Hydrothermal carbonization of wet biomass from nitrogen and phosphorus approach: A review

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Abstract

With increasing energy and resource consumption due to population growth, the biorefinery concept is becoming popular. This concept aims to harness all the properties of biomass by producing energy and recovering useful chemical products. Nutrients such as nitrogen and phosphorus play a key role in the world’s food production because they are the main elements used in fertilizer production. Hydrothermal carbonization (HTC) has been presented as a suitable option for energy recovery that can also be used as a pre-treatment for enhanced nutrient recovery. During the HTC process, part of the nitrogen and phosphorus are solubilized into the process water and the other part remains within the hydrochar. Hydrochars are mainly used as soil amendments due to their high content of phosphorus and nitrogen, but in this process, water still contains a considerable concentration of these compounds making it a potential source for their recovery. Therefore, HTC may boost the nutrient recovery strategy by extraction (process water) or densification (hydrochar) from biomass if it is coupled with another nutrient recovery process. This review presents an overview of the phosphorus and nitrogen fate during the HTC process from a perspective of nutrient recovery, presenting existing technologies and future trends.

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1. Introduction

1.1. Importance of phosphorus and nitrogen recovery

Nutrients such as phosphorus (P) and nitrogen (N) are vital for modern agriculture and fertilizer production and their utilization is closely related to population growth. At the same time, these nutrients represent a significant threat to the environment due to the volume that is disposed of on land and in water. Most of the nutrients disposed of in nature originate from manure production of cattle, pigs, and poultry, as well as the wastewater and organic residuals produced from human activities [1]. The traditional disposal method for manure is application in farmlands, however, the unequal portion of P and N in this waste exceed the nutrient demands of the crops and pasture land resulting in nutrient saturation in the soils [2,3]. Rainwater washes these excess nutrients into soils, taking them into rivers, lakes, aquifers, and oceans, causing algae growth in the water bodies. Algae consume the oxygen in the water bodies affecting the surrounding environment by killing the flora and fauna [4]. Furthermore, P is considered a non-renewable resource because its extraction depends on the mining of phosphate rock. The importance of P and N application, especially in agriculture, gives an extra added value to wastes with high P and N content and makes them a target for nutrient recovery strategies [5]. Some researchers have proposed different potential scenarios for the production of P and N rich products from different wastes, especially from manure: 1) production of elemental P or N from the solid fraction for the industrial market, such as the food and detergent industries, 2) production of a P–N rich fertilizer from the solid fraction (P and N salts) and 3) production of struvite from the liquid fraction for the agricultural market [5]. Therefore, the scientific community is under enormous pressure to develop technologies that can reutilize the nutrients, especially P, from the waste stream [6]. These will help to mitigate the environmental problems and alleviate the dependence on exhaustible resources like P.

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1.2. Phosphorus and nitrogen recovery strategies

N and P removal and recovery strategies are mainly focused on sewage sludge, manure, and digestates due to their high nutrient concentration and the high quantities of waste produced [4,7,8]. However, there are other high concentration P and N sources such as food waste, algae, or other industrial waste that should be considered within these strategies. P and N removal and recovery strategies are shown in Table 1. The most common strategies for P and N removal are biological nitrification and de-nitrification, and chemical precipitation. Nevertheless, in these processes, N and P cannot be recovered [8]. On the other hand, there are existing technologies for P and N recovery, such as struvite precipitation, air stripping, or acid washing, among others [8].

| Method | Focus | Description | Recovery -Removal | Reference |
|--------|-------|-------------|--------------------|-----------|
| Air stripping process | Nitrogen | The physicochemical process is carried out at high pH and is applied in a liquid mixture. The high pH converts ammonium ions into ammonia in solution and the air injected into the liquid mixture is used to volatilize the ammonia. Then, the ammonia is absorbed by a strongly acidic solution (i.e. H₂SO₄) to form mineral fertilizers. | 70–92% | Liu et al. [6] and Sengupta et al. [8] |
| Anaerobic ammonium oxidation (anammox) | Nitrogen | A biological process that converts the NH₄ and NO₂ to N₂ gas under anaerobic conditions. However, it is important to ensure an appropriate nitrate concentration within the liquid mixture to be able to carry out the anammox process. | 70–99% | Ge et al. [8], Zekker, et al. [19] and Li et al. [20] |
| Struvite precipitation | Phosphorus and Nitrogen | The process consists of precipitation of magnesium ammonium phosphate (MAP or Struvite) by balancing the magnesium, phosphate, and ammonium ions (ratio 1:1:1) at pH around 9. The precipitate (struvite) can be recovered by centrifugation or filtration. | 99–100% | Le Corre et al. [9] and Yu et al. [10] |
| Microalgae cultivation | Phosphorus and Nitrogen | A liquid with high P and N concentrations is removed by growing algae. Algae harvest is mainly through coagulation/flocculation, centrifugation, flotation, etc. Algae can be used for biofuel production. | 62–91% of Total nitrogen | Cai et al. [14] and Mulbry et al. [15] |
| Acid wash | Phosphorus | Application of acids (i.e. HCl or H₂SO₄) to a dry biomass (ash, biochar, or hydrochar) in order to solubilize the P as soluble phosphate. The P is recovered from the solution through an isolation process. | 48–83% of Total nitrogen | Heilmann et al. [4] |
| Washing method with extract | Phosphorus | Consists of extracting P from the solid sample with an extraction solution (i.e. CaCl₂, Olsen solution, LiCl, etc.) considering as variables the pH, solid to solution ratio, and extraction time. The solution that should be used for extraction depends on the species of P. | Not reported as | Wuenschers et al. [21] |
| Co-combustion | Phosphorus | Thermochemical conversion of the biomass into ashes at high temperatures (850–1250 °C). Most of the P-organic from the biomass is retained in ashes in the form of P-metal cations. The P is recovered through mineral or acid extraction. | Up to 100% | Cieslik and Koniczczka [7] |
| HTC | Phosphorus and Nitrogen | Solubilization of N and P from biomass through a high temperature (180–250 °C) and pressure (5–45 bar) process in the presence of water. The solid product also retains some of the P and N making it suitable as a potential fertilizer. | Up to 49% of P and up to 41% of N solubilization | Aragón-Briceno et al. [22], Heilmann, et al. [4] and Ekpo et al. [2] |
| Acid-supported HTC | Phosphorus and Nitrogen | Solubilization of N and P through HTC in acidic conditions. The acidic conditions promote the solubilization of the N and P into the process water and N solubilization, during the HTC process. The solid product also retains some of the P and N respectively but in a lower concentration. | Up to 100% and 63.4% of P and nitrogen | Dai et al. [1] |
| Alkali-supported HTC | Phosphorus and Nitrogen | Solubilization of N and P through HTC in alkaline conditions. The alkaline conditions promote the solubilization of the N and P into the process water during the HTC process. | Up to 16% of P and up to 48% of N solubilization | Ekpo et al. [2] |
| Electro dialytic process (ED) | Phosphorus and Nitrogen | This process was developed by the Technical University of Denmark in 1992 and is patented in 1995 (PCT/DE95/00290). ED is applied to the ashes (dried solids) in stationary cells for P recovery. | 32–84% | Cieslik and Koniczczka [7] and Guedes et al. [23] |
| Enhanced biological phosphorus removal (EBPR) | Phosphorus | Removal of P by microbes after producing a solid stream (sludge) that is suitable for P recovery. The solid product can contain from 5 to 7% of P. | 90–99% | Yuan et al. [24] |
| Ion exchange and adsorption-based methods | Nitrogen | This process is based on the recovery of the cation NH₄ from liquids by using an ion exchanger/adsorbent such as zeolite. | 65–80% | Sengupta et al. [8] |
| Bioelectrical systems | Nitrogen | This process aims at ammonium recovery in liquids. It uses low-grade substrates (organic matter) as an electron source in order to produce electricity and recover ammonia. The process is carried out at high pH conditions that allow ammonia recovery. | 79–96% | Sengupta et al. [8] |
| Membrane-based recovery | Nitrogen and Phosphorus | This process uses specialized membranes to recover specific chemical compounds. It has been used mainly for ammonia and dissolved phosphates recovery. The most predominant technologies are microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. | 99–100% | Sengupta et al. [8] |
Energy production from biomass, although it has limitations, can be considered one of the main alternative energy sources to complement or substitute for fossil fuels along with wind, solar, and wave power. There is a wide range of processes used nowadays for biomass transformation, e.g. thermochemical, biological, and mechanical [25]. In the past years, thermochemical conversion of biomass was one of the most studied and developed technologies such as air stripping, anammox, struvite precipitation, microalgae cultivation, ion exchange and adsorption methods, and bioelectrical systems are based on the transformation of N into ammonia form for the recovery process [8,10,16,17]. For instance, the ion exchange adsorption uses an ion exchanger/adsorbent (i.e. zeolite) to recover the cation NH₄⁺ as a salt precipitate [8]. Ammonia stripping is carried out at a high pH that converts the ammonium ions into ammonia (solubilization) followed by air injection into the liquid mixture to volatize the ammonia for recovery through an acidic solution [8,16]. Bioelectrical systems use low-grade substrates (organic matter) as an electron source to produce electricity and recover ammonia [8]. Lastly, anaerobic ammonium oxidation (anammox) is a biological process that converts NH₄ and NO₂⁻ to N₂ gas under anaerobic conditions [18].

N and P strategies have been developed and adapted depending on the recovery source, resources, and environmental conditions. The recovery source (biomass) is one of the main factors to be considered when selecting a recovery strategy due to the potential hazardous organic and inorganic pollutants (heavy metals, hydrocarbons, pesticides, etc.) or/and pathogens that might be contained in it or derived from it that could result in damage to the environment [7]. For this reason, the current strategies should consider the integration of pollutant removal and hygienization processes.

1.3. Hydrothermal carbonization

Energy production from biomass, although it has limitations, can be considered one of the main alternative energy sources to complement or substitute for fossil fuels along with wind, solar, and wave power. There is a wide range of processes used nowadays for biomass transformation, e.g. thermochemical, biological, and mechanical [25]. In the past years, thermochemical conversion of biomass was one of the most studied and developed fields worldwide and includes different processes such as combustion, pyrolysis, torrefaction, and hydrothermal treatments (carbonization, gasification, liquefaction) [25,26].

Table 2 shows the different thermal treatments for biomass conversion. Energy production from biomass via combustion processes can present some drawbacks that could affect the system's operation. These include increasing the cost of transportation, storage, and process efficiency [27]. These disadvantages are related to the high moisture content, fast biological degradation, low bulk density, low energy properties, heterogeneous chemical properties, and the milling of raw biomass, as well as fouling and corrosion problems caused by inorganics present in biomass [27]. On the other hand, hydrothermal treatments (HT) present an advantage over the other thermochemical treatments (combustion) as they are carried out in the presence of water, avoiding the drying pre-treatment step and reducing the energy requirements of the system [22,26]. The main target of HT is energy densification through the concentration of carbon and oxygen removal in the solid fraction. HT by-products and their characteristics will depend on the severity of the process (pressure, temperature, and reaction time), resulting in either a solid hydrochar, a bio-crude, or a syngas. However, one of the main disadvantages is the high setup requirements (energy and installation costs) for the equipment [28].

HTC is also known as wet torrefaction and it is carried out at temperatures ranging from 200 °C to 250 °C. HTC involves the application of high temperature and pressure to convert high moisture biomass into carbonaceous biofuel, gas (mainly CO₂), and process water rich in organic and inorganic compounds [22,26,28,29]. During the HTC process, a series of physicochemical reactions occur associated with hydrolysis, decarboxylation, and dehydration reactions [27,30–32]. Characteristics of by-products are strongly related to the severity of the process, which is ruled by the process conditions such as residence time and temperature but also related to the feedstock used for the treatment [33–35]. The solid product resulting from the HTC process is called hydrochar, which presents superior properties in comparison to the raw biomass in terms of higher mass and energy density. Moreover, the HTC process improves the dewaterability and the combustion performance as solid fuel [36]. The main applications for hydrochar are soil improvement, carbon sequestration, bioenergy production, and wastewater pollution remediation [28,37]. Furthermore, it has been demonstrated that the HTC process is not only used for the production of a solid by-product (hydrochar), but also produces a liquid product that is rich in organic and inorganic compounds [38–40]. This process water is considered as a product with no biological activity, but its main drawback is related to the presence and/or high concentration of recalcitrant products such as phenols, furfural, 5-HMF, their derivatives, and nutrients (ammonia), that are strongly related to the type of biomass treated and process parameters. Although the liquid products can contain complex compounds, the suitability of the process water for biogas production has been proven [22,34,38,40–50]. This is because the process water can contain up to 15% of the total carbon, mainly in the form of acetic and formic acid that is highly biodegradable [44].

HTC has grown up fast in the past years to the point that HTC technology has been developed on a commercial scale by companies based mainly in Europe and Asia (see Table 3). Every company presents its own design, process conditions, and additives, as summarized in Table 3. Most of these companies have focused on the HTC of sewage sludge and its integration within wastewater treatment plants in order to reduce the waste volume, obtain a pathogen-free solid product, and to reduce the energy consumption by improving the dewaterability of the solid fraction and by increasing the biogas production. Nonetheless, companies are still investing in technology to make more self-sustaining processes to better harness the properties of the biomass feedstock.

1.4. Importance of HTC integration with phosphorus and nitrogen recovery

There are some problems derived from HTC by-products: 1) the combustion of the solid by-products from HTC (hydrochars) releases NOx into the environment and 2) eutrophication can be caused by liquid or solid wastes with high N and P concentration,
resulting in permanent damage to the underground water. Therefore, it is important to create new strategies by combining or modifying the existing technologies to achieve higher P and N recoveries. Introducing the HTC process coupled with other technologies can enhance the P and N recovery strategies and, at the same time, minimize the risk of pathogens in the final products. In this regard, the potential advantages of the integration of HTC into a nutrient recovery strategy can be summarized as 1) the wide range of biowastes that can be treated despite their different characteristics, 2) the valuable by-products that can be obtained from the HTC (hydrochars, bio-oil, organic products), 3) the pathogen and organic decomposition during the HTC process, 4) the waste volume reduction, and 5) the potential as a P and N reclamation process [51]. Some authors have adopted the approach of using HTC as a process for P and N extraction from the solid fraction to the process water [1,39,52,54]. As a result, it has been found that the HTC process is very efficient in solubilizing and converting organic N into ammonium N, turning it into a good alternative for N solubilization for further recovery [1,51,55]. P conversion is similar to N conversion (from organic to inorganic), but its solubilization through HTC is not efficient if the conditions are not acidic [2,42].

| Table 2 | - Type of thermal treatments for biomass conversion. |
|---------|---------------------------------------------------|
| Hydrothermal process | Observations | Process conditions for biomass | Main product | References |
| Slow pyrolysis | Slow heating rates (1–30 °C/min) for a long period of time to produce solid char. Limited or free of oxygen. | Temperature range | Pressure |
| Fast pyrolysis | Rapid heating and fast volatilization of organic fuels by thermochemical processes in the presence of little or no oxygen. Favors liquid production. | 650–1000 | 1 atm |
| Torrefaction | Carried out at low heating rates and in the absence or with limited content of oxygen. | 250–300 | 1 atm |
| HTC | In presence of water. Produces mainly hydrochar. | 200–250 | 10 bar |
| HTL | In presence of water. Produces mainly bio-crude. | 280–370 | 20 MPa |
| HTG | In presence of water. Produces mainly syngas. | >370 | 25 MPa |

| Table 3 | HTC companies around the world. |
|---------|---------------------------------|
| Company | Process | Patent | Additives | Process conditions | Reactor type | Observations | Reference |
| TerraNova energy | Carbonization | Terranova® Catalyst | 200 | 2 | Pressure-cooker like vessel (batch) | Reduction of disposal volume by 75%, 80% less energy demand than drying, 15% higher biogas yield, up to 80% P recovery in the coal slurry and 24/7 supervision not required. | © TerraNova Energy GmbH [76] and Child [77] |
| SunCoal Industries | Carbonization | CarboREN® | Unknown | 200 | 6–12 | Continuous | Feedstock pre-treatment: Grind and remove impurities - Re-use of the process water (P.W.) - Stirring during the HTC process. | SunCoal Industries [78] and Child [77] |
| AVA-CO2 | Carbonization | HTC-0 Catalyst | 200 | 5–10 | 2.2–2.6 MPa | Several batch reactors | Some P.W. is recycled and other part goes to a waste water treatment plant (WWTP). P.W. is used for fertilizers and chemical recovery. | AVA-CO2 [79] and Child [77] |
| Ingelia | Carbonization | Ingelia S.L. | Unknown | 180 | 6–8 | Continuous (Inverted flow reactor) | The process itself uses between 12 and 15% energy. | Ingelia [80] and Child [77] |
| Antaco | Carbonization | Antaco | Unknown | 200 | 4–10 | 25 bar | Continuous | The process itself uses between 12 and 15% energy. | Antaco [81] and Child [77] |
| Shinko Holdings Co. Ltd | Hydrothermal treatment | HY-200/5000/10000 | Unknown | 230 | 0.5 | 25 bar or 3 MPa | Continuous | Plastic conversion. | Shinko Holdings Co. Ltd [82] and Child [77] |
| C-Green A.B. | HTC | FracFlow reactor | Unknown | 200 | 1 | 20 bar | Continuous | First full-scale HTC plant is being installed at Stora Enso’s Heinola fluting mill in Finland. Processing capacity of 16,000 tons/year. | C-GREEN TECHNOLOGY A [83] and Stora Enso [84] |
Hence, N and P recovery from the liquid fraction can be improved if acidic conditions are promoted because this in turn promotes the hydrolysis of the organic-N species and the solubilization of the inorganic P [1]. On the other hand, HTC also promotes P precipitation and crystallization that allows P extraction in the solid fraction [4,51,52,56]. Therefore, HTC has the potential to boost the nutrient extraction (process water) or densification (hydrochar) from biomass for further nutrient recovery [51,57]. These two approaches do not seem to be mutually exclusive. Nonetheless, only a few studies have included a small section discussing the fate of N or P during and after the HTC process [26,36,51,55,58–62].

HTC review papers are mainly focused on the type of feedstock, biomass chemical reactions, operation conditions, energy balance, product characteristics (hydrochar and process water), and perspectives for future research opportunities, applications, and gaps. For example, Funke and Ziegler [32] presented a review that summarized the knowledge about the chemical nature of the HTC process from a process design point of view and described the most important parameters qualitatively. Libra et al. [63] discussed the conversion process and chemistry involved in hydrochar production from different feedstocks (biomass residues and waste materials). Reza et al. [64] reviewed the HTC development considering process parameters, chemical reactions, and by-products characteristics for energy and crop production. Zhao et al. [38] focused on biofuel production from bio-waste (sewage sludge, municipal solid waste, and palm oil empty fruit bunches) by using hydrothermal treatments as pre-treatments, including HTC, highlighting advantages and disadvantages of the process and the economic viability of HT solid biofuel production. Kambo and Dutta [65] discussed the advantages of hydrochar over biochar. Jain et al. [86] presented a review of the conversion of biomass using HTC to activated carbon. Román et al. [67] focused on experimental and modeling studies of the HTC experimental parameters and hydrochar applications, with special emphasis on its use as a material for electrodes in supercapacitors. Li and Shahbazi [68] wrote a review about the carbon spheres formed through HTC. Zhou et al. [69] considered integration of HTC and anaerobic digestion technologies using food waste as a biomass source. Wang et al. [28] discussed hydrochar formation and characteristics during the HTC process for lignocellulosic biomass and sewage sludge, and Biller and Ross [26] summarized the state of the art of HT (including carbonization) in algal biomass. However, the biomass is not limited to the production of biofuels, and can also be used as a feedstock to recover or produce new sustainable chemical compounds such as N and P. Therefore, the challenge is to create new strategies by combining or modifying the existing technologies to achieve higher P and N recovery efficiencies from biomass waste. Introducing the HTC process, coupled with other technologies, could enhance the current P and N recovery strategies and, at the same time, minimize the risk of pathogens in the final products. In this review, the variables that influence the fate of P and N during HTC of biomass are discussed from a perspective of nutrient recovery, potential applications and future challenges, and trends.

2. Variables that influence N and P solubilization in HTC

When N and P are considered as targets in a nutrient recovery strategy, the understanding of how the variables affect the fate of both nutrients, especially their solubilization, becomes a key factor for the recovery efficiency of the process (see Table 3). During the HTC process, N and part of the P from the biomass is solubilized within the process water and this process is influenced by the reaction temperature, retention time, feedstock, solids loading, and pH, among other factors [22,51,53,55,59,62,85]. For instance, according to Kruse and Dahmen [86], around 80% of the phosphate content within the solid fraction of sewage sludge and digestate can be recovered by using HTC. The extracted phosphate can be used to produce fertilizers and, at the same time, will avoid over-fertilization, by using the digestate for land spreading. Nonetheless, the fate of P during hydrothermal treatment not only depends on the process conditions but also on the feedstock source which is strongly linked to the levels of metals present in the solid fraction [39]. For this reason, it is important to determine the main factors that affect the behavior of P and N during the HTC process in order to define better recovery strategies.

The first factor that should be considered in the recovery strategy that plays a key role in the N and P fate is the source of biomass treated. The N and P species are strongly related to the source of biomass and their determination could help to predict the potential products and the different pathways that N and P can take during the HTC process. Moreover, the N and P speciation could help to determine their mobility and bioavailability [51,59]. Another factor that could help to determine the fate of N and P during HTC is the presence and concentration of heavy metals such as Ca, Mg, Al, and Fe, because they can promote precipitation of N and P through mineralization or adsorption [51,54,59]. In Table 4, the characteristics that influence the fate of N and P for different biomass sources are presented. These bio-wastes are categorized into agricultural wastes, animal manures, sewage sludges, algae, food waste, and municipal solid waste. Elemental analysis (CHNS), proteins, total P (TP) and metals such as Ca, Mg, Al, and Fe and ash content can give an insight into the potential fate-transformations during the HTC process [51,53,59,87,88]. Elemental and total P analyses can provide information about the amount of P and N contained in the biomass. Nevertheless, it is necessary to consider more specific analyses to determine the organic and inorganic fractions of the N and P species of a given biomass. Ash content can provide an estimation of the total amount of metal contained in the biomass but only the concentration of specific metals such as Ca, Mg, Al, and Fe will provide more information about the potential salts that can be formed during the HTC process [51,62].

HTC process conditions such as process temperature, retention time, pH, and solids loading also influence the N and P solubilization. In the literature many studies can be found related to N and P extraction and recovery from HTC [2,4,10,22,39,52,55–57,89–96]. Ekpo et al. [2] stated that an acid medium could promote the hydrolysis of N and enhance the N recovery efficiency. This statement is supported by the research of Dai et al. [1] where they achieved the release of higher concentrations of total N and ammonia at low pH conditions using the acid-supported HTC. However, Ekpo, et al. [2] also stated that the N solubilization is mostly influenced by the severity of the reaction (temperature and retention time) rather than the pH conditions. He et al. [54] found that pressure is another factor that influences N dissolution. They concluded that higher pressures might result in a dramatic cracking or dissolution of N from the solid fraction. Furthermore, it was found that pressure also influences the N species distribution in the liquid fraction affecting mainly NO3−-N and CN−-N. Another factor that has a great influence on N solubilization is the type of feedstock treated because their specific properties influence the quality of the HTC by-products [34]. Some biomass possesses more nitrogenous compounds than others, making them more susceptible to this N solubilization. The raw material is closely related to the N species that will be formed during the HTC [93]. Thus, N solubilization increases as the temperature and retention time increases but reduces as the solids loading increases [22,39,41,53,85,97].

The reaction temperature is a factor that affects the fate of P in the HTC process. Some studies have found that higher reaction temperatures favor P densification within the hydrochar and reduce its solubilization in the liquid fraction [90,92,93]. In
addition, it has been suggested that this immobilization of P during the HTC process results in a stable form such as P-apatite [90]. The solubilization of the P species increases at low temperatures and longer residence times [92]. This can be related to the presence of multivalent metal ions, especially metal cations, that could be responsible for the formation of the insoluble phosphates at high temperatures during the HTC process [2]. The resident time is also a key factor that may have some influence on the nutrient behavior during the HTC process. Ghanim et al. [90] suggested that most of the insoluble P forms occur quickly, highlighting the importance of the residence time during the HTC treatment. The retention time might indirectly influence the P immobilization or solubilization. This is because the residence time influences the solubilization of the cations that are closely related to the P behavior, such as Ca, Mg, K, and Na. In general, the residence time may have a strong effect on the partitioning of P, but the effect is less pronounced at high temperatures. This may be due to precipitation of P occurring quickly at high temperatures [90]. The role of pH in P extraction-recovery is important. Regardless of the acid used (mineral or organic), the acidity favors the formation of soluble metal compounds [32]. Ekpo et al. [2] concluded that the pH, especially in acidic conditions, enhanced both N and P solubilization during the HTC process.

Hence, the main governing factors that influence the fate of N and P during the HTC process can be divided into two: HTC process conditions and biomass characteristics (see Fig. 1).

### Table 4

| Biomass                  | Dry basis | References                                      |
|--------------------------|-----------|-------------------------------------------------|
|                          | % C       | % H     | % N     | % S     | % O     | % Protein | TP (g/kg) | Ca (g/kg) | Mg (g/kg) | Al (g/kg) | Fe (g/kg) | Ash (%) |
| Sewage Sludge            | Max 18.30 | 2.90    | 2.70    | 0.30    | 14.60   | 9.80      | 13.00     | 12.47     | 7.33      | 6.60      | 13.70     |         |
|                          | Min 53.24 | 7.39    | 9.58    | 5.62    | 48.50   | 26.29     | 122.09    | 148.42    | 90.00     | 53.35     | 61.20     | [10,22,39,41,56,61,85,88,98–103] |
| Pig Manure               | Max 34.26 | 4.83    | 2.51    | 0.20    | 0.48    | 22.00     | 2.65      | 15.10     | 9.60      | 0.64      | 1.04      | 12.70    | [4,39,87,100,104–108] |
|                          | Min 51.18 | 6.82    | 4.88    | 21.18   | 37.89   | 22.00     | 25.80     | 36.77     | 16.80     | 4.10      | 2.73      | 41.20    |         |
| Cow Manure               | Max 31.70 | 4.20    | 1.56    | 0.37    | 29.03   | 11.00     | 2.50      | 6.80      | 5.00      | 3.70      | 1.70      | 7.16     | [1,4,52,87,104–115] |
|                          | Min 50.50 | 7.10    | 7.30    | 38.03   | 50.70   | 18.70     | 15.16     | 82.56     | 11.60     | 15.71     | 7.86      | 28.90    |         |
| Chicken Manure           | Max 22.07 | 1.90    | 1.30    | 0.20    | 23.10   | 31.60     | 0.16      | 14.50     | 4.73      | 0.76      | 0.01      | 10.90    | [4,39,87,100,104,108,116–118] |
|                          | Min 46.80 | 6.65    | 5.96    | 2.50    | 41.90   | 31.60     | 34.10     | 58.40     | 11.90     | 4.73      | 2.00      | 43.79    |         |
| Municipal Solid Waste    | Max 24.10 | 1.64    | 0.56    | 0.00    | 16.90   | 0.20      | 0.70      | 38.40     | 5.40      | 20.55     | 0.59      | 5.40     | [30,31,41,103,119–125] |
|                          | Min 52.00 | 6.70    | 3.60    | 0.20    | 38.70   | 6.80      | 5.90      | 287.34    | 15.32     | 57.80     | 132.20    | 100.00   |         |
| Food Waste               | Max 29.50 | 3.00    | 1.50    | 0.07    | 21.30   | 9.80      | 1.20      | 0.97      | 0.00      | 0.00      | 0.00      | 0.00     |         |
|                          | Min 56.30 | 8.01    | 4.85    | 0.50    | 57.20   | 24.31     | 52.00     | 1.51      | 43.00     | 8.00      | 1.20      | 230.70   |         |
| Algae                    | Max 26.00 | 5.00    | 1.00    | 0.30    | 18.60   | 23.95     | 0.80      | 7.30      | 4.50      | 0.05      | 0.10      | 5.00     | [30,39,100,134–143] |
|                          | Min 52.10 | 7.66    | 11.10   | 6.90    | 58.30   | 64.00     | 32.50     | 42.75     | 13.46     | 2.57      | 2.81      | 34.50    |         |
| Agricultural Waste       | Max 32.50 | 0.75    | 0.00    | 0.00    | 3.90    | 4.80      | 0.10      | 0.24      | 0.28      | 0.02      | 0.00      | 0.04     | [29,30,41,104,116,144–153] |
|                          | Min 66.90 | 9.20    | 5.96    | 0.97    | 61.55   | 17.70     | 11.00     | 43.81     | 3.11      | 4.66      | 9.40      | 16.24    |         |

**Fig. 1.** Main governing factors for Nitrogen and Phosphorus transformation during HTC process.

**Fig. 2.** Simplified scheme of the possible mechanisms involved in the transformation of nitrogen during HTC. Information redrawn and adapted from He et al. [54] and Wang et al. [59].

### 3. Nitrogen reaction pathways during HTC

A simplified scheme of the potential N transformation pathways during the HTC process is shown in Fig. 2 and was based on the studies carried out by He et al. [54] and Wang et al. [59]. The hydrothermal process leads the nitrogenous compounds to form several inorganic N ions such as NH₄⁺, CN⁻, NO₂⁻, and NO₃⁻ [54]. Furthermore, many studies agree that the N solubilized into the process water is mainly the ammonia form [2,22,39,53,54,59,85,154]. The increase of temperature suggests a transfer of solid-N into the liquid fraction whereas the inorganic species of N (including ammonium and nitrate salts) suffer hydrolysis to mainly form NH₄⁺-N and NO₃⁻-N [54,59,60]. The organic N, generally composed of proteins and pyridine-N compounds, also suffers a transformation through hydrolysis and deamination reactions into inorganic N (NH₄⁻-N). However, the hydrolysis of organic N (mainly proteins) is slow when the reaction temperature...
is below 230 °C, suggesting that higher temperatures may reduce the HTC process time if the target is the N solubilization [59,100]. Despite most of the N dissolving during the HTC process, some N still remains in the solid fraction due to chemical, precipitation, and crystallization reactions. Compounds such as proteins, pyrrole-N, pyridine-N, and quaternary-N have been found in the hydrochar [54,59,60]. The presence of sugars has also been found to promote the incorporation of N into heterocycles resulting in more stable N species (quaternary-N and pyridine-N) as the reaction temperature in the HTC process increases [39]. As a result, these stable species can be fixed within the hydrochar. Wang et al. [59] found that pyridine-N increased within the hydrochar as the temperature increased (180–200 °C), but decreased at temperatures above 260 °C. The presence of metal ions such as Ca²⁺, Mg²⁺, and PO₄³⁻ can promote N precipitation due to salt formation (struvite) [54,56,59,60]. For instance, CaCO₃ can promote precipitation via ureolysis accelerated deamination [59].

Few studies have extensively studied the effects of temperature and heating rate on N transformation and migration behaviors in thermal treatments [53,54,59,60]. He et al. [54] proposed eight routes for the N transformation during the HTC process of digestate from sewage sludge, including the addition of CaCO₃ as a N solubilization booster. They indicated that the majority of labile N-containing substances may be decomposed and released into liquid fraction at 220 °C. The novelty in this study was the integration of HTC + Air stripping for N recovery from the solid fraction which achieved a global N recovery of 62%. Zhuang et al. [53] studied the transformation pathways of N in sewage sludge during hydrothermal treatment. In this study, the detailed transformation of the N species during different treatment temperatures was reported for the liquid and solid by-products. Xiao et al. [60] and Wang et al. [59] studied the effect of temperature in the N speciation and transformation during the HTC process of Spirulina and food waste, respectively. They found that the N that remained in the solid fraction (hydrochar) after thermal treatment was composed of pyridine-N, pyrrole-N, quaternary-N, amino-N, and inorganic-N. It was suggested that amino-N was mostly converted into quaternary-N and the formation of the heterocyclic-N species was caused by crystallization and ring condensation of N-containing intermediates via the Dies-Alder reaction. The study also reported that N was solubilized during the thermal process due to the hydrolysis of the protein-N and inorganic-N that were transformed to a stable amide-N by the cleavage of peptide bonds that were subsequently transformed into NH₄⁻, via deamination and a ring-opening reaction.

4. Phosphorus reaction pathways during HTC

Compared with the dry thermochemical transformation where the P migrates into only the solid fraction, the P in hydrothermal treatments can migrate into both the solid and liquid fraction. The potential transformation pathways of P during HTC are summarized in Fig. 3. During the HTC process all the P species generally transform into orthophosphates [51]. Species such as pyrophosphates, polyphosphates, phytic acids, phosphate diesters, and others suffer hydrolysis, breaking down the molecular bonds and converting them into soluble orthophosphates that migrate into the liquid fraction. Nevertheless, the amount of metal ion content in biomass waste also defines the fate of P during the thermochemical reaction. Metals such as Ca, Mg, Cu, and Zn can react with P forming insoluble precipitates (phosphate salts) and adsorption can be promoted by Fe and Al hydroxides due to their high affinity with P [51,58,62].

Several studies have researched P transformation during the HTC process in order to get a better understanding of the transformation pathways. Ghanim et al. [90] and Dai et al. [52] have studied the speciation of P during HTC using poultry litter and cattle manure, respectively. Both concluded that identification of the different P forms in the feedstock is the key factor for controlling the solubility of P before treatment. Therefore, knowing the molar ratios of Ca, K, and Mg compared to P helps to identify if the mineral content is a sufficient amount to form precipitates that will result in the densification of the P within the hydrochars [22,90]. According to Huang et al. [51], P minerals such as Ca, K, and Mg phosphates are the most common found in biomass. For this reason, it is important to know the metal cation profile and the P forms contained within the biomass before thermal treatment to predict the P transformation pathways during the thermal treatment and design better strategies for P recovery. Furthermore, the P species within a char will determine its potential as a soil amendment because there are species that are more chemically and biologically available for the soil [155]. Several studies state that multivalent metal cations (for example, Ca, K, Mg, Na, Al, Fe) are strongly bonded with the P transformation pathways [52,80,92,93,155]. During thermal treatment there is a transformation of the P species, with the non-soluble P being the most dominant. The transformation to non-soluble P phosphates is attributed to the presence of multivalent metal elements (such as Ca, K, and Mg) reacting and forming precipitates that are mainly contained within the hydrochar [2,4,52,90]. It has been found that the organic P species break down as the process temperature increases, forming phosphates with the metal cations. Ghanim et al. [90] found that during the HTC process the P is immobilized into inorganic and apatite forms because of its stability. Although pyrolysis is a different thermal treatment from HTC, some studies might give an insight into the transformations of P when undergoing high-temperature treatments. For instance, Sun et al. [155] suggested that the organic P in biomass, such as phytates and lipids, suffers a transformation (the breakdown of phytate) during the thermal process (pyrolysis) forming inorganic metal-P consortiums. These consortiums are formed and chemo-adsorbed on the surface of the hydrochar during the HTC process as insoluble phosphates such as Ca₃(PO₄)₂ and Mg₆(PO₄)₂ [4,93,156].

5. Studies related to P and N recovery

The HTC studies related to P and N are mainly focused on the extraction and solubilization in the process water or nutrient densification in the hydrochar. In general, biomass feedstocks such as digestates and animal manure have been widely studied because of their high nutrient content (see Table 4). However, there are some other valuable and interesting biomass feedstocks that have been studied as well, such as food waste, microalgae, and agricultural waste [57,94,157].

The high N and P content in sewage sludge, especially digestate, makes this type of biomass attractive for the integration of the HTC process within wastewater treatment systems. Aragon-Briceño et al. [22] introduced an approach coupling HTC with anaerobic digestion within a wastewater treatment plant. They applied the HTC process for sewage sludge digestion at three different reaction temperatures, 180, 220, and 250 °C, followed by the anaerobic digestion of the HTC by-products. They obtained solubilizations of P and N up to 27 and 58%, respectively. They concluded that the N extraction is related to the reaction severity of the HTC process but they did not find a correlation with the P solubilization. Yu et al. [91] analyzed the HTC products from the granular digestate from an upflow anaerobic sludge blanket reactor (UASB). A reduction of N in the hydrochar from 9.58% to 5.49% was reported and an almost total immobilization of the P with a bioavailability > 80%. Zhao et al. [6] worked with the HTC process of digestate and evaluated the P
recovery and the feasibility of produce activated carbon from the hydrochar. The study reported a recovery of 92.6% of the P within the hydrochar, mostly as calcium phosphate. The hydrochar was acid washed to recover the P, achieving 88.9–94.3% recovery from the total P of the digestate. Zhuang et al. [53] obtained N recoveries from 36.9% to 75.5% in the process water from the HTC of sewage sludge by applying reaction temperatures up to 300 °C. He et al. [54] had an interesting approach, integrating the HTC process and air stripping process to recover N from dewatered sewage sludge. They obtained solubilization of 84% by the addition of CaCO3 and reported recovery of 62% of the total N. Huang et al. [55] did a similar study with chicken manure, obtaining a recovery of 57% of the total N of the initial biomass. Another study was carried out on septic tank waste and the HTC process at different reaction temperatures and retention times in which 70% of the N was solubilized in the process water [88].

Unlike sewage sludge that is treated in a continuous system, animal manure is usually treated in semi-continuous or non-continuous systems. Moreover, large amounts of different animal manure is generated around the world due to intensive farming to meet global food needs. Therefore, the interest in recycling or harnessing the different manures, especially for their high nutrient content, has led some researchers to investigate the benefits of applying HTC to these types of biomass. Heilmann et al. [4] examined the capture of P in the hydrochar of the HTC of the manure of three different animals (poultry, pigs, and cattle) under various reaction conditions (temperature, solids loading, and time). It was found that hydrochars coming from poultry litter retained 83–90% of the total P, 64–100% for hydrochars coming from swine manure, and 88–100% for hydrochars coming from cattle manure. The study concluded that the feedstock source determines the behavior and fate of the P. For example, for hydrochars coming from poultry litter, no correlation was found between the reaction conditions and the P retained within the hydrochar, but for cattle and swine manure the process temperature and solids loading (retention times above 1hr) enhanced the retention of P within the hydrochar. Reza et al. [110] found that around 50% of the N is solubilized during the HTC processing of cow manure.

There are few studies related to P and N regarding lignocellulosic biomass (mostly agricultural waste) because of its low P and N content and, for that reason, they are mainly focused on carbon densification and fuel properties. Nevertheless, some lignocellulosic biomass still contains sufficient amounts of N and P that can be recovered (see Table 4). Funke et al. [158] performed HTC of wheat straw and anaerobically digested wheat straw. They focused on the N and P retained within the hydrochar at different temperatures and retention times. It was found that between 55 and 65% of the N was retained within the hydrochar from digestate and 48–64% from wheat straw. P retention was higher compared to N. Between 77-80% and 36–78% was retained within the hydrochar of digestate and wheat straw, respectively. Gronwald et al. [159] investigated the nutrient adsorption capacity of the hydrochars from digestate, Miscanthus Andersson, and woodchips. It was concluded that hydrochars coming from 200 to 250 °C treatments presented a poor or negligible sorptive effect on NO3, NH4, and PO4. However, they found that hydrochars coming from digestates released PO4 into the aqueous solutions when the soils were washed. This was attributed to the high P content in the digestate. However, they stated that the nutrient retention potential of a hydrochar depends on the feedstock carbonized, process conditions, surface area obtained, and the interaction with the cations and anions of the material. Parmar and Ross [41] applied HTC in agricultural and sewage sludge digestates, municipal solid waste (organic fraction), and vegetable-garden-fruit waste. According to the results reported, they obtained better recovery rates (74–84%) of N in the hydrochar and process water for the lower reaction temperature (200 °C) rather than higher temperature (250 °C) using 20% of solids of each feedstock. Chen et al. [92] investigated the HTC of

Fig. 3. Scheme of the possible mechanisms involved in the transformation of P during HTC. Information redrawn and adapted from Huang et al. [51].
watermelon peel. They found densification of P in the hydrochar from 53 to 154% compared with the original feedstock. Moreover, they found that lower temperatures promoted P solubilization. On the other hand, the ammonia in the hydrochar reduced up to 11%, although the total N increased from 36 to 99%. For the process water, they obtained no difference in the total N concentration compared with the raw biomass. Vinasse and sugar cane bagasse as a biomass feedstock was studied by Silva et al. [93]. They investigated the addition of acid, base, and salts as promoters in order to immobilize nutrients within the hydrochars at different reaction temperatures. They concluded that the addition of H$_2$SO$_4$, H$_3$PO$_4$, and (NH$_4$)$_2$SO$_4$ promoted the immobilization of N and P.

Other studies have focused on the HTC of micro and macro algae [94,96,157,160]. Heilmann et al. [157] evaluated the nutrient solubilization through the HTC process using microalgae (Chlamydomonas reinhardtii) as a feedstock, achieving extractions of 80% of the total N and 100% of the P. Levine et al. [94] obtained retention of up to 48.7% and 43% for N and P, respectively, within the hydrochar by using HTC in algal biomass (Nannochloris Nau mann and Synnechocystis Sau.). The work carried out by Du et al. [56] studied the feasibility of growing algae (Chlorella vulgaris Beij.) in the process water coming from the HTC process of Nannochloropsis oculata (Droop). Dijkstra et al. observed a recovery rate of 45.5–59.9% of total N and 85.8–94.6% of total P were achieved.

Another promising biomass waste for nutrientclamation by the HTC process is food waste. Idowu et al. [57] evaluated the fate of nutrients resulting from the HTC of (restaurant) food waste, focused on the usage of the solid product as fertilizer. It was concluded that the majority of the N remains in the hydrochar and the P fate is dependent on the reaction time and temperature. Moreover, they estimated that up to 0.96% and 2.3% of the N and P-based fertilizers, respectively, can be replaced in the US with hydrochar and process water from restaurant food waste.

Compared with the traditional HTC process as a strategy for P and N extraction, the acid-supported HTC has shown higher efficiencies, especially for P [2,4]. The addition of acid (H$_2$SO$_4$ or HCl) can not only increase the extraction of cations (promoting the formation of soluble phosphates from Ca, K, Na, and Mg), but can also catalyze the conversion of organic acids through esterification and promote dehydration and decarboxylation [2]. Ekpo et al. [2] analyzed the effect of adding three types of acids, H$_2$SO$_4$, acetic and formic acids, into the HTC process for swine manure. Reaction temperatures of 120, 170, 200, and 250 °C were tested, achieving P recoveries of 79, 94, 80, and 60%, respectively. They found that sulfuric acid promotes better solubilization of P. Furthermore, 60–70% of the total N concentration determined in the process water corresponded to organic N and the rest to NH$_4$-N. Nonetheless, the addition of acids to the sample before thermal treatment had not significant effect. Dai et al. [1] achieved solubilization of up to almost 100% and 63% of the total P and N, respectively, in cattle manure with acid-supported HTC using HCl (2%) to lower the pH. As well as this, it was found that the acid-based HTC in corn stover led to N solubilization of 83–97% from the hydrochar to the liquid fraction [95]. Heilmann et al. [4] used HCl (4 M) to extract P from swine manure hydrochar, achieving 89% P extraction.

Some authors have proposed integrating HTC with the struvite process to recover P from the process water. Becker et al. [56] proposed a novel approach integrating HTC with P–Nclamation via struvite precipitation. The sewage sludge was acidified with nitric acid prior to HTC treatment in order to improve the P solubilization. Furthermore, the ammonium formation due to hydrolysis and deamination reactions during the HTC process, the addition of magnesium salts, and pH increase, all promoted struvite precipitation achieving P recovery up to 82.5% from the native sludge. Yu et al. [10] recovered up to 91.6% and 54.88% of P and N, respectively, from the process water of a carbonized sewage sludge digestate using struvite precipitation. Zhang et al. [89] performed hydrothermal treatment using HCl and H$_2$O$_2$ and reported recovery of 99.3% (Mg$^{2+}$.PO$_4$ $^{3-}$.184.1, pH 9.98) through struvite crystallization with a modest energy requirement reaching values as low as 768 kWh/kg of P. Overall, 16.6% of total P was recovered after P was solubilized, captured and made available.

6. Existing technology for nitrogen and phosphorus recovery

Many technologies have been developed for nutrient recovery in the last decades. Most of them were mainly focused on P recovery rather than N recovery. In addition, these technologies have been predominantly designed for wastewater, sewage sludge, and manure [161]. The final products from the P recovery process are mostly used for agricultural purposes as fertilizers given their important value in the market [3].

The selection of a P recovery process in a recovery strategy is strongly dependent on the properties of the biomass. In general, P recovery technologies consist of extraction (in acidic conditions) and precipitation (mainly in struvite form) with some differences depending on the properties and state of the biomass (solid or liquid). As according to Cieslik and Konieczka [7] there are several kinds of technologies and approaches for P recovery, especially for sewage sludge, but most of them lack management of the waste materials produced during the recovery processes or the operational costs are high. For instance, processes such as precipitation and crystallization are used for wastewater, Seaborne, KREPO, and Aqua-Reci processes for sludge, and BioCon process for biomass ashes. Therefore, it can be said that P recovery technologies for biomass (especially for sewage sludge) have been developed either for aqueous fraction, sludge, or ash [162,163]. On the other hand, N-focused recovery technologies are fewer compared with P and are mainly focused on recovery from liquid waste streams with high concentrations of NH$_4$-N. These technologies are based on N conversion through biological processes (i.e. anammox) or stripping, from ammonia to N$_2$, in combination with a fixation process, N$_2$ and H$_2$ to form NH$_3$ (i.e. Haber-Bosh) [161].

In Table 4, the N and P recovery technologies developed at a large scale are presented. Paques Technology B.V [164], has developed the PHOSPAQ™ and the ANAMMox® processes for P and N recovery, respectively. The PHOSPAQ™ process is mainly based on the recovery of phosphate as struvite, and ANAMMox® is a biological process that converts ammonium and nitrite into N gas for its recovery. Another process that has been developed and patented for P extraction from animal manure, is the "Quick Wash" process, which consists of the use of mineral or organic acid solutions to extract P and the addition of liquid lime and an organic poly-electrolyte to precipitate P to recover it. This process claims a recovery rate of 90% of P from pig manure [3]. Ostara [165] has developed PEARL® and WASSTRIP® processes for P recovery that produce a premium slow-release fertilizer called Crystal Green®. The Ostara PEARL® reactor employs the same chemical principle for the formation of struvite: in continuous aeration, high pH, and with magnesium dosage (Mg$^{2+}$). The company claims that their struvite recovery process decreases the operating cost in a wastewater treatment plant and, at the same time, its Crystal Green® fertilizer meets the relevant environmental regulations. GMB [166] Bioenergie has developed a technology to recover ammonia from compost using drying tunnels and recovering the ammonia through a sulfuric acid scrubber. Other processes that are being used for P recovery are BioCon and Cambi/Kempro [4]. The first process recovers P from the P-rich ashes of the previously incinerated sewage sludge through sulfuric acid. The second process combines the thermal hydrolysis of the Cambi technology and the
Kepro process. Some fraction of P is solubilized with a high temperature (around 150 °C) and extracted by addition of ferric chloride solution to produce ferric phosphate.

Nonetheless, technologies presented in Table 5 require either maximization of the soluble fraction of P and N or maximization of the retention of P within the solid fraction for subsequent recovery. For instance, in the route of P recovery from ashes, the moisture content of biomass should not be overlooked as this can exhibit a detrimental effect on the energy efficiency of the incineration process. In this scenario, the potential synergy offered by HTC, in terms of enhanced dewatering, could be beneficial and this is a reason why careful selection is the key to finding a middle ground between maximization of dewatering and minimization of the loss of P to liquid [167,168].

### Table 5

| Technology | Process | % of Recovery | Reference |
|------------|---------|---------------|-----------|
| BioCon process | A drying-incineration process of sewage sludge. The first process consists of spreading the sludge uniformly in a layering belt and the drying is achieved by hot air (180 and 80–100 °C). The incineration process is carried out at 850 °C. The P extraction process is carried out with sulfuric acid-producing soluble phosphate. This phosphate is extracted by ion exchange followed by acidification and evaporation. | Up to 60% of phosphorus recovery. | [4,163,169–171] |
| Cambi/KePro process | The process consists of using the Cambi process to hydrolyze the sewage sludge at high temperatures (~150 °C) and low pH (~1) to solubilize the P. This is followed by the separation of the solid and liquid fractions. The P is recovered from the liquid fraction using ferric chloride to produce insoluble ferric phosphate (Kepro process). | Up to 70% phosphorus recovery. | [4,171] |
| "Quick Wash" Technology | Technology that uses mineral or organic solutions to extract P. The P recovery is through the addition of liquid lime and organic poly-electrolyte to the liquid extract. The P is recovered as calcium-P precipitate. This process produces a manure low in P and a P precipitate. | Claims to recover 90% of phosphorus in the pig manure. | [3] |
| PHOSPAQ™ Technology | Based on the struvite precipitation process. The P is extracted by the addition of magnesium oxide, causing precipitation of the ammonium and phosphate as struvite. In addition, this process removes chemical oxygen demand (COD) from wastewater. | Removal efficiency of 70–95% of phosphate. | [164] |
| ANAMMox® Technology | The biological process that removes ammonia from liquid wastes converting it into gas N. This process reduces the CO2 emissions and reports to have cheaper operation costs (up to 60%) than the nitrification/denitrification process. | Over 95% of ammonia removal. | |
| PEARL® Technology | Technology based on the struvite precipitation process. The process consists of injecting magnesium salts into a controlled pH reactor. This produces crystal granules called Crystal Green®. Crystal Green® is a highly pure fertilizer that is commercialized. | Claims to remove more than 85% of the phosphorus and 40% of nitrogen. | [162,165] |
| WASSTRI® Technology | Technology that works as a complementary technology for PEARL®, removing the internal P from the waste of activated sludge via stripping. This process is commonly placed before an anaerobic digester. The extra added value is the protection of the anaerobic digesters from the formation of struvite that could block the pipelines. | Up to 85–95% of the formerly dissolved P can be recovered. | |
| Seaborne process | A process created by German Seaborne Environmental Research Laboratory GmbH for sewage sludge treatment that recovers P and N as struvite and purifies the biogas, harnessing the sewage sludge’s biogas, ashes, and biomass. | Not reported. | [169] |
| Ammonium sulfate | Technology for N recovery from compost or solid biomass that releases gases with a high concentration of ammonia. The process uses biological drying tunnels to volatilize the ammonia that is recovered with sulfuric acid (air washer) in ammonium sulfate form. | Recovery of 80 kg N and 90 kg sulfur per ton of sludge treated. | [166] |
| RAVITA process | Technology for N and P recovery developed by Helsinki Region Environmental Services Authority (HSY) for a wastewater treatment plant. The process combines struvite precipitation and ammonia stripping. The N and P recovered as phosphoric acid are used in the air washer to form ammonium phosphate. | Potential phosphorus recovery is around 70% of the total phosphorus inlet. | [161] |
| ANITA™Mox Technology | This process combines an aerobic and an anoxic process into one moving bed biofilm reactor. Up to 85% total nitrogen removal and up to 95% phosphorus removal. | Not reported. | [170] |
| ANITA™Shunt Technology | This process integrates the nitrate-shunt principle into the traditional activated sludge system. Up to 95% of total nitrogen removal. | The bacteria used are nitrate producers and specific Anammox biomass. The advantages of this technology are that it does not use external carbon sources and has a very low energy cost. | |
| Airprex® Technology | The process consists of the increase of pH through CO2 stripping. The process is followed by the addition of MgCl2 in order to precipitate the P as struvite. This process was developed to prevent struvite incrustation at EBPR WWTP. | Up to 7% of the sludge input. | [172,173] |
| Ashdeo® Technology | The process is aimed at recovering P from sewage sludge ash (SSA). The SSA is used as a reducing agent and is mixed with Na salts to form NaCaPO4. The reaction is carried out at 900 °C sewage sludge ash. | 98% of phosphorus recovery from the sludge/ash input in the process. | [172] |
| Gifhorn® Technology | This is the modified-optimized version of the seaborne process. The first step consists of 40% of the total phosphorus from the sewage sludge is transformed into silico-phosphates and recovered as slag. The P precipitation is carried out by the addition of Mg(OH)2 at high pH (9) to form struvite. | Not reported. | [3] |
| Mephrec® Technology | The sludge is dried to 80% DM and pressed into briquettes. The briquettes or ash from sludge are treated with gasification at 1450 °C. During gasification, the phosphates present in SS are the sludge/ash input in the process. | Claims to recover 90% of phosphorus in the pig manure. | [4,171] |

7. Future challenges and trends

As reviewed in previous sections, there is some information about the N and P transformation fate during the HTC process, but a better understanding is still needed, especially due to the wide range of biomass that can be subject to P and N recovery. Information about N and P speciation is one of the key factors that is needed to obtain a better picture of N and P behavior during the thermal process. However, this is not an easy task since every type of biomass has different properties and the HTC conditions are not always the same. Previous studies have demonstrated that the HTC...
process is a feasible process to be included in the N and P recovery strategies. Nevertheless, more studies related to the combination of HTC with more nutrient recovery processes are needed, focused on the recovery efficiency and the reduction of operational costs. Furthermore, it is important to take into account the environmental implications of the disposal of by-products. The process water not only contains organic matter and nutrients that can be harnessed and recovered, but also contains chemical compounds that can damage the environment or affect other subsequent treatment processes. Therefore, more studies related to the process of water purification are needed. Moreover, there are not many studies related to hydrochars and their applications in soils. For that reason, it is important to continue research into this area, to tackle the negative implications, and to ensure the harnessing of the benefits of using hydrochars as soil amenders. Thus, one of the challenges is the standardization of the processes involved with the nutrient recovery strategies to be able to design and construct commercial units.

The current trend is focused on the integration of HTC into wastewater treatment systems to improve energy production and recovery. The approach taken by most of the companies and current research projects is the design of a portable and flexible unit for the HTC process that is able to be integrated within wastewater treatment plants (see Table 3). Another interesting proposed approach is focused on the design of a portable HTC unit for integration into a municipal solid waste treatment plant, but with the aim of recovering water for agricultural purposes [174]. Indeed, all the previously mentioned approaches are novel, but they are focused on waste reduction, energy, and water recovery.

The existing HTC technology has the potential to be coupled with the N and P recovery process, especially because the HTC process has proved to be a good option for solubilizing N and P or densify it within the solid fraction. The concepts of biorefinery and waste reduction are leading to a new trend in which HTC is coupled with other N and P reclamation technologies in order to better harness the properties of the biomass and, at the same time, make the whole N and P reclamation process energy self-sustainable (see Fig. 4). The first steps have been taken towards designing these new N and P reclamation strategies. CarboRem has developed C700, a portable HTC unit integrated with a nutrient recovery system (N, P, and magnesium) [175]. This product is aimed at integration into wastewater treatment plants and claims benefits such as waste volume reduction, enhanced biogas production (increase up to 50%), nutrient recovery, and self-sustained energy process.
8. Conclusions

There is a wide range of methods and technologies developed for P and N recovery and the HTC process is an attractive process that can be used as a step to complement the N and P reclamation strategies. However, a better understanding of the factors that affect the N and P transformations and fate during the HTC process is necessary. This would help to predict the resulting chemical by-products and help to assertively select a recovery process. Therefore, in order to implement better nutrient recovery strategies, potential routes for integrating P and N reclamation and recycling into the treatment of nutrient-rich biowastes via HTC are needed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] L. Dai, et al., A synergistic combination of nutrient reclamation from manure and resultent hydrochar upgradation by acid-supported hydrothermal carbonization, Bioresour. Technol. 243 (2017) 860–866, 2017/11/01.
[2] U. Ekpo, A.B. Ross, M.A. Camargo-Valero, L.A. Fletcher, Influence of pH on hydrothermal treatment of swine manure: impact on extraction of nitrogen and phosphorus in process water, Bioresour. Technol. 214 (2016) 637–644, 2016/09/01.
[3] A.A. Szogi, M.B. Vanotti, P.G. Hunt, U.S. Patent 8,673,046 B1, Process for Removing and Recovering Phosphorus from Animal Waste, U.S. Patent and Trademark Office, 2014. Available: https://patents.google.com/patent/US8673046B1/en
[4] O. Schoumans, W. Bilkens, O. Oenema, P. Ehler, Phosphorus Recovery from Animal Manure: Technical Opportunities and Agro-Economic Perspectives, 2010. Alterl1566-7197.
[5] X. Zhao, et al., Fertilizer and activated carbon production by hydrothermal carbonization of digestate, Biomass Conversion and Biorefinery, journal article 8 (2) (June 01 2018) 423–436.
[6] B. Cieslik, P. Konieczka, A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of “no solid waste generation” and analytical methods, J. Clean. Prod. 142 (2017) 1728–1740, 2017/01/20.
[7] S. Sengupta, T. Nawaz, J.I.C.P.R. Beaudry, Nitrogen and phosphorus recovery from wastewater, journal article 1 (3) (September 01 2015) 155–166.
[8] K.S. Le Corre, E. Valcami-Jones, P. Hobbs, S.A. Parsons, Phosphorus recovery from wastewater by struvite crystallization: a review, Crit. Rev. Environ. Sci. Technol. 39 (6) (2009) 433–477, 2009/06/01.
[9] Y. Yu, et al., Simultaneous phosphorus and nitrogen recovery from anaerobically digested sludge using a hybrid system coupling hydrothermal pre-treatment with MAP precipitation, Bioresour. Technol. 243 (2017) 634–640, 2017/11/01.
[10] T. Nakatko, A. Tokai, K. Ohno, Comparative assessment of technological systems for recycling sludge and food waste aimed at greenhouse gas emissions reduction and phosphorus recovery, J. Clean. Prod. 32 (2012) 157–172, 2012/09/01.
[11] S. Katakai, H. West, M. Clarke, D.C. Barush, Phosphorus recovery as struvite: recent concerns for use of seed, alternative Mg source, nitrogen conservation and fertilizer potential, Resour. Conserv. Recycl. 107 (2016) 142–156, 2016/02/01.
[12] L.E. de-Bashan, Y. Bashan, Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003), Water Res. 38 (19) (2004) 4222–4246, 11.
[13] W. Cai, Z. Zhao, D. Li, Z. Lei, Z. Zhang, D.-J. Lee, Algae granulation for nutrients uptake and algae harvesting during wastewater treatment, Chemosphere 214 (2019) 55–59, 2019/01/01.
[14] W. Mulbry, S. Kondrad, C. Pizarro, E. Kebede-Westhead, Treatment of dairy manure effluent using freeze-dried algae: algal productivity and recovery of manure nutrients using pilot-scale algal turf scrubbers, Bioresour. Technol. 99 (17) (2008) 8137–8142, 2008/11/01.
[15] B. Liu, A. Giannis, J. Zhang, V.W.-C. Chang, J.-Y. Wang, Air stripping process for ammonia recovery from source-separated urine: modeling and optimization 90 (12) (2015) 2208–2217.
[16] T. Cai, S.Y. Park, Y. Li, Nutrient recovery from wastewater streams by microalgae: status and prospects, Renew. Sustain. Energy Rev. 19 (2013) 3669, 2013/01/01.
[17] C.-H. Ge, et al., Nitration-anammox process – a realistic and satisfactory way to remove nitrogen from high saline wastewater, Bioresour. Technol. 275 (2019) 86–93, 2019/03/01.
[18] I. Zekker, et al., ANAMMox-denitriﬁcation biomass in microbial fuel cell to enhance the electricity generation and nitrogen removal efficiency, Biodegradation 31 (4) (2020/12/01 2020) 249–264.
[19] J. Li, et al., Insight into the impacts of organics on anammox and their potential linking to system performance of sewage partial nitrification-anammox (PN/A): a critical review, Bioresour. Technol. 300 (2020) 122655, 2020/03/01.
[20] W. Cai, Z. Zhao, D. Li, Z. Lei, Z. Zhang, D.-J. Lee, Algae granulation for nutrients uptake and algae harvesting during wastewater treatment, Chemosphere 214 (2019) 55–59, 2019/01/01.
[21] M. Wilk, A. Magdziarz, Hydrothermal carbonization, torrefaction and slow pyrolysis of Miscanthus giganteus, Energy 140 (2017) 1292–1304, 2017/12/01.
[22] T. Wang, Y. Zhai, Y. Zhu, C. Li, G. Zeng, A review of the hydrothermal carbonization of biomass for hydrochar formation: process conditions, fundamentals, and physicochemical properties, Renew. Sustain. Energy Rev. 90 (2018) 233–247, 2018/07/01.
[23] M. Wnukowski, P. Owczarek, L. Niedziwiecki, Wet torrefaction of Miscanthus – characterization of hydrochars IN view OF handling, storage and combustion properties, Journal of Ecological Engineering, journal article 16 (3) (December 01 2017) 565–578.
[24] A.M. Smith, S. Singh, A.B.J.F. Ross, Fate of inorganic material during hydrothermal carbonisation of biomass, Energy 300 (2020) 122655, 2020/03/01.
[25] N.D. Berge, K.S. Ro, E. Frølandsdottir, M.A. Chappell, S. Bae, Hydrothermal carbonization of municipal waste streams, Environ. Sci. Technol. 45 (13) (2011) 5969–5973.
[26] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining 4 (2) (2010) 160–177.
[27] K. Wiedner, C. Naisse, C. Rumpel, A. Pozzi, P. Wieczorek, B. Glaser, Chemical modification of biomass residues during hydrothermal carbonization – what makes the difference, temperature or feedstock? Org. Geochem. 54 (2013) 91–100, 2013/01/01.
[28] E. Danso-Boateng, G. Sharma, A.D. Wheatley, S.J. Martin, R.G. Holdich, Hydrothermal carbonisation of sewage sludge: effect of process conditions on product characteristics and methane production, Bioresour. Technol. 177 (2015) 318–327, 2017.
[29] Q. Xu, Q. Qian, A. Quek, N. Ai, G. Zeng, J. Wang, Hydrothermal carbonization of macroalgae and the effects of experimental parameters on the properties of hydrochars, ACS Sustain. Chem. Eng. 1 (9) (2013) 1092–1101, 2013/09/03.
[30] P. Zhao, Y. Shen, S. Ge, Z. Chen, K. Yoshikawa, Clean sold biofuel production from high moisture content waste biomass employing hydrothermal treatment, Appl. Energy 131 (2014) 345–367, 2014/10/15.
[31] R. Saidur, E.A. Abdelaziz, A. Demirbas, M.S. Hossain, S. Mekhilef, A review on hydrothermal carbonization of sewage sludge with different reaction conditions, in: Presented at the 13th IWA Specialized Conference on Small Water and Wastewater Systems & 5th IWA Specialized Conference on Resources-Oriented Sanitation, Athens, Greece, 14–16

Renewable Energy 171 (2021) 401–415
terms of production, physico-chemical properties and applications, Renew. Sustain. Energy Rev. 45 (2015) 359–378, 2015/01/01.

[66] A. Jain, R. Balasubramanian, M.P. Svensson, Hydrothermal conversion of biomass to activated carbon with high porosity: a review, Chem. Eng. J. 283 (2016) 789–805, 2016/01/01.

[67] S. Roman, et al., Hydrothermal carbonization: modeling, final properties and applications, Energy 11 (1) (2014) 216.

[68] R. Li, A. Shahbazi, A review of hydrothermal carbonization of carbohydrates for carbon spheres preparation, Trends in Renewable Energy, Hydrothermal Carbonization (HTC); Carbohydrates; Carbon Gases; Sugar; Process Parameters; HTC Mechanism; HTC user info.; History of HTC: Temperature; Residence Time; Precursor Concentration; pH; Pressure 1 (1): 45–53, 2015/03-15.

[69] Y. Zhou, N. Engler, M. Nelles, Symbiotic relationship between hydrothermal carbonization technology and anaerobic digestion for food waste in China, Biosustain. Technol. 260 (2018) 404–412, 2018/07/01.

[70] P.T. Williams, S. Besler, The influence of temperature and heating rate on the slow pyrolysis of biomass, Renew. Energy 7 (3) (1996) 233–250, 1996/03/01.

[71] F. Fonse, S.V. Hecke, D. Dickinson, W. Prins, Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions, GCB Bioenergy 5 (2) (2013) 104–115.

[72] J. W. Lee, Y.-H. Kim, S.-M. Lee, H.-W. Lee, Optimizing the torrefaction of mixed softwood by response surface methodology for biomass upgrading to high energy density, Biosustain. Technol. 116 (2012) 471–475, 2012/07/01.

[73] D. Chen, Z. Zheng, K. Fu, Z. Zeng, J. Wang, M. Lu, Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products, Fuel 159 (2015) 27–32, 2015/11/01.

[74] S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: a review of subcritical water technologies, Energy 36 (5) (5/2011) 2328–2342.

[75] A. Kruse, A. Krupka, V. Schwarzkopf, C. Gamard, T. Henningsen, Influence of proteins on the hydrothermal gasification and liquefaction of biomass. 1. Comparison on different feedstocks, Ind. Eng. Chem. Res. 49 (9) (2005) 3013–3020, 2005/04/01.

© TerraNova Energy GmbH, Available: http://terranova-energy.com/en/, 2019, 20-Oct.

[76] M. Child, Industrial-scale Hydrothermal Carbonization of Waste Sludge Materials for Fuel Production, Master of Science of Master of Science Thesis, Faculty of Technology, Lappeenranta National University of Technology, Finland, 2014.

[77] SunCoal Industries, Available: https://www.suncosal.com/company/, 2019, 18-Oct.

[78] Ava-CO2, Available: http://ava-htc.com/, 2019, 16-Oct.

[79] Ingelia, Available: https://www.ingelia.com/?lang=en, 2019, 16-Oct.

[80] Antaco, Available: http://www.antaco.co.uk/technology/, 2019, 16-Oct.

[81] Shinko Holdings Co, Ltd, Available: http://www.shinko-mfg.co.jp/, 2019, 16-Oct.

C-GREEN TECHNOLOGY A, 7-5-2020, https://www.c-green.se/, 2020.

[82] Stora Enso, From hard-to-handle waste to pure bioenergy, 7-5-2020, https://www.storaenso.com/en/newsroom/news/2019/12/from-hard-to-handle- waste-to-pure-bioenergy, 2019.

[83] C. Aragón-Briceno, A.K. Pozzalek, E.A. Brajer et al., Renewable Energy 171 (2021) 401–415
[149] O. Çepelioğlu, A.E. J.W.m. Pütün, Research, A pyrolysis study for the thermal and kinetic characteristics of an agricultural waste with two different plastic wastes 32 (10) (2014) 971–979.

[150] V. Strezov, T.J. Evans, C. Hayman, Thermal conversion of elephant grass (Pennisetum Purpureum Schum) to bio-gas, bio-oil and charcoal, Bioresour. Technol. 99 (17) (2008) 8394–8399, 2008/11/01.

[151] M.J. Jahirul, M.G. Rasul, A.A. Chowdhury, N. Ashwath, Biofuels production through biomass pyrolysis—a technological review, Energies 5 (12) (2012) 4952–5001.

[152] M.T. Reza, J.C. Lynam, M.H. Uddin, C.J. Coronella, Hydrothermal carbonization: fate of inorganics, Biomass Bioenergy 49 (2013/02/01/2013) 86–94.

[153] X. He, et al., Effects of pyrolysis temperature on the physicochemical properties of gas and biochar obtained from pyrolysis of crop residues 143 (2018) 746–756.

[154] M. Toufiq Reza, et al., Hydrothermal carbonization (HTC) of cow manure: carbon and nitrogen distributions in HTC products 35 (4) (2016) 1002–1011.

[155] M.T. Reza, J. Nover, B. Wirth, C.J. Coronella, Hydrothermal Carbonization of Glucose in Saline Solution: Sequestration of Nutrients on Carbonaceous Materials, 2016.

[156] S.M. Heilmann, et al., Hydrothermal carbonization of microalgae II. Fatty acid, char, and algal nutrient products, Appl. Energy 88 (10) (2011) 3286–3290, 2011/10/01.

[157] A. Funke, J. Mumme, M. Koon, M. Diakité, Cascaded production of biogas and hydrochar from wheat straw: energetic potential and recovery of carbon and plant nutrients, Biomass Bioenergy 58 (2013) 225–237, 2013/11/01.

[158] M. Gronwald, A. Don, B. Tiemeyer, M. Helfrich, Effects of fresh and aged chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils, SOIL 1 (1) (2015) 475–489.

[159] A.M. Smith, A.B. Ross, Production of bio-coal, bio-methane and fertilizer from seaweed via hydrothermal carbonisation, Algal Research 16 (2016) 1–11, 2016/06/01.

[160] L. Rossi, S. Reuna, T. Fred, M. Heinonen, RAVITA Technology – new innovation for combined phosphorus and nitrogen recovery, Water Sci. Technol. 78 (12) (2019) 2531–2537.

[161] L. Egle, H. Rechberger, J. Krampe, M. Zessner, Phosphorus recovery from municipal wastewater: an integrated comparative technological, environmental and economic assessment of P recovery technologies, Sci. Total Environ. 571 (2016) 522–542, 2016/11/15/.

[162] M. Kasprzyk, M.H. Gajewska, S. Molendowska, Possibilities OF phosphorus recovery from reject waters, sewage sludge and ashes after thermal sewage sludge treatment, journal article 18 (4) (2017) 65–78.

[163] B.V. Paques Technology, Products, 3-12-2019, https://en.paques.nl/products/other/phospaq, 2019.

[164] Ostara, Technology, Available: https://ostara.com/nutrient-management-solutions/, 2019.

[165] GMB, Nutrient recovery, 4-12-2019, https://www.gmb.eu/gmb-clusters/gmb-bioenergie/nutriententerugwinning, 2019.

[166] L. Rossi, S. Reuna, T. Fred, M. Heinonen, RAVITA Technology – new innovation for combined phosphorus and nitrogen recovery, Water Sci. Technol. 78 (12) (2019) 2531–2537.