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COMPARISON OF NUTRIENT RELEASE STRATEGIES IN HYDROTHERMALLY TREATED DIGESTED SEWAGE SLUDGE

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Abstract

This work studies the fate of nutrients (N, P and K) during the hydrothermal treatment of anaerobically digested sewage sludge to raise their concentrations in the liquid phase and facilitate their recovery as solid mineral by chemical precipitation. The hydrothermal process has been optimized by evaluating temperature (170 – 230 °C) and reaction time (5 – 60 min) in an acid-free medium or with the addition of HCl (0.1 – 0.5 M). In the acid-free hydrothermal reactions, nutrients were mainly concentrated in the hydrochar, which were extracted with 0.5 M HCl (10% w/v). Following this route, 6.9 g N/kg, 13.8 g P/kg, and 8.8 g K/kg contained in the feedstock were extracted from the hydrochar produced at 230 ºC, which considering direct nutrient solubilization to process water by acid-free HTT, accounts for 82, 83, and 78% N, P, and K release, respectively. In the HCl-assisted hydrothermal treatment, the release of nutrients directly into the process water was improved and depended mainly on the acid concentration used and to a lesser extent on the reaction temperature. Operating at 230 °C and 0.5 M HCl, a release of 98% N (more than 45% as NH_4-N), 87% P (as PO_4-P) and 70% K contained in the feedstock was achieved in the process water. Chemical precipitation of phosphorus and nitrogen from the process water allowed the recovery of a solid identified as crystalline struvite, with a high content in P, Mg, NH_4-N and negligible heavy metals

content. The estimated cost of digested sewage sludge treatment could reach 13.7 euros per ton, considering the energy inputs required in the hydrothermal treatment.

Keywords: Biomass valorization, Digested sewage sludge, Hydrochar, Hydrothermal carbonization, Nutrient solubilization.

Abbreviation list

AD, anaerobic digestion.

FC, fixed carbon.

HCT-[HCl], hydrochar, T represents reaction temperature (ºC) and [HCl] the added HCl concentration (M), if applicable.

HC-W, washed hydrochar

HHV, higher heating value.

HTT, hydrothermal treatment.

L-T, leachant from hydrochar acid washing, T represents reaction temperature (ºC) for hydrochar obtaining.

PWT-[HCl], process water, T represents reaction temperature (ºC) and [HCl] the added HCl concentration (M), if applicable.

RSM, response surface methodology.

VM, volatile matter.

W_{DSS}, digested sewage sludge weight.

W_{HC}, hydrochar weight.

W_{ST}, struvite weight.

W_{TSPW}, total solid weight in process water.

Y_{HC}, hydrochar mass yield.

Y_{PW}, process water yield.

Y_{ST}, struvite recovery yield.

Introduction

Anaerobic digestion (AD) is a widely used mature and economically viable technology that biochemically transforms sewage sludge to biogas. The biogas is often used to obtain heat and energy, improving the economic and environmental benefits of the process. Digested sludge is generally stable and devoid of pathogens and odor[1]. Importantly, digested sludge is an organic waste that contains large amounts of nutrients (> 40 g N/kg; > 20 g P/kg; 5 g K/kg)[2–4], comparable to the nutrient content of other biomass wastes, such as animal manure (30 – 60 g N/kg; 15 – 20 g P/kg; 10 – 25 g K/kg)[5–7] and food waste (25 – 35 g N/kg; 3 – 6 g P/kg; 3 – 12 g K/kg)[8–10]. These nutrients represent the primary components found in agricultural fertilizers. It is estimated that more than 250 million tonnes of fertilizers will be needed by 2050[8,11]. However, the scarcity of nitrogen and phosphorus naturally in the soil, in particular, has been well-documented[10,12,13], prompting work evaluating options to replace their production from natural sources, which are energetically and environmentally expensive[13]. Recovering the phosphorus, nitrogen, and potassium found in digested sludge would be highly beneficial for their use as a sustainable source of nutrients for fertilizers.

Hydrothermal treatments (HTT) have the potential to sustainably recover nutrients from wet biomasses[8,10,14,15]. Under hydrothermal carbonization conditions (180 – 250 ºC and self-generated pressure), wide range of wet biomasses, including digested sewage sludge, are

chemically transformed[16]. HTT process has been shown to be advantageous when compared to other thermochemical processes such as pyrolysis[17], gasification[18] or combustion[19], which all require initial feedstock drying. More research is needed on HTT chemical reactions, the kinetics, the effect of operating conditions and use of catalysts, energy and heat recovery, combination with other technologies, and technical and economic aspects[20]. The hydrothermal process yields a carbonaceous solid, called hydrochar, with physical and energetic properties similar to those of lignite coal; a process water, which acts as a solvent and contains a large amount of organic compounds and mineral salts; and a small gaseous phase composed primarily of CO_2[21].

Hydrothermal treatment has been used to recover a variety of resources from wastes, including nutrients. Many papers found in the literature have addressed the fate of nutrients (N, P and K) during the HTT of wastes. Idowu et al. (2017)[8] studied the nutrient recovery from food waste (225 – 275 °C for 24 h) observing that most of the N remained integrated in the hydrochar (> 50%), regardless of the reaction temperature, while the highest release of P (70%) and K (96%) occurred at 225 °C and 4 h reaction time. In the case of digested sludge, a lower temperature (170 °C for 1 h) allowed 80% release of the N to the process water, yielding a P release lower than 40%[15]. Recent studies have also shown that HTT under acidic conditions can enhance P leaching to process water[5,7,10,22], since most of the P is in the form of insoluble inorganic P linked to multivalent metal elements (Fe, Ca, Al, Mg) present in the feedstock. Acid-assisted HTT of animal manure showed that the addition of inorganic acids (HCl, H_2SO_4) allowed the release of more than 95% of P and 60% of N at a lower acid concentration than using organic acids (citric acid, acetic acid) at temperatures below 200 °C[5,7,22]. Food waste has also been treated by acid-assisted HTT to solubilize nutrients in the process water, being reported that more than 95% of N, P and K were solubilized using an inorganic acid (0.5 M HCl) at 170 °C[10].

Nutrient-rich process water could have potential use as a liquid fertilizer, with prior pH conditioning being necessary[23]. However, fertilization studies should be carried out to ensure the suitability of the process water for plant growth, which can occasionally be negative due to the presence of phytotoxic substances[24]. Another possibility, once the nutrients have been concentrated in the process water, is to recover them by physicochemical processes. P and N are usually the main concern, and are commonly recovered as struvite by chemical precipitation[25]. Struvite obtained from biomass waste-derived solutions is more advantageous and effective than a liquid fertilizer because of the high content of slow-release available P, and low presence of pathogen and heavy metal[26]. Becker et al. (2019)[27] hydrothermally treated digestate at 180 ºC in the presence of 2 M HNO_3 for 2 h and precipitated a struvite-like solid by mixing PO_4-P rich hydrochar leachant, obtained by washing hydrochar with 2 M citric acid in a 1:10 w:v ratio, and NH_4-N-rich process water. Zhang et al. (2020)[25] treated swine manure digestate to HCl plus H_2O_2 assisted hydrothermal treatment at 60 – 180 ºC for 15 – 45 min, and then the process water was derived to crystallization of a struvite-like solid. Both studies used $MgCl_2$ as an ionic exchange reagent to set the molar ratio of PO_4:Mg:NH_4 to a value of 1:1.3:1 at pH 8.5-9. Sometimes the cost of these reagents is too high to ensure the economic feasibility of the process. For this reason, other cheaper reagents are often used, such as CaO, which allows the precipitation of apatite-like materials instead of struvite-like ones[28].

Since nutrient solubilization in process water could be negatively affected by the presence of inorganic elements[8], the nutrient leaching pathway through acid washing of hydrochar has been widely considered. However, little information exists on the behavior of nutrients over the reaction time. This work aims to analyze the evolution of nutrients (N, P and K) and that of other inorganic elements (Al, Ca, Fe and Mg) in process water over the reaction time, and at different temperatures (170 – 230 °C) under acid-free and acid-assisted HTT (0.1 – 0.5 M

HCl), which could be advantageous in providing new routes for the management of a digested sewage sludge containing large amounts of nutrients and inorganic elements, allowing to understand about the interaction between them throughout the reaction. The main novelty of this work lies in comparing nutrient solubilization between HCl-assisted HTT and that which combines acid-free HTT with acid washing of hydrochar, for the subsequent nutrient recovery of nutrients by chemical precipitation of struvite-like material. The hydrochar and struvite-like material characterization results are expected to provide understanding on the conditions necessary for its suitable use for industrial purposes.

Materials and methods

Digested sewage sludge

Digested sewage sludge was collected from a municipal wastewater treatment plant (located in the north of the Community of Madrid, Spain), after mixed (primary plus secondary) sewage sludge stabilization in a mesophilic anaerobic reactor, and subsequent dewatering process. The feedstock was homogenized with an industrial mixer and stored in 1.5 kg portions at -20 ºC. Before use, the feedstock was defrosted and characterized, presenting a moisture content close to 90 wt.%. The main characteristics of the digested sewage sludge were: pH 8.2 ± 0.1; total solids, 101.8 ± 0.6 g/kg; volatile solids, 60.7 ± 0.8 g/kg; and total chemical oxygen demand (TCOD), 84.2 ± 6.5 g/L. Proximate and elemental composition, and HHV of dry feedstock are shown in **Table 1**. The composition of inorganic elements is reported in the results and discussion section "Characterization of raw material and hydrochars", and the content of the main heavy metals is shown in **Table S1**.

Hydrothermal treatment

HTT of digested sewage sludge was carried out in an electrically heated 316 ZipperClave stainless steel pressure reactor, with a working volume of 4 L (Autoclave Engineers, USA). In

each experiment, the reactor was loaded with 1.5 kg of wet digested sewage sludge. The operating temperature (170, 200, and 230 ºC) was reached by heating the reactor at a rate of 3 ºC/min and was maintained for 1 h. The impact of reaction temperature and acid concentration (0.1, 0.3, and 0.5 M HCl, PanReac) on nutrient fate was studied. Response surface methodology (RSM) based on a first-degree model was used to design the experimental matrix used in this work to analyze the effect of temperature and acid addition on the fate of nutrients during the HTT. RSM is a tool that has been used to determine optimal HTT conditions for other pre-defined goals. In this work, an experimental matrix was generated based on a central composite rotatable design with a duplicate of the central point. Using Minitab 19 software, a matrix of 6 acid-assisted experiments (4 factorial point and 2 central point replicates) was generated. In addition, 3 acid-free experiments were also performed. All the tests were performed by duplicate (amounting 12 and 6 reactions for HCl-assisted and acid-free HTT, respectively).

For all experiments, reaction samples (40 mL) were withdrawn from the reactor at 5, 15, 30 and 60 min. Then, the reaction was stopped by cooling with an internal heat exchanger using tap water. The resultant slurry was separated into solid (hydrochar) and process water by filtration with a 250-µm membrane vacuum filter. The hydrochar was weighed after oven-drying of the solid fraction overnight at 105 ºC, with subsequent grinding and sieving to a particle size between 100 and 200 µm. The liquid fraction was filtered with 0.45 µm Scharlab glass filters and the obtained process water was stored at 4 ºC. The hydrochar and process water were labeled as HCT-[HCl] and PWT-[HCl], respectively, where T represents reaction temperature (ºC) and [HCl] the added HCl concentration (M), if applicable. The mass yield of hydrochar (Y_{HC}) was calculated by **Eq. 1** and defined as the weight ratio of recovered hydrochar (W_{HC}) to feedstock (W_{DSS}) on a dry basis.

$$Y_{HC}\ (\%) = (W_{HC}/W_{DSS}) \cdot 100 \quad (1)$$

Likewise, the process water yield (Y_{PW}) expresses the mass ratio of total solids in process water (W_{TSPW}) to that of digested sewage sludge (W_{DSS}) on a dry basis, and was calculated with Eq. (2):

$$Y_{PW}\ (\%) = W_{TSPW}/W_{DSS} \quad (2)$$

Nutrient leaching from plain hydrochar

A hydrochar sample (5 g) from each acid-free run was mixed with 50 mL of 0.5 M HCl using an orbital shaker (Julabo SW22, Germany) at 150 rpm for 2 h to evaluate the leaching of N, P and K[10]. The resultant leachant (L-T) and the washed hydrochar (HC-W) were separated by vacuum filtration (250 μm). The leachant was filtered with 0.45 μm Scharlab glass filter and stored at 4 ºC. Both leachant and washed hydrochar were subsequently analyzed using the abovementioned methodology for process water and hydrochar.

Nutrient recovery from process water

A magnesium salt ($MgCl_2$) was added to a 50 mL sample of process water to promote the struvite formation according to the molar ratio of Mg:PO_4 at 1.3:1[29]. The mixture was basified with 2 M NaOH up to pH 9 and kept under stirred for 20 min. The precipitated solid was separated by filtration through 0.45 μm and dried overnight at 105 ºC, being labelled as ST (in terms of struvite) followed to the HTT operating conditions (i.e., ST230, ST230-L or ST230-A, where the term L refers to acid-free HTT plus leachant from hydrochar acid washing, and the term A refers to HTT assisted by 0.5 M HCl). The struvite recovery yield (Y_{ST}) was calculated by **Eq. 3** and defined as the weight ratio of recovered struvite (W_{ST}) to total solids in process water (W_{TSPW}) in the precipitation step per process water yield (Y_{PW}) on a dry basis.

$$Y_{ST}\ (\%) = (W_{ST}/W_{TSPW}) \cdot Y_{PW} \quad (3)$$

Analytical methods

The elemental composition (C, H, N and S) of the feedstock, process water, leachant from char washing, and hydrochar samples (including HC-W) was determined by duplicate on a CHNS analyzer (LECO CHNS-932). A proximate analysis by thermogravimetry, according to ASTM methods D3173-11, D3174-11, and D3175-11, was performed by duplicate to determine the moisture, ash, volatile matter (VM) content and fixed carbon (FC) (by difference), respectively, of the feedstock and hydrochar. The higher heating value (HHV) of the dried feedstock and hydrochar was determined by **Eq. 4**, an unified correlation to calculate the HHV from C, H, N, S, O and ash content (in wt.%) according to Channiwala et al. (2002)[30].

$$HHV\ (MJ/kg) = 0.349 \cdot C + 1.178 \cdot H + 0.100 \cdot S - 0.103 \cdot O - 0.015 \cdot N - 0.021 \cdot Ash \quad (4)$$

The concentration of inorganic elements in the feedstock, hydrochar and process water was determined by inductively coupled optical emission spectroscopy (ICP-OES) on an IRIS INTREPID II XDL instrument from ThermoFisher Scientific. Solid samples were firstly digested in a microwave digester using a mixture of hydrochloric acid, nitric acid and hydrogen peroxide. The Standards Measurements and Testing (SMT) protocol, a sediment P fractionation method, harmonized and validated in the frame of the standards, measurements and testing program[31] , was applied to the HC-W to analyze P speciation (organic and inorganic P)[29]. Total P was obtained by mixing 0.2 g of hydrochar (previously calcined at 450 ºC for 3 h) with 20 mL of 3.5 M HCl under continuous stirring at room temperature for 16 h. Orthophosphate (PO_4-P) was determined by mixing 0.2 g of hydrochar with 20 mL of 1 M HCl under continuous stirring at 25 ºC for 16 h[4]. Total P and PO_4-P from supernatant and those from process water were analyzed photometrically with a Hach Lange LCK350 cuvette test. In the process water, NH_4-N content was assessed by distillation and titration according

to the standard method 4500-NH_3-B-C published by the American Public Health Association[32]. Nitrite (NO_2-N) and nitrate (NO_3-N) were quantified on a Dionex ICS-900 ion chromatograph with chemical suppression, fitted with a 4 × 250 mm Dionex IonPac AS22 column, using a 1 mL/min mobile phase of 1.4/4.5 mM $NaHCO_3$ and Na_2CO_3. The results corresponding to P and N solubilization were also expressed as grams of P or N per kg of dry feedstock.

Results and discussion

Characterization of digested sewage sludge and hydrochar

Table 1 includes the proximate and ultimate analysis of the feedstock and hydrochar, including those obtained after acid washing step. Digested sewage sludge showed a nutrient content of 28.4 g P/kg, 56.2 g N/kg, and 32.7 g K/kg on a dry basis, and a remarkable ash content (around 30 wt.%) attributed to the presence of Al (0.1 g/kg), Ca (20.1 g/kg), Mg (4.4 g/kg) and Fe (47.0 g/kg) (d.b.).

Table 1. Main characteristics of digested sewage sludge and hydrochar[a] on a dry basis.

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%)					HHV
	Yield	FC	VM	Ash	C	N	S	H	O	(MJ/kg)
Digested sludge	-	10.8 (0.3)	59.4 (0.4)	29.8 (0.2)	30.5 (0.3)	5.6 (0.1)	1.4 (0.1)	4.6 (0.1)	28.1 (0.1)	12.6
HC170	76.4	11.1 (0.2)	49.9 (0.3)	39.0 (0.1)	28.3 (0.1)	3.7 (0.1)	1.1 (0.1)	4.2 (0.1)	23.7 (0.1)	11.5
HC200	57.6	11.3 (0.1)	45.3 (0.8)	43.4 (0.1)	27.7 (0.1)	3.3 (0.1)	1.2 (0.1)	3.9 (0.1)	20.5 (0.1)	11.4
HC230	57.1	11.4 (0.1)	43.9 (0.1)	44.7 (0.1)	27.3 (0.2)	3.0 (0.1)	0.7 (0.1)	3.9 (0.1)	20.4 (0.1)	12.5
HC170-W	50.8[b]	19.2 (0.1)	70.3 (0.1)	10.5 (0.1)	42.7 (0.6)	2.6 (0.1)	0.4 (0.1)	5.1 (0.1)	38.7 (0.1)	18.1
HC200-W	39.7[b]	18.7 (0.1)	71.2 (0.1)	10.1 (0.1)	52.3 (0.2)	2.1 (0.1)	0.2 (0.1)	5.9 (0.1)	29.4 (0.1)	21.9
HC230-W	40.1[b]	19.0 (0.1)	71.3 (0.1)	9.7 (0.1)	52.4 (0.1)	2.0 (0.1)	0.2 (0.1)	5.7 (0.1)	30.0 (0.1)	21.9
HC170-0.1	53.7	12.1 (0.5)	50.2 (0.1)	37.7 (2.3)	28.4 (0.1)	3.7 (0.1)	1.0 (0.1)	4.1 (0.1)	25.1 (0.1)	11.3
HC170-0.5	25.9	16.7 (0.3)	48.3 (0.1)	35.0 (0.7)	30.9 (0.4)	3.3 (0.1)	0.9 (0.1)	4.2 (0.1)	25.7 (0.1)	12.4
HC200-0.3	31.9	12.6 (0.1)	47.4 (0.1)	40.0 (0.1)	31.2 (0.6)	3.5 (0.1)	0.8 (0.1)	4.2 (0.1)	20.3 (0.1)	13.2
HC230-0.1	51.4	12.5 (0.2)	47.4 (0.1)	40.1 (0.3)	31.5 (0.6)	3.5 (0.1)	1.0 (0.1)	4.2 (0.1)	19.7 (0.1)	13.1
HC230-0.5	31.5	17.4 (0.1)	43.9 (0.1)	38.7 (0.1)	29.1 (0.2)	2.3 (0.1)	1.2 (0.1)	3.8 (0.1)	24.9 (0.1)	12.7

Standard deviation is reported in brackets.

[a] Data obtained after 60 min reaction time.

[b] Values obtained considering mass hydrochar yield and mass lost due to acid washing.

The hydrochar yield was mainly influenced by temperature, decreasing by 19 percentage points when the temperature increased from 170 ºC to 200 ºC in acid-free HTT experiments. This fact could be explained by the effect of temperature on the degradation of organic compounds of the digested sludge and their subsequent release into the process water[12]. In the case of acid-assisted HTT, the decrease in Y_{HC} (by 22 – 26 percentage points) is accentuated by the role of strong acids to facilitate the solubilization of organic compounds[6]. In addition, acid played a remarkable role in the solubilization of inorganic matter, leading to a decrease in the hydrochar ash content, which accounts around 40 – 50% of the lost yield of hydrochar with respect to acid-free HTT. This fact is also observed in the HC-W (decreasing by 17 – 26 percentage points but being this Y_{HC} related to that reported for acid-free hydrochars plus the weight lost obtained after washing step).

The fixed carbon content in hydrochar did not vary throughout the acid-free HTT (10.8% in the feedstock to 11.1 – 11.4% in HC170, HC200, and HC230), but the volatile matter content decreased by about 16 percentage points under the same conditions. This evolution is related to the decrease of C, H and O content of hydrochar because of decarboxylation and dehydration of organic compounds (e.g. alcohols or ketones) of the feedstock [25]. Ash content increased by 10, 13 and 15 percentage points in HC170, HC200 and HC230, respectively. HTT temperature increased the solubilization of N and S in the process water, thus decreasing their content in the hydrochar by 47 and 50%, respectively, at 230 ºC. In the case of acid-assisted HTT, a similar trend was observed with temperature of the main characteristics of hydrochar, although strongly influenced by the acid concentration used. Acid washing of hydrochar from acid-free HTT promoted the increase in fixed carbon and volatile matter content and ash solubilization, obtaining materials with around 30 percentage points less ash than the original hydrochar, without remarkable differences obtained at different

temperatures. Likewise, the N and S contents of the HC-W were substantially reduced to values below 3 and 0.5%, respectively, resulting in hydrochar with the highest HHV values. In general, the effect of acid seems to depend on how it is used. Added HCl during HTT seemed to mainly influence the organic matter solubilization, because of the catalytic effect of acid on hydrolysis, dehydration and condensation reactions, but did not prevent ash agglomeration. However, HCl positively affected hydrochar ash removal during acid washing step but did not show volatile matter solubilization, because of under non-hydrothermal conditions, HCl mainly solubilizes phosphates and carbonates from the structure of the hydrochar[33].

The characteristics of the hydrochar were compared with the values established by ISO 17225-8 for the use of thermally treated and densified biomass fuels. This standard indicates that the HHV of digestate-based hydrochar should reach 18 MJ/kg and contain no more than 2% N, 0.2% S, 10% ash and 75% volatile matter. Therefore, only HC-W have the potential to be used directly as solid fuels for industrial use. In a different way, hydrochar was evaluated as crop support and soil amendment according to Regulation (EU) 2019/1009[34] on fertilizing products, which establishes a minimum dry mass content of 20 wt.%, organic carbon content of 7.5 wt.%, and specifies metal concentration limits for the application on various soils of these hydrochars, which are as follows (in mg/kg): As < 40, Cd < 1.5, Cr < 2, Cu < 200, Hg < 1, Ni < 50, and Pb < 120. Therefore, those hydrochars from acid-free HTT would be suitable as a solid organic fertilizer because they contain N, P, and K, and those from HCl-mediated HTT would be suitable as soil amendment (nutrients have been mostly extracted) (**Table S1**). However, beyond complying with the limits established by current regulations, some authors have reported that the presence of certain organic compounds in hydrochars could inhibit plant growth, highlighting the importance of conducting studies to ensure proper synergy between HTC products and plant metabolism[35,36]. Eskandari et al. (2019)[37] tested the effects

of paper mill sludge-based hydrochar on pine seedling growth and reported that the application of adequate rates of hydrochar can reduce fertilizer requirements and showed positive effects on germination, shoot biomass and stem diameter compared with control seedlings (without hydrochar) under the fertilizer levels tested."

Nutrient release in process water

Fate of phosphorus

Fig. 1 shows the evolution of P concentration (as PO_4-P) in the process water during the hydrothermal reactions. All the P in the process water was detected as PO_4^{3-}. In acid-free HTT (**Fig. 1a**), the maximum P concentration (equivalent to 13.9 g P/kg feedstock) was reached at 170 ºC after 60 min reaction time. In contrast, at 230 ºC, the P concentration slightly decreased with time, obtaining a concentration of 1.2 g P/L (equivalent to 9.7 g P/kg feedstock) at the same reaction time. An increase in temperature favors hydrothermal mechanisms and plays a key role in the fate of phosphorus, keeping it retained in the hydrochar[38,39]. During HTT, hydrolysis, decarboxylation and polymerization reactions occur, promoting the hydrolysis of organic polyphosphates into orthophosphate (PO_4^{3-}). As a result, metal cations such as Al^{3+}, Ca^{2+}, $Fe^{2+/3+}$ and Mg^{2+}show affinity for the PO_4^{3-} anion and leads to the formation of complexes[40]. Increasing temperature increases the crystallinity of these metal phosphates by reducing their solubility[41], which explains the decrease of P concentration in the process water and the consequent increase of P in hydrochar (14.1 and 18.6 g P/kg feedstock in HC170 and HC230, respectively). This effect of temperature has been previously described by Becker et al. (2019)[27], who hydrothermally treated a digested sewage sludge observing that P solubilization in the process water at 220 ºC was 14% lower than at 190 ºC. To analyze the effect of the presence of dissolved metal cations, **Fig. 2a** and **2b** show the evolution of Al^{3+}, Ca^{2+}, $Fe^{2+/3+}$ and Mg^{2+} in the process water in acid-free HTT at

170 and 230 ºC, respectively. At 170 ºC, the concentration of Al^{3+}, Ca^{2+}, $Fe^{2+/3+}$ and Mg^{2+} slightly increases during the reaction, which is equivalent to a total concentration of 8.1×10^{-3} mol/L. This trend is similar to the trend obtained with P at that temperature (about 6.3×10^{-3} mol P/L was solubilized in the process water). According to the molar ratios of phosphates that can be formed with these metallic elements (Al:P (1:1), Ca:P (3:2), Fe:P (1:1 or 3:2, depending to the Fe oxidation state), and Mg:P (3:2)), an excess of solubilized P in the process water (around 1.3×10^{-3} mol P/L) not related with solubilization of metal phosphates exists. This excess P may be associated with organic P from the hydrolysis of organic matter (e.g. proteins, amino-acids) present in feedstock. At 230 ºC, the concentration of all cations decreased with time, similar to that of P. The drop in metal cation concentration (equivalent to a total of 1.5×10^{-2} mol/L) is similar to the drop in the P concentration (equivalent to 1.8×10^{-2} mol/L), suggesting it is feasible to that the P drop is related to the formation of insoluble phosphates precipitated on the hydrochar[42]. Marin-Batista et al. (2020)[4] worked on HTT of digested sewage sludge observed a higher release of organic P to the process water as PO_4-P, related to the increasing temperature. The solubilized PO_4-P reacted with other inorganic ions to form phosphate salts. In this way, higher HTT temperature resulted in an increase in inorganic P in the hydrochar (about 80% of the total P appears in the hydrochar)[4].

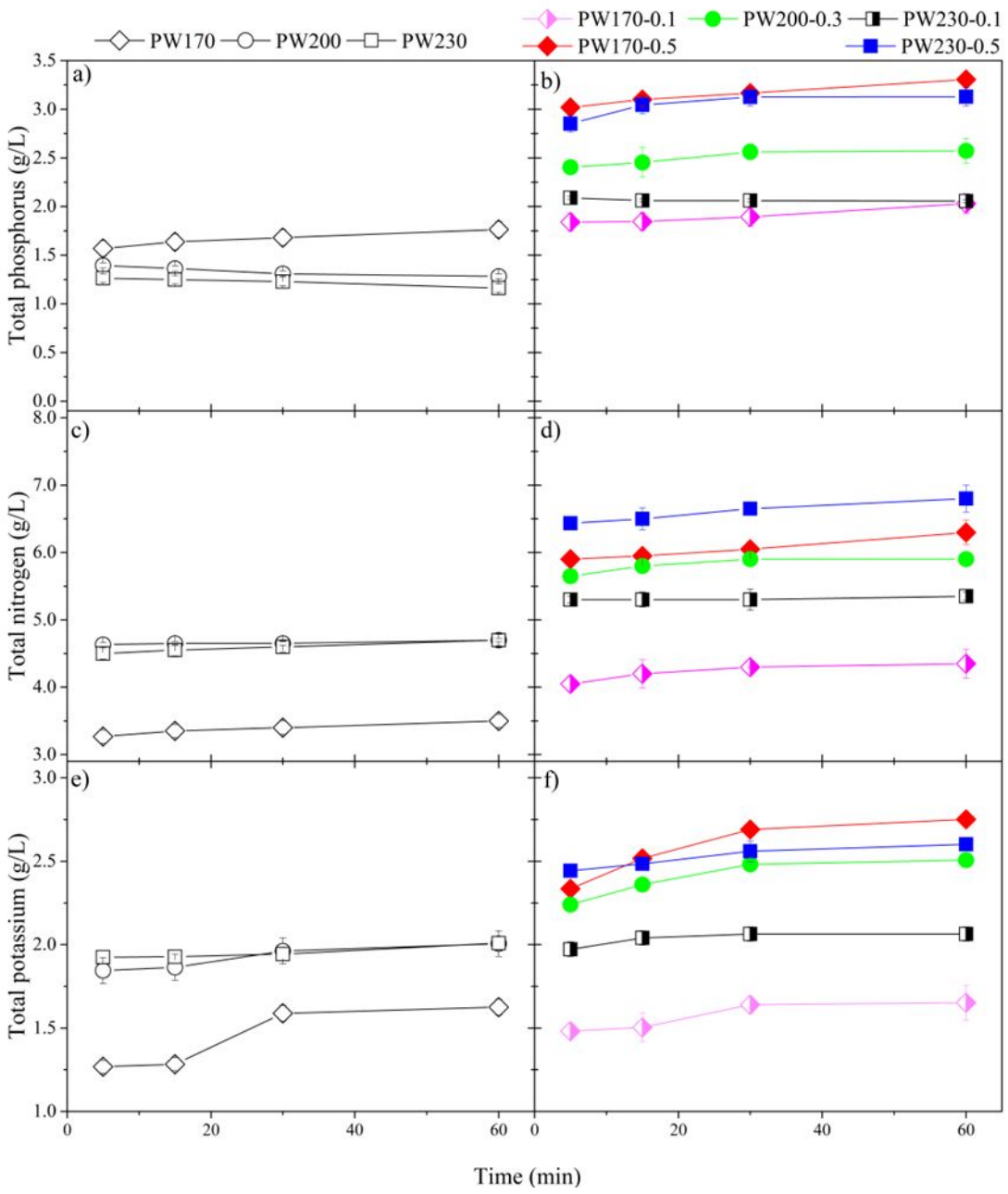


Fig. 1. Time course of phosphorous, nitrogen and potassium in process water for acid-free (a, c and e) and HCl-assisted HTT (b, d and f).

In the case of HCl-assisted HTT (**Fig. 1b**), the P concentration in PW170-0.5, PW200-0.3, and PW230-0.5 slightly increased with reaction time, while remained almost constant in PW170-0.1 and PW230-0.1. The leaching of P from the solid to the process water increased with increasing HCl concentration, showing no significant differences with temperature, and reaching maximum values of 3.0 and 3.1 g P/L (equivalent to 24.9 and 25.5 g P/kg feedstock)

after 60 min reaction time at 170 and 230 ºC, respectively, at the highest HCl concentration (0.5 M). This observation is likely due to the fact that mineral acids facilitate the transformation and dissolution of organic P (mainly proteins and amino acids) contained in the digested sewage sludge and its subsequent release to process water[5,7,43]. Attending to literature, not only the acid concentration but also the type of acid and the characteristics of the feedstock seem to have an influence on the P release. In the case of manure wastes, most of the P appears as organic P (proteins, lipids, among others), which is easily hydrolyzable at acidic pH, regardless of the type of acid used. This observation suggests that the addition of organic or inorganic acids that result in a low pH value may be enough to solubilize most of P in the process water. Qaramaleki et al (2020)[7] indicated that almost all the P contained in a fresh animal manure was leached into the process water using 0.5 M citric acid or 0.5 M HCl at 170 ºC. However, P from biomasses such as sewage sludge or digestates (from sewage sludge, animal manure or agri-food wastes) usually appear as inorganic complexes[44], requiring a strong inorganic acid to promote the solubilization of these complexes. Rodriguez Correa et al. (2017)[45] reported that citric acid-assisted HTT of digested sewage sludge evolved to new acids that did not promote P solubilization. Becker et al. (2017)[27] hydrothermally carbonized digested sewage sludge at 190 ºC, previously acidified at pH 4.0 by addition of HNO_3, and observed that P was mainly retained in the hydrochar, indicating that the pH of the process water after reaction was 4.8, which was not enough to achieve solubilization of PO_4-P. In the present study, a positive effect of HCl addition on metal solubilization was observed (**Fig. 2c** and **2d**), showing that acidic conditions (pH 3.1 and 2.8 at 170 ºC and 230 ºC, respectively) do not favor the formation of precipitable metal phosphates. This is mainly due to the effect of pH on the phosphate species present in the medium. At pH values below 4.8, phosphate anions were mainly in their monobasic form ($H_2PO_4^-$), which facilitates the formation of acid phosphates with cations such as Al^{3+}, whose

bonding is favored by the decrease amount in OH^- anions[46]. However, the formation of phosphates with divalent cations such as Ca^{2+}, $Fe^{2+/3+}$ or Mg^{2+} is not favored at very acidic pH values (< 4.8) because a decrease in the oversaturation of the medium occurs as a result of protonation of the dibasic phosphate species (HPO_4^{2-})[47]. In the present study, an increase in the concentration of divalent cations and $Fe^{2+/3+}$ was observed in the process along the 0.5 M HCl-assisted HTT (equivalent to 1.3×10^{-2} and 1.4×10^{-2} mol/L at 170 ºC and 230 ºC, respectively), together with a slight drop in Al^{3+} concentration (equivalent to 6.4×10^{-5} and 5.0×10^{-5} mol/L at the mentioned reaction temperatures), which can be related to the increase in P concentration (equivalent to 9.2×10^{-3} and 8.9×10^{-3} mol/L at 170 ºC and 230 ºC, respectively) to explain this trend.

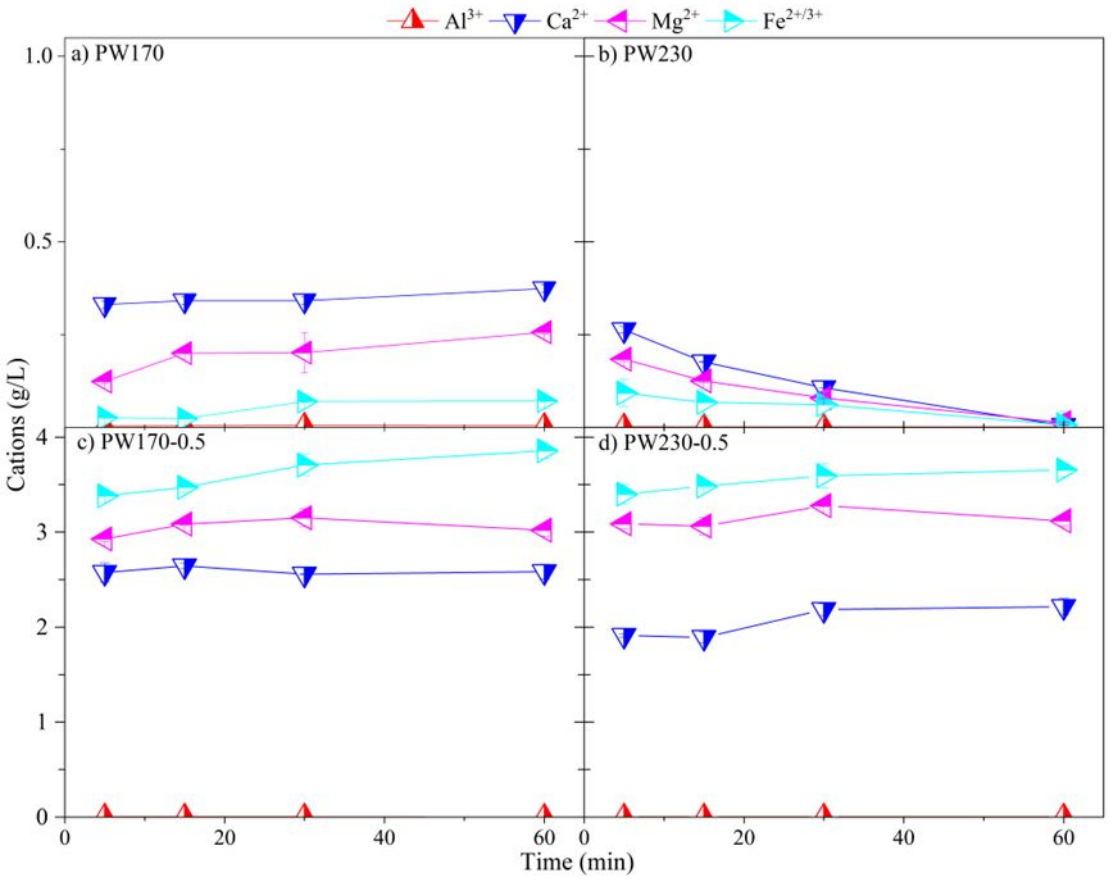


Fig. 2. Time course of main cations in the process water.

Fate of nitrogen

The fate of N during HTT of digested sewage sludge was analyzed by evaluating the evolution of N concentration in the process water corresponding to acid-free and HCl-assisted HTT (**Fig. 1c** and **1d**). In the acid-free HTT systems (**Fig. 1c**), the effect of temperature under hydrothermal conditions favored the hydrolysis of proteins, amino acids, and multi-peptides present in the feedstock, resulting in the release of different N compounds to the process water[48]. N release was remarkable above 200 ºC (with similar values at 200 and 230 ºC), obtaining a N concentration of approximately 38.5 g N/kg feedstock. This value is 39% higher than that obtained at 170 ºC (27.9 g N/kg feedstock).

In the case of HCl-assisted HTT (**Fig. 1d**), an increase in N release with reaction time was observed in most of cases except for PW230-0.1, where N concentration remained constant, promoting the addition of acid a more positive effect than the increase in temperature. With the addition of 0.1 M HCl, a 15% increase in the maximum N concentration in the process water obtained at 170 ºC and 230 ºC (equivalent to 36.5 and 44.5 g N/kg feedstock, respectively) was found compared to that obtained in acid-free reactions. Similarly, an increase in HCl concentration appeared to favor N solubilization, with a maximum N concentration of 6.8 g/L (55.4 g N/kg feedstock) at 230 ºC and 0.5 M HCl. These results are in accordance with those reported by others. Dai et al. (2017)[22] concluded that an increase in HCl concentration (0.25 – 2%) in the hydrothermal treatment of animal manure favored N solubilization (from 1.6 to 2.6 g N/L). Also, Zhang et al. (2019)[49] reported that increasing the temperature from 160 to 260 ºC in acidic conditions (2% HCl) was essential for maximizing the release of N (up to 85%) from corn stover to process water, while Qaramaleki et al. (2020)[7] observed that the best N leaching from animal manure into the process water was obtained at temperatures above 200 ºC using 0.5 M HCl (approximately 60% N from the feedstock was solubilized in the process water).

An analysis of nitrogen species in the process water (**Fig. 3**) revealed concentrations of organic N, NH_4-N, NO_3-N and NO_2-N equivalent to the total nitrogen in the feedstock. Increasing the temperature from 170 to 230 ºC along the acid-free reactions resulted in a 73 and 95% increase in organic N and NO_3-N, respectively, in the process water. Some studies suggest that an increase of temperature enhances N solubilization to the process water, while organic and inorganic nitrogen-bearing species undergo hydrolysis to generate NH_4-N and NO_3-N[50,51]. However, the increase in NH_4-N is less evident because the hydrolysis of organic N (mainly as proteins and amino-acids) and its subsequent deamination to form NH_4-N is a slow step at temperatures below 200 ºC[52,53].

In HCl-assisted HTT, a significant effect of acid concentration on the solubilization of organic N to process water was observed. Thus, in HTT assisted with 0.1 M HCl at 170 and 230 °C, the solubilized organic N was 220% and 43% higher than in acid-free HTT, respectively, while in HTT assisted with 0.5 M HCl, the organic N solubilization was even higher (430% at 170 ºC and 230% at 230 °C) than plain HTT. Furthermore, increasing the reaction temperature increased the transformation of organic N to NH_4-N (with a maximum value of 26.1 g NH_4-N/kg feedstock at 230 ºC and 0.5 M HCl) was observed. The NO_3-N concentration was largest at higher temperatures, but decreased with increasing HCl concentration because deamination to form NH_4-N is promoted under acidic conditions[5], while the NO_2-N concentration was lower than 0.1% in all cases.

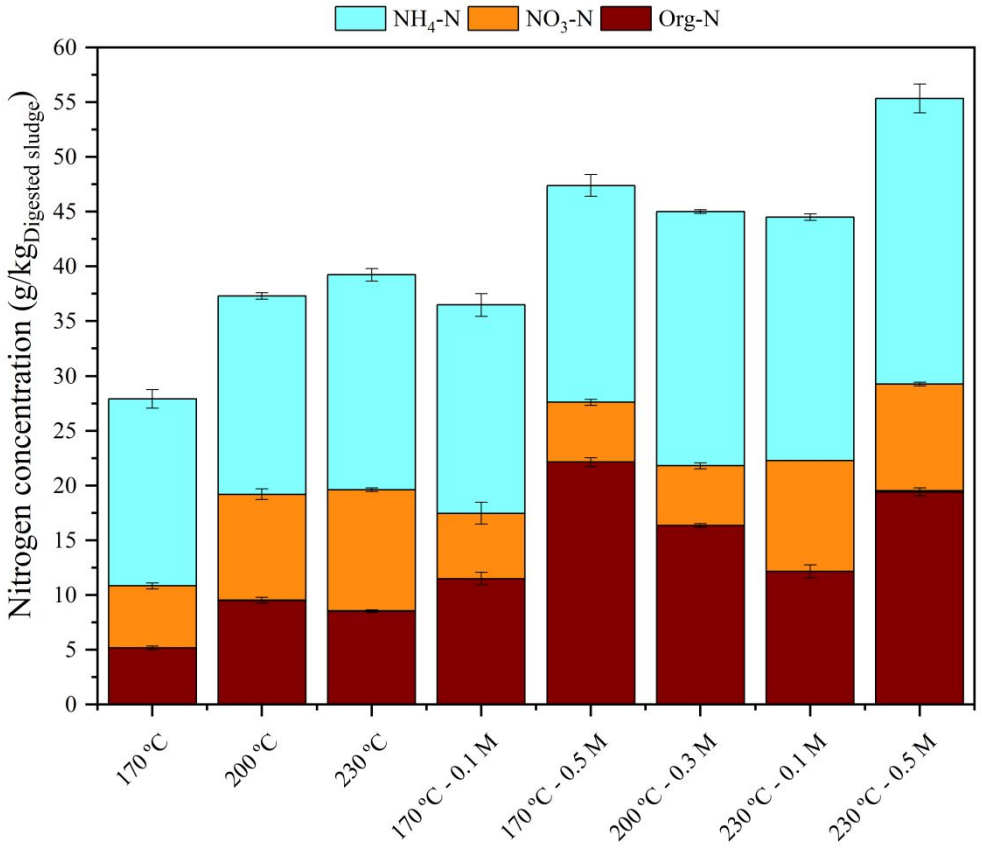


Fig. 3. Distribution of nitrogen species in the HTT process water after 60 min reaction time.

Fate of potassium

The leaching of K in the process water in acid-free HTT (**Fig. 1e**) increased with temperature and reaction time, increasing the K concentration by 25% at 60 min of reaction at 200 – 230 ºC with respect to 170 ºC. The addition of 0.1 M HCl in HTT (**Fig. 1f**) did not influence the K release compared to the results obtained in acid-free HTT. This could be related to the easy solubilization of K salts before medium saturation. Higher K solubilization was observed with the addition of 0.5 M of HCl, regardless of reaction temperature, because of an increase in K solubilization with decreasing pH. In general, total K solubilization is achieved after HTT of different biomass wastes (animal manure, microalgae, food waste, agricultural-digestate)[8,15,54], but in the case of digested sewage sludge, the high K concentration in the feedstock (32.7 g K/kg), reduced its total release because the equilibrium between all

solubilized elements was reached. This fact was also observed by Ekpo et al. (2015)[15] who reported a partial K solubilization (60% of the K of digested sewage sludge) due to the saturation of the process water with the large amount of elements in the feedstock and the retention of some salts within the solid product formed during HTT. Alhnidi et al. (2022)[55] hydrothermally treated mimic anaerobically digestate at 180 – 260 ºC for 3 h and observed that most of K was solubilized in the process water but around 10 – 16 % remained sorbed in the hydrochar structure.

Strategies to promote nutrient release from digested sewage sludge

Fig. 4 shows a distribution of N_0, P_0 and K_0 (56.2 g/kg, 28.4 g/kg, and 32,7 g/kg dry feedstock, respectively) along the acid-free HTT (process water plus leachant and HC-W) and HCl-assisted HTT (process water plus hydrochar) (at 60 min reaction time). The fate of P for all acid-free HTT processes appears to have been controlled by temperature. P was predominantly retained in the hydrochar at the highest temperature (which corresponds to 18.6 g P/kg dry feedstock, equivalent to 65.5%, at 230 ºC), likely due to the formation of phosphate-metallic complexes that inhibited P solubilization. Diversely, an increase in reaction temperature favored the release of N from the solids to the process water (corresponding to the release of 39.2 g N/kg dry feedstock, equivalent to 69.8%, at 230 ºC), resulting from the hydrolysis and deamination of organic N. Similarly, K release to the process water was also controlled by temperature (corresponding to the release of 16.8 g/kg dry feedstock, equivalent to 51.4%, at 230 ºC). The hydrochar washing with 0.5 M HCl is more effective for nutrient release, especially P, from HC230, and promoted additional release of P (corresponding to 13.8 g P/kg dry feedstock), N (equivalent to 7.0 g N/kg dry feedstock) and K (equal to 8.8 g K/kg dry feedstock) to the leachant. Considering the nutrient release both in the leachant and in the amount of nutrients solubilized directly in the process water, the best operating condition was found at 230 ºC, achieving a release of 83%, 82% and 78%

of P (as PO_4-P), N and K, respectively, from the raw digested sewage sludge thermally treated.

In the case of HCl-assisted HTT, temperature showed a significant effect on nutrient release to the process water regardless of HCl concentration. The highest HCl concentration (0.5 M) favored N, P and K leaching, being this variable more significant in the case of N. Comparing these results with those of acid-free HTT combined with hydrochar washing, the direct nutrient release to the process water (using 0.5 M HCl) achieved the highest solubilization of N and P (20 and 10% higher, respectively) than those obtained with combined route. In the case of K, the best option to maximize its solubilization may be combining acid-free HTT and acid washing of the hydrochar. However, considering the importance of nutrients for fertilization purposes, P and N (as NH_4-N) recovery is more attractive. For this reason, HCl-assisted HTT is considered a better option than acid-free HTT combined with hydrochar washing for releasing nutrients directly in liquid phase and, therefore, amenable to in-depth analysis.

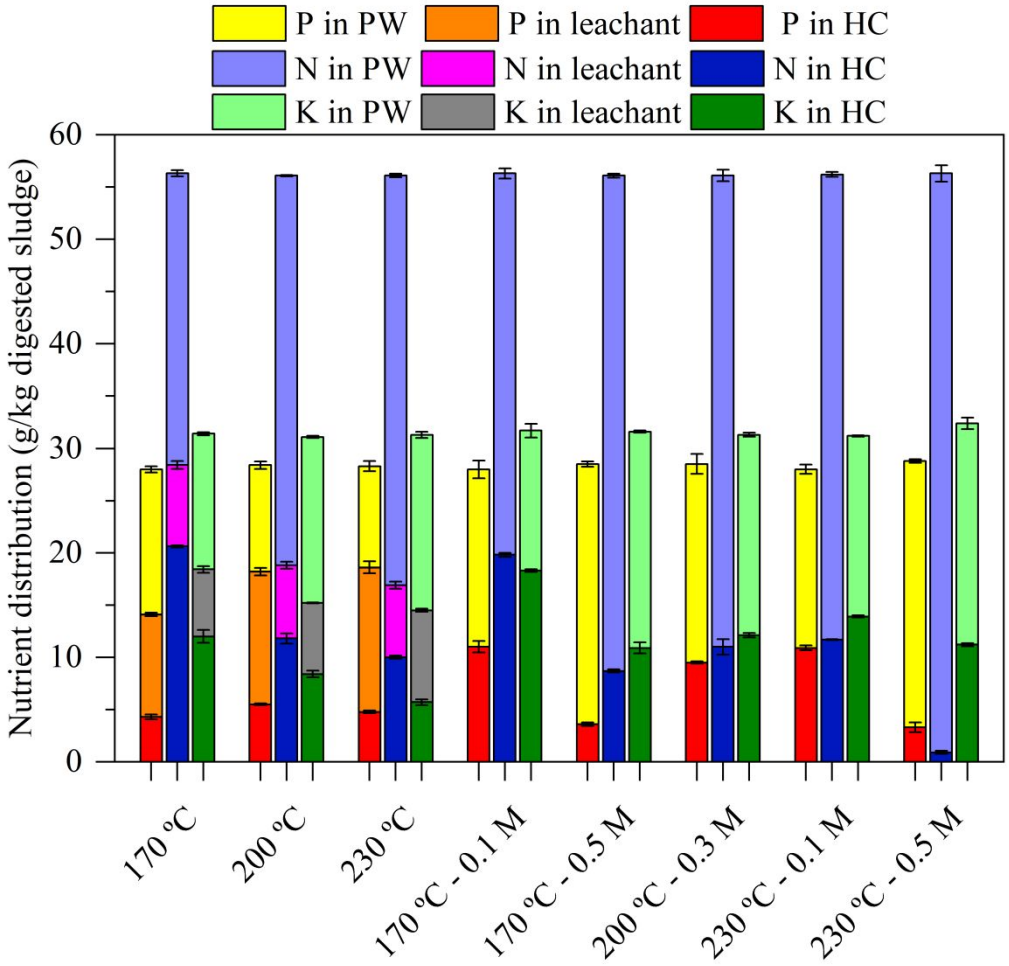


Fig. 4. Distribution of nutrients (P, N and K) in acid-free HTT (washed hydrochar, leachant and process water) and HCl-assisted HTT (hydrochar and process water) of digested sewage sludge.

A three-dimensional response surface study was conducted to evaluate the importance of operating conditions (temperature and HCl concentration) in maximizing nutrient release (**Fig. 5**). The third variable that could affect nutrient release is the reaction time, but as previously shown, the acidic medium allows obtaining the maximum nutrient concentration at 60 min reaction time, thus this was the time selected to carry out this analysis. **Table 2** contains the equations of the factorial design that determine the solubilization of P (**Eq. 5**), N (**Eq. 6**), NH_4-N (**Eq. 7**), and K (**Eq. 8**), as a function of temperature (ºC) and HCl concentration (M). Fitting of experimental data showed statistical significance ($p < 0.05$ and $R^2 > 99.5\%$).

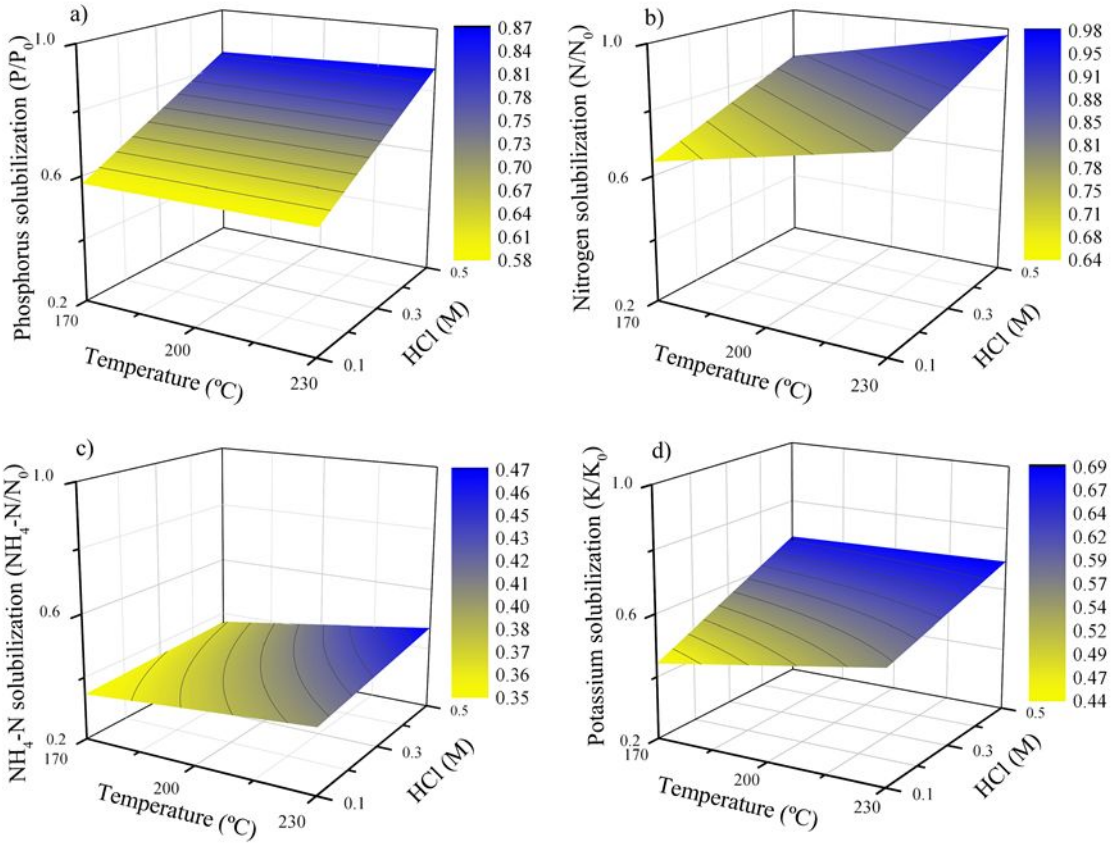


Fig. 5. Response surface of phosphorus (a), nitrogen (b) NH_4-N (c), and potassium (d) solubilization in process water of HCl-assisted HTT after 60 min reaction time.

Table 2. Descripting equations of normalized P, N, NH_4-N, and K solubilization in HCl-assisted HTT as a function of temperature (T, ºC) and HCl concentration (C, M) at 60 min reaction time.

Equation	R^2 (%)	Eq.
$P/Po = 0.5134 - 0.000035 \cdot T + 0.56 \cdot C + 0.00076 \cdot T \cdot C$	99.73	(5)
$N/No = 0.002392 \cdot T + 0.4981 \cdot C - 0.000067 \cdot T \cdot C + 0.1888$	99.98	(6)
$NH_4 - N/No = 0.000749 \cdot T - 0.2715 \cdot C + 0.001929 \cdot T \cdot C + 0.199$	99.56	(7)
$K/Ko = 0.002399 \cdot T + 1.305 \cdot C - 0.004254 \cdot T \cdot C - 0.02268$	99.61	(8)

As can be seen in **Fig. 5**, the surfaces are plain, and it do not present any curvature because the factorial design generates a first-order equation since only two factors (temperature and HCl concentration) were considered. In **Fig. 5b**, the coupled effect between temperature and HCl addition mainly influenced N release, obtaining a maximum value of 98% at the most

severe HTT conditions (230 ºC and 0.5 M HCl). Maximum N release as NH_4-N (47%) was achieved under these conditions (**Fig. 5c**). Increasing the HCl concentration to 0.5 M was also crucial in enhancing leaching of P as PO_4-P (≈ 87%) and K (≈ 69%) to the process water (**Fig. 5a** and **5d**, respectively), with the reaction temperature used not being decisive. From these premises, HCl-assisted HTT of digested sewage sludge appears to be a promising alternative to release N (as NH_4-N), P (as PO_4-P) and K in the process water in a single step. This alternative treatment allows the recovery of nutrients with a higher yield to those obtained by Ekpo et al. (2015)[15] by acid-free HTT of digested sewage sludge at 170 and 250 ºC for 60 min, and comparable, in the case of P, to those reported by Zhao et al. (2018)[56], who valorized a digested farm sludge by HTT at 190 ºC and then washing of the hydrochar with 1.5 M H_2SO_4.

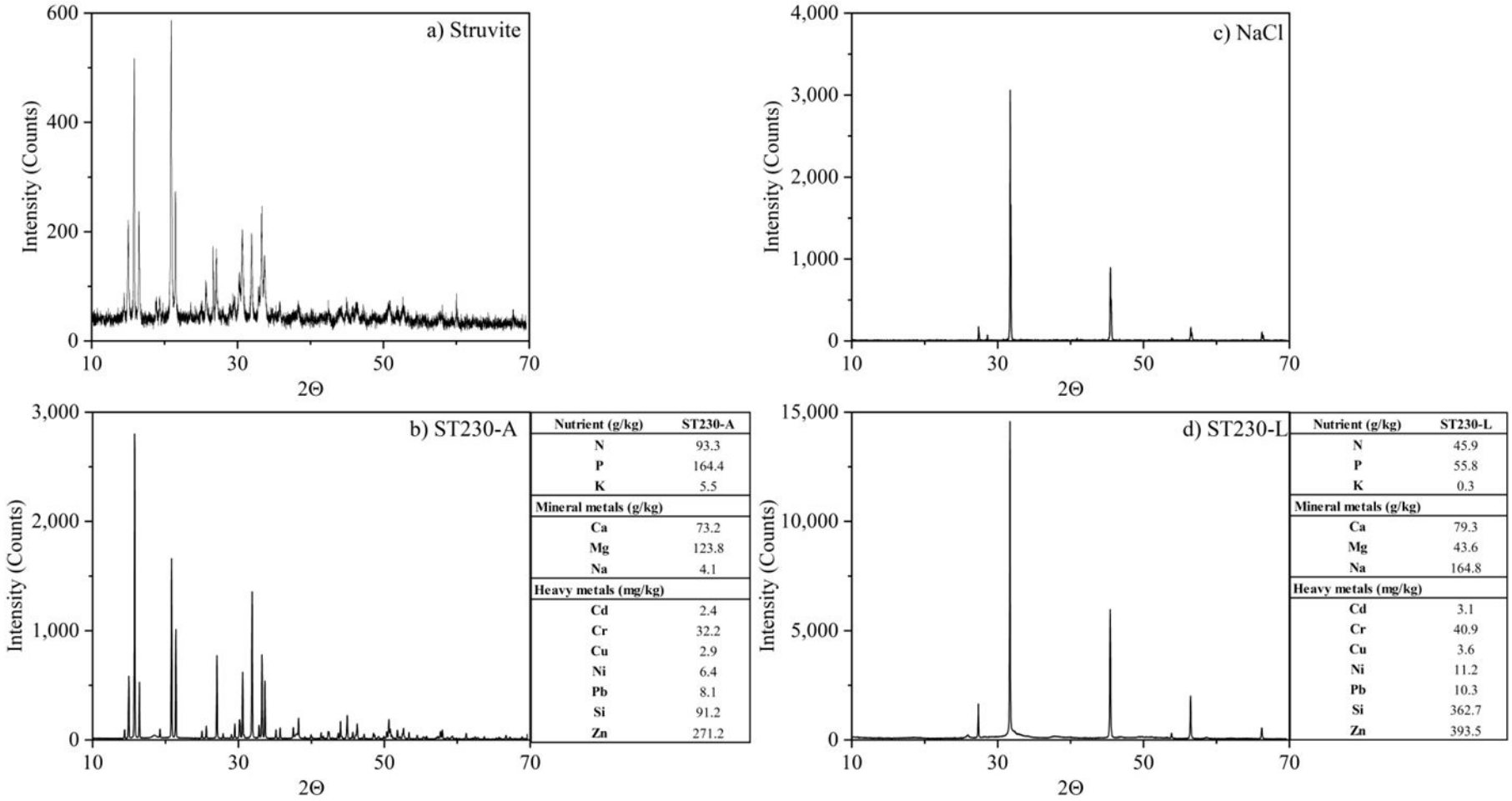
The nutrient-enriched liquid phases (PW230-0.5 or combined PW230 and L-230) could be pH-adjusted for direct use as liquid fertilizer[23]. However, this liquid stream would be susceptible of containing high amount in organic compounds whose effect on plant growth should be evaluated by fertilization analysis. Celleti et al. (2021)[24] studied the phytotoxic effect of process water derived from HTT of swine manure used for hydroponic growth of maize. They observed that process water rich in potentially phytotoxic substances (mainly Na) and with a very alkaline pH reduced nutrient bioavailability and thus led to growth arrest. However, they indicated that diluted process water with low levels of phytotoxins and adequate content of essential nutrients could be adequate for appropriate germination and growth of plants. Alternatively, nutrient recovery via chemical precipitation of struvite could appear as an interesting option. This might be a crucial point to make the products profitable in future for agricultural applications[12]. This method allows obtaining a mineral rich in P and NH4-N, of growing interest due to the increasing scarcity of P. The recovery of K as KNO_3 could be possible by adding tartaric acid at controlled pH[57] or as potassium struvite

($MgKPO_4$) from a liquid source with higher K content than NH_4-N[58]. In this way, the process water obtained under optimum conditions for nutrient solubilization (PW230-0.5) and that liquid phase corresponding to mixed PW230 plus L-230, were subjected to struvite precipitation to compare their characteristics. PW230-0.5 stands out for its PO_4-P (3.1 g/L), NH_4-N (3.2 g/L), and Mg (0.5 g/L) concentration, essentials for struvite precipitation. However, both PW230 (containing 1.0 g PO_4-P/L, and 2.3 g NH_4-N/L) and L-230 (containing 2.4 g PO_4-P/L, and 0.4 g NH_4-N/L) require mixing to achieve adequate nutrient concentration for struvite precipitation. **Fig. 6** shows the mineral and heavy metals content and diffraction patterns of solid precipitates (ST230-A and ST230-L), respectively. The structure of ST230-A presented clear crystalline peaks (**Fig. 6b**) similar to pure struvite (**Fig. 6a**) and remarkable N (93.3 g/kg), PO_4-P (164.4 g/kg), and Mg (123.8 g/kg) contents. On the contrary, ST230-L (**Fig. 6d**) did not show struvite peaks, but corresponded to NaCl (**Fig. 6c**), due to the neutralization of hydrochloric acid from the leachant during the precipitation step, and presented lower N (45.9 g/kg), PO_4-P (55.8 g/kg), and Mg (43.6 g/kg) contents than ST230-A. In addition, a higher Si concentration was observed in ST230-L (362.7 g Si/kg) with respect to ST230-A (91.2 g Si/kg). This fact is correlated with the ash content of the hydrochars shown in **Table 1,** showing HC230-0.5 a higher ash content than HC230-W. Then, a lower inorganic concentration was released to process water during HCl-assisted HTT in comparison to those inorganics transferred to leachant after hydrochar washing, which may precipitate together with struvite. The higher retention of inorganic elements in the hydrochar during HCl-assisted HTT, which did not precipitate together with struvite, contributed to improve final product specifications. In this way, only ST230-A considered as a potential struvite. The ST230-A recovery yield was 223.2 g struvite per kg dry digested sewage sludge, and the N/P/K content of the struvite was 9.3/37.5/0.7, following the same considerations as for an industrial fertilizer (the N/P/K of the commercial struvite was 10.1/51.5/0). In addition,

the struvite contained 1.9% total organic C and heavy metals content was negligible. According to metal composition, some impurities including Cl^- containing compounds (such as NaCl or $MgCl_2$) could be present, whose excess is considered harmful to agriculture because of its toxic effects and its antagonistic interaction with NO_3^-, which impairs NO_3^- nutrition and reduces crop yield[59]. However, the use of struvite-like precipitate as a fertilizer is potentially suitable according to Regulation (EU) 2019/1009 on fertilizing products[34].

The integration of HTT with nutrient recovery for digested sewage sludge management can be a potential source of value-added products. Following the methodology reported by Mannarino et al. (2022)[60] for the estimation of the energy input of a similar process using food waste as feedstock, the cost of the process at the optimum operating conditions to obtain the highest nutrient solubilization (230 ºC and 1h, considering the HCl requirements negligible) is estimated to be approximately 13.7 € per tonne of treated digested sewage sludge. This economic approximation takes into account the electricity input of the HTT reactor (3,800 to 5,200 kWh per tonne of dry raw material), together with additional units such as slurry separation, drying and pelletizing of the hydrochar. Furthermore, it considers both the electricity price for non-household customers[61] and the output associated to the energy content of the hydrochar[21]. Moreover, the energy valorization of process water by anaerobic digestion for obtaining biogas[62], or by dark fermentation[63] or aqueous phase reforming[64] to produce hydrogen add outputs to the process. According to Medina-Martos et al. (2020)[65] energy input for HTT of sewage sludge at 210 ºC for 1 h coupled to an anaerobic digestion stage resulted in an energy cost around 10 € per tonne of treated sewage sludge, which is in accordance with the cost estimation of our process. This value is significantly lower than other alternatives such as anaerobic fermentation plus P releasing from dewatered anaerobic sludge by sequential extraction with H_2SO_4 acidified water and sulphur-reducing bacteria, which is around 110 € per treated tonne of sludge[66], and even the HCl plus H_2O_2-

assisted hydrothermal carbonization of digestate (around 50 € per tonne of digestate) with subsequent struvite crystallization from the process water[25]. Regarding struvite precipitation, the cost of the required reagents ($MgCl_2$ and NaOH) results in about 1.6 € per tonne of digested sewage sludge[25,27,67], which is in the cost range of chemicals for struvite precipitation using biomass waste (1 – 2 € per tonne of biomass waste[25,68–70]). This prediction of the cost could be improved in a continuous HTT setup, where energy recovery can be optimized by integrating the streams involved in the process, which significantly saves the required energy inputs[65,71].



Nutrient (g/kg)	ST230-A
N	93.3
P	164.4
K	5.5
Mineral metals (g/kg)	
Ca	73.2
Mg	123.8
Na	4.1
Heavy metals (mg/kg)	
Cd	2.4
Cr	32.2
Cu	2.9
Ni	6.4
Pb	8.1
Si	91.2
Zn	271.2

Nutrient (g/kg)	ST230-L
N	45.9
P	55.8
K	0.3
Mineral metals (g/kg)	
Ca	79.3
Mg	43.6
Na	164.8
Heavy metals (mg/kg)	
Cd	3.1
Cr	40.9
Cu	3.6
Ni	11.2
Pb	10.3
Si	362.7
Zn	393.5

572

573 **Fig. 6**. X-ray diffractogram and nutrient content of a) commercial struvite, b) ST230-A, c) commercial NaCl, and d) ST230-L.

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Conclusions

Two nutrient release strategies based on HTT of digested sewage sludge were studied in this work. The HCl-assisted HTT showed the best performance on nutrient solubilization directly into process water, achieving under optimum conditions (230 ºC, 60 min, and 0.5 M HCl), up to 87% of P (as PO_4-P), 98% of N (as organic N and 47% of NH_4-N) and 69% of K release. The combined strategy based on acid-free HTT (nutrient solubilization into process water) and hydrochar acid washing (nutrient concentrated in a leachant) showed lower nutrient release yield (80 – 82% P, 60 – 82% N, and 59 – 78% K). Only using the best HCl-assisted HTT conditions yielded a solid with struvite-like characteristics through chemical precipitation from the process water.

Supporting information

Heavy metal content in digested sewage sludge and hydrochar according to Regulation (EU) 2019/1009.

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Data availability

Data will be made available on request

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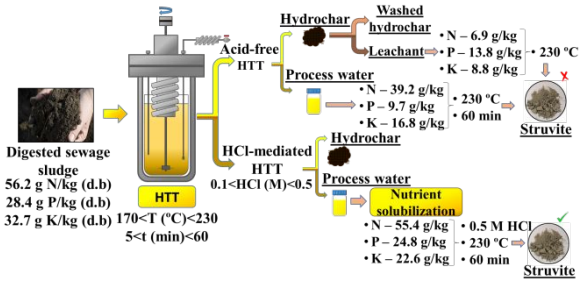

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Synopsis: Scheme of the different hydrothermal treatment routes of digested sewage sludge for nutrient solubilization and their subsequent recovery as struvite.