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Transformation of Phosphorus during (Hydro)thermal Treatments of Solid Biowastes: Reaction Mechanisms and Implications for P Reclamation and Recycling

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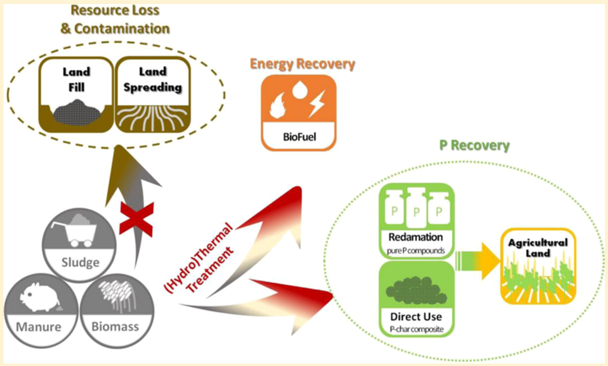
Supporting Information

ABSTRACT: Phosphorus (P) is an essential nutrient for all organisms, thus playing unique and critical roles at the food−energy−water nexus. Most P utilized by human activities eventually converges into various solid biowastes, such as crop biomass, animal manures, and sewage sludges. Therefore, integration of efficient P recovery practices into solid biowaste management will not only significantly reduce the dependence on limited geological P resources but also reduce P runoff and related water contamination issues associated with traditional waste management strategies. This study reviews the applications of (hydro)thermal techniques for the treatment of solid biowastes, which can greatly facilitate P recovery in addition to waste volume reduction, decontamination, and energy recovery. Research showed that P speciation (including molecular moiety, complexation state, and mineralogy) can experience significant changes during (hydro)thermal treatments, and are impacted by treatment techniques and conditions. Changes in P speciation and overall properties of the products can alter the mobility and bioavailability of P, and subsequent P reclamation and recycling efficiency of the treatment products. This review summarizes recent progresses in this direction, identifies the challenges and knowledge gaps, and provides a foundation for future research efforts targeting at sustainable management of nutrient-rich biowastes.



1. INTRODUCTION

1.1. Critical Role of Phosphorus at the Food−Energy−Water Nexus. In recent years, it has been increasingly recognized that a better understanding and management of the food−energy−water nexus is critical for meeting the increasing demands of growing population while maintaining the service of the ecosystem.[1−4] Phosphorus (P) is an essential element for all living life, thus playing an unique and critical role at the food−energy−water nexus.[5] In particular, sustainable food production for the fast-growing population relies heavily on P fertilization in agriculture.[6,7] In addition, biofuel production constitutes a growing portion in the agriculture sector, which has also induced increasing demands for P fertilizers.[8] These human utilized P fertilizers are produced from the mining of geological phosphate rocks, the location and total reservoir of which are both globally limited.[9] In fact, several recent studies have projected that at the current mining rates, current minable geological phosphate reserves will be depleted in 50−100 years.[6] Such imbalance between P demand and P resource has evoked great concerns over its depletion and food security. On the other hand, human utilization of P is rather inefficient, with significant amounts of P being lost during fertilizer production and soil application, food production and processing, as well as waste handling.[7] P runoff from these processes is one of the main contributors to eutrophication in aquatic environments, which possesses great threats to ecosystem and human health.[10,11] Therefore, from the perspectives of P resource conservation, sustainable food production, and environment protection, it is critical to better manage the anthropogenic P cycle[7,12−15] and improve P utilization and recycling/reclamation.

1.2. Integrating P Recovery into Solid Biowaste Management: Opportunities for (Hydro)thermal Treatments. The key to close the anthropogenic P cycle is to improve the efficiency of both P utilization and recovery, which can reduce P resource consumption and P loss into the environment.[12,13,15] Briefly, the anthropogenic P cycle starts

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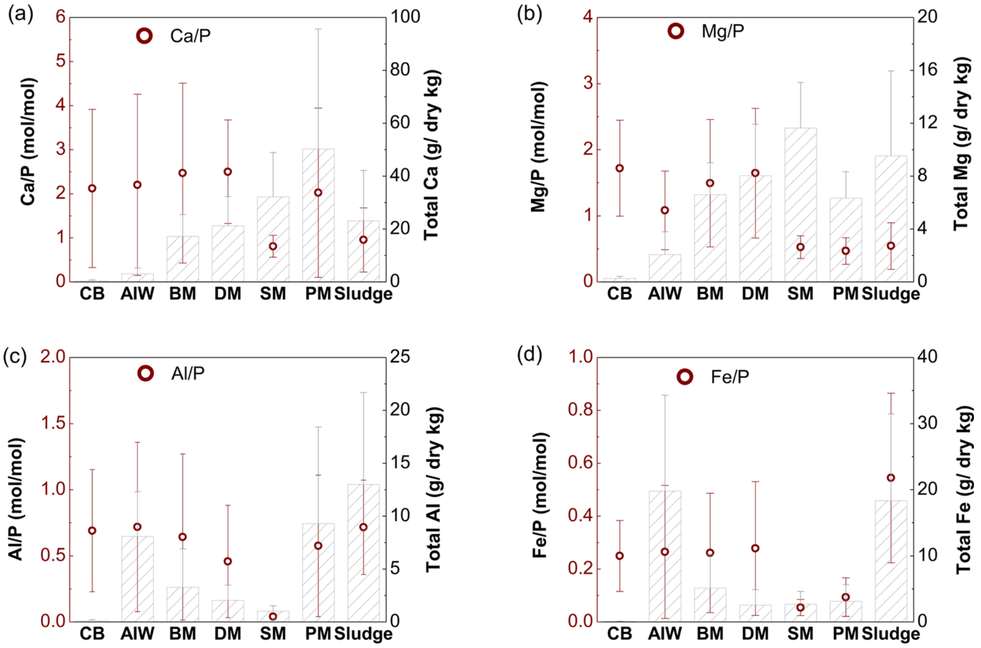

Figure 1. Major cation concentrations (vertical bars) and their molar ratios to P (red circles) for common solid biowastes (CB - crop biomass, AIW - agri-industrial wastes, BM - beef manure, DM - dairy manure, SM - swine manure, PM - poultry manure, Sludge - various biosolids from WWTPs). Data compiled from journal publications (see Supporting Information SI Table S1 for details).

with the production of P-containing materials such as fertilizers and industrial/daily products from geological phosphate rocks. For P applied as fertilizers, after utilization by crops, P is diverged into food processing and livestock sectors and subsequently consumed by humans.[6,16] In addition to the P embedded in wastes that are generated during agriculture (e.g., crop residue), livestock farming (e.g., animal manures), and food processing processes (e.g., slaughterhouse wastes and agro-industrial wastes), P consumed by human is mostly converged into wastewater treatment plants (WWTPs).[15] For P in wastewater, although many chemical methods have been developed for its recovery, biological treatments remain as the primary strategies through the accumulation of P by microbial biomass. All these processes produce P-rich biowastes, broadly categorized into agricultural wastes, animal wastes, and sewage sludges. P in these wastes adds up to 64% of human mined P,[6,12] and is the focus of discussion for this review.

How we manage the above-mentioned P-rich biowastes determines whether we can improve the efficiency of anthropogenic P cycle and the resilience of related systems at the food−energy−water nexus. Common disposal methods for sewage sludges include direct land spreading, landfill, incineration, or addition to cement products after drying. However, each of these methods has inherent disadvantages and a significant amount of resources (including P) are typically wasted during the treatment and/or disposal process.[17] Animal manures are commonly applied as soil amendments directly or after simple pretreatments, such as compost, lime treatment, or alum treatment. Although soil application of manures is a convenient and cost-effective waste disposal and P recycling strategy, there are several associated problems: (1) P in manure is highly mobile and can outpace plant utilization rate, resulting in the soil runoff of excess P and serious water pollution problems,[6,18] (2) the embedded organic contaminants (e.g., antibiotics, pesticides) and pathogens can cause human and environmental hazards.[19,20]

In general, the treatment of solid biowastes is a complex issue that involves technological, socioeconomic, and environmental factors. Sustainable waste management calls for system-level approaches that consider innovations and improvements in both treatment techniques and management strategies.[21,22] Any improved treatment techniques should aim for maximum resource recovery and minimum waste disposal, thus simultaneously address the challenges with waste management and maximize the overall socioeconomic benefits. In this regard, there have been increasing interests in the application of (hydro)thermal techniques for biowaste managements, because (1) they can accommodate a broad range of wastes with different properties (dry vs wet, uniform vs heterogeneous);[23,24] (2) they are highly tunable techniques that can convert solid biowastes into products with broad applications (for example, chars, fuel, and organic products),[25,26] thus achieving effective resource recovery; (3) (hydro)thermal techniques can serve as sanitation methods to decompose pathogens and organic contaminants,[27,28] and can significantly reduce waste volume and reduce the stress on ecosystem. In addition, these techniques also have great potentials for P recovery/reclamation, which is a less explored research area. This review summarizes the working principles of common (hydro)thermal techniques and discusses their efficiency and great potentials in facilitating P recovery from solid biowastes.

1.3. Importance of P Speciation in P Recovery. For any P recycling/reclamation methods, one fundamental influencing factor is the P speciation in the raw feedstock and treatment products, because speciation largely determines an element's mobility and bioavailability. For P reclamation (via methods such as precipitation, adsorption, or ion-exchange), the speciation of P in biowastes and the derived products controls its extractability and speciation in the liquid extracts,[29,30] and ultimately its reclamation efficiency. For P recycled through direct soil applications of manures and other P-rich wastes, the soil runoff problem is largely caused by the abundant mobile P

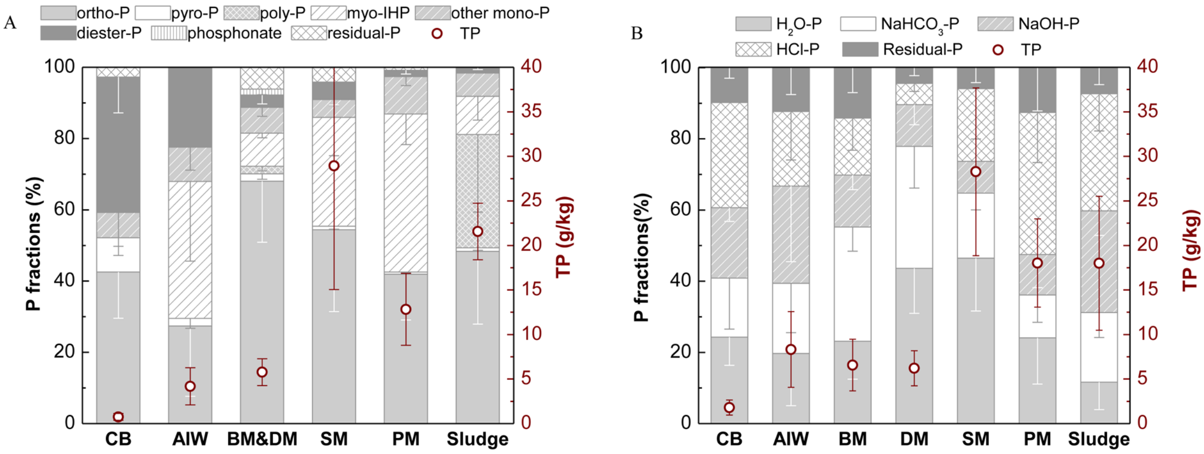

Figure 2. Total P content (TP; red circles) and fractions of different P species in various solid organic wastes determined by (A) coupled chemical extraction and ^{31}P liquid NMR, and (B) sequential extraction. CB - crop biomass, AIW - agri-industrial wastes, BM - beef manure, DM - dairy manure, SM - swine manure, PM - poultry manure, Sludge - various biosolids from WWTPs. Panel (A) ortho-P (orthophosphate), pyro-P (pyrophosphate), poly-P (polyphosphates), myo-IHP (myo-inositol hexakisphosphate or phytic acid), other mono-P (e.g., nucleic acids), diester-P (phosphate diesters). Panel (B) H_2O-P, $NaHCO_3$-P, NaOH-P, HCl-P, and residual P are water-, $NaHCO_3$-, NaOH-, and HCl-extractable P and residual P according to the Hedley protocol. Data compiled from journal publications (see SI Table S2 and S3 for details).

species embedded in these wastes, thus chemical adjustments of P speciation has been a common practice to address this problem.[31−33] In this regard, the potential of (hydro)thermal treatments for P reclamation/recycling is largely determined by the P speciation in the treated products. In the past few years, there has been a growing number of studies on P transformation during (hydro)thermal treatments of various biowastes. These studies suggest that (hydro)thermal treatments are highly tunable toward modulating P migration and speciation, and might be able to serve specific P reclamation or recycling practices. However, systematic investigation and understanding of the controlling factors are still missing, which hampers the optimization of these (hydro)thermal techniques for efficient P recovery. This review summarizes results from these investigations, identifies the challenges and knowledge gaps, and presents perspectives for future research and development. Particularly, the mechanisms behind P transformation in different types of biowastes and the controlling factors (i.e., treatment techniques and conditions) are summarized, and the implications for P reclamation and recycling are critically evaluated.

2. PHYSICOCHEMICAL CHARACTERISTICS OF P-RICH SOLID BIOWASTES

2.1. Overview of Chemical Composition. The resource recovery potential of a waste stream is largely determined by its chemical composition. First of all, P content in biowastes largely determines their value as P source and the benefits of P recycling. Second, the composition and relative abundance of metals (particularly metals with strong affinities for P) affect the speciation of P in both the raw biowastes and treatment products (see Section 2.2 and Section 3). Below we briefly summarize the compositional characteristics of the main groups of solid biowastes: agriculture biomass, agro-industrial wastes, animal manures, and sewage sludges.

Wasted agricultural biomass (such as wheat and rice straw, corn stalk, and switchgrass) takes up a significant fraction of P fertilizers applied to soils.[6] They have relatively uniform composition with high organic matter contents, primarily cellulose, hemicelluloses, and lignin.[34] Ash contents in agriculture biomass range from 5 to 20%, and the main components are silica (SiO_2, 40−70% of ash mass) and potassium (K_2O, 8−20% of ash mass), whereas other metals (e.g., Ca, Mg, Al, and Fe) present at concentrations of ∼100s mg/kg dry biomass (Figure 1).[35] P contents in agriculture biomass are ∼2 g/kg (Figure 2),[36,37] whereas plant seeds are generally more enriched in P (∼10 g/kg for common cereals and legumes, which consist of mostly phytic acid)[38] compared to other plant tissues. Therefore, agro-industrial wastes derived mostly from seeds (e.g., peanut shell and niger seed) have relatively higher P contents (Figure 2).

Animal manures, depending on dietary composition, animal species and physiology, and manure handling process, can vary broadly in their chemical compositions (Figure 1). Manures have high organic matter contents, which primarily consist of protein (10−30%), lipids, and undigested carbohydrates (e.g., cellulose, hemicelluloses, and lignin).[39,40] Ca is the most abundant metal in animal manures, with concentrations ranging from 10 to 100 g/kg dry manure. Mg is the second most abundant metal and its concentrations are around 10 g/kg. Al and Fe are generally present at concentrations bellow 10 g/kg (typically < 5 g/kg). Average P contents in manures are ∼5−30 g/kg dry mass (Figure 2).

The elemental compositions of sewage sludges depend strongly on the sewage source, wastewater treatment techniques, and subsequent handling processes. The organic matters in sewage sludges are primarily microbial biomass, thus the main organic components in sludges are organic compounds constituting cellular structures, such as polysaccharides, proteins, lipids, and DNA. Compared to crop biomass and manures, sewage sludges have much higher ash contents and more diverse metal compositions.[41] Major metals (Na, K, Ca, Fe, Mg, and Al) commonly present at a few weight percent (Figure 1), whereas concentrations of other metals (e.g., Ti, Zn, Cu, Mn, Cr, Sr) are typically 1 order of magnitude lower.[41] P contents can range from 1000s mg/kg to several weight percent, depending on the sludge sources and types of biological treatment methods (e.g., polyphosphate accumulating bacteria or microalgae).[42−44]

2.2. P Speciation in Solid Biowastes and the Governing Factors. Besides chemical composition, P speciation is also an important factor controlling P recyclability. P can exist in different molecular configurations (moieties), such as phosphonate, orthophosphate, polyphosphates, and organophosphates. These different moieties can also present in different chemical states, such as cation complexes, surface adsorbed species on other minerals, incorporated into other mineral phases, or precipitated as P-containing minerals. Overall, P speciation in the surveyed biowastes is highly heterogeneous, and is affected by similar factors that control the overall chemical compositions of these wastes.

For P speciation in crop biomass and agro-industrial wastes, based on chemical extraction and liquid ^{31}P nuclear magnetic resonance (NMR) spectroscopy analysis, organophosphorus (for example, phytic acid, phosphate mono- or diesters) can account for 40−70% of the total extractable P, whereas orthophosphate contributes for 30−40% (Figure 2A). In terms of mobility and bioavailability, P in crop biomass and agro-industrial wastes is relatively mobile, with an average 40% of the total P being water- and NaHCO$_3$-extractable (Figure 2B).[36]

P speciation in animal manures has been extensively studied. It is highly variable and dependent on animal physiology, species,[45] age,[45] diet,[46−48] and manure handling (e.g., storage duration).[49] Phytic acid from animal feeds remains abundant in all types of animal manures, ranging from a few weight percent to more than half of total P in liquid extracts (Figure 2A).[45,46,48,50] Other organic phosphorus (such as phosphate diester, phospholipids, DNA, and phosphonates) are also present, but usually only account for a minor fraction and are mainly contributed by microbial biomass.[29,46,51] On the basis of the overall elemental contents as discussed in Section 2.1, it is anticipated that P complexation and mineral states are primarily controlled by Ca and Mg (Figure 1). Indeed, various Ca-phosphate minerals and struvite ($MgNH_4PO_4{\cdot}6H_2O$) are frequently identified in animal manures.[33,52] Because most of the organophosphorus and inorganic phosphates are readily soluble, P species in manures are highly mobile. Sequential extraction of various manures showed that soluble and Olsen P can account for 50−80% of total P in manures, with chicken and turkey manures having less mobile P than swine, diary, and beef manures (Figure 2B).[29,50,51,53]

P speciation in sewage sludges is largely dependent on wastewater treatment techniques and sludge handling processes. Activated sludge generally consists of inorganic phosphates, diverse organophosphorus species, and polyphosphates (Figure 2A), with their relative abundance dependent on the treatment techniques (e.g., activated sludge process, membrane bioreactor, and enhanced biological phosphorus removal).[54−57] Following sludge processing (dewatering, mixing of other sludge sources, and anaerobic digestion), organophosphate and polyphosphate are gradually degraded into orthophosphates that are increasingly associated with metals (especially Ca, Fe, and Al) and their minerals.[58−60] This is likely due to the release and hydrolysis of intracellular P species and their subsequent interaction with metals and minerals.

2.3. Characterization Techniques for P Speciation in Solid Wastes. Several analytical techniques are commonly used to characterize P speciation in environmental matrices, each with strengths and limitations. The main tools that are capable of in situ characterization of solid phases are ^{31}P solid state NMR spectroscopy, P X-ray absorption spectroscopy [XAS, mainly X-ray absorption near edge structure (XANES) spectroscopy], and X-ray diffraction (XRD). Both NMR and XAS are elemental sensitive techniques that provide information on local coordination environment and phase identification. ^{31}P solid state NMR provides good molecular moiety information (e.g., phosphonate, orthophosphate, pyrophosphate, and polyphosphate), but is limited in identifying and quantifying these molecular moieties in heterogeneous matrix due to difficulties in obtaining high resolution data (e.g., presence of broad and overlapping peaks).[61] The presence of abundant paramagnetic elements (Fe and Mn), which is very common in environmental samples such as sewage sludges, also hampers the observation of P species associated with these elements.[62] P XAS is relatively more sensitive to distinguishing inorganic orthophosphate species in different chemical states (e.g., surface complexation, mineral phases, phosphate incorporated in other mineral phases), whereas relatively insensitive to differentiating organophosphates, monomeric P, and polymeric phosphates.[63−65] Coupled chemical extraction (NaOH-EDTA)[66,67] and ^{31}P liquid NMR can be used for P molecular moiety identification and quantification in complex matrices where direct solid state ^{31}P NMR can be challenging.[61,68] However, this approach does not probe the in situ chemical states of P, and can only characterize the P species that are solubilized into the extraction solution. It can also cause potential alteration to P complexation forms during the extraction process, such as dissolution, desorption, and precipitation.[61−63]

Sequential extraction based on the Hedley protocol and its modified versions have been extensively used to evaluate the relative mobility and abundance of different P species.[29,30,69] In this protocol, water and NaHCO$_3$ extractable P species are attributed to readily soluble phosphates and organophosphates. NaOH extractable P species are considered to be P sorbed on Fe/Al mineral phases. HCl extractable P species are considered to be insoluble phosphate minerals such as Ca, Al, and Fe phosphates. However, P speciation by sequential extraction is operationally defined and can only be semiquantitatively correlated with the assigned chemical species, not to mention potential alterations to P speciation during the extraction reactions.[30,70]

On the basis of the above-discussed advantages and disadvantages of different approaches and techniques, it is recommended that multiple complementary techniques should be combined to obtain a full picture of the P speciation information (both molecular moiety and their chemical states), in order to fully understand the transformation pathways during solid biowaste treatments. Many excellent reviews exist on the principles and applications of these techniques, and interested readers are referred to these publications for details.[61−63]

3. THERMOCHEMICAL TRANSFORMATION OF P DURING WASTE TREATMENTS

3.1. Classification of (Hydro)thermal Techniques and Their Applications for Biowaste Management. In general, (hydro)thermal techniques can be divided into two main categories: thermal treatments (operating under inert atmosphere and dry conditions) and hydrothermal treatments (operating in a closed pressurized system and under wet conditions). Each category can be further divided into carbonization, liquefaction, and gasification treatments, based on the operating temperature and phase partitioning of the products (Figure 3).[71,72] Carbonization (or pyrolysis, for dry

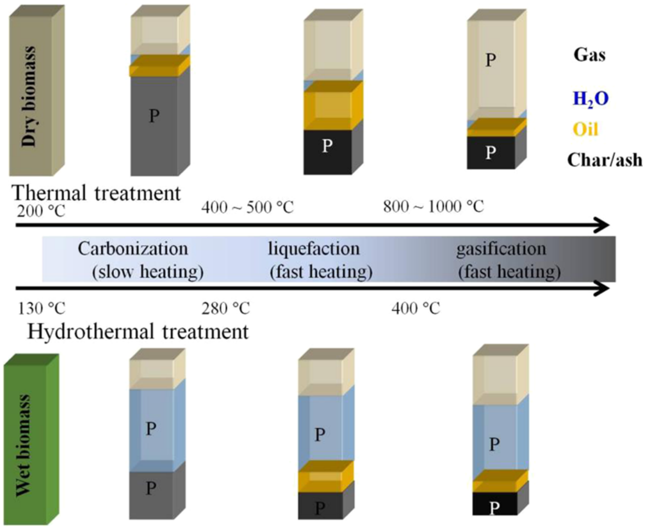

Figure 3. Classification of different (hydro)thermal treatments, their working conditions, product phase distribution, and P distribution in different phases. Mass distribution in the gas, liquid, oil, and solid phases is arbitrary. Temperature boundaries for the different thermochemical processes are based on previous studies.[71,72]

thermochemical processes) and hydrothermal carbonization (HTC; for wet thermochemical processes) occur at low heating temperatures with slow heating rate, where the mass predominantly remains in the solid products. Liquefaction and hydrothermal liquefaction occur at medium temperature range, with a fast heating rate and short residence time, where liquid products account for a large fraction of the mass.[73] Gasification and hydrothermal gasification are the processes occurring at higher temperatures, where gas products become dominant.[74]

With regard to solid biowaste treatment, hydrothermal techniques possess certain advantages over thermal techniques: (1) Many solid biowastes have high water contents, with a significant fraction present in the form of intracellular or bound water that cannot be efficiently predried for thermal treatments. In these cases, hydrothermal treatments can be used to avoid expensive drying processes.[23,75] (2) Hydrothermal treatments generally operate in closed systems and at lower temperatures, compared to the higher operating temperatures required by thermal treatments. Hydrothermal treatments are also exothermic processes.[76] These features make hydrothermal treatments more energy efficient. (3) Similar to thermal treatments, hydrothermal treatments can also serve as sanitation methods to degrade pathogens and organic

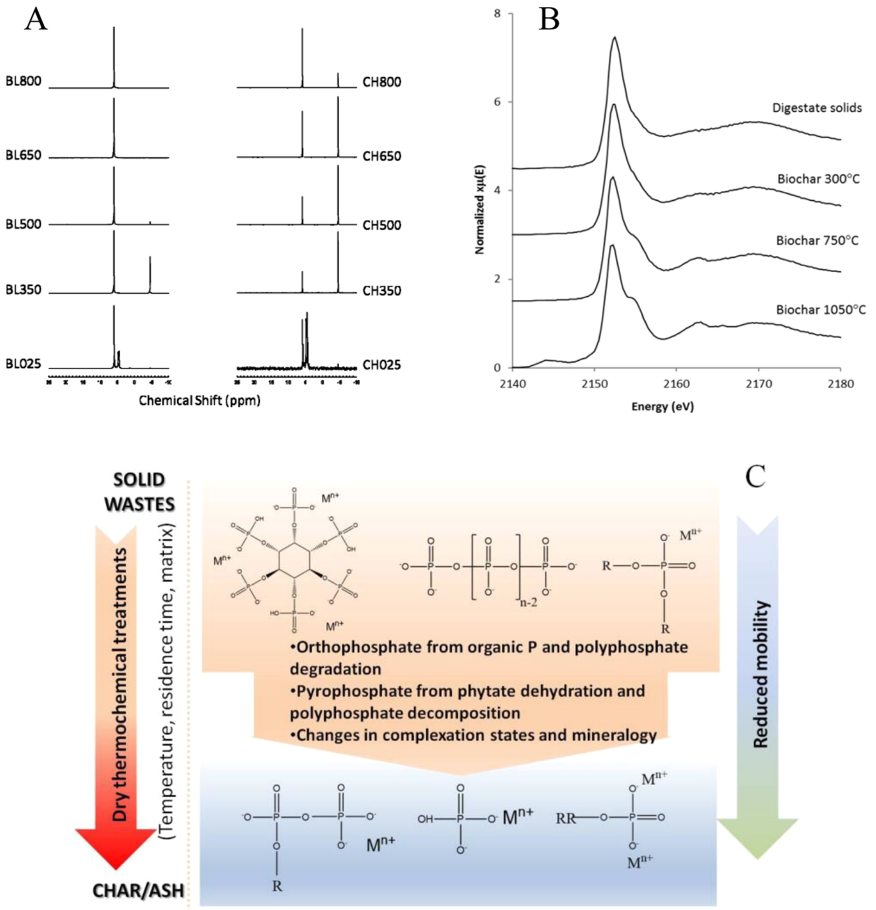

Figure 4. (A) ^{31}P NMR spectra of solution extracts from raw broiler litter (BL025) and cottonseed hull (CH025) and their pyrolyzed biochars produced at 350, 500, 650, and 800 °C. (B) P K-edge XANES spectra of pyrolyzed biochar produced from the solid residue of anaerobically codigested animal slurry (75%, pig and dairy farms) and food waste (25%).[85] Linear combination fitting revealed the transformation of $CaHPO_4$ (representing soluble Ca phosphate species) into apatite (representing insoluble Ca phosphate species). (C) Schematic illustration of the primary transformation pathways of representative P species during dry thermochemical treatments. Panel A was adapted from Uchimiya et al.,[82] copyright 2014 American Chemical Society. Panel B was adapted from Bruun et al.,[85] copyright 2017 Elsevier.

contaminants. Studies have shown that organic contaminants in sewage sludge can be significantly degraded after HTC treatment, with more than 90% of common pharmaceuticals degraded following HTC treatment at 210 °C.[27,28]

Because (hydro)thermal techniques can achieve waste volume reduction and production of value-added materials (e.g., energy materials, functional materials),[25,26,35,71,74] they can facilitate resource recovery from biowastes and reduce the environmental burdens associated with traditional treatment methods. Extensive studies have been devoted to understand and manipulate the transformation of carbohydrates during (hydro)thermal treatments for energy recovery, and excellent reviews exist on the transformation and reaction mechanism of organic matters.[24,71,72]

In addition to the transformation of carbon, the evolution of nutrients and metals have also gained increasing interests over the past few years, because these elements also account for a significant fraction of solid biowastes.[35] Understanding their transformation during waste treatments is important for fully understanding the reaction mechanisms, and can also help optimize treatment techniques for nutrient recovery. Sections 3.2 and 3.3 summarize and critically review the transformation of P during thermal and hydrothermal treatments, including the transformation of P molecular moiety, complexation and mineralogy states, and mobility/bioavailability determined by sequential extraction.

3.2. P Transformation during Dry Thermochemical Treatments.

P Phase Partitioning. During dry thermochemical treatments, feedstock mass is fractionated into solid, liquid (water, oil), and gas phases, with their relative distributions depending on the treatment conditions (Figure 3). P remains mostly in the solid phase and its partitioning in liquid and gas phases is limited. The relative fractions of P in solid, liquid, and gas phases are related to feedstock type, P speciation, and treatment conditions (primarily temperature). For example, when pyrolyzed at 250−600 °C, P recovery in the solid phase is ~80% for wheat straw, ~100% for maize straw and peanut husk,[36] and ~100% for sewage sludges and manures.[59,77,78]

In general, organic P species are more susceptible to thermal decomposition than inorganic P species, and feedstocks containing high organic P species are more likely to release P into gas phase. Copyrolysis of organic tris(2-butoxyethyl) phosphate with lignin at 400−600 °C resulted in ~25−50% P release into the gas phase.[81] For the same feedstock, higher treatment temperatures also promote P migration into the gaseous phase. For example, P can be volatilized into gas phase during gasification,[79,80] and the main gaseous P species was PO_2^+ during gasification of biomass (900−1400 °C), whereas hydrogen phosphate and two organophosphates were also identified in the volatiles of pyrolyzed tris(2-butoxyethyl) phosphate.[79,81] However, few studies have examined P vaporization and a systematic understanding of the influencing factors is still missing.[80]

Transformation of P Molecular Moieties. Regarding the transformation of P molecular moiety during pyrolysis, several consistent trends have been observed on the effect of treatment temperature (Figure 4): (1) Organic P are decomposed even at relatively low temperatures (250 °C);[36,59,82] (2) Pyrophosphate forms during pyrolysis and is mostly abundant at medium temperature ranges (300−600);[36,82] (3) Almost all P exists as orthophosphate in pyrochars produced at high temperatures (dependent on feedstocks, mostly >700 °C).[82,83]

Organophosphates such as phytic acid are abundant in various biowastes (Figure 2) and can undergo dramatic transformations during pyrolysis, such as dehydration, decarboxylation, and polymerization.[72] These reactions can lead to the decomposition of organophosphates and formation of orthophosphates, pyrophosphates, and/or organophosphates with more condensed functional groups. For example, pyrolysis of sewage sludge and pure organophosphate led to the decrease of organophosphates and increase of inorganic phosphate;[60,81] whereas pyrolysis of tris(2-butoxyethyl) phosphate produced phosphates linked to aromatic structure.[81] In general, orthophosphates and pyrophosphates are the two main species identified in NMR analysis of the liquid extracts of pyrolyzed biochars (Figure 4A).[36,82] The formation of condensed organophosphates is a possible reason that no organophosphates were identified in liquid extracts, because they may not be extractable by NaOH/EDTA solution.

The formation of pyrophosphate has been observed for the pyrolysis of various feedstocks, including sewage sludges, animal manures (e.g., swine manures and poultry litter), and biomass (e.g., wheat straw, maize straw and corn stove).[36,59,60,82−84] Pyrophosphate typically only exist in small fractions in raw feedstocks (Figure 2A), but can readily form at temperatures above 200 °C.[30,82] Both treatment temperature and feedstock characteristics affect the abundance of formed pyrophosphate. Compared to other feedstocks, plant biomass generates higher amount of pyrophosphate and over a broader range of treatment temperatures. Pyrophosphate can account for more than 50% of the extractable P from the pyrochars of cottonseed hull and pecan shell,[82,83] and remains relatively abundant at up to 800 °C.[36] Animal manures seem to generate abundant pyrophosphate at only low temperature range (<350 °C), and little pyrophosphate is identified at high temperature ranges.[82] Pyrophosphate is most likely formed via the dehydration of two adjacent orthophosphate groups, such as those in phytic acid, as biomass (particularly the seed parts) with high phytate content tends to generate more pyrophosphate than manures and sewage sludges.[36,82] For feedstocks containing polyphosphates (mainly sludges and some types of manures) (Figure 2A), polyphosphates were found to degrade into shorter chain lengths (including pyrophosphate) during slow pyrolysis, with the chain length decreasing with increasing pyrolysis temperature.[59]

In addition to soaking temperature, other frequently investigated parameters are heating rate, soaking duration, and types of atmosphere.[83,84] Heating rate seems to have minimal effects on the decomposition of organophosphate and formation of pyrophosphate. For example, no obvious differences were observed for the liquefaction (500 °C) and flash carbonization of corn stove, sludge, and sawdust.[83] Pyrolysis under different inert atmospheres seems to have little influence on P molecular transformation. For sewage sludges pyrolyzed under N_2 and CO_2, similar P speciation and relative abundance were observed in the liquid extracts from pyrochars.[84]

P Complexation and Mineralogy. The complexation and mineralogical states of P in the treatment products differ greatly among feedstocks (Section 2.2), and their transformations largely depend on feedstock composition (e.g., metal species and content), initial P speciation, and treatment conditions. Only a few studies have investigated the transformation of P complexation and mineralogy during thermal treatments.[60,85−87] Although much still remain unknown, two general trends were observed in these studies (Figure 4):

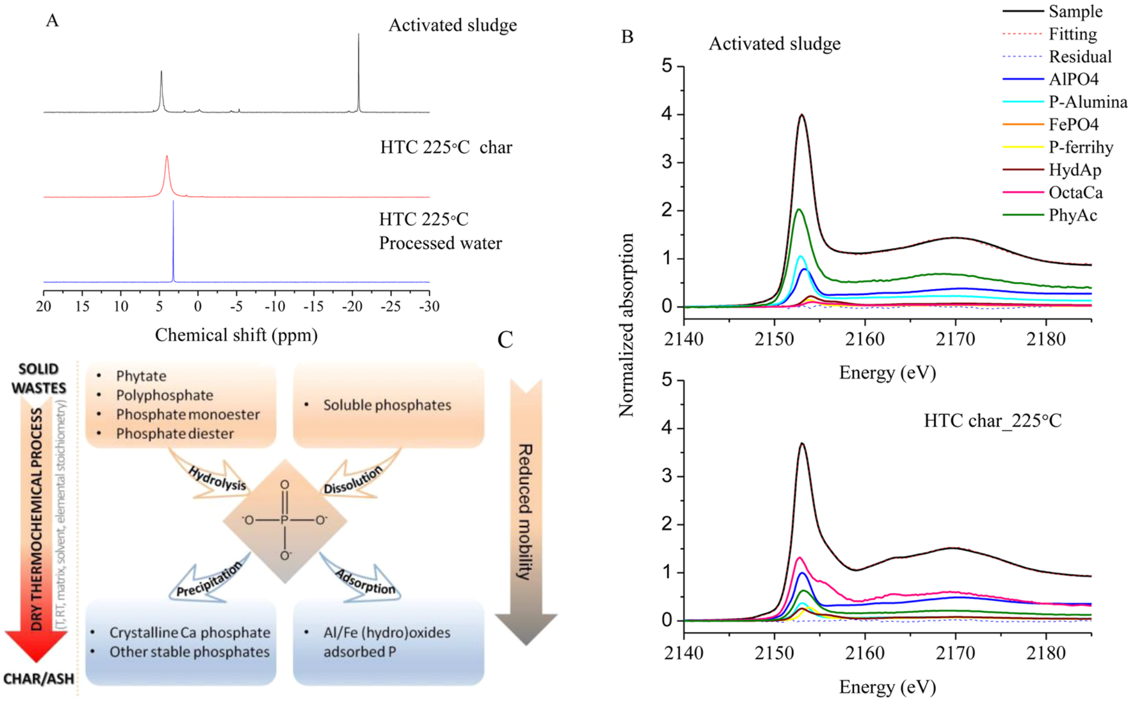

Figure 5. (A) ^{31}P liquid NMR spectra of liquid extracts from raw activated sludge and its HTC (225 °C) produced hydrochar and processed water, showing the degradation of phytic acid (representing organophosphorus) and polyphosphates into orthophosphate in both the solid and liquid products. (B) P K-edge XANES spectra of raw activated sludge and its HTC (225 °C) produced hydrochar. Linear combination fitting of the spectra showed the increasing abundance of Ca-phosphate mineral phases and phosphate sorption on Fe minerals P following HTC treatment. P-Alumina (phosphate sorption on γ-alumina), P-ferrihy (phosphate sorption on ferrihydrite), HydAp (hydroxaylapatite), OctaCa (octa-calcium phosphate), PhyAc (phytic acid). (C) Schematic illustration of the possible mechanisms involved in the transformation of P during hydrothermal treatments. Panels A and B were modified from Huang and Tang,[59,60] copyright 2015 @American Chemical Society.

(1) The decomposition of organophosphates and/or polyphosphates resulted in increasing association of P with metals or minerals. As discussed above, the decomposition of organophosphates can result in the degradation of one or more organic functional groups linked to the phosphate groups and/or the release of orthophosphates. Subsequently, the degraded organic functional groups can be substituted by metal cations, and the released orthophosphates can participate in mineral formation with metal cations or directly adsorb onto other solid phases. Similarly, fragmentation of polyphosphates into shorter chained polyphosphates and the accompanied release of orthophosphate can also create additional P–O bonds for complexation with metal cations.[60] Overall, little is known about the metal cations or minerals involved in these complexation processes, as well as the effects of feedstock characteristics and treatment conditions.

(2) Solid phase transformation of inorganic phosphates. As discussed in Section 2.2, a great portion of P in solid biowastes exists as inorganic phosphate species, likely in the forms of metal complexes, phosphate minerals, and/or mineral adsorbed species. These species can also undergo phase transformations during the anoxic heating processes, such as the dehydration of hydrated phosphate minerals and (re)crystallization of amorphous phases. For example, pyrolysis of sewage sludges showed the increase of octacalcium phosphate.[60] Pyrolysis of animal manures showed observable crystallization of Ca-phosphate phases at temperatures above 600 °C, demonstrating the importance of treatment temperature (Figure 4B).[85] Incineration of sewage sludge and model inorganic phosphate phases at 750–950 °C also showed the formation of apatite from Al and Fe phosphates and amorphous Ca phosphate phases.[87]

P Mobility and Bioavailability. Solution extraction and sequential extraction are frequently used to evaluate P mobility and indirectly probe P speciation. In general, thermal treatments reduce the amount of mobile P phases (water and $NaHCO_3$ extractable, Olsen P) and migrates more P into less mobile phases (NaOH and HCl extractable). For example, decreases of soluble and Olsen P was observed during the pyrolysis of sewage sludges,[60,77] plant biomass,[36] and animal manures.[82,88] In these cases, the fractions of HCl extractable P increased after pyrolysis, consistent with the decrease of organophosphates and increase of more crystalline Ca phosphates as revealed by P XANES analyses (Figure 4B). Such immobilization effect generally increases with increasing pyrolysis temperature.[36,82]

It is worth noting that the observed P fractionation behaviors are affected by not only P chemical speciation but also the matrix characteristics. Different feedstocks and treatment condition can produce pyrochars with varied chemical composition and structure, which can affect the physical distribution of P species and their partitioning behavior during extraction reactions. For example, although only small differences in P speciation (from P K-edge XANES and NMR) were observed after pyrolysis of sewage sludge[73] and biomass,[82] their NaOH and HCl extraction efficiencies were significantly different.

3.3. P Transformation during Wet Thermochemical Treatments.

P Phase Partitioning. Different from dry thermochemical treatments, hydrothermal treatments can migrate P into both solid and liquid phases,[89,90] because these treatments use wet feedstocks and phosphate is readily soluble. Again, the transformation of P species and their partitioning into solid and liquid phases are determined by the interplay between feedstock characteristics and treatment conditions, as discussed below.

First, feedstock composition can affect the phase migration and distribution of P. Feedstocks with high metal contents generally result in more P retention in the solid hydrochars.[89,91] This is because metals such as Ca, Mg, Cu, and Zn can form insoluble phosphate precipitates, and Fe and Al (hydr)oxide minerals have high affinities for P adsorption. For example, P recovery in HTC produced hydrochars from animal manures and sludges is commonly above 80%, whereas that for crop refinery products or algae is almost zero.[40,92,93] Moreover, similar to thermal treatments, metal-complexed and mineral-associated P species in the feedstocks can also be transformed into more stable species under hydrothermal conditions (more to follow).

Second, hydrothermal conditions (i.e., treatment temperature and duration, solid/liquid ratio, and liquid chemistry) can greatly affect the decomposition of organic P and the dissolution/precipitation of inorganic phosphate species, thus the final P speciation. HTC treatments of various animal manures showed that P recovery in the hydrochar was affected by treatment temperature, duration, solid/solvent ratio, and feedstock types.[40,94] Hydrothermal liquefaction of algae showed that P was mostly retained in the solid and liquid phases (no P in the bio-oil), with the relative abundance dependent on treatment temperature and duration.[90,95,96] Comparison of hydrothermal carbonization, liquefaction, and gasification of microalgae, digestate, and manures showed increasing P retention in the hydrochar with increasing treatment temperature.[89]

P Molecular Moieties. The transformation of P molecular moieties during hydrothermal treatments is relatively simple, compared to that of thermal treatments. Regardless of feedstock types and initial P speciation, hydrothermal treatments generally transform all the P species into orthophosphates (Figure 5).[59,91,97]

P Complexation and Mineralogy. In general, hydrothermal treatments impose more extensive alterations to P speciation than thermal treatments. Under hydrothermal conditions, reactions occur homogeneously in the mixed slurry, and the reaction intensities are also promoted by the pressurized high temperature environment. Orthophosphates dissociated from organophosphates are available for forming phosphate precipitates or adsorption to minerals. Unstable inorganic P species may also undergo dissolution and reorganization/recrystallization (Figure 5). These two processes will lead to the formation of more stable and insoluble species. Thus, P speciation in the treatment products is largely governed by the presence of P-binding metals (which determines the complexation and mineralogy state of phosphate species) and the hydrothermal conditions (which determines the stability of different P species). For example, HTC treatment of sewage sludge at 225 °C induced the increasing association of phosphate with Fe (as Fe oxide adsorbed species) and Ca (as Ca-phosphate minerals), because both cations are abundant in sludges and have high affinities for P to form precipitates and/or surface complexes (Figure 5).[60] As summarized in Section 2, Ca is dominant in most animal manures and Ca phosphate phases (mostly amorphous) are commonly found in raw manures. The transformation of Ca phosphate phases is thus an important reaction during hydrothermal processes. Indeed, the formation of crystalline Ca phosphate phases under hydrothermal conditions has been well studied in material and geothermal studies.[98,99] Apatite is the stable Ca phosphate phase under hydrothermal conditions, and can be a main form of P species in hydrochars produced from wastes containing abundant Ca.

P Mobility and Bioavailability. Results from chemical extraction or sequential extraction were also consistent with speciation results. Sequential extraction of sewage sludge hydrochars produced by hydrothermal carbonization/gasification showed significant decreases of soluble and Olsen P fractions, and increases of both NaOH and HCl fractions.[60,97] HTC of animal manures similarly reduced the soluble and Olsen P fractions, whereas most of the P partitioned in acid extractable fraction.[40,91] The abundance of NaOH fraction in hydrothermal treatment products from sewage sludges is consistent with the presence of abundant Fe and Al minerals in sewage sludges, whereas the dominance of HCl extractable fraction after hydrothermal treatments of animal manures agrees with the predominance of Ca compared to other metals in animal manures (Section 2).

3.4. Future Perspectives on the (Hydro)thermal Transformation of P.

As reviewed in Section 3.2 and 3.3, recent endeavors in studying the (hydro)thermal treatments of nutrient-rich biowastes have begun to uncover the behaviors of P during these processes. Despite the efforts on the phase partitioning and speciation evolution of P under different treatment techniques and conditions, an in-depth and systematic understanding of P transformation is still missing. Because this research direction is still at its early stage, studies to date have not covered all (hydro)thermal treatments and the broad ranges of treatment conditions, and not all aspects of P speciation were characterized in these studies. Many questions warrant further investigation, such as the effects of organic matrix on P transformation, solid state phase transformation of different inorganic phosphates, and the thermodynamics of thermochemical reactions involved in P transformation.

Moreover, technical challenges in probing P speciation in highly heterogeneous matrices such as sewage sludges and animal manures also contribute to this knowledge gap. The main technical challenges are (1) the chemical speciation of P includes not only molecular structure but also complexation and mineralogical states, and (2) most P are similarly coordinated (as tetrahedral PO_4 units), which produces relatively small changes that are not easily differentiated by spectroscopic techniques (see Section 2.3 for details). In this regard, future studies might consider well-controlled model systems to better understand the transformations of different P species and the effects of treatment conditions. For example, simulated biosolid matrix (e.g., mixtures of phytate, cellulose, and various salts) can be used to investigate the influence of individual components on P transformation. Because P speciation is closely associated with metals Ca, Fe, Al, Mg, and their minerals, quantification of metal contents and speciation can be useful for constraining P speciation results.

4. IMPLICATIONS FOR P RECLAMATION AND RECYCLING

In general, P recovery from solid biowastes can be achieved via two different strategies: reclamation of P as pure P compounds, or direct application of the P-rich products as P fertilizers

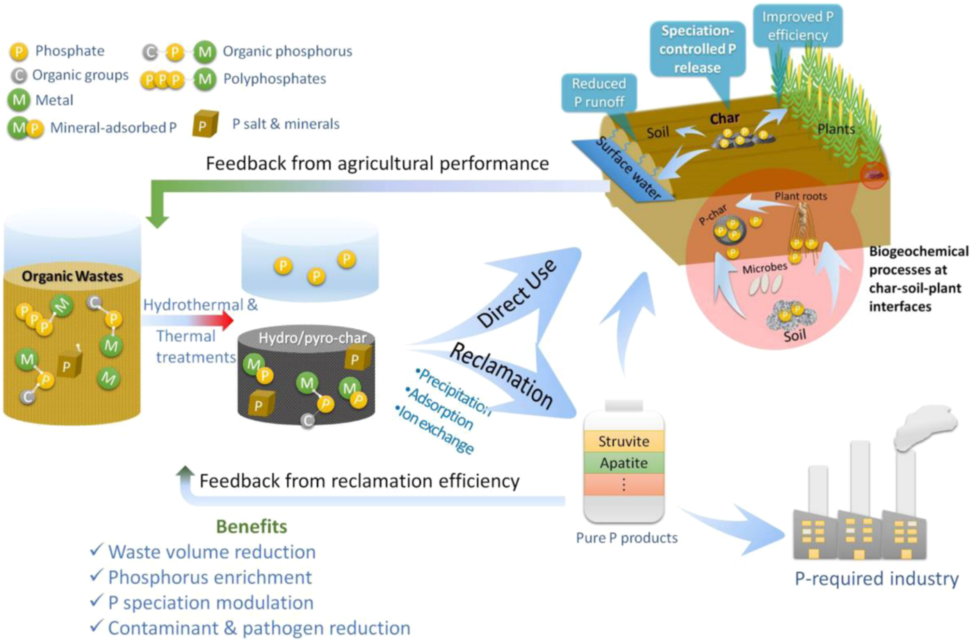

Figure 6. Schematic illustration of the potential routes for integrating P reclamation and recycling into the treatment of nutrient-rich biowastes via (hydro)thermal treatment techniques.

(Figure 6). The potentials of (hydro)thermal treatments in facilitating P recovery from nutrient-rich biowastes have been demonstrated in recent studies, and are based on two features of these techniques. They can facilitate more effective P recovery via waste volume reduction and P speciation modulation. They can also accommodate biowastes (such as sewage sludges with high contaminant contents) that are technically or environmentally unfavorable for P recovery via conventional practices (such as land applications). In the following sections, research progress in this direction is summarized and evaluated. Particularly, the critical roles of P speciation and the effects of thermochemical transformation in P recovery practices are discussed.

4.1. P Reclamation. Direct extraction and reclamation of P from raw solid biowastes are generally not effective or efficient, due to the physicochemical properties of the feedstocks (e.g., high water content, strong buffering capacity, diverse P speciation). Conventional strategies for P reclamation from solid biowastes generally involve an initial step that solubilizes P into aqueous phase (via anaerobic digestion or chemical extraction), followed by the recovery of solubilized P via precipitation (in the forms of struvite, monoammonium phosphate, or other phosphate phases), adsorption, or ion exchange.[12,100] The optimal scenario is to achieve maximum P recovery with least operational steps and low costs. Recent studies have demonstrated that (hydro)thermal treatments of biowastes have the potential to tackle these challenges for effective P reclamation.

First, (hydro)thermal treatments can significantly reduce waste volume and enrich P in the solid phase (see Section 3), allowing P extraction to be performed at smaller processing scales (less solution consumption and smaller containers). Particularly, it has been demonstrated that hydrothermal treatments can efficiently facilitate the drying of feedstocks with high water contents, by destructing cellular structure and hydrophilic groups in the biomass and release intracellular and adsorbed water. For example, sewage sludges usually contain more than 90% water following thickening. Conventional dewatering techniques (e.g., filter presses, decanter centrifuges, belt presses) can only lower the water content to about 60–75% unless further treated with thermal drying.[101,102] Sewage sludges following HTC treatment can reach a low water content of 20–30% after mechanical pressing, and with much less energy consumption compared to conventional dewatering and drying processes.[23,103,104] Hydrothermal treatments can also be applied to the drying of other wet solid wastes (such as algae, animal manures, and crop biomass), not to mention their existing applications for biofuel and chemical production.[105−107] In addition to significant volume reduction, P contents in the treated solids are also increased because P in many biowastes tends to remain in the solid phase (see Section 3.2 and 3.3).

Second, (hydro)thermal treatments can extensively destruct and transform the chemical structures of biowastes, through which the physically and chemically constrained P species can be released or become more available for extraction. For biomass with low contents of P-complexing metals, hydrothermal treatment conditions might be tuned to release P into the aqueous phase, which can be directly used as liquid P fertilizer or sources for phosphate precipitation or adsorption. For example, more than half of the total P can migrate into the aqueous phase after hydrothermal liquefaction of algae.[90,95] For feedstocks with high metal contents, P partition in the aqueous phase can be controlled by tuning the treatment conditions, such as solvent chemistry, temperature, and duration.[94]

Third, (hydro)thermal treatments can transform diverse P species in the feedstocks into orthophosphates, which can enhance P recovery via chemical extraction and subsequent precipitation, adsorption, or ion-exchange. The most desirable P species for P reclamation is orthophosphate,[12] whereas many biowastes contain significant fractions of organophosphorus species (Section 2). These organophosphorus species, even if efficiently extracted, cannot be efficiently recovered. As summarized in Section 3, various (hydro)thermal techniques can readily decompose complex P species into orthophosphates. For example, regardless of sludge or manure types and their contained P speciation, all the P were transformed into orthophosphates that mostly remained in the solid phase as metal complexes or mineral bound species, and can be efficiently extracted by acid.[40,59,60,108]

The reclaimed P can be used as raw materials for producing P-containing industrial products or directly used as P fertilizer. Extensive studies have been devoted to understand struvite formation and evaluating its value as slow release P fertilizer (see relevant references[109−113]).

4.2. Recycling through Soil Application: Improved P Efficiency and Less P Runoff? Soil applications of the products from (hydro)thermal treatments of biowastes have been proposed to serve as a carbon sequestration strategy in the context of climate change and to improve soil fertility and productivity.[114−119] Considering the critical roles of P, its cycling from these products to soils is no less important than that of carbon.[120] As analyzed in Section 1, P runoff from inefficient P fertilizer usage in agriculture is one of the main contributors to eutrophication of water bodies.[121,122] Conventional inorganic P fertilizers or biowastes (such as animal manures and biosolids) have rapid P release rates (due to highly mobile P speciation, Figure 2) that can outpace plant needs and soil retention capacity, thus causing large amount of P loss into water bodies. Thus, it is increasingly recognized that improving P fertilizer efficiency is a key to solve P runoff problems.[13,123,124] Recent studies have shown that (hydro)-thermal treatments have the potential to tackle the P runoff problems mentioned above, by modulating P speciation and properties of the solid products (more to follow).

The ultimate recyclability of P from the (hydro)thermally produced char products depends on the interplay among char, plants, and soils, and a range of biogeochemical processes, including: (1) P release from or adsorption on to chars, (2) transformation of the released P at soil−char−plant interfaces, (3) response of soil, microbial community, and plants to char application (Figure 6).

The immediate effect following soil application of the char products is the leaching of P from chars. Many studies have used simulated leaching experiments to evaluate P mobility of chars produced from a broad range of feedstocks, including crop biomass,[125,126] manures,[88,127,128] and sewage sludge.[129,130] These experiments used either pure chars or char/soil mixtures, in the presence of flow solutions with controlled compositions, and generally lasted within 1 month. Compared to that of raw feedstocks, P leaching rates from (hydro)thermally produced chars were significantly reduced.[85,88,127,128] This is consistent with chemical speciation and sequential extraction results, both showing decreased abundance of soluble and Olsen P after treatments. These leaching experiments also showed that the treatment products have low but relatively steady P leaching rates compared to the raw feedstocks.[88,126,131] In addition, adsorption of soluble P onto chars may also contribute to the reduced P leaching, because chars typically have high adsorption capacities.[130,132−134] P leaching from chars can also be affected by electrolyte type,[125] solution pH,[127,131] and dissolved organic matters.[130] For example, P leaching from rice husk biochar was found to be facilitated by anions (Cl^-, NO_3^-, and SO_4^{2-}) and inhibited by phosphate precipitating cations (Ca^{2+}, Mg^{2+}, and NH_4^+), because anions may inhibit the readsorption of dissolved P and cations can precipitate with dissolved P.[125] P leaching is generally enhanced at acidic pH range, because most P is transformed into inorganic phosphates after (hydro)thermal treatments.[127,131] P leaching experiments involving soils demonstrated the important interplays between char and soil properties, because the factors controlling P leaching (e.g., solution pH, dissolved organic matter, adsorption capacity) are influenced by both char and soils.[128,131,133,135]

Only a few studies have conducted long-term plant growth experiments to determine the actual P recyclability by plants. These studies demonstrated that P species in the chars were available to plants. Compared to controls without char application, char application generally enhanced plant growth and P uptake by the plants.[126,136−138] In addition to the physicochemical processes governing P release from chars and availability in soil solutions, other factors become more important, such as the alteration of soil properties by chars (e.g., release of char components and their interaction with soils), change of microbial community and activities,[135,139,140] and the response of plants to the modified soil environments.[141,142]

In summary, studies to date have revealed P leaching behaviors from various (hydro)thermal treatment products and the factors governing these processes. Studies have also demonstrated the potential of (hydro)thermal treatment products as alternative P fertilizers, in terms of P supply and crop growth enhancement. P speciation and the physicochemical properties of the products play pivotal roles in these aspects, because they control the types of P species (e.g., orthophosphate, organophosphate, and pyrophosphate) that can be released, and the release kinetics and extents under specific conditions (Figure 6). In addition to other benefits such as effective decontamination and volume reduction, the advantages of (hydro)thermal treatments in this aspect include: (1) they are highly tunable to modulate P speciation and mobility in the products, leading to slow P release rate and potentially high P recyclability; and (2) the overall properties of the treatment products might be tuned for their usage in different soil types. These advantages can potentially enhance the recycling of more biowastes and the recyclability of P in these wastes. Because the recyclability of P in (hydro)thermal treatment products (in terms of P percentage used by plants compared to runoff) is determined by complex processes in soil environments, future studies are needed to quantitatively measure the P recyclability of the products and explore the governing factors and mechanisms. Results from these studies can provide useful feedbacks for the optimization of (hydro)-thermal treatments for this purpose (Figure 6).

4.3. Future Perspectives on P Reclamation and Recycling. Previous studies have demonstrated the potentials of (hydro)thermal treatments in facilitating P reclamation and recycling, and the critical role of P speciation in these processes. Further studies are needed to technically improve the application of these techniques for P reclamation and recycling. Regarding the application for P reclamation, (1) the treatment and P reclamation processes need to be integrated and optimized to efficiently recover P at low cost. For example, whether precipitation or adsorption is a better P reclamation option for the processed water and extracts from different HTC conditions needs to be tested; (2) because heavy metals commonly present in some feedstocks (e.g., sewage sludges), the treatment and reclamation methods need to be optimized to minimize metal contents and/or bioavailability in the reclaimed P products.

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Regarding soil application of (hydro)thermal treatment products as a P recycling strategy, further research efforts are needed to gather relevant information to evaluate the economic and environmental benefits and provide guidance for regulations and usages. (1) A systematic comparison of products from different treatment conditions and their correlations to P speciation is needed. Particularly, most studies focused on products from pyrolysis (pyrochar or biochar), whereas very few focused on products from hydrothermal treatments (hydrochar). In addition, P speciation in the products were rarely characterized and related to the product performance. This information is necessary for providing feedbacks for waste treatment processes, in order to select the optimal treatment technique and condition. (2) In order to evaluate the overall benefits of soil application of the treated products, measurements on the recycling of other nutrients, carbon sequestration potential, and crop productivity should also be conducted and compared to those of conventional fertilization strategies. (3) Standardized test procedures need to be developed in order to generate quantitative parameters that will allow the comparison among different studies. For example, in existing literature, different leaching protocols (e.g., different leaching solutions and soil mixing ratios) were used for the assessment of P mobility, and different soil and plant tests (e.g., different application levels, plant species, and sampling intervals) were used in evaluating the fertilizer potentials of waste treatment products.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b02011.

> Data of major element contents, sequential fractionation of P, and P speciation (by ^{31}P liquid NMR) in various biowastes compiled from previous studies (PDF)

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Notes

The authors declare no competing financial interest.

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