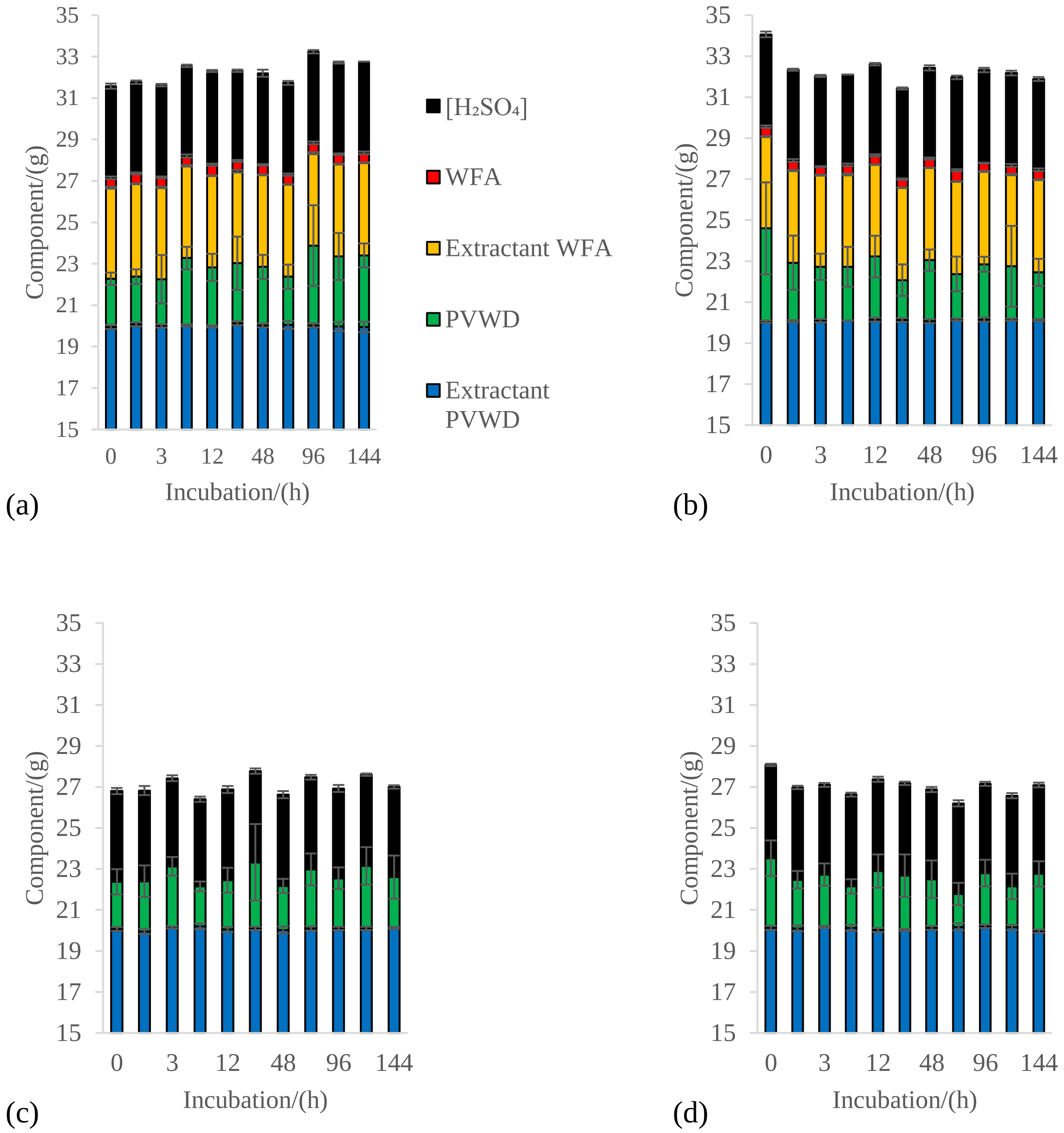


Figure A.20. Detailed amounts of [H_2SO_4], WFA, WFA extractant, PVWD and PVWD extractant used for the preparation of the blends (Table 6.1): (a) HCl-WFA+PVWD, (b) HCl-WFA+HCl-PVWD, (c) PVWD and (d) HCl-PVWD (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

Table A.8. Different types of chambers are employed to measure the ammonia volatilisation and GHGs emissions during the storage and after the land application of organic amendments (Moure Abelenda, Semple, Herbert, *et al.*, 2022).

Headspace	**Type of manure**	**Incubation**	**H_2SO_4 trap**	**Analysis**
300-mL static chamber (Velthof *et al.*, 2005)[a].	200 mL manure (2.0 – 4.8 g NH_4^+-N/kg fresh material) from manipulation of pig diet.	Anaerobic incubation at 35 ºC. No shaking 90 days	3 mL 3.2 mol/L Minimum recharge of 24 hours (Flux with N_2 for 10 minutes after measurement).	Mix all H_2SO_4 samples to quantify total NH_3 emission.
500-mL static chamber (Van der Stelt *et al.*, 2007)[a].	500 g biologically treated (Agri-mest®, Effective micro-organism® and Euro Mest-mix®) manure slurry (18.2 g inorganic N/kg DM).	Incubation at 4, 20 and 35 ºC. Shaking every even day. Removing the acid trap. 223 days	12.5 mL 3.2 mol/L Minimum recharge of 24 hours.	Segmented flow analysis. Dilution to 50 mL total volume with milli-Q water.

Headspace	**Type of manure**	**Incubation**	**H_2SO_4 trap**	**Analysis**
1000-mL static chamber (Whelan *et al.*, 2010)[a].	120 mL digestate (5775 mg NH_4^+-N/L) obtained from ruminant slurry and food waste. Model to assess impact (*e.g.* depth to surface ratio) on NH_3 volatilisation.	25 ºC No shaking (12 mm depth) 15 days	1 mol/L 10 mL Minimum recharge of 24 hours.	Indophenol blue method photometer. Dilution with milli-Q water and adjustment to pH 4.
700-mL (assuming density slurry 1 g/mL) static chamber (Regueiro, Coutinho, & Fangueiro, 2016)[a].	300 g chemically treated (CH_3COOH, citric acid, $CH_3CH(OH)COOH$, H_2SO_4, $Al_2(SO_4)_3$) pig and dairy slurry.	15 ºC No shaking 60 days	100 mL 0.1 mol/L H_3PO_4 Minimum recharge of 12 hour (10-minute aeration after sampling).	Autoanalyzer™ Skalar, Breda (segmented flow colorimetry).
200-mL closed chamber employed in the Chapter 6, Chapter 7 and Chapter 8[b].	Approximately 30 mL of blend of post-harvest vegetable waste digestate (689.74 mg NH_4^+-N/L)	25 ºC Continuous shaking at 100 rpm. 6 days	10 mL 1 mol/L Minimum recharge of 1 hour	Autoanalyzer™, SEAL analytical (segmented flow

Headspace	**Type of manure**	**Incubation**	**H_2SO_4 trap**	**Analysis**
	trated with HCl acidified wood bottom ash.		(destructive sampling).	indophenol blue photometer).
12 to 27 L -closed dynamic chamber (Berg *et al.*, 2006)[c]. Flowrate during sampling was changed once per minute. Ventilation only during sampling.	5 and 8 % DM pig slurry (2,570 mg NH_4^+-N/kg).	Room temperature 49 cm diameter 65-L Open container ≥ 162 days		Photoacoustic gas monitor once per week.
500-mL closed dynamic chamber (Dinuccio, Berg, *et al.*, 2008)[c]. Flow rate compressed air 500 mL/min. Open storage and dynamic chamber only used for sampling gaseous emissions.	1,000 mL cattle (1160 to 1,490 mg NH_4^+-N/kg) and pig (4,050 to 4,330 mg NH_4^+-N/kg) slurry and their solid and liquid fractions (obtained through mechanical separation).	5 ± 0.5 ºC and 25 ± 0.2 ºC. No shaking (crust formation was allowed). 95c m top diameter 100 cm base diameter 200 cm depth 30 day		Photo-acoustic multi-gas monitor.

Headspace	**Type of manure**	**Incubation**	**H_2SO_4 trap**	**Analysis**
500 to 1100 -mL closed dynamic chamber (Dinuccio, Balsari, *et al.*, 2008)[c].	1 kg whole pig slurry and liquid fractions. 0.4 kg solid fraction	25 ± 0.2 ºC 74 cm^2 1500 mL open container.		Photo-acoustic multi-gas monitor.
400-mL (assuming density slurry 1 g/mL) closed dynamic chamber (Kavanagh *et al.*, 2019)[c].	1.6 kg dairy and cattle slurry (4 and 7 % DM) treated with H_2SO_4, CH_3COOH, $AlK(SO_4)_2 \cdot 12H_2O$ and $FeCl_3 \cdot 6H_2O$.	Irish farm winter conditions 8.6 ºC and 60 % moisture. 14 days.		Glass wool soaked with 0.05 M oxalic acid to strip the moisture from the air before reaching the photo-acoustic monitor.
1.57-L open dynamic chamber (Brennan *et al.*, 2015)[d]. 5.1 L air/min	Chemically treated dairy cattle slurry treated with $AlK(SO_4)_2 \cdot 12H_2O$, $FeCl_2$, $AlCl_3$, biochar and lime.	Application of the treated slurry at a rate of 33 m^3/ha over the soil.	3 % of oxalic acid in acetone (Leuning *et al.*, 1985).	

Headspace	Type of manure	Incubation	H_2SO_4 trap	Analysis
		20 cm diameter	Minimum recharge of 1 hour.	
80-L wind tunnels (Dinuccio *et al.*, 2012) evenly distributed over manure surface (spaced 1 m apart)[e]. 0.6 m/s air flow. 4 L/min	Pig slurry and liquid fraction (900 m^3 cylinder 314 m^2) and 6.6 m^3 truncated cone heap (solid fraction; 21 m^2).	Summer (15-25 ºC) and winter (3-10 ºC) seasons in Piemonte (Italy). Area measurement (no shaking).	80 mL 18.65 mol/L Minimum recharge of 24 hours.	Ammonium sensitive electrode (ISO TC 147/6778).
58-m^3 open dynamic chamber (Balsari *et al.*, 2007)[d]. 37,650 m^3/h air flowrate. Air velocity 2 m/s.	200 kg farmyard manure heaps.	Torino University (Grugliasco) 850 mm of rain per year and 12.3 ºC.	Collection of samples of outgoing air from 15 sampling points. 6 days of sampling.	Ion-meter equipped with a gas-sensitive combined electrode for NH_3 measurement in the 1 % H_2SO_4 traps.

Headspace	Type of manure	Incubation	H_2SO_4 trap	Analysis
9-L open dynamic chamber (assuming height of 0.2 m for the inverted PVC funnel covering 0.138 m^2 of surface)[a,d]. Air flow 9 L/min. Air velocity 0.05 – 0.01 m/s (Balsari *et al.*, 2007). 80-L wind tunnel (Dinuccio et al., 2012; Schmidt & Bicudo, 2002). Covering an area of 0.32 m^2. Air flow 4 L/min. Air velocity 0.5 m/s (Balsari *et al.*, 2007)[e].	Pig slurry Dairy cattle slurry	North Western Po Valley (Italy). 314 m^3; 10 m diameter and 4 m depth. Average rainfall 900 mm/year and 12 ºC.	1 % boric acid solution. Minimum recharge of 24 hours. 6 days of sampling.	Titration of the ammonium borate with a H_2SO_4 solution 0.2 N.
Open environment (Leuning *et al.*, 1985; Maffia *et al.*, 2021)[f].	Any	Continuous	40 mL 3 % oxalic acid in acetone 20 mL 0.5 N H_2SO_4	Spectrophotometry

[a] In the static chamber there is no flux of air allowing the convective movement of the ammonia volatilised. As described by Van der Stelt *et al.* (2007): "*In this method transport of NH_3 by air movement was excluded and so NH_3 volatilisation occurred in a passive way*".

[b] The method used in this thesis is a modification of the static chamber procedure (Velthof *et al.*, 2005) and these were considered to be the best conditions for representing the current practices of storage of the anaerobic digestate and the preparation of a novel fertiliser. The effect of the mixing have been tested in other systems such as the closed dynamic chamber (Perazzolo *et al.*, 2015) and the wind tunnel (Blanes-Vidal *et al.*, 2012).

[c] In the dynamic chamber the direction of the flux of air in the headspace is not clearly defined. A dynamic chamber is regarded as closed if the air comes from a known supply (*i.e.* gas bottle).

[d] On the other hand, in an open dynamic chamber, is the air from the environment outside of the chamber what is pumped to allow the convective movement of the gases in the headspace. In the latter case, it is required to measure the composition of the air at the entrance of the chamber and/or use filters.

[e] The wind tunnel allows laminar flux of air in the headspace. These are the conditions that better represent the open storage of the organic amendments (*i.e.* digestate, manure and slurry). Nevertheless, according to Schmidt & Bicudo (2002), small wind tunnels may not meet all the criteria and should be more accurately referred to as flux chambers.

[f] Passive techniques for measuring the NH_3.

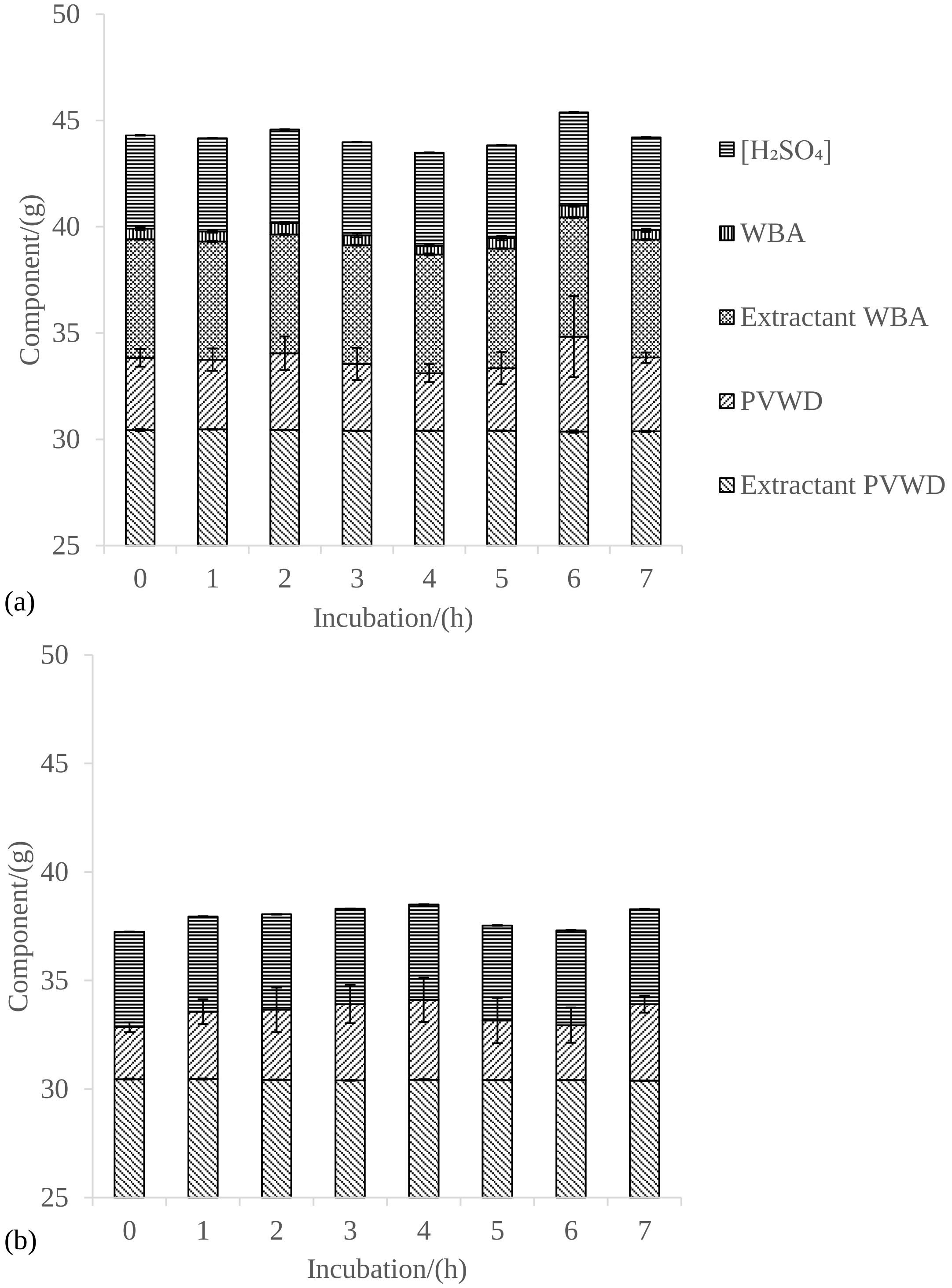


Figure A.27. Detailed amounts of samples and extractant (*i.e.* ultrapure milli-Q® water) used for the preparation of (a) WBA+PVWD and (b) PVWD in a closed chamber with a 0.11 M H_2SO_4 solution (Table 7.1). The Y axis does not start at zero in order to appreciate the amounts of [H_2SO_4], WBA, Extractant of WBA and PVWD (Moure Abelenda *et al.*, 2021d).