

**MACRONUTRIENT SOLUBILISATION DURING HYDROTHERMAL
TREATMENT OF SEWAGE SLUDGE**

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ABSTRACT

A first step in assessing the potential of the hydrothermally treated sludge as a fermentation medium or as fertiliser, among other more innovative uses, is to study in depth the compositional changes that take place during the hydrothermal treatment of secondary sewage sludge. Thus, the present study analyses, for the first time, the effects of the reaction time, temperature, pressure and atmosphere on the properties of the hydrolysates obtained and, in particular, on the fate of the four main macronutrients (C, N, P and K). Under the most aggressive operational conditions tested (200 °C, 50 bar, 210 min and oxidising atmosphere), 76% of total suspended solids were disintegrated and 94%, 96%, 12% and 41% of C, N, P, and K were solubilised, with the majority of these changes occurring during the first 60 min of treatment. Nevertheless, these conditions also resulted in significant mineralisation of the organic carbon (77% total Chemical Oxygen Demand reduction) and the formation of notable concentrations of ammonium (around 64 g/kg dry matter) and small amounts of nitrates and nitrites (0.14 g/ kg dry matter). After long reaction times, the re-alkalinisation of the reaction medium favoured the binding of soluble P to dissolved metal ions and its subsequent precipitation. Temperature and type of atmosphere did not significantly influence the soluble K concentration, suggesting that this element mainly interacts with tightly bound extracellular polymeric substances in the raw sludge. Finally, pressure did not have significant effects on the final macronutrient composition of the treated sludge.

KEYWORDS

Sludge, nitrogen, phosphorus, potassium, hydrothermal treatments.

1. INTRODUCTION

The huge amounts of sludge that are unavoidably generated during the secondary treatment of municipal wastewaters continue to be one of the main problems in wastewater treatment plants (WWTP) (Malhotra and Garg, 2020). Within the European Union, the latest data available for Spain on sewage sludge production (2016) place it as the second largest producer, with 1174.4 thousand tonnes generated (European Commission, 2020).

As its management represents up to 50% of the total operational costs in WWTP (Malhotra and Garg, 2019), valorisation strategies are being developed as a way of reducing the environmental and economic impact (Lamastra *et al.*, 2018). Due to its composition, sludge can be used as a cheap renewable source of energy and/or materials such as nutrients, proteins and adsorbents (Gherghel *et al.*, 2019; De Carvalho *et al.*, 2019; Ma and Liu, 2019; Świerczek *et al.*, 2018; Kacprzak *et al.*, 2017; Kelessidis *et al.*, 2012). However, sludge also contains organic pollutants such as polycyclic aromatic hydrocarbons (PAH), dioxins and furans (PCDD/F), polychlorinated biphenyls (PCB), detergent and pharmaceutical residues, personal care products, endocrine disruptors, synthetic steroids, pathogens and heavy metals (Hudcová *et al.*, 2019).

Currently, the main research efforts on sludge management are being focused on optimising traditional sludge treatments, such as anaerobic digestion (Kor-Bicakci *et al.*, 2019; Ma *et al.*, 2017), pyrolysis (Karaca *et al.*, 2018; Jaramillo-Arango *et al.*, 2016) or gasification (Oladejo *et al.*, 2018); and on developing new ways of valorising sludge to recover energy and new resources such as proteins, enzymes, bioplastics, volatile fatty acids and new biofuels (Yuan *et al.*, 2019; Gherghel *et al.*, 2019; Xu *et al.*, 2018; Zhao *et al.*, 2014).

It is interesting to point out that many of these traditional and new ways of sludge management require sludge solubilisation as a previous and necessary step (Chang *et al.*, 2020; Perendeci *et al.*, 2020; Hii *et al.*, 2014; Fenga *et al.*, 2014; Morgan-Sagastume *et al.*, 2010; Bougrier *et al.*, 2007). Among the techniques available for this purpose, hydrothermal treatments are one of the most attractive alternatives (Zhan *et al.*, 2020; Chen *et al.*, 2020; Chang *et al.*, 2020; Urrea *et al.*, 2018). Sludge is subjected, in a dense liquid phase to reduce volume, to high temperatures and pressures (above 100 °C and 0.101 MPa), which destroy cells and hydrolyse molecules (Su *et al.*, 2019; Urrea *et al.*, 2017; Hii *et al.*, 2014). Compared to other methods, they do not require expensive devices, do not release harmful emissions into the air, improve the characteristics of settleability and filterability, stabilise the sludge and reduce energy consumption (Moon *et al.*, 2015). Hydrothermal treatments are categorised depending on the type of atmosphere that is employed. If this atmosphere includes air, pure oxygen or any other oxidant, the process is called wet oxidation (WO), whereas if treatment is carried out under an inert atmosphere, it is known as thermal hydrolysis (TH) (Hii *et al.*, 2014).

There is a large amount of literature on hydrothermal sludge treatments, analysing the effect of the main operating variables (temperature, pressure, pH and gas flow rate) (Malhotra and Garg, 2020; Suárez-Iglesias *et al.*, 2017; Farno *et al.*, 2015; Hii *et al.*, 2014; Appels *et al.*, 2010) and promoters (such as metal salts, H₂O₂ and persulfate) (Ning *et al.*, 2020; Song *et al.*, 2016; Gao *et al.*, 2015; Devlin *et al.*, 2011) on a large number of physical, chemical, rheological and texturometric parameters, as well as on the final composition of the hydrolysate (Urrea *et al.*, 2018; Suárez-Iglesias *et al.*, 2017; Urrea *et al.*, 2014; Donoso-Bravo *et al.*, 2011).

Despite the extensive research on the effect of thermal hydrolysis or wet oxidation on the solubilisation and transformations of C from sludge, their impacts on

other macroelements have scarcely been studied. To the best of our knowledge, the most complete studies to date covering this topic correspond to Sun *et al.* (2013), who analysed the evolution of the main macronutrients during the thermal hydrolysis of a 50% diluted, dewatered sewage sludge at temperatures between 180 °C and 240 °C and to Lu *et al.* (2021), who analysed the release of C, N, P, K, amino acids and metals after 30 min of thermal hydrolysis at different temperatures. Apart from this, Malhotra and Garg (2019) studied carbon and ammonium concentrations during the hydrothermal treatment of secondary sludge at different temperatures (140, 160 and 180 °C), pH (3.3, 6.3 and 9.3), times (2, 3.5 and 5 h after reaching the set temperature) and oxidation coefficients (0, 0.25 and 0.5). However, only one nitrogen species (ammonium) was analysed, and no attention was paid to the evolution of other nitrogen species such as nitrites, nitrates or organic nitrogen, either soluble or not. Similarly, different studies have examined the redistribution of nitrogen in different products, but during hydrothermal liquefaction or carbonisation treatments of sludge, where dewatered sludge was employed as the raw material and hydrochars and oily phases were also formed (Zhuang *et al.*, 2017, Wang *et al.*, 2019). Regarding phosphorus, research efforts have focused on its recovery after combining hydrothermal treatments or carbonisation with other subsequent separation methods, but not on its behaviour during these treatments nor the effect of oxygen (Blöcher *et al.*, 2012; Munir *et al.*, 2017; Li *et al.*, 2020; Zheng *et al.*, 2020; Liu *et al.*, 2020). Therefore, there are no studies specifically dealing with the effect of the main operational parameters (time, pressure, temperature and atmosphere) during the hydrothermal treatments of wet sewage sludge on the fate of the four macroelements (C, N, P and K) simultaneously. What stands out most is that neither the changes occurring during the heating period, when the solubilisation rate is the highest, nor the effect of an oxidising atmosphere has been

thoroughly analysed yet. Moreover, dewatered sewage sludge is commonly used as a feedstock, despite the fact that previous drying is unnecessary because hydrothermal treatments use water as a reagent (Chen *et al.*, 2020).

The aim of this research was to study in depth the compositional changes that take place during the hydrothermal treatment of secondary sewage sludge. For this purpose, the effects of the main operational parameters (time, temperature, pressure and atmosphere) on the fate of the four macronutrients (C, N, P and K) and the most important physicochemical parameters were analysed. Such knowledge would be very useful when deciding the use of hydrothermally treated sludge as a fermentation medium for the bioproduction of metabolites (biogas, VFA, bioplastics and so on) (Tu *et al.*, 2019; Zhang *et al.*, 2019) or as fertiliser (directly or after a previous transformation) (Seleiman *et al.*, 2020), among others.

2. MATERIALS AND METHODS

2.1. Sewage sludge

Secondary sludge, thickened by dissolved air flotation, was collected from a wastewater treatment plant in Baiña (Asturias). The sludge samples were immediately stored at 4 °C until being used. Table 1 shows the main characteristics of this sludge.

Table 1. Physicochemical properties of sewage sludge.

Parameters	Mean values
pH	6.9 ± 0.1
Colour Number (CN)	0.08 ± 0.02
Dry matter (g DM/kg sludge)	34 ± 3
Total Suspended Solids (g TSS/kg sludge)	27 ± 3
Volatile Suspended Solids (g VSS/kg sludge)	23 ± 1
Soluble Extracellular Polymeric Substances (g sEPS/kg dry matter)	5.2 ± 0.1
Bound Extracellular Polymeric Substances (g bEPS/kg dry matter)	100 ± 2
Total Chemical Oxygen Demand (tCOD) (g O ₂ /kg dry matter)	1050 ± 30
Soluble Chemical Oxygen Demand (sCOD) (g O ₂ /kg dry matter)	40 ± 20
Total carbon (g C/kg dry matter)	415 ± 1
Total nitrogen (g N/kg dry matter)	70 ± 1
Total phosphorus (g P/kg dry matter)	16.0 ± 0.4
Total potassium (g K/kg dry matter)	5.5 ± 0.3

2.2. Experimental setup

The hydrothermal reactions were carried out in a 1 L 316 SS semi-batch reactor (Parr Instrument Co.) with two magnetically driven six-blade turbine agitators. Additionally, the reactor was also equipped with temperature and pressure controllers and the corresponding indicators, a sampling system and a heating blanket. In order to prevent the pressure from exceeding 120 bar, rupture disks and vent valves were

included in the setup. Pressure was adjusted by means of a back-pressure valve located at the end of the gas line. To saturate the gas flow (N₂ for thermal hydrolysis or O₂ for wet oxidation), it was previously bubbled through a 2 L stainless steel water tank. To ensure safe operating conditions, the reactor and the humidifier were initially loaded to 70% of the maximum capacity. A scheme of the experimental setup can be seen in Figure S.1 in the Supplementary Material.

For all the experiments, the volume of the sludge was 700 mL; the stirrer speed, 150 rpm; the flow rate of O₂ or N₂, 1800 mL/min and the reaction time, 210 min. Samples were periodically withdrawn from the beginning of the experiment, including the heating and pressurisation period, which lasted around 45 min, and subsequently analysed in triplicate.

2.3. Analytical methods

2.3.1. Physicochemical parameters

Total and volatile solids concentrations (TSS and VSS) and total and soluble chemical oxygen demands (tCOD and sCOD) were measured according to Standard Methods (APHA *et al.*, 2005). pH was determined with a pH-meter (Basic 20 Crison Instruments) at room temperature.

Colour number (CN) was obtained using the absorbance values at three wavelengths (436, 525 and 620 nm) measured with a T80 UV/VIS spectrophotometer (PG Instruments Ltd) according to equation 1 (Urrea *et al.*, 2017):

$$C.N = (ABS^2_{436} + ABS^2_{525} + ABS^2_{620}) / (ABS_{436} + ABS_{525} + ABS_{620}) \quad (1)$$

CN and sCOD, as well as the macronutrient concentrations (see section 2.3.2), were measured in the supernatant, obtained after centrifuging the samples at 10000 g for

20 min in a Thermo Scientific centrifuge. The precipitate was used to determine the composition of the solid phase. All parameters, whether measured in the liquid or solid phase, have been expressed in g/kg dry matter in the initial sludge, in order to compare results with those from other sludges used by different researchers, regardless of the solid content of the feedstock.

Dry matter content was obtained by difference in weight between raw sewage sludge and after drying at 105 °C.

2.3.2. Elemental analysis

Soluble total organic (sTOC) and inorganic (IC) carbon concentrations were measured using a Shimadzu TOC-V CSH device.

Concentrations of nitrogen as nitrites, nitrates, ammonium and organic nitrogen in the supernatant were measured using a Segmented Flow Self-Analyzer, SKALAR SAN PLUS, based on colourimetric reactions. The system is composed of a dialyzer, an ultraviolet digester, photometric detectors and the respective cadmium columns for the reduction of nitrate. Before the analysis, the samples were diluted 1:250 with distilled water.

Total nitrogen in the raw sludge and in the hydrolysed solid fractions was determined with a C, N, H, S Elemental Analyzer, Elementar Vario EL.

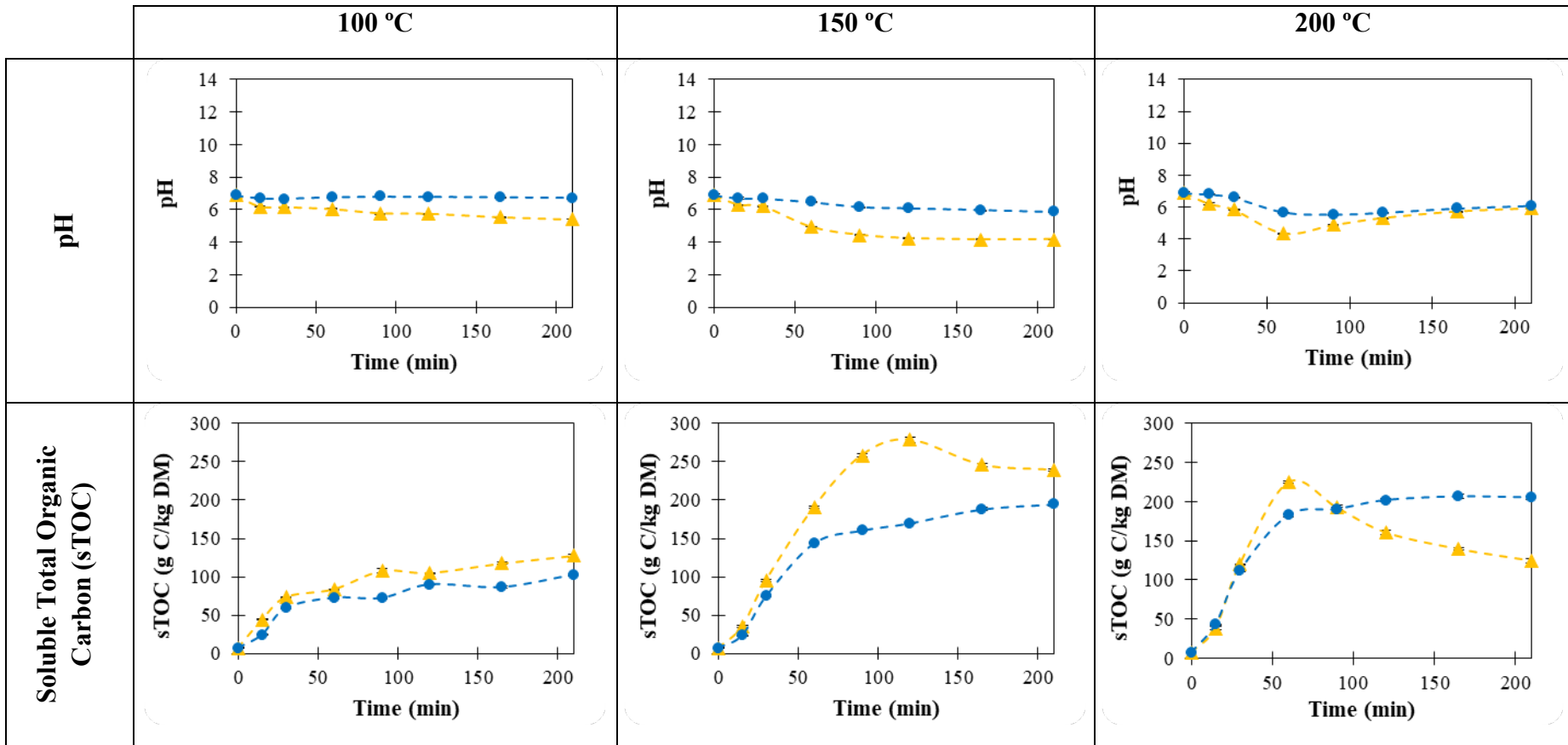
Concentrations of K and P were measured in the supernatant by quantitative analysis with a Thermo Scientific's Neptune plus ICP-MS (Inductively Coupled Plasma Mass Spectrometer), equipped with an integrated I-AS autosampler. The collision/reaction cell used 4.3 mL/min of He to eliminate interferences. An Sc internal standard was used because its mass is similar to the measured elements. In order to determine the total concentration of K and P, a sample of raw sludge, previously dried

at 105 °C for 24 h and subsequently digested by the microwave acid digestion method, was also analysed. 6 mL of HNO₃ and 2 mL of a 30% H₂O₂ solution were added to 100 mg of dried sludge and a microwave instrument was used (Ethos One, Milestone Systems). The procedure employed is described in the application note HPR-EN-25 of Milestone (Milestone, 2009).

3. RESULTS AND DISCUSSION

3.1. Effect of operational conditions on carbon solubilisation

Figure 1 shows the changes in the main physicochemical properties, including the soluble organic carbon concentration, during the hydrothermal treatment of sludge under different temperatures and atmospheres. As the effects of the main operating conditions on these parameters have already been profusely studied (Xue *et al.*, 2015; Baroutian *et al.*, 2015), they will be briefly explained in this section. Additionally, Figure S.2 in the Supplementary Material shows the evolution of TSS.



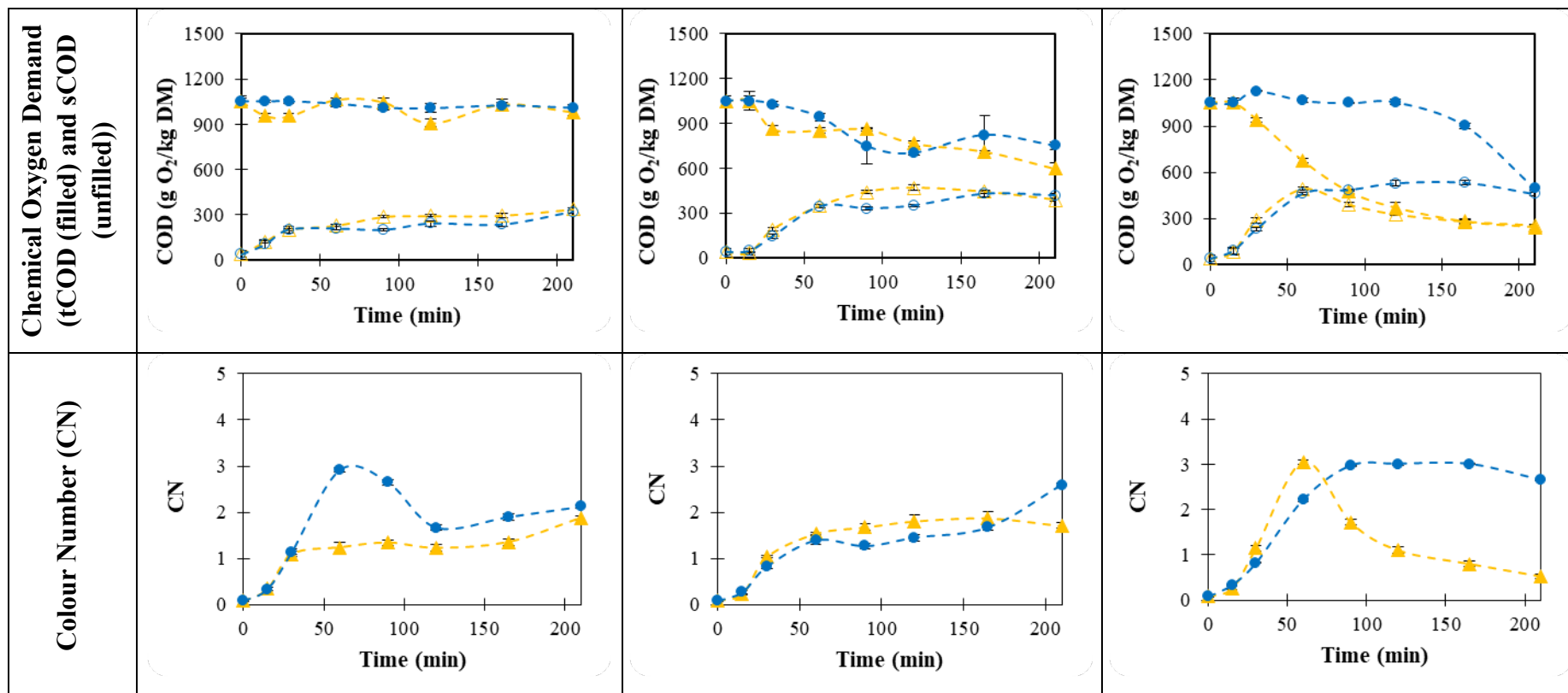


Fig. 1. Effect of temperature on the main physicochemical properties (pH, sTOC, tCOD (filled symbol), sCOD (unfilled symbol) and CN) during wet oxidation (▲) and thermal hydrolysis (●) of sludge at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen or nitrogen flow rate, 1800 mL/min.

The first observation to make is that during the hydrothermal treatment of sludge under an inert atmosphere a higher and faster release of soluble compounds was observed when the temperature was increased. In this sense, both sCOD and sTOC increased at first as a result of the initial breakage of cells produced by the hydrolysis reactions and then, they remained constant because the released compounds were not oxidised due to the absence of oxygen (Suárez-Iglesias *et al.*, 2017). This absence of oxidation reactions under inert atmospheres also explained why tCOD remained almost constant during all the thermal hydrolysis experiments, regardless of the temperature selected. Moreover, the hydrolysis caused a change in the colour of the supernatant, it being more intense at high temperatures. This was attributed to the formation of biorefractory molecules called melanoidins due to Maillard reactions (Dwyer *et al.*, 2008).

Regarding the effect of an oxidising atmosphere, the presence of oxygen was only relevant at high temperatures. In fact, sCOD, tCOD and sTOC behaved quite similar under both atmospheres at 100 °C, indicating the little oxidation of organic matter at low temperatures. Once the temperature was increased, the impact of an oxidising atmosphere, in comparison to an inert one, on the main physicochemical sludge properties became noticeable. For temperatures higher than 150 °C, oxidation reactions began to be important, so sCOD initially increased due to hydrolysis reactions but, after reaching a maximum, it decreased due to the oxidation of the previously solubilised organic matter to CO₂ and water (Urrea *et al.*, 2014). It is interesting to point out that high temperatures not only accelerated the oxidation reactions, but also the hydrolysis ones. It was also conspicuous that sTOC also initially increased from 7.2 ± 0.6 g C/kg dry matter to 278 ± 4 g C/kg dry matter during the wet oxidation of sludge at 150 °C but, after 165 min, this value remained constant for the rest of the reaction

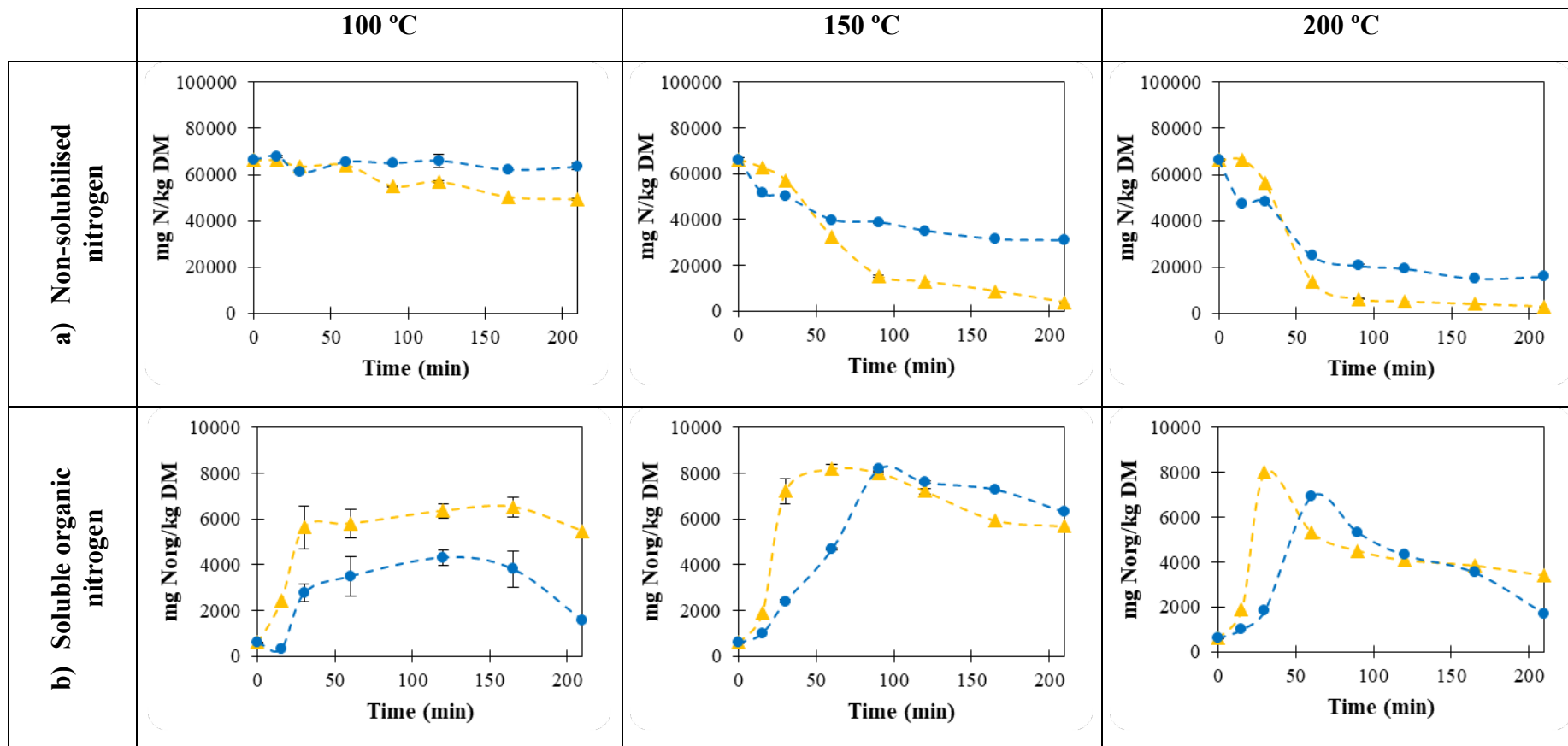
time. On the other hand, when the temperature was stepped up to 200 °C, the sTOC value reached a maximum (225 ± 2 g C/kg dry matter) after only 60 min, but then decreased to 125 ± 3 g C/kg dry matter during the last 150 min of reaction. Thus, comparing sCOD and sTOC values, it was deduced that the oxidation reactions were negligible at 100 °C but, as the temperature rose, the dissolved organic matter was partially oxidised (at 150 °C, sTOC remained constant but sCOD decreased) or even totally mineralised to carbon dioxide, if the temperature was high enough (at 200 °C, both sCOD and sTOC decreased). In fact, the accumulation of partially oxidised intermediate compounds at high temperatures (200 °C) was indirectly confirmed by the increase in the colour number, which also registered a maximum after 60 min of the experiment, coinciding with the maximum of the sCOD. After this time, the coloured compounds started to be degraded, as shown by the sTOC behaviour.

Additionally, the concentration of inorganic carbon in the liquid fraction was negligible regardless of treatment and reaction time, since the CO₂ formed during wet oxidation was desorbed by the gas stream. As for the evolution of carbon in the solid fraction (see Figure S.3 in the Supplementary Material), it agrees with the solubilisation trend previously described for sTOC. Furthermore, the mineralisation of the compounds during wet oxidation can be observed in the balance included in Figure S.4 in the Supplementary Material, since CO₂ formation only occurred in the presence of oxygen.

Finally, the effect of oxygen pressure on the main physicochemical characteristics of the hydrolysed sludge was studied by carrying out experiments at 10, 50 and 90 bar (see Figure S.5 in the Supplementary Material). Results revealed that an increase in the dissolved oxygen concentration had a positive impact on the sludge solubilisation but also speeded up the subsequent mineralisation of the solubilised organic matter to CO₂ and water (Urrea *et al.*, 2014).

3.2. Effect of operational conditions on nitrogen solubilisation

Research continued by investigating the effects of temperature and type of atmosphere (oxidising or inert) on the concentrations of the different nitrogen species during the hydrothermal treatment of sludge in the presence of oxygen (wet oxidation) and nitrogen (thermal hydrolysis) at different temperatures (100, 150 and 200 °C) (Figure 2).



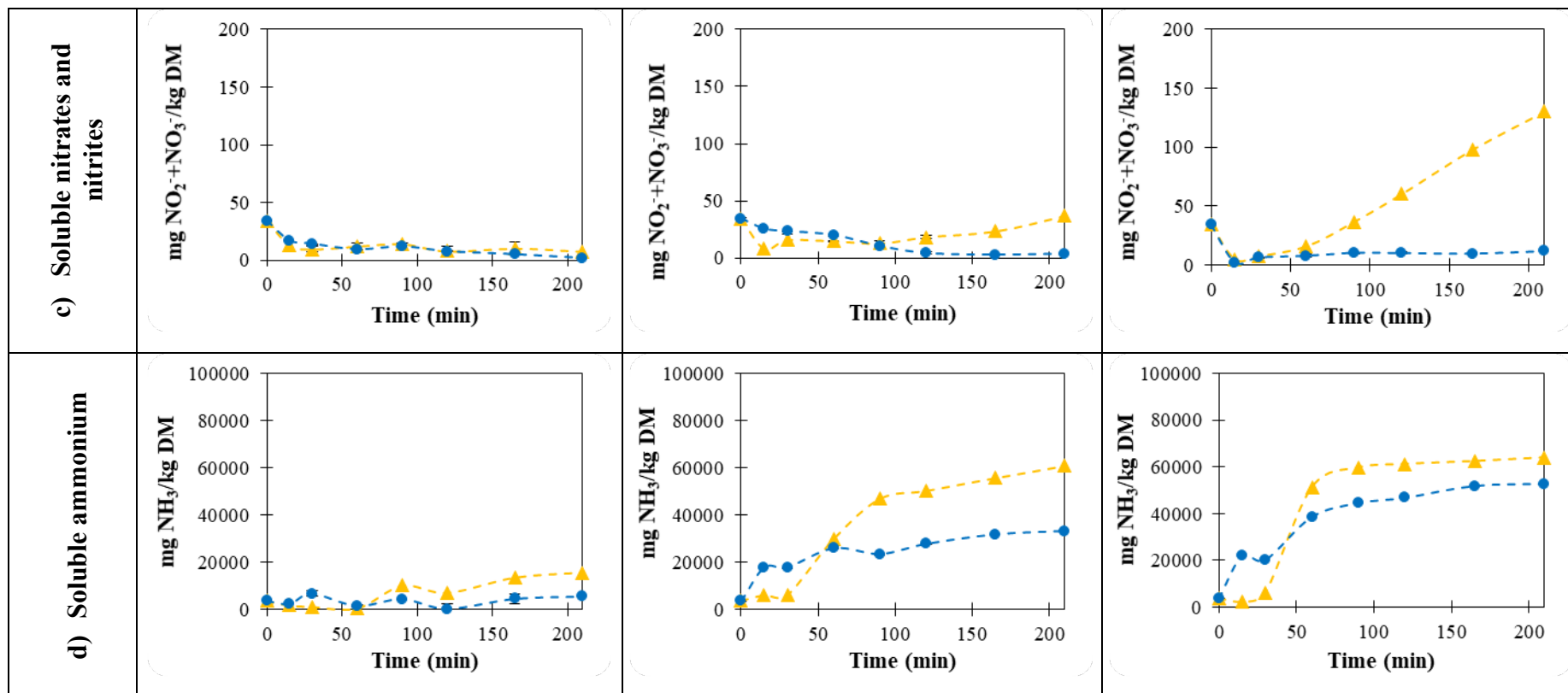


Fig. 2. Evolution of nitrogen in the solid fraction (a); and organic nitrogen (b), nitrogen as nitrates and nitrites (c) and nitrogen as ammonium (d) in the liquid fraction during wet oxidation (▲) and thermal hydrolysis (●) of sludge at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen or nitrogen flow rate, 1800 mL/min.

As in the case of carbon, at the lowest temperature tested (100 °C), the changes in the concentrations of the different types of nitrogen during wet oxidation and thermal hydrolysis were quite similar. Figure 2a showed that the percentage of nitrogen in the non-solubilised sludge barely decreased during the experiments at 100 °C. This suggests that there was no preferential solubilisation of nitrogen in comparison with other chemical elements of the sludge at low temperatures. In presence of oxygen, this final reduction was slightly higher than under an inert atmosphere, as would be expected, because the degradation was speeded up by the oxidising atmosphere. It can also be deduced from Figure 2b that the solubilisation of organic nitrogen mainly occurred during the first 60 min, probably due to the release of extracellular polymeric substances with nitrogen in their composition (Malhotra and Garg, 2019). After this time, the concentration of soluble organic nitrogen increased slightly, suggesting that the breaking up of cells at this temperature took place slowly. The final decrease observed in the soluble organic nitrogen concentrations during the last 50 min of treatment at 100 °C could be explained by the hydrolysis and/or oxidation of organic nitrogen to inorganic compounds. Regarding the inorganic nitrogen species formed, the concentration of nitrogen as nitrates or nitrites species was negligible, so their formation from organic nitrogen could be discarded. Ammonium, however, was the main inorganic nitrogen species generated, being its concentration in the liquid phase doubled in absence of oxygen and quadrupled in its presence at the end of the hydrothermal treatments at 100 °C.

Nevertheless, the effects of the atmosphere on the fate of soluble and non-soluble nitrogen became evident at higher temperatures due to nitrogen speciation is attributed to oxidation reactions and the degradation of proteins (Malhotra and Garg, 2019; Xue *et al.*, 2015). This was also in line with the absence of significant differences

in the evolution of the main physicochemical parameters for those same conditions (Figure 1). So, although increasing the temperature above 100 °C involved a significant reduction in the percentage of non-solubilised nitrogen in the solid sludge fraction, this was more pronounced under an oxidising atmosphere and at higher temperatures. As an example, the nitrogen content of the non-solubilised sludge fraction decreased from an initial value of 66300 ± 600 mg N/kg dry matter to 16000 ± 800 or 2906 ± 4 mg N/kg dry matter after 210 min of hydrothermal treatment in absence or presence of oxygen, respectively, at the highest temperature (200 °C). Moving on to soluble organic nitrogen, its concentration increased during the first minutes of reaction, reaching a maximum, and then started to decrease. This was attributed to the existence of two reactions in series: the initial solubilisation of nitrogen from the solid phase of the sludge due to bacterial lysis and the subsequent degradation of the solubilised proteins, with ammonium as the final product (Malhotra and Garg, 2019). It can be easily deduced from Figures 2a and 2d that both reactions are favoured by high temperatures and/or the presence of oxygen during the hydrothermal treatment, which is reasonable, taking into account that more aggressive conditions caused not only faster bacterial lysis but also a higher degree of denaturation and degradation of proteins, with the corresponding generation of ammonium as a by-product. At this point, it should be stressed that, due to the high temperatures and the constant gas flow passing through the reaction medium, ammonium was partially desorbed, so its concentration was deduced from a nitrogen mass balance (see Figure S.4 in the Supplementary Material). As expected, the rate of formation of ammonium during the hydrothermal treatment of sludge was accelerated by employing higher temperatures and/or the presence of an oxidising atmosphere, which involved faster degradation of the solubilised proteins. So, around 47% of the initial nitrogen in the sludge was converted to ammonium after 210

min of treatment at 150 °C under an inert atmosphere, whereas this percentage increased to 75% or 87% if temperature was 200 °C or oxygen was employed as oxidant, respectively. In fact, under the most severe conditions (200 °C and oxygen) only 5% of the solubilised nitrogen remained in organic form. In this specific case, it is also interesting to note a gradual increase in the nitrate concentration during the hydrothermal treatment from 60 min to the end of the experiment, reaching a final value of 130 mg $\text{NO}_2^- + \text{NO}_3^-$ /kg dry matter. This suggests a low degree of nitrification of ammonium, which was only appreciable under the most aggressive conditions tested (200 °C and with oxygen).

Regarding the effect of the oxygen pressure on nitrogen speciation during the hydrothermal treatment of sludge (see Figure S.6 in the Supplementary Material), results revealed that no significant differences were to be observed in the changes undergone by the main nitrogen species at the different pressures tested, which ranged from 10 to 90 bar. Only a slight increase in the concentration of nitrates and nitrites concentration was observed at high oxygen pressures due to a lower solubilisation of the organic nitrogen at 10 bar. Therefore, it can be concluded that this operational parameter is not determining during the hydrothermal treatment of sludge.

3.3. Effect of operational conditions on phosphorus solubilisation

Figure 3 shows the behaviour of solubilised phosphorus and potassium during the hydrothermal treatment of sludge at different atmospheres and temperatures. Their non-solubilised concentrations and the mass balances before and after the treatments at different temperatures can be seen in Figures S.3 and S.4 in the Supplementary Material.

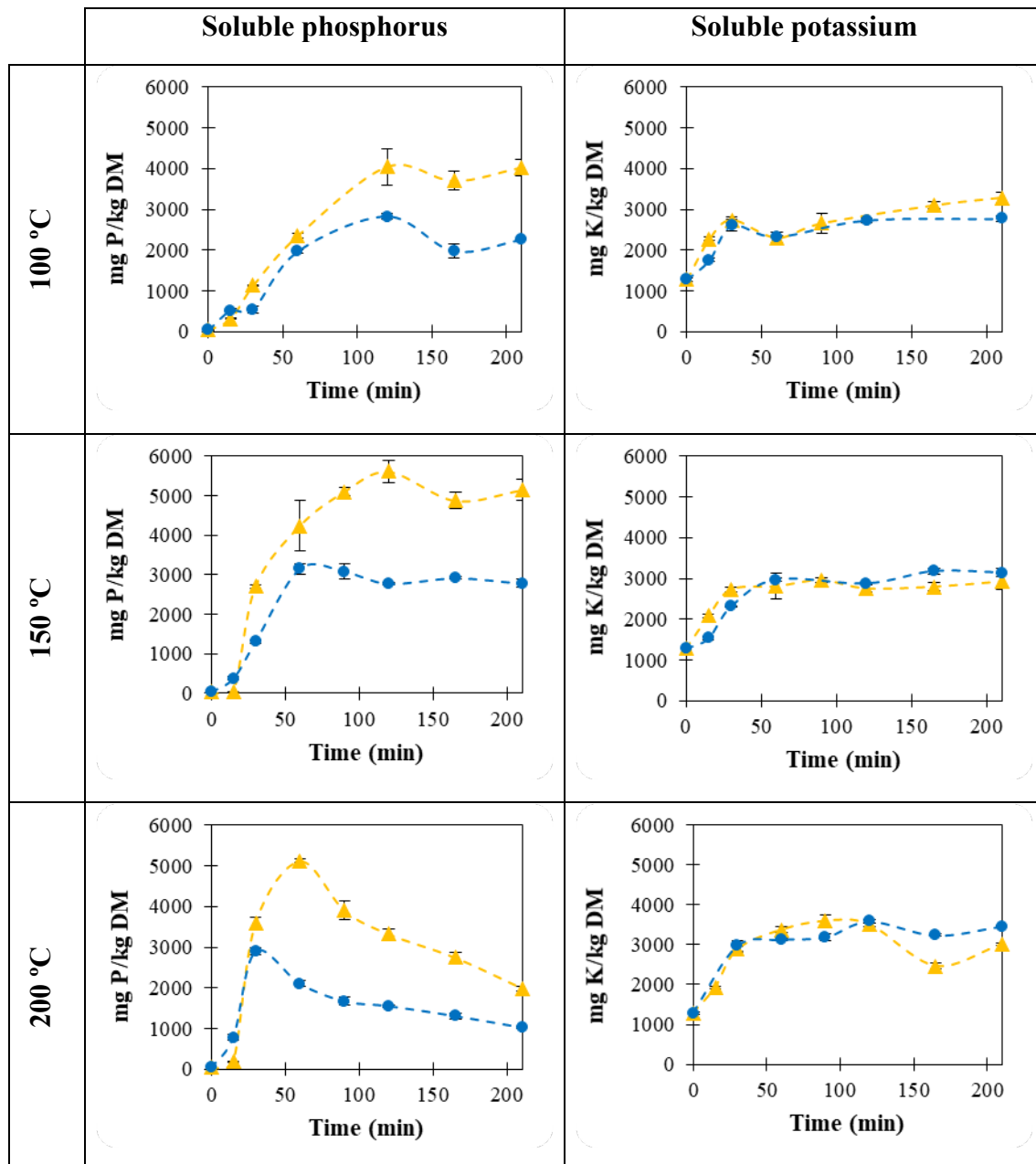


Fig. 3. Evolution of solubilised P and K during wet oxidation (▲) and thermal hydrolysis (●) at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen or nitrogen flow rate, 1800 mL/min.

Before discussing the effect of operational conditions on phosphorus and potassium solubilisation, it is important to note that both have been considered as inorganic nutrients. In the case of phosphorus, this was because sludge is mainly

composed of inorganic phosphorus and its main form in solution is phosphate (Xie *et al.*, 2011; Xu *et al.*, 2015).

When analysing the effect of temperature on phosphorus evolution, as was observed for carbon and nitrogen, this parameter also increased the phosphorus solubilisation rate, which was to be expected, due to higher cellular lysis. Nevertheless, temperature did not have any significant effect on the maximum solubilised amount, only on the time required to achieve it. Thus, focussing on wet oxidation at 100 °C, the maximum concentration of soluble P was reached after 120 min with a value of 4000 ± 400 mg P/kg dry matter; at 150 °C, this was reached after 120 min as well, with a value of 5600 ± 300 mg P/kg dry matter and at 200 °C, after 60 min with a value of 5120 ± 40 mg P/kg dry matter. These values for solubilised phosphorus corresponded to around 30% of the initial amount in the raw sludge. It should be also stressed that soluble phosphorus only decreased after reaching a maximum at the highest temperature tested. This was related to variation in the pH: high temperatures caused faster TSS reduction (see Figure S.2 in the Supplementary Material) and higher initial acidification of the solution, resulting in increased formation of PO_4^{3-} in the liquid phase. After a while, the pH increased again (Figure 1) and the alkaline medium favoured the binding of phosphorus with metal ions present in the solution (Fe, Ca, Al...) and its subsequent precipitation, which involved a reduction in the soluble P concentration (Xu *et al.*, 2015).

Regarding its evolution during thermal hydrolysis, the degree of solubilisation achieved was lower in absence of oxygen. Thus, maximum phosphorus solubilisation during the hydrothermal treatment of sludge in absence of oxygen was around 18% for all the temperatures, in comparison to the 32% achieved under an oxidising atmosphere. Again, this behaviour is closely related to the changes in pH during the hydrothermal

treatment: thermal hydrolysis caused lower acidification of the hydrolysed sludge, leading to the formation of PO_4^{3-} in the liquid phase to a lesser extent than during wet oxidation.

Further experiments were conducted to better understand the oxygen effect. Figure S.7 in the Supplementary Material shows the changes in soluble phosphorus during the hydrothermal treatment at different pressures. It was observed that increasing the dissolved oxygen concentration produced greater solubilisation of P, reaching a maximum value of 5700 ± 600 mg P/kg dry matter at 90 bar, in comparison to 5600 ± 300 mg P/kg dry matter at 50 bar and 4410 ± 40 mg P/kg dry matter at 10 bar. As can be seen in Figure S.5 in the Supplementary Material, the higher the pressure employed, the greater was the acidification of the sample during the treatment and, therefore, the higher the formation of PO_4^{3-} in the liquid phase.

3.4. Effect of operational conditions on potassium solubilisation

Finally, soluble potassium concentrations were also measured during the hydrothermal treatment of sludge carried out at different temperatures and atmospheres (Figure 3). Results revealed that neither changing the temperature nor the type of atmosphere produced significant impacts on the solubilisation rate or the final soluble potassium concentration, which reached a maximum of around 3100 ± 400 mg K/kg dry matter after approximately 30 min, regardless of the temperature, atmosphere or pressure tested (see Figure S.7 in the Supplementary Material). This constant value corresponds to around 57% of the total potassium in the raw sludge and suggests that potassium was mainly associated with tightly bound EPS. These extracellular polymers are easily solubilised, even at low temperatures, explaining the increase in the soluble concentration during the first minutes of treatment, when the heating up of the reactor occurred (Urrea *et al.*, 2017; Sheng *et al.*, 2010).

3.5. Comparison

Figure 4 shows the proportions of the non-solubilised macroelements in the dry matter of the sludge before being treated or after 210 min of thermal hydrolysis or wet oxidation at 100, 150 and 200 °C.

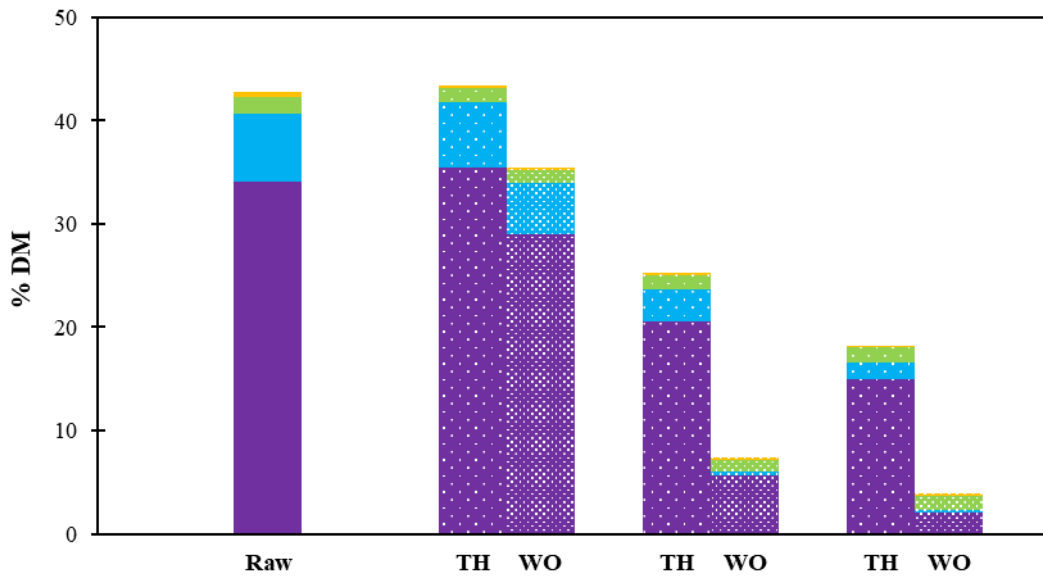


Fig. 4. Proportion of non-solubilised C (■), N (■), P (■) and K (■) before treatment (raw) and after 210 min of thermal hydrolysis (TH) or wet oxidation (WO) at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen or nitrogen flow rate, 1800 mL/min.

As previously explained, slight TSS reductions were observed at the lowest experimental temperature (100 °C), regardless of the atmosphere selected (see Figure S.2 in the Supplementary Material). At this temperature, the possibility of preferential solubilisation of some elements in comparison to others could also be discarded, the proportions of each element remaining approximately constant after the treatments. However, when the temperature was increased to 150 °C or 200 °C, solubilisation of the sludge was clearly evident, as was a decrease in the proportion of nitrogen in the non-

solubilised fraction in comparison to the other elements. These effects were more marked under the most aggressive conditions, that is to say, at high temperatures and/or in presence of oxygen. So, nitrogen represented 6.6% of the initial weight of the dried sludge, but this percentage decreased to 0.3% in the non-solubilised sludge fraction after wet oxidation at 200 °C. Under the same conditions, the percentages of solid carbon, phosphorus and potassium changed from 34.1, 1.6 and 0.4% in the raw sludge to 2.0, 1.4 and 0.3%, respectively, after the hydrothermal treatment. It is interesting to remember that these conditions also caused a 76% reduction in TSS, which decreased from 27 g TSS/kg sludge in the initial sample to 7 g TSS/kg sludge in the sample treated at 200 °C under an oxidising atmosphere. Nevertheless, no significant effect of the dissolved oxygen concentration on the final elemental composition of the non-solubilised fraction of the sludge was observed, at least over the range of pressures studied (see Figure S.8 in the Supplementary Material).

Focusing now on the liquid phase, Figure 5 shows the proportions of the main elements in the liquid phases of the initial sludge and the hydrolysates obtained after 210 min of the corresponding hydrothermal treatment.

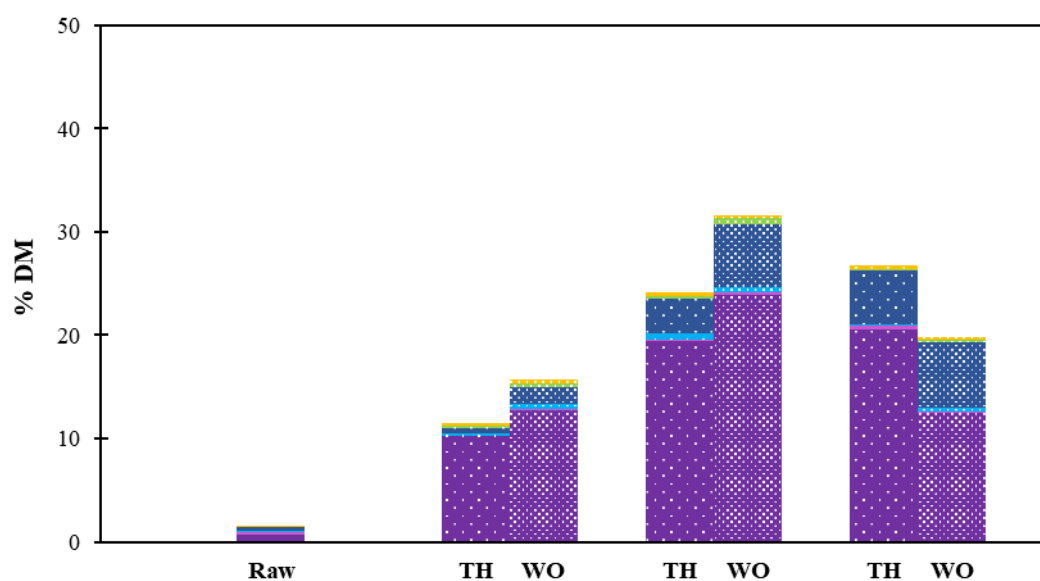


Fig. 5. Proportion of solubilised organic C (■), inorganic C (■), organic N (■), inorganic N (■), P (■) and K (■) before treatment (raw) and after 210 min of thermal hydrolysis (TH) and wet oxidation (WO) at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen or nitrogen flow rate, 1800 mL/min.

As might be expected, a significant increase in the solubilised amount of the different elements studied was observed after the hydrothermal treatments. Nevertheless, as has already been explained, a higher temperature and/or the employment of an oxidising atmosphere did not necessarily imply a higher content of these elements in the liquid phase, even when these conditions improve the disintegration of the solid fraction. This is due to two previously mentioned processes, the formation of carbon dioxide by oxidation reactions and the precipitation of phosphorus at alkaline pH. In addition, an increase in the amount of inorganic nitrogen also occurred due to the degradation of organic nitrogen-containing compounds into ammonium, the formation of which was accelerated under the most aggressive conditions of temperature and in presence of oxygen.

It is interesting to stress that the Corg:Norg:P:K mass ratio for the liquid phase of the raw sludge was 100:8.3:0.5:17.9, whereas this parameter after 210 min at 200 °C of thermal hydrolysis was 100:0.8:0.5:1.7 or, in the case of wet oxidation, 100:2.7:1.6:2.4. Therefore, it can be concluded that, at the highest temperature tested, an inert atmosphere produced a decrease in either the Norg/Corg or K/Corg ratios due to the faster solubilisation of carbon in comparison with the rates corresponding to the other elements. Moreover, part of the organic nitrogen was converted into ammonium and released from the liquid medium. In contrast, the P/Corg ratio was maintained, owing to their solubilisations were comparable. On the other hand, the oxidising atmosphere caused smaller reductions in the Norg/Corg and K/Corg ratios in

comparison to an inert one, because a fraction of the solubilised organic carbon was oxidised to CO₂. Nevertheless, the P/C_{org} ratio increased during the wet oxidation treatment because the formation rate of CO₂ was higher than the precipitation rate of PO₄³⁻. Nevertheless, it should be remembered that the content of the four elements here discussed increased in terms of their absolute concentrations.

Eventually, as demonstrated above, increasing the dissolved oxygen concentration did not produce significant impacts on the final elemental composition in the liquid phase, at least over the range of pressures tested (10-90 bar) (see Figure S.9 in the Supplementary Material).

4. CONCLUSIONS

This study has provided, for the first time, a profound understanding of the effect of the hydrothermal treatments on the fate of the four main macronutrients (C, N, P and K) in sewage sludge, which is important, because this hydrolysed feedstock is of considerable interest for use as a fertiliser or as a fermentation medium. Regarding carbon, results revealed that the oxidation reactions were negligible at 100 °C but, as the temperature rose, the dissolved organic matter was mineralised to carbon dioxide. Focusing on nitrogen, increasing the temperature led, under both types of atmosphere, to a higher degree of solubilisation of this element, the effect being greater in presence of oxygen. In the specific case of soluble organic nitrogen, its solubilisation occurred mainly during the first minutes of treatment due to the release of extracellular polymeric substances and, afterwards, this organic nitrogen was degraded to ammonium, especially at high temperatures and under an oxidising atmosphere. With phosphorus, solubilisation also occurred at the beginning of the treatments, but then, as the temperature increased, it re-precipitated in the form of PO₄³⁻, resulting in a decrease in the soluble phosphorus. In addition, for all the conditions tested, fast initial

solubilisation of potassium was observed during the first 30 min and then the soluble concentration achieved remained almost constant until the end of the experiments. Finally, pressure did not have significant effects on the final macronutrient composition of the sludge hydrolysate over the range tested (10-90 bar).

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Supplementary Material

MACRONUTRIENT SOLUBILISATION DURING HYDROTHERMAL TREATMENT OF SEWAGE SLUDGE

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Figure S.1. Scheme of the experimental setup: (B1) compressed bottle of oxygen or nitrogen, (H1) humidifier, (R1) reactor with heating jacket, (C1) condenser, (E1) PID controller (gas flow, humidifier and reactor temperature, stirrer speed and pressure). Streams: (1) gas, (2) saturated gas, (3) gas outlet, (4) sample outlet. 4

Figure S.2. Effect of temperature on total suspended solids (TSS) during wet oxidation or thermal hydrolysis at 100 (◆), 150 (▲) and 200 °C (■). In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 5

Figure S.3. Evolution of C, P and K in the solid fraction during wet oxidation or thermal hydrolysis at 100 (◆), 150 (▲) and 200 °C (■). In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 6

Figure S.4. C, N, P and K balance (solid (■), liquid organic (▣) and inorganic (▢) and gas (■) fractions) before treatment (raw) and after 210 min of thermal hydrolysis (TH) or wet oxidation (WO) at 100, 150 and 200 °C. In all cases: pressure, 50 bar; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 7

Figure S.5. Effect of pressure on the main physicochemical properties (pH, sTOC, tCOD (filled symbol), sCOD (unfilled symbol) and CN) during wet oxidation at 10 (◆), 50 (▲) and 90 bar (■). In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 8

Figure S.6. Evolution of nitrogen in the solid fraction (a); and organic nitrogen (b), nitrogen as nitrates and nitrites (c) and nitrogen as ammonium (d) in the liquid fraction during wet oxidation at 10 (◆), 50 (▲) and 90 bar (■). In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min. 9

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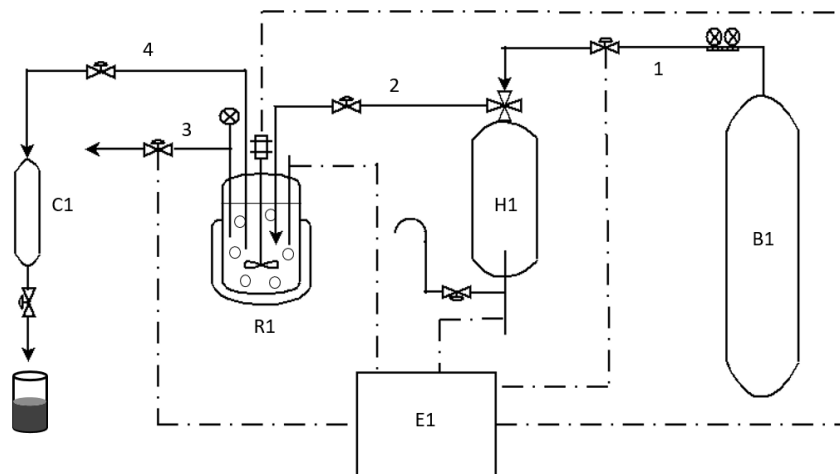


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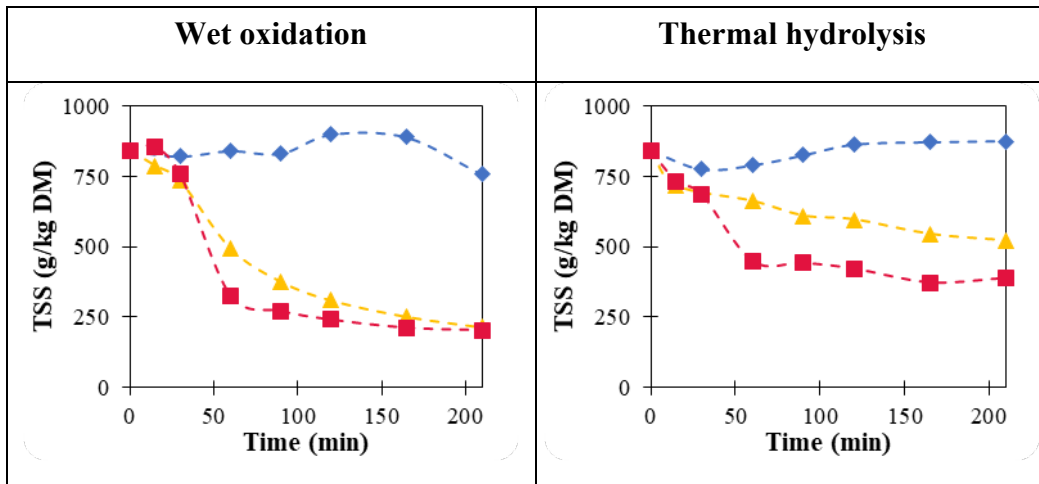


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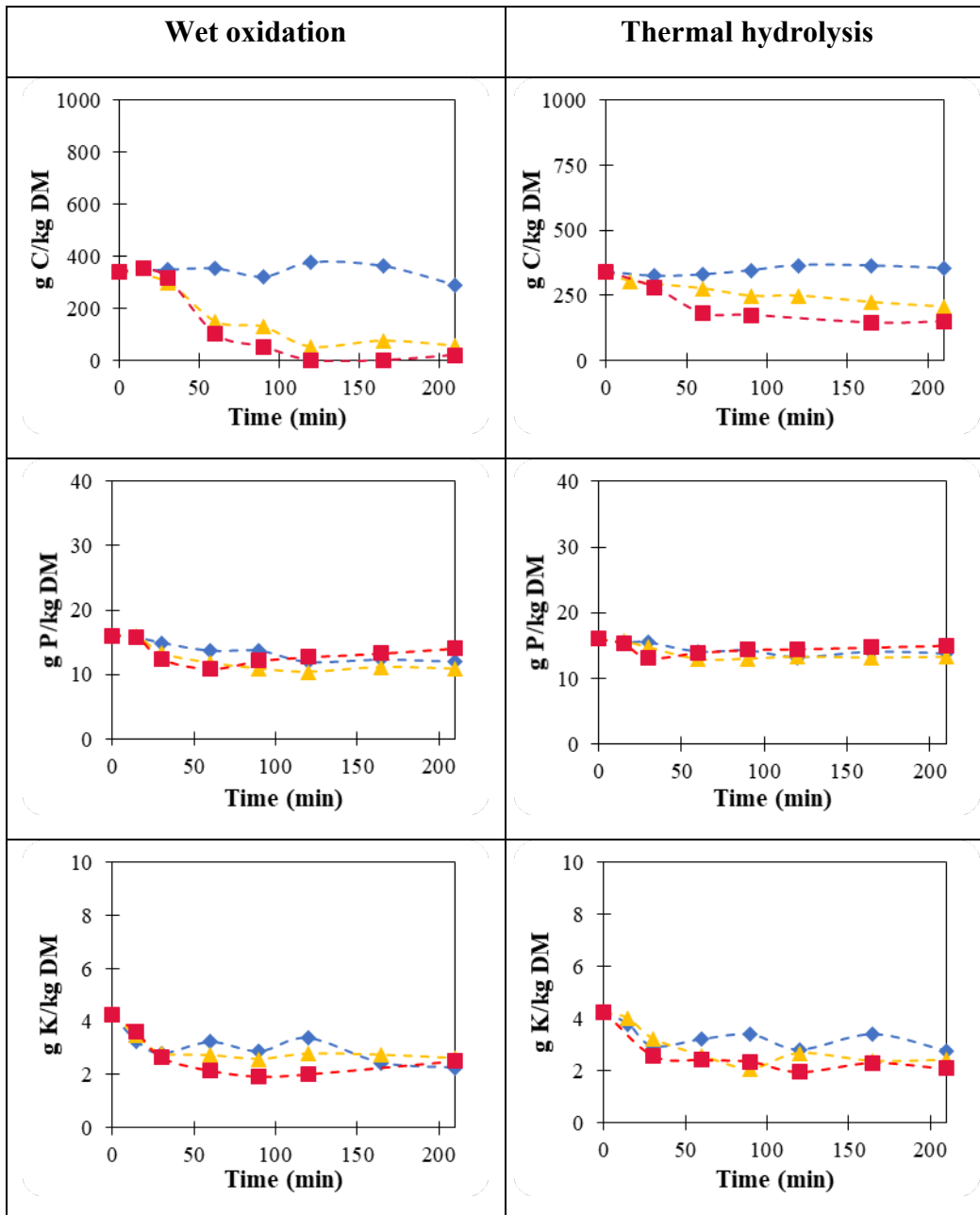


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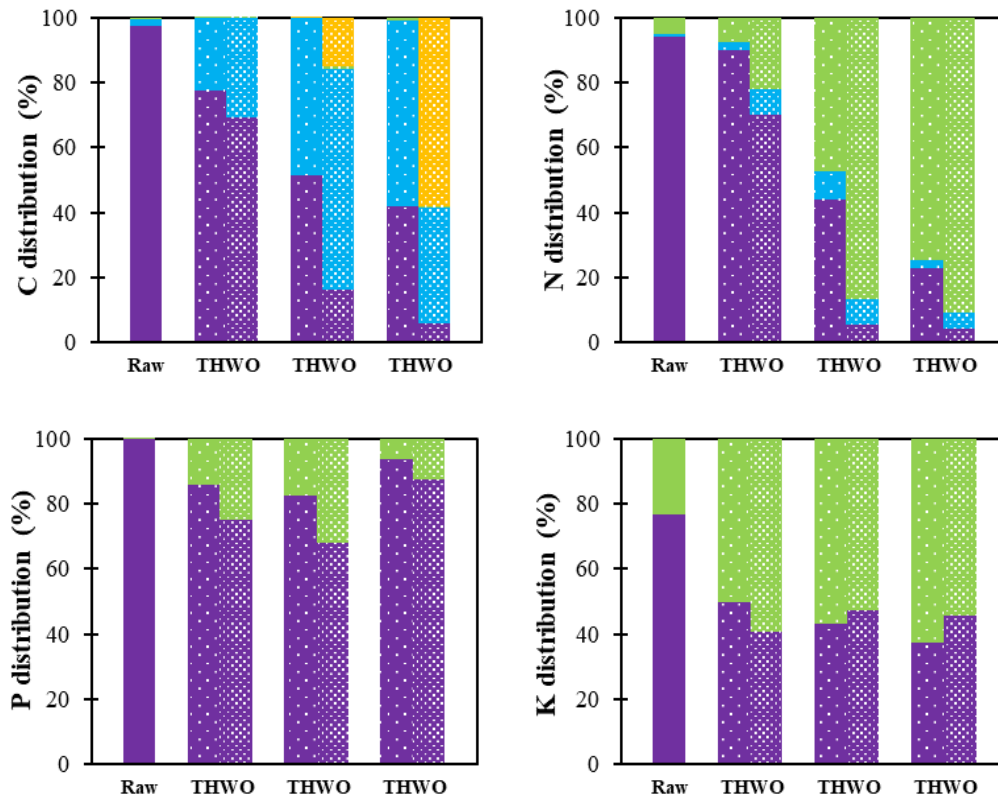


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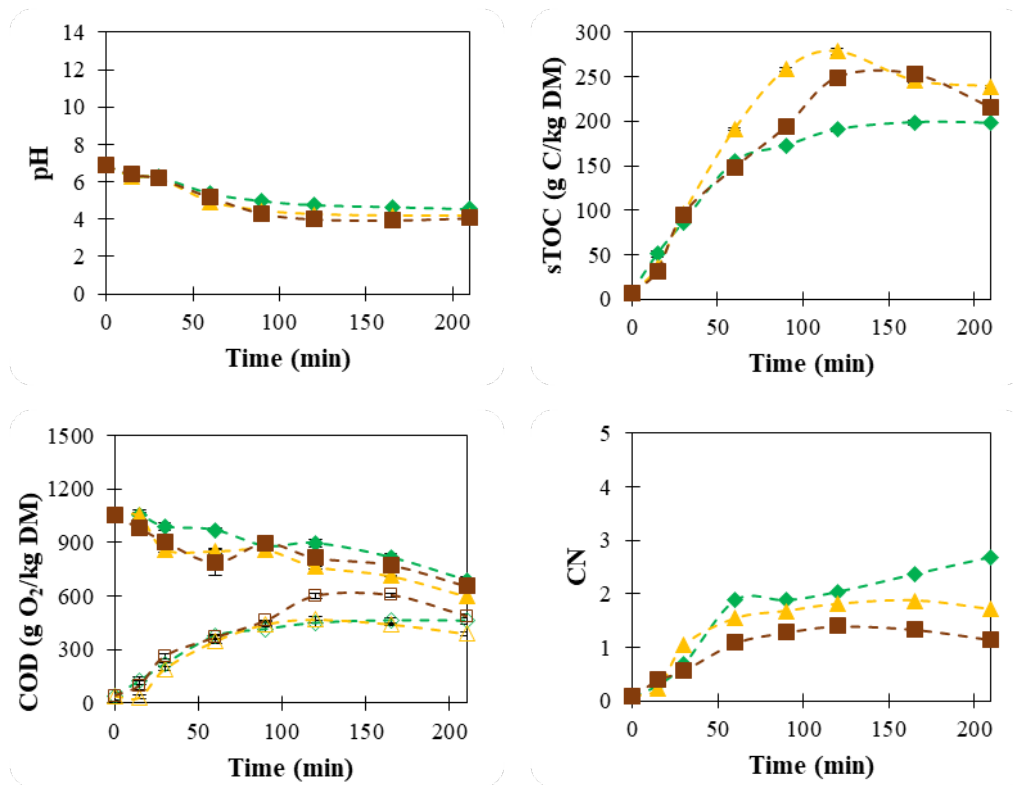


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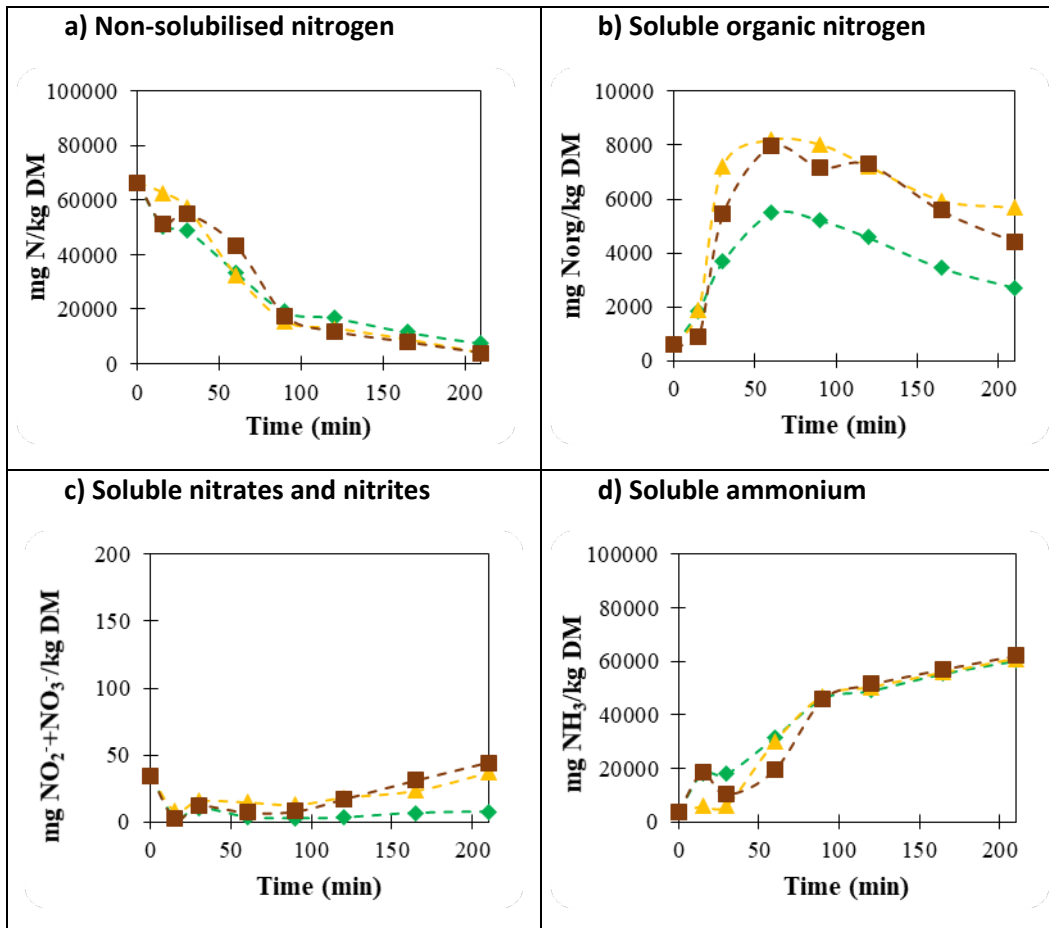


Figure S.6. Evolution of nitrogen in the solid fraction (a); and organic nitrogen (b), nitrogen as nitrates and nitrites (c) and nitrogen as ammonium (d) in the liquid fraction during wet oxidation at 10 (◆), 50 (▲) and 90 bar (■). In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

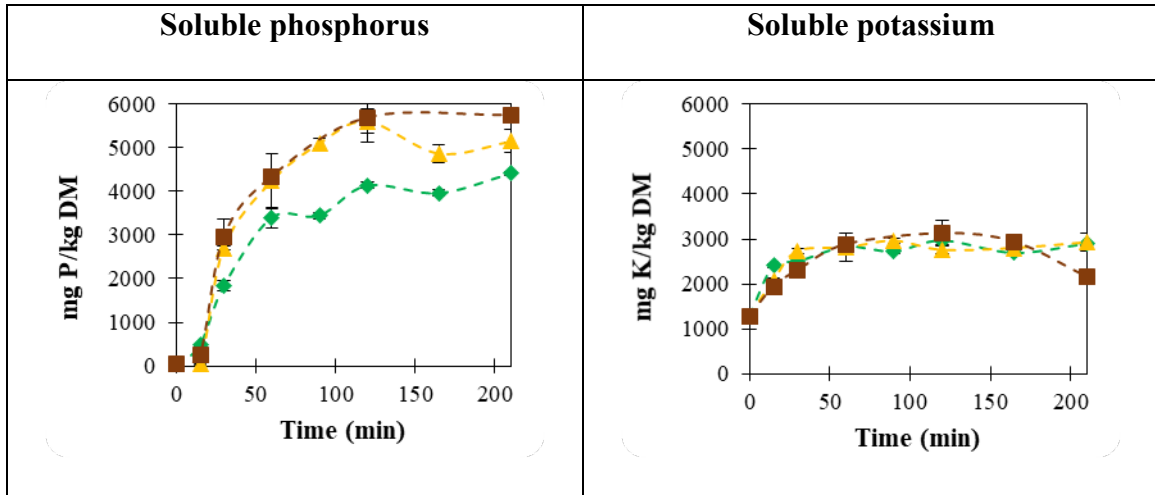


Figure S.7. Evolution of solubilised P and K during wet oxidation at 10 (◆), 50 (▲) and 90 bar (■). In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

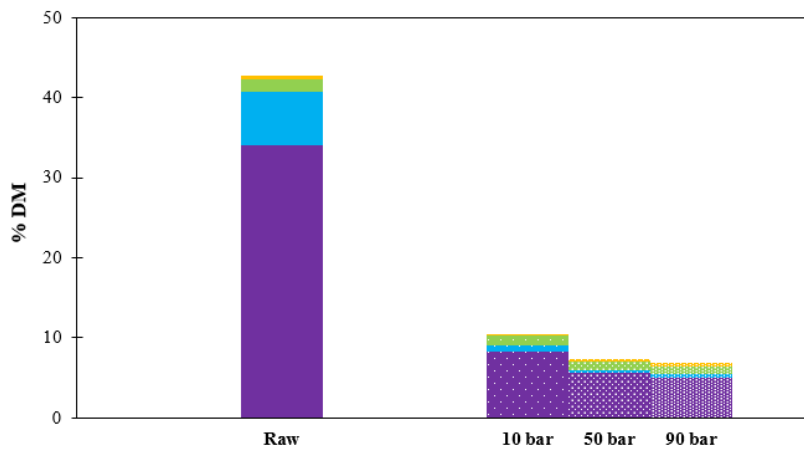


Figure S.8. Proportion of non-solubilised C (■), N (■), P (■) and K (■) before treatment (raw) and after 210 min of wet oxidation at 10, 50 and 90 bar. In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.

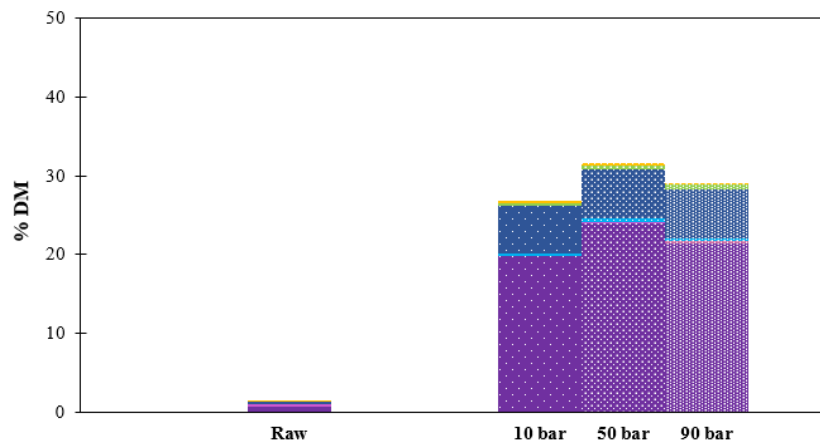


Figure S.9. Proportion of solubilised organic C (■), inorganic C (■), organic N (■), inorganic N (■), P (■) and K (■) before treatment (raw) and after 210 min of wet oxidation at 10, 50 and 90 bar. In all cases: temperature, 150 °C; stirrer speed, 150 rpm; oxygen flow rate, 1800 mL/min.