

Article

Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar

Vicky Shettigondahalli Ekanthalu ^{1,*}, Satyanarayana Narra ^{1,2} , Tommy Ender ¹, Edward Antwi ¹ and Michael Nelles ^{1,2}

- ¹ Department of Waste and Resource Management, Faculty of Agricultural and Environmental Sciences, University of Rostock, D-18059 Rostock, Germany; satyanarayana.narra@uni-rostock.de (S.N.); tommy.ender@uni-rostock.de (T.E.); edward.antwi2@uni-rostock.de (E.A.); michael.nelles@uni-rostock.de (M.N.)
- ² Deutsches Biomasseforschungszentrum GmbH (DBFZ), D-04347 Leipzig, Germany
- * Correspondence: vicky.ekanthalu@uni-rostock.de

Abstract: Phosphorus (P) recovery from alternative P-rich residues is essential to meet the growing demands of food production globally. Despite sewage sludge being a potential source for P, its direct application on agricultural land is controversial because of the obvious concerns related to heavy metals and organic pollutants. Further, most of the available P recovery and sludge management technologies are cost-intensive as they require mandatory dewatering of sewage sludge. In this regard, hydrothermal carbonization (HTC) has gained great attention as a promising process to effectively treat the wet sewage sludge without it having to be dewatered, and it simultaneously enables the recovery of P. This study was conducted to analyse and compare the influence of acid (H₂SO₄) addition during and after HTC of sewage sludge on P leaching and the characteristics of hydrochar. The obtained results suggested that despite using the same amount of H₂SO₄, P leaching from solid to liquid phase was significantly higher when acid was used after the HTC of sewage sludge in comparison with acid utilization during the HTC process. After HTC, the reduction in acid-buffering capacity of sewage sludge and increase in solubility of phosphate precipitating metal ions had a greater influence on the mobilization of P from solid to liquid phase. In contrast, utilization of H₂SO₄ in different process conditions did not have a great influence on proximate analysis results and calorific value of consequently produced hydrochar.



Citation: Shettigondahalli Ekanthalu, V.; Narra, S.; Ender, T.; Antwi, E.; Nelles, M. Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar. *Processes* **2022**, *10*, 151. <https://doi.org/10.3390/pr10010151>

Academic Editors: Bipro R. Dhar and Biplob Pramanik

Received: 21 December 2021

Accepted: 10 January 2022

Published: 12 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: hydrothermal carbonization; sewage sludge; phosphorus; phosphorous recovery; hydrochar; pH; leachate

1. Introduction

Phosphorus (P) is an indispensable element for all life forms, and its continuous supply is vital for sustainable food production globally. Further, P is also used in various industrial applications, such as production of detergents, paints, food and beverages [1]. As a result of the versatility P possesses, the natural source of P is being unsustainably exploited. The overexploitation of the P-rock from its natural source for manufacturing fertilizers and other industrial applications will create severe problems in the coming 50 to 100 years [2]. The nonrenewable nature of P and its vulnerability to become scarce in the coming years will exert a serious burden on agricultural production costs and could question global food security. Due to the combination of concerns such as its nonrenewable nature, importance concerning global food security, and significant price volatility, P and its future availability are drawing growing attention, and there are calls for an immediate need to find an alternative P source [3]. Wastewater and sewage sludge are the carriers of P, and wastewater treatment plants (WWTP) act as a viable source substituent for the production

of phosphate fertilizers. Further, in selected countries of Europe, P in the WWTP accounts for about >70% of the total P imported [4], which indeed shows the potential of WWTP as an alternative source for the production of P fertilizer.

Conventional sewage sludge management involves its direct application to farmland as fertilizer. Nevertheless, sewage sludge is contaminated with heavy metals and organic pollutants, making its direct application onto farmland controversial. Despite sewage sludge being a potential source for P, its management and nutrient recovery is still a crucial global issue due to the presence of high water content and poor dewaterability characteristics [5]. Currently, most of the available sewage sludge management technologies require mandatory dewatering of sewage sludge, making its management cost-intensive. Incineration of sewage sludge might be widely accepted, however, its prerequisite of having sludge be dewatered makes the process cost-intensive and poses concerns related to the release of toxic air pollutants (NO_x, SO₂ and dioxins) if the process is not managed properly [6].

In the year 2020, nearly 16% of sewage sludge produced in Germany was managed by material recycling in agriculture or landscaping measures, and approximately 77% of the produced sewage sludge was incinerated [7]. As a result of stringent environmental policies and laws placed by Germany, sewage sludge management options are becoming progressively limited. The German sewage sludge ordinance (AbfKlärV), structured on enabling principles of the Circular Economy Act [8], is not only making it obligatory to recover phosphorus from sewage sludge, but also outlaws the direct utilization of sewage sludge on farmland [9]. This new obligation from AbfKlärV applies from January 2029 for larger WWTP (>100,000 populations equivalent), and is planned to be followed by medium and smaller WWTP. Considering the situation and the readiness of available technology, increasing the number of incineration plants might seem like an easy solution, but this would not only be expensive also might create political, public, and environmental contentions. One among the best possible approach to tackling this dual problem associated with the management of sewage sludge and foreseen concern on P scarcity is by introducing a technology where not only is P recovered from sewage sludge but where sludge could also be transformed into a value-added product. However, the technical potential of the value-added product has to be proved with a practical market value.

Hydrothermal carbonization (HTC) has gained greater attention as an environmentally friendly and promising technology to treat sewage sludge without it having to be dewatered. The HTC process utilizes the excess moisture present in sewage sludge as a catalyst, reactant, and solvent, to convert sewage sludge into a carbonaceous product (hydrochar) and simultaneously enables recovery of P. The consequently produced hydrochar after HTC is essentially easy to dewater, is hygienic, potentially free of pharmaceuticals, and likely to exhibit moderate energy density [10,11]. Generally, after HTC of sewage sludge, a significantly higher portion of P is transferred and accumulated onto hydrochar. The building-up of P in hydrochar produced after HTC of sewage sludge is mainly influenced by the utilization of coagulant in the WWTP [1]. Metal salts such as Al₂(SO₄)₃ and FeCl₃ are generally utilized in the WWTP to precipitate P from wastewater [12]. During HTC, the presence of metal salts in sewage sludge, in turn, fosters the P transformation into hydrochar, along with the majority of heavy metals [13]. An effective method for leaching the trapped P in hydrochar is by treating hydrochar in inorganic acid solutions at an extremely low pH [1,14].

Recently, several studies have reported the influence of feed-water pH on the distribution and transformation of P during HTC of sewage sludge [6,15–17], the potential risk concerning heavy metals in hydrochar [18], physical and chemical characteristics of hydrochar [5,19], value-addition of hydrochar by converting it into effective adsorbents [11,20], and utilization of hydrochar as soil amender [21]. The primary focus of studies so far has been to increase the efficiency of P recovery and to understand the physicochemical behaviour of hydrochar. Even though these studies address the P recovery and speciation under the specific HTC process and acid-leaching conditions, the influence

of acid utilization at different stages of the HTC process on P transformation and hydrochar characteristics are yet to be understood.

The primary objective of this investigation is to analyse and compare the influence of acid addition during HTC, after HTC, and during-and-after HTC of sewage sludge on P transformation and hydrochar characteristics. Acid leaching at different stages of HTC was facilitated by the addition of strong acid (H_2SO_4) at different concentrations. The subsequently produced leachate was analysed for P and major multivalent metal ion concentrations, and hydrochar was examined for proximate analysis and fuel characteristics.

2. Materials and Methods

2.1. Feedstock and Initial Analysis

The feedstock used in this study is a sewage sludge that was initially digested, followed by mechanical dewatering. The sewage sludge in digested and dewatered form was collected directly from the wastewater treatment plant located in Rostock, Germany, with an initial dry matter content of 22.00% (dried at 105 °C). The sewage sludge utilized in the entire investigation was collected on a single occasion, during the stable operation condition of the treatment plant, to enable consistent results during the analysis. The sewage sludge from WWTP was collected in an airtight container and transferred instantly to the laboratory and refrigerated at 4 °C. The refrigerated samples were taken directly for HTC investigation. Before HTC, a homogeneous sewage sludge slurry was prepared (this aids better workability) by thoroughly mixing sewage sludge with deionised water or H_2SO_4 of known concentration and quantity.

The proximate analysis of the sewage sludge was performed using a Thermogravimetric Analyser (TGA) unit LECO TGA701 (LECO Instrumente GmbH, Mönchengladbach, Germany), and moisture content, volatile content, fixed carbon, and ash content were determined. The ultimate analysis of the sewage sludge was performed in an external laboratory using an organic elemental analyser following EN ISO 16948, 2015. The calorific value of the sewage was determined by Parr 6400 calorimeter (Parr Instruments Inc., Moline, IL, USA) following the method described in EN 14918, 2010. Total phosphate content in the sewage sludge was analysed in an external laboratory according to EN ISO 11885, 2009. All analyses were repeated thrice and the mean value was reported.

2.2. Hydrothermal Carbonization

A Parr 4523 reactor (Parr Instrument (Deutschland) GmbH, Zeilweg 15, Frankfurt, Germany) operating at an autogenic pressure was used to hydrothermally carbonise sewage sludge. The HTC reactor consists of a 1 litre-capacity reactor vessel with a maximum pressure threshold of 138 bar. Further, the reactor is equipped with a 2 kW heating coil, a stirrer with an attached motor, and a pressure and temperature sensor. The stirrer and the heating coil were regulated using a Parr 4848 PID reactor controller. HTC was carried out in three different scenarios and resultant products were recovered and analysed. An overview of the experimental methodology is provided in Figure 1. For scenario 1 and scenario 3, the investigation was carried out by charging the reactor vessel with 318.18 g sewage sludge (22.0% DM) and filling it up with 381.8 g and 331.8 g of 0.25 M or 0.35 M H_2SO_4 , respectively. For scenario 2, the investigation was carried out by charging the reactor vessel with 318.18 g sewage sludge (22.0% DM) and filling it up with 331.8 g of deionised water. In all three scenarios before starting the investigation, sewage sludge and co-substrate were mixed inside the reactor to form a homogeneous slurry, and the initial pH of mixed feedstock slurry was recorded. The defined quantity of sewage sludge to co-substrate was used to produce coal slurry of 10% DM, and a comparatively equal quantity of H_2SO_4 was used before solid–liquid separation, which facilitates fair evaluation of the products. The homogeneously mixed sewage sludge slurry was hydrothermally carbonized with a retention time of 2 h at a temperature of 220 °C and an autogenic pressure was generated during the process. The 220 °C reaction temperature was achieved by heating the reactor with a constant heating rate of 4 K/min. Further, the feedstock was continuously kept

stirring during the entire process stage. After the HTC, the reactor was cooled to room temperature without any additional cooling mechanism. Later, solids and liquids were separated from the HTC slurry and further analysis was carried out.

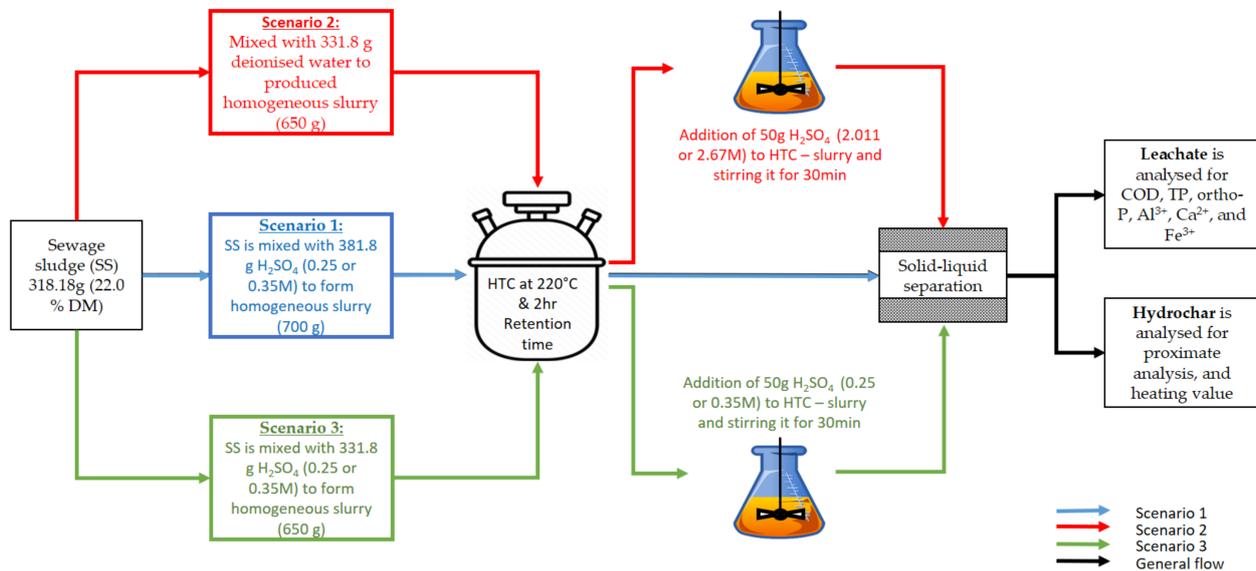


Figure 1. Overview of the experimental methodology.

2.3. Acid Leaching

The experimental analysis for three scenarios was designed in a way to analyse and compare the influence of adding H_2SO_4 during and after HTC of sewage sludge on P transformation. In scenario 1, the entire quantity (381.8 g) of H_2SO_4 (0.25 M or 0.35 M) was mixed with sewage sludge (318.18 g) to form a homogeneous slurry, followed by hydrothermal treatment. In scenario 2, the initial homogeneous slurry was prepared by mixing deionized water (331.8 g) with sewage sludge (318.18 g) and HTC was carried out. Later, 50 g H_2SO_4 (2.011 or 2.67 M) was added to the coal slurry and stirred for 30 min to facilitate acid leaching. In scenario 3, the initial homogeneous slurry was prepared by mixing 331.8 g of H_2SO_4 (0.25 M or 0.35 M) with sewage sludge (318.18 g) and HTC was carried out. After HTC, 50 g H_2SO_4 (0.25 or 0.35 M) was added to the coal slurry and stirred for 30 min to facilitate further acid leaching.

As shown in Table 1, irrespective of process conditions, sample number L1.1, L2.1, L2.2, and L3.1 were produced using a comparatively equal amount of the H_2SO_4 (5.29 g of 18 M H_2SO_4). Similarly, leachate L1.2, L2.3, L2.4, and L3.2 were produced using a comparatively equal amount of the H_2SO_4 (7.41 g of 18 M H_2SO_4), facilitating an impartial comparison of final products.

Table 1. Utilization of H_2SO_4 during the experimental procedure.

Sample Description		Quantity of 18 M H_2SO_4 Used	H_2SO_4 Addition		Weight of Coal Slurry before Solid-Liquid Separation
Scenario	Sample Id		during HTC	after HTC	
Scenario 1	L1.1	5.29 mL	381.8 g 0.25 M	-	700 g
	L1.2	7.41 mL	381.8 g 0.35 M	-	
Scenario 2	L2.1	5.29 mL	-	50.0 g 2.01 M	700 g
	L2.2				
	L2.3	7.41 mL	-	50.0 g 2.67 M	
	L2.4				
Scenario 3	L3.1	5.29 mL	331.8 g 0.25 M	50.0 g 0.25 M	700 g
	L3.2	7.41 mL	331.8 g 0.35 M	50.0 g 0.35 M	

2.4. Product Recovery and Analysis

The final pH of the coal slurry was noted after the HTC of sewage sludge. For scenario 1, the coal slurry was directly sent for vacuum filtration, however, for scenario 2 and scenario 3, acid leaching was performed post-HTC, as explained in Section 2.3. Vacuum filtration for all three scenarios was carried out at in a similar process condition, via top-feeding procedure using a Büchner funnel. The following process conditions were kept constant for solid-liquid separation of the coal slurry; (1) entire contents of coal slurry after carbonization/acid-leaching was emptied into the Büchner funnel, (2) the vacuum pump was turned on to generate enough vacuum pressure for separating solids and liquids. The filtrate (leachate) produced after the filtration was collected in a volumetric flask and stored at 4 °C until it was analysed for COD, TP, ortho-P, Al³⁺, Ca²⁺, Fe³⁺, and Mg²⁺. Similarly, the obtained solids (hydrochar) were oven-dried at 105 °C for 24 h and stored in airtight containers for further examination.

The calorific value and proximate analysis of the hydrochar was determined in a similar way to sewage sludge, using a Parr 6400 calorimeter and TGA unit LECO TGA701, respectively. COD, TP, ortho-P, Al³⁺, Ca²⁺, Fe³⁺, and Mg²⁺ were analysed spectrophotometrically. Triplicates of all investigated results were obtained, and the resultant mean value was reported.

3. Results and Discussion

3.1. Characteristic of Sewage Sludge

The proximate and ultimate analysis results of feedstock are shown in Table 2. The utilized sewage sludge in this study had a moisture content of 78.00% and total solids were 22.00%. The proximate analysis depicted that the sewage sludge had an ash content of 33.64% DM at 815 °C and volatile solids (VS) of 65.00% DM, which was consistent with the previous investigation range concerning the proximate analysis results [15,22,23]. The ultimate analysis results had a typical value for carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O) content for sewage sludge in Germany [24] with; C: 34.70%; H: 4.90%; N: 4.80%; S: 1.60% and O: 17.60% on a dry basis. Dried sewage sludge is known to contain a higher concentration of P and moderate calorific value. The TP content in the sewage sludge was examined to be 3,440,000 mg/kg, accounting for 3.4% of total dry sludge, and the calorific value was observed to be relatively higher with 14.72 MJ/kg (HHV) in comparison with previous studies [15,22,24]. The overall characteristics of the feedstock have the typical composition of sewage sludge in Germany.

Table 2. Proximate and ultimate analysis of sewage sludge.

Parameters	Units	Value
Moisture content	%OS	78.00
Total solids	%OS	22.00
Volatile solids	%DM	65.00
Ash (815 °C)	%DM	33.64
Ash (550 °C)	%DM	35.00
Fixed carbon (FC)	%DM	1.36
HHV	MJ/kg, DM basis	14.72
Nitrogen	%DM	4.80
Carbon	%DM	34.70
Sulphur	%DM	1.60
Oxygen	%DM	17.60
Hydrogen	%DM	4.90
Total phosphorus	mg/kg DM	34,400.00

OS = Original Sample, DM = Dry Matter, HHV = Higher Heating Value.

3.2. P-Transformation from Solids to the Liquid Phase of Sewage Sludge

Figure 2 shows the concentration of TP and ortho-P in leachate after the solid-liquid separation of HTC coal slurry produced in three different scenarios. For each experiment,

TP and ortho-P in the leachate were analysed spectrophotometrically. In brief, results from the experimental analysis clearly depicted that even after the utilization of the same amount of acid, a higher amount of P-transformation from solids to liquids was observed in the leachate produced using scenario 2 experimental setup in comparison to scenario 1 and scenario 3.

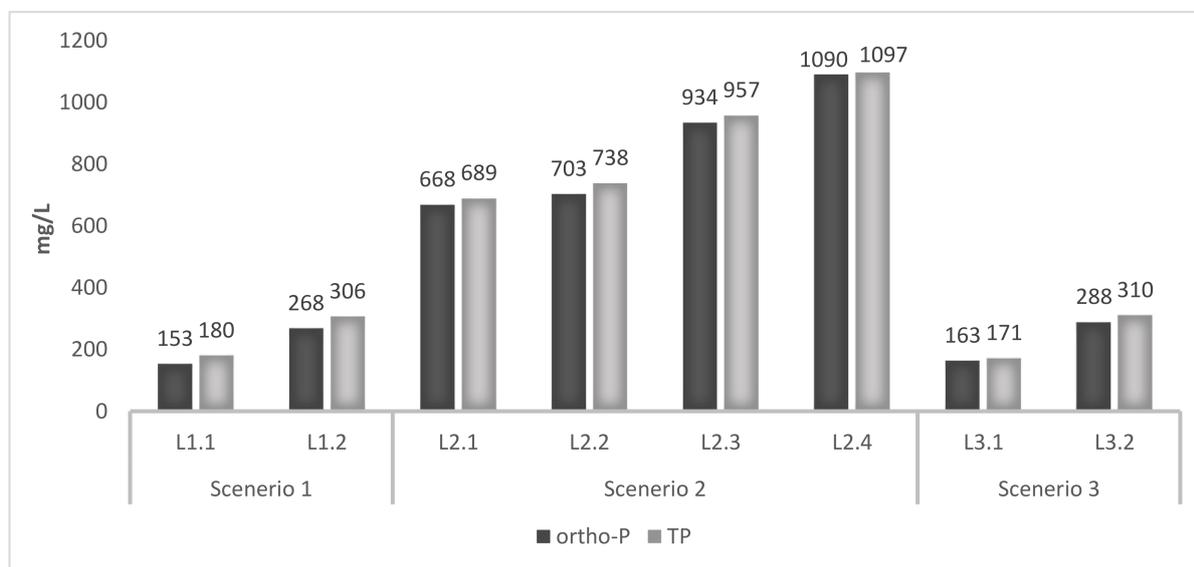


Figure 2. Concentration of TP and ortho-P in the leachate after solid–liquid separation.

In the leachate L1.2, L2.3, L2.4, and L3.2, despite using the same amount of acid, the highest TP transformation into the leachate was observed in L2.3 (957 mg/L) and L2.4 (1097 mg/L), which was >300% higher in comparison with L1.2 at 306 mg/L and L3.2 at 310 mg/L. Similarly, between L1.1, L2.1, L2.2, and L3.1; the higher TP transformation into the leachate was observed during scenario 2 in L2.1 (689 mg/L) and L2.2 (738 mg/L) which was almost 400% higher in comparison with L1.1 (180 mg/L) and L3.1 (171 mg/L). The obtained results suggested that during HTC of sewage sludge, P leaching from solids to the liquid phase is highly favourable when acid (H_2SO_4) is used after the HTC of the sewage sludge in comparison with the acid utilization during the HTC process. This could be explained by the influence of acid-buffering capacity on the mobility of P.

3.2.1. Influence of Acid-Buffering Capacity of Sewage Sludge on the Mobilization of P

The buffering capacity of any solution medium can be defined as the ability of the solution to inhibit the pH change caused by the addition of a strong acid or base [25]. The buffer capacity (β) represents the tendency of the solution to change its pH upon addition of acid (dC_A) or base (dC_B) (see Equation (1)).

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \quad (1)$$

In general, sewage sludge suspension consists of a liquid and a solid phase. The liquid phase of the sewage sludge contains amphoteric organic matter, strong alkaline and weakened acidic salts with a high tendency to inhibit acidification. The acid-buffering capacity in the solid phase of sewage sludge is attributed to the acid-consuming components, carbonate minerals, metal oxide, hydroxide, alkaline mineral, etc. [26]. Further, the presence of abundant organic matter such as protein and volatile fatty acids also greatly contributes to the inhibition of acidification [27].

However, the acid-buffering substance present in the solid and liquid phase of the sewage sludge suspension has different neutralising points. Upon the addition of acids

into sewage sludge suspension, primarily, acid (H^+) would start reacting with carbonates in the suspension with a relatively higher neutral point (see Equation (2)). Soon after the exhaustion of carbonates in the system, the additional H^+ will undergo a cation exchange reaction ($5.5 < pH < 6.2$) (see Equation (3)). Further, additional H^+ will be then reacted and consumed by the organic matter present in the suspension. Ultimately, the presence/addition of further H^+ induces dissolution of aluminium phosphates (Al-P), and finally leads to the dissolution of ferric phosphate (Fe-P) (see Equations (4)–(6)) [27–29].



Equations (4)–(6) theoretically depict that 3 mol of H^+ is required to dissolve each mol of P. However, actually more H^+ is required since sewage sludge usually contains significantly more acid-consuming compounds of both organic and inorganic origin [5]. Nevertheless, during the leaching process, it is difficult to predict the exact influence of organic and inorganic compositions and forms, as they greatly vary with the sludge origin.

3.2.2. Influence of HTC on Buffering Capacity of Sewage Sludge and Mobilization of P

During HTC, both the temperature and the feedstock composition significantly regulate the chemical reaction pathways and the thermochemical breakdown of the biomass structure. The composition of the sewage sludge is diverse and includes lipids, polysaccharides, proteins, and lignin. This diversity in the composition makes it challenging for defining the kinetics and reaction pathways during HTC [30]. In the HTC process, hydrolysis of lipids, polysaccharides, protein, and lignin is deemed to be the primary reaction that takes place due to the low activation energy, which is then immediately followed by dehydration, decarboxylation, condensation, and aromatization [31,32]. As the reaction begins, carbonaceous compounds hydrolyse almost entirely into free fatty acids [33]. These fatty acids have been recognized primarily as acetic acid and propionic acid, and are mostly derived from unsaturated lipids [34]. Further, with an increased reaction time, aldehydes, ketones, and monosaccharides degrade and form organic acids such as formic, lactic and acetic acid [35].

As a result of all these chemical reactions and thermochemical breakdown pathways, the acid-buffering capacity of sewage sludge significantly reduces after HTC. In scenario 2, as the acid leaching was carried out after HTC of sewage sludge, the majority of the H^+ in added H_2SO_4 is utilized to induce dissolution of Al-P and Fe-P. This in turn justifies the increased TP and ortho-P. However, in scenario 1 and scenario 3, despite using the same amount of acid as in scenario 2, it was observed that significantly less P was leached into the leachate. During scenarios 1 and 3, most of the H^+ ions added in the form of acid are utilised to offset buffering resistance provided by carbonates, cation exchange reaction, and organic matter. This resistance provided by buffering agents present in the system greatly depletes the available H^+ before it reaches proper conditions to react with P-holding metals.

3.2.3. Influence of Temperature during Acid Leaching of Coal Slurry (Sewage Sludge) on the Mobilization of P

The temperature of the HTC slurry during acid leaching also had an influence on the transformation of P into the leachate. In scenario 2, despite using a similar amount of acid during P leaching, L2.2 (738 mg/L) had higher TP leached into the leachate in comparison to L2.1 (689 mg/L). Similar phenomena were observed between L2.3 (957 mg/L) and L2.4 (1097 mg/L). The leachates L2.2 and L2.4 had about 7.2 and 14.6% higher TP in comparison with the leachates L2.1 and L2.3, respectively. The only difference between these treatment

processes was temperature. The acid leaching for L2.1 and L2.3 was carried out directly after the HTC (between 47 °C to 50 °C), before allowing the temperature to come down to room temperature. In contrast, acid leaching for leachate L2.2 and L2.4 was carried out after letting the HTC slurry cool down to room temperature (between 26 °C to 29 °C).

Usually, in a solution medium with an increasing temperature, the solubility of a salt increases. However, this is not always the case. The equilibrium constant for a sludge suspension at a changing temperature can be estimated using the van't Hoff equation (Equation (7)) [36].

$$\frac{d(\ln k_{eq})}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (7)$$

In a process, k_{eq} is the change in equilibrium constant of a chemical reaction at temperature T , the standard enthalpy change is ΔH° , and R is the ideal gas constant. Evidently, if the dissolution of the salts is exothermic ($\Delta H^\circ < 0$), an increase in the reaction temperature of the solution will negatively influence the leaching of the TP into the leachate. However, if the dissolution of the salt is endothermic ($\Delta H^\circ > 0$), the reaction process will receive benefit from the high temperature of the medium. Nevertheless, in acid leaching, the mass diffusivity is also vital and increases with increasing temperature, this, in turn, will boost the rate of dissolution of a compound in the reaction medium. Therefore, a higher temperature might enhance the mass transport but might have a contrary effect on the dissolution of some particular salts [37].

3.2.4. Influence of Metal Ion Migration (Al^{3+} , Ca^{2+} and Fe^{3+}) on TP Transformation into the Leachate

The element composition of the sewage sludge, predominantly the presence of phosphate-precipitating metals (viz., Fe, Al, and Ca), has a greater influence on deciding the P transformation from the solid to the liquid phase [38,39]. During HTC of sewage sludge, the presence of multivalent metal ions (such as Al^{3+} , Ca^{2+} , Fe^{3+} , and Mg^{2+}) in higher concentrations is responsible for forming phosphate with low solubility, and in turn enabling P accumulation onto hydrochar. The study carried out by Ekpo et al. indicated that the HTC of swine manure using H_2SO_4 as an additive tends to decrease the level of Ca, Fe, and Mg in hydrochar and simultaneously enable P transformation from a solid to a liquid phase [39].

Despite using the same amount of acid, the leachate produced using scenario 1 (0.96 and 1.59 mg/L) and scenario 3 (1.79–9.53 mg/L) had significantly lower Al^{3+} concentration in comparison with scenario 2 (87.5–134 mg/L) (see Figure 3). Similarly, considerably high Fe^{3+} migration from solid to liquid was observed in scenario 2 in comparison with scenario 1 (L1.1) and scenario 3 (L3.1). Nevertheless, following the use of H_2SO_4 at higher concentration, scenario 1 and scenario 3 had similar Fe^{3+} migration from solid to liquid phase in comparison with scenario 2. Thus, the obtained results suggest that the utilization of H_2SO_4 after HTC of sewage sludge tends to increase the solubility of phosphate-precipitating metal ions (Al^{3+} and Ca^{2+}), simultaneously increasing the P transformation from solid to liquid phase (see Figure 2). In contrast, utilization of H_2SO_4 during HTC of sewage sludge negatively influenced the metal ions and P migration. Further, irrespective of the H_2SO_4 utilization in different process conditions, the COD of the leachate had comparatively similar results.

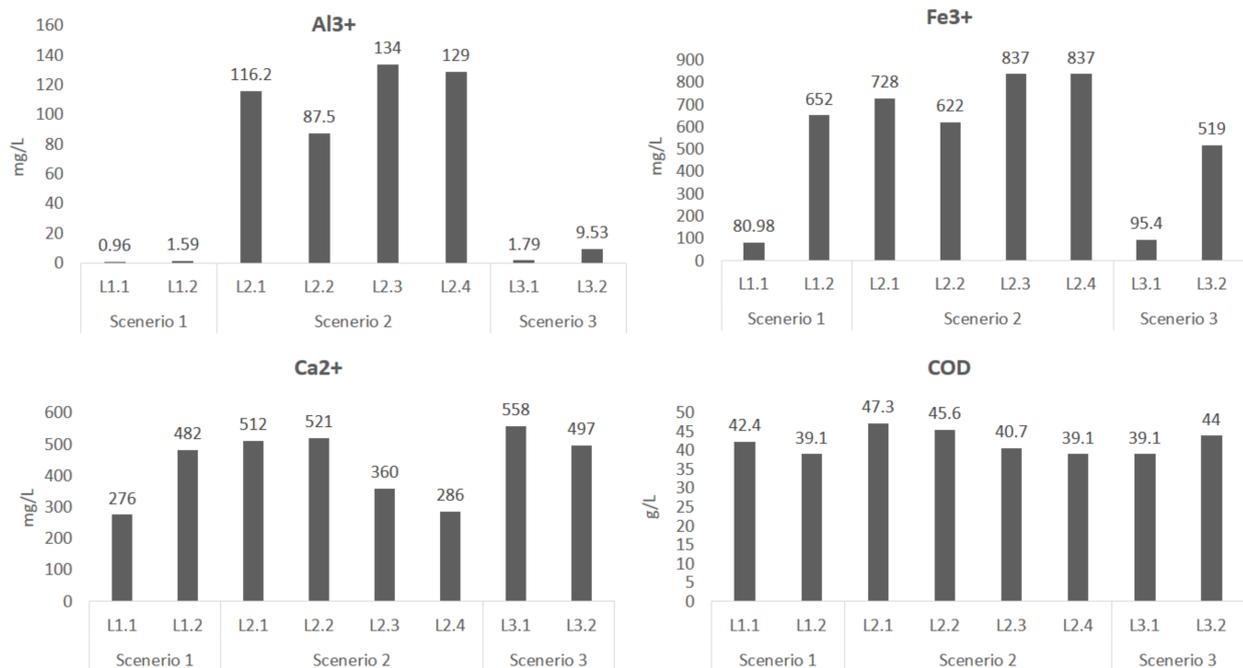


Figure 3. Metal ions' concentrations and COD of the leachate after solid–liquid separation.

3.3. Fuel Characteristic of the Hydrochar

The proximate analysis and calorific value (HHV) of the hydrochar are presented in Table 3. Following HTC, sewage sludge was carbonized to a brown-grey char, and the physical appearance implied that the produced hydrochar had a uniform composition and could be easily moulded into dense pellets. The proximate analysis and calorific value were investigated to comprehend the fuel property of the produced hydrochar. Despite using H_2SO_4 as an additive in the different process conditions, hydrochar produced from the investigated three different scenarios for HTC had comparatively similar results for proximate analysis and calorific value. However, with the utilization of H_2SO_4 as an additive at higher concentrations, in scenario 2 (L2.3 and L2.4) there was a slight increase in VS and decrease in ash content of hydrochar in comparison with scenario 1 (L1.2) and scenario 3 (L3.2). Nevertheless, the difference is too insignificant to draw any conclusion.

Table 3. Proximate analysis and calorific value of hydrochar produced under different reaction conditions.

Sample Description		Proximate Analysis (% DM)			Acid Utilization		pH (HTC)		Acid Leaching		Calorific Value
Scenario	Sample Id	VS	Ash	FC	during HTC	after HTC	Initial pH	Final pH	Initial pH	Final pH	HHV (MJ/Kg)
Scenario 1	L1.1	47.89	44.37	7.74	✓	-	3.16	5.12	-	-	13.22
	L1.2	50.12	41.72	8.18	✓	-	2.26	4.67	-	-	13.49
Scenario 2	L2.1	50.76	42.63	6.61	-	✓	7.46	6.77	2.99	3.65	14.10
	L2.2	47.80	43.82	8.38	-	✓	7.47	7.12	2.96	3.34	14.09
	L2.3	53.97	38.37	7.67	-	✓	7.56	7.01	2.71	3.13	14.02
	L2.4	52.97	39.56	7.47	-	✓	7.34	6.74	2.51	3.12	14.08
Scenario 3	L3.1	51.74	41.04	7.23	✓	✓	3.95	5.69	-	-	13.82
	L3.2	50.04	42.17	7.80	✓	✓	2.33	5.12	3.83	4.057	13.70

The hydrochar produced using different scenarios in this study had HHV ranging between 13.22–14.09 MJ/kg, which is comparable to the results from earlier studies demonstrating fuel characteristics of hydrochar produced using sewage sludge [5,40].

The volatile solids (VS) concentration of sewage sludge (65.00%) decreased after carbonization (47.80–53.97%), and this loss of VS could be partially related to the increase in fixed carbon (FC) of the produced hydrochar. On average, the FC content in hydrochar produced using three different scenarios was about 7.60% (6.61–8.38%) which was about a 6-fold increase in comparison with the FC content of sewage sludge at 1.3%. FC can be defined as combustible residue existing in the hydrochar after the volatile solids are burned. Generally, sewage sludge before HTC contains high VS and low FC content, however, FC content significantly increases after HTC [41]. One explanation for the increase in FC content of hydrochar could be due to the breakdown of sewage sludge under the influence of aromatization, polymerization, and condensation during the HTC process [42]. There are several studies showcasing a strong relationship between FC content and the heating value of hydrochar; an increase in the FC content of the hydrochar can directly raise the calorific value of the hydrochar [41,43]. However, hydrochar produced in this study, despite having higher FC content, had a comparatively lower calorific value in comparison with the sewage sludge. The decrease in the heating value of hydrochar can be attributed to the reaction severity due to the utilization of H₂SO₄ and the dissolution of organic material into the liquid phase.

The ash content of the hydrochar increased from 33.64% in sewage sludge to about 41.75% (38.37–44.37%) in hydrochar. The increase in ash content can be attributed to the excess loss of VS and the retainment of minerals onto the hydrochar. Similarly, the increase in FC of the hydrochar can be correlated to the devolatilization of VS and the mass conversion through HTC. Nevertheless, concerning the mass balance during the HTC process, the loss of VS in hydrochar was higher than that of the increased FC, indicating that VS was also converted into other products such as CO₂ or dissolved into the liquid phase [44,45].

4. Conclusions

The influence of H₂SO₄ utilization during and after HTC of sewage sludge on P leaching, metal ion transformation, and characteristics of hydrochar was analysed. The experimental results clearly depict that even after the utilization of the same amount of acid, a higher amount of TP (300–400%) and metal ion transformation from solid to liquid was observed when H₂SO₄ was used after HTC, in comparison with H₂SO₄ utilization during HTC. As a result of chemical reactions and the thermochemical breakdown pathway that occurs during HTC, the acid-buffering capacity of sewage sludge is significantly reduced. Upon addition of acid to the HTC slurry produced after HTC of sewage sludge, the majority of the H⁺ in the added H₂SO₄ is utilized to induce dissolution of Al-P and Fe-P, aiding significantly increased P transformation from solid to a liquid phase. Further, the temperature of the HTC slurry during acid leaching also had an influence on the transformation of P into the leachate. Comparatively higher P leaching (increase in 7.20% and 14.60% with utilization of acids at lower and higher acid concentrations, respectively) from solid to liquid phase was observed when the acid was added to the HTC slurry at room temperature than with acid addition to the HTC slurry (between 47 °C to 50 °C) directly after the HTC process. In contrast, despite using H₂SO₄ in the different process conditions, hydrochar produced from the investigated three different scenarios had comparatively similar results for proximate analysis and calorific value.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr10010151/s1>, Table S1. Concentrating of TP, ortho-P, metal ions, and COD in the leachate after solid-liquid separation (three different trials).

Author Contributions: Conceptualization, V.S.E. and S.N.; methodology, V.S.E.; formal analysis, V.S.E.; investigation, V.S.E.; writing—original draft preparation, V.S.E.; writing—review and editing,

V.S.E., S.N., T.E., E.A. and M.N.; visualization, V.S.E.; supervision, S.N. All authors have read and agreed to the published version of the manuscript.

Funding: This publication was funded by the German Research Foundation (DFG) and the Open Access Publication Fund of the University of Rostock.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article or Supplementary Materials.

Acknowledgments: The authors would like to thank Ruth Gebauer, Jan Sprafke, and Kersten Eckermann for their kind assistance during the preparation of this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Pérez, C.; Boily, J.-F.; Jansson, S.; Gustafsson, T.; Fick, J. Acid-Induced Phosphorus Release from Hydrothermally Carbonized Sewage Sludge. *Waste Biomass Valor.* **2021**, *12*, 6555–6568. [CrossRef]
- Nenov, V.; Peeva, G.; Yemendzhiev, H.; Stancheva, M.; Zerouq, F. Phosphorus consumption. From linear to circular flow. *Moroc. J. Chem.* **2020**, *8*, 819–829.
- Heckenmüller, M.; Narita, D.; Klepper, G. *Global Availability of Phosphorus and Its Implications for Global Food Supply: An Economic Overview*; Kiel Institute for the World Economy: Kiel, Germany, 2014.
- Jama-Rodzeńska, A.; Białowiec, A.; Koziel, J.A.; Sowiński, J. Waste to phosphorus: A transdisciplinary solution to P recovery from wastewater based on the TRIZ approach. *J. Environ. Manag.* **2021**, *287*, 112235. [CrossRef]
- He, C.; Giannis, A.; Wang, J.-Y. Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior. *Appl. Energy* **2013**, *111*, 257–266. [CrossRef]
- Ekanthalu, V.S.; Narra, S.; Nelles, M. Hydrothermal Carbonization: A Robust Technology to Effectively Manage Sewage Sludge Produced in Germany—Review. 2019. Available online: <https://www.researchgate.net/publication/338544309> (accessed on 30 November 2021).
- Statistisches Bundesamt Destatis. Erhebung der öff. Abwasserentsorgung—Klärschlamm. 2021. Available online: <https://www-genesis.destatis.de/genesis/online?operation=statistic&levelindex=0&levelid=1639500438707&code=32214#abreadcrumb> (accessed on 18 December 2021).
- Kreislaufwirtschaftsgesetz—KrWG, Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der Umweltverträglichen Bewirtschaftung von Abfällen*; Bundesministeriums der Justiz und für Verbraucherschutz sowie des Bundesamts für Justiz: Berlin, Germany, 2012.
- Abfklär, V. *Verordnung über die Verwertung von Klärschlamm, Klärschlammgemisch und Klärschlammkompost*; Bundesministeriums der Justiz und für Verbraucherschutz und Bundesamts für Justiz: Berlin, Germany, 2017.
- Crocker, M.; Andrews, R. Chapter The Rationale for Biofuels. In *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*; Royal Society of Chemistry (RSC): London, UK, 2010; pp. 1–25.
- Saetea, P.; Tippayawong, N. Recovery of Value-Added Products from Hydrothermal carbonization of Sewage Sludge. *Int. Sch. Res. Not.* **2013**, *2013*.
- Park, T.; Ampunan, V.; Lee, S.; Chung, E. Chemical behavior of different species of phosphorus in coagulation. *Chemosphere* **2016**, *144*, 2264–2269. [CrossRef] [PubMed]
- Becker, G.; Wüst, D.; Köhler, H.; Lautenbach, A.; Kruse, A. Novel approach of phosphate-reclamation as struvite from sewage sludge by utilising hydrothermal carbonization. *J. Environ. Manag.* **2019**, *238*, 119–125. [CrossRef]
- Heilmann, S.M.; Molde, J.S.; Timler, J.G.; Wood, B.M.; Mikula, A.L.; Vozhdayev, G.V.; Colosky, E.C.; Spokas, K.A.; Valentas, K.J. Phosphorus Reclamation through Hydrothermal Carbonization of Animal Manures. *Environ. Sci. Technol.* **2014**, *48*, 10323–10329. [CrossRef]
- Wang, T.; Zhai, Y.; Zhu, Y.; Peng, C.; Wang, T.; Xu, B.; Li, C.; Zeng, G. Feedwater pH affects phosphorus transformation during hydrothermal carbonization of sewage sludge. *Bioresour. Technol.* **2017**, *245*, 182–187. [CrossRef]
- Ovsyannikova, E.; Arauzo, P.J.; Becker, G.C.; Kruse, A. Experimental and thermodynamic studies of phosphate behavior during the hydrothermal carbonization of sewage sludge. *Sci. Total Environ.* **2019**, *692*, 147–156. [CrossRef]
- Shi, Y.; Luo, G.; Rao, Y.; Chen, H.; Zhang, S. Hydrothermal conversion of dewatered sewage sludge: Focusing on the transformation mechanism and recovery of phosphorus. *Chemosphere* **2019**, *228*, 619–628. [CrossRef]
- Zhai, Y.; Liu, X.; Zhu, Y.; Peng, C.; Wang, T.; Zhu, L.; Li, C.; Zeng, G. Hydrothermal carbonization of sewage sludge: The effect of feed-water pH on fate and risk of heavy metals in hydrochars. *Bioresour. Technol.* **2016**, *218*, 183–188. [CrossRef] [PubMed]
- Liu, X.; Zhai, Y.; Li, S.; Wang, B.; Wang, T.; Liu, Y.; Qiu, Z.; Li, C. Hydrothermal carbonization of sewage sludge: Effect of feed-water pH on hydrochar’s physicochemical properties, organic component and thermal behavior. *J. Hazard. Mater.* **2020**, *388*, 122084. [CrossRef] [PubMed]

20. Leng, L.; Yuan, X.; Huang, H.-J.; Shao, J.; Wang, H.; Chen, X.; Zeng, G. Bio-char derived from sewage sludge by liquefaction: Characterization and application for dye adsorption. *Appl. Surf. Sci.* **2015**, *346*, 223–231. [[CrossRef](#)]
21. Wang, L.; Chang, Y.; Liu, Q. Fate and distribution of nutrients and heavy metals during hydrothermal carbonization of sewage sludge with implication to land application. *J. Clean. Prod.* **2019**, *225*, 972–983. [[CrossRef](#)]
22. Peng, C.; Zhai, Y.; Zhu, Y.; Xu, B.; Wang, T.; Li, C.; Zeng, G. Production of char from sewage sludge employing hydrothermal carbonization: Char properties, combustion behavior and thermal characteristics. *Fuel* **2016**, *176*, 110–118. [[CrossRef](#)]
23. Ekanthalu, V.S.; Morscheck, G.; Narra, S.; Nelles, M. Hydrothermal Carbonization—A Sustainable Approach to Deal with the Challenges in Sewage Sludge Management. In *Urban Mining and Sustainable Waste Management*; Springer: Singapore, 2020; pp. 293–302.
24. Roskosch, A.; Heidecke, P. *Sewage Sludge Disposal in the Federal Republic of Germany*; German Environment Agency: Dessau-Roßlau, Germany, 2018.
25. Golterman, H.; Stumm, W.; Morgan, J.J. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. *J. Ecol.* **1982**, *70*, 924. [[CrossRef](#)]
26. Yong, R.N.; Mohamed, A.-M.O.; Warkentin, B.P. *Principles of Contaminant Transport in Soils*; Elsevier: Ann Arbor, MI, USA, 1992.
27. Zhang, H.-Y.; Ju, Y.-Y.; Fan, Z.-M.; Wang, B. Acid buffer capacity of sewage sludge barrier for immobilization of heavy metals. *Huan Jing Ke Xue* **2010**, *31*, 2956–2964.
28. Bozkurt, I.; Moreno, L.; Neretnieks, I. Long-term processes in waste deposits. *Sci. Total Environ.* **2000**, *250*, 101–121. [[CrossRef](#)]
29. Petzet, S.; Peplinski, B.; Cornel, P. On wet chemical phosphorus recovery from sewage sludge ash by acidic or alkaline leaching and an optimized combination of both. *Water Res.* **2012**, *46*, 3769–3780. [[CrossRef](#)]
30. Wang, L.; Chang, Y.; Li, A. Hydrothermal carbonization for energy-efficient processing of sewage sludge: A review. *Renew. Sustain. Energy Rev.* **2019**, *108*, 423–440. [[CrossRef](#)]
31. Libra, J.A.; Ro, K.S.; Kammann, C.; Funke, A.; Berge, N.D.; Neubauer, Y.; Titirici, M.-M.; Fühner, C.; Bens, O.; Kern, J.; et al. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* **2011**, *2*, 71–106. [[CrossRef](#)]
32. Reza, M.T.; Uddin, M.H.; Lynam, J.G.; Hoekman, S.K.; Coronella, C.J. Hydrothermal carbonization of loblolly pine: Reaction chemistry and water balance. *Biomass Convers. Biorefinery* **2014**, *4*, 311–321. [[CrossRef](#)]
33. Blach, T.; Engelhart, M. Optimizing the Hydrothermal Carbonization of Sewage Sludge—Response Surface Methodology and the Effect of Volatile Solids. *Water* **2021**, *13*, 1–19. [[CrossRef](#)]
34. Wilson, C.A.; Novak, J.T. Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water Res.* **2009**, *43*, 4489–4498. [[CrossRef](#)] [[PubMed](#)]
35. Asghari, F.S.; Yoshida, H. Acid-Catalyzed Production of 5-Hydroxymethyl Furfural from d-Fructose in Subcritical Water. *Ind. Eng. Chem. Res.* **2006**, *45*, 2163–2173. [[CrossRef](#)]
36. Hoff, J.H. Studies in Chemical Dynamics. *Nature* **1896**, *55*, 98.
37. Ehrnström, M.S. *Recovery of Phosphorus from HTC Converted Municipal Sewage Sludge*; Luleå University of Technology: Luleå, Sweden, 2016.
38. Huang, R.; Fang, C.; Zhang, B.; Tang, Y. Transformations of Phosphorus Speciation during (Hydro)thermal Treatments of Animal Manures. *Environ. Sci. Technol.* **2018**, *52*, 3016–3026. [[CrossRef](#)] [[PubMed](#)]
39. Ekpo, U.; Ross, A.B.; Camargo-Valero, M.A.; Fletcher, L.A. Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus in process water. *Bioresour. Technol.* **2016**, *214*, 617–644. [[CrossRef](#)] [[PubMed](#)]
40. Ekanthalu, V.S.; Narra, S.; Sprafke, J.; Nelles, M. Influence of Acids and Alkali as Additives on Hydrothermally Treating Sewage Sludge: Effect on Phosphorus Recovery, Yield, and Energy Value of Hydrochar. *Processes* **2021**, *9*, 618. [[CrossRef](#)]
41. Putra, H.; Damanhuri, E.; Dewi, K.; Pasek, A.D. Hydrothermal carbonization of biomass waste under low temperature condition. *MATEC Web Conf.* **2018**, *154*, 01025. [[CrossRef](#)]
42. Mazumder, S.; Saha, P.; Reza, M.T. Co-hydrothermal carbonization of coal waste and food waste: Fuel characteristics. *Biomass Convers. Biorefinery* **2020**, *12*, 3–13. [[CrossRef](#)]
43. Anshariah; Imran, A.; Widodo, S.; Irvan, U.R. Correlation of fixed carbon content and calorific value of South Sulawesi Coal, Indonesia. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *473*, 012106. [[CrossRef](#)]
44. Berge, N.D.; Ro, K.S.; Mao, J.; Flora, J.R.V.; Chappell, M.A.; Bae, S. Hydrothermal Carbonization of Municipal Waste Streams. *Environ. Sci. Technol.* **2011**, *45*, 5696–5703. [[CrossRef](#)]
45. Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal. *Ind. Eng. Chem. Res.* **2012**, *51*, 9023–9031. [[CrossRef](#)]