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Dissertation

Vicky Shettigondahalli Ekanthalu

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Preface

The worlds demand for Phosphorous in the recent decades has increased exponentially creating a huge pressure on the global mining industries. This increased pressure on phosphorous as a resource is indirectly contributing to the global climate negatively demanding for alternative solutions. The alternative solutions would be to recycle the available phosphorous from non-conventional alternatives such as from sewage sludge at the wastewater treatment plants using different technologies. These non-conventional approaches reduce the global burden and tries to recycle the resource locally. The Professorship for Waste and Resource Management as well as the Professorship for Material and Energy valorization of Biogenous Residues at the University of Rostock try to address the above stated issue and focus on developing processes to optimize the recycling of valuable resources from waste and residues.

The PhD thesis of Mr. Vicky Shettigondahalli Ekanthalu started in the year 2019 and focuses on the optimization of the recycling of Phosphorous using Hydrothermal Carbonization process with pre- and post-treatments of the substrates using various acids and bases. This thesis is a practice-oriented research evaluating various pH variations including treatment of char demonstrating sustainable recycling pathways.

The PhD work of Mr. Shettigondahalli Ekanthalu was carried out within the framework of the PhD program "Material and energetic utilization of waste and biomass", which is coordinated by the Professorship of Waste and Resource Management as well as by the Professorship of Material and Energy Valorization of Biogenous Residues at the University of Rostock.

The PhD was financially supported under the projects 1.) RePhoR-MV: Regionales Phosphor-Recycling aus Klärschlämmen in Mecklenburg-Vorpommern (funded by BMBF), 2.) Waste2Energy: Hybrid waste to energy as a sustainable solution for Ghana (funded by BMBF), 3.) Perival: Waste to Value Chains in Peri-Urban Environments (Waste-value – Wertschöpfungsketten in der Peripherie Urbaner Regionen). Zhaoquanying Town - Beijing (Shunyi District) (funded by BMBF), 4.) MOWI: Management of Organic Waste in India (funded by GIZ). The results of the thesis were evaluated in the form of a cumulative dissertation. Mr. Shettigondahalli Ekanthalu submitted the work to the Faculty of Agricultural and Environmental Sciences in Fall 2023.

From the perspective of the reviewers, the scientific significance of the present work results in particular from the following points:

- In the past 5 years, Mr. Shettigondahalli Ekanthalu has dealt very intensively with the possibilities and limits of the combined recycling and resource recovery of phosphorous from wastewater treatment plants

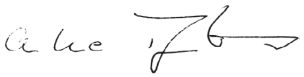
- For this purpose, Mr. Shettigondahalli Ekanthalu developed specific technical recovery concepts based on the treatment processes that are technically feasible using hydrothermal carbonation process. Extensive practical tests were carried out on a laboratory scale. The results show that the applied processes are technically and economically feasible for addressing the phosphorous recovery from non-conventional resources. In addition, a significant contribution to climate protection and sustainable regional application can be made possible.

Finally, we wish you interesting technical suggestions and a lot of fun reading the dissertation of Dr.-Eng. Vicky Shettigondahalli Ekanthalu.

Sending warm greetings from Rostock, Tier and Innsbruck

Prof. Dr. habil. Satyanarayana Narra
Universität Rostock

Dr.-Ing. Susanne Hartard
Hochschule Trier



Prof. Dr.-Ing. Anke Bockreis
Universität Innsbruck

Universität Rostock Traditio et Innovatio

Professorship for Waste and Resource Management
Faculty of Agriculture and Environmental Science

HYDROTHERMAL CARBONIZATION OF SEWAGE SLUDGE AND THE INFLUENCE OF pH ON PHOSPHORUS TRANSFORMATION AND HYDROCHAR PROPERTIES

Cumulative Dissertation

Submitted in the fulfillment for the award of

Doctor of Engineering (Dr.-Ing.)

At the Faculty of Agriculture and Environmental Sciences

University of Rostock

Vicky Shettigondahalli Ekanthalu (M.Sc.)

Rostock

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I would like to thank my parents for their unwavering support and belief throughout my academic career and doctoral work. Prof. Mont Michael Nelles and Dr. habil Satyanarayana Narra are the first people I'm grateful to on a professional level. They accepted me into their workgroup and supervised the completion of this thesis. I would like to once again acknowledge and thank Dr. habil Satyanarayana Narra, with whom I have worked directly for the past five years. His insightful advice, comments, and suggestions have substantially influenced the direction of this thesis.

I am extremely thankful to Dr. Jan Sprafke and Dr. Nils Engler, who supervised most of the laboratory work and gave me the necessary freedom at the lab to complete the work. I am also grateful to Kersten Eckermann and Annabell Apitz, members of the technical staff, who were always willing to aid me with my experiments. Thank you to Dr. habil. Abdallah Nassour, Prof. Gert Morsheck, and Dr. Ruth Gebauer. In some way or another, they have motivated me by bringing out the best in me. Thanks to Christine Herz, who helped me with the complex administrative processes during my studies and work at the department. My special thanks also go to Vidhi Singh, Tommy Ender, and Dr. Edward Antwi for their input, suggestions, and useful discussions over the past years. Not to forget the contributions of Jan Klein, Mona-Maria Narra, Sebastian Foth, Dr. Haniyeh Jalalipour, Dr. Qahtan Thabit, and Zipporah Asiedu, especially for your friendship and productive academic discussions. For the incredibly fruitful time spent together, a big thanks to all the other staff members at the University of Rostock's Department of Waste and Resource Management who aren't specifically named here.

I would like to express my sincere gratitude to the BioGRAG-DEF, MOWI, PERIVAL, RePhor-MV, and Waste2Energy projects and their respective grant givers for their invaluable contributions to my doctoral journey. The insights gained and skills developed while working with these projects have undoubtedly played a crucial role in shaping and enriching the quality of my research.

Last but not least, I would like to express my gratitude to my loving wife and a great friend Anju for being a constant source of inspiration. I am not sure how long this journey would have taken me if you have not provided me with constant encouragement and pep talks. Thank you and love you!

ABSTRACT

The availability of phosphorus is crucial for all life forms on the planet Earth and absolutely essential for meeting global agricultural and industrial demands. The world's demand for phosphorus has progressively risen due to the accelerated progress of the global economy and the increasing population. In contrast, the global phosphate mineral deposit is nonrenewable in nature, its origin is limited to a few geographical locations, and it is expected to be depleted in a few decades. To meet the global demand for this indispensable element, there is an immediate need for the effective management and recycling of residues containing high levels of phosphorus. One such potential possibility is to recover phosphorus from sewage sludge generated by a wastewater treatment plant (WWTP). The present-day techniques at municipal WWTPs capture up to 95% of phosphorus from wastewater into sewage sludge, producing a highly desirable product consisting of significantly higher concentrations of phosphorus with an opportunity to recycle. Many countries prohibit the direct use of sewage sludge for agricultural purposes due to its complex composition, which includes hazardous substances of organic origin, various pathogens, microplastics, and heavy metals. The presence of heavy metals in sewage sludge is a particularly major cause of concern. The direct recovery of phosphorus from sewage sludge is also challenging and cost-intensive due to the high moisture content present in the sewage sludge. Given this context, hydrothermal treatment of sewage sludge has drawn increased attention as an environmentally appropriate and practically feasible technique for treating moist sewage sludge without the requirement of pre-drying. In contrast to conventional sewage sludge valorization pathways like incineration, the hydrothermal carbonization (HTC) process obviates the limitation of moisture present in sewage sludge. The hydrothermal technique uses the surplus moisture in sewage sludge in the reaction process and makes it as a catalyst to transform sewage sludge into a lignite-like hydrochar that is phosphorus -rich, hygienic, and readily dewaterable.

This study examines the effect of pH and various acid-base additives on the mobilization of phosphorus from solids to the liquid phase. The various process conditions during HTC affect the properties of hydrochar and the process water. The impacts of varying HTC process parameters and pH during various stages of the process were also investigated. Additionally, a study is also done to compare the economic viability of the sulfuric acid requirements for leaching phosphorus from sewage sludge hydrochar and compares it with the traditional phosphorus -leaching techniques for other sewage sludge derivatives.

The first set of experiments examines how changing the pH (from 3.5 to 11) during hydrothermal carbonization of sewage sludge affects phosphorus transformation, yield, proximate analysis, and calorific value of the resulting hydrochar. Using organic acids, inorganic acids, and alkali, a broad pH range was achieved during the analysis. The results indicate that pH and temperature are significant factors in phosphorus leaching into the process water, hydrochar yield, and the heating value of produced hydrochar, with inorganic acids having a substantial effect.

Based on these results, further investigation was carried out to analyze the influence of acid addition pre- and post-HTC on sewage sludge. This particular research result demonstrated that the acid buffer capacity of sewage sludge is drastically reduced due to chemical reactions and the thermochemical degradation pathway during the HTC process. The H^+ in H_2SO_4 is used to promote Al-P and Fe-P dissolution. The reduction in the acid buffer capacity of sewage sludge after HTC results in greatly accelerated phosphorus transformation from solid to liquid phase, compared to acid addition before HTC.

The latest experimental analysis involved acid leaching the sewage sludge hydrochar at pH of 1.5, 2.125, and 2.75 and studying their impacts on phosphorus leaching and hydrochar properties. Formic acid, sulfuric acid, and acetic acid were used to achieve different pH during the leaching process, and their results were compared. The research's findings demonstrated that the acid dissociation constant and pH have influenced the solubility and mobility of phosphorus in the acid-leaching medium.

The economic feasibility study conducted on the sulfuric acid needed to leach phosphorus from sewage sludge derivatives showed that phosphorus leaching from sewage sludge hydrochar can compete with conventional phosphorus recovery methods that use sewage sludge ash and sulfuric acid. The HTC process offers the supplementary benefit of generating climate-neutral fuel in addition to its ability to economically leach phosphorus.

KURZFASSUNG

Die Verfügbarkeit von Phosphor ist für alle Lebensformen auf unserem Planeten von entscheidender Bedeutung und für die Deckung des weltweiten Bedarfs in der Landwirtschaft und Industrie absolut notwendig. Der weltweite Bedarf an Phosphor ist aufgrund des beschleunigten Fortschritts der Weltwirtschaft und des Bevölkerungswachstums immer weiter gestiegen. Die weltweiten Phosphatvorkommen sind jedoch nicht erneuerbar, ihr Vorkommen ist auf einige wenige geografische Gebiete beschränkt, und es wird erwartet, dass sie in wenigen Jahrzehnten erschöpft sein werden. Um den weltweiten Bedarf an diesem unverzichtbaren Element zu decken, besteht ein unmittelbarer Bedarf einer nachhaltigen Bewirtschaftung und Verwertung von Rückständen mit hohem Phosphorgehalt. Eine dieser Möglichkeiten ist die Rückgewinnung von Phosphor aus Klärschlamm, der in Kläranlagen während der Abwasserreinigung anfällt. Mit den heutigen Techniken in kommunalen Kläranlagen werden bis zu 95% des Phosphors aus dem Abwasser im Klärschlamm angereichert, wodurch ein Produkt mit deutlich höheren Phosphorkonzentrationen entsteht. Viele Länder verbieten jedoch die direkte Verwertung von Klärschlamm für landwirtschaftliche Zwecke aufgrund seiner komplexen Zusammensetzung, den organischen Schadstoffen, verschiedenen Krankheitserregern, Mikroplastik und Schwermetallen. Vor allem das Vorhandensein von organischen Schadstoffen und Schwermetallen im Klärschlamm gibt Anlass zu großer Sorge. Auch die direkte Rückgewinnung von Phosphor aus Klärschlamm ist aufgrund des hohen Feuchtigkeitsgehalts von Klärschlamm eine Herausforderung und kostenintensiv. Vor diesem Hintergrund bietet die hydrothermische Behandlung von Klärschlamm als umweltverträgliches und praktikables Verfahren zur Behandlung von entwässertem Klärschlamm ohne Vortrocknung eine Alternative.In der Forschung gewinnt sie zunehmend an Bedeutung. Im Gegensatz zu konventionellen Verwertungsmethoden wie der Verbrennung entfällt bei der hydrothermalen Karbonisierung (HTC) die Begrenzung durch die im Klärschlamm vorhandene Feuchtigkeit. Der hydrothermale Prozess nutzt die überschüssige Feuchtigkeit im Klärschlamm im Reaktionsprozess und verwendet sie als Katalysator, um den Klärschlamm in eine braunkohleähnliche Hydrokohle umzuwandeln, die phosphorreich, hygienisiert und leicht zu entwässern ist.

In der vorliegenden Studie wird der Einfluss des pH-Wertes und verschiedener Säure-Base-Zusätze auf die Rücklösung von Phosphor aus den Feststoffen in die flüssige Phase untersucht. Die verschiedenen Prozessbedingungen während der HTC beeinflussen die Beschaffenheiten von Hydrokohle, Prozesswasser und Leachwasser. Die Auswirkungen unterschiedlicher HTC-Prozessparameter und des pH-Werts während verschiedener Prozessphasen wurden ebenfalls untersucht. Darüber hinaus wurde eine Studie durchgeführt, um die Wirtschaftlichkeit der Schwefelsäureanforderungen für die Auslaugung von Phosphor aus Klärschlamm-Hydrokohle zu prüfen und sie mit den traditionellen Phosphor-Rücklösungstechniken für andere Klärschlammderivate zu vergleichen.

In der ersten Versuchsreihe wird untersucht, wie sich die Änderung des pH-Werts (von 3,5 auf 11) während der hydrothermalen Karbonisierung von Klärschlamm auf die Phosphorumwandlung, die Ausbeute, die Immediatanalyse und den Heizwert der resultierenden Hydrokohle auswirkt. Mit Hilfe von organischen Säuren, anorganischen Säuren und Basen wurde bei der Analyse ein breiter pH-Bereich abgedeckt. Die Ergebnisse zeigen, dass der pH-Wert und die Temperatur wesentliche Faktoren für die Phosphorauswaschung in das Prozesswasser, die

Hydrokohleausbeute und den Heizwert der erzeugten Hydrokohlesind. Anorganische Säuren haben einen besonders positiven Einfluss.

Auf Grundlage dieser Ergebnisse wurde eine weitere Untersuchung durchgeführt, um den Einfluss der Säurezugabe vor und nach der HTC auf den Klärschlamm zu untersuchen. Dieses spezielle Forschungsergebnis zeigte, dass die Säurepufferkapazität von Klärschlamm aufgrund chemischer Reaktionen und des thermochemischen Abbaupfades während des HTC-Prozesses drastisch reduziert wird. Das H^+-Ionin der Schwefelsäure (H_2SO_4) wird zur Förderung der Al-P- und Fe-P-Auflösung verwendet. Die Verringerung der Säurepufferkapazität des Klärschlamms nach der HTC führt zu einer stark beschleunigten P-Umwandlung von der festen in die flüssige Phase, verglichen mit der Säurezugabe vor der HTC.

Die letzte experimentelle Analyse umfasste die saure Säurerücklösung der Klärschlamm-Hydrokohle bei einem pH-Wert von 1,5, 2,125 und 2,75 und die Untersuchung ihrer Auswirkungen auf die Rücklösung und die Eigenschaften der HTC-Kohle. Ameisensäure, Schwefelsäure und Essigsäure wurden verwendet, um unterschiedliche pH-Werte während des Auslaugungsprozesses zu erreichen, und die Ergebnisse wurden verglichen. Die Forschungsergebnisse zeigten, dass die Säuredissoziationskonstante und der pH-Wert die Löslichkeit und Mobilität von Phosphor im sauren Auslaugungsmedium beeinflusst haben.

Die Wirtschaftlichkeitsstudie zur Schwefelsäure, die für die Auslaugung von Phosphor aus Klärschlammderivaten benötigt wird, zeigte, dass die Phosphor-Rücklösung aus Klärschlamm-Hydrokohle mit konventionellen Phosphor-Rückgewinnungsmethoden konkurrieren kann, die Klärschlammasche und Schwefelsäure verwenden. Das HTC-Verfahren bietet neben der wirtschaftlichen Auslaugung von Posphor aus Klärschlämmen den zusätzlichen Vorteil der Erzeugung eines klimaneutralen Brennstoffs.

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
AD	Anaerobic digestion
ANOVA	Analysis of Variance
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DM	Dry matter
DOC	Dissolved organic carbon
DoE	Design of experiments
EBPR	Enhanced biological phosphorus removal
EU	European Union
FC	Fixed carbon
HC	Hydrochar
HHV	Higher heating value
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquification
ISSA	Incinerated sewage sludge ash
kW	Kilowatt
LHV	Lower heating value
MSW	Municipal solid waste
OS	Original Sample
PE	Population equivalent
PSS	Primary sewage sludge
PSSA	Pyrolysis sewage sludge ash
PSSC	pyrolysis sewage sludge char
PSSCA	Pyrolysis sewage sludge char ash
RSM	Response surface model
RQ	Research question
SI	Saturation index
SS	Sewage sludge
SSA	Sewage sludge ash
SSH	Sewage sludge hydrochar
TOC	Total organic carbon
TGA	Thermogravimetric Analyzer
TN	Total Nitrogen
TP	Total Phosphorus
VFA	Volatile fatty acids
VS	Volatile solids
WO	Wet oxidation
WWTP	Wastewater treatment plant

1. Introduction and research questions

Sewage sludge management and nutrient recovery have emerged as critical waste management subjects among the scientific community. Sewage sludge management strategies that are efficient and ecologically acceptable have become a regulatory priority in many nations as concerns about environmental sustainability and resource conservation continue to develop. According to projections issued by the United Nations Food and Agriculture Organization global demand for fertilizers is expected to rise continuously (FAO 2019). Increasing resource scarcity and rising demand for phosphorus (P)-based products serve as a wake-up call regarding resource scarcity and the imperative need to investigate alternative sources (Brownlie et al., 2023). Within the context of this issue, municipal sewage sludge that contains around 3% P has the potential to be an advantageous secondary source for the production of P (Cydzik-Kwiatkowska 2020).

Germany produced around 1.74 million metric tons of sewage sludge in the year 2020 (Statistisches Bundesamt, Destatis 2023). The agricultural consumption of the nutrient P_2O_5 was approximately 0.192 million metric tons (FAO 2023) in the same year. Taking into account the 50% P recovery from sewage sludge, Germany may produce approximately 0.06 million metric tons of nutrient P_2O_5. It is 31% of Germany's annual nutrient P_2O_5 demand. This highlights the importance of sewage sludge as an alternative P resource. In addition to significantly enhancing resource efficiency, proper sewage sludge usage can also facilitate effective sewage sludge management.

The use of sewage sludge in agriculture and landscaping has been a popular method of recycling sewage sludge. The present trend in sewage sludge utilization is however moving away from land-based applications and heading toward thermal treatment. In addition to nutrients, sewage sludge contains heavy metals and pollutants of organic and inorganic origin (Aragón-Briceño et al., 2021). The presence of these pollutants complicates its direct application to farmland. The German Sewage Sludge Ordinance regulates the handling and treatment of sewage sludge in Germany (AbfKlärV 2017). German Sewage Sludge Ordinance prohibits the land-based recycling of sewage sludge in Germany from 2029 for wastewater treatment plants (WWTPs) with a capacity of >100,000 population equivalent (PE). Similar rules will be applied in 2032 for sewage treatment plants with a capacity of >50,000 PE. Producers of sewage sludge in Germany are now required by law to extract phosphorus from sludge with a phosphorus concentration of ≥20 grams of P per kg of dry sewage sludge.

The abundance of volatile organic compounds present in sewage sludge on the other hand can be used to boost the efficiency of energy production. Although drying and incineration are the most popular methods, the presence of significant moisture content in the feedstock could incur higher management costs (Wilk et al., 2022). An effective treatment option is required to address the issue of higher moisture content in sewage sludge and enhance energy management. The hydrothermal treatment process is currently evolving as a promising know-how due to its potential to handle sewage sludge with high moisture content. The dewatering capacity of sewage sludge is greatly improved through hydrothermal conditioning and also reduces the overall energy demand. Hydrothermal carbonization (HTC) as a technology aligns with the European Key Objectives Action Plan, which emphasizes "waste-to-energy" in the circular economy and encourages waste prevention, reuse, and recycling.

HTC as a technology is however not yet been proven in continuous industrial operation in sewage sludge treatment. The reason for this mainly includes the limitation of cost-effective technology to treat process water produced after HTC of sewage sludge (Reißmann et al., 2021), and limited knowledge of acid leaching of sewage sludge hydrochar and P recovery. With a detailed understanding of the above-mentioned aspects, HTC is anticipated to play a significant role, particularly in sewage sludge management. The recent literature on HTC of sewage sludge tries to understand the effect of process conditions such as temperature (Liu et al. 2021), moisture content (Wang, Chang and Li 2019), heating rate (Brand et al., 2014), and reaction time (Wang et al., 2020), on the properties of hydrochar and process water. Extensive research has also been conducted to comprehend the reaction pathway and kinetics of the HTC of sewage sludge (Takamatsu, Hashimoto and Sioya 1970). According to Web of Science search results, there have been less than 15 research articles published on the topic of acid-leaching sewage sludge hydrochar to date (see Figure 2-5).

The leaching of P from sewage sludge derivative using the chemical leaching process has shown that pH plays a significant role in the migration of P to leachate. In this concern understating the influence of pH during HTC on sewage sludge and on the sewage sludge hydrochar will be crucial to have an efficient and cost-effective P recovery from hydrothermally carbonized sewage sludge. The primary objective of this study is to gain a deeper understanding of the effects of pH and acid characteristics during the HTC of sewage sludge and their influence on the solid-to-liquid P transformation. The study objective is thus divided into six research questions (RQ) which were answered through this cumulative dissertation based on the preceding research outcomes.

RQ 1: What is the influence of acid and base as additives during HTC of sewage sludge?

RQ 2: What effect does acid utilization pre- and post-hydrothermal carbonization have on phosphorus mobilization and hydrochar characteristics in sewage sludge? what chemical reaction kinetics impact the phosphorus-transformation from sewage sludge to leachate?

RQ 3: What are the effects of leaching sewage sludge hydrochar using organic and inorganic acids at various pH on phosphorus-mobilization?

RQ 4: In addition to pH what are the other characteristics of acids influencing the phosphorus mobilization from sewage sludge hydrochar to leachate?

RQ 5: Is it economically viable to leach phosphorus from sewage sludge hydrochar in comparison to the conventional sewage sludge derivatives such as sewage sludge ashes and pyrolysis sewage sludge ashes?

RQ 6: What is the current status and future of HTC as a technology to treat sewage sludge?

These research questions and objectives are addressed via a literature review and extensive experimental work. This will be described and discussed in the subsequent chapters. The cumulation of all work is the incorporation of three original articles and one review article into this dissertation. Additional published and unpublished data were used to support the validity of the described findings. Figure 1-1 provides an overview of the chapters linked to the research questions of this cumulative dissertation. Chapter 4 and chapter 5 of this thesis consist of the first and second articles of this cumulative dissertation which aim to address RQ 1 and 2, respectively. The 6th chapter of this thesis comprises the third article that seeks to address RQ 3 and 4. Chapters 7 and 8 of this thesis consist of the 4th article as well as extended analysis and discussion that address RQ 5 and 6. Detailed overview on articles and authors contribution is provided in chapter 3.

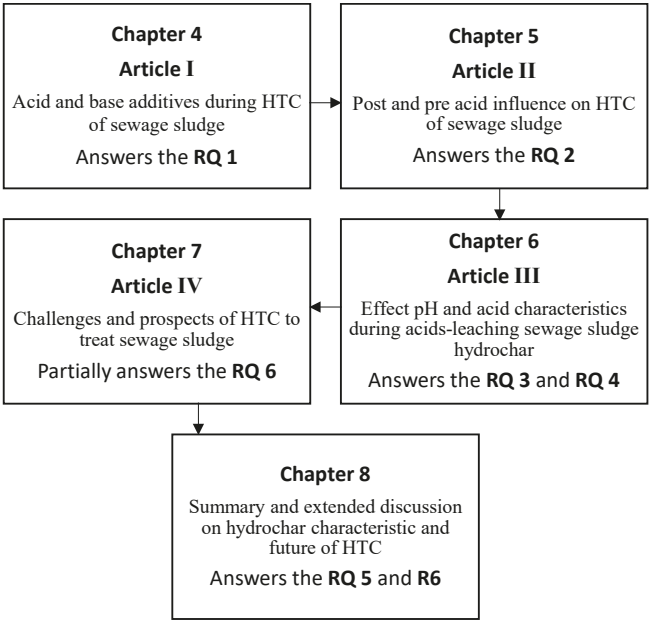

Figure 1-1 Chapters and their connections to the research question.

2. Background

2.1. State of art in HTC technology

HTC was first described by a German chemist named Friedrich Bergius. In 1913, he successfully imitated natural coalification in a controlled environment by hydrothermally transforming cellulose into substances resembling coal (Bergius 1913). Friedrich Bergius was awarded the Nobel Prize in 1931 for developing chemical high-pressure methods with the goal of elucidating the mechanism of natural coalification by hydrothermal transformation. HTC was rediscovered in recent years and has gained a great deal of research community interest over the past two decades. The primary reasons for the increasing research interest in this field are mainly due to: 1) The exploration of HTC's potential to valorize a wide range of biomass and waste streams into renewable biofuels and value-added products, 2) lower operating temperature in comparison to conventional thermochemical treatment processes, and 3) its potential to reduce energy demand. Numerous researchers have investigated the underlying mechanisms of HTC using model biomass compounds such as cellulose, lignin, glucose, sucrose, starch, xylose, etc. (Falco, Baccileb and Titirici 2011; Sevilla and Fuertes 2009; Li and Shahbazi 2015). Thousands of publications have been written about HTC since its discovery and research on HTC of sewage sludge has begun to receive increasing attention in the last decade (see Figure 2-1). The interest in this topic is only anticipated to expand.

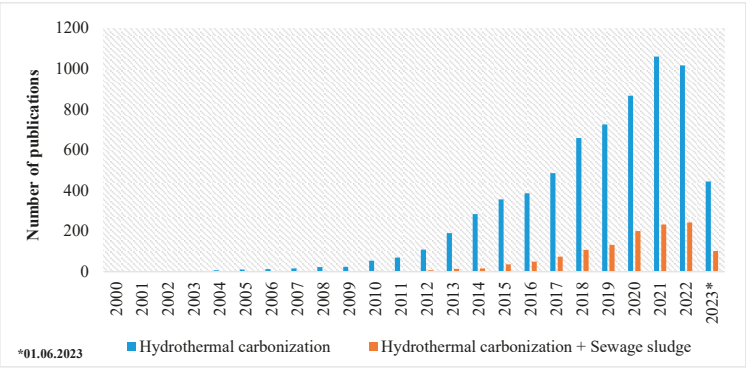

Figure 2-1 Number of published scientific articles based on Web of Science search for "Hydrothermal carbonization" and "Hydrothermal carbonization AND Sewage sludge".

Hydrothermal carbonization is an exothermic thermochemical process that can convert sewage sludge or any biomass into carbonaceous products called hydrochar at high temperatures of 180–250 °C and autogenous pressures for several hours. The initial biomass changes in both its morphology and its chemical structure under these conditions. The morphological changes include the change in the properties of biomass, such as the structure of the pores, the structure of the surface, and its affinity towards water. The changes in the molecular structure can be used to describe the chemical structure. In addition to hydrochar, the byproducts include a considerable amount of liquid (process water) and a small amount of gas (primarily CO_2). The schematic representation of the HTC process in an autoclave is depicted in Figure 2-2. The quantity and distribution of hydrochar, process water, and gases are highly variable and dependent on various

factors such as biomass type, moisture content, reaction temperature, and heating rate; these aspects are thoroughly explained in Section 2.1.1. Among the various influencing factors, the reaction temperature and pressure in the autoclave have the greatest impact compared to other factors (Möller et al., 2011).

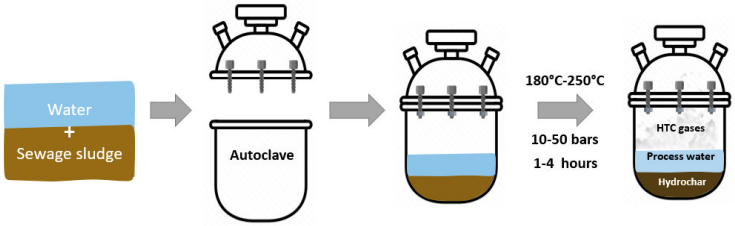

Figure 2-2 Schematic representation of HTC process in an autoclave.

2.1.1. Role of fundamental influencing process parameters

2.1.1.1. Temperature

Temperature plays a crucial role in determining the reaction network, product distributions, and characteristics of hydrothermal carbonization. The essential function of temperature is to provide the heat required to decompose organic macromolecules. This allows the fragmentation and recombination of chemical bonds with increased reactivity. Hydrothermal reactions become more pronounced with the rising temperature thereby accelerating the degradation and polymerization rates of sewage sludge compounds by a significant amount (Jellali et al., 2022). Higher temperatures have shown to promote the formation and enrichment of aromatic structures within hydrochar (Liu et al. 2021).

The effect of temperature on the breakdown of major macromolecular components in sewage sludge has found to be significant. Polysaccharides generally hydrolyze faster than proteins, followed by lipids (Liu et al., 2021). HTC of sewage sludge at higher temperatures decomposes proteins higher rate than polysaccharides, showing that proteins are more sensitive to temperature (Babu et al., 2023). The complex nature of sewage sludge thus affects process kinetics by influencing macromolecular breakdown. Hydrothermal reactions between 130-150 °C accelerate soluble biopolymer concentrations and further increases the hydrothermal reaction at temperature >150 °C (Wang and Li 2015). Hydrothermal decomposition of soluble polysaccharides and proteins occurs at temperatures above 180 °C facilitating maillard reactions producing hydrochar with dark brown color (Inoue et al., 1997). Hydrothermal carbonization uses mild-subcritical temperatures to enhance carbonization while preventing liquefaction and gasification (Lachos-Perez et al., 2022). At a temperature higher than 250 °C hydrothermal treatment causes the immiscible liquid in the processwater indicating the occurrence of hydrothermal liquefaction (Elhassan et al., 2023). This suggest that the temperature below 250 °C is optimum for HTC. The Figure 2-3 depicts the phase diagram for hydrothermal processes in relation to temperature and pressure.

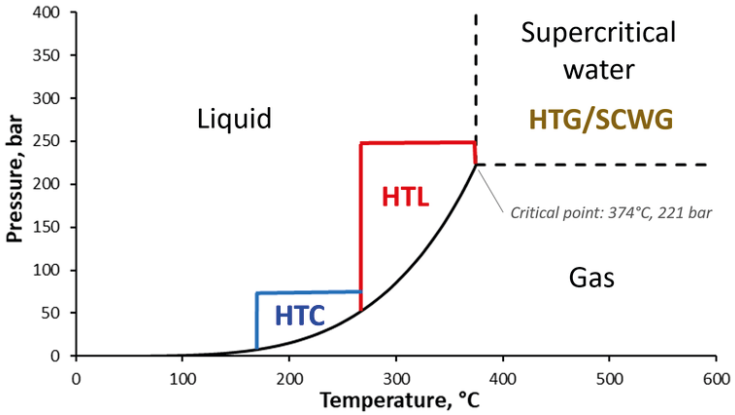

Figure 2-3 Phase diagram for hydrothermal processes in relation to temperature and pressure (Judd 2020)

2.1.1.2. Moisture content

In hydrothermal processes, moisture is essential to drive the chain of chemical reactions like hydrolysis, dehydration, decarboxylation, polymerization, and coalification (Wang, Chang and Li 2019). Water improves preheating efficiency and prevents local overheating from exothermal reactions that occur during HTC.

According to Watanabe et al., at higher temperature water experiences lower density, a decline in dielectric constant, and an increase in ionic product. The hydrogen bonding structure of water changes with the dielectric constant, making it act like a polar organic solvent. The solvent nature of water tends to intensify with increasing temperature as water molecules gain kinetic energy. This leads to increased molecular motion and stronger interactions with solutes enabling the non-reactive organic molecules to undergo chemical reactions due to their improved water solubility.

Water molecules can participate in carbonization reactions as reactants and the amount of water necessary to sustain these influences is minimal. Gong et al., observed that subcritical water induces considerable carbonization reactions and hydrochar production from sewage sludge at lower moisture content. Maintaining a large solid load maximizes hydrochar generation; however, transport of hydrolysis fragments from the sewage sludge matrix can be limited (Hashaikeh et al., 2007). Hydrothermal carbonization of sewage sludge usually occurs at around 75%–99% moisture (Wang, Chang and Li 2019). Both chemical and economic factors are crucial considerations in selecting an appropriate moisture content.

2.1.1.3. Reaction time

Reaction time plays a critical role in the hydrothermal carbonization of sewage sludge. It influences a variety of factors including energy balance, product distribution, chemical composition, and product characteristics (Wang et al., 2020). Compared to the natural coalification process, the reported residence times for the HTC process range from a few minutes to several hours (~8 hours vary greatly depending upon the composition of biomass) (Yoganandham, Sathyamoorthy and Renuka 2020), which are considerably shorter than the

natural coalification process. Merely adjusting the residence time duration is likely to produce the same outcomes as higher temperatures. Research shows that shorter reaction durations yield more hydrochar from sewage sludge and longer retention times decrease the hydrochar yield (Jaruwat et al. 2018). At a longer retention time together with depolymerization and the degradation of biomacromolecules, further degradation of reactive fragments occurs (Wang et al., 2020; Nizamuddin et al., 2017). Nevertheless, the composition of sewage sludge can also play a crucial role here. HTC of sewage sludge can produce hydrochar with a comparatively higher heating value by removing oxygen-rich compounds within a reaction time of 30 to 60 minutes due to an increase in ash content resulting from the dissolution of biopolymers (H, Apostolos and Wang 2013; Peng et al., 2016). Extended reaction durations and higher temperatures have a negative impact on the porous structure of hydrochar, limiting its applicability in adsorption (Wang, Li and Chang 2017; Zhao et al., 2023). Therefore, depending on the application needs and requirements, it is crucial from an industrial standpoint to execute HTC with a short residence time in order to increase efficiency and reduce costs.

2.1.1.4. Heating rate

The heating rate as a process parameter is an important factor in hydrothermal carbonization process after the reaction temperature. It has a significant influence on intermediate formation and product distribution. The degree of dehydration and decarboxylation reactions that occur during the hydrothermal process can be influenced by the rate of heating. Higher heating rates during the hydrothermal processes reduce hydrochar yield as a result of incomplete carbonization. On other hand, lower heating rates may extend reaction duration and increase energy consumption (Czerwińska, Śliz and Wilk 2022). Brand et al., observed that a lower heating rate (2 °C min^{-1}) produces a solid residue with a greater heating value and lower O/C and H/C ratios than a high heating rate (20 °C min^{-1}) (Brand et al., 2014). A lower rate of heating provides sufficient time for biomolecule decomposition and intermediate recombination. Likewise, the rate of cooling, which is usually uncontrollable during water/air cooling, follows a similar pattern (Wang, Chang and Li 2019). The heating rate also affects the hydrochar's morphology, diameter, and particle size distribution (Tasca et al., 2019). However, it is observed that the porous structure of hydrochars can be damaged by higher reaction temperatures and rapid heating rates. This damage may be caused by the condensation of volatile organic matter in the pores or by dissolving alkaline and alkaline elements within the matrix (Tasca et al., 2019).

2.1.2. Reaction pathway and kinetics during hydrothermally carbonizing sewage sludge

The extensive research in the field of hydrothermal carbonization has the potential to enable the large-scale reforming of sewage sludge in the near future. At present, most of the available technologies for sewage sludge treatment using HTC are only used on a small scale for testing purposes. TerraNova® intends to build a 3,000 ton/year HTC facility in Poland to process biowaste along with sewage sludge (TerraNova Energies 2022). This would be the first industrial-scale plant that will be installation in Poland or in Europe. The quantity of sewage sludge currently produced in Poland or Europe; however, renders the installation capacity of 3,000 tons per year inadequate. Hydrolysis, dehydration, decarboxylation, polymerization, and aromatization have qualitatively recognized in hydrothermal carbonization with the help of intensive research and literature. The previous literature on hydrothermal carbonization for sewage sludge research has mostly examined how reaction variables, particularly temperature and retention time, influence

product fraction yields, compositions, and morphology of the end product. Due to the intricacy of the hydrothermal reaction network in sewage sludge, only a few large investigations have reported reaction routes.

The fundamental reaction mechanism of the hydrothermal carbonization process includes depolymerization of sewage sludge, degradation of biopolymers, and reactive intermediate recombination. Takamatsu, Hashimoto and Sioya (1970) were the first to attempt and describe the sewage sludge hydrothermal breakdown reaction routes (Takamatsu, Hashimoto and Sioya 1970). They presented a scheme that describes the degradation of solid components into soluble evaporative and non-evaporative substances and their transformation between these states. Funke and Ziegler (2010) have provided a comprehensive study that includes a distinct explanation of the general reaction mechanisms. Wang, Chang and Li (2019) have made an extensive review of the reaction pathway and kinetics on hydrothermal carbonization of sewage sludge. The development of reaction pathways is crucial to understanding the mechanism and kinetics of sewage sludge hydrothermal carbonization's product synthesis. Most recently, Ischia at el., (2022) have studied the systematic insight kinetics and characterization of glucose decomposition during hydrothermal carbonization (Ischia et al., 2022).

The proposed simplified reaction pathways for the hydrothermal conversion of sewage sludge are depicted in Figure 2-4. Due to its lower activation energy compared to other hydrothermal reactions such as dehydration, decarboxylation, aromatization, and condensation, hydrolysis is considered as the beginning phase of the HTC process (Libra et al., 2011). Water and biopolymers react during hydrolysis, weakening their chemical bonds and generating a range of products, including soluble oligomers (low molecular weight polymers), monomer compounds, and various other intermediaries (Jamal-Uddin et al., 2023). The hydrolyzed products quickly dehydrate and decarboxylate after hydrolysis (Reza, Uddin et al., 2014).

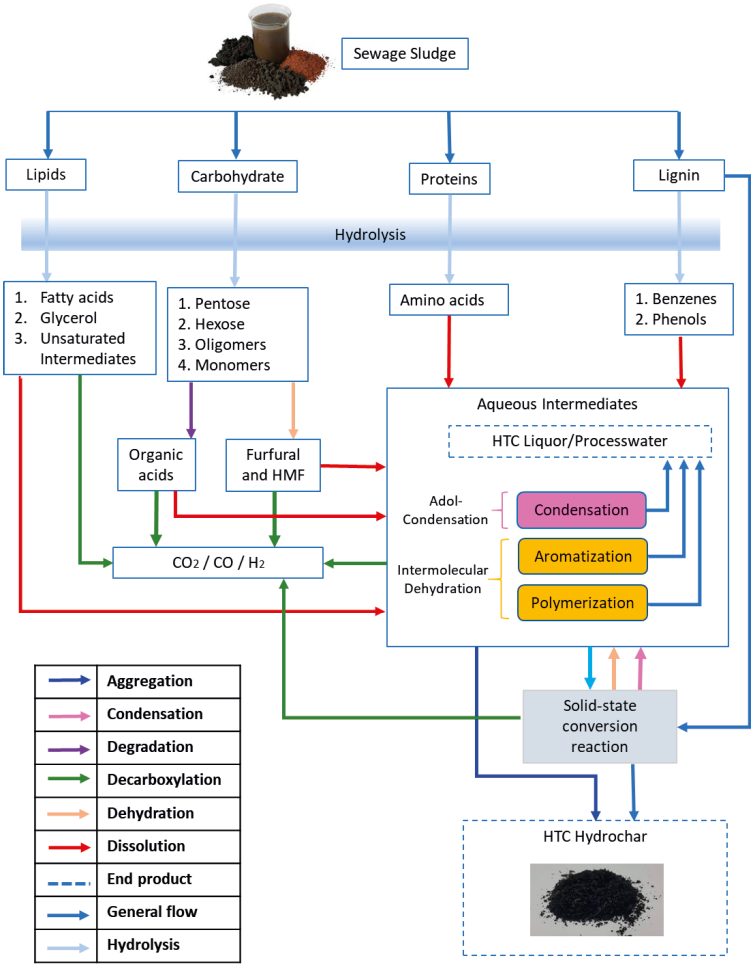

Figure 2-4 Chemical reaction pathway that occurs during hydrothermal carbonization of sewage sludge (Zhou 2020; Wang, Chang and Li 2019; He et al., 2014).

Following the dehydration of monosaccharides, a significant portion of furan compounds undergo condensation, polymerization, and aromatization in the liquid phase. This process occurs concurrently with the formation of N-containing ring structures from maillard reactions, phenolic compounds resulting from lignin hydrolysis, and extremely reactive substrates such as organic acid compounds, alditols, and aldehydes (Guo et al., 2022). Subsequently, these intermediates transform into solid products via auto-nucleation (He et al., 2014; Reza, Andert et al., 2014). Through aggregation and carbonization, as well as liquid-solid and solid-solid reactions, the solid products contribute to the formation of hydrochar. Additional intermolecular dehydration, devolatilization, condensation, and decarboxylation occur during this process (Kruse, Funke and Titirici 2013). Condensation polymerization dominates the chemical process for hydrochar

formation (Wang et al., 2020). Higher temperatures and longer reaction periods accelerate step-growth polymerization, which dominates this process.

2.1.2.1. Sewage sludge hydrochar characteristics

When sewage sludge is hydrothermally carbonized, the amount of carbon in it increases while the amounts of oxygen, nitrogen, and hydrogen decrease drastically. It is observed that the carbon content of hydrochar is higher than that of the original sewage sludge and the fixed carbon content tends to rise with the severity of carbonization (Roslan et al., 2023). The nature of the sewage sludge and the hydrothermal conditions determine the fuel characteristics of the consequently produced hydrochar. Dehydration and decarboxylation, which are regulated by reaction intensity play a major role in carbonizing sewage sludge, and decreasing the H/C and O/C ratios. Hydrothermal carbonization appears to mostly remove oxygen, as the O/C ratio decreases more than the H/C ratio (Roslan et al., 2023). The carbonization impact of activated sludge is stronger than that of anaerobic digested sludge. There is a noticeable discrepancy in the carbon content of hydrochar samples produced from these different types of sludge due to the wide range in chemical composition that results from different sewage sludge sources and treatment methods (Escala et al., 2013). Hydrochar from activated sludge contains H/C and O/C ratios similar to those of lignite and sub-bituminous coal, whereas primary sludge hydrochar is far from natural coal. Thus, activated sludge is preferable over anaerobic digested and primary sludge for energy-related hydrochar production (Wang, Chang and Li 2019).

Hydrothermal carbonization provides an additional benefit by easing the removal of nitrogen and sulfur from the feedstock and altering the routes for the release of N during hydrochar combustion. The enhanced interaction between NH_3 and NO is analogous to the selective non-catalytic reduction process and this modification improves the release of volatile nitrogen in the form of NH_3 (Chen et al., 2023). When sludge hydrochar is utilized as a solid fuel alternative for fossil fuel the risk of creating gaseous pollutants such as NO_x and SO_x is reduced (Gerner et al., 2021). The retention of about 90% of the phosphate salts that precipitate during hydrothermal carbonization in hydrochar necessitates additional P removal steps for efficient resource recovery.

Hydrochar has a decreased volatile matter content, a greater ash content, and a minor increase in fixed carbon content when compared to the initial feedstock. This decrease in volatile matter content is mostly due to the removal of oxygen-containing functional groups (hydroxyl and carboxyl groups) within biopolymers (Wang and Li 2015). The decrease in volatile content confirms the presence of carbonization and has a positive influence on the prospective use of hydrochar as a solid fuel. The combustion performance of sewage sludge hydrochar is superior to that of raw sewage sludge due to its simpler and more stable ignition and burning processes. One downside of hydrothermal carbonization is the concurrent rise in ash content caused by excessive loss of volatile matter and mineral retention. The degree of ash content growth in hydrochar is closely proportional to both the original ash level of the sewage sludge and the hydrothermal conditions used.

2.1.2.2. Characteristics of process water after HTC of sewage sludge

Hydrothermal treatment is known to be the most efficient preconditioning method for improving sludge dewaterability by disrupting the hydrophilic character of extracellular polymeric molecules (Chen et al., 2022). A simple centrifuge dewatering process can be used to easily separate the liquid component of hydrochar slurry produced from hydrothermal treatment of

sewage sludge. The liquid phase produced after HTC is also known as process water. Process water contains short-chain organic acids such as acetic, benzene, propionic, butanoic acids, furanic, phenolic, aromatic, alkene, and aldehyde components (Danso-Boateng et al., 2015). Higher temperatures and longer residence times increase acetic acid concentration in the liquid fraction due to the formation of volatile fatty acids from lipid and protein degradation (Chen et al., 2019). However, stronger reaction conditions which includes higher temperature and retention time lower propionic acid (a type of volatile fatty acid) concentration in the reaction medium with the formation of CO_2, CO, and H_2 (Xue et al., 2015). Primary sewage sludge could produce much more volatile fatty acids than activated sewage sludge. This is due the presence of higher unsaturated lipid content in primary sewage sludge in comparison to activated sewage sludge.

The process water obtained after hydrothermally treating sewage sludge contains a variety of organic compounds, including short-chain organic acids, various other organics, and melanoidins. At the HTC reaction temperature above 180 °C, maillard reactions are responsible for producing melanoidins and refractory polymers in the process water phase. Melanoidins give the process water its distinctive dark brown color and are poorly biodegradable as they include aldehydes, pyrroles, pyrazines, and pyridines (Faixo et al., 2021). This water also serves as a carrier for the transfer of nutrients from the sludge into the liquid phase. It is possible to partially dissolve the nutrients in sewage sludge by transferring them into the liquid fraction. About 35-70 percent of nitrogen, ~50 percent of potassium and ~10 percent of phosphorus can be transferred to processwater depending on the characteristics of sewage sludge (Hämäläinen et al., 2021; Sarrion et al., 2023). It is important to note that the reaction temperature greater than 200 °C plays a crucial role than residence time in the solubilization of these nutrients.

The process water of the hydrothermally treated activated sludge has an acidic pH of ~5.0 due to the presence of organic acids produced during the breakdown of biopolymers. On the contrary, the process water derived from digested sewage sludge that has undergone hydrothermal treatment exhibits a higher pH potentially due to its elevated buffering capacity (Escala et al., 2013). With an increasing reaction temperature the pH of the liquid phase initially decreases, but then begins to rise around 210–220 °C. This change is attributed to the increased production of alkaline groups, such as ammonia at higher reaction temperatures (Liang et al., 2021). Since proteins in sewage sludge are particularly susceptible to ammonification at high temperatures, the concentration of NH4eN (ammonia-nitrogen) increases as reaction severity increases.

The reaction severity of carbonization in sewage sludge has significant effects on the solubilization of biopolymers. Soluble chemical oxygen demand (COD) as an important indication of biopolymer solubilization shows a linear increase with increasing temperature and residence time which is in good agreement with the degree of the reaction. The effect of reaction temperature on COD solubilization was shown to be more significant than that of residence time (Bougrier, Delgenès and Hélène 2008). Hydrothermal carbonization results in the solubilization and subsequent breakdown of macromolecules, and these changes in soluble COD are obvious. Proteins make up about 55-70% of soluble COD, with lipids coming in at 15-25% and polysaccharides at 13-15% (Donoso-Bravo et al., 2011). Nevertheless, depending on the type of sewage sludge used, the COD concentrations in the resultant process waters may range from the thousands to the tens of thousands of milligrams per liter.

2.1.3. Acid leaching sewage sludge hydrochar

HTC has attracted increasing attention as an eco-friendly and dependable technology to treat sewage sludge without the need for pre-drying processes. The HTC process uses the moisture

existing in sewage sludge as a catalyst, reactant, and solvent, eventually converting the sewage sludge into hydrochar and enabling the recovery of P. The produced hydrochar after HTC is hygienic, free of pharmaceuticals, easily dewaterable and likely to have moderate energy density (Crocker and Andrews 2010; Saetea and Tippayawong 2013). The presence of metal salts in sewage sludge is responsible for the P retention in the sewage sludge hydrochar after HTC process (Becker et al., 2019). Hydrochar produced after HTC of sewage sludge accumulates >90% of P from sewage sludge, but its direct application to agriculture is limited due to the presence of heavy metals. The possibilities to address this issue are either by eliminating the heavy metals from the hydrochar or by recovering the P from the hydrochar. Recovering P from sewage sludge hydrochar by treating it with inorganic acids at an extremely low pH can be an effective method for addressing this problem.

Ashes from incinerated sewage sludge have been the subject of extensive research on phosphorus release by leaching. Ash2Phos, Ash Dec, LEACHPOS, Parforce, Mephrec®, TertaPhos®, BioCon®, SEPHOS, PASH, and a number of other P recovery technologies are currently available and are used to recover P from sewage sludge ashes (Ehrnström 2016). Several studies have examined the efficiency of acid leaching and precipitation to extract P from sewage sludge incinerated ash (Kalmykova and Fedje 2013; Gorazda et al., 2016; Fang et al., 2018; Liang et al., 2019; Luyckx and Caneghem 2022). Guedes et al., (2014) and Ottosen, Jensen and Kirkelund (2014) employed the electro-dialytic separation process to sewage sludge ash in an effort to recover phosphorus. The composition of sewage sludge ashes and sewage sludge hydrochar changes greatly. This limits the employment of the same technique of acid leaching sewage sludge ashes to sewage sludge hydrochar. The organic content is nonexistent in sewage sludge ashes but between 50 and 70 percent in sewage sludge hydrochar. This is the key difference between sewage sludge ashes and sewage sludge hydrochar. Furthermore, metals occur in many forms of complexes and as counterions to organic components in HTC processed sewage sludge (Ehrnström 2016). Metals are also present in significant amounts as oxides in sewage sludge ashes.

Leaching of phosphorus from hydrothermally treated sewage sludge has not been investigated on a large scale. There are only a handful of studies including the research by AVA Cleanphos (AVA Cleanphos 2018), HTCycle, and TerraNova®, thus data on the topic is limited. The AVA Cleanphos solution allows the production of a heavy metal-free phosphoric acid without an additional purification stage - an important difference compared to recovery from sewage sludge ash. The AVA Cleanphos process entails the acid treatment of sewage sludge hydrochar, followed by the separation of phosphoric acid from metal sulfates via nanofiltration, and the recovery of concentrated phosphoric acid. The company claims that its extraction technique results in a phosphorus dissolution rate of 80%, while the hydrochar itself absorbs approximately 90% of the heavy metal content (AVA-CO2 Schweiz AG 2014). The TerraNova® process recovers phosphorus from hydrothermally carbonized sewage sludge coal slurry by decreasing its pH, mechanically separating the phosphorus-rich liquid, adding calcium silicate hydrate granules, and precipitating struvite (TerraNova Energies 2021).

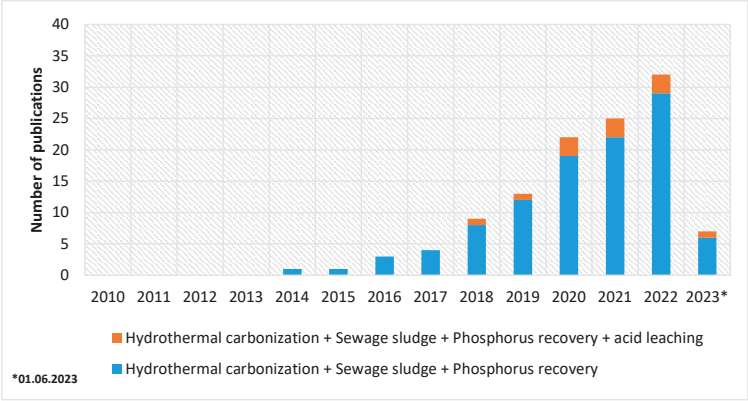

Figure 2-5 Number of published scientific articles based on Web of Science search for "Hydrothermal carbonization AND Sewage sludge AND Phosphorus recovery" and "Hydrothermal carbonization AND Sewage sludge AND Phosphorus recovery AND Acid leaching".

In addition to the pilot and industrial scale research conducted by the above-mentioned private companies, only a small number of research papers have published on the topic of acid-leaching sewage sludge hydrochar, including the scientific papers included in this dissertation. The fate of P and its transformation during HTC of sewage sludge has gained a significant amount of interest lately (Wang et al., 2020; Shi et al., 2019; C. Pérez et al., 2021; Marin-Batista et al., 2020). Pérez et al., (2021) studied the acid leaching of sewage sludge and hydrochar using 2.5 M acid solutions of H_2SO_4 and HCl. Pérez et al., (2022) have further studied the influence of organic acid (citrate and oxalate) leaching on the P transformation from sewage sludge hydrochar. Becker et al., proposed citric acid-mediated acid leaching of digestate sewage sludge hydrochar for phosphorus recovery (up to 82.5 wt%), followed by the use of process water as a source of ammonia (Becker et al., 2019). Gerner et al. have reported the phosphorus stripping and phosphorus leaching of sewage sludge hydrocar using sulfuric acid and recovery of about 84% and 71% of phosphorus respectively from solids to liquid phase (Gerner et al., 2021).

The previous research has intensively studied the process condition during the hydrothermal treatment of sewage sludge. So far the research on acid influence at various stages of the HTC process, as well as the P leaching efficiency and cost viewpoint of the acid needed in leaching P from sewage sludge hydrochar, has done only to a limited extent. In this concern understating the influence of pH and acid characteristics during HTC of sewage sludge and on the sewage sludge hydrochar will be crucial to have an efficient and cost-effective P recovery from hydrothermally carbonized sewage sludge.

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3. List of publications

This cumulative dissertation is based on following four articles and additional unpublished data. Three of the four articles are original research articles while the last one is the review article. All the articles are published.

I. **Vicky Shettigondahalli Ekanthalu**, Satyanarayana Narra, Jan Sprafke, and Michael Nelles (2021) Influence of Acids and Alkali as Additives on Hydrothermally Treating Sewage Sludge: Effect on Phosphorus Recovery, Yield, and Energy Value of Hydrochar. Processes 9(4) 618, DOI: 10.3390/pr9040618

II. **Vicky Shettigondahalli Ekanthalu**, Satyanarayana Narra, Tommy Ender, Edward Antwi and Michael Nelles (2022) Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar. Processes 10(1), 151; DOI: 10.3390/pr10010151

III. **Vicky Shettigondahalli Ekanthalu**, Tommy Ender, Satyanarayana Narra, Edward Antwi, Saptarshi Bej and Michael Nelles (2023) Acid Leaching of Hydrothermally Carbonized Sewage Sludge: Phosphorus Release and Hydrochar Characteristics. Front. Environ. Eng. 2:122347, DOI: 10.3389/fenve.2023.1223247

IV. Tommy Ender, **Vicky Shettigondahalli Ekanthalu** and Michael Nelles (2023) Hydrothermal Carbonization of Sewage Sludge – An Effective Approach to Treat and Manage Sewage Sludge in Rural Areas of Germany?. Detritus, 24, 70–77. DOI: 10.31025/2611-4135/2023.18308

3.1. Author's contribution:

Chapter no	Article number	Article title	Contribution to the article	Estimated contribution in percentage
4	I	Influence of Acids and Alkali as Additives on Hydrothermally Treating Sewage Sludge: Effect on Phosphorus Recovery, Yield, and Energy Value of Hydrochar	Vicky Shettigondahalli Ekanthalu wrote the entire article, is the corresponding author, interpreted the results, and was solely responsible for the experimental work.	90%
5	II	Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar	Vicky Shettigondahalli Ekanthalu wrote the entire article, is the corresponding author, interpreted the results, and was solely responsible for the experimental work.	90%
6	III	Acid Leaching of Hydrothermally Carbonized Sewage Sludge: Phosphorus Release and Hydrochar Characteristics.	Vicky Shettigondahalli Ekanthalu wrote the entire article, is the corresponding author, interpreted the results, and was solely responsible for the experimental work.	90%
7	IV	Hydrothermal Carbonization of Sewage Sludge – An Effective Approach to Treat and Manage Sewage Sludge in Rural Areas of Germany?	Vicky Shettigondahalli Ekanthalu wrote the article together with other authors, and worked together equally till the acceptance of this publication.	40%

3.2. Authors declaration

AUTHORS DECLARATION

Article

"Shettigondahalli Ekanthalu, V.; 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. https://doi.org/10.3390/pr9040618"

As the co-authors of the above article, we have no conflicts of interest to declare. We confirm that Vicky Shettigondahalli Ekanthalu being a corresponding author of the above article has written the complete article, interpreted the results, and was solely responsible for the experimental work. We are aware that Vicky Shettigondahalli Ekanthalu is using the above article for the partial fulfillment of his cumulative PhD dissertation. We confirm that we have not submitted or intend to submit the above article elsewhere (partially or fully) to achieve any scientific title or grade.

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Article

"***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***"

As the co-authors of the above article, we have no conflicts of interest to declare. We confirm that Vicky Shettigondahalli Ekanthalu being a corresponding author of the above article has written the complete article, interpreted the results, and was solely responsible for the experimental work. We are aware that Vicky Shettigondahalli Ekanthalu is using the above article for the partial fulfillment of his cumulative PhD dissertation. We confirm that we have not submitted or intend to submit the above article elsewhere (partially or fully) to achieve any scientific title or grade.

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"Shettigondahalli Ekanthalu, V.; Ender, T.; Narra, S.; Antwi, E.; Bej, S.; Nelles, M. Acid leaching of hydrothermally carbonized sewage sludge: Phosphorus release and hydrochar characteristics. Front. Environ. Eng. 2023, Volume 2. DOI: 10.3389/fenve.2023.1223247"

As the co-authors of the above article, we have no conflicts of interest to declare. We confirm that Vicky Shettigondahalli Ekanthalu being a corresponding author of the above article has written the complete article, interpreted the results, and was solely responsible for the experimental work. We are aware that Vicky Shettigondahalli Ekanthalu is using the above article for the partial fulfillment of his cumulative PhD dissertation. We confirm that we have not submitted or intend to submit the above article elsewhere (partially or fully) to achieve any scientific title or grade.

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Article

"Ender, T.; Shettigondahalli Ekanthalu, V; Nelles, M. HYDROTHERMAL CARBONIZATION OF SEWAGE SLUDGE – AN EFFECTIVE APPROACH TO TREAT AND MANAGE SEWAGE SLUDGE IN RURAL AREAS OF GERMANY?."
Detritus. Accepted 04.08.2023

As the co-authors of the above article, we have no conflicts of interest to declare. We confirm that Vicky Shettigondahalli Ekanthalu and Tommy Ender have worked equally and written the complete article. We are aware that Vicky Shettigondahalli Ekanthalu is using the above article for the partial fulfillment of his cumulative PhD dissertation. We confirm that we have not submitted or intend to submit the above article elsewhere (partially or fully) to achieve any scientific title or grade.

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4. Influence of acids and alkali as additives on hydrothermally treating sewage sludge: Influence on phosphorus recovery, yield, and energy value of hydrochar

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Exclusive overview of the article and its connection to the research question

The article titled "Influence of acids and alkali as additives on hydrothermally treating sewage sludge: Influence on phosphorus recovery, yield, and energy value of hydrochar" tries to answer the below RQ of this cumulative dissertation.

- **RQ 1**: What is the influence of acid and base as additives during HTC of sewage sludge?

The primary aim of this article is to understand and compare the effects of organic acids, inorganic acids, and alkali as additives during HTC of sewage sludge on P transformation. In addition to the primary aim, this study also shed light on the effect of additives on the dewaterability, yield, and heating value of hydrochar.

4.1. Abstract

The high moisture content present in sewage sludge hinders the use of sewage sludge in incineration or energy application. This limitation of moisture present in sewage sludge can be obviated by using the hydrothermal carbonization (HTC) process. In sewage sludge management, the HTC process requires less energy compared to other conventional thermo–chemical management processes. The HTC process produces energy-rich hydrochar products and simultaneously enables phosphorus recovery. This study investigates the influence of organic acids, inorganic acid, and alkali as additives on phosphorus transformation, yield, proximate analysis and the heating value of subsequently produced hydrochar. The analysis includes various process temperatures (200 °C, 220 °C, and 240 °C) in the presence of deionized water, acids (0.1 M and 0.25 M; H_2SO_4, HCOOH, CH_3COOH), and alkali (0.1 M and 0.25 M; NaOH) solutions as feed water. The results show that phosphorus leaching into the process-water, hydrochar yield, proximate analysis, and the heating value of produced hydrochar is pH- and temperature-dependent, and particularly significant in the presence of H_2SO_4. In contrast, utilization of H_2SO_4 and NaOH as an additive has a negative influence on the heating value of produced hydrochar.

Keywords: Hydrothermal carbonization; Sewage sludge; Phosphorus recovery; Hydrochar; Process-water; pH

4.2. Introduction

The management of sewage sludge produced from wastewater treatment plants is an important global issue due to the presence of high moisture content, harmful pathogens, and poor dewaterability. Conventional sewage sludge management involves the direct application on farmland as fertilizer. However, sewage sludge has attracted greater attention as a feedstock for nutrient recovery and renewable biofuels production (He, Giannis and Wang 2013; Shettigondahalli Ekanthalu et al., 2020). In the year 2018, about 23% of sewage sludge produced in Germany was managed by applying directly on farmland, and about 65% of the produced sewage sludge was incinerated (Statistisches Bundesamt Destatis 2020). Since 2017, new regulation was placed by the German sewage sludge ordinance (AbfKlärV) based on enabling principles of the Circular Economy Act (Kreislaufwirtschaftsgesetz - KrWG 2017) on sewage sludge management. This new regulation is not only making it mandatory to recover phosphorus from sewage sludge in Germany but also prohibits the direct use of sewage sludge on farmland (AbfKlärV 2017). According to AbfKlärV, sewage sludge must undergo mandatory phosphorus recovery if the phosphorus content is ≥20 g/kg total dry matter (DM) or ≥2% DM. The thermal pretreatment of sewage sludge is still possible; however, the subsequent recovery of phosphorus in the produced incinerated ash or the carbonaceous residue has to be guaranteed. This new obligation applies from January 2029 for the wastewater treatment plants with size >100,000 populations equivalent (PE). The treatment facilities with >50,000 PE must also comply with the new regulation to recover phosphorus from January 2032. After these dates, soil-related disposal of sewage sludge is no longer permitted. Only the smaller wastewater treatment plants (≤50,000 PE) can use their sewage sludge as a soil amender when the phosphorus content in sludge is <20 g/kg total DM.

The option for managing sewage sludge is getting progressively limited as the result of strict environmental legislation placed by Germany over the last decade. The actual problem exists in states of Germany such as Mecklenburg–Western Pomerania, Lower Saxony, and Rhineland–Palatinate where >50% of the produced sewage sludge is managed by direct application for agriculture and landscaping (Statistisches Bundesamt Destatis 2020). In this concern, the current number of thermal treatment facilities might not be able to handle the amount of sludge produced, eventually triggering the new problem associated with the storage of untreated sewage sludge.

Incineration is a widely accepted technique to treat sewage sludge in Germany which can significantly reduce the sludge volume and produce reactively hygiene sludge ash residue with high phosphate content (Wang et al., 2017). Yang et al. (2019) studied the effect of chlorine-based additives on phosphorus recovery during sewage sludge incineration. The addition of Magnesium chloride ($MgCl_2$) and Calcium chloride ($CaCl_2$) during incineration increases the fixation rate of total phosphorus (TP) to a maximum of 98.5% in sewage sludge treated with 3% (Magnesium) Mg at 900 °C and 97.8% in sewage sludge treated with 5% Calcium (Ca) at 800 °C. Similar to incineration, pyrolysis can also be an effective alternative process to treat and recover phosphorus from sewage sludge. The study by Atienza–Martínez et al. (2014) indicated phosphorus recovered from pyrolysis is temperature-dependent and that more than 90% of phosphorus can be recovered using pyrolysis followed by char combustion in sulfuric acid.

In recent years, hydrothermal carbonization has gained greater attention for treating sewage sludge as it is greatly regarded as an eco-friendly and promising technology. Hydrothermal carbonization is a technology that demonstrates the high potential to treat the moist/wet biomass without it having to be dewatered. HTC uses moisture present in sludge as the reaction medium

to process the sewage sludge without pre-drying. During HTC, higher temperature and pressure will aid the moisture present in sewage sludge to serve as a solvent, reactant, and catalyst for converting sewage sludge into hydrochar. The product hydrochar is hygienic, essentially free of pharmaceuticals, easily dewaterable, and likely to be a coal-like product with high energy density (Crocker 2010; Saetea and Tippayawong 2013). Additionally, the HTC process is proved to save up to 53% thermal energy and 69% electrical energy compared to conventional sludge drying methods (Stucki et al., 2015). Currently, there are several studies on HTC of sewage sludge, particularly in producing hydrochars and subsequent utilization of hydrochar as effective adsorbents (Leng et al., 2015; Saetea and Tippayawong 2013), soil amendment (Wang, Chang and Liu 2019), or as feedstock for energy production (He, Giannis and Wang 2013; Kim, Lee and Park 2014). Further, there are few studies that are explaining the effects of additives during HTC of lignocellulosic biomass (Lynam et al., 2011; Lynam et al., 2012; Reza et al., 2015). The investigation carried out by Lynam et al., (2012) identifies the benefit of the increased heating value of resulting hydrochar produced using Ca salts (Ca chloride and Ca lactate) as additives during HTC of Lignocellulosic biomass.

Previous studies on understanding the effect of feed-water pH during HTC of sewage sludge have mainly focused on investigating phosphorus transformation (Wang et al., 2017; Ovsyannikova et al., 2019; Shi et al., 2019), risk of heavy metals in hydrochar (Zhai et al., 2016), physicochemical properties of hydrochar (Liu et al., 2020). Shi et al., studied the effect of initial pH and HTC reaction temperature on the mobilization of phosphorus (Shi et al., 2019). They found that at higher temperatures phosphorus is more likely to be more present in the hydrochar; however, using acid additives in large amounts could shift phosphorus into the liquid phase. Further, the phosphate leached into the process-water can be chemically precipitated by the addition of a coagulant and a mixing of process-water and coagulant. The multivalent metal ions most commonly used are calcium, aluminium, and iron (Lenntech 2020; TerraNova 2016). To the author's knowledge, very few investigations compare the influence of organic acids, inorganic acids, and alkali additives on the HTC of sewage sludge. Wang et al., 2017 investigated the influence of feed water pH (altered by the addition of acetic acid or sodium hydroxide) on phosphorus transformation during HTC of sewage sludge. The results showed that during the HTC of sewage sludge, metal cations and pH played vital roles in the transformation of phosphorus. The observation made by Ekpo et al., (2016) shows that 94% of the phosphorus in feedstock was recovered into the process-water after hydrothermal treatment of pig manure with a sulfuric acid additive at 170 °C. Reza et al., studied the influence of using acid and alkali additives on the HTC of wheat straw (Reza et al., 2015). However, the behavior of phosphorus transformation greatly differs from the types of biomasses, and HTC process conditions and techniques.

The main purpose of this study is to investigate and compare the influence of organic acids (acetic acid and formic acid), inorganic acids (sulfuric acid), and alkali (sodium hydroxide) as additives on the hydrothermal treatment of sewage sludge. Despite the primary objective of this study being to understand the influence of different additives on the P transformation during HTC of sewage sludge, this study also shed light on the effect of additives on dewaterability, yield, and heating value of hydrochar.

4.3. Material and methods

4.3.1. Material

The sewage sludge used in this study was obtained directly from the wastewater treatment plant, Rostock, Germany. The central wastewater treatment plant in Rostock treats both industrial (1/3) and municipal wastewater (2/3) with the capacity to treat wastewater from 320,000 inhabitants (UBC Sustainable Cities Commission 2017). The freshly digested and dewatered sludge was collected in an airtight specimen container and transported immediately to the laboratory. The sewage sludge, after being received in the laboratory, is refrigerated at 4 °C before use. The refrigerated representative samples were directly taken for HTC investigation and respective additives of deionized water, organic acid, inorganic acids, and alkali with known concentrations were added and mixed to make a homogeneous slurry. The respective additive solution of 0.1 and 0.25 M concentration was prepared by diluting acetic acid (100%, p.a.), formic acid (≥98.0%, p.a.), sulfuric acid (1 M), and sodium hydroxide (≥97.0% (T), pellets) in the deionized water. The produced additive solution was used on the same day of preparation. The ultimate analysis of the sewage sludge was performed using an organic elemental analyzer by following EN ISO 16948, 2015. Proximate analysis was performed using a LECO Thermogravimetric Analyser (TGA) unit TGA701 to determine moisture content, volatile organic compound, fixed carbon and ash content. The heating value of the sewage sludge and resulting char was determined by Parr 6400 calorimeter (Parr Instruments Inc., Moline, IL, USA) following the method described in EN 14918, 2010. Total phosphate in the obtained sewage sludge was analyzed in an external laboratory following the method described in EN ISO 11885, 2009. All measurements were made in duplicate, and the mean value is reported.

4.3.2. Hydrothermal carbonization treatment

Hydrothermal carbonization of sewage sludge was carried out in a Parr 4523 reactor (Parr Instrument (Deutschland) GmbH, Zeilweg 15, Frankfurt, Germany) at an autogenic pressure. The processing unit 4523 consists of a reaction vessel of 1-L capacity that can withstand a maximum pressure of 138 bar, a heating jacket equipped with a 2 kW heating coil, a temperature and a pressure sensor, and a stirrer with an attached motor. The reactor temperature and the speed of the stirrer were controlled using a Parr 4848 PID reactor controller. Figure 4-1 provides an overview of the experimental methodology. The analysis was carried out by charging the reactor with 297.00 g raw sewage sludge (23.5% DM) and it was topped up with 402.00 g of deionized water or additive solution of acetic acid, formic acid, sulfuric acid, or sodium hydroxide in 0.1 M or 0.25 M concentration. The sewage sludge and additives were mixed homogeneously inside the reactor before starting the investigation, and the initial pH of mixed feedstock slurry was noted using WTW pH 3310 m. The defined ratio of sewage sludge to additives was used to produce a homogeneous slurry of 10% DM. The mixture was hydrothermally carbonized at autogenic pressure with a constant heating rate of 4 K/min. The investigation was carried out with the varying temperature of 200 °C, 220 °C, and 240 °C for a retention time of 2 h while keeping the stirrer switched on during the entire process. Later, the reactor was allowed to cool down to room temperature without any additional cooling mechanism.

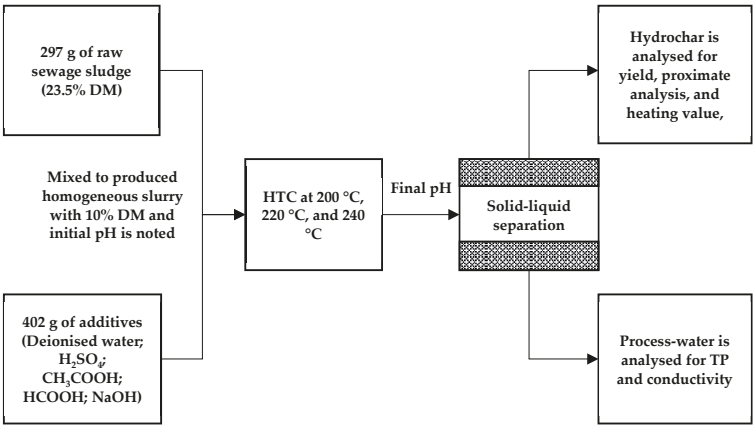

Figure 4-1 Schematic representation of experimental methodology

4.3.3. Product recovery and analysis

The final pH of the HTC-slurry obtained after HTC of sewage sludge was noted, and the resulting hydrochar and process-water were separated by using a vacuum filtration apparatus. Vacuum filtration was carried out at the constant process conditions using a top-feeding procedure in a Büchner funnel. The following rules were kept constant for solid-liquid separation of the HTC-slurry and analyzing the dry matter concentration of hydrochar: (1) entire content HTC-slurry after carbonization was poured into the Büchner funnel, (2) the vacuum pump was switched on to generate the vacuum pressure for solid–liquid separation, (3) the solids (hydrochar) thus obtained using vacuum filtration were oven-dried at 105 °C for 24 h and stored in sealed containers for further analysis or usage. Similarly, process-water produced after filtration was collected and stored in a volumetric flask and refrigerated at 4 °C until it was analyzed for total phosphorus (TP) concentration and conductivity.

The yield of the produced hydrochar is calculated as explained in equation (4.3. The Lower heating value (LHV) of the hydrochar was determined in a similar way to sewage sludge using a Parr 6400 calorimeter following the method described in EN 15170, 2010. TP in the process-water was analyzed spectrophotometrically after acid hydrolysis and oxidation following EN ISO 6878, 2004. The conductivity of the process-water was measured using a Hach HQ 40 d multifunction meter. By determining the conductivity, it was possible to understand the variations of salt content in the process-water produced at different process parameters. Triplicates of all analyzed results were obtained and the mean value was reported.

4.3.4. The fraction phosphorus recovered on hydrochar

The TP recovered on the hydrochar was mathematically calculated using the experimental data obtained on TP concentration in sewage sludge and process-water, and the total yield of the hydrochar after HTC. TP recovered from the hydrochar ($TP_{(h)}$) can be mathematically defined as follows:

$$TP_{(h)} = 100 - \left(\frac{Y_{(pw)} \times TP_{(pw)}}{TP_{(fs)}} \times 100\right) \quad (4.1)$$

Where $TP_{(pw)}$ and $TP_{(fs)}$ is the TP content in process-water and the initial feedstock slurry respectively, and $Y_{(pw)}$ is the total yield of the process-water after filtration which is calculated as follows:

$$Y_{(pw)} = \mathrm{m} - \left(\frac{m_o \times Y_{(h)}}{DM_{(h)}}\right) \quad (4.2)$$

Where m is the total weight of the feedstock, m_o is the dry weight of the feedstock, $DM_{(h)}$ is the dry matter percentage of hydrochar after filtration, and $Y_{(h)}$ is the yield (%) of produced hydrochar and was calculated as the applied formula.

$$Y_{(h)}(\%) = \frac{m_h}{m_o} \times 100 \quad (4.3)$$

Where m_h is the total dry weight of produces hydrochar.

4.4. Results and discussion

4.4.1. Characteristic of sewage sludge

The results of the proximate and ultimate analysis of sewage sludge are presented in Table 4-1. The moisture content of sewage sludge was determined to be 76.53% leaving behind the total solids content of 23.48%. The analysis also demonstrates noticeably lower ash content of 32.83% DM and higher volatile solids (VS) of 61.46% DM, which was inconsistent with the previous investigation ranges (Peng et al., 2016; Wang et al., 2017). The ultimate analysis of the sewage sludge specified the typical C-H-N-S-O content for sewage sludge in Germany (Roskosch and Heidecke 2018) with; C: 32.5; H: 5.0; N: 4.98; S: 1.50 and O: 21.4 on a dry basis. The dry sewage sludge is known to contain a higher concentration of phosphorus and a relatively higher heating value. The TP content in the feedstock was determined to be 36.1 g/kg, accounting for 3.6% of total dry sludge, and the heating value was observed to be relatively higher with 13.56 MJ/kg (LHV) in comparison with previous studies (Peng et al., 2016; Wang et al., 2017; Roskosch and Heidecke 2018). One possible explanation for increased LHV can be the presence of higher volatile solids and lower ash content. Nevertheless, the overall characteristics of the feedstock have the typical composition of sewage sludge in Germany.

Table 4-1 Proximate and ultimate analysis of sewage sludge.

Parameters	Units	Value
Moisture content	%OS	76.53
Total solids	%OS	23.48
Volatile solids	%DM	61.46
Ash (850 °C)	%DM	32.83
Fixed carbon (FC)	%DM	5.71
LHV	MJ/kg, DM basis	13.56
HHV	MJ/kg, DM basis	14.66
Nitrogen	%DM	4.98
Carbon	%DM	32.5
Sulphur	%DM	1.50
Oxygen	%DM	21.4
Hydrogen	%DM	5.00
Total phosphorus	mg/kg DM	36100.00

OS = Original Sample, DM = Dry Matter

4.4.2. Effect of additives and reaction temperature on yield of hydrochar

Figure 4-2 compares the total yield (%) of hydrochar produced at different temperatures using various additives. An increase in the process temperature from 200 °C to 240 °C has decreased the hydrochar yield on average by about 10%, which agrees with the earlier investigation results demonstrating a decrease in hydrochar yield with an increase in reaction temperature (Kalderis et al., 2014; Jaruwat et al., 2018). The maximum hydrochar yield was observed with the carbonization method using inorganic acid as additives in comparison with the carbonization method using organic acid, alkali, and deionized water as additives. The maximum hydrochar yield of 69.09% was achieved using a 0.25 M H_2SO_4 additive in feedstock (pH 3.78), with the carbonization temperature of 200 °C and 2 h retention time. In contrast, the same reaction temperature and retention time, using 0.25 M CH_3COOH (pH 5.44), HCOOH (pH 5.38), NaOH (pH 10.68) and deionized water (pH 7.8) additives has resulted in the hydrochar yield of 62.74%, 63.79%, 55.47%, and 59.66%, respectively. Nevertheless, it is interesting to see that at the lower additive concentration (0.1 M), despite having comparatively similar initial pH range (5.8–6.3) of sewage sludge slurry prepared using CH_3COOH (pH 6.3), HCOOH (pH 6.2), and H_2SO_4 (pH 5.8), hydrochar yield was significantly higher with using H_2SO_4 as an additive in comparison with other organic acids.

The increases in reaction temperature will directly influence eliminating the moisture content in the biomass structure as the effect of hydrolysis reaction and simultaneously foster biomass degradation; this, in turn, decreases hydrochar yield (Sermyagina et al., 2015; Jaruwat et al., 2018). Further, the investigation conducted by Jaruwat et al. (2018) has shown that a longer retention time will increase the yield of the hydrochar as the result of repolymerization of decomposed biopolymers.

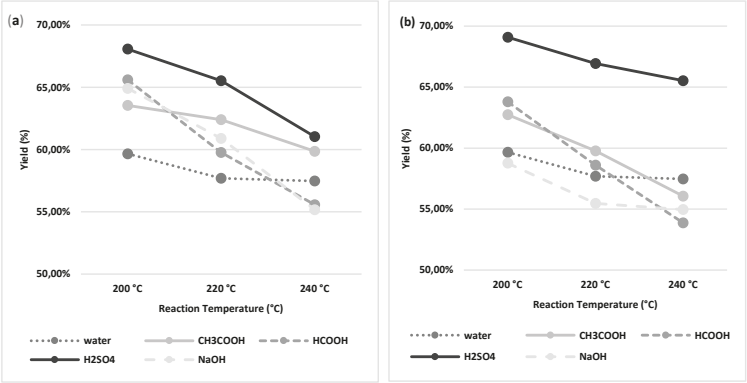

Figure 4-2 Influence of additives and temperature on yield of hydrochar; (a) represents the hydrochar yield produced using additives of 0.1M concentration; (b) represents the hydrochar yield produced using additives of 0.25M concentration.

Similar to reaction temperature and retention time, the addition of additives also influences the yield of the hydrochar. Temperature undoubtedly has a greater influence on the mass yield of hydrochar. Nevertheless, similar to temperature, despite having similar pH, retention time, and reaction temperature, using inorganic acid has increased the hydrochar yield in comparison to using organic acids or alkali as additives. An increase in the hydrochar yield can be co-related with the higher molecular mass of H_2SO_4 and changing pH due to strong acid additive utilization in comparison with the utilization of CH_3COOH, HCOOH, NaOH, and deionized water as an additive.

4.4.3. Effect of additives and HTC process conditions on solid-liquid separation

The dry matter concentration of the various hydrochar residue after filtering the process-water using a vacuum filter at the constant process conditions (top-feeding procedure with a Büchner funnel) is depicted in Figure 4-3. The HTC treatment was advantageous to sludge dewatering. The dry matter concentration of hydrochar residue after solid-liquid separation increased significantly after the HTC- reaction and the use of H_2SO_4 as an additive, significantly favored dewatering. When 0.25 M H_2SO_4 solution was used as an additive, the dry matter of hydrochar residue was 27.68 - 31.75%, which was significantly higher in comparison with using deionized water as an additive (20.70 - 24.83%). The influence of H_2SO_4 in enhancing the dewaterability of sewage sludge has also been explained previously (Statistisches Bundesamt Destatis 2020). The use of organic acids as an additive did not show any greater difference in the dry matter of hydrochar residue (20.68 - 26.38%) in comparison with using deionized water as an additive. In contrast, the use of NaOH as an additive had considerably decreased the dry matter of hydrochar residue (1.28 - 16.51%) at the lower reaction temperature (200 °C), however, at the higher reaction temperatures (220 °C and 220 °C) dry matter of hydrochar residue was higher (27.27 - 28.82%).

The extracellular polymeric materials in the sewage sludge contain viscous protein material which is extremely hydrophilic (Wang et al., 2020). The effective way to enhance the sludge dewatering performance is by breaking the cell wall and destroying the sludge flocs to release and hydrolyze the organic matter present in sewage sludge. This phenomenon can be effectively achieved alongside the higher temperature and pressure that occur in the HTC process. The reduction in

the binding force of the sludge particles achieved during the HTC process improves the dewatering performance after HTC and is significantly enhanced using H_2SO_4 in the reaction medium. In contrast, the use of NaOH additive at lower reaction temperature (200 °C) was not effective in hydrolyzing the organic matter. This could have influenced in retaining of the viscous protein material in sewage sludge, making the HTC-slurry hard to dewater. Nevertheless, using NaOH additive at higher reaction temperatures (220 °C and 240 °C) was effective in hydrolyzing the organic matter present in sewage sludge.

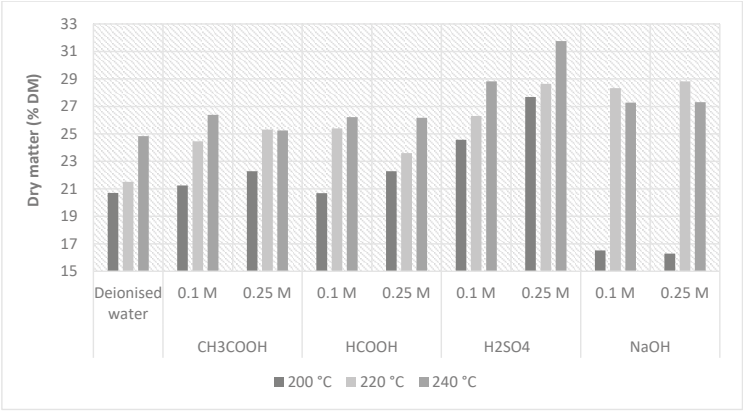

Figure 4-3 Dry matter concentration of hydrochar residue after filtering the process-water.

4.4.4. Effect of additives on hydrochar properties: proximate analysis and heating value

Following HTC, sewage sludge was carbonized into a brownish-grey solid hydrochar with a nutlike smell. The physical appearance of produced hydrochar implied that hydrochar had a uniform composition and could be readily molded into dense pellets. The proximate analysis and LHV were determined to understand the fuel characteristics of the produced hydrochar.

Table 4-2 represents the results comprising volatile matter, ash content, fixed carbon, and LHV of various hydrochar produced at different process conditions. The hydrochar produced using various additives in this investigation had LHV in the range of 14.24–15.63 MJ/kg, which is similar to the results of earlier studies demonstrating fuel characteristics of hydrochar produced using sewage sludge (He, Giannis and Wang 2013).

Table 4-2 Proximate analysis and heating value of hydrochar produced using various additives and reaction conditions. (AC-Additive concentration; RT- Reaction temperature; Initial and final pH represents the pH of feedstock slurry before and after HTC. All hydrochars were produced at 2 h retention time.)

Sample description			pH		Proximate analysis (wt.% dry basis)			LHV
Additive	AC	RT (°C)	Initial pH	Final pH	VS	Ash	FC	MJ/kg
Deionized water	-	200	7.8	6.6	49.29	41.89	8.83	15.03
		220	7.9	6.7	44.52	46.55	8.94	15.40
		240	7.8	6.9	47.10	44.31	8.59	15.16
CH3COOH	0.1 M	200	6.32	6.16	49.77	41.73	8.51	15.02
		220	6.39	6.28	44.97	46.58	8.46	15.41
		240	6.32	6.73	46.24	45.14	8.63	15.20
	0.25 M	200	5.44	5.3	50.45	40.89	8.66	15.50
		220	5.63	5.66	47.25	43.92	8.84	15.56
		240	5.71	5.7	44.74	46.34	8.93	15.75
HCOOH	0.1 M	200	6.23	6.48	49.38	42.94	7.68	15.37
		220	6.22	6.83	44.26	47.57	8.17	15.63
		240	6.14	7.83	46.62	44.90	8.48	14.78
	0.25 M	200	5.38	5.46	52.52	39.76	7.72	15.60
		220	5.45	6.15	48.08	43.49	8.44	15.37
		240	5.28	6.8	44.62	47.35	8.03	14.99
H_2SO_4	0.1 M	200	5.85	6.15	51.59	39.62	8.80	14.70
		220	6.01	6.39	48.90	42.27	8.84	15.19
		240	5.7	6.84	46.84	45.76	7.41	14.83
	0.25 M	200	3.78	4.32	52.37	42.51	5.13	14.24
		220	3.47	4.77	51.09	44.50	4.41	14.32
		240	3.81	5.64	49.16	45.57	5.27	14.68
NaOH	0.1 M	200	9.88	6.92	50.04	43.10	6.87	14.77
		220	9.94	8.4	45.21	48.40	6.40	14.50
		240	9.9	7.02	43.74	47.89	8.37	14.84
	0.25 M	200	10.68	7.5	45.67	48.53	5.81	14.24
		220	10.98	7.7	43.66	49.46	6.88	14.46
		240	10.76	7.9	42.18	50.72	7.11	14.90

The breaking down of biomass at higher temperatures to influence aromatization, polymerization, and condensation to produce hydrochar can be a reason for the increase in fixed carbon content (FC) with increasing reaction temperature (Mazumder, Saha and Reza 2020). Fixed carbon can be defined as combustible residue present in the char after the volatile matter is burned. In general, biomass before carbonization contain high VS content and low FC, but high moisture content (Putra et al., 2018). Previously several studies are showing a strong correlation between FC content and calorific value; an increase in the FC content in char can directly increase the heating value of the char (Anshariah et al., 2020; Putra et al., 2018). The use of H_2SO_4 and NaOH as an additive has negatively influenced the LHV of the produced hydrochar in comparison with the hydrochar produced using organic acids and deionized water as an additive.

The hydrochar produced using organic acids and deionized water as an additive has increased the FC content (7.72 - 8.94%) in comparison to the FC content of the initial feedstock (5.71%). Here, the increase in the FC content in hydrochar might have influenced in increasing the LHV (14.99 – 15.75 MJ/kg). However, the use of H_2SO_4 as an additive at higher concentrations (0.25 M) has negatively influenced the FC content of produced hydrochar (4.41 - 5.27%). Similarly, the use of NaOH as an additive at lower reaction temperature (200 °C and 220 °C) has no noticeable

influence on FC% (5.81 – 6.87%) in comparison with initial feedstock. On other hand, it was also observed that there was a significant decrease in the VS content and increase in the ash content after HTC of sewage sludge. The decrease in VS content can be attributed to the reaction severity and dissolution of organic material into the liquid phase, and an increase in the ash content can be correlated with the decrease in the mass percentage of VS composition of the hydrochar. However, it is interesting to perceive that the ash content in the hydrochar produced using H_2SO_4 (0.25 M) as an additive is offset more so by decreasing FC content than VS content; similar phenomena can also be seen with the hydrochar produced using NaOH as an additive at 200 °C and 220 °C. The decrease in the FC content with the use of H_2SO_4 at higher concentration and NaOH at lower reaction temperatures (200 °C and 220 °C) as an additive can explain the lower LHV in the respectively produced hydrochars.

4.4.5. Conductivity of process-water

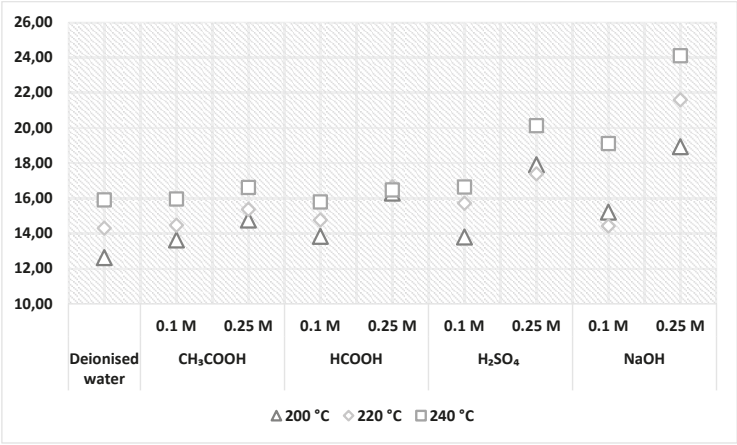

Figure 4-4 Conductivity of process-water produced using acids and alkali additive at different concentration.

Figure 4-4 is the graphical representation of the conductivity of the process-water produced using different acids and alkali as additives. The conductivity measurement, in general, provides a reliable means to understand the ions concentration of a solution. The maximum conductivity of 24.10 µS/cm was observed in the process-water produced using alkali additive. Among acid-based additives, the utilization of inorganic acid (H_2SO_4) as an additive had process-water with higher conductivity (17.4 - 20.12 µS/cm) in comparison with organic acid additives (CH_3COOH and HCOOH).

4.4.6. Effect of HTC organic acids, inorganic acids, and alkali additive on P-transformation

4.4.6.1. The pH of feedstock slurry, before and after HTC

Table 4-2 depicts the pH of the feedstock slurry before and after HTC at various temperatures, additives, and additive concentrations. The HTC process comprises hydrolysis, dehydration, decarboxylation, aromatization, and condensation polymerization (Funke and Ziegler 2010).

During HTC the pH of the feedstock slurry decreases as the result of the degradation of macromolecular organic matter into an acidic substance (viz., volatile fatty acids) and subsequent dissolution into the liquid phase. Further, the reaction time and temperature also influence the pH of the sludge hydrolysate. The use of organic acids and inorganic acid as additives resulted in the feedstock initial pH between 3.4 and 6.4. In contrast, the use of NaOH additive resulted in the feedstock initial pH ranging from 9.9 – 11.0. In the baseline condition, the deionized water additive has an initial pH of 7.8. The final pH represents the pH of the feedstock slurry after HTC. The experimental observation depicts that, regardless of variations in the initial pH, the final pH value after HTC always tends to move towards neutral. The obtained results were consistent with an idea that the acids formed during hydrolysis were subsequently decomposed or repolymerized at a higher temperature, which influences the pH of feedstock slurry after HTC (Wang et al., 2020). Further, it is also possible that the buffering function of the sewage sludge might have a significant effect on the final pH. The obtained results of the shift in final pH towards neutral agree with several earlier HTC research carried out on sewage sludge (Wang et al., 2017), swine manure (Ekpo et al., 2016), and wheat straw (Reza et al., 2015).

4.4.6.2. Effect of additives on Phosphorus transformation

Figure 4-5 shows the concentration of TP in the process-water produced after the HTC of feedstock slurry at various temperatures. For each experiment, TP in the process-water was analyzed spectrophotometrically after acid hydrolysis and oxidation of the process-water sample. Further, the TP in the hydrochar was calculated mathematically using equation (*4.1*). Figure 4-6 depicts the influence of additives, additive concentration, and pH of the feedstock slurry on the recovering TP from the raw feedstock into hydrochar after HTC at various temperatures. In brief, the results show that even at a similar pH, higher leaching of TP into process-water is achieved by the utilization of inorganic acid (H_2SO_4) as an additive in comparison with organic acids.

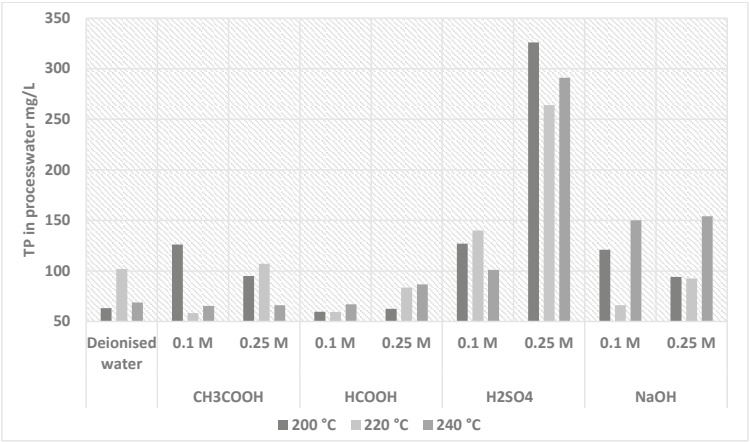

Figure 4-5 TP concentration of the process-water.

Following the HTC of sewage sludge, the highest TP leaching into the process-water (326 mg/L) was observed by using H_2SO_4 as an additive (pH 3.78), which represents about 93% of TP being recovered from raw feedstock into consequently produced hydrochar. Irrespective of process temperature, using deionized waste as an additive did not have any significant influence on the

TP leaching. TP leaching into process-water using deionized water as an additive was observed to be 63–101 mg/L, which represents about 97.7–98.7% of TP being recovered from raw feedstock into consequently produced hydrochar. The TP concentration in the process-water following the treatment at various temperatures and organic acid additives—formic and acetic acid—was observed to be in the range of 58.3–126 mg/L and 59.3–86.6 mg/L, respectively. Likewise, using NaOH as an additive also had comparatively similar TP leaching (66.2–154 mg/L) into the process-water after HTC at various temperatures. The obtained results suggested that organic acids and alkali had a very limited impact on extracting TP from raw feedstock into the process-water, which agrees with the similar results demonstrated by earlier studies (Wang et al., 2017; Ekpo et al., 2016).

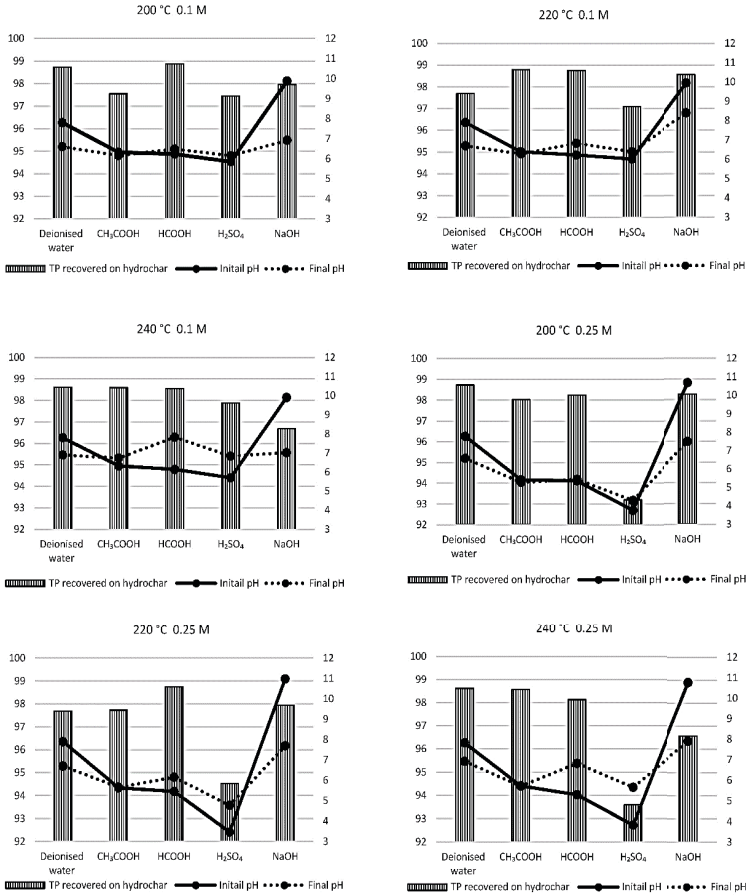

Figure 4-6 Influence of additives, additive concentration, temperature, and pH on the recovery of TP into the Hydrochar.

During HTC, the extraction of phosphorus into the process-water was generally lower with the utilization of organic acids as additives in comparison with an inorganic acid, regardless of temperature. An increase in H_2SO_4 additive concentration from 0.1 M to 0.25 M, increased the

TP leaching into process-water by about 3 folds from 101 - 127 mg/L to 264 - 326 mg/L respectively. However, increase the concentration of organic acid additives from 0.1 M to 0.25 M has obviously decreased the pH of the resulting feedstock slurry, but it did not greatly influence TP leaching into process-water.

The initial pH of feedstock slurry produced using CH_3COOH and HCOOH additive was ~6.3 and ~5.6, and ~6.2 and ~5.3 respectively at 0.1 and 0.25 M concentration. The TP in the process-water was observed to be in the range of 65.5 - 126 mg/L and 66 – 105 mg/L when produced using CH_3COOH additive at 0.1 and 0.25 M concentration. Similarly, the TP in process-water was in a similar range with 59.3 - 66.9 mg/L and 62 – 86.3 mg/L when produced using HCOOH additive at 0.1 and 0.25 M concentration.

Factors influencing the TP immobilization during the HTC process include treatment conditions (temperature, reaction time, and additive properties), and the feedstock itself (Wang et al., 2020). The formation of phosphorus salts (calcium phosphate, magnesium ammonium phosphate, and magnesium phosphate) are known to immobilize phosphorus into the hydrochar and this immobilization is influenced by the presence of higher inorganic content of the feedstock (such as the level of Ca, Mg, and others), pH, temperature and additives during HTC.

The element composition of the feedstock, particularly the presence of phosphate precipitating metals (viz., Fe, Al, and Ca) has a higher potential in deciding the phosphate retention in the hydrochar product (Huang et al., 2018). During HTC of sewage sludge, the presence of a higher concentration of multivalent metal ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} are responsible for forming phosphate with low solubility and in turn enabling the phosphate to be retained in subsequently produced hydrochar. However, the previous studies indicated that the treatment using H_2SO_4 as an additive tends to reduce the level of Ca, Fe, and Mg in hydrochar (Ekpo et al., 2016). Analyzing the conductivity aids in understanding the metal ion concentration in the process-water, and the experimental analysis indicated higher conductivity in the process-water following the use of H_2SO_4 additives in comparison with other organic acids as additives (see Figure 4-4). The presence of increasing metal ion concentration can explain the higher level of P immobilization into the process-water, particularly with H_2SO_4 additives. Nevertheless, despite having relatively higher conductivity following the use of NaOH as an additive, TP concentration in the process-water was comparatively less. One explanation for increased conductivity following the use of alkali additive can be simultaneously induced ionic salts with NaOH additive utilization. The investigated results suggest that HTC of sewage sludge significantly immobilizes phosphorus into hydrochar in all but mineral acid additives. Results are consistent with another study carried out by Ekpo et al. (2016) demonstrating lower TP leaching into the process-water during HTC of swine manure in the presence of CH_3COOH, HCOOH, and NaOH as additives.

4.5. Conclusion

The influence of organic acids, an inorganic acid and, alkali as an additive on phosphorus mobilization, energy value, yield, dewaterability by hydrothermally carbonizing sewage sludge was analyzed. Phosphorus extraction into the process-water is pH-dependent and particularly significant in presence of inorganic acid (H_2SO_4). The use of H_2SO_4 and NaOH as an additive has decreased the FC content of produced hydrochar, which negatively influences the heating value of the consequently produced hydrochar. A relatively higher reduction in the binding force of the sludge particles was observed during HTC using H_2SO_4 in the reaction medium, this in turn improved the hydrochar dewatering performance in comparison with other additives. In

conclusion, if the HTC of sewage sludge is designated to leach the phosphorus into the process water, the use of inorganic acid at a higher concentration is favorable; however, compromise will be made in concern to the fuel characteristic of the hydrochar.

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

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Exclusive overview of the article and its relevance to the research question

The article titled “Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar” tries to answer the below RQ of this cumulative dissertation.

- **RQ 2:** What effect does acid utilization after and before hydrothermal carbonization have on phosphorus mobilization and hydrochar characteristics in sewage sludge? Moreover, what chemical reaction kinetics impact the phosphorus transformation from sewage sludge to leachate?

The primary aim of this study is to understand the influence of acid utilization at different stages of the HTC process on P transformation and hydrochar characteristics. In addition to the primary aim, this study attempts to demonstrate the chemical reaction kinetics during the HTC of sewage sludge and provides an overview of chemical reactions that influence P-transformation from solid to liquid phase.

5.1. 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 analyze and compare the influence of acid (H_2SO_4) 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 H_2SO_4, 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 H_2SO_4 in different process conditions did not have a great influence on proximate analysis results and calorific value of consequently produced hydrochar.

Keywords: Hydrothermal carbonization; Sewage sludge; Phosphorus; Phosphorous recovery; hydrochar; pH; leachate

5.2. 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 (Pérez et al., 2021). 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 (Nenov et al., 2020). The non-renewable 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 non-renewable 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 (Heckenmüller, Narita and Klepper 2014). 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 (Jama-Rodzeńska et al., 2021), 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 higher water content and poor dewaterability characteristics (He, Giannis and Wang 2013). 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, SO_2 and dioxins) if the process is not managed properly (Shettigondahalli Ekanthalu et al., 2020).

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 (Statistisches Bundesamt Destatis 2021). 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 (Kreislaufwirtschaftsgesetz - KrWG 2012), is not only making it obligatory to recover phosphorus from sewage sludge, but also outlaws the direct utilization of sewage sludge on farmland (AbfKlärV 2017). 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 (Crocker and Andrews 2010; Saetea and Tippayawong 2013). Generally, after HTC of sewage sludge 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 (Pérez et al., 2021). Metal salts such as $Al_2(SO_4)_3$ and $FeCl_3$ are generally utilized in the WWTP to precipitate P from wastewater (Park et al., 2016). 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 (Becker et al., 2019). An effective method for leaching the trapped P in hydrochar is by treating hydrochar in inorganic acid solutions at an extremely low pH (Heilmann et al., 2014; Pérez et al., 2021).

Recently, several studies have reported the influence of feed-water pH on the distribution and transformation of P during HTC of sewage sludge (Wang et al., 2017; Ovsyannikova et al., 2019; Shi et al., 2019; Shettigondahalli Ekanthalu et al., 2020), the potential risk concerning heavy metals in hydrochar (Zhai, Liu et al., 2016), physical and chemical characteristics of hydrochar (Liu et al., 2020; He, Giannis and Wang 2013), value –addition of hydrochar by converting it into effective adsorbents (Leng et al., 2015; Saetea and Tippayawong 2013), utilization of hydrochar as soil amender (Wang, Chang and Liu 2019). The primary focus of studies so far has been to increase the efficiency of P recovery and to understand the physicochemical behavior 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 analyze 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 analyzed for P and major multivalent metal ion concentrations, and hydrochar was examined for proximate analysis and fuel characteristics.

5.3. Materials and Methods

5.3.1. 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, US) 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.

5.3.2. 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 5-1. 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.

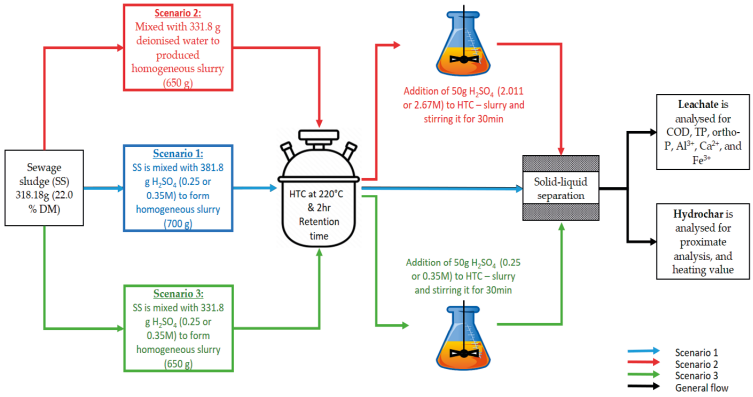

Figure 5-1 Overview of the experimental methodology.

5.3.3. Acid leaching

Table 5-1 Utilization of H_2SO_4 during the experimental procedure

Sample description		Quantity of 18M 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	381.8g 0.25M	-	700g
	L1.2	7.41 ml	381.8g 0.35M	-	
Scenario 2	L2.1	5.29 ml	-	50.0g 2.01M	700g
	L2.2				
	L2.3	7.41 ml	-	50.0g 2.67M	
	L2.4				
Scenario 3	L3.1	5.29 ml	331.8g 0.25M	50.0g 0.25M	700g
	L3.2	7.41 ml	331.8g 0.35M	50.0g 0.35M	

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 5-1, 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.

5.3.4. 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, Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+}. 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, Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} were analysed spectrophotometrically. Triplicates of all investigated results were obtained, and the resultant mean value was reported.

5.4. Results and discussion

5.4.1. Characteristic of sewage sludge

The proximate and ultimate analysis results of feedstock are shown in Table 5-2. 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 (Peng et al., 2016; Wang et al., 2017; Shettigondahalli Ekanthalu et al., 2020). The ultimate analysis results had a typical value for C-H-N-S-O content for sewage sludge in Germany (Roskosch and Heidecke 2018) 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 34.4 g/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 (Peng et al., 2016; Wang et al., 2017; Roskosch and Heidecke 2018). The overall characteristics of the feedstock have the typical composition of sewage sludge in Germany.

Table 5-2 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	34400.00

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

5.4.2. P-transformation from solids to the liquid phase of sewage sludge

Figure 5-2 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 analyzed 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.

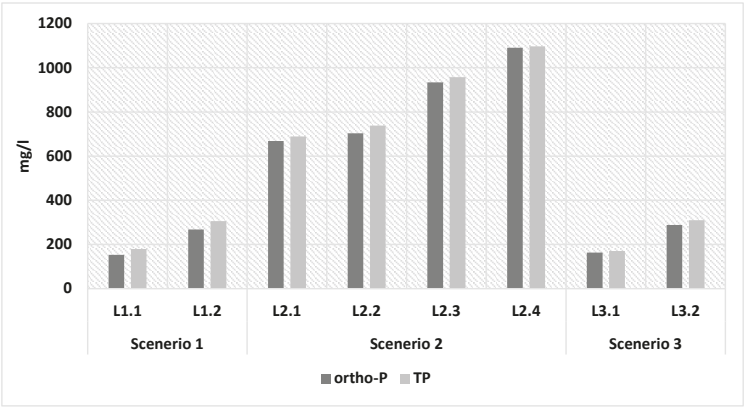

Figure 5-2 Concentrating of TP and ortho-P in the leachate after solid-liquid separation

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.

5.4.3. 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 strong acid or base (Stumm and Morgan 1981). 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 5.1).

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \tag{5.1}$$

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 viz., carbonate minerals, metal oxide, hydroxide, alkaline mineral etc. (Yong et al., 1992). Further, the presence of abundant organic matter such as protein and volatile fatty acids also greatly contributes to the inhibition of acidification (Zhang et al., 2010).

However, the acid buffering substance present in the solid and liquid phase of the sewage sludge suspension has different neutralizing 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 (5.2)). 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 (5.3)). 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 aluminum phosphates (Al-P), and finally leads to the dissolution of ferric phosphate (Fe-P) (see equation ((5.4)-(5.6)) (Zhang et al., 2010; Bozkurt et al., 2000; Petzet, Peplinski and Cornel 2012).

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \tag{5.2}$$

$$\text{Primary rock mineral} + 2H^+ + H_2O \rightarrow \text{cations} + H_4SiO_4 + \text{Secondary minerals} \tag{5.3}$$

$$AlPO_4 + 3H^+ \rightarrow Al^{3+} + H_3PO_4 \tag{5.4}$$

$$Fe_3(PO_4)_2 + 6H^+ \rightarrow 3Fe^{2+} + 2H_3PO_4 \tag{5.5}$$

$$FePO_4 + 3H^+ \rightarrow Fe^{3+} + H_3PO_4 \tag{5.6}$$

The equation (5.4) - (5.6) theoretically depicts 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 higher acid-consuming compounds of both organic and inorganic origin (He, Giannis and Wang 2013). 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.

5.4.4. Influence of HTC on buffering capacity of sewage sludge and mobilization of P

During HTC, both the temperature and the feedstock composition significantly regulates 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 (Wang, Chang and Li 2019). 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 (Libra et al., 2014; Reza et al., 2014). As the reaction begins carbonaceous compounds would hydrolyze almost entirely into free fatty acids (Blach and Engelhart 2021). These fatty acids have been recognized primarily as acetic acid and propionic acid and are mostly derived from unsaturated lipids (Wilson and Novak 2009). Further, with an increased reaction time; aldehydes, ketones, and monosaccharides would be degraded forming organic acids such as formic, lactic and acetic acid (Asghari and Yoshida 2007).

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.

5.4.5. 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 (5.7)) (Hoff 1896).

$$\frac{d(ln\, k_{eq})}{dT} = \frac{\Delta H°}{RT^2} \tag{5.7}$$

In a process, k_{eq} is the change in equilibrium constant of a chemical reaction at temperature *T*, the standard enthalpy change is $\Delta H°$, and R is the ideal gas constant. Evidently, if the dissolution of the salts is exothermic ($\Delta H°$ <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 ($\Delta H°$ <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 (Ehrnström 2016).

5.4.6. Influence of metal ion migration (Al^{3+}, Ca^{2+} and, Fe^{3+}) on TP-transformation into the leachate

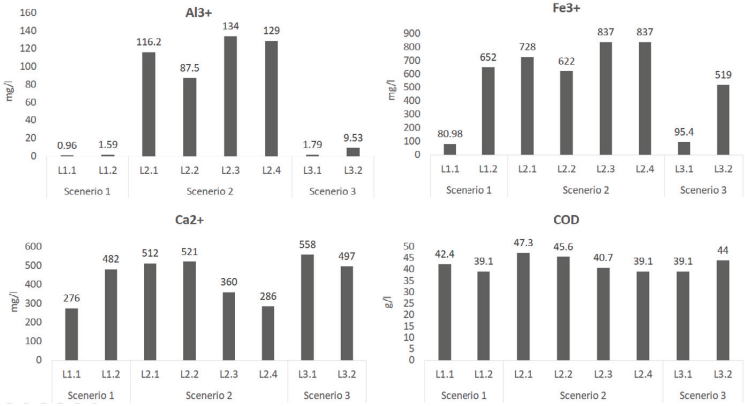

Figure 5-3 Metal ions concentration and COD of the leachate after solid-liquid separation.

The element composition of the sewage sludge, predominantly the presence of phosphate precipitating metals (viz., Fe, Al, and Ca) has a higher potential in deciding the P transformation from the solid to liquid phase (Manures 2018; Ekpo et al., 2016). 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 (Ekpo et al., 2016).

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 5-3). 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 5-2). 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 at different process conditions, the COD of the leachate had comparatively similar results.

5.4.7. Fuel characteristic of the hydrochar

The proximate analysis and heating value (HHV) of the hydrochar are presented in Table 5-3. 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 5-3 Proximate analysis and heating value of hydrochar produced at different reaction conditions.

Sample description		**Proximate analysis (Wt.% dry basis)**			**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 investigation had the HHV in the range of 13.22 - 14.09 MJ/kg, which is similar to the results from earlier studies demonstrating fuel characteristics of hydrochar produced using sewage sludge (He, Giannis and Wang 2013; Shettigondahalli Ekanthalu et al., 2021).

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 (Putra et al., 2018). 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 (Mazumder, Saha and Reza 2020). There are several studies to showcase 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 (Anshariah et al., 2020; Putra et al., 2018). 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 H_2SO_4 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 CO_2 or dissolved into the liquid phase (Berge et al., 2011; Kang et al., 2012).

5.5. Conclusion

The influence of H_2SO_4 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 H_2SO_4 was used after HTC, in comparison with H_2SO_4 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 H_2SO_4 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 H_2SO_4 in the different process conditions, hydrochar produced from the investigated three different scenarios had comparatively similar results for proximate analysis and calorific value.

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5.7. Supplementary information

The 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).

6. Acid leaching of hydrothermally carbonized sewage sludge: Phosphorus release and hydrochar characteristics

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Exclusive overview of the article and its connection to the research question

The article titled "Influence of acids and alkali as additives on hydrothermally treating sewage sludge: Influence on phosphorus recovery, yield, and energy value of hydrochar" tries to answer the following RQ of this cumulative dissertation.

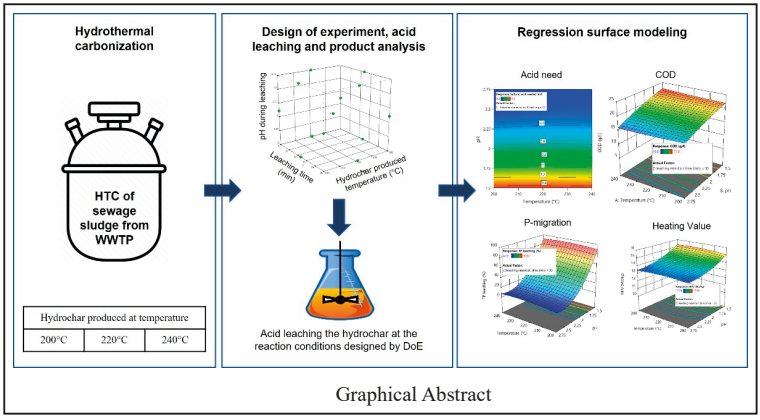
- **RQ 3**: What are the effects of leaching sewage sludge hydrochar using organic and inorganic acids at various pH on phosphorus mobilization?
- **RQ 4**: In addition to pH what are the other characteristics of acids influencing the phosphorus mobilization from sewage sludge hydrochar to leachate?

The article tries to integrate experimental analysis and regression modeling to understand the impacts of acid leaching hydrochar at varied pH utilizing organic and inorganic acids on P transformation and hydrochar characteristics. Together with the influence of varying pH, an investigation is made to explore the other acid feature that affects P mobilization during acid leaching of hydrochar. The outcomes of this study provide a comprehensive overview of the effects of pH and acid characteristics on the leaching of phosphorus from the solid to liquid phase as well as the properties of hydrochar after acid treatment.

6.1. Abstract

The options for managing sewage sludge and its utilization as fertilizer are becoming progressively limited as a result of stringent environmental regulations imposed by the European Union over the past 10 years. The limitation of moisture present in sewage sludge that affects conventional treatment options like incineration can be obviated by using the hydrothermal carbonization (HTC) process. This research investigates the acid leaching of hydrochar produced by hydrothermally carbonizing sewage sludge. The objective is to investigate and compare the effects of formic acid (HCOOH), sulfuric acid (H_2SO_4), and acetic acid (CH_3COOH) at varying pH levels on total phosphorus (TP) mobilization and hydrochar properties. The impact of independent parameters such as carbonization temperature of hydrochar, acid type, acid concentration, and acid leaching retention time on the TP mobilization, chemical oxygen demand (COD) of the leachate, and the fuel characteristic of the hydrochar was explored. A quadratic and cubic model was proposed to correlate the effects of independent parameters on TP and ortho-P mobilization, acid need, COD of leachate, and fuel characteristics of hydrochar using Design of Experiments and Response Surface Modelling. This approach was chosen in order to maximize the amount of data from a constrained number of experimental trials. The outcome of the study indicated a fractional amount of H_2SO_4 was enough to reach and maintain the lower pH in hydrochar slurry compared to HCOOH and CH_3COOH. TP mobilization from solid to liquid is highly favorable in the presence of H_2SO_4 at lower pH compared to HCOOH and CH_3COOH under similar reaction conditions. In addition, it was discovered that lowering the pH using HCOOH and H_2SO_4 to acid-leach the hydrochar boosted the caloric value of the hydrochar. However, CH_3COOH has a contradictory effect.

Keywords: Hydrothermal carbonization; response surface model; design of experiments; regression model; sewage sludge treatment; phosphorus recovery; pKa; organic and inorganic acids



Graphical Abstract

6.2. Introduction

Phosphorus (P) is a critical element whose availability is vital for meeting agricultural and industrial demands across the world. In recent years, global phosphate demand has steadily increased due to the accelerated growth of the economy (Cieślik and Piotr Konieczka 2017). However, the global phosphate mineral resource is nonrenewable, limited to a few countries, and is projected to be exhausted in 50–100 years (Poirier, Jaskolowski and Clúa 2022). As a result, there is an urgent need for the efficient management and recycling of phosphorus rich by-products in order to meet future global demands. Recovering P from sewage sludge produced in a wastewater treatment plant (WWTP) is one such potential approach. Municipal WWTPs often convert phosphate from wastewater into sludge, making sewage sludge the most popular by-product with a substantial source of P. Recent estimates indicate that the quantity of industrial and domestic wastewater generated annually on a global scale is in the order of billions of tons and is anticipated to increase due to population growth and rising standards of living (Bora, Gupta and Durbha 2019). The production of sewage sludge in Europe (EU27) is estimated to be approximate 10 million tonnes annually dry matter (DM) (Domini et al., 2022). In comparison Germany has produced 1.72 million tonnes DM of sewage sludge in 2022, demonstrates the potential of sewage sludge as an alternative source for P mineral (Statistisches Bundesamt, Destatis 2022). Most WWTPs treat phosphorus-containing wastewater with enhanced biological phosphorus removal or chemical precipitation, which transfers >90% of the phosphorus from the unprocessed wastewater to the sewage sludge (Liang et al., 2019). The primary utilization pathway for sewage sludge includes thermal disposal in mono- and co-incineration facilities, recycling in agriculture, recycling in landscaping, and recycling of other materials through humification and composting. The management of sewage sludge varies significantly among EU Member States. In Spain, Ireland, Finland, Hungary, and Cyprus, land-based utilization or composting is the most popular method, whereas Netherlands, Belgium, Germany, and Austria mostly employ incineration (Domini et al., 2022). The availability of agricultural areas and local regulations are the key factors affecting the decision to recover or dispose of sludge. The direct use of sewage sludge for agricultural purpose is however restricted in many countries due to the presence of harmful substances such as heavy metals, organic residues, microplastics, and various pathogens. The sustainable management of sewage sludge is a global concern due to its potential for negative environmental effects. Nevertheless, the organic matter and nutrients present in sewage sludge have the potential to be utilized for the production of renewable energy and are essential for the production of fertilizers.

The German Sewage Sludge Ordinance (AbfKlärV) is a particular regulation under German waste law that specifies the application and utilization of sewage sludge (AbfKlärV 2017). The new rule set by the German sewage sludge ordinance restricts the direct use of sewage sludge to agriculture and also mandates the recovery of phosphorus from sewage sludge in Germany (AbfKlärV 2017). Following the 1999 ban on landfilling in the European Union (EU), incineration has become the preferred waste disposal method in the EU-15 (Raheem et al., 2018). In 2022, 1.3 million tons DM (approximately 77% of the total generated sewage sludge) have been thermally recycled (mono-incineration, co-incineration, and other thermal disposals), and the trend of sewage sludge being managed by land-based utilization/landscaping is decreasing (Statistisches Bundesamt, Destatis 2022). Although thermal treatment of sewage sludge is generally accepted, the most significant drawback of incineration is the high energy requirements of thermal dewatering (Werther and Ogada 1991). In this regard, hydrothermal carbonization (HTC) has received increased attention as an environmentally acceptable and viable approach for treating sewage

sludge without dewatering it. The HTC process uses the excess moisture in sewage sludge as a catalyst and converts the sewage sludge into a carbonaceous product at reaction temperatures ranging from 180 °C to 260 °C at 0.5 to 24 hours retention time and at elevated autogenous pressures (Jellali et al., 2022).

In recent years, there has been considerable interest in the investigation of HTC as a potential treatment option for sewage sludge, as well as studies examining the P transformation during and after HTC. There are several studies that reported the distribution and transformation of P during HTC of sewage sludge (Wang et al., 2017, Ovsyannikova et al., 2019; Shi et al., 2019), acid leaching of sewage sludge and hydrochar using 2.5 M acid solutions of H_2SO_4 and HCl (Pérez et al., 2021), the influence of organic acid (citrate and oxalate) leaching on the P transformation from sewage sludge hydrochar (Pérez et al., 2022), migration and transformation of phosphorus during hydrothermal carbonization of sewage sludge (Zheng et al., 2020), and phosphorus recovery from sewage sludge incineration ash (Liang et al., 2019). Numerous previous studies have demonstrated that a significant amount of P after HTC of sewage sludge is retained in the hydrochar (Heilmann et al., 2014; Wang et al., 2017; Wang, Chang and Li 2019). The previously published results indicate that 97.7-98.7% of TP has retained in the resulting hydrochar after HTC treatment of sewage sludge (Shettigondahalli Ekanthalu et al., 2021). Nevertheless, variation of pH has a major effect on the transformation of P from solid to liquid phase and the alteration of pH after HTC is found to be highly efficient (Shettigondahalli Ekanthalu et al., 2022). Prior research has examined the independent effects of organic and inorganic acids on the acid leaching of sewage sludge hydrochar. The effect of acid leaching of sewage sludge hydrochar utilizing organic and inorganic acids under varying conditions of acid strength and time has not been investigated yet, to the author's knowledge.

This study focuses on acid leaching the sewage sludge hydrochar with formic acid (HCOOH), sulfuric acid (H_2SO_4), and acetic acid (CH_3COOH) at varying pH to determine its effect on P mobilization, hydrochar characteristics, and leachate characteristics. In addition to comprehending the impact of pH on P leaching, the purpose of this study is to investigate what other acid properties influence P leaching from solids to liquid. A Design of Experiments (DoE)/Response Surface Model (RSM) method facilitates the investigation of the selected reaction conditions within a defined reaction space. The DoE/RSM has been widely used in HTC (Mäkelä, Benavente and Fullana 2015; Mäkelä, Benavente and Fullana 2016; Román et al., 2018), for sewage sludge dewatering (Lühmann and Wirth 2020, Danso Boateng et al., 2015), optimization of hydrochar production (Guo et al., 2021, Akbari et al., 2022, Zheng et al., 2020B), and the influence of pH on P release and transformation in hydrothermally carbonized sewage sludge (Lühmann and Wirth 2020). Although acid leaching hydrochar process parameters such as acid usage and the role of pH in P transformation, as well as hydrochar characteristics, have only been studied separately with particular acid utilization so far. The DoE/RSM methodology employed in this study seeks to comprehend the impacts of various acids and their interactions with hydrochar on the characteristics of hydrochar and leachate, with a specific emphasis on P mobilization. The results of this study offer an in-depth overview of the impact of pH and acid characteristics on the leaching of phosphorus from the solid to liquid phase as well as the properties of hydrochar.

6.3. Materials and methods

6.3.1. Material

The digested and mechanically dewatered sewage sludge used in this investigation was directly obtained from Nordwasser GmbH in Rostock, Germany. The primary wastewater treatment facility in Rostock can handle the wastewater from 320,000 inhabitants and treats both industrial (1/3) and municipal (2/3) wastewater (UBC Sustainable Cities Commission 2017). This WWTP produced 4482 tonnes of dry sewage sludge per year on average between the years of 2014 and 2018, and all of the generated sewage sludge is currently incinerated (Tränckner 2023). Sewage sludge was only sampled once during the treatment plant's steady operation state to ensure consistency of results throughout the investigation. The sewage sludge sample was collected in a sealed sample container and immediately transferred to the laboratory, where it was refrigerated at 4 °C till used for HTC. The dry matter content of the sewage sludge was 22.0% and the ash content was 7.4% (815 °C in% original substance). The refrigerated sewage sludge samples were allowed to warm up to room temperature before HTC.

To evaluate moisture content, volatile organic compound, fixed carbon (FC), and ash content of sewage sludge, a LECO Thermogravimetric Analyzer (TGA) unit TGA701 was used. The ultimate analysis was carried out using an organic element analyzer in accordance with EN ISO 16948, 2015 (EN ISO 16948 2015). The calorific value of the sample material was evaluated using a Parr 6400 calorimeter (Parr Instruments Inc., USA) in accordance with EN 14918, 2010 (EN 14918 2010). The total phosphate content of the sewage sludge was determined in an external laboratory using EN ISO 11885, 2009 (EN ISO 11885 2009).

Acid-leaching of hydrochar is facilitated using either Formic acid 98% pure, Sulfuric acid 72%, or Acetic acid 100% (All the acid reagents were obtained from AppliChem GmbH, Darmstadt). The amount of acid required for attaining the targeted pH was achieved by following the methodology of DIN EN 15933:2012 (Deutsches Institut für Normung 2012).

6.3.2. Experimental method

An overview of the experimental methodology is provided in Figure 6-1. The experimental methodology was planned in four stages; stage 1: HTC of sewage sludge, stage 2: DoE using StatEase Design Expert Software (Version 22.0.0), stage 3: acid leaching of hydrochar, and Stage 4: product recovery, experimental analysis, and regression surface modeling

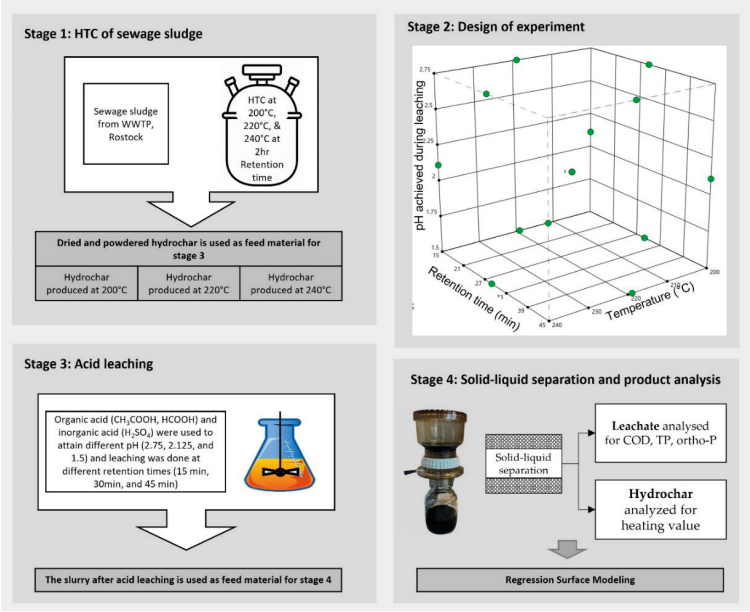


Figure 6-1 Overview of the experimental methodology.

6.3.3. Hydrothermal carbonization of sewage sludge

A Parr 4523 reactor (Parr Instrument GmbH, Zeilweg 15, 60439 Frankfurt, Germany) was used to hydrothermally carbonize sewage sludge. The reactor operates at autogenic pressure and is equipped with a 1-L reaction vessel that can tolerate a maximum pressure of 138 bar. The heat for the reactor is provided by a 2 kW heating coil, and the stirring is facilitated by a stirring unit with a connected drive. The pressure and temperature sensors of the reactor are controlled and monitored using a Parr 4848 PID controller unit.

To understand the influence of HTC temperature on the acid leaching of consequently produced hydrochar, HTC was carried out at temperatures of 200 °C, 220 °C, and 240 °C and a retention time of 2 h while continuously stirring the substrate at 150 rpm. Before beginning HTC, certain volumes of sewage sludge and distilled water were combined within the reactor and mixed to generate a homogenous slurry of 10% DM, and the initial pH was noted using a pH meter (WTW pH 3310, Xylem Analytics Germany Sales GmbH). The HTC of sewage sludge slurry was carried out at an autogenic pressure with a continuous heating rate of 4 K/min. Following HTC, the reactor vessel was left to cool to room temperature, and the final pH was recorded. Following the top-feeding method, solids and liquids were separated from the HTC slurry in a Büchner funnel. The hydrochar produced at three different temperatures was oven-dried at 105 °C for 24 h. The dried hydrochar was collected separately (according to the temperature at which it was produced), crushed to produce fine powder, and stored in an airtight container at room temperature until used.

6.3.4. Design of experiments

The Design-Expert program from Stat-Ease, Inc., was used to design the experiments, perform regression analysis, and model the response surface. The experiments were designed to reveal the interactions of three independent variables with the targeted responses. The three independent variables selected include the following process conditions: 1) the carbonization temperature at which the hydrochar was produced: 200 °C, 220 °C, and 240 °C, 2) pH during the acid leaching process: 1.5, 2.125, and 2.75, and 3) acid leaching time: 15 min, 30 min, and 45 min. Using Box–Behnken design, three replications at the central points and one point in the middle of each edge of the cubical surface were employed, resulting in 15 experimental runs for every acid used. The product of each experimental run was recovered and experimentally analyzed to generate six different targeted responses. The following responses were considered in this study: TP in leachate, ortho-P in leachate, COD of leachate, acid needed, % TP leached, and higher heating value (HHV) of hydrochar. Figure 6-1 (stage 2) is a graphical representation of the experimental design space, and supplementary material S1 includes the randomized experimental design.

6.3.5. Acid leaching process

In the experimental design described in Figure 1, three different acids were used to achieve the targeted pH, and the effects of different acids (HCOOH, H_2SO_4, and CH_3COOH) on the TP-transformation, ortho-P transformation, COD, acid need, and HHV of hydrochar were experimentally analyzed. The experimentally analyzed results of the defined responses were fitted into the RSM model to generate respective 3D-surface models. During the acid-leaching process, the amount of acid required to attain the targeted pH was determined following the methodology of DIN EN 15933:2012 (Deutsches Institut für Normung 2012). The standard DIN EN 1593:2012 specifies a method for determining the pH in suspension of sludge within the pH range of 2–12. However, to maintain uniformity in the experimental procedure, the same standards were used to determine and achieve a pH of 1.5.

A measure of 5 g of hydrochar (produced at 200 °C, 220 °C, and 240 °C) was mixed with 45 mL of deionized water, and a homogeneous slurry was prepared by mixing the content for 15 min on a magnetic stirrer at 250 rpm. After preparing the homogeneous slurry, concentrated acids (one each of HCOOH, H_2SO_4, or CH_3COOH) were slowly titrated against the slurry whilst constantly stirring the content until the desired pH was attained and held constant for 15 min. Later, the pH was held constant for 15 min, 30 min, and 45 min to facilitate the acid leaching of the hydrochar.

6.3.6. Product recovery experimental analysis and regression modeling

6.3.6.1. Product recovery experimental analysis

The hydrochar slurry produced after the acid leaching was sent directly to the polysulfone bottletop vacuum filter for the separation of solids and liquids. The following process conditions were maintained during the solid–liquid separation of the hydrochar slurry: 1) the entire content of the hydrochar slurry after acid-leaching was poured into the polysulfone bottletop vacuum filter and 2) the vacuum pump was turned on to create sufficient vacuum pressure for separating solids and liquids. After the filtering, the liquid was collected in a volumetric flask and kept at 4 °C until it was tested for TP, ortho-P, and COD. Similarly, the resulting solids (hydrochar) were oven-dried at 105 °C for 24 h before being kept in sealed containers for further examination.

Following the procedure outlined in EN 15170, 2010, the caloric value of the hydrochar was analyzed using a Parr 6400 calorimeter in a manner identical to that of sewage sludge. Liquid (leachate) was analyzed spectrophotometrically for TP and ortho-P using the NANOCOLOR ortho- and total-Phosphate tube test kits in accordance with DIN EN ISO 6878-D11. Lastly, following the standards specified in DIN ISO 15705, the COD of the leachate was analyzed using a NANOCOLOR COD 1500 tube test kit. All the spectrophotometric testing kits were obtained from MACHEREY-NAGEL GmbH & Co. KG, Germany. The studied findings were obtained in triplicate, and the mean value is presented.

6.3.6.2. Regression modeling

The DoE/RSM approach was chosen to understand the interaction between selected independent variables and their resulting responses. A DoE/RSM strategy was used in order to maximize the amount of data from a constrained number of experimental trials (Lühmann and Wirth 2020). The DoE was designed with a Box-Behnken Design of RSM methodology using Design Expert software. Box-Behnken Design is an approach that use the minimum square technique to fit the model and defines the interactions of parameters and their influence on responses (Akbari et al., 2022).

The regression modelling was performed as described by Montgomery (Montgomery 2013), and the interaction between the selected variables and the resulting responses were modeled using quadratic (6.1) and cubic equations (6.2).

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{1 \le i \le j \le n}^{n} \beta_{ij} x_i x_j + e \tag{6.1}$$

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{1 \le i \le j \le n}^{n} \beta_{ij} x_i x_j + \sum_{1 \le i \le j \le k \le n}^{n} \beta_{ijk} x_i x_j x_k + e \tag{6.2}$$

Where y denotes the predicted response, β_0 represents the constant co-efficient, β_i $(1 \le i \le n)$ are the coefficients of the linear terms, β_{ij} $(1 \le i \le j \le n)$ represent co-efficients of the quadratic terms (Equation (6.1), and β_{ijk} $(1 \le i \le j \le k \le n)$ represent the co-efficients of the cubic terms (Equation (6.2). x_i, x_j, and x_k are the coded values of the independent variables in the regression function and e is the vector for random error.

A specific model was chosen for every particular response to reduce the lack of fit value in relation to the pure error. For the quadratic and cubic models, the respective lack of fit values were analyzed with respect to the pure error. A non-significant lack of fit value (p-value greater than 0.05) indicates good predictive generalizability of the regression model. In some cases, reduced versions of the original quadratic and cubic models were used to ensure that the lack of fit value was non-significant. This ensures that the potential for overfitting of simpler or reduced versions of the original models decreases by improving their overall predictive reliability on an unseen data space. Table 6-1 and supplementary material S2, illustrates the specifications of the quadratic and cubic regression models that were obtained in the current study.

Table 6-1 Process order of every analyzed response.

Response	HCOOH	H_2SO_4	CH3COOH
TP in leachate	Reduced Quadratic	Quadratic	Reduced Cubic
Ortho-P in leachate	Quadratic	Quadratic	Reduced Cubic
Acid needed	Reduced Quadratic	Quadratic	Quadratic
%TP in leached	Reduced Cubic	Quadratic	Reduced Cubic
COD of leachate	Quadratic	Reduced Cubic	Reduced Cubic
HHV	Quadratic	Reduced Cubic	Quadratic

6.4. Results and discussion

6.4.1. Characteristics of sewage sludge and consequently produced hydrochar

The results of the proximate and ultimate analysis of sewage sludge are shown in Table 6-2. The sewage sludge used in this study had a moisture content of 78.00% and a total solid content of 22.00%. The initial 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 ranges (Peng et al., 2016; Wang et al., 2017; Shettigondahalli Ekanthalu et al., 2020). The ultimate analysis results had a typical value for C-H-N-S-O content for sewage sludge in Germany (Roskosch and Heidecke 2018) with; C: 34.70%; H: 4.90%; N: 4.80%; S: 1.60% and O: 17.60% on a dry basis. The dry sewage sludge is known to contain a higher concentration of phosphorus and moderate heating value. The TP content in the feedstock was determined to be 34.4 g/kg, accounting for 3.4% of total dry sludge, and the heating value was observed to be relatively higher with 14.72 MJ/kg (HHV) than was observed in previous studies (Peng et al., 2016; Wang et al., 2017; Roskosch and Heidecke 2018). The overall characteristics of the feedstock have the typical composition of sewage sludge in Germany.

Table 6-2 Proximate and ultimate analysis of sewage sludge and hydrochar.

Parameters	Units	Sewage sludge	Hydrochar produced at 200 °C	Hydrochar produced at 220 °C	Hydrochar produced at 240 °C
Moisture content	%OS	79.37	-	-	-
Total solids	%OS	20.63	100	100	100
Volatile solids	%DM	65.00	45.63	44.53	42.32
Ash	%DM	33.64	47.25	48.35	50.23
Fixed carbon	%DM	1.36	7.124	7.124	7.45
HHV	MJ/kg, DM	14.72	13.43 (± 0.11)	13.72 (± 0.04)	13.95 (± 0.35)
Nitrogen	%DM	4.71	3.05	2.89	2.66
Carbon	%DM	31.8	30.30	30.40	30.60
Sulphur	%DM	1.66	1.68	1.80	1.95
Hydrogen	%DM	4.81	3.94	3.91	3.84
Total phosphorus	mg/kg DM	34200.0	50300.00	50800.00	53900.00
Total phosphorus	% DM	3.42	5.03	5.08	5.39

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

6.4.2. RSM process optimization

Table 6-3 shows the analysis of variance (ANOVA) and Fit Statistics for the regression model. These quantities signify the reliability of the regression model based on the experimental data that was used to model the response surface. Fischer (F) test results and probability (p-value) can be used to gauge the regression model's effectiveness. F-value is the ratio of two group variations used to determine the statistical significance between the means of the groups. A p-value is a statistical measurement used to validate a hypothesis against observed data. A regression model with higher F values and lower p values is more reliable. As depicted in Table 6-3, all the analyzed responses have p-value <0.05 and a higher F-value portraying a greater statistical significance of the designed models.

The ANOVA of the residual data depicts unexplained variation in the response. Lack of fit refers to the situation where a statistical model fails to adequately fit the underlying data. In other words, it occurs when the model does not capture the relationship between the independent variables and the dependent variables in a regression model. A strong lack of fit (p-value smaller than 0.05) is an undesirable property because it indicates that the model does not fit the data well. It is desirable to have an insignificant lack of fit (p-value greater than 0.05). As shown in Table 6-3 the lack of fit p-value for all the obtained responses were not significant relative to the pure error, meaning the model fits well and there is a significant effect on parameters on output response.

Table 6-3 Analysis of variance (ANOVA) fit statistics of modeled responses.

Responses	ANOVA			Fit Statistics			
	Model		Residual				
	F-value	p-value	lack of fit p-value	R2	R2adj	R2pred	Adeq Precision
HCOOH							
TP in leachate	232.10	<0.0001	0.06	0.9968	0.9925	0.9678	43.11
Ortho-P in leachate	269.69	<0.0001	0.63	0.9979	0.9942	0.9807	46.94
Acid needed	191.45	<0.0001	0.05	0.9961	0.9909	0.9615	37.02
%TP in leached	1398.19	<0.0001	0.07	0.9992	0.9991	0.9701	68.07
COD of leachate	22.64	0.0016	0.34	0.9760	0.9329	0.7110	14.48
HHV of hydrochar	50.31	0.0002	0.74	0.9891	0.9694	0.9140	22.07
H_2SO_4							
TP in leachate	486.85	<0.0001	0.87	0.9989	0.9968	0.9936	55.12
Ortho-P in leachate	352.53	<0.0001	0.08	0.9984	0.9956	0.9760	50.48
Acid needed	42.82	0.0003	0.23	0.9872	0.9641	0.8229	16.15
%TP in leached	515.76	<0.0001	0.91	0.9989	0.9970	0.9946	54.64
COD of leachate	66.08	0.0027	0.07	0.9959	0.9808	-	27.69
HHV of hydrochar	212.86	0.0005	0.92	0.9987	0.9940	-	41.37
CH3COOH							
TP in leachate	146.86	<0.0001	0.11	0.9962	0.9894	0.9288	39.77
Ortho-P in leachate	63.33	0.0001	0.08	0.9913	0.9757	0.8331	22.51
Acid needed	3491.70	<0.0001	0.31	0.9998	0.9996	0.9979	157.09
%TP in leached	40.75	0.0001	0.06	0.9866	0.9623	0.7427	22.24
COD of leachate	4.10	0.0353	0.54	0.7545	0.5704	0.3200	6.18
HHV of hydrochar	25.38	0.0012	0.48	0.9786	0.9400	0.7621	15.25

The Fit statistics shown is Table 6-3 are intended to provide the reader with an understanding of the quality of the regression model. Fit statistics includes the data on R^2, predictive $R^2(Pred.R^2)$, adjusted R^2 $(Adj.R^2)$, and adequate precision. R^2 measures the amount of variation around the mean explained by the model. If the model captures all variations around the mean, R^2 equals one, and if the model cannot account for any variation, R^2 equals zero. R^2 is closest to 1 when all terms are still in the model; it is possible to not include terms in the model that do not have a statistically significant effect (Lühmann and Wirth 2020). $Adj.R^2$ is the measure of the amount of variation around the mean explained by the model. The $Adj.R^2$ decreases as the number of terms in the model increases if those additional terms do not add value to the model. $Pred.R^2$ measure of the number of variations in new data explained by the model. The $Adj.R^2$ and $Pred.R^2$ should be within approximately 0.20 of each other to be in "reasonable agreement". If they are not, there may be a problem with either the data or the model (Stat-Ease, Inc. 2022). In this study, $Pred.R^2$ was in reasonal agreement with the $Adj.R^2$ value in majority of cases; in turn, depicts the reliability of the model (see Table 6-3).

Adequate precision is a measure of the range in predicted response relative to its associated error; in other words, it is a signal to noise ratio. A ratio greater than four is desirable (Stat-Ease 2022). All the obtained adequate precision values in this study were >4, confirming an adequate signal and the possibility to use the model to navigate the design space with greater reliability.

6.4.3. Acid requirement in achieving the targeted pH

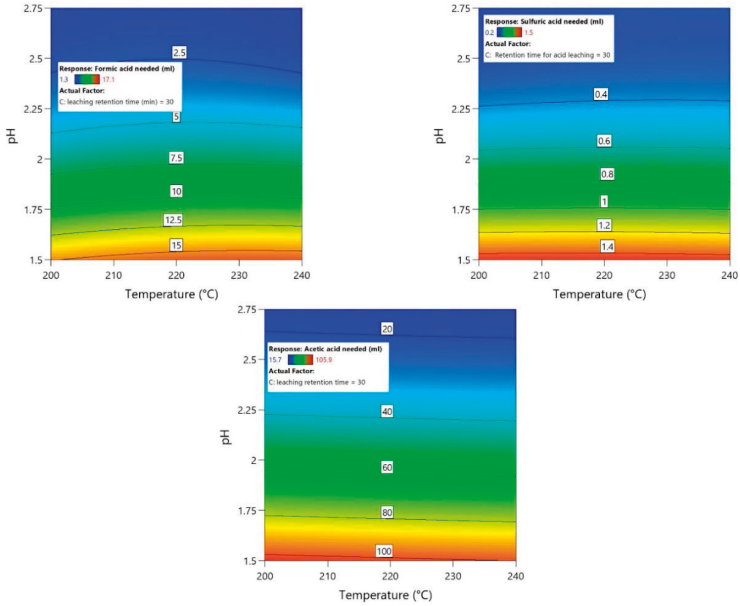


Figure 6-2 Regression model contour plot depicting the influence of acids on reaching the targeted pH.

Figure 6-2 displays the response surface plot of the amount of acid required to achieve and maintain the desired pH in the hydrochar slurry for 30 min of acid leaching. The demand for acid was unaffected by a 15-min change in leaching time either way (See Supplementary Figure S3). In comparison to organic acids, using inorganic acid required less acid to achieve and maintain the desired pH. Among the organic acids, acetic acid required ~seven-fold more acid than formic acid to achieve a similar pH. For instance, ~1.5 mL of H_2SO_4 (72% sulfuric acid) is required to achieve and maintain the pH of 1.5 in a 50 g hydrochar slurry of 10% dry matter with an initial pH of ~5.73 (+/− 0.2); ~15 mL of formic acid (98% formic acid) is required to achieve the same conditions, and the acid requirement for acetic acid (100% acetic acid) increases significantly to ~100 mL. Several parameters influence the target of achieving and maintaining a lower pH during acid leaching of hydrochar. The primary influencing parameter is the type of acid; acid strength and other parameters include the HTC process and diverse chemical reaction that occurs within the process.

It was seen in the experimental analysis that H_2SO_4 needed a fractional amount of acid compared to CH_3COOH and HCOOH to reach and maintain the lower pH. Similarly, HCOOH also needed less acid than CH_3COOH. This phenomenon can be explained using the strength of the acid. One approach for describing the strength of any acid is its pKa value. The negative log of the Ka value, also known as the acid dissociation constant, is the pKa value (Helmenstine 2020). A stronger acid is indicated by a lower pKa value and the lower pKa value indicates that the acid can be fully dissociated in the water (Helmenstine 2020). Of the different acids used in this investigation, H_2SO_4 is the strongest acid with a pKa value of −3.0, indicating the presence of highly acidic components that can readily donate protons in water (Stumm and Morgan 1981). Formic acid is

a simple carboxylic acid with a pKa value of 3.75 is a weaker acid than H_2SO_4 and relatively stronger than Acetic acid with a higher pKa value of 4.7 (Stumm and Morgan 1981). Hence, H_2SO_4, with its lower pKa value, needs only a fraction of the amount of acid required to achieve and maintain lower pH in hydrochar slurry compared to the amount needed for CH_3COOH and HCOOH with their higher pKa values.

When half of the acid has dissociated, pKa and pH are equal. When the pKa and pH values are close, the buffering capacity of a species, or its ability to maintain the pH of a solution, is greatest. Therefore, the optimal choice for a buffer is one with a pKa value close to the desired pH of the chemical solution (Helmenstine 2020). In the hydrolysis phase of the HTC process, volatile fatty acids (VFAs) are created, which results in the production of organic acid molecules and contributes to acidification (Woriescheck 2019; Danso-Boateng et al., 2015). The presence of increased VFAs after the HTC of sewage sludge could also be one parameter influencing the larger amount of an organic acid (CH_3COOH and HCOOH) required to achieve a lower pH compared to the amount of inorganic acids (H_2SO_4) required.

6.4.4. Effect of different acid utilization and acid leaching retention time on COD of leachate

The HTC process water is organically and inorganically contaminated, and COD is characterized as one of several organic contaminants. The organic contaminants in the process water produced by HTC usually have high levels of COD that depend upon the HTC process conditions and input materials (Woriescheck 2019). During the HTC of sewage sludge, the decomposition of the organic acidic compounds and their displacement from the solid to the liquid phase contributes to the acidification of the liquid phase and simultaneous increase in COD (Jellali et al., 2022). In general, the HTC process decreases the pH and increases the soluble COD content, particularly for the digested and dewatered sludge (Merzari et al., 2020). Several organic compounds, especially the VFAs, create a major organic load in the process water after HTC, in turn increasing the COD of the process water. VFAs are formed during the hydrolysis stage of the HTC process and produce acids such as acetic acid, propionic acid, butyric acid, valeric acid, and levulinic acid (Danso-Boateng et al., 2015). The presence of these acids in the liquid phase increases the concentration of protons or hydroxide ions, further catalyzing decarboxylation and dehydration reactions (Guo et al., 2021; Reza et al., 2015). Among VFAs, acetic acid is the main organic acid produced during HTC through the hydrolysis and dehydration of straight-chain polymers, such as cellulose and hemicellulose, or simple monomers in the presence of subcritical water (Liu et al., 2020).

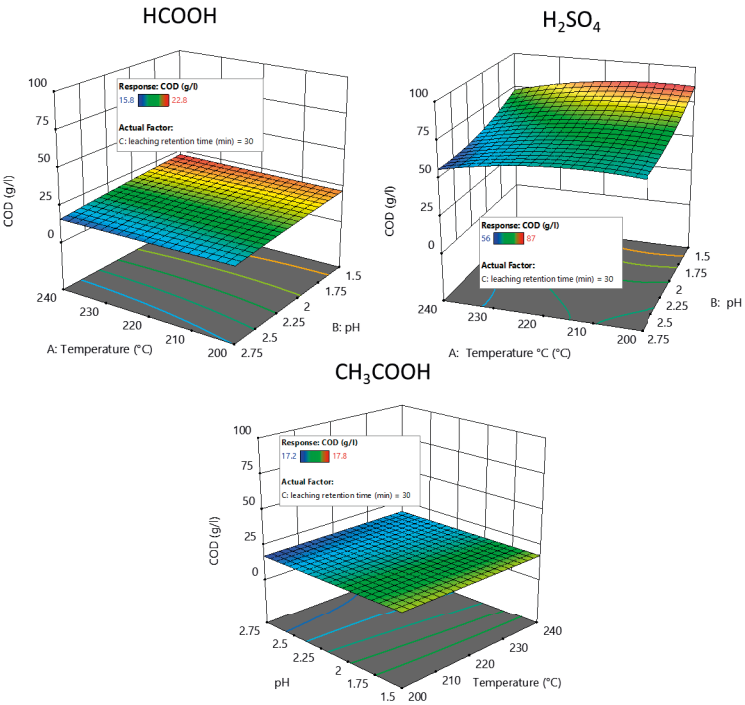


Figure 6-3 Regression mode three-dimensional response surface plot showing COD of the leachate produced after acid leaching using H_2SO_4, HCOOH, and CH_3COOH

Figure 6-3 depicts the response surface plot of the COD of the leachate obtained after acid leaching the hydrochars using different acids at different pH levels with a 30 min retention time. The influence of acid leaching retention time on COD was insignificant with varying acid leaching retention time (+/−15 min) (see Supplementary Figure S4). In general, during the acid leaching process, using organic acids (HCOOH and CH_3COOH) to achieve the targeted pH results in higher COD in the leachate compared to the use of an inorganic acid (H_2SO_4). COD was found to increase with increasing pH when H_2SO_4 and HCOOH were used for acid leaching. However, the use of CH_3COOH for acid leaching did not have a greater influence on the COD, irrespective of varying pH. Compared to the use of organic acids, the use of inorganic acids might have leached a larger amount of organic material, furfural, and 5-HMF, together with nutrients. This could explain the significantly increased COD with H_2SO_4 compared to organic acid utilization. Additionally, an increased COD can be seen with formic acid utilization as well as an increase in the acid concentration. However, there is no increase in COD with the use of acetic acid despite the increase in the pH. One reason for such phenomena could be that acetic acid is the main organic acid produced during the HTC process, and further addition of acetic acid during acid leaching processes decreases the pH but does not increase the organic load or influence the COD concentration.

6.4.5. Effect of different acids on P-transformation from solids to the liquid phase

Figure 6-4 displays the response surface plot showing the effects of the different acid types and their concentration (pH) on the transformation of TP from solid to liquid phase during an acid-leaching process. TP in the leachate was analyzed spectrophotometrically after acid hydrolysis and oxidation of the sample, and the results were used to plot the RSM plot. Figure 6-4 depicts the results from an acid leaching retention time of 30 min. Altering the acid leaching retention time by +/−15 min did not have a great influence on TP transformation (See Supplementary Figure S5, S6). In brief, the results show that acid leaching the hydrochar slurry using H_2SO_4 at pH 1.5 transformed approximately 90% (+/−1%) of TP from the solid to the liquid phase, whereas HCOOH and CH_3COOH transformed only approximately 36% (+/−6%) and 2.5% (+/−1%), respectively, under similar reaction conditions. The ortho-P transformation from solid to liquid also had a similar trend to that of TP and is depicted in the response surface plot of Figure 6-5.

Following the acid leaching of hydrochar, the highest TP transformation from solid to liquid (5,268 mg/L or 90.87%) was observed by using H_2SO_4 and acid leaching at pH 1.5. The maximum TP transformation from solid to liquid following acid leaching at pH 1.5 using HCOOH and CH_3COOH was 1,721 mg/L (42.08%) and 59.5 mg/L (3.36%), respectively. The results suggested that compared to inorganic acid (H_2SO_4), organic acids (HCOOH and CH_3COOH) with similar pH have a limited impact on transforming TP from solid to liquid, which agrees with the previous studies (Wang et al., 2017; Ekpo et al., 2016; Shettigondahalli Ekanthalu et al., 2021). In addition to the acid used and the pH, the reaction temperature at which the hydrochar was produced also had a slight influence on the TP transformation. The hydrochar generated at 240 °C had an 8.7% greater TP transition from solid to liquid than the hydrochar produced by acid-leaching (H_2SO_4, pH 1.5) at 200 °C. The TP transformation of HCOOH was 11.5% higher under identical reaction circumstances, while the impacts of CH_3COOH were too small to support any conclusion.

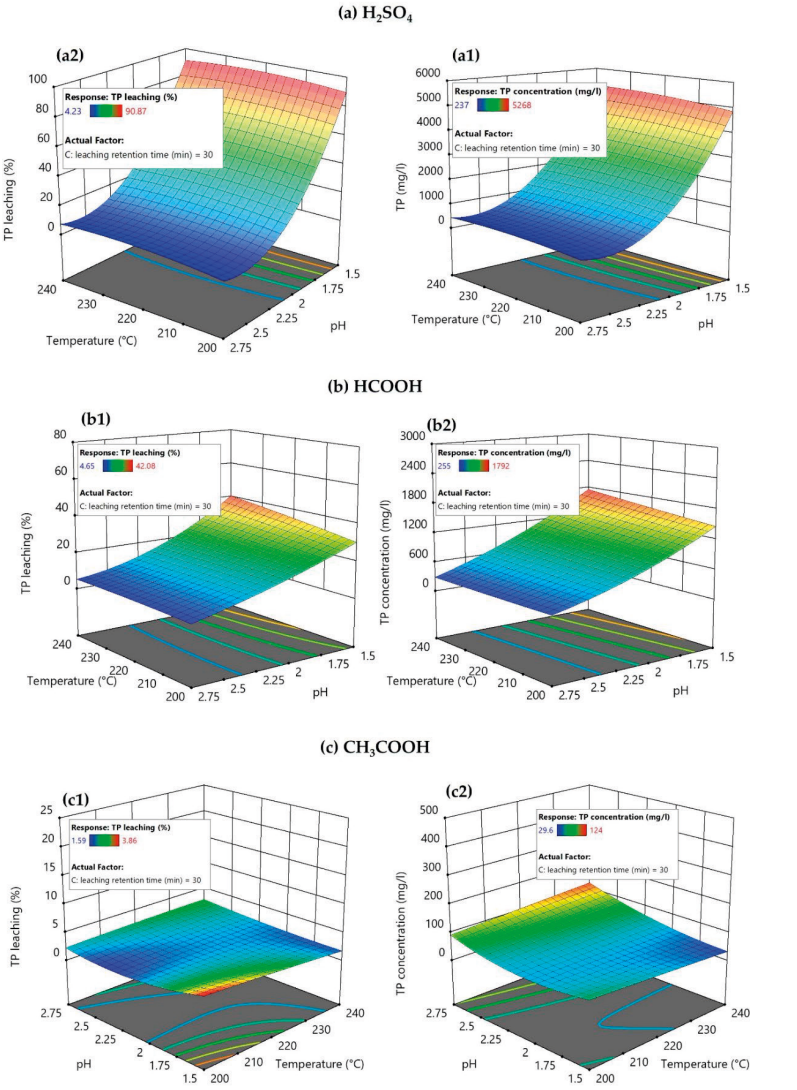


Figure 6-4 Regression mode three-dimensional response surface plot showing the effect of hydrochar produced temperature and acid leaching pH on the transformation of TP from solid to liquid phase.

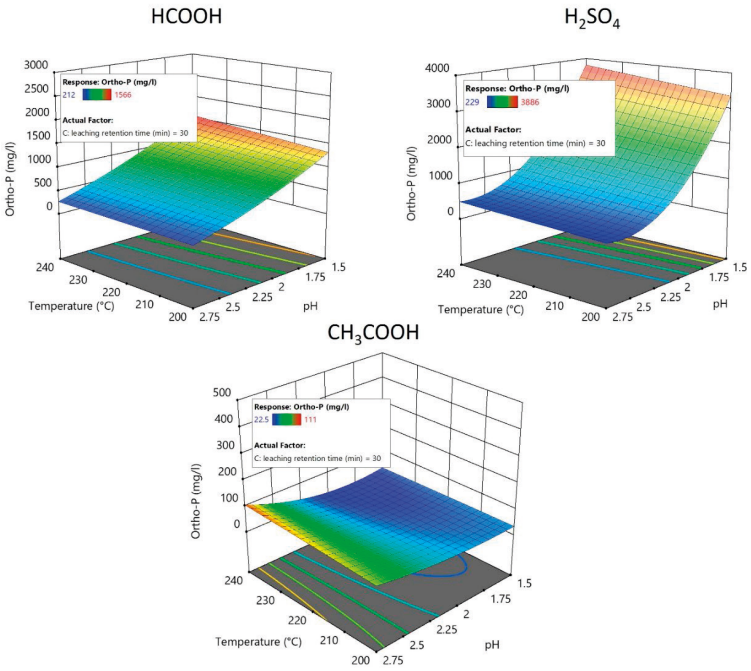


Figure 6-5 Regression mode three-dimensional response surface plot showing the effect of hydrochar produced temperature and acid leaching pH on the transformation of Ortho-P from solid to liquid phase

During HTC of sewage sludge, the presence of a higher concentration of multivalent metal ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} is responsible for forming phosphate with low solubility and, in turn, enabling the phosphate to be retained in subsequently produced hydrochar (Huang et al., 2018). The solubility of these multivalent metal ions has a significant impact on the TP mobility from a solid to a liquid during the acid-leaching procedure. Factors influencing the TP transformation from solid to liquid include the strength of the acid (Dai et al., 2017), the pH of the leaching medium (Petzet, Peplinski and Cornel 2012), and the ability of the acid to mobilize the phosphorus-holding compounds (ferric phosphate, ferrous phosphate, aluminum phosphate, calcium phosphate, and magnesium phosphate). The primary chemical reactions for the TP transformation from solid to liquid are included in the following equation.

$$AlPO_4 + 3H^+ \rightarrow Al^{3+} + H_3PO_4 \quad 6.3$$

$$Fe_3(PO_4)_2 + 6H^+ \rightarrow 3Fe^{2+} + 2H_3PO_4 \quad 6.4$$

$$FePO_4 + 3H^+ \rightarrow Fe^{3+} + H_3PO_4 \quad 6.5$$

$$Ca_9(Al)(PO_4)_7 + 21H^+ \rightarrow 9Ca^{2+} + Al^{3+} + 7\,H_3PO_4 \quad 6.6$$

The reactions in equations (6.3) - (6.6) are highly favourable in strongly acidic conditions and particularly in the presence of strong acids like H_2SO_4. To facilitate the primary reactions for TP transformation, there is a requirement for greater acid concentration to overcome the buffering

resistance provided by the hydrochar slurry (Shettigondahalli Ekanthalu et al., 2022). Figure 6-6 displays the concentration of Al^{3+} and Fe^{3+} ions in the leachate produced by acid-leaching hydrochar with HCOOH, H_2SO_4, and CH_3COOH at pH values of 1.5, 2.125, and 2.75. The use of stronger acids or acids with lower pKa values has a substantially greater effect on the dissolution of Al^{3+} and Fe^{3+} ions and their corresponding P, as demonstrated by the experimental findings. Using H_2SO_4, which has a pKa value of −3.0, resulted in the greatest Al^{3+} and Fe^{3+} ion discharge, followed by HCOOH and CH_3COOH, which have pKa values of 3.75 and 4.70, respectively. The use of CH_3COOH for acid leaching has shown visibly poor dewaterability compared to H_2SO_4 and HCOOH. The hydrophilic nature of hydrochar slurry produced by the addition of CH_3COOH can also hinder the migration of phosphorus-containing compounds from solid to liquid.

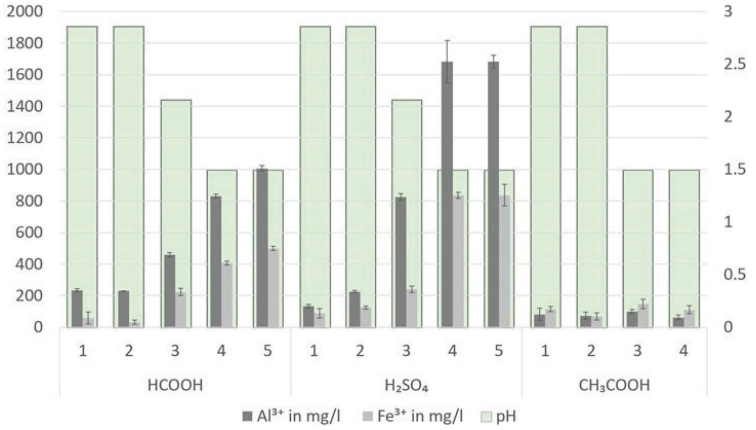


Figure 6-6 Al^{3+} and Fe^{3+} concentration in the leachate produced after acid leaching the hydrochar.

With the utilization of H_2SO_4, a slight decrease in the pH of the acid-leaching medium significantly increased the TP mobilization from solids to liquid. This is because at lower acid concentrations, most of the acid present in the reaction medium is utilized to offset the buffer resistance provided by acid-consuming compounds present in the reaction medium with relatively higher neutral points; see equations 6.7 and 6.8.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \quad 6.7$$

$$\text{Primary rock mineral} + 2H^+ + H_2O \rightarrow \text{cations} + H_4SiO_4 + \text{Secondary minerals} \quad 6.8$$

6.4.6. Effects of different acid utilization on the calorific value of hydrochar produced after acid leaching

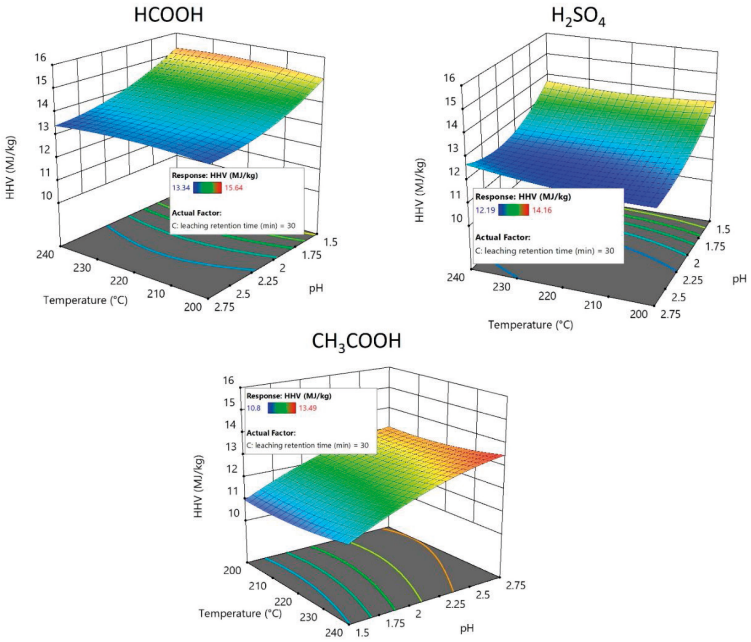


Figure 6-7 Regression mode three-dimensional response surface plot showing influence of acid leaching using H_2SO_4, HCOOH, and CH_3COOH on the calorific value of hydrochar.

The calorific value of the hydrochar produced after acid leaching the hydrochars using different acids at different pH levels is illustrated in the Figure 6-7. The illustrated Figure 6-7 particularly shows the caloric value of hydrochar produced at an acid leaching retention time of 30 min. Increasing or decreasing the leaching time by 15 min did not have any greater influence on the caloric value of the hydrochar produced (See Supplementary Figure S7). Treating the hydrochar with different acid-leaching conditions influenced its caloric value. Prior to acid leaching, hydrochar had a caloric value ranging between 13.43 MJ/kg and 13.95 MJ/kg, and after acid leaching, the caloric value of hydrochar ranged between 10.97 MJ/kg and 15.64 MJ/kg. The caloric value for the hydrochar after acid leaching using HCOOH and H_2SO_4 ranged between 15.64 MJ/kg and 13.43 MJ/kg and between 14.16 MJ/kg and 12.19 MJ/kg, respectively, which is comparable to the findings of other research examining the caloric value of hydrochar produced by hydrothermally carbonizing digested sewage sludge (He, Giannis and Wang 2013; Shettigondahalli Ekanthalu et al., 2021; Shettigondahalli Ekanthalu et al., 2022). However, the caloric value for the hydrochar after treatment with CH_3COOH was in the range of 13.49–10.97 MJ/kg, which is less than that of hydrochar treated using different acids in this study. Furthermore, it was also noticed that decreasing the pH during acid leaching using HCOOH and H_2SO_4 increased the caloric value of hydrochar. In contrast, the use of CH_3COOH for acid leaching adversely affected the caloric value of hydrochar with decreasing pH.

Several previous studies showed a strong correlation between the increase in HTC reaction temperature and the caloric value (Danso-Boateng et al., 2015); similar results were found during this research that an increase in reaction temperature has increased the calorific value of the produced hydrochar (see Table 6-2). The heating value of the sewage sludge tends to increase after HTC due to aromatization, polymerisation, and condensation reactions that occur during the HTC process (Mazumder, Saha and Reza 2020).

Numerous studies have demonstrated a significant correlation between FC content and caloric value. FC is the remaining combustible material that is present after the volatile solids in the hydrochar are burnt. The caloric value of hydrochar increases with the increasing FC concentration of hydrochar (Anshariah et al., 2020; Putra et al., 2018; Shettigondahalli Ekanthalu et al., 2022). Before HTC, sewage sludge typically has high VS and low FC content, but a series of reactions that occurs during HTC considerably increase FC and also the calorific value of hydrochar (Putra et al., 2018). The proximate analysis and calorific value of selected hydrochar samples obtained after 30 min acid leaching time are shown in Table 6-4.

Table 6-4 Proximate analysis and calorific value of hydrochar samples obtained after 30 min acid leaching time.

Sample description			**Proximate analysis of solids after acid leaching**			**HHV**
Acid used	Acid leaching pH	Temperature	Volatile solids	Fixed carbon	Ash	MJ/kg
HCOOH	2.75	200	47.26	6.76	45.98	13.49 (± 0.04)
	2.75	240	43.41	7.25	49.34	13.34 (± 0.02)
	2.125	220	49.16	7.2	43.63	13.93 (± 0.05)
	1.5	200	51.99	8.31	39.7	15.16 (± 0.02)
	1.5	240	51.31	8.8	39.8	15.28 (± 0.02)
H_2SO_4	2.75	200	45.49	7.25	47.26	12.2 (± 0.11)
	2.75	240	41.73	8.77	49.5	12.71 (± 0.2)
	2.125	220	46.69	8.24	45.07	12.36 (± 0.13)
	1.5	200	51.97	9.15	38.88	13.78 (± 0.02)
	1.5	240	50.69	8.93	40.38	13.74 (± 0.14)
CH_3COOH	2.75	200	45.9	6.23	47.87	12.93 (± 0.02)
	2.75	240	42.46	6.56	50.98	13.49 (± 0.2)
	2.125	220	44.92	5.76	49.32	12.59 (± 0.08)
	1.5	200	42.88	6.18	50.94	10.97 (± 0.1)
	1.5	240	44.13	5.33	50.54	11.51 (± 0.23)

When H_2SO_4 was used for acid leaching, the FC value of the hydrochar was found to increase with decreasing pH. Acid leaching the hydrochar using H_2SO_4 and decreasing the pH from 2.75 to 1.5 increased the FC content of the hydrochar from 7.25% to 9.15%. A similar effect was observed when HCOOH was used for acid leaching: decreasing the pH from 2.75 to 1.5 increased the FC content of the hydrochar from 6.76% to 8.93%. In contrast, when CH_3COOH was used, decreasing pH from 2.75 to 1.5 adversely affected the FC content of hydrochar by decreasing it from 6.23% to 5.33% and decreasing the caloric value from 12.93 MJ/kg to 10.97 MJ/kg.

6.5. Conclusion

The acid leaching of hydrothermally carbonized sewage sludge was studied to understand and compare the effects of independent parameters like carbonization temperature of hydrochar, acid type (H_2SO_4, HCOOH, and CH_3COOH), acid concentration (pH), and acid leaching retention time on the P mobilization, hydrochar properties, acid need, and COD of the leachate. The results of the study indicated that the use of acids with lower pKa values has a significantly greater impact on the solubility and mobility of phosphorus-containing compounds from solids to liquids. TP mobilization from solid to liquid is highly favorable in the presence of H_2SO_4 (~90%) at lower pH (1.5) in comparison with HCOOH (~36%) and CH_3COOH (~2.5%) at similar acid-leaching reaction conditions. It was also observed that a smaller amount of acid (H_2SO_4) with a lower pKa value is enough to achieve and maintain a lower pH in hydrochar slurry when compared to acids with a higher pKa value (CH_3COOH and HCOOH). Regarding the COD of the leachate, the use of organic acid, specifically CH_3COOH, tends to induce additional organic acidic compounds, which simultaneously contributes to an increase in COD. Concerning the energy characteristic of hydrochar, the utilization of CH_3COOH negatively impacted the FC content of hydrochar while concurrently decreasing its caloric value. In contrast, the use of H_2SO_4 and HCOOH had positive effects on the FC content and the caloric value of hydrochar. Future research should evaluate and compare the economic effectiveness of using sulfuric acid to leach sewage sludge hydrochar with sewage sludge ash in order to provide an economic viewpoint of P recovery.

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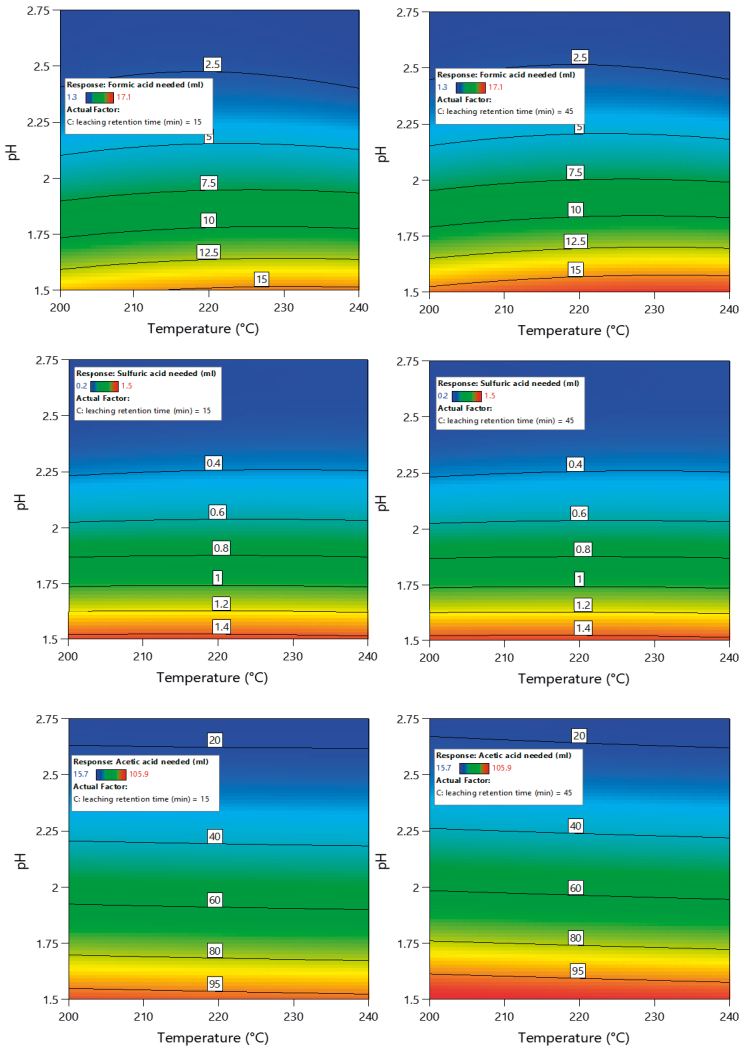
6.7. Supplementary information

S1 Randomized experimental design space suggested by Design Expert program

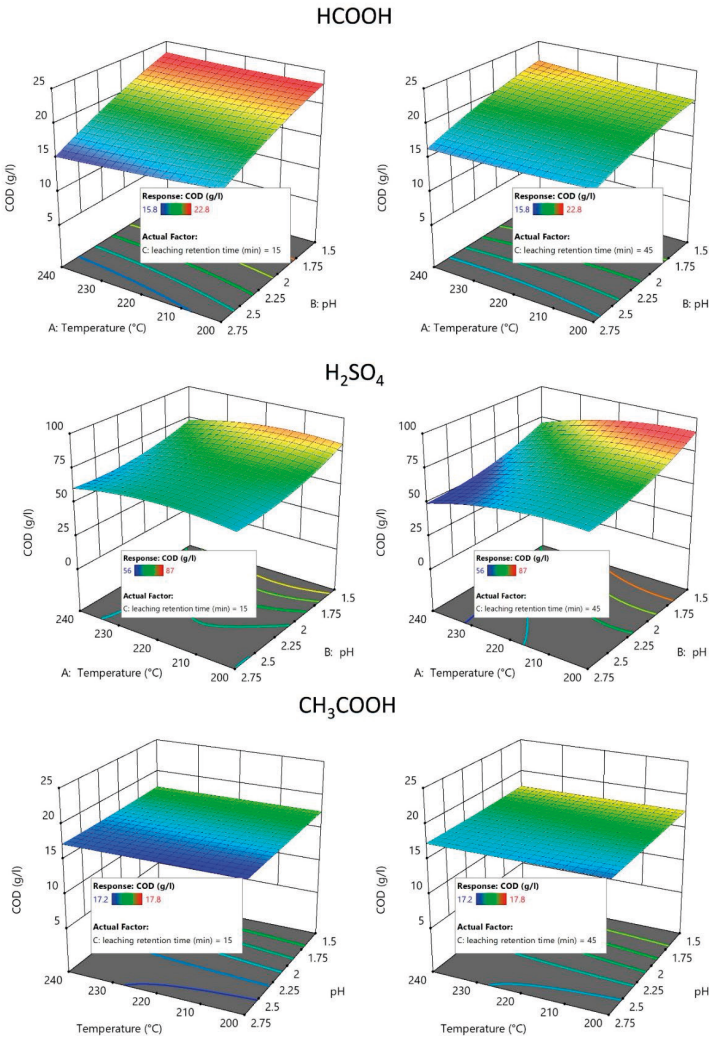
	Factor 1	Factor 2	Factor 3
Run	A: Temperature	B: pH	C: Leaching retention time
	°C		minute
1	240	2.125	45
2	220	1.5	45
3	200	2.125	45
4	220	2.125	30
5	220	2.125	30
6	220	2.75	15
7	240	2.75	30
8	200	2.75	30
9	220	2.75	45
10	220	2.125	30
11	200	2.125	15
12	220	1.5	15
13	240	2.125	15
14	200	1.5	30
15	240	1.5	30

S2 Order specifications of the quadratic and cubic regression models that were obtained in the current study

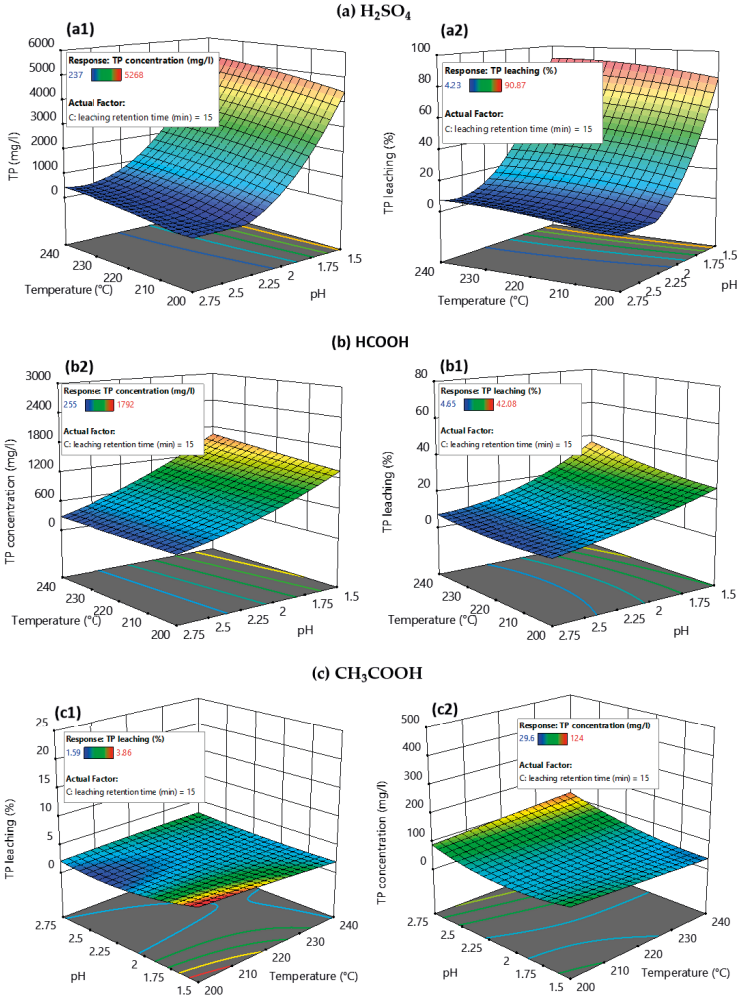
Target value	Coded Regression Model Coefficients														ANOVA		Fit Statistics		
	Intercept	A	B	C	AB	AC	BC	A^2	B^2	C^2	A^2B	A^2C	AB^2	F-value	p-value	lack of fit F-value	R^2_{adj}	R^2_{pred}
HCOOH																			
TP in leachate	825,69	72,25	-659,13	55,13	-78,00	2,50	-53,75	6,29	117,54					232,10	<0.0001	17,12	0,9925	0,9678
Ortho-P in leachate	766,00	66,75	-596,12	42,88	-51,25	10,75	-32,50	-',00	83,25	-13,25				269,69	<0.0001	0,72	0,9942	0,9807
Acid needed	5,61	0,16	-7,09	0,30	-0,35	0,03	-0,33	-0,41	3,14					191,45	<0.0001	18,04	0,9909	0,9615
%TP in leached	16,46	0,26	-15,58	3,14	-2,47	0,03	-2,92	-0,42	4,12		0,78	-2,21	2,49	1398,19	<0.0001	5,49	0,9991	0,9701
COD of leachate	19,80	-0,10	-2,89	-0,31	-0,48	0,28	0,60	0,15	-0,48	-0,13				22,64	0,0016	1,66	0,9329	0,711
HHV of hydrochar	14,07	0,04	-0,86	0,15	-0,07	-0,11	-0,13	-0,15	0,40	0,06				50,31	0,0002	0,46	0,9694	0,914
H_2SO_4																		
TP in leachate	1249,00	125,38	-2336,12	3,50	-63,25	-210,00	-8,00	-103,62	1563,88	-214,88				486,85	<0.0001	0,22	0,9968	0,9936
Ortho-P in leachate	1029,33	147,25	-1578,88	24,38	-73,00	-200,50	-30,25	7,21	964,46	-195,04				352,53	<0.0001	11,80	0,9956	0,976
Acid needed	0,53	0,01	-0,59		0,01			-0,01	0,34	-0,02				42,82	0,0003	3,56	0,9641	0,8229
%TP in leached	22,39	1,11	-42,29	0,14	0,30	-3,69	-0,19	-2,69	28,53	-3,46				515,76	<0.0001	0,17	0,997	0,9946
COD of leachate	7,03	-0,55	-0,83	-0,18	0,13	-0,28	-0,23	-0,50	0,50	-0,10	-0,25	0,25		66,08	0,0027	13,50	0,9808	
HHV of hydrochar	12,36	-0,11	-0,65	-0,10	0,14	0,33	0,10	0,16	0,60	0,37		-0,37	0,23	212,86	0,0005	0,01	0,994	
CH_3COOH																		
TP in leachate	53,48	4,78	28,50	-2,30	16,63	-0,48	4,38	-0,59	25,26				-6,00	146,86	<0.0001	8,65	0,9894	0,9288
Ortho-P in leachate	34,10	-9,05	32,63	-0,23	8,08	-2,15	3,61	-0,79	29,27				13,62	63,33	0,0001	11,90	0,9757	0,8331
Acid needed	45,53	-1,10	-42,76	1,66	0,65	-0,35	-1,63	0,12	13,30	0,45				3491,70	<0.0001	2,42	0,9996	0,9979
%TP in leached	1,93	0,09	-0,17	-0,09	0,69	-0,02	0,20	-0,10	0,83				-0,53	40,75	0,0001	15,92	0,9623	0,7427
COD of leachate	17,38	-0,03	-0,18	0,05	0,03				0,04				0,05	4,10	0,0353	1,15	0,5704	0,32
HHV of hydrochar	12,37	0,19	1,08	-0,06	0,01	-0,01	0,08	0,18	-0,33	0,04				25,38	0,0012	1,12	0,94	0,7621



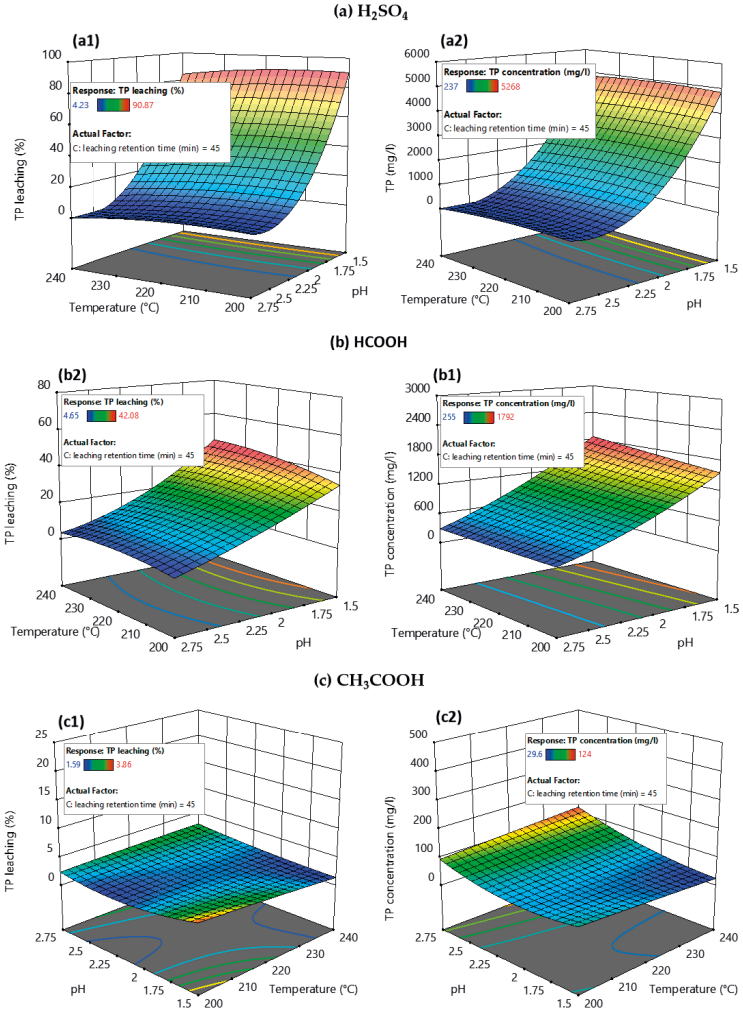
S3 Regression model contour plot depicting the influence of acids on reaching the targeted pH for the retention time of 15 and 45 min



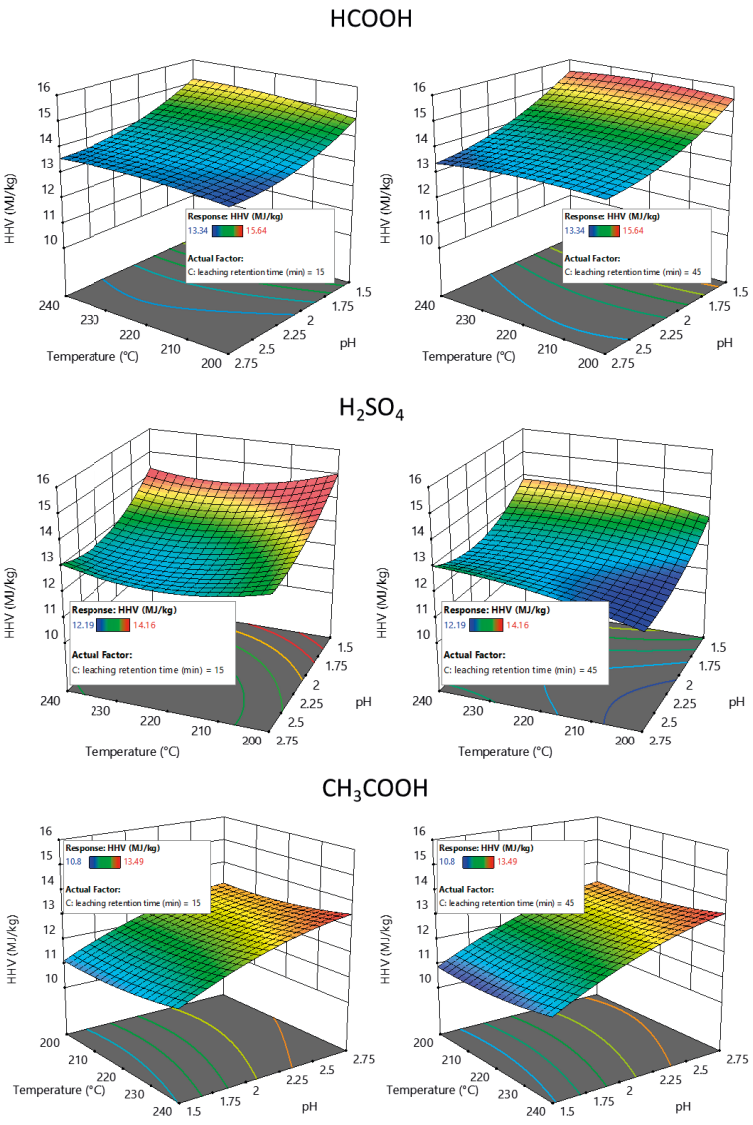
S4 Response surface plot showing COD of the leachate produced after acid leaching using H_2SO_4, HCOOH, and CH_3COOH at 15 and 45 min of retention time



S5 Response surface plot showing the effect of carbonization temperature of hydrochar and acid leaching pH on the transformation of TP from solid to liquid phase at 15 min of acid leaching time



S6 Response surface plot showing the effect of carbonization temperature of hydrochar and acid leaching pH on the transformation of TP from solid to liquid phase at 45 min of acid leaching time



S7 Response surface plot showing the influence of carbonization temperature of hydrochar and acid leaching pH on the calorific value of hydrochar at 15 and 45 min of acid leaching retention time

7. Hydrothermal Carbonization of Sewage sludge – An Effective Approach to Treat and Manage Sewage Sludge in Rural Areas of Germany?

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Exclusive overview of the article and its connection to the research question

The article titled "Hydrothermal Carbonization of Sewage sludge – An Effective Approach to Treat and Manage Sewage Sludge in Rural Areas of Germany?" tries to partially answer the below RQ of this cumulative dissertation:

- **RQ 6**: What is the current status and future of HTC as a technology to treat sewage sludge?

This review article tries to integrate the regulations in Germany concerning sewage sludge management and the current status of hydrothermal carbonization as a technology to treat sewage sludge on an industrial scale.

7.1. Abstract

As the result of new regulation from the German Sewage Sludge Ordinance (AbfKlärV 2017) and the future obligation to recover phosphorus, thermal treatment (mono-incineration) has become increasingly popular, whereas land-based utilization has decreased. Germany has produced 1.71 million metric tons (dry matter) of sewage sludge in the year 2021. Sewage sludge contains important nutrients such as phosphorus but also heavy metals and organic pollutants making the direct utilization of sewage sludge in agriculture controversial. Rural areas in particular have benefited from land-based sewage sludge utilization however the future ban on direct land-based utilization is forcing them to find alternative solutions for sewage sludge treatment and management. Hydrothermal carbonization (HTC) has developed considerably over the last 15 years and offers a viable alternative for the utilization of municipal and industrial organic waste such as sewage sludge. The process takes place in an aqueous environment without the need for pre-drying sewage sludge and thereby facilitating direct processing. HTC is especially suitable in combination with the recovery of nutrients like phosphorus. Technologies to recover this essential resource are important because phosphorus is an element that cannot be substituted and is therefore essential. HTC could make a significant contribution to sewage sludge management in combination with phosphorus recovery. However, the technology has yet to establish itself as a sewage sludge valorization process (2023) and is not yet a recognized state-of-the-art. Nevertheless, the HTC technology could gain greater relevance in the future, especially as an alternative valorization pathway for sewage sludge in rural areas of Germany.

Keywords: Hydrothermal carbonization, nutrient recovery, phosphorus recovery, sewage sludge utilization, rural areas

7.2. Introduction

Sewage sludge is the waste generated from the treatment of wastewater in wastewater treatment plants (WWTP). The sludge is a by-product in addition to the treated wastewater which contains nutrients and has to be utilized (Huezo et al., 2021). Sewage sludge can be divided into primary, secondary and tertiary sludge (Roskosch et al., 2018). Primary sludge is also known as pre-sludge, is produced through sedimentation in primary clarifiers during the mechanical-physical treatment of effluent. Secondary sludge is divided into return sludge and activated sludge. Secondary sludge is separated from treated wastewater in secondary clarifiers. The sludge produced during further wastewater treatment is called tertiary sludge. For instance, phosphate elimination processes used in downstream chemical purification produce this (Roskosch et al., 2018). The term raw sludge refers to non-stabilized or partially stabilized sludge (AbfKlärV, 2017).

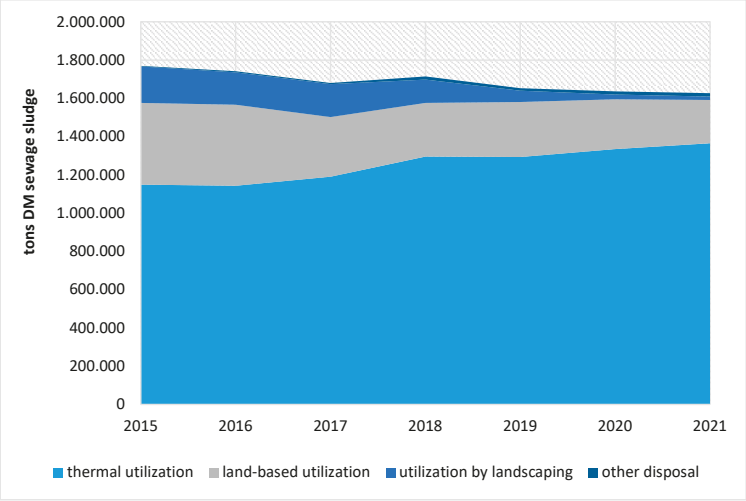

Figure 7-1 Development of the sewage sludge utilization in Germany 2015-2021 (DESTATIS, 2022).

The Federal Statistical Office of Germany indicates that 1,717,803 t DM (dry matter) of sewage sludge was generated in the year 2021 (Destatis, 2023). The current trend of sewage sludge utilization is greatly shifting towards thermal utilization and no longer towards land-based utilization. In addition to nutrients, sewage sludge also contains heavy metals and organic pollutants making its direct application for agriculture purposes difficult (Aragón-Briceño et al., 2021). In Germany, sewage sludge disposal options have become progressively limited as a result of advanced environmental policies and the laws that have been adopted over the last decade. According to the German Sewage Sludge Ordinance (AbfKlärV 2017), sewage treatment facilities larger than 100,000 population equivalent (PE) and 50,000 population equivalents (PE) will no longer be allowed to recycle sewage sludge for land-based utilization starting in 2029 and 2032, respectively. About 79% of the total amount of sewage sludge generated in 2021 (1,364,890 t DM) in Germany was thermally utilized (including mono- and co-incineration among other thermal disposals) and the amount of sewage sludge managed through land-based use and landscaping is gradually declining. (Destatis, 2023). Figure 7-1 shows the trend in sewage sludge utilization in Germany from 2015-202.

The sewage sludge producers are required by the German Sewage Sludge Ordinance to recover phosphorus from the sludge on a mandatory basis. Phosphorus recovery from the ash or carbonaceous residue is done after the mono-incineration of sewage sludge. Alternatively, the co-incineration of sewage sludge can be done only after reducing the phosphorus content to at least 50% or to <20 g P/kg DM. The sewage sludge that resulted could only be used thermally in co-incineration (e.g., cement plant, power plant, waste incineration) after meeting this requirement (AbfKlärV 2017; Mix-Spagl, 2017). All sewage sludge producers are required to voluntarily inform the relevant authority by 31st December 2023 of their future plans for recovering phosphorus. An obligation to recover phosphorus will come into existence in the year 2029 for all WWTP that treat municipal wastewater (Montag et al., 2022). Another considerable regulation in the context of land-based utilization is the German Fertilizer Ordinance (DüMV 2012). Among the other regulations, this ordinance regulates the placing on the market of fertilizers that are not designated as EG-fertilizers (Roskosch et al., 2018). Furthermore, this regulation classifies sewage sludge as an organic or organic-mineral fertilizer and makes a provision to be used as fertilizer if it meets the specified limits (Roskosch et al., 2018). In addition to the limit values in the Sewage Sludge Ordinance (AbfKlärV 2017), those in the Annex to the German Fertilizer Ordinance (DüMV 2012) also apply to the agricultural-based utilization of sewage sludge. As a result, the possibilities for direct land-based utilization are limited especially in the case of heavy metals.

The typical composition of sewage sludge is shown in Table 7-1 below. Table 7-1 also depicts the limit values of the German Fertilizer Ordinance (DüMV 2012) and German Sewage Sludge Ordinance (AbfKlärV 2017) for direct land-based applications. If sewage sludge does not comply with the qualitative requirements of the German Fertilizer Ordinance and German Sewage Sludge Ordinance, it has to be recycled in other ways (Langenohl, 2015).

Stringent regulations from the German Sewage Sludge Ordinance, (AbfKlärV 2017) and the future obligation of phosphorus recovery has made thermal valorization increasingly popular whereas land-based utilization and landscaping have decreased. Rural areas in particular have benefited from land-based sewage sludge utilization.

Table 7-1 Composition of digested and dewatered sewage sludge according to (Basse et al., 2012) and (Roskosch et al., 2018).

Parameter	Unit	Range for sewage sludge	Limit values according to DüMV 2012 or AbfKlärV 2017 (mg/kg DM)
Moisture	Wt.-% (raw)	65 - 75	-
Ash	Wt.-% (wf)	30 - 50	-
LHV	MJ/Kg (raw)	1 - 2 / 10 - 12	-
C	Wt.-% (wf)	33 - 50	-
H	Wt.-% (wf)	3 - 4	-
O	Wt.-% (wf)	10 - 20	-
N	Wt.-% (wf)	2 - 6	-
S	Wt.-% (wf)	0.5 - 1.5	-
Fl	Wt.-% (raw)	aprox. 0.01	-
Cl	Wt.-% (raw)	0.05 - 0.5	-
P	g/kg (raw)	2 - 55	-
Sb	mg/kg (raw)	5 - 30	-
As	mg/kg (raw)	4 - 30	40
Pb	mg/kg (raw)	70 - 300	150
Cd	mg/kg (raw)	1.5 – 4.5	1.5
Cr	mg/kg (raw)	50 - 80	-
Cu	mg/kg (raw)	300 - 350	-
Mn	mg/kg (raw)	600 - 1,500	-
Ni	mg/kg (raw)	30 - 35	80
Se	mg/kg (raw)	1 - 5	-
Tl	mg/kg (raw)	0.2 - 0.5	1
V	mg/kg (raw)	10 - 100	-
Hg	mg/kg (raw)	0.3 - 2.5	1
Zn	mg/kg (raw)	100 - 300	4,000
Sn	mg/kg (raw)	30 - 80	-
AOX	mg/kg DM	200 - 400	400
PCB6	mg/kg DM	0.01 - 0.02	0.1
PCDD/dl-PCB	mg/kg DM	0.000005 – 0.0001	0.00003

As previously stated, land-based application of sewage sludge was the most common method for managing and utilizing sewage sludge in rural areas. Since this recycling method is about to be phased out, there is growing interest in finding alternative ways to recycle sewage sludge and recover phosphorus. In this concern, thermal valorization (mono-incineration) of sewage sludge in combination with phosphorus recovery from ash might be widely accepted. The primary requirement of sludge to be dewatered and dried however makes the incineration process cost-intensive and poses concerns related to the release of toxic air pollutants (NO_x, SO_2, and dioxins) if the incineration process is not managed properly (Shettigondahalli Ekanthalu et al., 2022). Small and medium-sized WWTPs and municipalities will need to find alternative methods of sewage sludge management and treatment in the future if they do not have access to such thermal sludge valorization opportunities.

7.3. Hydrothermal carbonization of sewage sludge

7.3.1. Operating conditions and reaction pathway

Hydrothermal carbonization (HTC) is a promising alternative for the management of sewage sludge and the process used moist waste as a reaction medium to convert biomasses into a lignite-like hydrochar. In contrast, other thermo-chemical conversion processes such as incineration and pyrolysis, are not suitable particularly for moist municipal and industrial organic waste like sewage sludge as it requires pre-drying (Wang et al., 2019B). A major advantage of the HTC technology is the possibility of processing the sewage sludge directly without further drying. As a result, the mechanically dewatered sewage sludge generated at WWTP could be processed directly (Wang et al., 2020). HTC has gained increasing interest from the research community and there are many scientific studies dealing with the hydrothermal treatment of sewage sludge like digested sludge (Huzeo et al., 2021), and raw sludge (Blach and Engelhart, 2020) or primary sludge (Danso-Boateng et al., 2015).

HTC converts sewage sludge into a carbonaceous product (hydrochar) while simultaneously recovering phosphorus from it by utilizing moisture present in sewage sludge as a catalyst, reactant, and solvent (Kruse et al., 2013). The sewage sludge is converted to a carbonaceous product under temperatures (180 °C - 280 °C) and pressures below the saturation vapor pressure in several parallel or serial chemical reaction mechanisms (Reza et al., 2014a). During the process a series of reactions results in numerous dissolved intermediates. Polymers like carbohydrates first break down into simpler components (e.g., di- and monosaccharides) by hydrolysis. The hydrolysis of cellulose produces glucose and fructose. Lignin, on the other hand, is converted to phenol (Kruse et al., 2013). As the HTC process continues, various platform chemicals such as 5-HMF (5-(Hydroxymethyl)-2-furaldehyde), furfural, or levulinic acid are formed. Furthermore, Maillard reactions take place at certain reaction temperatures and reaction times, which contributes to the formation of hydrochar but also leads to high contents of total organic carbon (TOC) and total nitrogen (TN) in the resulting HTC process water (Xu et al., 2022; Djandja et al., 2021). The decisive reaction that leads to the formation of hydrochar is aldol condensation (Shi et al., 2019). The resulting hydrochar from HTC of sewage sludge is essentially hygienic, easy to dewater, free of pharmaceuticals, and expected to exhibit moderate energy density (Crocker et al., 2011; Saetea and Tippayawong, 2013). The yield of hydrochar produced depends on various reaction parameters, of which temperature and reaction time play a decisive role (Huezo et al., 2021; Djandja et al., 2021; Blach and Engelhart, 2020).

7.3.2. Fate and behavior of heavy metals and organic pollutants during HTC

As described in the introduction section, sewage sludge contains heavy metals along with organic pollutants. They are omnipresent in the environment and end up in sewage sludge from households and industries, among others (Roskosch et al., 2018). The sludge absorbs the heavy metals by passive sorption and active uptake through the accumulation of living cells (Geng et al., 2020).

Hydrothermal carbonization of sewage sludge has effects on the distribution of heavy metals. Wang et al., 2019A concluded that the heavy metal distribution depends on the reaction severity and suspected immobilization into the hydrochar. Wang et al, 2020 confirmed the assumption of redistribution of heavy metals in the liquid and solid phases. In particular, the metals Al, Fe, Zn, and Mn are immobilized in the char during the process under neutral conditions. Less than 5% of the heavy metals were detected in the resulting process water. However, acidic conditions result in a weaker enrichment of heavy metals into the solid phase. The immobilization depends mainly on the

reaction temperature and reaction time (Wang et al., 2020). Furthermore, due to the immobilization of the heavy metals, the ecotoxicity is low (Liu et al., 2018; Wang et al., 2020). In addition to heavy metals, the fate of organic contaminants in sewage sludge, such as drug residues, is important. Vom Eyser et al., 2015, studied the removal of twelve pharmaceuticals (including ibuprofen and erythromycin) in sewage sludge during HTC. Seven of the pharmaceutical substances were either or the proportion in the hydrochar was reduced (39% to ≥97%) (vom Eyser et al., 2015). The heavy metals and organic impurities in the hydrochar from sewage sludge turn its suitability as fertilizer into a critical issue. However, vom Eyser et al., 2015 only investigated the fate of the pharmaceuticals in the respective hydrochar and not in the process water (PW). The PW can contain organic pollutants like phenols, aromatic compounds, alkenes, and pyrazines (Usman et al., 2019).

7.3.3. Process water as a by-product

The solid-liquid separation after hydrothermal carbonization of the sewage sludge produces two phases. On one side is the hydrochar and on the other side is the process water (PW). The PW is inorganically and organically polluted and has to be treated. Quicker and Weber, 2016 give ranges of values for COD from 4,900.00 - 78,000.00 mg l-1, for BOD5 1,700.00 - 42,000.00 mg l-1 and TOC 4,000.00 - 31,700.00 mg l-1. If left untreated, it would be a burden on water bodies and thus on the environment (Leng et al., 2021). Particularly, the formation of persistent and toxic organic compounds during HTC that can leach into the PW remains a challenge. These substances are occasionally difficult to degrade biologically and may complicate the PW treatment. The composition of the PW depends primarily on the waste biomass used at the beginning and the reaction parameters (Woriescheck, 2019; Usman et al., 2019). Chen et al., 2019 found that PW from HTC of dewatered sewage sludge contains mainly proteins and short-chain fatty acids, but also poorly degradable compounds such as humic acids, melanoidins, nitrogen heterocycles, and phenols. A major challenge of PW management besides the actual contamination of the PW is the large quantities that would be produced during the industrial, continuous process of an HTC plant. Additionally, the legal requirements for PW treatment can also pose additional challenges. HTC-PW in Germany is categorized as wastewater and has to be treated and disposed of as such (§ 56 German Federal Water Act, WHG). This is done either to a direct discharge quality which allows direct discharge into the environment (§ 57 WHG) or to an indirect discharge quality which allows discharge and subsequent treatment in a municipal WWTP (§ 58 WHG). Respective requirements and limit values must be met for both alternatives.

The minimum requirement values for the discharge of wastewater into a water body or municipal WWTP are described in the German Waste Water Ordinance (AbwV) and the associated annexes. The treatment must be carried out according to the state of the art. For process waters from hydrothermal treatment, the requirements of Annex 27 "Treatment of waste by chemical and physical processes (CP plants) and waste oil regeneration" apply (AbwV 1997).

There is currently no continuous industrial implementation of HTC technology that includes process water management and treatment. One opportunity to manage the large quantities of PW is to reuse it as a partial flow in the HTC process and therefore save fresh water (if needed) and reduce the costs associated with it (Kambo et al., 2018). This step should be chosen to reduce costs and to benefit from the positive effects of recirculation. The aforementioned inorganic and organic load necessitate the use of PW treatment technologies. Biological processes such as anaerobic digestion proved to be feasible from various publications. Anaerobic degradation enables a reduction of chemical oxygen demand (COD) by up to 75% (Wirth et al., 2015). Another utilization pathway for PW is to recover nutrients from it. Malhotra and Garg, 2020 performed recovery of humic acids from PW

using ammonium sulfate and were able to recover ~70% of humic acids. Subsequent growth trials showed positive effects (Malhotra and Garg, 2020). However, subsequent treatment of PW is necessary. Various providers of HTC solutions have their treatment technologies, like nanofiltration and reverse osmosis (Kläusli, 2014; Fettig et al., 2018) or aerobic treatment in a constructed wetland (Fettig et al., 2018). However, no data was available on the efficiency of these technologies and continuous large-scale operation is lacking. For a commercial realization of HTC technology, efficient and cost-effective processes for process water treatment are required.

7.3.4. Industrial readiness and industrial application

In addition to the mature technology, sufficient quantities of sewage sludge are required for the successful implementation of HTC technology for sewage sludge management and valorization in rural areas. The HTC technology must also be competitive with other thermal processes like incineration or pyrolysis to make its implementation successful. Reißmann et al., 2020 created a base model for HTC as a sewage sludge utilization method in Germany for 2030 assuming the currently best available techniques (BAT). In this model, 65,000 t FM sewage sludge per year is utilized (14,300 tons of dry matter per year with 22% DM). Due to the continuous industrial operation and the knowledge gained from it, learning effects can be observed in operational management. Nutrient recycling (e.g., phosphorus) is integrated in addition to the basic model. The authors concluded that production costs, phosphorus recovery, and process water treatment have a significant impact on the competitiveness of HTC compared to conventional processes such as incineration. According to this study, competitive production costs for the final HTC product must be less than € 325 per ton of hydrochar produced. Reißmann et al., 2020 point out that only the delivery of the product up to mono-incineration and not beyond was taken into account in this cost calculation. The HTC technology however has not yet (2023) been able to establish itself as a valorization process for the treated sewage sludge in Germany and especially for rural areas. The technology was temporarily tested on a sewage treatment plant in Düsseldorf but was discontinued after a test phase (Schnell et al., 2020). There are several methods for industrializing the technology at the moment, including multi-batch processes (quasi-continuous) and processes in tubular reactors (Blöhse, 2017; Quicker and Weber, 2016). There are some providers of commercial HTC solutions which includes TerraNova Energy, HTCycle, and SunCoal Industries (Aragón-Briceño et al., 2021).

7.4. HTC and nutrient recovery

7.4.1. Need for phosphorus recovery and recovery technics

Phosphorus is a critical resource and a non-renewable essential element for all living organisms on the earth. The European Commission designated phosphorus as a "critical raw material" in 2014. (Wang et al., 2020; Aragón-Briceño et al., 2021). According to Krüger and Adam, 2015, more than 550,000 t/a of phosphorus was applied to German farmlands in 2015. The global phosphorus reserves are limited and the over-exploitation of natural reserves of phosphorus is anticipated to create severe problems in the next 50-100 years. Current phosphorus reserves are located in the US, Morocco, Jordan, China, and South Africa, assuming that Germany and Europe are entirely dependent on imports. The remaining phosphate reserves are however contaminated with heavy metals such as cadmium or uranium (Krüger and Adam, 2015). Various studies have assumed that the available phosphorus reserves will soon be exhausted (Pérez et al, 2021). Increasing population growth leads to higher consumption of energy and resources and to meet the phosphorus demand of the raising population, there is an immediate need for intelligent phosphorus recovery technologies

and alternative sources of phosphorus. The integrated concerns such as; non-renewable nature, significance on global food security, and serious cost volatility, the future of phosphorus availability is drawing greater attention and poses an urgent need to find an alternative phosphorus source (Heckenmüller et al., 2014). As waste biomasses such as sewage sludge contain high phosphorus concentrations, several phosphorus recovery technologies are now available (Aragón-Briceño et al., 2021). The easiest way is land-based recycling with phosphorus being returned to the natural cycle. Rural areas in particular have benefited from land-based sewage sludge utilization. However, sewage sludge contains heavy metals and organic pollutants which makes the direct-recycling route more difficult (Aragón-Briceño et al., 2021). In this concern, the direct utilization of sewage sludge on agricultural land is prohibited. Several recovery technologies are based on the recovery of phosphorus from the sewage sludge ash, requiring incineration of the sewage sludge to produce phosphorus-rich ash (Kwapinski et al, 2021; Krüger and Adam, 2015). Hydrothermal carbonization in combination with subsequent phosphorus recovery would be an attractive option for rural regions without sewage sludge incineration (Kwapinski et al, 2021; Pérez et al, 2021).

7.4.2. Influence of acid utilization during HTC sewage sludge

7.4.2.1. Effects of Post- and Pre-Acid Treatment During HTC

HTC significantly reduces sewage sludge's acid buffering capacity due to the chemical reactions and thermochemical breakdown that occurs during the process. Carrying out acid leaching after HTC of sewage sludge, the majority of the H^+ in added acids will be utilized to induce the dissolution of Al-P and Fe-P and transformation of higher phosphorus from solid to liquid phase (Shettigondahalli Ekanthalu et al., 2022). In contrast, when the acids are used during or before the HTC process, a significantly lower concentration of phosphorus will be transformed from the solid to the liquid phase. When acids are used before or during HTC, the majority of H^+ ions added in the form of acids are used to overcome buffering resistance provided by carbonates, cation exchange reactions, and organic matter. Due to the buffering agents present in the system, the available H^+ is greatly depleted before it can react with metal ions that hold phosphorus.

The presence of phosphate-precipitating metals such as Fe, Al, and Ca in sewage sludge plays a more significant role in determining the degree of conversion of phosphorus from solid to liquid (Huang et al., 2018; Ekpo et al., 2016). The presence of multivalent metal ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} during the HTC of sewage sludge contributes to the formation of phosphate with low solubility, which then facilitates the accumulation of phosphorus onto hydrochar. Similarly, the acid buffering resistance of the sewage sludge also regulates the phosphorus transformation from the solid to liquid phase upon the addition of acids. Sewage sludge suspension in general consists of a liquid and a solid phase. The solid and liquid phase of the sewage sludge contains several compounds with a high tendency to inhibit acidification (Shettigondahalli Ekanthalu et al., 2022). The acid-inhibiting substance present in sewage sludge suspension tends to have different neutralizing points. Upon adding acids to sewage sludge suspension, H^+ would initially react with carbonates existing in the sewage sludge with relatively higher neutral points in the suspension. The additional H^+ will undergo a cation exchange after the carbonate in sewage sludge is exhausted. Later the presence of additional H^+ would be consumed in offsetting the buffering resistance provided by organic matter present in sewage sludge. In the end, the presence of any further H^+ would be utilized in the dissolution of aluminum phosphates (Al-P) and ferric phosphates (Fe-P) (Zhang et al., 2010; Bozkurt et al., 2000; Petzet et al., 2012). The HTC process however contributes considerably to reducing the acid buffering capacity of sewage sludge. By acid leaching the sewage sludge after HTC, there will

be maximum utilization of added acids to induce the dissolution of Al-P and Fe-P and significantly increase the phosphorus-leaching from the solid to the liquid phase.

7.4.2.2. Recovery of Phosphorus from HTC-treated sewage sludge hydrochar

The utilization of H_2SO_4 and HCl at higher concentrations increases the mobilization of phosphorus (80-100%) from the solid to the liquid phase in hydrochar derived from sewage sludge (Pérez et al., 2021). Phosphorus leaching and the subsequent mobilization of heavy metals from hydrochars were investigated by Pérez et al., 2022, using oxalate and citrate across a pH range of 0 to 4. Oxalate resulted in nearly full P release from hydrochars at pH 1, whereas both oxalate and citric acids achieved P extraction efficiencies that were better than 75% even at the lowest pH. Acid leaching of the sewage sludge hydrochar results in a high phosphorus and multivalent cation recovery. Nevertheless, heavy metal concentrations must be monitored throughout the process since they affect the product's potential use as fertilizer. According to Gerner et al., hydrochar has an affinity towards heavy metals and will retain a significant portion of them, releasing very little into the liquid phase. The presence of a higher concentration of heavy metal in hydrochar makes the land-based application restricted under the German Fertilizer Ordinance. The most practical use option is then the energy recovery from hydrochar. HTC process also transfers around 50% of nitrogen from the solid to liquid phases, increasing hydrochar combustion performance in terms of NO_x emissions reduction (Gerner et al., 2021).

Calcium phosphate salt is a desirable product for recovering phosphorus from leachate. Calcium phosphate is similar to phosphate rock, the primary basic material for the fertilizer industry. The phosphorus product extracted from the effluent can be incorporated directly into the process as a by-product. The filtrate after leaching is believed to have a high ionic strength, which influences ion-association and solubility. Due to the decreased concentration of free ions caused by ion association, supersaturation may be required for the formation of solid deposits (Ehrnström, 2016). In order to recover all dissolved phosphorus, excess calcium ions must be introduced to the leachate. Increasing the pH could have a comparable effect.

7.5. Conclusion

The use of agriculture and landscaping as traditional treatment methods will soon be phased out in Germany due to new regulations on the management of sewage sludge (2029). Rural areas where sewage sludge is usually disposed of by agriculture and landscaping will be particularly challenged by the forthcoming situation. Hydrothermal carbonization (HTC) is receiving increased attention as an eco-friendly and promising technology for treating and managing sewage sludge without the need for drying. It is possible to effectively manage sewage sludge by using HTC technology not only by recovering phosphate but also by complying with German Sewage Sludge Ordinance requirements. HTC offers major potential for the valorization of sewage sludge and could be an interesting alternative for sewage sludge treatment and nutrient recovery in rural areas of Germany. Especially for nutrient recovery, HTC could be an opportunity to close loops. However, sufficient quantities of sewage sludge are needed to enable continuous operation. The HTC plant with subsequent process water treatment and nutrient recovery facilities should be built on the site of a WWTP to enable indirect discharge of pre-treated PW. The HTC process water is another challenge, as significant amounts are produced during continuous operation. The PW is organically contaminated and has to be treated before discharge into the environment. A functional and eco-economic concept for PW-management is necessary for a commercial implementation of HTC technology. Future research

should focus on methods to minimize the amount of heavy metal in hydrochar and its use as fertilizer in accordance with the legal requirements of the German Fertilizer Ordinance and other relevant regulations. The technology has not yet (2023) been able to establish itself in an industrial continuously operated HTC plant for sewage sludge utilization in Germany. The technology readiness to manage and handle processwater produced from HTC of sewage sludge is the major concern. A practical, dependable, and affordable processwater disposal method is essential for the successful commercialization of HTC technology. Given the current rate of scientific development in the area, this is probably anticipated to happen in the near future.

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8. Summary and extended results and discussion

The results that were collected throughout this dissertation are summarized and discussed in this chapter. The source articles contain more in-depth descriptions of the findings. This chapter also includes a discussion on process water treatment, further unpublished experimental results, economic analysis, and P precipitation from leachate. This particular chapter together with summarizing the main results also tries to answer the below RQ of this cumulative dissertation

- **RQ 5**: Is it economically viable to leach P from sewage sludge hydrochar relative to the conventional sewage sludge derivatives such as incinerated sewage sludge ash and pyrolysis sewage sludge ash?
- **RQ 6**: What is the current status and future of HTC as a technology to treat sewage sludge?

The economic feasibility analysis of the sulfuric acid demand to leach P from sewage sludge hydrochar has been calculated and compared with other sewage sludge derivatives such as incinerated sewage sludge ash, pyrolysis sewage sludge ash, and pyrolysis sewage sludge char. This chapter also provides a summary of the current knowledge and future stand of HTC as a technology to manage sewage sludge and recover value-added products from it.

8.1. Pre and post-acid utilization and the transformation of P

Within the boundaries of this research, the influence of acid base utilization during and after HTC of sewage sludge on P leaching, metal ion transformation, and the characteristics of hydrochar were analyzed. The ultimate analysis and heavy metal analysis of hydrochar samples were however not carried out in the initial articles due to a lack of access to the specific apparatus and funding. The extended results of this chapter fill that gap and provide the results and detailed discussion on the characteristics of hydrochar. The following section of this chapter, together with summarizing the results from the published manuscript that are presented in chapter 4, chapter 5, chapter 6, and chapter 7, it also provides additional data on the experimental findings of hydrochars and their discussion.

8.1.1. Acid utilization before and after hydrothermal carbonization of sewage sludge[1]

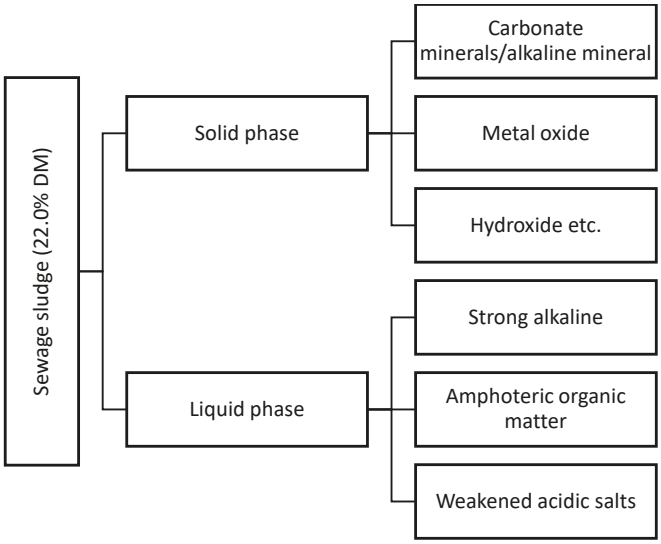

Figure 8-1 Solid and liquid components of sewage sludge that provide resistance to acidification

Sewage sludge suspension in general consists of a liquid and a solid phase with higher buffering resistance (see Figure 8-1). The liquid phase of sewage sludge in particular contains amphoteric organic matter with an ability to act as both acid and base, and strong acidic and alkaline salts. This diverse combination is sewage sludge has a higher tendency to inhibit acidification during the acid treatment. On the other hand, the solid phase of sewage sludge also contains alkaline minerals, hydroxide, metal oxides, carbonate minerals, etc., with the potential to inhibit acidification during the acid treatment. In addition, the composition of sewage sludge greatly comprises of organic matter such as volatile fatty acids, protein, and volatile fatty acids with the potential to inhibit acidification during acid treatment (Zhang et al., 2010).

The diverse components present in sewage sludge (both of solid and liquid origin) with a greater potential to inhibit acidification have a different neutralizing point when treated with acids. When sewage sludge suspension is treated with acids, initially the H^+ ions present in the treatment medium will be consumed by the carbonates present in the sewage sludge suspension which has a relatively high neutralizing tendency (see equation (5.2)). After neutralizing the carbonates present in the sewage sludge suspension, additional H^+ ions present in the acid treatment medium will undergo a reaction that leads to cation exchange (see equation(5.3)). The further H^+ ions present in the reaction medium will be consumed sequentially by the organic matter such as volatile fatty acids and protein that are present in the sewage sludge suspension. The ultimate H^+ ions that still exist in the treatment

[1] This section contains experimental findings and discussion from the published articles titled "Influence of Acids and Alkali as Additives on Hydrothermally Treating Sewage Sludge: Effect on Phosphorus Recovery, Yield, and Energy Value of Hydrochar" and "Influence of Post- and Pre-Acid Treatment during Hydrothermal Carbonization of Sewage Sludge on P-Transformation and the Characteristics of Hydrochar" which are part of this cumulative dissertation and has been included under Chapter 4 and Chapter 5.

medium will then react and induce the successive dissolution of aluminum phosphates and ferric phosphate (see equation (5.4) - (5.6)).

The thermochemical breakdown and the reaction pathway of the HTC process significantly influence and alter the chemical and morphological structure of sewage sludge after HTC. As explained earlier, sewage sludge has a diverse chemical composition with the presence of varying portions of lipids, proteins, polysaccharides, and lignin. The primary reaction during the hydrothermal treatment of sewage sludge involves the hydrolysis of lipids, proteins, polysaccharides, and lignin. Hydrolysis of these compounds is deemed as a primary reaction because of their low activation energy. Dehydration, decarboxylation, condensation, and aromatization are the sequential reactions after hydrolysis (see Figure 2-4). As the reaction continues, carbonaceous compounds get hydrolyzed into free fatty acids, primarily acetic acid and propionic acid derived from unsaturated lipids (Blach and Engelhart 2021; Wilson and Novak 2009). Aldehydes, ketones, and monosaccharides are degraded as the reaction progresses, forming organic acids like formic acid, lactic acid, and acetic acid (Asghari and Yoshida 2007).

The tendency of sewage sludge to inhibit acidification reduces drastically after hydrothermal treatment as a result of reaction severity, thermochemical breakdown pathways, and the complex chemical reactions that occur during the process. With the acid utilization after hydrothermal treatment of sewage sludge, the majority of H^+ ions in added H_2SO_4 are used in inducing the dissolution of Al-P and Fe-P. This eventually results in increased P leaching from sewage sludge into leachate. With the acid utilization before hydrothermal treatment of sewage sludge, the majority of H^+ ions in the added H_2SO_4 will be used to offset buffering resistance provided by carbonates, cation exchange reactions, and organic matter. This eventually depletes H^+ before it can react with P-holding metals and eventually leads to low P leaching from sewage sludge to leachate.

8.1.2. Acid leaching of sewage sludge hydrochar[2]

The maximum P leaching from sewage sludge hydrochar to leachate was obtained at pH 1.5 of the leaching medium and by using H_2SO_4 as acid to reach the targeted pH. Figure 8-2 shows a detailed RSM model overview of acid leaching process conditions that include the hydrochar produced temperature, pH of the leaching medium, and leaching retention time that influenced the highest P transformation from solid to liquid. Figure 8-2 also provides the results for the influence of the above-mentioned process conditions on the heating value of hydrochar after acid leaching and COD of the leachate. According to the experimental analysis conducted in Shettigondahalli Ekanthalu et al., (2023), the maximum TP leaching from sewage sludge hydrochar to leachate was achieved following the use of sulfuric acid at pH 1.5 (90 ± 1.5%). At similar reaction conditions, formic acid and acetic acid leached about 36% (± 6%) and 2.5% (± 1%) of P from sewage sludge hydrochar to leachate, respectively. The results obtained from this study suggested that, in comparison to inorganic acid, organic acids have a substantially small impact on leaching P from sewage sludge hydrochar to leachate. The type of acids used significantly contributed to the TP leaching in addition to the acid leaching pH. The reaction temperature at which the hydrothermal reaction was carried out also had a minor effect on the P leaching, with the higher reaction temperature range being slightly more effective.

[2] This section contains experimental findings and discussion from the published article titled “Acid leaching of hydrothermally carbonized sewage sludge: phosphorus recovery and hydrochar characteristics” which is part of this cumulative dissertation and has been included under Chapter 6.

During hydrothermal treatment of sewage sludge, the existence of a higher amount of metal ions such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Mg^{2+} in sewage sludge greatly influences the formation of phosphate compounds with low solubility. This will provide optimum conditions for phosphate present in sewage sludge suspension to be retained in subsequently produced hydrochar after HTC (Huang et al., 2018). During the sewage sludge hydrochar acid leaching process, the solubility of the above-mentioned multivalent metal ions will substantially influence the leaching of P from sewage sludge hydrochar to leachate. The strength of the acid, pH during the leaching process, and the potential of the acids to mobilize the phosphorus-holding compounds play a crucial role in influencing the P leaching from sewage sludge hydrochar to leachate.

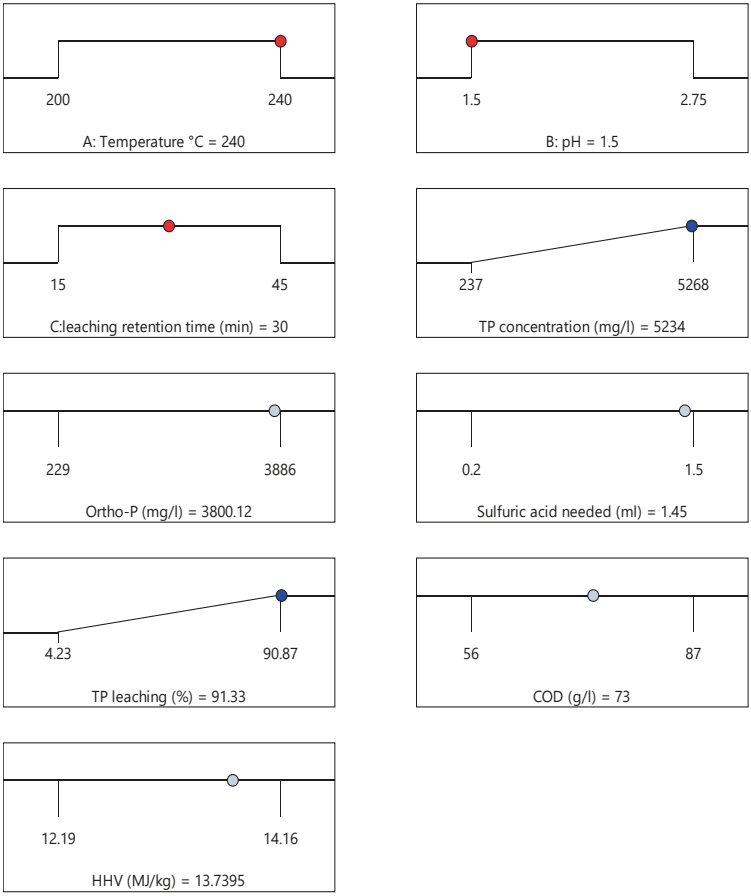

Figure 8-2 Overview of acid leaching process conditions that resulted in highest P transformation from sewage sludge hydrochar to lechate.

The finding of Shettigondahalli Ekanthalu et al. (2023) depicts that the use of acid with a lower pKa value provides a condition for a considerably greater dissolution rate of aluminum and ferric ions

and their P derivatives. The negative log of the Ka value, in other words also known as the acid dissociation constant and called as pKa value (Helmenstine 2020). Sulfuric acid being an inorganic acid has a pKa value of -3.0, and formic acid and acetic acid being an organic acid has a pKa value of 3.75 and 4.70, respectively (Stumm and Morgan 1981). The use of sulfuric acid with a lower pKa value has a substantially higher dissolution rate of aluminum and ferric ions and their P derivatives in comparison with organic acids with higher pKa values. The use of acetic acid during the leaching process has specifically resulted in poor dewaterability of sewage sludge hydrochar. This tendency of sewage sludge hydrochar slurry to retain a higher moisture content during the acid leaching process could have additionally hindered the leaching of phosphorus-containing compounds from sewage sludge hydrochar to leachate.

The experimental analysis revealed that a fractional amount of sulfuric acid is enough to maintain a lower pH when compared to acetic acid and formic acid. Formic acid need was also lower in comparison to acetic acid, this phenomenon can be explained by the strength of the acid. Sulfuric acid is the strongest acid with a pKa value of -3.0. This indicates the presence of highly acidic compounds that can donate protons to water. Formic acid is a weaker carboxylic acid and has a pKa value of 3.75 making it relatively stronger than acetic acid, which has a higher pKa value of 4.7. Therefore, sulfuric acid with a lower pKa value requires only a fractional quantity of acids to achieve and maintain a lower pH in acid leaching medium.

8.1.3. Influence of various acid utilization stages on the ultimate analysis characteristic of hydrochar

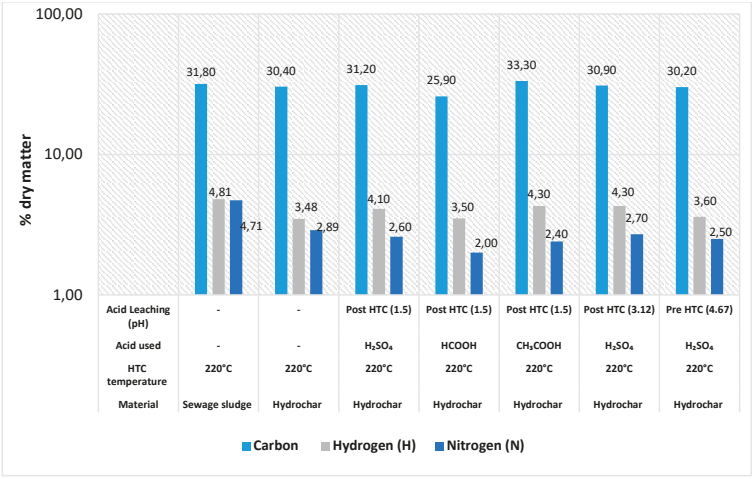

Figure 8-3 H%, C%, and N% in sewage sludge and consequently produced hydrochar at various conditions.

Figure 8-3 compares the hydrochar findings for H%, C%, and N% with the initial sewage sludge. All three parameters were calculated using DIN EN 15407: 2011-05 standard method in an external lab. The results demonstrate that the effects of HTC and acid leaching on the C and H content of the resulting hydrochar were less significant in comparison with N. N% has decreased by approximately 38.64% following HTC of sewage sludge, and further acid leaching under varied

reaction conditions has reduced N% by about 51 (±6.5) %. This considerable drop in N% will significantly assist the energy-related usage of hydrochar by lowering NO_x emissions.

The main constituent of sewage sludge is organic matter such as carbohydrates and proteins which make energy recovery from sewage sludge feasible. In terms of toxicity reduction, volume reduction, and heavy metal management, direct sewage sludge valorization via incineration could be advantageous. Direct combustion could also be cost-intensive and possible gaseous pollutant emissions could be triggered by the unstable burning resulting from the presence of high moisture content in sewage sludge. Another potential issue with direct sewage sludge incineration is its high nitrogen content. The nitrogen in sewage sludge would eventually be converted into NO_x associated with direct combustion in the thermal utilization process of sewage sludge (Yang et al., 2022). Nitrogen oxides (NO_x) are the primary contributors to air pollution, both at the point of origin and in down-winding regions. NO_x refers to various nitrogen and oxygen compounds, including NO, NO_2, N_2O, N_2O_3, N_2O_4, and N_2O_5. NO_x, which are hazardous pollutants with negative impacts on the environment and are responsible for acid rain, tropospheric ozone interference, and secondary aerosol formation (Shah et al., 2018). The N content in biomass, the N species, and the formation mechanism during biomass combustion are the primary deciding factors for the formation of NO_x. Modifying the N functionalities prior to combustion can have a substantial effect on the transformation of N to NO_x (Rocha et al., 2020). The formation of NO_x during the combustion of sewage sludge can be reduced by reducing the N content of the sewage sludge. It is possible to turn moist sewage sludge into hydrochar with lower the nitrogen content using HTC. The emission of NO_x during the combustion of hydrochar can be further decreased by reducing the hydrochar N content.

The increase in temperature during the HTC process aids the solid-N transfer into the liquid phase. The inorganic species of N however undergo hydrolysis, mainly forming NO_3—N and NH_4^+-N. The organic N (generally proteins and pyridine-N compounds) also undergoes a transformation into inorganic N (NH_4^+-N) via hydrolysis and deamination reactions (Xiao et al., 2019, Wang et al., 2018B). Even though the majority of the N will dissolve as part of the HTC process, some N will still be present in the solid fraction as a result of chemical reactions, precipitation, and crystallization. Hydrochar has been found to contain a variety of compounds, including proteins, pyrrole-N, pyridine-N, and quaternary-N (Aragón-Briceño et al., 2021). A decrease in the pH during the acid leaching process has also led to the decrease of N content in the consequently produced hydrochar. As the reaction temperature in the HTC process rises, it has also been discovered that the presence of sugars encourages the incorporation of N into heterocycles, producing more stable N species (quaternary-N and pyridine-N) (Wang et al., 2018B). These stable N-species can then be fixed inside the hydrochar as a result. The decrease in N content following HTC has increased the potential for producing clean solid fuel from sewage sludge and also provided a successful method for limiting N during sustainable sludge management.

8.1.4. Influence of acid leaching hydrochar on the transformation of heavy metals

The levels of sulfur and heavy metals found in sewage sludge and hydrochar are compared in Table 8-1. The percentage of sulfur and heavy metals that were retained on the hydrochars following HTC and acid leaching is also displayed in Table 8-1. All parameters were experimentally examined in an external lab using the DIN EN ISO 11885: 2009-09 standard method. The results show that all heavy metals except Arsenic (<8.65% retained in hydrochar) had a larger affinity for hydrochar and retained in it even after acid leaching at pH 1.5 using H_2SO_4, and CH_3COOH. Acid leaching the

hydrochar with HCOOH at pH 1.5 however retained Arsenic in larger amounts (66.93%) in hydrochar, along with the other heavy elements tested.

Table 8-1 Sewage sludge sulfur and heavy metals compared to hydrochar produced at 220 °C and acid leached at pH 1.5 using organic and inorganic acids.

Material (Acid used)	**Sewage Sludge (-)**	**Hydrochar (H_2SO_4)**		**Hydrochar (HCOOH)**		**Hydrochar (CH_3COOH)**	
Parameter/ Unit	mg/kg DM	mg/kg DM	% Retained in hydrochar*	mg/kg DM	% Retained in hydrochar*	mg/kg DM	% Retained in hydrochar*
Sulfur	1.66	7.13	220.77%	1.59	46.55%	1.71	49.65%
Arsenic	5.94	<1.00	<8.65%	8.18	66.93%	<1.00	<8.11%
lead	13.90	26.00	96.14%	24.70	86.36%	29.10	100.91%
Cadmium	0.60	0.69	59.11%	0.93	75.33%	0.89	71.50%
Chromium	38.60	45.40	60.45%	68.60	86.37%	68.20	85.16%
Copper	575.00	968.00	86.53%	981.00	82.92%	1060.00	88.86%
Nickel	16.50	26.40	82.24%	24.50	72.16%	27.50	80.33%
Mercury	0.55	0.91	85.95%	1.00	88.92%	0.56	49.79%
Zinc	786.00	821.00	53.69%	1120.00	69.25%	874.00	53.60%

*% retained in hydrochar is calculated with reference to hydrochar yield after HTC and acid leaching

The use of H_2SO_4 in acid leaching the hydrochar has greatly enhanced the P and N transition from solid to liquid phase but has resulted in larger levels of sulfur and heavy metals in the resulting hydrochar. The existence of decreased N content in hydrochar improves combustion by reducing NOx, but its application is severely limited to energy consumption in industrial recycling operations with proper fume cleaning systems due to its high sulfur and heavy metal content.

8.2. Economic feasibility of the chemical need to leach P from sewage sludge HTC char

The use of sulfuric acid methods for the leaching of P from sewage sludge products has attracted a lot of attention due to their high P extraction efficiency, ease of operation, and low cost. In the vast majority of instances, this procedure can result in the simultaneous leaching of heavy metals from ISSA, which in turn complicates the application of recovered phosphorus as fertilizer (Le et al., 2020). In contrast, using a similar method to recover P from sewage sludge hydrochar could adsorb a significant portion of heavy metals onto the hydrochar itself, leaving the P-rich leachate with a lower concentration of heavy metals. Figure 8-4 compares the of P material flow during the treatment of sewage sludge using pyrolysis, HTC, and incineration, followed by acid leaching with sulfuric acid. Figure 8-5 provide a summary of the acid demand per kilogram of phosphorus removal and the cost associated with leaching one metric ton of P recovery from incinerated sewage sludge ash (ISSA), pyrolysis sewage sludge char (PSSC), pyrolysis sewage sludge char ash (PSSCA), and HTC-Char methods based on experimental and literature data. Additionally, Table 8-2 provides an overview of sewage sludge treatment pathways and the P recovery efficiency of the procedures illustrated in Figure 8-5. The economic efficiency of sulfuric acid leaching methods was assessed

by comparing the amount of sulfuric acid required to leach one kilogram of phosphorus from various sewage sludge products to the cost of sulfuric acid required to leach one metric ton of phosphorus. The cost of sulfuric acid is the sole direct cost that was taken into account in this evaluation. The market price of sulfuric acid was considered to be 157 USD per metric ton, which is equivalent to 144.44 euros per metric ton as of March 2023 (Chemanalyst 2023).

The P concentration in the ISSA, PSSC, PSSCA and HTC- sewage sludge hydrochar was 3.99-8.60%, 5.60%, 4.70-8.10%, and 3.2-5.60% respectively (see Table 8-2). The initial percentage of P in the sewage sludge greatly depends on several factors including the influent wastewater, the sewage sludge treatment process, and subsequent sludge treatment operations such as the choice of any inorganic flocculants and sludge dewatering aids (Le et al., 2020, Sichler et al., 2022). Additionally, different sewage sludge treatment techniques such as incineration, pyrolysis, or HTC cause a different degree of burnout in sewage sludge and vary the characteristic of the consequently produced product and its P content.

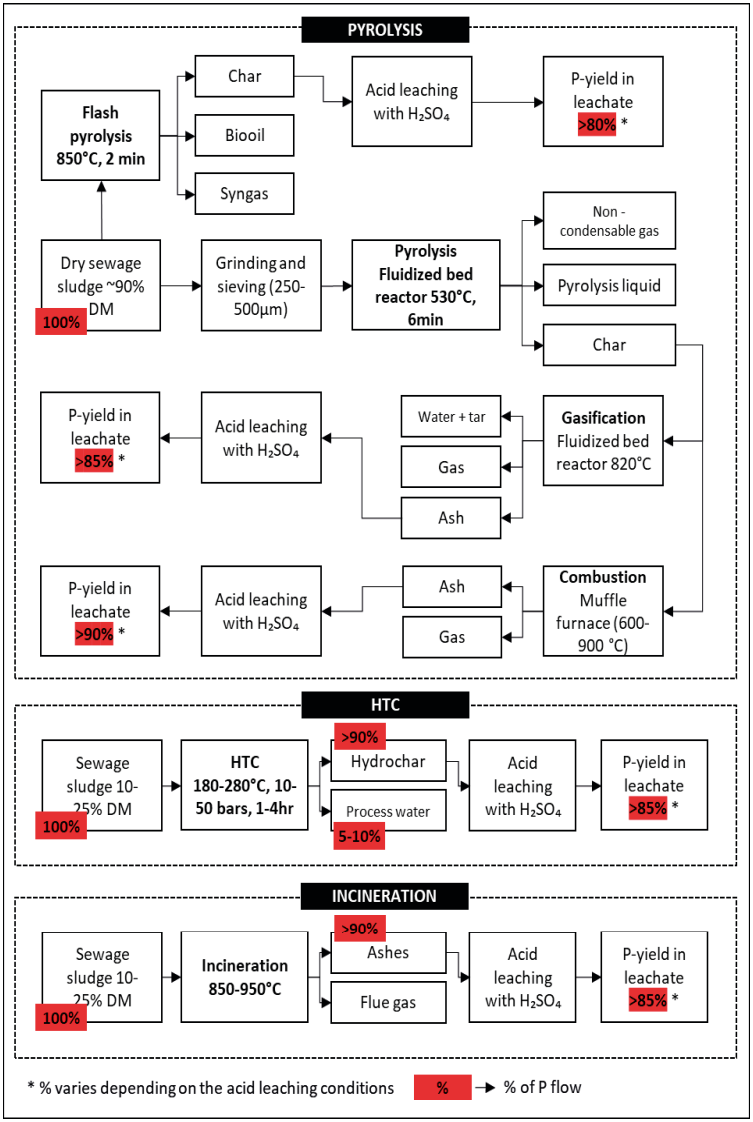

Figure 8-4 Phosphorus material flow during the treatment of sewage sludge with pyrolysis, HTC, and incineration, followed by acid leaching with sulfuric acid.

Table 8-2 Overview of sewage sludge treatment pathways and the P leaching efficiency with H_2SO_4 utilization

Reference	Type of sewage sludge	Treatment technology	P% before acid leaching	P leaching efficiency using sulfuric acid
(Luyckx, Geerts and Caneghem 2020)	SSA	Fluidized bed furnace (840-850 °C)	7.80%	93%
(Fang, Li and Guo et al., 2018)		Fluidized bed furnace (>850 °C)	3.99%	94%
(Liang et al., 2019)		Muffle furnace (900 °C)	5.76%	82%
(Wang et al., 2018)		Fluidized bed furnace (850 °C)	4.07%	88%
(Cohen 2009)		Incineration (900 °C)	6.80%	89%
(Kleemann et al., 2016)		Incineration (850-950 °C)	7.50%	90±1%
(Kleemann et al., 2016)		Incineration (850-950 °C)	7.16%	93 ±2%
(Boniardi et al., 2021)		laboratory standard muffle (900 °C)	7.60%	90%
(Boniardi et al., 2021)		Fluidized bed furnace (850-950 °C)	8.60%	92%
(Kleemann et al., 2016)	PSSC	Flash-pyrolysis (850 °C)	5.60%	89% ±9%
(Atienza–Martínez et al., 2014)	Combustion ash produced from PSSC	pyrolysis of SS at 530 °C followed by combustion in muffle furnace at 900 °C	4.70%	90% ±5%
(Atienza–Martínez et al., 2014)	Gasification ash produced from PSSC	pyrolysis of SS at 530 °C followed by gasification in fluidized bed reactor at 820 °C	8.10%	94% ±3%
(Gerner et al., 2021)	HTC sewage sludge char	HTC sewage sludge char produced at 200 °C with reaction time of 4hr	4.95%	71 ±1%
Current study		HTC sewage sludge char produced at 240 °C with reaction time of 2hr	5.39%	90 ±1%
(AVA Cleanphos 2018)		HTC sewage sludge (Bio-P) char produced at 210 °C with a reaction time of 5hr - pilot scale	3.2-3.6%	>95%
(AVA Cleanphos 2018)		HTC sewage sludge (Chem-P) char produced at 210 °C with a reaction time of 5hr - Pilot scale	5.60%	>95%

Figure 8-5 compares the sulfuric acid demand to leach one kilogram of phosphorus from the sewage sludge products produced by incineration, pyrolysis, and HTC. The lowest sulfuric acid demand for one kilogram of phosphorus leaching from solids to liquid phase was observed in ISSA at 4.92 kg H_2SO_4/1 kg P leaching, followed by HTC-SS char at 4.88 kg H_2SO_4/1 kg P leaching, and PSSA at 10 kg H_2SO_4/1 kg P leaching. The extraction efficiency in this study for HTC-SS char was 6.23 kg H_2SO_4/1 kg P leaching. This is in line with the previously reported results (AVA Cleanphos 2018).

The economic aspect of sulfuric acid demand for P leaching from HTC sewage sludge char can readily compete with the conventional P leaching from ISSA, as shown in Figure 8-5. In addition to exceeding the regulatory requirement for P recovery, acid-leaching HTC sewage sludge char transfers approximately 50 percent of N into the liquid phase while retaining a significantly greater proportion of heavy metals in hydrochar. The reduced nitrogen content in char enhances combustion by reducing NO_x. Its application is severely limited to energy utilization in industrial recycling plants with suitable fume cleaning systems due to its high sulfur and heavy metal content. After recycling the P from sewage sludge hydrochar, it will remain available as a climate-neutral fuel source for the cement sector and coal power plants.

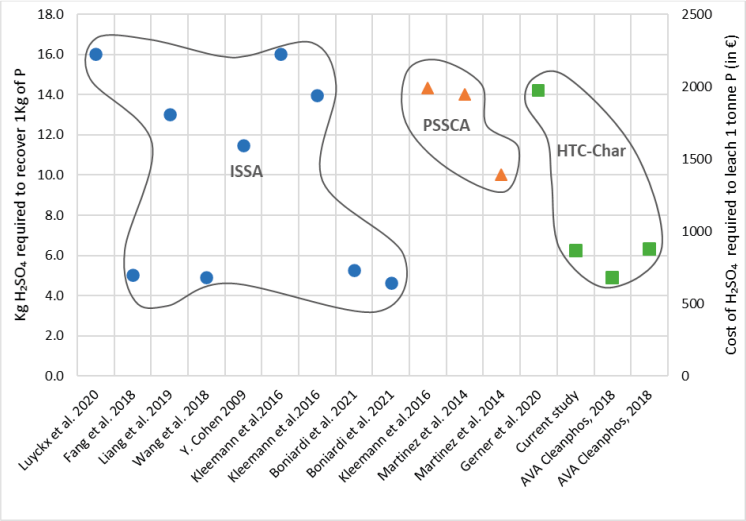

Figure 8-5 H_2SO_4 demand per kilogram of phosphorus leaching and H_2SO_4 cost associated with leaching one metric ton of phosphorus from different sewage sludge derivative.

P recovery from HTC char can compete with existing traditional SSA recovery technologies that employ sulfuric acids and also provide the added advantage of producing climate-neutral fuel. However, the most essential question that needs to be answered is whether or not such high recovery rates of over 90% P are necessary and reasonable. The German Sewage Sludge Ordinance requires only 50% phosphorus reclamation (or 20 g P/kg DM) in sewage sludge. Is it possible to economically and environmentally justify the recovery of 40% more phosphorus than what is required by the German Sewage Sludge Ordinance, given the necessity of recovering phosphorus minerals, in connection with the management of the leachate that is produced following the recovery of phosphorus? It is possible to reduce the amount of phosphate that is released from sewage sludge hydrochar by optimizing the process. This could mean that the consumption of significant quantities of sulfuric acid is no longer required. As a consequence of this, it will be possible to significantly cut down on the overall cost of the procedure because the quantity of chemicals that are required will be decreased.

8.3. Recovery of phosphorus from leachate

Recovery of P from ISSA through wet-chemical techniques has been intensively studied and applied on an industrial scale. An increasing number of studies have concentrated on P recovery from hydrochar in addition to the numerous studies interested in HTC (Ovsyannikova et al., 2019; Liu et al., 2021). Production of hydrochar from the municipal sludge carries a significant amount of heavy metals which makes it highly unsuitable for direct use as a fertilizer. Further, P available in biological forms is restricted as it is a compound to minerals (Xiangdong et al., 2019; Fei et al., 2019). These impurities make hydrochar difficult to use; thus removing heavy metals and increasing bio-available P through recovering P is the primary objective. Wet-chemical and thermochemical processes are the most prevalent techniques and are accepted greatly at an industrial scale. In the thermochemical process, the volatilization of P takes place in a reducing atmosphere at a heating range of 900–950 °C

for 15–20 min with a dosage of sodium, potassium, or magnesium (Liu et al., 2021). This treatment process results in the formation of Ca-P. Although Ca-P is greatly bioavailable the thermochemical recovery process requires intense energy input along with the need for inorganic chloride for efficient removal of heavy metals (Fang, Wang et al., 2021; Luyckx, Geerts and Caneghem 2020). Wet chemical technology has two major steps; a) Initially leaching P from a solid to a liquid medium in the presence of strong acids. b) subsequent chemical precipitation of bioavailable P from leachate. The wet-chemical P recovery process also projects high economic efficiency, a simpler process, and industrial-scale application. The process of crystallization and precipitation can be divided into the following three steps (Abel-Denee, Abbott and Eskicioglu 2018; Stumm and Morgan 1981; Ehrnström 2016).

1. *Nucleation or crystal formation* occurs either homogenously or heterogeneously when the formed nuclei overgrow their critical sizes. The impulsive growth of crystallites in solution is known as homogeneous nucleation, whereas heterogeneous nucleation occurs when crystallites are deposited on existing surfaces.
2. *Secondary nucleation* results in *crystal growth* by transporting ions from the bulk to the nuclei surface, where they are adsorbed.
3. *Aggregation of the crystals* leads to precipitation when enough crystal growth is achieved.

The following are the primary crystallization products that are widely taken into account for the synthesis of phosphorus fertilizer from wastewater streams and products (Liu et al., 2021):

1. Struvite ($MgNH_4PO_4{\cdot}6H2O$),
2. Calcium phosphates (Ca-P), and
3. Vivianite ($Fe_3(PO4)_2{\cdot}8H_2O$

The saturation index (SI) indicates the solution saturation condition. SI is determined by dividing the ion activity product of constituent ions by the precipitate's equilibrium solubility product (Ksp). The range of the saturation index below zero indicates that precipitation cannot occur as the system is unsaturated (SI <0). The saturation index above zero (SI >0) is considered as a supersaturated condition where precipitation can take place. Figure 8-6 is the representation of pK_{sp} (-log K_{sp}) constant precipitates of the salts and solubility at 25 °C for some relevant precipitates discussed in this section. The solubility of salts and kinetics of a precipitate can be influenced by the nature of the deposits of the solid phase.

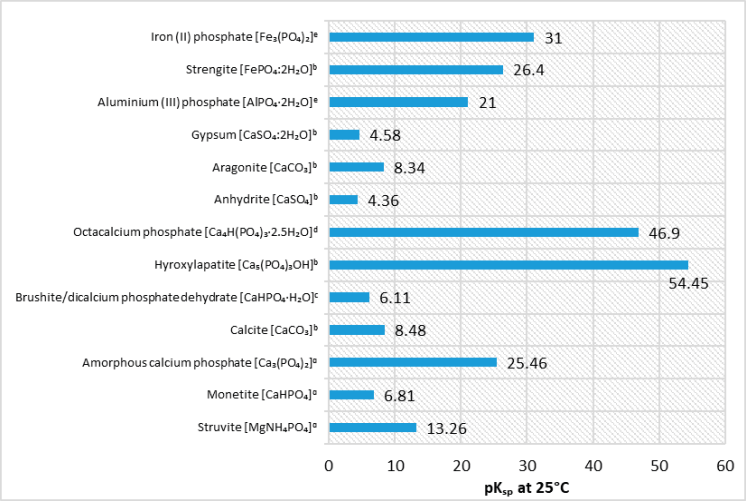

Figure 8-6 Salts and solubility product constant at 25 °C. [a] (Daneshgar et al., 2019), [b] (Ball and Nordstrom 1991), [c] (Allison, Brown and Novo-Gradac 1991), [d] (Tung et al., 1988)[e] (Ebbing and Gammon 2009)

8.3.1. Struvite

Crystallization of struvite is a widely accepted method for the recovery of P from sewage sludge and its derived products. In principle, struvite formation begins at the molar ratio of 1:1:1 (Mg^{2+}:NH_4^+:PO_4^{-3}) under saturated conditions (see eq. 8.1). Phosphate in solution may also exist in the $H_2PO_4^{2-}$ and $H_2PO_4^-$ forms and contribute to the formation of struvite (see eq 8.2 and 8.3).

$$Mg^{2+} + NH^+_4 + PO_4{}^{3-} + 6H_2O \longrightarrow MgNH_4PO_4{:}6H_2O\downarrow \quad 8.1$$

$$Mg^{2+} + NH^+_4 + H_2PO_4{}^{2-} + 6H_2O \longrightarrow MgNH_4PO_4.6H_2O\downarrow + H^+ \quad 8.2$$

$$Mg^{2+} + NH^+_4 + H_2PO_4{}^- + 6H_2O \longrightarrow MgNH_4PO_4{:}6H_2O\downarrow + 2H^+ \quad 8.3$$

The saturation point for struvite formation is strongly influenced by solution pH and has a favorable range of 8-10. An increase in ion concentrations and pH can increase the saturation of the solution. However a pH above 10.5 causes a significant drop in NH_4^+ that subsequently prevents the struvite formation (Kumar and Pal 2015). Because of the diversity in the composition of sludge-derived hydrochar, the optimum pH conditions, and an ideal stoichiometric molar ratio of magnesium, nitrogen, and phosphorus fluctuate during the precipitation process (Liu et al., 2021). An additional supply of chemicals rich in Mg^{2+} and NH_4^+ is necessary to increase their concentration in the extracts. Studies have obtained >98% P precipitation with a short duration of <2 hours at the pH range of 9-9.5 and with the molar ratio of 1:1:1 (Mg:N:P) (Liang et al., 2019). Other studies have also reported that higher Mg:P (>1.5) and lower N:P (0.6) molar ratios at a pH greater than 9.3 can recover >97% P and >70% N. Another form of struvite is K-struvite ($MgKPO_4{\cdot}6H_2O$), which is formed at the replacement of NH_4^+ with K^+ at a pH of 11. According to Li et al., potassium hydroxide extraction and consequent crystallization in the presence of magnesium dichloride recovered ≥88% P as K-struvite (Ksp = 10-22) (Li et al., 2020). Considering the cost perspective of potassium hydroxide and magnesium dichloride, the extraction process can become cost-intensive.

8.3.2. Calcium Phosphates

Calcium phosphate compounds are commercially accessible, and their recovery from sewage sludge derivatives is well-accepted. Kinetics and pH play a major role in the precipitation process. Calcium phosphate precipitate takes various forms at different pHs; Dicalcium phosphate at pH 5 (see equation 8.4), Octacalcium phosphate at pH 6 (see equation 8.6), and hydroxyapatite at pH 7 and above (see equation 8.7) (Desmidt et al., 2015). The changing phosphate molar concentration from 0.01 – 0.5 in a control pH results in precipitates in the order of brushite → monetite, → and amorphous Ca-P (Abbon, Lundager and Boistelle 1986). Ca-P can attain supersaturation and precipitation even at a low pH of less than 4, which is not the case in struvite. The Eq 8.4-8.7 depicts the process of crystallization for calcium phosphate.

$$Ca^{2+} + HPO_4^{2+} \rightarrow CaHPO_4 \quad 8.4$$

$$3Ca^{2+} + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \quad 8.5$$

$$Ca2+ + 2HPO_4^{2-} + 4PO_4^{3-} \rightarrow Ca_8(HPO_4)_2(PO_4)_4 \quad 8.6$$

$$5Ca^{2+} + 2\ PO_4^{3-} + OH^- \rightarrow Ca_5(HPO_4)_3OH \quad 8.7$$

Efficiency as high as >89% can be achieved in precipitating P from the leachate of hydrochar by adding Ca chemicals in the solution form with a pH >5 (Zhai et al., 2014). However, the undesirable formation of $AlPO_4$ (pKsp = 20) and/or $FePO_4$ (pKsp = 15) can occur because of co-dissolved Al and Fe cations during the acidic extraction. These undesirable formations when combined with the hydroxides at a range of pH 4.4 to 6.5 can reduce the bio-availability of the recovered products (Fang, Li and Donatello et al., 2018). The formation of $Al(C_2O_4)_2^-$, $Al(C_2O_4)_3^{3-}$, $Fe(C_2O_4)_2^-$, and $Fe(C_2O_4)_3^{3-}$ complexes during oxalic acid extraction was hypothesized to render aluminum and ferric ions unremovable by cation exchange resin. These complex's formation lowers the P recovery value (Liang et al., 2019). Increasing the pH of the leaching medium (pH >10) could also stop aluminum from co-precipitating since aluminum is mostly a soluble anion at pH >10 (Fang, Li and Donatello et al., 2018). It is important to validate the feasible combinations of the extractants and the targeted fertilizers beforehand to overcome the odds of producing inferior-quality aluminum phosphates and ferric phosphates (Peng et al., 2018). For the precipitation of Ca-P, a specific molar ratio of 1 (Ca): 1.67 (P) can be achieved by supplying lime (CaO), $Ca(OH)_2$, and $CaCl_2$. Whereas the high demand for Ca could be created due to co-precipitation and the formation of gypsum and carbonate (Peng et al., 2018). This increases the chemical requirement while also lowering the overall phosphorus recovery (Desmidt et al., 2015). Even though there are high precipitation and recovery rates observed in various research, the effective cost-effective technique for precipitation and recovery to calcium phosphate from the hydrothermally treated sewage sludge hydrochar is still lacking. One factor that needs greater attention in creating a cost-effective technique is the balance between the demand for chemicals and its relation to the P recovery percentage.

8.3.3. Vivianite

Vivianite is a hydrated iron phosphate mineral and generally consists of ferrous ions in its chemical structure. Vivianite precipitation is particularly interesting and effective in recovering P from the sewage sludge and its derivative which contains a higher iron composition. It has a higher market price and potential as a Fe and P fertilizer, preventing Fe chlorosis and enhancing crop yield (Liu et al., 2021). Lab-scale studies show vivianite crystallization is feasible under complex environments, with enhanced precipitation efficiency nearing 100% and high purity (82% vivianite) (Liu et al.,

2018; Priambodo, Shih and Huang 2017; Zhang et al., 2020) However, there is a lack of studies on recovering P as vivianite from sludge-derived hydrochar due to challenges like adding expensive iron salts, requiring reductive and anoxic conditions, and requiring high purity demand (Liu et al., 2021). Vivianite is only metastable at room temperature, and impurities can cause it to completely oxidize in two days.

To make the Vivianite precipitation process more stable and robust, future research should optimize operational parameters. Contaminants and their potential risks in the overall process and in the recovered products should be studied carefully. The life cycle and economic assessment should be considered for its production, used chemicals, and effectiveness in the complete process.

8.4. Process water handling and treatment

Process water is the byproduct of the HTC process and is a filtrate that is produced after the separation of solids. The composition of processwater is complex and is contaminated with inorganic and organic contaminates, and has a high organic load as well. The combination indicators like total nitrogen (TN) or total phosphorus (TP) define the inorganic load, whereas chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), and dissolved organic carbon (DOC) characterize the organic contamination in process water. As explained in the earlier section 2.1.1 the composition of the hydrothermally carbonized sewage sludge process water greatly depends on the input material and the process parameters during the HTC process.

The presence of acids, sugars, furans, phenols, alcohols, ketones, aldehydes, and N-containing compounds in process water (Lin et al., 2015) could increase HTC waste disposal costs (Lu et al., 2022). Following the hydrothermal carbonization of sewage sludge, the COD of the process water rises. In addition, despite the majority of heavy metals being adsorbed onto hydrochar, some heavy metals may be discharged into the aqueous phase during the hydrothermal carbonization of sewage sludge (Lin et al., 2015). As a result, the direct discharge of the aqueous phase may give rise to issues regarding biosafety for both humans and the environment (Danso-Boateng et al., 2015). In concern to the characteristic of process water, according to the German Federal Water Act (WHG 2009), the processwater produced from the hydrothermal carbonization of waste biomass is considered as wastewater and is obliged to be treated. The discharge to process water directly to the water bodies or indirectly into the public WWTP requires legal compliance and approval as per the German Federal Water Act and German Wastewater Ordinance. The stringent regulatory compliances and disposal challenges that are involved with processwater could potentially exceed the economic and environmental benefits that are associated with an HTC process. The following section gives an overview of possible utilization and treatment pathways for processwater with the objective of lowering economic costs and minimizing environmental risk.

8.4.1. Recirculation

Recirculation of the processwater could be considered as a primary approach to handle large quantities of processwater generated during hydrothermal carbonization. Recirculation of processwater refers to the reuse of the liquid phase of HTC product within the HTC process to meet the water demand. The reuse or recirculation of the HTC process water carries with it a number of benefits, some of which are detailed here.

1. Due to the fact that process water is reused within the facility and offers the opportunity to derive additional value, recirculation of process water is unaffected by legal requirements for disposal.

2. A decrease in the amount of process water, which would result in a decrease in the costs associated with treating process water at the HTC facility (Kambo, Minaret and Dutta 2018).
3. Recirculating process water has been proposed as the most effective approach for the recovery of heat, with the potential to lower external heat demand by tenfold (Stemann, Erlach and Ziegler 2013).
4. The inclusion of organic acids in the process water may further catalyzes the process during recirculation, reducing pressure and temperature requirements during HTC while also promoting dehydration and decarboxylation reactions (Picone, Volpe and Messineo 2021; Arauzo et al., 2020).
5. Hydrochar with a porous structure has the potential to accumulate degraded sugar molecules from the recirculated HTC process water, thereby increasing the energy density of the produced hydrochar (Kambo, Minaret and Dutta 2018).
6. For additional energy recovery, the recirculated processwater can be handled via anaerobic digestion or co-digestion (discussed in section 8.4.2).

The recirculation of processwater produced by miscanthus in the HTC process at 260 °C has shown a gradual increase in the mass yield of hydrochar samples of 5–10% with each subsequent recirculation (Kambo, Minaret and Dutta 2018). Nonetheless, the third recirculation of the PW had no discernible effect on mass yield. Furthermore, as compared to the initial run's hydrochar sample, the energy yield of the recirculated processwater hydrochar increases by up to 15%. An increase in hydrochar yield can be achieved by recycling the process water, as indicated by (Catalkopru, Kantarli and Yanik 2017), because this reduces the ease with which soluble bits of degraded biomass diffuse from the particle surface into the solution. Hydrochar is produced via condensation and re-polymerization processes. The organic acids in the recirculated process water can act as a catalyst and further stimulate dehydration events, considerably boosting the carbonization process (Arauzo et al., 2020). The presence of organic acids in the process water has a tendency to accelerate the conversion rate of the feedstock by fostering the dehydration of hydrolytic products formed from hemicellulose and cellulose. This can be understood as an acceleration of the conversion rate. This ultimately leads to the creation of intermediates that are soluble in water (Wang-Tengfei et al., 2018). These intermediates have the capability of undergoing a polymerization process. This can contribute in the formation of solid particles having high energy density (Wang-Ruikun et al., 2020). The greater synthesis of polymerized solid microparticles coming from the organic matter within PW leads to an elevation in the carbon content of hydrochars, which in turn results to an increase in the energy content of hydrochars. This occurs as a consequence of the enhanced formation of polymerized solid microparticles (Picone, Volpe and Messineo 2021).

The majority of the scientific evidence to date indicates that PW recirculation lowers wastewater volume and hence operating costs and has a number of beneficial benefits on the HTC process; however, there is a lack of research on material addressing processwater recirculation. For instance, prior research has shown that the hydrochar output during recirculation operations does not follow a typical trend (Catalkopru, Kantarli and Yanik 2017; Picone, Volpe and Messineo 2021), although the impact specifically on processwater is unknown. Therefore, more research is needed to determine how the recirculation stages influence the hydrochar mass yield, energy content and characteristics of the ultimate PW in particular for sewage sludge utilization.

8.4.2. Anaerobic digestion and Co-digestion

The high concentration of protein and volatile fatty acids found in HTC processwater makes it suitable for anaerobic digestion (Tasca et al., 2019). It is possible that the problem of processwater handling might be solved by combining HTC with anaerobic digestion, which would also result in the recovery of additional energy. In addition, the digested processwater can be easily handled at the location where it was produced, which is typically a municipal water treatment facility. The amount of methane yielded would increase with increasing volatile fatty acid concentration in the liquid fraction (Danso-Boateng et al., 2015). Wirth et al., (2015) investigated the Anaerobic digestion of process water from hydrothermal carbonization of sewage sludge and found that AD is a promising technique for the treatment of processwater in an energy-efficient and sustainable manner. In their research, Wirth et al. found that using sewage sludge HTC process water as the only material for anaerobic digestion produced up to 180 mL CH_4/g COD, with a steady-state COD removal efficiency of between 68 and 75%. Chen et al. 2019 investigated the impact of HTC reaction parameters such as temperature and retention time on the methane yield of the consequently produced processwater. According to their findings, increasing the HTC reaction temperature decreased the methane production from 286 mL CH4/g COD to 136 mL CH4/g COD for processwater produced at HTC temperatures of 170 °C and 320 °C, respectively. Additionally, a similar effect of lower methane output was detected with increasing retention time. An increase in the synthesis of more organic compounds such as humic acid, nitrogen heterocycle, recalcitrant organic compounds, and phenols that are resistant to reaction can be ascribed to the decreased methane yield with increasing HTC reaction severity (Chen et al., 2019).

Anaerobic digestion of individual substrates may have drawbacks associated with substrate characteristics (Rubia et al., 2018). In contrast, anaerobic co-digestion involves the combined digestion of two or more substrates, is an effective approach for overcoming the disadvantages of mono-digestion and enhancing the economic viability of a treatment plant (Mata-Alvarez et al., 2014). Anaerobic co-digestion offers numerous benefits compared to the digestion of a single substrate. Co-digestion improves the stability of the process stability, allows higher organic loading rates as well as increases methane yield, lowers the risk of toxic compounds due to dilution, and balances solid content and nutrients (Wang-Fang et al., 2020). Rubia et al. (2018) studied the anaerobic co-digestion of organic fractions from MSW with sewage sludge HTC processwater. The results indicated that the co-digestion of organic fraction from MSW and sewage sludge processwater in a ratio of 3:1 yields a comparable amount of methane relative to the digestion of organic fraction from MSW alone, thereby providing an alternative method for managing processwater. The co-digestion of processwater with primary sewage sludge, according to a different study by Villamil et al. 2019, may offer a feasible approach for integrating HTC technology and WWTPs. In comparison to the digestion of processwater alone, their findings showed that co-digestion of processwater and PSS in the ratio of 1:3 produced the highest methane yields (1.76 and 1.30-fold with granular sludge inoculum and flocculent sludge inoculum, respectively). However, increasing the processwater to primary sewage sludge ratio reduces the methane yield because the sewage sludge HTC process water contains inhibitory nitrogen-containing aromatic chemicals (Villamil et al., 2019).

Taking into account the properties of the process water generated by the HTC of sewage and carefully optimizing the process of integrating the HTC with AD can result in the creation of a prospective treatment method with the option of energy recovery.

8.4.3. Wet oxidation

In the year 1950, Zimmerman put forth the idea of using a wet oxidation process to eliminate organic compounds in the liquid phase. During the wet oxidation process, biomass is subjected to high temperatures (120 °C to 238 °C) and pressures (3 to 33 bar) in the presence of water and oxygen as oxidants to totally oxidize organic materials into carbon dioxide and water (Zhang et al., 2020).

Weiner et al. (2018) combined the hydrothermal carbonization (HTC) of sewage sludge with the wet oxidation of the resulting process waters. Their research findings demonstrated that the Wet oxidation (WO) of PW is likely to eliminate 50–70% COD and dissolve organic carbon. The WO treatment of PW has increased the concentration of organic acids, particularly acetic acid, which is a positive indicator that oxidized PW can be utilized in anaerobic digestion (Weiner et al., 2018). Stutzenstein et al. 2018 show a method for using iron (III) nitrate as a substitute for molecular oxygen as an oxidizing agent during wet oxidation of processwater. Iron (III) nitrate proved to be an effective oxidant at a relatively low process operating temperature of 120 °C and substantially decreased equipment costs when compared to oxygen oxidation at 200 °C. In the first hour of the reaction, 50% of the COD and 30% of the DOC were removed, whereas increasing the reaction time by more than one hour did not show any noticeable difference (Stutzenstein et al., 2018).

The application of non-catalytic WO to the PW from hydrothermally liquified (HTL) sewage sludge was investigated by (Thomsen et al., 2022). The results from their studies indicated that at the maximum temperature (350 °C) and retention time (180 min), the WO of the aqueous phase from the HTL of sewage sludge could remove 97.6% of COD and 96.1% of TOC. The WO process is exothermic, generating up to 28.3% of the reaction heat demand. The minimum energy demand per kilogram of COD removed is 9.6 kWh at 200 °C for 180 minutes without consideration of the utilization of recovered heat during the WO process (Thomsen et al., 2022).

8.4.4. Overview of other additional treatment methods for process water

A number of approaches have been looked into for treating and valorizing PW in addition to the methods already discussed, some of which are mentioned here. Separation of chemicals such as carboxylic acids from PW (Dutta et al., 2020), furans separation from PW using vacuum separation (Huang et al., 2019), and conversion of PW components to bioelectricity, biohydrogen, syngas, and bioethanol (Leng et al., 2021).

On the other hand, the performance of these technologies is still a long way from satisfactory, and they cannot be industrialized for the most part due to the complex nature of PW. In the vast majority of thermochemical conversion processes, recovering useful chemical co-products from diluted and heterogeneous PW streams is a considerable difficulty. According to (Wilson et al., 2019), it is difficult to separate nutrients and chemicals in a way that is cost-effective due to the stringent purity standards that are necessary for the production of bulk chemicals. Furthermore, the use of a hazardous solvent for the processing of PW can impair subsequent wastewater treatment regardless of whether only a trace of the solvent is detected in the PW (Leng et al., 2021).

Future research should concentrate on improving already existing technologies and filling in any knowledge gaps on PW valorization in order to minimize the environmental impact of PW disposal and maximize the amount of value that can be extracted from it. Future research should focus on developing existing technologies by scaling up valorization processes, techno-economic analysis, and life-cycle assessment. Figure 8-7 provides an overview of some of the challenges and potential research prospects for the treatment and valorization of PW.

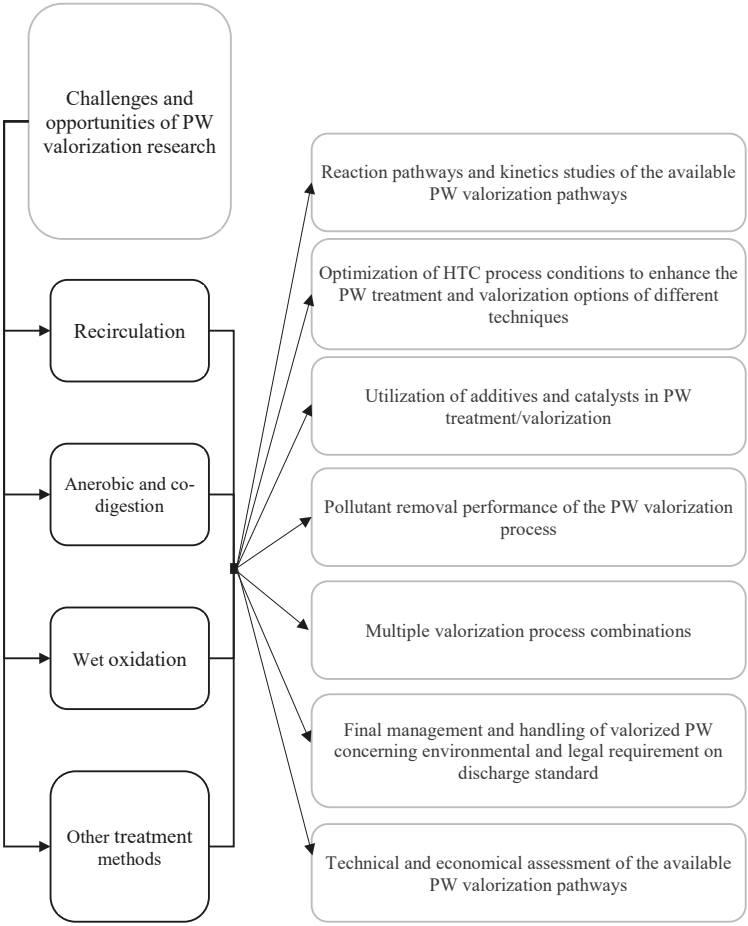

Figure 8-7 Challenges and the potential research prospects for the treatment and valorization of process water

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9. Conclusion

The current chapter provides the conclusion and thesis by answering the research questions underlying this cumulative dissertation.

RQ 1: What is the influence of acid and base as additives during HTC of sewage sludge?

During hydrothermal treatment of sewage sludge, phosphorus leaching from solids to the liquid phase is highly effective at lower pH levels and particularly significant with sulfuric acid use. The use of sulfuric acid as an additive during hydrothermal treatment of sewage sludge improves the dewatering efficiency and yield of the of sewage sludge hydrochar in comparison to the use of formic and acetic acids. Similar to organic acids, the use of base (sodium hydroxide) as an additive has significantly less effect on the leaching of phosphorus.

RQ 2: What effect does acid utilization after and before hydrothermal carbonization have on phosphorus mobilization and hydrochar characteristics in sewage sludge? Moreover, what chemical reaction kinetics impact the phosphorus transformation from sewage sludge to leachate?

The characteristics of sewage sludge are complex by nature and have the tendency to resist acidification. Using acids before the hydrothermal treatment of sewage sludge results in lower phosphorus leaching efficiency in comparison to acid utilization after hydrothermal treatment. The series of chemical reactions that occur under high pressure and high temperature in a hydrothermal treatment process reduces the acid buffering resistance provided by sewage sludge. This reduction in buffering resistance provides an ideal condition for H^+ ions in acid to interact with the phosphate-holding compounds and improve the phosphorus leaching efficiency in an acid-leaching medium. The use of acids before or after hydrothermal treatment of sewage sludge has a very small difference in the heating value and proximate analysis results.

RQ 3: What are the effects of leaching sewage sludge hydrochar using organic and inorganic acids at various pH on phosphorus mobilization?

Leaching phosphorus from sewage sludge hydrochar is influenced by two process parameters: Firstly, the process conditions during the hydrothermal treatment process, which include temperature and reaction time; and secondly, the process conditions of the leaching medium, which include the pH range and the type of acid used. The influence of process conditions in the acid-leaching medium has a substantially greater effect in comparison to the process conditions during the hydrothermal treatment, which have a less significant effect. The use of organic acids (formic and acetic acids) in the acid-leaching medium has very little impact on the phosphorus leaching from the solid to liquid phase, irrespective of their concentration and pH in the leaching medium. In contrast, the use of inorganic acid (sulfuric acid) in the acid-leaching medium has significantly higher efficiency in leaching phosphorus from sewage sludge hydrochar to leachate at pH <2.

RQ 4: In addition to pH what are the other characteristics of acids influencing the phosphorus mobilization from sewage sludge hydrochar to leachate?

Together with the pH, the strength of the acid used in the leaching medium plays a crucial role in deciding the migration efficiency of phosphorus from sewage sludge hydrochar to leachate. The acids with a lower pKa have a higher tendency to donate H^+ in the acid-leaching medium in

comparison to the acids with a higher pKa value. The use of acids with a lower pKa value presents a higher number of H^+ ions in the leaching medium and the greater possibilities of chemical interaction with phosphate-holding compounds in sewage sludge hydrochar. In contrast, using acids with a higher pKa value results in poor phosphorus leaching due to lower availability of H^+ ions and higher chemical costs. This difference in the pKa value directly influences the phosphorus leaching percentage from sewage sludge hydrochar to leachate, from ~90% with the use of sulfuric acid (pKa value of -3), ~36% with the use of formic acid (pKa value of 3.75), and ~2.5% with the use of acetic acid (pKa value) at similar conditions in the leaching medium.

RQ 5: Is it economically viable to leach phosphorus from sewage sludge hydrochar in comparison to the conventional sewage sludge derivatives such as sewage sludge ashes and pyrolysis sewage sludge ashes?

Sulfuric acid methods are popular for leaching phosphorus from sewage sludge products due to their high extraction efficiency, ease of operation, and low cost. The lowest sulfuric acid demand for one kilogram of phosphorus leaching from sewage sludge hydrochar to leachate was observed to be 4.88 kg sulfuric acid and this leach efficiency is comparable with the conventional phosphorus leaching efficiency from incinerated sewage sludge ashes. Leaching phosphorus from incinerated sewage sludge ashes can result in the simultaneous leaching of heavy metals and complicate the application of recovered phosphorus as fertilizer. On the other hand, recovering phosphorus from sewage sludge hydrochar can adsorb a significant portion of heavy metals onto the hydrochar, leaving the phosphorus-rich leachate with a lower concentration of heavy metals. Phosphorus leaching from hydrothermally carbonized sewage sludge char can readily compete economically with conventional phosphorus leaching from incinerated sewage sludge ashes and transfer ~50% of nitrogen into the liquid phase while retaining a greater proportion of heavy metals in hydrochar. The reduced nitrogen content in char enhances combustion by reducing NO_x. However, the high sulfur and heavy metal content of hydrochar after acid leaching limits its energy-related utilization in industrial recycling plants with suitable fume cleaning systems.

RQ 6: What is the current status and future of HTC as a technology to treat sewage sludge?

The current state of know-how in the field of HTC has extensively studied the reaction pathway and kinetics of the HTC of sewage sludge. This particular research has extensively studied the acid leaching of hydrochar and the economic comparison with the conventional acid leaching process. The economic aspect of sulfuric acid demand for phosphorus leaching from HTC sewage sludge char can readily compete with the conventional phosphorus leaching processes that utilize H_2SO_4. HTC as a technology has however not yet been proven in continuous industrial operation in sewage sludge treatment. One of the major drawbacks to the large-scale application of the HTC process in sewage sludge management is the readiness of technologies that can handle and manage processwater. The presence of high amounts of organic and inorganic pollutants in process water could increase HTC waste disposal costs. The stringent regulatory compliance and disposal challenges that are involved with processwater could potentially exceed the economic and environmental benefits that are associated with an HTC process. For the HTC technology to be successfully commercialized, a functional, dependable, and cost-effective disposal technique for processwater is crucial. This is likely to occur within the next few years given the rate of scientific advancement in the field right now.

10. Outlook

Phosphorus leaching from sewage sludge hydrochar using sulfuric acid can economically compete with conventional methods involving acid leaching of phosphorus from sewage sludge ashes. With the current leaching processes, there is a possibility to leach over 90% phosphorus from sewage sludge hydrochar. In addition to this, phosphorus recovery from sewage sludge hydrochar provides the added advantage of producing climate-neutral fuel. Given the context of this study, the most important questions that have to be answered are: 1) whether or not such high phosphorus recovery rates of over 90% are necessary and reasonable; 2) the economically and technologically effective method to precipitate phosphorus after the leaching process; 3) what is the environmentally and economically viable technique to handle the leachate after precipitating phosphorus; and 4) the development of effective technology to handle the processwater within the premises of the HTC treatment facility. Considering this research gap, the following aspects require detailed research for the success of HTC in treating sewage sludge on an industrial scale:

1. In view of the regulations from the German Sewage Sludge Ordinance, what should be the economically and environmentally optimum P recovery percentage from sewage sludge hydrochar considering: 1) efficient nutrient recovery; 2) minimum chemical demand; and 3) ease of handling the leachate after phosphorus precipitation.
2. Optimization of existing process water treatment techniques for maximum value extraction and less environmental impact. It is recommended that the study on this aspect be supplemented with techno-economic and life-cycle assessments.
3. Detailed research to valorise the hydrochar after acid leaching to create value added products.

APPENDIX

Declaration of independency

I hereby declare that I have written the submitted dissertation independently and without outside help, and I have not used sources and aids other than those indicated by me, and I have marked as such the passages taken from the works used, either literally or in terms of content.

Vicky Shettigondahalli Ekanthalu

Rostock, 22.01.2024

Curriculum Vitae

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WORK EXPERIENCE

Aug. 2018 - Present	**Scientific Research Assistant** at the Faculty of Agriculture and Environmental Science, Department of Waste and Resource Management, **University of Rostock, Germany** Recently completed project: Management of Organic Waste in India (MOWI). BMU Global project
Nov. 2014 - Feb. 2015	**Intern**, Environment and Information Technology Centre-UIZ, Berlin
Aug. 2013 - Feb. 2014	**Lecturer** at Gnana Vikas Polytechnic, Chitradurga, India

ACADEMIC QUALIFICATION

April 2019 - Present	**Ph.D. scholar** Department of Waste and Resource Management, University of Rostock Research topic: Hydrothermal carbonization of sewage sludge and the influence of pH on phosphorus transformation and hydrochar properties.
October 2014 – September 2017	**Master of Science** in Environmental Resource Management at **Brandenburg Technical University,** Cottbus, Germany. Master Thesis: Technical Investigations on Agglomeration of Material Containing Iron Hydroxide and its Application in Adsorption of Phosphorous. (**Thesis grade: 1.3**)
April 2009 – April 2013	Bachelor's in civil engineering at S.J.M Institute of Technology, Karnataka, India. Bachelor Thesis: Physico-Chemical Analysis of Ground Water in Chitradurga, Karnataka, India.

PROJECTS EXPERIENCE

August 2020 – Present	**Waste to energy as a Sustainable Solution for Ghana** **Funded by the Federal Ministry of Education and Research, Germany (6.2 million Euros).** The aim of to develop a novel, hybrid waste-to-energy plant based on photovoltaics, biogas, and pyrolysis. The plant will use energy from the sun as well as various degradation processes to convert waste to green energy. Responsibility – **Supporting Technical Expert**.
October 2021 – February 2023	**Management of Organic Waste in India:** **Funded by GIZ GmbH in collaboration with Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.** With a focus on integrated waste management, the MOWI module to improve sustainable organic waste management practices in the selected states of India. As part of the project, we were responsible for developing an organic waste management master plan in three states of India. Responsibility – **Supporting Technical Expert.**
August 2019 - December 2020	**Waste-value – Wertschöpfungsketten in der Peripherie Urbaner Regionen (PERIVAL)** Funded by the Federal Ministry of Education and Research, Germany (555,270 Euros). The core research aim of the PERIVAL project is to plan, calculate and work out steps of an optimized waste value separation and recycling system in the pilot region of Zhaoquanying Town, Beijing (Shunyi District), China been implemented finally in the research and development phase. Responsibility – **Supporting Technical Expert.**
February 2019 – July 2019	**Regionales Phosphor-Recycling aus Klärschlämmen in Mecklenburg-Vorpommern** This proposed project aims to develop a holistic strategy for phosphorus recycling from sewage sludge in the state of Mecklenburg Vorpommen as a model region in Germany. Responsibility – **Supporting Technical Expert.**
August 2018 - January 2019	**Bioenergy for the production and utilization in Ghana (BioGRAG-DEF).** Funded by the Federal Ministry of Education and Research, Germany (58,000 Euros). Responsibility – **Supporting Technical Expert.**

COMPUTER SKILLS

Software and Language	MS Office, Design of Experiments/Response Surface Modelling, and GIS(Basic)

LIST OF PUBLICATIONS AND CONFERENCE

(Peer-reviewed journal)

1. Ender, T; **Shettigondahalli Ekanthalu, V**; Jalalipour, H; Sprafke, J; Nelles, M. Process Waters from Hydrothermal Carbonization of Waste Biomasses like Sewage Sludge: Challenges and Opportunities in Germany. Front. Environ. Eng. **(under review since 27.07.2023)**
2. Ender, T; **Shettigondahalli Ekanthalu, V**; Nelles, M. Hydrothermal Carbonization of Sewage sludge – An Effective Approach to Treat and Manage Sewage Sludge in Rural Areas of Germany? Detritus **(Accepted on 04.08.2023)**
3. **Shettigondahalli Ekanthalu, V**; Ender, T.; Narra, S.; Antwi, E.; Bej, S.; Nelles, M. Acid leaching of hydrothermally carbonized sewage sludge: Phosphorus release and hydrochar characteristics. Front. Environ. Eng. 2023, Volume 2. DOI: 10.3389/fenve.2023.1223247
4. Williams, P.A.; Narra, S.; Antwi, E.; Quaye, W.; Hagan, E.; Asare, R.; Owusu-Arthur, J.; **Shettigondahalli Ekanthalu, V**. Review of Barriers to Effective Implementation of Waste and Energy Management Policies in Ghana: Implications for the Promotion of Waste-to-Energy Technologies. Waste 2023, 1, 313-332. https://doi.org/10.3390/waste1020021
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8. P.J. Sajil Kumar; Andezhath Mohanan, Anju; **Shettigondahalli Ekanthalu, V.** Hydrogeochemical analysis of Groundwater in Thanjavur district, Tamil Nadu; Influences of Geological settings and land use pattern., Geology, Ecology, and Landscapes, DOI:10.1080/24749508.2019.169
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2. **Shettigondahalli Ekanthalu, V**; Satyanarayana Narra; Haniyeh Jalalipour; Edward Antwi; Vidhi Singh; Mona Maria Narra; Michael Nelles Review of the existing organic waste management situation in Kerala. 12th IconSWM-CE & IPLA Global Forum 2022.
3. Ender, T; **Shettigondahalli Ekanthalu, V**; Michael Nelles. Hydrothermal carbonization of sewage sludge – an effective approach to treat and manage sewage sludge in rural areas of Germany. 9TH INTERNATIONAL SYMPOSIUM ON ENERGY FROM BIOMASS AND WASTE 2022.
4. **Shettigondahalli Ekanthalu, V**; Narra, S; Nelles, M. Pre- and post-acid treatment effects during hydrothermal carbonization of sewage sludge on Phosphorus-transformation characteristics and the properties of hydrochar. 7th HTP Expert Forum "Hydrothermal Processes" 2022.
5. Narra, S., **Shettigondahalli Ekanthalu, V**., Antwi, E., Nelles, M. (2021). Effects of Marine Littering and Sustainable Measures to Reduce Marine Pollution in India. In: Baskar, C., Ramakrishna, S., Baskar, S., Sharma, R., Chinnappan, A., Sehrawat, R. (eds) Handbook of Solid Waste Management. Springer, Singapore. https://doi.org/10.1007/978-981-15-7525-9_60-1

6. **Shettigondahalli Ekanthalu, V**; Hemidat, S.; Hartard, S.; Morschek, G.; Narra M.; Narra S.; Sprafke J.; Nelles M. (2020) Waste value potential analysis of municipal solid waste produced in the Peri-Urban Area of Zhaoquanying, China. WIT Transactions on Ecology and the Environment. DOI: 10.2495/WM200031
7. **Shettigondahalli Ekanthalu, V**., Morscheck, G., Narra, S., Nelles, M. (2020). Hydrothermal Carbonization—A Sustainable Approach to Deal with the Challenges in Sewage Sludge Management. In: Ghosh, S. (eds) Urban Mining and Sustainable Waste Management. Springer, Singapore. https://doi.org/10.1007/978-981-15-0532-4_29
8. **Shettigondahalli Ekanthalu, V**; Narra, S; Nelles, M. (2019) Hydrothermal carbonization: An emerging technology to effectively manage sewage sludge – Review. 2nd International Symposium on Hydrothermal Carbonization.
9. **Shettigondahalli Ekanthalu, V**; Narra, S; Nelles, M. (2019) Hydrothermal Carbonization: A robust technology to effectively manage sewage sludge produced in Germany -Review. ISBN: 978-3-86009-487-7
10. Morschek, G; **Shettigondahalli Ekanthalu, V**; Narra, S; Gruenes, J; Nelles, M. (2018) Sewage sludge disposal in Germany – Status and need for change. IconSWM 2018.

SCHOLARSHIPS AND AWARDS

1. Best research paper award in the "9th **International Conference on Solid Waste Management towards Circular Economy – 2019,** Bhubaneswar, India**".**
2. **National overseas studies scholarship from the Government of Karnataka**, during M.Sc. program at BTU Cottbus-Senftenberg, Germany for a period of 2 years from 2014 to 2016.
3. **Engineering student scholarship from the Government of Karnataka**, during my Bachelor of Engineering at S.J.M Institute of Technology, India for a period of 4 years from 2009 to 2013.

LANGUAGE COMPETENCIES

- Fluent in **English, Kannada, Hindi, Telugu,** and intermediate in **German (A2).**

Place: Rostock

Date: 01 September 2023

In dieser Reihe bisher erschienen

Band I
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