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Phosphorus transformation during HCl and NaOH assisted microwave hydrothermal conversion of sewage sludge

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ABSTRACT

Due to the global shortage of P ore, it is critical to reclaim P from sewage sludge. This study investigated the transformation mechanism of P from sewage sludge during HCl and NaOH assisted microwave hydrothermal (MHT) conversion process. The results revealed that the MHT process enhanced the aromaticity and reduced the polarity of the solid products. The addition of HCl or NaOH can promote the release of P into the MHT liquid products. NaOH can facilitate the transfer of Al/Fe-mineral adsorbed P into the MHT liquid products. The addition of HCl during the MHT process can promote the dissolution of mineral P in the sewage sludge. The orthophosphate diester transformed to orthophosphate with the addition of NaOH in the MHT process, while the addition of HCl facilitated the formation of polyphosphate in the solid products. P K-edge X-ray absorption near edge structure (XANES) analysis demonstrated that the Ca-P minerals decreased first and then increased with the MHT temperature from 120 to 220 °C. The extend of MHT holding time at 170 °C can promote the dissolution of Ca-P minerals in the solid products. The addition of HCl in the MHT process enhanced the release of Ca-P minerals, while NaOH can promote the formation of Ca-P minerals in the solid products. This study provides fundamental knowledge on P transformation during MHT processes for the design of treatment methods to utilize P in sewage sludge.

1. Introduction

Phosphorus (P) is an essential nutrient for all living organisms, and it also plays a vital role in modern industry [1]. With the continuous increase in global population, the demand for P in agricultural and industrial sectors is growing gradually. Traditional supply of P largely relies on the mining of phosphate ore, a finite and nonrenewable resource. It is predicted that the global P rock resources will be exhausted within 100 years [2]. In addition, the global distribution of P ore is extremely uneven, with more than 70 % phosphate rock reserved in Morocco and Western Sahara [3]. Furthermore, the utilization efficiency of P minerals is low. It is reported that approximately 1.3 million tons of P are removed and lost during wastewater treatment every year globally [4]. Excessive discharge of P can also lead to eutrophication and biodiversity deterioration of aquatic environment [5]. The eutrophication phenomenon was once perceived as a pollutant due to the excessive proliferation of algae in the Northern Adriatic Sea, which degraded the water quality, benthic habitats, and community structures [6]. Therefore, it is crucial to remove and recover P from waste streams for sustainable development and environmental remediation.

Waste water treatment plants (WWTPs) is an important sector for the recovery of P, which is estimated to meet 15 %–20 % of the global P demand [1]. P can be recovered at WWTPs by different technologies, such as biological processes, chemical precipitation, or crystallization [7,8]. Sewage sludge is the major byproduct of WWTPs, which accumulates more than 90 % of P from wastewater [9]. Therefore, P recovery from sewage sludge holds great potential. However, due to its diverse sources, sewage sludge exhibits a highly complex composition. Multiple media (solid, liquid, and gas) and various interactions (organics-inorganics) are existed in the sewage sludge system. It contains inorganic minerals, various transition metals, microorganisms, biomacromolecules, toxic organic contaminants, etc. In addition, the water content of sewage sludge is very high (> 80 %), leading to unstable and changeable property [10,11]. It is important to find an effective way to dispose sewage sludge while reclaiming valuable resources such as P.

The traditional methods for treating sewage sludge includes landfill, anaerobic digestion, incineration, and so forth [6,12]. Landfill of sewage sludge occupied large area of land, and it may cause serious problems on

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soil contamination and odor gas emission. Anerobic digestion can convert sewage sludge to biogas, but it needs a long processing time and the system is vulnerable to the changes of surrounding environment. Incineration can obtain the best volume reduction of sewage sludge, but it consumes large energy. Hydrothermal conversion has emerged as a promising way to treat biomass wastes with high water content. The wet biomass wastes were exposed to high temperature and autogenous pressure in hydrothermal treatment, and the biomass were converted into high-value byproducts through energy densification, carbon concentration, and oxygen elimination [13]. During the hydrothermal process, the water in sewage sludge serves as both reaction medium and reactant, promoting the polymerization, decarboxylation, dehydration, and hydrolysis reactions [14]. Numerous studies have investigated the properties of sewage sludge hydrochar produced by hydrothermal processes [15–18]. The characteristics and distribution of the hydrothermal products depend on various factors, including temperature, pressure, reaction time, liquid to solid ratio, acidic-basic treatment, addition of additives, etc. Reaction temperature is the most critical parameter affecting the reaction mechanism and product characteristics [19,20]. The transformation of P during hydrothermal conversion also gained great interest. It was shown that most P is retained in the hydrothermal solid product, and organic P and pyrophosphate can be converted into orthophosphate after the hydrothermal process [21]. In addition, P species in hydrothermal products are affected by the chemical of sewage sludge and hydrothermal conditions [22].

Compared with conventional hydrothermal conversion, microwave hydrothermal conversion of biomass wastes has attracted extensive attention. Microwave treatment has the advantages of rapid heating combined with better penetrability [23]. Microwave hydrothermal conversion has been widely applied in the disposal of lignocellulose. It exhibits higher process efficiency and improved product yield and quality [20]. Recently, there are also some studies on the microwave hydrothermal conversion of sewage sludge. These studies mainly focused on the decomposition of organic matters, the properties of hydrochar, and dewaterability. For example, Chen et al. found that increasing microwave power can improve the yield of bio-oil from sewage sludge [23]. Wang et al. demonstrated that the hydrochar products have higher aromaticity, carbonization degree, porosity, and polarity than the raw sewage sludge [20]. Rao et al. showed that microwave irradiation can be used to synchronously evaporate water and reduce the bound water of sludge [24]. Microwave hydrothermal conversion is an advanced technology for the disposal and recycling of sewage sludge. However, there is very limited research on speciation evolution and transformation of P during microwave hydrothermal conversion of sewage sludge.

In this study, we investigated the effect of different microwave hydrothermal conditions, including temperature, holding time, acid additive, and alkaline additive on the reaction mechanism and P transformation of sewage sludge. To identify the P speciation and associated reaction mechanisms, a suite of complementary characterization techniques was conducted, including Hedley's sequential chemical extraction, ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectroscopy, and P K-edge X-ray absorption near edge structure (XANES) spectroscopy. Since the transformation of P during the microwave hydrothermal conversion process is highly related to some metal elements, inductively coupled plasma mass spectrometry (ICP-MS) was conducted to test the metal elements concentration of the hydrothermal liquid products. The results provide fundamental knowledge and insights for the recovery and reutilization of P from sewage sludge.

2. Materials and methods

2.1. Sewage sludge

The sewage sludge with a water content of 80 % and ash content of 27.6 % was obtained from F. Wayne Hill Water Resources Center (Buford, Georgia, USA). Details of the facility can be found in our previous studies [25,26]. Primary (physical), secondary (biological), anaerobic digestion, and tertiary treatments are conducted in the center. The primary sludge and waste activated sludge are treated by enhanced biological phosphorus removal. The sludge was formed after anaerobic digestion of primary and secondary sludge, as well as the mixing of chemical sludge from the tertiary treatment. The final sewage sludge used in this research was collected after centrifuge dewatering. Detailed contents of metal elements are shown in Table S1.

2.2. Microwave hydrothermal treatment

Microwave hydrothermal treatment (MHT) of sewage sludge was conducted in Teflon reactors with a total volume of 50 mL (Anton Paar Multiwave 5000, Austria). In each experiment, sewage sludge of 20 g was added to the reactor. To obtain the subcritical hydrothermal condition, as well as to study the effect of temperature and holding time on the hydrothermal performance, the MHT processes were performed with different temperatures (120, 170, and 220 °C) and the same holding time (60 min), or with different holding time (10, 60, and 120 min) at the same temperature (170 °C). In addition, MHT processes with different HCl and NaOH contents were also conducted at 170 °C and a holding time of 60 min. The heating time of each experiment was uniformly set as 10 min. After the MHT processes, the reactors were slowly cooled down to 60 °C. The MHT products were then collected and separated by centrifugation (10,000 rpm, 10 min). The liquid products were filtered and stored at 4 °C for further analysis. The solid products were dried in an oven (80 °C, 24 h), then ground to fine powder for further analysis.

2.3. Sequential chemical extraction using Hedley's method

Hedley's method is widely used to characterize P speciation in sewage sludge [27–29]. Raw sewage sludge and MHT solid products were sequentially extracted by deionized water, 0.5 M $NaHCO_3$, 0.1 M NaOH, and 1.0 M HCl. All extraction steps were conducted on a shaker (200 rpm) at 25 °C for 16 h. The P concentration of the supernatant collected after extraction was detected in triplicate using the molybdenum blue method on an UV–vis spectrometer [30].

2.4. ^{13}C solid state NMR analysis

The C speciation of the sewage sludge and the MHT solid products were investigated using ^{13}C solid state NMR. The NMR data were collected using a Bruker AVIII HD 300 spectrometer operating at a ^{1}H frequency of 300 MHz. A fine powder of the sample was packed into a 4 mm diameter zirconia rotor with Kel-F cap. A ramped cross polarization pulse program coupled with magic angle spinning at a rate of 10 kHz was conducted. The spectra were obtained at a ^{13}C frequency of 75.5 MHz, with a contact time of 3 ms, and a repetition delay of 4 s. The ^{13}C chemical shifts are referenced to adamantane.

2.5. ^{31}P NMR analysis

Solid state ^{31}P NMR was used to identify P speciation in the raw sewage sludge and MHT solid products. Direct polarization data were collected by a Bruker AVIII HD 300 spectrometer. The spectra were obtained at a ^{31}P frequency of 121.5 MHz, with a repetition delay of 4 s. The magic angle spinning rate was set as 10 KHz. The ^{31}P chemical shifts presented here are referenced to $NH_4H_2PO_4$.

2.6. ^{1}H—^{31}P 2D NMR analysis

The ^{1}H—^{31}P heteronuclear correlation 2D NMR spectra were performed to further illustrate the P speciation in the raw sewage sludge and MHT solid products. Data were collected on a Bruker AVIII 400

spectrometer, with the magic angle spinning rate of 12 kHz using a phase modulated Lee Goldberg sequence in the indirect ^{1}H dimension followed by cross polarization and detection to ^{31}P. The spectra were obtained at a ^{1}H frequency of 400.3 MHz, a ^{31}P frequency of 162.0 MHz, and a repetition delay of 4 s. The contact time of 500 μs for cross polarization was used as a compromise to achieve a reasonable signal to noise, while setting the contact time as short as possible such that only correlations between ^{1}H and ^{31}P sites in direct vicinities are observed. The ^{1}H and ^{31}P chemical shifts are referenced to $NH_4H_2PO_4$.

2.7. P K-edge XANES analysis

The P K-edge XANES data of the sewage sludge and MHT products were obtained at 4B7A beamline of Beijing Synchrotron Radiation Facility. The sewage sludge and MHT solid products were ground into fine powders and brushed evenly on conductive tape sticked to a sample holder. The XANES data were obtained in fluorescence mode using a Si drift detector (Si111). The reference compounds included $Mg_3(PO_4)_2$, $AlPO_4$, $FePO_4$, $Ca_8H_2PO_4{\cdot}6.5H_2O$ (OCP), and $Ca_5(PO_4)_3(OH)$. All the XANES spectra were collected from 2120 to 2200 eV. The data collection and analysis methods followed our previous study [31].

2.8. ICP-MS analysis

The metal elements concentration of the MHT liquid products was detected by an inductively coupled plasma mass spectrometry (Agilent, 7500a). Each sample was tested in duplicate, and the average was performed.

3. Results and discussion

3.1. Reaction mechanism of sewage sludge during the MHT process

Fig. 1 presents ^{13}C NMR spectra of the sewage sludge and different MHT solid samples. The chemical structure and properties of sewage sludge changed obviously after the MHT processes. The original sludge is mainly composed of carbohydrates, proteins or peptides, humic substances, lipids (e.g., fatty acids or fats), lignin, etc. The peaks at 23 and 32 ppm were assigned to methyl carbons (CH_3) and mobile methylene carbons (CH_2), respectively [32]. The peak at 55 ppm represents alkyl carbon substituted by oxygen or nitrogen atoms, e.g., methoxyl group (O-CH_3) or NCH. The alkyl carbon singly bonded to one oxygen atom was identified by the peak at 73 ppm, which can be attributed to O-alkyl in carbohydrate-like structures. The peak at 104 ppm, which was characterized as alkyl carbon bonded to two oxygen atoms, indicating the existence of O-C-O in carbohydrates. The peak at 130 ppm was related to proton and alkyl-substituted aromatic carbon. The peak at 173 ppm represented carboxyl, ester, and amide carbon, e.g., COO and N-C=O [33]. Generally, the ratio of peak integrals in ^{13}C CP-MAS spectra does not reflect molar ratios. However, comparing changes in

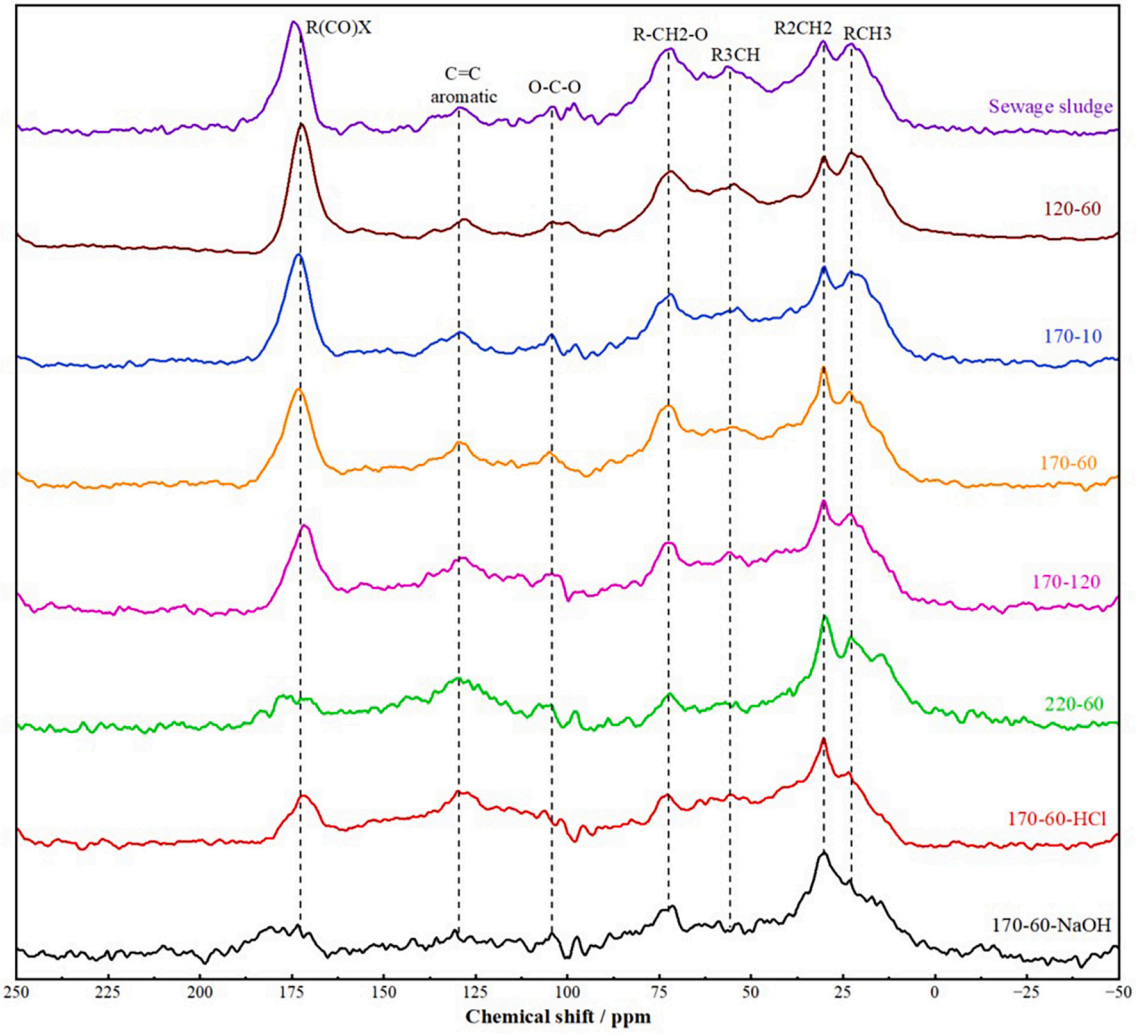

Fig. 1. ^{13}C NMR spectra of the sewage sludge and MHT solid products.

relative peak intensities in a defined series of samples such as ours provides semi-quantitative to qualitative results. It can be found that the peak intensity of oxygen-containing groups decreased gradually with the increase in MHT temperature and holding time, while the peak intensity of methyl carbons, mobile methylene carbons, and aromatic carbon increased. This indicates that the carbohydrates, proteins, and lipids hydrolyzed and decomposed into small monomers under the subcritical water conditions. In addition, the MHT processes enhanced the aromaticity and reduced the polarity of the solid products.

With the same MHT temperature (170 °C) and holding time (60 min), the addition of HCl (pH = 3.54) and NaOH (pH = 11.22) further decreased the peak intensity of oxygen containing groups, and the peaks assigned to methyl carbons and mobile methylene carbons were enhanced. The peak intensity of carboxyl, ester, and amide carbon was lowest in the solid product under NaOH enhanced MHT treatment. This is because the alkaline condition generated by NaOH during the MHT process can facilitate the hydrolysis and decomposition of organic matters, including carbohydrates, proteins, and lipids [34].

Table S2 presents the water and ash contents of the sewage sludge and MHT solid products. The water content of the MHT solid products decreased gradually with increasing temperature and holding time. The water content of the samples without any additives is the lowest at 220 °C (65.1 %) with a holding time of 60 min, which is much lower than that of the original sewage sludge (80.0 %). Water within sewage sludge can act as a good absorber of microwave irradiation, which enhances the rotation of water molecules. Consequently, the binding force between extracellular polymers and water molecules reduced, leading to the release of bound water [35]. In addition, the high-frequency electric field can destroy the stable structure of the sewage sludge, thereby making it easier to be dewatered [36]. The addition of NaOH can further promote the dewaterability of sewage sludge, which may lead to enhanced hydrolysis of sewage sludge during the MHT process.

The ash content of the MHT solid products increased after the MHT processes. With increasing temperature, the ash content increased from 34.9 % (120 °C) to 45.1 % (220 °C). The increase in MHT holding time also facilitated the increase of ash content. This is due to the dissolution and release of organic matters in sewage sludge, as well as the substantial reduction of volatile matter. However, minerals phases were relatively stable during the MHT process, leading to the increase in ash content. This result is consistent with the NMR results as discussed above.

The addition of HCl in the MHT process decreased the ash content in the solid product, indicating the release of inorganic substances into the liquid products. In contrast, the MHT solid product with NaOH addition obtained the highest ash content (50.3 %), which is likely due to the enhanced effect of NaOH on the organic hydrolysis of the sewage sludge. In addition, NaOH can also facilitate the precipitation of some minerals in the solid product, leading to the increased ash content.

3.2. Effect of MHT conditions on P transformation

3.2.1. P content and distribution of MHT products

As shown in Fig. 2, with the same MHT holding time of 60 min, the P concentration of the liquid products increased from 183.1 to 223.3 mg/L as the temperature increased from 120 to 170 °C, but decreased to 105.1 mg/L as the temperature further increased to 220 °C. At the same MHT temperature of 170 °C, the P concentration increased from 112.5 to 223.3 mg/L as the holding time increased from 10 to 60 min, but then decreased to 129.8 mg/L as the holding time further increased to 120 min. In addition, the P content of the solid products increased with the increase in MHT temperature and holding time. During hydrothermal conversion process, reactions such as hydrolysis, dissolution, adsorption, and precipitation occurred on phosphates [37]. Within a certain range, the increase in MHT temperature and holding time can promote the hydrolysis and dissolution of P into the liquid products, leading to the increased P concentration of the liquid products. When the

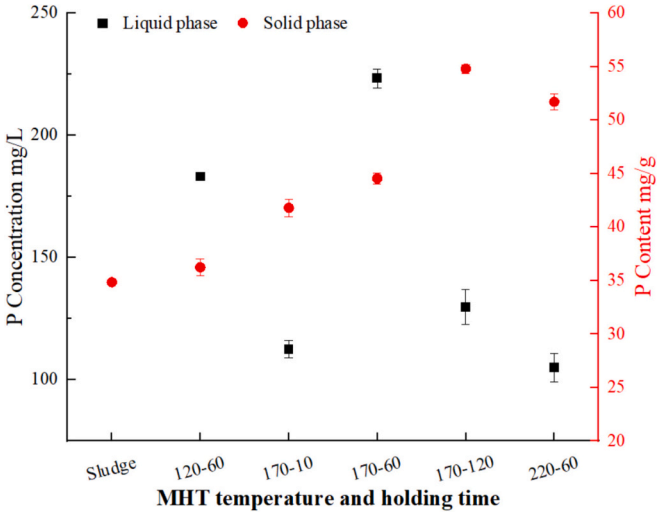

Fig. 2. Effect of temperature and holding time on P contents of the MHT products.

temperature and holding time further increased, the increased metal ions activity can promote precipitation, surface adsorption, and complexation [37]. Therefore, the released P would transfer to the solid products, resulting in increased P content of the solid products. As shown in Table. S3, the concentration of Mg, Al, Ca, and Fe in the hydrothermal liquid products decreased from 108.6 mg/L, 35.96 mg/L, 86.98 mg/L, and 67.93 mg/L to 64.21 mg/L, 10.81 mg/L, 44.53 mg/L, and 38.76 mg/L with the temperature increased from 170 °C to 220 °C. It indicates that the dissolved phosphate in the liquid products further precipitated with some metal ions at the temperature of 220 °C. Even though the effect of MHT temperature and holding time was obvious on the changes of P concentration in the hydrothermal products, there is no obvious change in the distribution of P. As presented in Table. S4, most P was distributed in the hydrothermal solid products. This is because the P concentrations of the solid products were much higher than that of the liquid products, implying the enrichment effect of P in the solid products during the MHT process.

To further investigate the transformation of P during MHT conversion process, the effect of pH with different HCl or NaOH addition were investigated. As shown in Fig. 3 and Fig. 4, with the different addition of HCl and the pH value decreased from 6.92 to −0.05, the P concentration of the liquid products increased from 223.3 mg/L to 6876.8 mg/L, and the P distribution in liquid products increased from 1.0 % to 97.9 %. With the different addition of NaOH and the pH value increased from 6.92 to 14.48, the P concentration of the liquid products increased from 223.3 mg/L to 5080.3 mg/L, and the P distribution of the liquid products increased from 1.0 % to 51.4 %. When the addition of NaOH further increased and the pH value increased to 14.53, the P concentration and distribution of the liquid product decreased to 4099.8 mg/L and 41.5 %, respectively. It indicates that the increase in HCl addition and the decrease in pH value can promote the release of P into the MHT liquid products continuously. However, the P concentration and distribution of the liquid products increased first and then decreased with the increase in NaOH addition and the pH value. This is mainly due to the precipitation of the released P and metal ions into the solid product under highly alkaline environment. The changes of P speciation and the associated transformation mechanism during the MHT processes are discussed below.

3.2.2. P speciation changes after MHT processes

Based on Hedley's sequential extraction method, the P extracted from the four steps corresponds to readily soluble P (extracted by H_2O), exchangeable P (by $NaHCO_3$), Al/Fe adsorbed P (by NaOH), and mineral

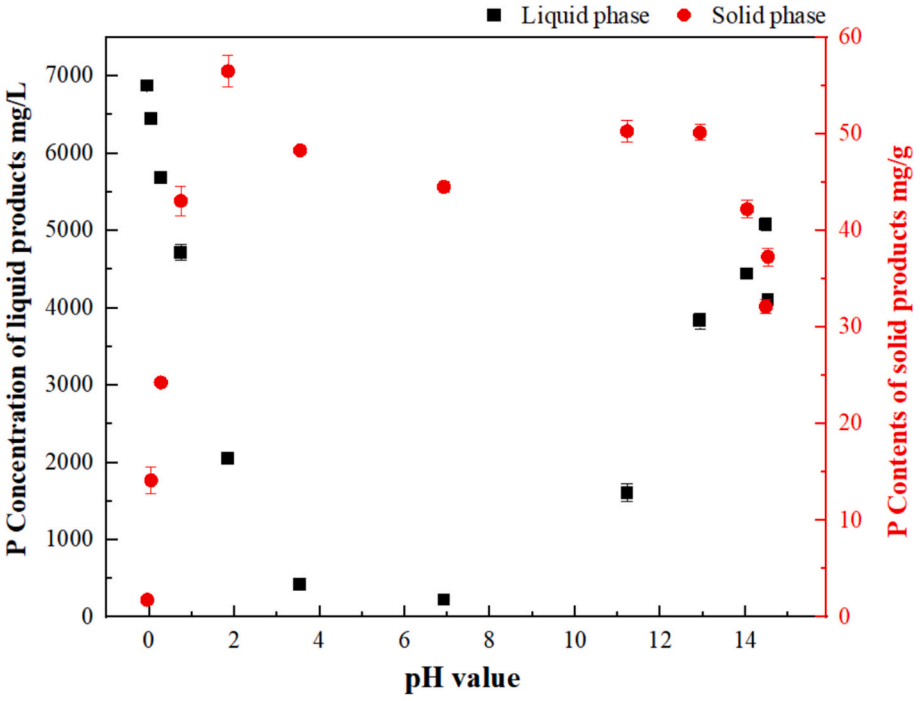

Fig. 3. Effect of pH on P contents of the MHT liquid and solid products.

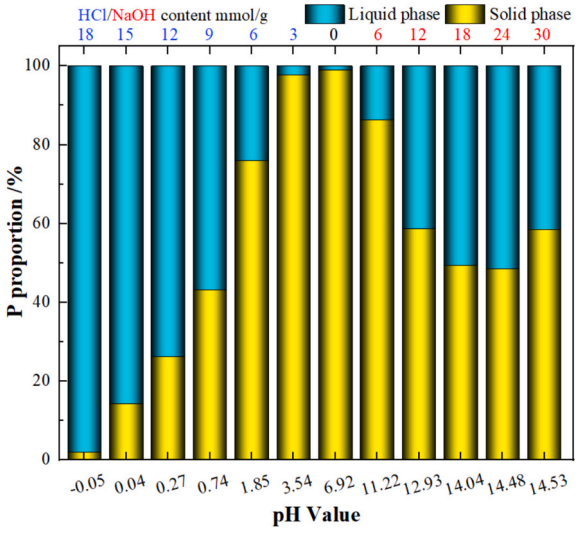

Fig. 4. Effect of pH on P distribution in the MHT liquid and solid products.

P (by HCl). [22,38] It can be found from Fig. 5 that, Al/Fe adsorbed P was the majority species in the sewage sludge (57.1 %). The proportion of mineral P was the second largest (30.4 %), which was much higher than that of readily soluble P (5.32 %) and exchangeable P (7.23 %). The content and proportion of readily soluble P and exchangeable P decreased after the MHT process, except for the sample treated by NaOH. With the MHT temperature increased from 120 to 220 °C, the proportion of mineral P increased from 36.4 % to 56.5 %, while the proportion of Al/Fe adsorbed P decreased from 55.3 % to 38.4 %. With the same MHT temperature of 170 °C, the proportion of Al/Fe adsorbed P decreased from 47.7 % to 39.5 % as the holding time increased from 10 to 120 min, and the mineral P proportion increased from 47.8 % to 55.0 %. This indicates that the increase in MHT temperature and holding time can promote the transfer of Al/Fe adsorbed P to mineral P. The adsorbed P on Al/Fe oxides would firstly be released to the liquid products, and

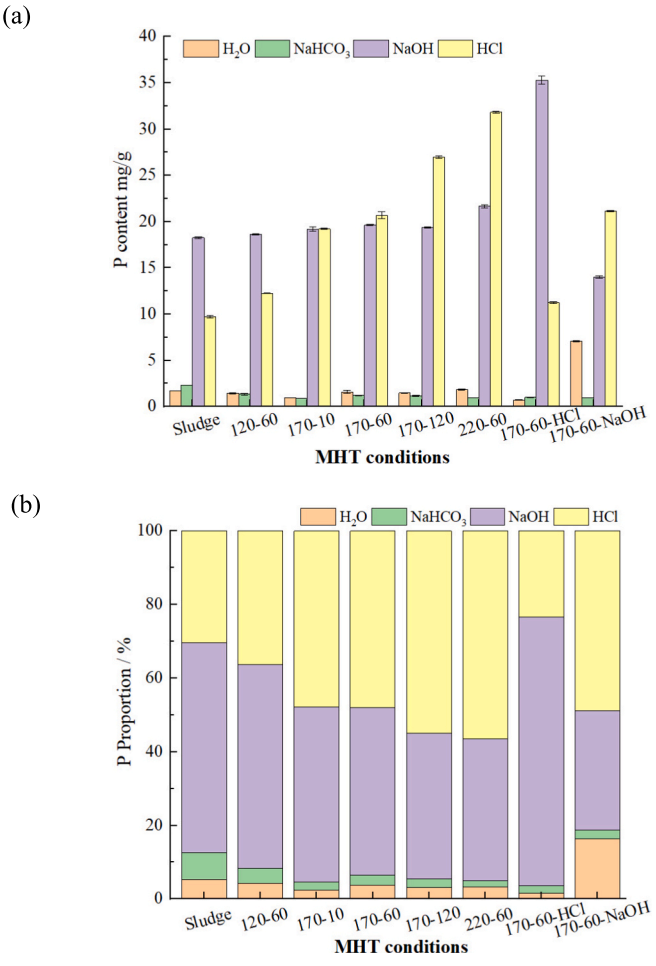

Fig. 5. Effect of MHT conditions on the concentration (a) and relative percentage (b) of different P species in the solid products.

then precipitate with Mg or Ca ions to form more stable mineral P. It is reported that H_2O-P and $NaHCO_3$-P can be categorized as labile P, while NaOH-P and HCl-P are classified as moderately labile P and non-labile P, respectively [39]. Therefore, the high temperature and long holding time of the MHT process can promote the transformation of labile P to non-labile P.

It is worth noting that the MHT process with HCl addition (pH = 3.54) decreased the proportion of mineral P (23.3 %). This is because the mineral P, including some Ca and Mg associated phosphate, becomes soluble under acidic condition [40]. The released phosphate further absorbed on some Al/Fe compounds, leading to the increased proportion of Al/Fe adsorbed P (73.1 %). Furthermore, the addition of NaOH in the MHT process (pH = 11.22) significantly decreased the concentration and proportion of Al/Fe adsorbed P, and increased the content of readily soluble P. This is because NaOH can promote the decomposition of organic matters, and the Al/Fe adsorbed P was desorbed under the alkaline condition. Therefore, the P concentration of the liquid products increased significantly, and the readily soluble P of the solid product also increased.

3.2.3. ^{31}P NMR analysis of sewage sludge and MHT solid products

Solid state ^{31}P NMR is a critical tool for characterizing P speciation in sewage sludge due to the relatively high P content. It is a non-destructive technique that requires minimum sample preparation [41]. In addition, the presence of Fe in organic matter may not influence the line-width of ^{31}P spectra [42]. As shown in Fig. S1, sewage sludge consists of orthophosphate, phosphate monoester, phosphate diester, and pyrophosphate. At 120 °C, there is no significant changes of P speciations in the MHT solid products. When the temperature increased to 170 and 220 °C, the spectra shifted to pyrophosphate area, suggesting the transformation of phosphate monoester and phosphate diester to pyrophosphate with the increase in MHT temperature. At the MHT temperature of 220 °C, there is also an obvious shoulder peak at orthophosphate area, indicating that high MHT temperature can further promote the decomposition of organic phosphate and pyrophosphate to orthophosphate. This result is different from some previous literature. Some studies have found that orthophosphate was the principal P species in the sewage sludge and hydrochar [43,44]. This is because the P species of hydrochar was extracted to test liquid state NMR in the literature. It is inevitable that some recalcitrant P species still remained in the hydrothermal solid products. Solid state NMR can detect the P species directly, thereby avoiding the issue of incomplete extraction of P species. With the addition of NaOH (pH = 11.22), the spectra shifted to the orthophosphate area. It indicates that the addition of NaOH during the MHT process can facilitate the decomposition of organic phosphate to orthophosphate even in the low MHT temperature (170 °C). When HCl was added in the MHT process (pH = 3.54), polyphosphate was the dominant P speciation. This is mainly because of the catalytic reaction of protons in the acidic MHT process, which facilitated the formation of polyphosphate from orthophosphate. The detailed reactions were shown in Fig. S2. With the pH value of 3.54, orthophosphate is mainly in the form of $H_2PO_4^-$ [45]. Upon the influence of protons, the orthophosphate was initially protonated to form a transient orthophosphate species. Subsequently, the water molecule was stripped from the protonated intermediate to form metaphosphate (HPO_3). Secondly, the metaphosphate reacted with $H_2PO_4^-$, leading to the formation of pyrophosphate and the release of H^+. Thirdly, the pyrophosphate was attacked by protons and formed instantaneous protonated pyrophosphate, which subsequently underwent dehydration to yield $HP_2O_6^-$. Finally, the $HP_2O_6^-$ reacted with $H_2PO_4^-$, resulting in the formation of polyphosphate and the release of H^+. In this process, protons reacted as a catalyst, promoting the formation of polyphosphate. Chtouki et al. presented that ammonium polyphosphate is produced from aqueous phosphoric acid and gaseous ammonia at elevated temperatures. Water molecules were driven off and orthophosphate molecules began to link together to form pyrophosphate, and then tripolyphosphate [46]. To further illustrate the P speciation changes during the MHT process, ^1H - ^{31}P 2D HETCOR NMR spectra were performed.

Fig. 6 displays the ^1H - ^{31}P 2D HETCOR NMR spectra recorded from the sewage sludge and MHT solid products. These spectra provide spatial information on the proximity between protons and phosphate species through pairwise correlations observed at specific 2D coordinates. The corresponding 2D projections display the ^1H (vertical) and ^{31}P (horizontal) spectra, highlighting only those resonances that reflect sufficiently strong ^1H—^{31}P interactions. A “strong” (or “weak”) ^1H—^{31}P contact suggests a short (or long) internuclear distance and/or a higher (or lower) local proton density in the vicinity of ^{31}P nuclei [47]. The signal appearing at δ_H = 0–2 ppm represents PO_4^{3-}/OH corresponding phosphate, and the signal with δ_H = 2–6 ppm is assigned to PO_4^{3-}/H_2O phosphate and PO_4^{3-}/CH_n phosphate, manifesting some hydrated phosphate and organic phosphate. Based on the 2D NMR spectra, the original sewage sludge consists of hydroxyl phosphate, hydrated phosphate, and organic phosphate. After the MHT process (170 °C, 60 min), the signal feature of the 2D NMR spectra attenuated significantly, especially for the hydrated phosphate and organic phosphate, indicating the dehydration and decomposition effects of MHT process on sewage sludge. With the addition of NaOH in the MHT process, hydroxyl orthophosphate was the principal P species. It further verified that NaOH can enhance the transformation of organic P into inorganic P. The addition of HCl also enhanced the dehydration and decomposition of hydrated phosphate and organic phosphate. Furthermore, it promoted the formation of polyphosphate in the MHT process, which is consistent with the result of ^{31}P NMR analysis. This is because the acidic conditions created by HCl promoted the polymerization of orthophosphate by proton catalysis.

3.2.4. P K-edge XANES analysis of the sewage sludge and MHT solid products

To further illustrate the phosphate composition changes of the MHT solid products during the MHT processes, XANES analysis was conducted. The spectra of the reference compounds are shown in Fig. S3. The different phosphates show specific absorption at different energy range. Fig. 7 presents the P K-edge XANES LCF spectra of the sewage sludge and MHT solid products. The parameters of the LCF results are shown in Table S5. The R values of all the samples are less than 0.02, which means high reliability of the results obtained by the LCF spectra. The relative abundances of the sewage sludge and MHT solid products are shown in Fig. 8. It can be found that the relative abundance of Ca-P ($Ca_5(PO_4)_3(OH)$ and OCP) increased after the MHT processes. Under the same MHT holding time of 60 min, the Ca-P content decreased first and then increased with the increase in MHT temperature. When the MHT temperature increased from 120 to 170 °C, the Ca-P content decreased from 68.8 % to 62.9 %. This trend can be attributed to the increased formation of acidic byproducts as the MHT temperature increased from 120 to 170 °C, resulting in a pH decrease from 7.12 to 6.92 (Table S6). The Ca-P minerals are very sensitive to acidic condition, which can promote the dissolution of Ca-P minerals. Therefore, the relative abundance of Ca-P decreased in this temperature range. With the MHT temperature further increased to 220 °C, the Ca-P content increased to 65 %. Under high hydrothermal temperature, reactions of acetal, decarboxylation, and polymerization occurred on small molecules, which led to the decrease in acidic matters [48,49]. As shown in Table S6, the pH value increased from 6.92 to 7.63 with the temperature increased from 170 to 220 °C, which promoted the formation of Ca-P in the MHT solid products. Additionally, with the same MHT temperature of 170 °C, the Ca-P content decreased gradually from 70.1 % to 59.6 % with the holding time increased from 10 min to 120 min. This is also due to the decrease in pH value in the MHT products.

It is worth noting that, when HCl was added in the MHT process (pH = 3.54), the Ca-P content decreased significantly. There is no $Ca_5(PO_4)_3(OH)$ maintained in the MHT solid products, and the relative abundance of OCP decreased to 31.7 %. The relative abundances of

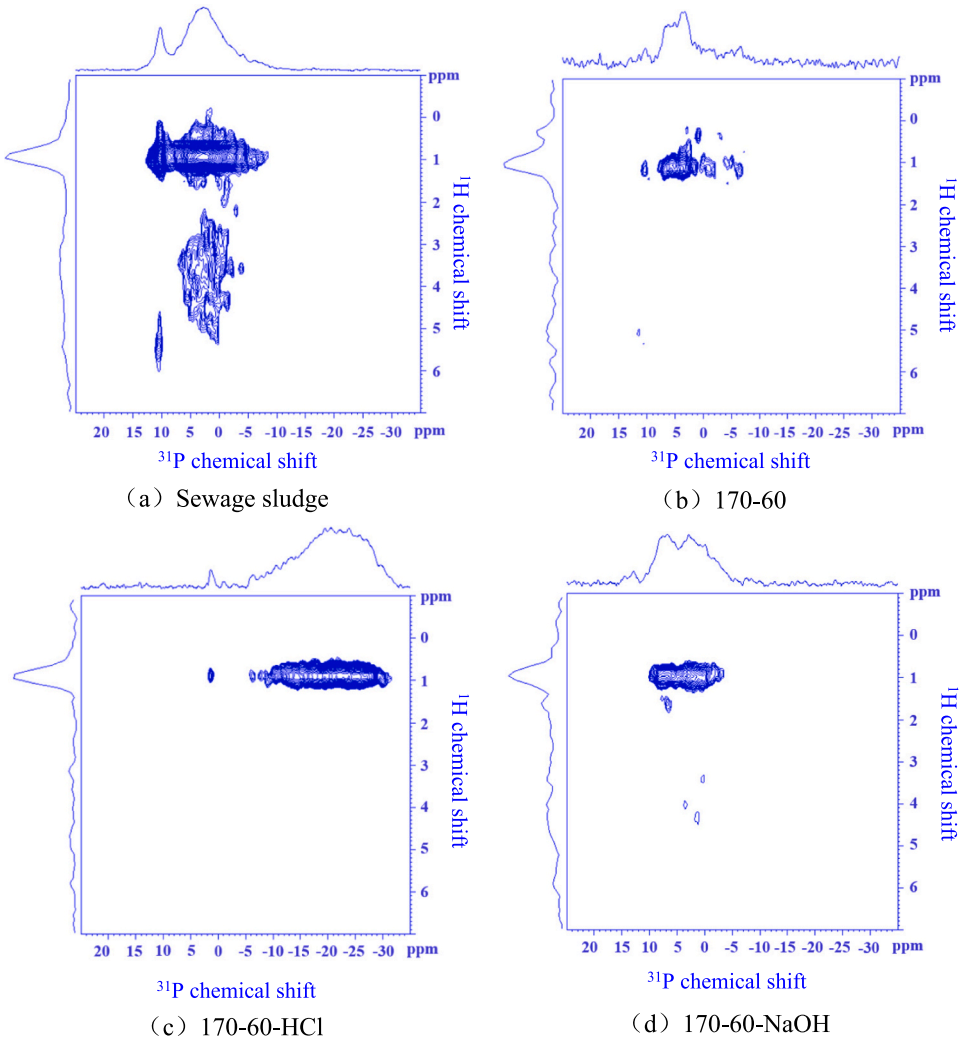

Fig. 6. ^{1}H—^{31}P 2D HETCOR NMR spectra of the sewage sludge and MHT solid products.

$FePO_4$ and $AlPO_4$ obtained the highest proportion, which is consistent with the analysis obtained in section 3.2.2. It further confirmed that the Ca-P minerals are more susceptible to acidic conditions, compared with other phosphates. In contrast, the addition of NaOH in the MHT process (pH = 11.22) promoted the formation of Ca-P, with the relative abundance increased to 70 %. The relative abundance of $Ca_5(PO_4)_3(OH)$ obtained the highest value of 19.2 %, which indicates that the alkaline MHT condition can facilitate the conversion of other phosphates to $Ca_5(PO_4)_3(OH)$. It is also consistent with the ^{1}H—^{31}P 2D HETCOR NMR results.

4. Conclusions

This study investigated the P transformation of sewage sludge during the HCl and NaOH assisted microwave hydrothermal conversion processes. The increase in MHT temperature (120-220 °C) and holding time (10–120 min) can promote the transformation of Al/Fe adsorbed P to mineral P. The phosphate esters of sewage sludge were gradually decomposed to pyrophosphate and orthophosphate. Both acidic and alkaline MHT conditions can promote the release of P into the hydrothermal liquid products. The acidic MHT condition with HCl addition (pH = 3.54) facilitated the dissolution of mineral P, including OCP and $Ca_5(PO_4)_3(OH)$ of the sewage sludge. Polyphosphate was formed in the solid product with the addition of HCl (pH = 3.54) in the MHT process. The alkaline MHT condition with NaOH addition (pH = 11.22) promoted the formation of orthophosphate and the release of adsorbed Al/Fe P into the liquid products. The production of $Ca_5(PO_4)_3(OH)$ was further enhanced via the addition of NaOH in the MHT process.

Compared with conventional heating, MHT conversion has the advantage of rapid heating and higher energy efficiency. By adjusting the MHT conditions, we can obtain phosphate with different speciations and optimize the recovery efficiency. The increase in MHT temperature and holding time can transform the phosphate of sewage sludge to stable mineral form, which will decrease the potential risk of eutrophication. The released P into the MHT liquid products via the acidic and alkaline conditions can be further recovered by crystallization of struvite, hydroxyapatite, and vivianite. The enriched orthophosphate in the MHT solid products is an essential nutrient and P source for organisms, which can be utilized as a fertilizer. This study provides some fundamental insights on P transformation of sewage sludge during acidic and alkaline MHT processes, which would be critical for the further utilization of P from sewage sludge.

CRediT authorship contribution statement

Yan Shi: Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Johannes Leisen:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Yinghao Wen:** Investigation. **Simin Zhao:** Investigation. **Yuanzhi Tang:** Writing – review &

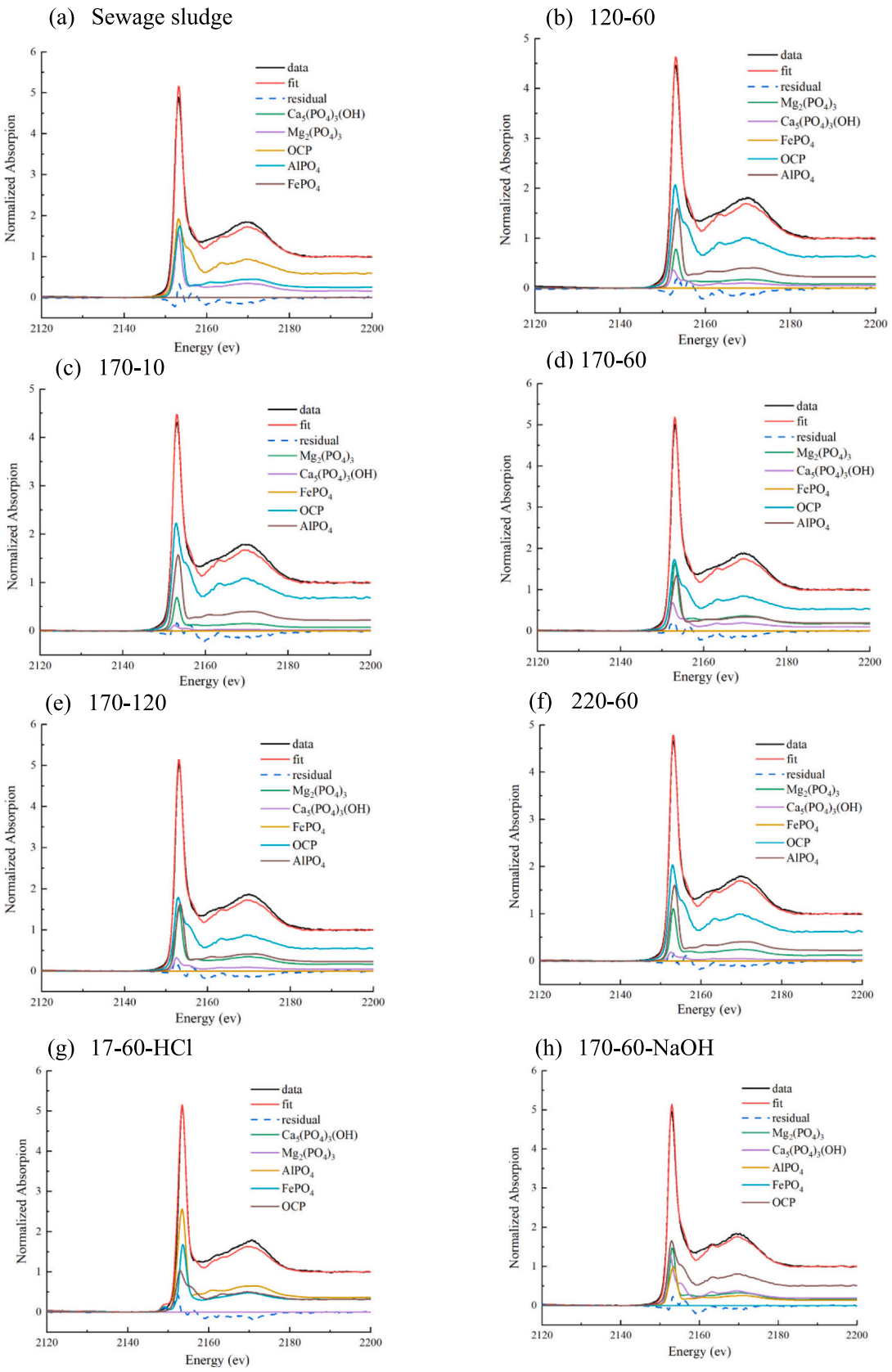

Fig. 7. P K-edge XANES spectra and LCF results of the sewage sludge and MHT solid products.

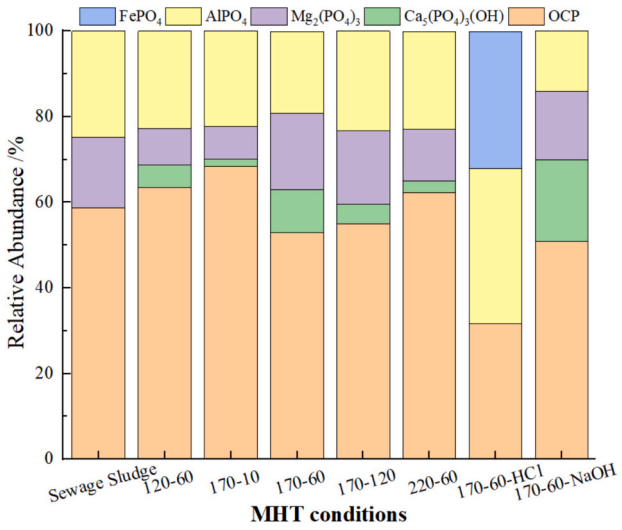

Fig. 8. Relative abundances of different phosphate species in the sewage sludge and MHT solid products.

editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2025.169129.

Data availability

Data will be made available on request.

References

[1] K. Venkiteshwaran, P.J. McNamara, B.K. Mayer, Meta-analysis of non-reactive phosphorus in water, wastewater, and sludge, and strategies to convert it for enhanced phosphorus removal and recovery, Sci. Total Environ. 644 (2018) 661–674.
[2] D. Cordell, J.O. Drangert, S. White, The story of phosphorus: global food security and food for thought, Glob. Environ. Chang. 19 (2) (2009) 292–305.
[3] H. Liu, G. Hu, I.A. Basar, J. Li, N. Lyczko, A. Nzihou, C. Eskicioglu, Phosphorus recovery from municipal sludge-derived ash and hydrochar through wet-chemical technology: a review towards sustainable waste management, Chem. Eng. J. 417 (2021) 129300.
[4] R.H. Li, X.Y. Li, Recovery of phosphorus and volatile fatty acids from wastewater and food waste with an iron-flocculation sequencing batch reactor and acidogenic co-fermentation, Bioresour. Technol. 245 (2017) 615–624.
[5] M. Kończak, M. Huber, Application of the engineered sewage sludge-derived biochar to minimize water eutrophication by removal of ammonium and phosphate ions from water, J. Clean. Prod. 331 (2022) 129994.
[6] M. Kacprzak, E. Neczaj, K. Fijałkowski, A. Grobelak, A. Grosser, M. Worwag, A. Rorat, H. Brattebo, A. Almås, B.R. Singh, Sewage sludge disposal strategies for sustainable development, Environ. Res. 156 (2017) 39–46.
[7] J. Tian, X. Cheng, S. Deng, J. Liu, B. Qiu, Y. Dang, D. Holmes, T.D. Waite, Inducing in situ crystallization of vivianite in a UCT-MBR system for enhanced removal and possible recovery of phosphorus from sewage, Environ. Sci. Technol. 53 (15) (2019) 9045–9053.
[8] J. Zhang, Z. Chen, Y. Liu, W. Wei, B.J. Ni, Phosphorus recovery from wastewater and sewage sludge as vivianite, J. Clean. Prod. 133439 (2022).
[9] Y. Shi, Z. Chen, K. Zhu, J. Fan, J.H. Clark, G. Luo, S. Zhang, Speciation evolution and transformation mechanism of P during microwave hydrothermal process of sewage sludge, Sci. Total Environ. 815 (2022) 152801.
[10] Z. Mei, D. Chen, J. Zhang, L. Yin, Z. Huang, Q. Xin, Sewage sludge pyrolysis coupled with self-supplied steam reforming for high quality syngas production and the influence of initial moisture content, Waste Manag. 106 (2020) 77–87.
[11] J. Wang, H. Liu, H. Deng, M. Jin, H. Xiao, H. Yao, Deep dewatering of sewage sludge and simultaneous preparation of derived fuel via carbonaceous skeleton-aided thermal hydrolysis, Chem. Eng. J. 402 (2020) 126255.
[12] F. Di Capua, D. Spasiano, A. Giordano, F. Adani, U. Fratino, F. Pirozzi, G. Esposito, High-solid anaerobic digestion of sewage sludge: challenges and opportunities, Appl. Energy 278 (2020) 115608.
[13] A. Tangredi, C. Barca, J.H. Ferrasse, O. Boutin, Effect of process parameters on phosphorus conversion pathways during hydrothermal treatment of sewage sludge: a review, Chem. Eng. J. 463 (2023) 142342.
[14] X. Zhang, X. Li, R. Li, Y. Wu, Hydrothermal carbonization and liquefaction of sludge for harmless and resource purposes: a review, Energy Fuel 34 (11) (2020) 13268–13290.
[15] Q. Chu, L. Xue, B.P. Singh, S. Yu, K. Müller, H. Wang, Y. Feng, G. Pan, X. Zheng, L. Yang, Sewage sludge-derived hydrochar that inhibits ammonia volatilization, improves soil nitrogen retention and rice nitrogen utilization, Chemosphere 245 (2020) 125558.
[16] H. Liu, I.A. Basar, A. Nzihou, C. Eskicioglu, Hydrochar derived from municipal sludge through hydrothermal processing: a critical review on its formation, characterization, and valorization, Water Res. 199 (2021) 117186.
[17] X. Liu, Y. Zhai, S. Li, B. Wang, T. Wang, Y. Liu, Z. Qiu, C. Li, Hydrothermal carbonization of sewage sludge: effect of feed-water pH on hydrochar's physicochemical properties, organic component and thermal behavior, J. Hazard. Mater. 388 (2020) 122084.
[18] A.L. Tasca, M. Puccini, R. Gori, I. Corsi, A.M.R. Galletti, S. Vitolo, Hydrothermal carbonization of sewage sludge: a critical analysis of process severity, hydrochar properties and environmental implications, Waste Manag. 93 (2019) 1–13.
[19] L. Wang, Y. Chang, A. Li, Hydrothermal carbonization for energy-efficient processing of sewage sludge: a review, Renew. Sust. Energ. Rev. 108 (2019) 423–440.
[20] Y.J. Wang, Y. Yu, H.J. Huang, C.L. Yu, H.S. Fang, C.H. Zhou, X. Yin, W.H. Chen, X. C. Guo, Efficient conversion of sewage sludge into hydrochar by microwave-assisted hydrothermal carbonization, Sci. Total Environ. 803 (2022) 149874.
[21] Y. Shi, G. Luo, Y. Rao, H. Chen, S. Zhang, Hydrothermal conversion of dewatered sewage sludge: focusing on the transformation mechanism and recovery of phosphorus, Chemosphere 228 (2019) 619–628.
[22] R. Huang, C. Fang, X. Lu, R. Jiang, Y. Tang, Transformation of phosphorus during (hydro) thermal treatments of solid biowastes: reaction mechanisms and implications for P reclamation and recycling, Environ. Sci. Technol. 51 (18) (2017) 10284–10298.
[23] G. Chen, M. Hu, G. Du, S. Tian, Z. He, B. Liu, W. Ma, Hydrothermal liquefaction of sewage sludge by microwave pretreatment, Energy Fuel 34 (2) (2020) 1145–1152.
[24] B. Rao, J. Su, S. Xu, H. Pang, P. Xu, Y. Zhang, J. Zhu, H. Tu, Thermal and non-thermal mechanism of microwave irradiation on moisture content reduction of municipal sludge, Water Res. 226 (2022) 119231.
[25] Q. Wang, C. Zhang, P. Liu, H. Jung, B. Wan, D. Patel, S. Pavlostathis, Y. Tang, Effect of interstage hydrothermal treatment on anaerobic digestion of sewage sludge: speciation evolution of phosphorus, iron, and sulfur, ACS Sustain. Chem. Eng. 8 (44) (2020) 16515–16525.
[26] R. Huang, Y. Tang, L. Luo, Thermochemistry of sulfur during pyrolysis and hydrothermal carbonization of sewage sludges, Waste Manag. 121 (2021) 276–285.
[27] S. Adhikari, G. Gasco, A. Mendez, A. Surapaneni, V. Jegatheesan, K. Shah, J. Paz-Ferreiro, Influence of pyrolysis parameters on phosphorus fractions of biosolids derived biochar, Sci. Total Environ. 695 (2019) 133846.
[28] G.C. Becker, A. Kruse, Discussion of classical phosphate extraction schemes to identify speciation in (hydro-) Thermochemically treated sewage sludge, ACS Sustain. Chem. Eng. 11 (44) (2023) 15841–15850.
[29] D.S. Hansen, A.E. Turcios, A.M. Klamt, C. Wieth, K. Reitzel, M.H. Thomsen, J. Papenbrock, Characterization of biochar produced from sewage sludge and its potential use as a substrate and plant growth improver, J. Environ. Manag. 348 (2023) 119271.
[30] J. Murphy, J.P. Riley, A modified single solution method for the determination of phosphate in natural waters, Anal. Chim. Acta 27 (1962) 31–36.
[31] Y. Shi, Z. Chen, Y. Cao, J. Fan, J.H. Clark, G. Luo, S. Zhang, Migration and transformation mechanism of phosphorus in waste activated sludge during anaerobic fermentation and hydrothermal conversion, J. Hazard. Mater. 403 (2021) 123649.
[32] L. Wang, A. Li, Y. Chang, Relationship between enhanced dewaterability and structural properties of hydrothermal sludge after hydrothermal treatment of excess sludge, Water Res. 112 (2017) 72–82.
[33] C. He, J. Zhao, Y. Yang, J.Y. Wang, Multiscale characteristics dynamics of hydrochar from hydrothermal conversion of sewage sludge under sub-and near-critical water, Bioresour. Technol. 211 (2016) 486–493.
[34] G. Izydorczyk, K. Mikula, D. Skrzypczak, K. Trzaska, K. Moustakas, A. Witek-Krowiak, K. Chojnacka, Agricultural and non-agricultural directions of bio-based sewage sludge valorization by chemical conditioning, Environ. Sci. Pollut. Res. 28 (2021) 47725–47740.

[35] B. Rao, X. Su, X. Lu, Y. Wan, G. Huang, Y. Zhang, P. Xu, S. Qiu, J. Zhang, Ultrahigh pressure filtration dewatering of municipal sludge based on microwave pretreatment, J. Environ. Manag. 247 (2019) 588–595.
[36] G. Zhen, J. Wang, X. Lu, L. Su, X. Zhu, T. Zhou, Y. Zhao, Effective gel-like floc matrix destruction and water seepage for enhancing waste activated sludge dewaterability under hybrid microwave-initiated Fe (II)-persulfate oxidation process, Chemosphere 221 (2019) 141–153.
[37] Z. Fang, X. Zhuang, X. Zhang, Y. Li, R. Li, L. Ma, Influence of paraments on the transformation behaviors and directional adjustment strategies of phosphorus forms during different thermochemical treatments of sludge, Fuel 333 (2023) 126544.
[38] J. Li, J. Jin, Y. Zhao, Z. Zou, Y. Wu, J. Sun, J. Xia, Enhancing phosphorus bioavailability in sewage sludge through co-hydrothermal treatment with biomass, J Water Process Eng 51 (2023) 103448.
[39] S. Song, J. Zhang, Y. Liu, H. Wang, Accumulation of labile P forms and promotion of microbial community diversity in mollisol with long-term manure fertilization, Agronomy 13 (3) (2023) 884.
[40] A. Sarrion, A. de la Rubia, C. Coronella, A.F. Mohedano, E. Diaz, Acid-mediated hydrothermal treatment of sewage sludge for nutrient recovery, Sci. Total Environ. 838 (2022) 156494.
[41] L.B. Staal, A.B. Petersen, C.A. Jørgensen, U.G. Nielsen, P.H. Nielsen, K. Reitzel, Extraction and quantification of polyphosphates in activated sludge from waste water treatment plants by 31P NMR spectroscopy, Water Res. 157 (2019) 346–355.
[42] C.A. Shand, M.V. Cheshire, C.N. Bedrock, P.J. Chapman, A.R. Fraser, J.A. Chudek, Solid-phase 31P NMR spectra of peat and mineral soils, humic acids and soil solution components: influence of iron and manganese, Plant Soil 214 (1) (1999) 153–163.
[43] S. Li, W. Zeng, Z. Jia, G. Wu, H. Xu, Y. Peng, Phosphorus species transformation and recovery without apatite in $FeCl_3$-assisted sewage sludge hydrothermal treatment, Chem. Eng. J. 399 (2020) 125735.
[44] Y. Zhang, H. Yuan, S. Cai, Y. Zhang, D. Wang, W. Zhang, Molecular transformation pathway and bioavailability of organic phosphorus in sewage sludge under hydrothermal treatment: importance of biopolymers interactions, J. Clean. Prod. 385 (2023) 135746.
[45] R.F. Chen, T. Liu, H.W. Rong, H.T. Zhong, C.H. Wei, Effect of organic substances on nutrients recovery by struvite electrochemical precipitation from synthetic anaerobically treated swine wastewater, Membranes 11 (8) (2021) 594.
[46] M. Chtouki, R. Naciri, A. Oukarroum, A review on phosphorus drip fertigation in the Mediterranean region: fundamentals, current situation, challenges, and perspectives, Heliyon 10 (2024) 25543.
[47] R. Mathew, C. Turdean-Ionescu, Y. Yu, B. Stevensson, I. Izquierdo-Barba, A. García, D. Arcos, M. Vallet-Regí, M. Edén, Proton environments in biomimetic calcium phosphates formed from mesoporous bioactive $CaO–SiO_2–P_2O_5$ glasses in vitro: insights from solid-state NMR, J. Phys. Chem. C 121 (24) (2017) 13223–13238.
[48] C. Falco, N. Baccile, M.M. Titirici, Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons, Green Chem. 13 (11) (2011) 3273–3281.
[49] H. Wang, Z. Yang, X. Li, Y. Liu, Distribution and transformation behaviors of heavy metals and phosphorus during hydrothermal carbonization of sewage sludge, Environ. Sci. Pollut. Res. 27 (2020) 17109–17122.