

Lappeenranta University of Technology

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Programme in Green Chemistry

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**HYDROTHERMAL CARBONIZATION IN WOOD INDUSTRY
SIDESTREAMS**

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Supervisor: Eveliina Repo, Associate Professor

ABSTRACT IN ENGLISH

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Hydrothermal carbonization in wood industry sidestreams

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Supervisor: Eveliina Repo, Associate Professor

The main goal of this research project is to study opportunities of Hydrothermal carbonization (HTC) method to treat pulp & paper process sewage streams. HTC is a thermochemical conversion method of organic compounds in order to create carbonated material. HTC experiments were done for various sludges, which were obtained from UPM Kaukas pulp & paper factory. Adsorption properties of prepared carbonated materials were compared by various analysis. Biosludge was noted to be a great adsorbent. Its adsorption capacity was measured with methylene blue to be 60 mg/g. It also contained suitable amount of water and therefore did not require drying or moistening.

Keywords: Adsorption, carbon, Hydrothermal carbonization, HTC, sludge treatment, pulp & paper

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Tämän diplomityön tavoitteena oli selvittää märkäpyrolyysin mahdollisuudet paperin valmistuksesta syntyvän orgaanisen lietten hyötykäyttöä varten. Märkäpyrolyysi on lämpökemiallinen menetelmä orgaanisten yhdisteiden muuntamiseksi hiillytetyiksi materiaaleiksi. Märkäpyrolyysiä kokeiltiin usealle erilaiselle lietteelle, joita saatiin UPM Kaukaan paperinvalmistustehtaalta. Valmistettujen hiilten adsorptiokykyä vertailtiin eri analyyseillä. Biolietteestä tuotettu hiili havaittiin hyväksi adsorptiomateriaaliksi. Sen adsorptiokapasiteetiksi määritettiin metyleenisisällä 60 mg/g. Lisäksi se sisältää runsaasti vettä valmiaksi, joten prosessointi ei vaadi kuivausta eikä kostutusta.

Hakusanat: Adsorptio, hiili, märkäpyrolyysi, HTC, lietten käsittely, metsäteollisuus

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LIST OF SYMBOLS AND ABBREVIATIONS AND DEFINITIONS

ADS	Anaerobically digested sludge	
COD	Carbon Oxygen Demand	
HTC	Hydrothermal carbonization	
HHV	High Heating Value	
TOC	Total Organic Carbon	
Biochar	Soil additive	
Biocoal	Product of HTC, look-alike coal.	
Bio-carbon	technical carbon	
q	Loading capacity	[mg/g] or [mmol/g]
q _e	Loading capacity at equilibrium state	[mg/g] or [mmol/g]
q _{max}	Maximum loading capacity	[mg/g] or [mmol/g]
C _i	Concentration of substance i	[mg/L] or [mmol/L]
C _e	Concentration in equilibrium	[mg/L] or [mmol/L]
K _S	affinity constant	[L/mg] or [L/mmol]

1 INTRODUCTION

Carbon is one of the key elements in life and can be found from all over where is organic matter. Carbon and its compounds are key matter in various fuels. Due to the global warming and high dependency of oil makes scientists all over the world constantly seeking green alternatives for fuel production. This is why hydrothermal carbonization (HTC) has gained more interest in recent years because it is simple and suitable method to treat biomass to produce, for example, bio-oils. Whether the product is fuel or something else, producing carbon is the key element in the process.

Biomass is considered as a renewable source of energy, because the source of carbon is from the nature. Biomass refers to organic matter originating from the living organisms such as plants, and it is usually recovered through the process as a waste. Utilization of biomass is important factor especially in recycling of wastes towards more sustainable development. Coal is the most used option in electricity production worldwide and it has the largest share in global CO₂ emissions. After coal comes oil.

Biomass can be utilized to substitute coal by co-firing technologies to increase sustainability in the energy production. Biomass usually needs to be treated before it can be utilized as a source of energy or product. This thesis focuses to the hydrothermal carbonization, which can be used to treat biomass in order to increase its compounds value. Hydrothermal carbonization does not produce pure carbon but it significantly increases biomass composition quality making it usable in various applications.

Pulp & paper processes generates mainly two types of sludge: primary sludge which consists high concentration of fibers and biosludge which consists high amount of water and organic matter. Primary sludge can be utilized quite well in these days, but utilization of biosludge is complicated because separation of low concentration organic matter from water can raise the expenses of the process while environmental requirements must be fulfilled. HTC can be advantageous method to convert organic matter into concentrated carbon while having low costs due to the mild temperature uses.

This thesis focuses to produce carbonized matter from the pulp & paper mills side streams. These streams are treated hydrothermally in the sealed space where the pressure forms after heating. As a part of the project *minimizing the hazard and maximizing the efficiency* produced carbon materials are then researched and optimized towards adsorbents to be utilized in the wastewater treatment.

1.1 Goals and delimitations

The main goal of this research project was to study opportunities of the HTC method to treat the pulp & paper process side streams and test the applicability of the produced carbon materials as adsorbents. HTC experiments were done for the various sludges and residues, which were obtained from UPM pulp & paper processes. The studied materials were very different from each other but in this thesis they are named as:

- Biosludge
- Primary sludge
- Wooden crust
- BioPiva 100
- Wastewater (alkaline/acidic/to water treatment)

Sources and names of sludges are discussed in Section 2.3. This contains basic information about UPM wastewater treatment process and source of each sludge type because name itself does not give a great picture of its sources or its type.

The research was a part of the research project “Sustainable Chemistry for the Low Carbon Society” of Lappeenranta University of Technology (LUT) funded by the Regional Council of South-Savo.

Differences between the carbon materials made from sludge by HTC treatment were studied by various methods. Main methods in testing were adsorption tests with methylene blue, CHNS-O-elemental analysis and surface area measurements, which were based on BET theory. Extract liquids were in some cases researched with measurements of TOC (total

organic content) and COD (chemical oxygen demand). However, liquids contained so many various compounds that their analyzation in detailed was practically impossible.

Lignin is troublesome substance especially in processes containing wood but it has many potential applications. That is why separation of lignin with adsorbent materials were one of the goals of this thesis. However, due to problems with analysis, methylene blue was used as a model compound to evaluate the adsorption performance of the produced HTC materials.

1.2 Structure of the thesis

Chapter 1 gives a general introduction for recent interest of hydrothermal carbonization treatment. In addition, goals and delimitations of this thesis are explained in Section 1.1.

Detailed theory of hydrothermal carbonization is conducted in Chapter 2. General information of biomass and its uses are discussed in Sections 2.1 and 2.2. Sludge types and sources are discussed thoroughly in Section 2.3 considering area of this thesis. Key factors considering HTC in pulp & paper sludges are noted in section 2.4. Also some current industrial applications are presented in Section 2.5.

Chapter 3 contains brief showcase of biomass conversion technologies that does not include HTC treatment.

Reaction parameters are discussed in Chapter 4. Hydrolysis, dehydration, decarboxylation and polymerization are the most significant phenomena during the HTC reactions are presented in 4.1-4.4. Significant physical factors are presented in Sections 4.5-4.9 which include residence time, temperature, loading amount, pressure and effect of pH.

Chapter 5 contains information about the main components sources and their reactions. Brief discussion about tree types are discussed in section 5.1. Main components, lignin, cellulose and hemicellulose are briefly discussed and their reactions are explained thoroughly during HTC in Sections 5.2-5.4 regarding subject of this thesis.

Adsorption is the main phenomena in this thesis when considering HTC applications as a part of the project and therefore it is discussed thoroughly in Chapter 6.

Experimental part is presented in Chapter 7. Section 7.1 contains procedure method of carbonated materials. Adsorption studies and isotherms are in sections 7.2-7.3. Surface area experiments based on Brunauer-Emmett-Teller are in section 7.4. Composition experiments (CHNS-O elemental analysis) are presented in section 7.5. TOC and COD analyses made for the liquid fraction are shown in Section 7.6. Structural analysis with FTIR is presented in Section 7.7.

Chapter 8 contains discussion about the results and conclusions based on the experimental studies. Main results from experiments are presented and compared to other experimental findings found in literature.

2 HYDROTHERMAL CARBONIZATION

Hydrothermal carbonization is an old but simple coalification technique. It is known for a century, but it has gained more interest in the recent years as it has been noted to be possible method to produce bio-fuels. Despite the simple technique, reaction mechanism is rather ambiguous (Funke & Ziegler, 2009). A major advantage of this method is that the mixed waste used as a raw material requires only minor process steps for the treatment.

The method itself was discovered in 1911 by German chemist Friederich Bergius who was able to synthesize CO and H₂ from carbon and water with less than 600°C temperature and aid of transition metals. Pressure of 200 bars was reached. Bergius noted, that the when the source of carbon was peat, the large amounts of CO was formed and the carbonaceous residues had similar elemental composition as natural coal. After researching more Bergius suggested that the carbonaceous residue is due to the similar reaction as in the natural coalification. He also discovered that biomass-type matter required contact with liquid water during the process and therefore could not decompose into gases but instead formed “hydrothermal carbon”. Bergius continued researching with his assistant on the coal liquefaction process and received Nobel Prize from it during the year 1931. Despite the early research, this subject was left alone until new interest in 21th century. The synthesis of carbon spheres from sugars at low temperatures by hydrothermal treatment were conducted and increasing number of articles were published, which led to new interest towards HTC. (Titirici et al., 2015).

When considering hydrothermal treatment, it is nearly always linked with a source material such as biomass. This can be due to that biomass includes so many different sources as a term, but there is still many ways to operate and process biomass. Biomass conversion technologies can be divided in the thermochemical and biochemical conversion technologies. The hydrothermal treatment offers one benefit that can be crucial when selecting efficient processing method; water is required through the treatment and therefore biomass can be wet. Generally, biomass does have high moisture content so instead of drying process, hydrothermal treatment can be more efficient. (Tekin, Karagöz & Bektaş, 2014).

Hydrothermal carbonization is probably the most common term, which is also used in this thesis, but method is also known for other terms such as: hydrothermal fractionation, autohydrolysis, water prehydrolysis, hot water treatment, pressurized liquid water extraction, hydrothermolysis, etc. (Borrega, 2015).

Hydrothermal treatment is conducted in mild temperature, usually between 180-300°C. This can also be referred as torrefaction. At these temperatures the product is usually referred as biocoal. When HTC temperatures are operated over 400°C product is often referred as biochar when the HTC product looks more like charcoal. Other thermochemical technologies such as flash carbonization, torrefaction and fast pyrolysis often refer processes where used temperatures are in range of 300-600°C and reaction time is rather short, like 30 minutes.

2.1 Biomass properties

Biomass is heterogenous organic matter, which is treated to gain more homogenous material to enhance its better utilization. Biomass can be categorized based on the physical properties, elemental analysis, moisture analysis, volatile content, and the high heating value (HHV). Typical biomass fractions for cellulose are 35-50%, 20-35% for hemicellulose and 15-20% for lignin (Nizamuddin et al., 2017). The reactions during HTC treatment are complex. Reaction mechanisms for these are briefly explained in Chapter 4 and complete reaction pathways of cellulose, lignin and hemicellulose are presented in Section 5.2-5.4.

Carbonized material functionalities can be manipulated in many ways all the way from the process parameters till post treatment. Biomass itself has a high impact on the compounds in the process which is why the feedstock of biomass is important. Moisture analysis can be used to determine if water needs to be added to the process.

Biomass such as wooden source contains various carbohydrates. Even though complex reactions occur, research can be simplified using glucose as feedstock. Most of HTC reaction mechanisms are based on hydrothermal reactions of glucose. (Alatalo, 2016).

Biochar properties can vary a lot and there is not much regulations for them. However, International Biochar Initiative (IBI) has divided biochars in three classes based on the carbon content. Class 1 biochar contains 60% or more carbon, class 2 biochar contains 30-60% of carbon and class 3 contains between 10-30% of carbon. Besides carbon content, other important factors are particle size, pore structure and chemical composition. (Moshan et al., 2014)

2.2 Biocoal applications

Hydrothermal carbonization can be used to alter biomass to more useful matter. Biochar applications, especially wastewater treatment based, are in need of development from the industrial point of view. Organic waste concludes all matter that comes from plants or living organisms that are biodegradable. Organic matter requires treatment before it can be released into the nature. For example, in the wastewater treatment nutrients are removed from water to prevent eutrophication. European Comission definition for biomass is: “*organic material such as trees, plants, and agricultural and urban waste*”. (European Comission, 2017).

Biomass based wastes are found from industry and the amount of biomass based processes is increasing as industry is moving towards sustainable development. This brings new requirements and needs to industry. Processes always produce by-products or waste which in this situation contains high amount of organic matter. This is where hydrothermal carbonization is researched to see its possible applications and advantages in current situations. Hydrothermal carbonization can be used as wastewater treatment method for high organic content in water. The idea of this method is to utilize organic matter and transform it to matter that is easier to utilize further. In most cases the utilized product is biochar.

Process itself is simple and very stable since it works in autogenous pressure. This provides cheap treatment costs. The product, biochar, is quite homogenous despite the type of input biomass. Biochar has good logistic qualities since it is easy to recover and transfer. (Hernandez, 2015.)

Carbon content can be increased significantly making the matter easier to utilize in further processes. Biochar can be used in energy production, agricultural landfill and even as adsorbent. Biochar main focus have been co-firing technologies where coal can be substituted. Biomass can be utilized to substitute coal by co-firing technologies to increase sustainability in energy production. Biomass usually needs treatment before it can be utilized as source of energy or product. This thesis focuses to the hydrothermal carbonization which can be used to treat biomass in order to increase its compounds value. Hydrothermal carbonization does not produce pure carbon, but it significantly increases biomass composition quality which is important from its applications point of view.

2.2.1 Biochar as soil amendment

Biochar can be used as porous soil amendment which improves soil quality as it adsorbs nutrients. Biochar does have good adsorption properties due its high porosity. It adsorbs heavy metals and other toxic pollutants keeping plants safe. Besides that, it also adsorbs nitrate and phosphorus-based nutrients, so the nutrients will not be washed away from the soil which is illustrated in Figure 1. Biochar provides better utilization of fertilizers as nutrients stay at the surface of soil. These together lower the risk of eutrophication, which is a common risk in the river basins near agricultural areas, and lower the required amount of fertilizers needed. (Nirex, 2013)

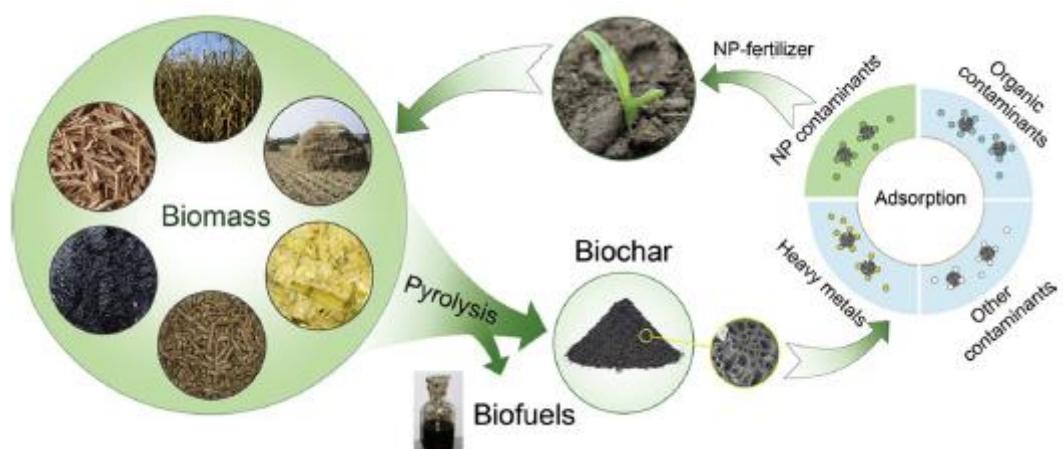


Figure 1. Simple cycle of biomass and possible uses of biochar (Xiaofei et al., 2015).

2.2.2 Biochar in water treatment

Biochar qualities, like large specific surface area, porous structure and surface functional groups, make it plausible low-cost solution for the pollutants removal from water. Chemical precipitation is a common water treatment method in the municipal water treatment. Downside of this method is formation of sludge, which requires disposal. Activated carbon is considered as an alternative option instead of conventional water treatment, however, it is still considered as an expensive method. (Mohan et al., 2014).

According to Mohan et al. (2014) biochar could be used to replace coal-, coconut shell-, and wood-based activated carbons. Biochar carbon content is less than in the activated carbon since it contains more hydrogen and oxygen functional groups due to the biomass structure. Hydrocarbons, organic matter and some inorganic metal ions can be adsorbed very well with biochars.

2.2.3 HTC in energy production

Coal is still most used option in electricity production worldwide. According to International Energy Agency 40% of global electricity production is from coal. Besides that, 46% of global CO₂ emissions comes from coal. CO₂ emissions from oil are currently 34% of the global CO₂ emissions. (IEA, 2016). Biomass can be used to substitute coal by co-firing technologies, which makes it interesting renewable source of energy. Biomass itself usually needs processing before utilization. Hydrothermal carbonization method is thoroughly introduced in Section 2.4. Even though the heating values are considered as the most important factors they are not in the main role in this thesis because the study of the carbon production rates and adsorption capabilities was the main task. That is why the discussion related to biomass use in the energy production is kept short.

Energy content of biomass is important factor in sustainable development. Renewable petroleum products can be manufactured from biomass. Biomass is renewable material where CO₂ emissions are absorbed via photosynthesis by the plants and it can be used for example as pellets for energy production. Biofuels are considered to be in the key role in

CO₂ emission reduction. Emission reduction also includes reduction in sulfur content during burning. Biomass in energy production already offers profitable production. In the future its share might increase as the fossil fuels price will increase. (Nizamuddin et al., 2017).

Carbohydrates energy contents can be calculated based on the chemical bonds of glucose and its products from the process. Titirici et al. (2007) has conducted comparison of energy and carbon exploitation schemes from carbohydrates between various processing methods. This is presented below in Figure 2. It contains combustion, fermentation, anaerobic digestion and hydrothermal carbonization methods.

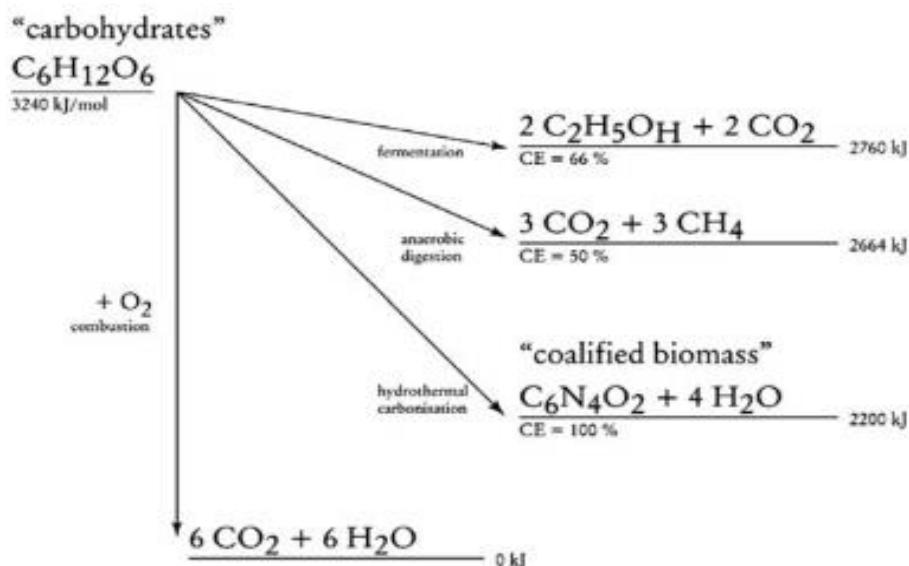


Figure 2. Various common carbon processing pathways with their stored combustion energy. CE refers to Carbon Efficiency which is calculated based of the ‘product carbons’ rate to side product carbons. (Titiriciti et al., 2007).

Hydrothermal carbonization has the best carbon efficiency because only side product is theoretically water. Carbohydrate in the form of glucose contains 3240 kJ/mol energy. During HTC one third of the energy is released via dehydration resulting 2200 kJ/mol stored combustion energy. Even though fermentation and anaerobic digestion has higher stored combustion energy hydrothermal carbonization could be considered more sustainable method because of the carbon efficiency. (Titiriciti et al., 2007).

Biomass can be used to produce various fuels. Possibilities varies from gases like hydrogen and methane to liquid fuels like biodiesel, fischer tropsch diesel, vegetable oil, ethanol, methanol, various biosynthetic oils and also solid fuels like biochar and hydrochar. (Nizamuddin et al., 2017).

2.3 Case UPM

As mentioned in Section 1.1 researched sludge types are, secondary sludge, primary and secondary sludge mix, grinded wooden crust, commercial BioPiva 100 powder and actual wastewater from the pulp & paper process. For the waste treatment UPM uses the activated sludge treatment process (Immonen, 2014). The process schematic is presented in Figure 3. to give better understanding of from where the researched sludge types were collected.

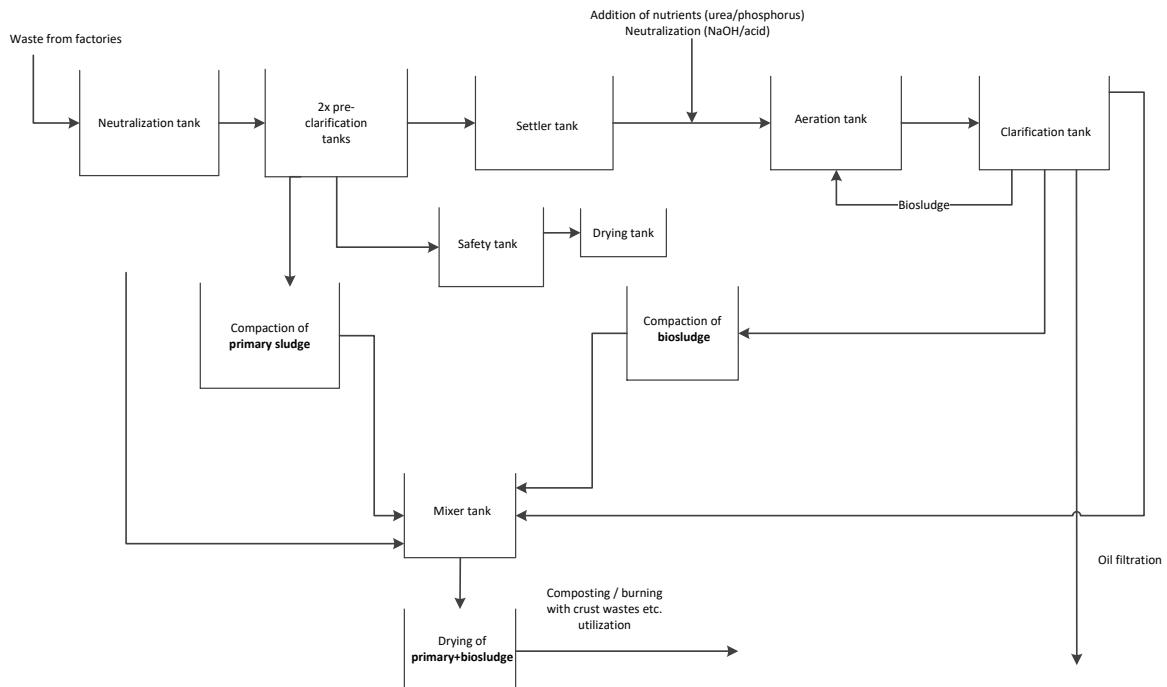


Figure 3. Schematic picture of UPM wastewater treatment process. (Immonen, 2014).

Waste streams from factories and sanitary water nearby are collected and neutralized with calcium oxide or sulfuric acid. Targeted pH for wastewater is 6-8. This is followed with pre-clarification where separated sludge is led to its own tank for compaction. Rest of the flow

is led to the settlement tank where nutrients, urea and phosphorus are added. The settler tank is made to control wastewater flow and quality. After settling, wastewater can be neutralized with sodium hydroxide or sulfuric acid. (Immonen, 2014).

After settling wastewater is led to the aeration tank where required nutrients, phosphorus and nitrogen, are added to assure microbiological treatment. Residence time of wastewater in aeration tank is one day. Afterwards wastewater is led to secondary settling tank for sedimentation. Sludge is formed to the bottom of the settling tank and most of it is recycled back to the aeration tank. Excessive sludge, *biosludge* in this thesis, is collected and led to compacting. The compacted primary and biosludge are led to the mixer. Combination of these sludges (bio- and primary sludge) is simplified and called as *primary sludge* in this thesis.

Wastewaters used in the laboratory experiments are collected before and after bleaching pulp. Also actual wastewater that goes to water treatment facility was collected. BioPiva 100 is purified kraft lignin powder manufactured by UPM. It was also tested with HTC treatment. (UPM Biochemicals, 2015). The grinded wooden crust is from UPM Pellos plywood mill. Sludge from the process does not have other uses than landfill. This is researched as plausible raw material for HTC treatment.

Considering UPM wastewater treatment process HTC could be applied to reduce amount of primary sludge and biosludge during the process. This would produce low-cost biochar, which is easier and more efficient to be utilized further while lowering amount of sludge that requires the conventional treatment.

2.4 Hydrothermal carbonization in pulp & paper mill streams

Usually hydrothermal treatment is linked to lignocellulosic biomass treatment (Borrega, 2015). Nearly 30% of wood contains lignin which cannot be utilized. This is why waste streams from pulp & paper processes usually contains high doses of lignin. Lignin is hard to separate from the wastewater but during the HTC treatment it is a good source of

hydrocarbons. Also, the waste streams contain a high volatile amount of water which is required in the HTC treatment. Therefore, the method can be utilized as low-cost depending on the used temperature that can vary a lot. For the biofuel production used temperatures are over 400°C, over the water critical temperature. For coalification used temperatures starts around 200°C in subcritical area of water.

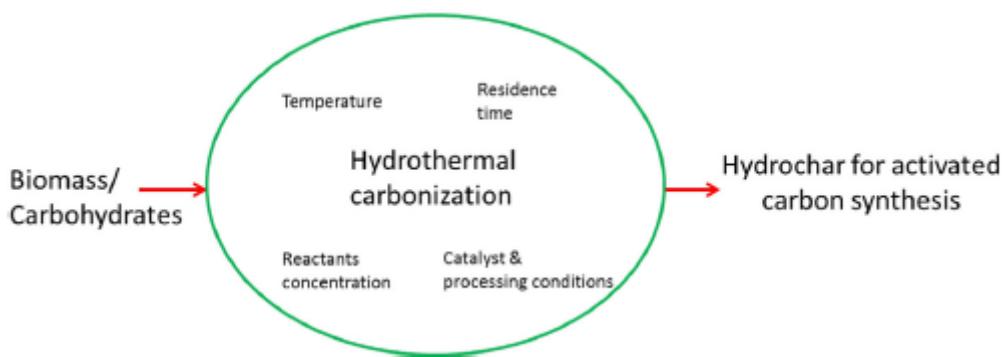


Figure 4. Most important factors in hydrothermal carbonization treatment (Jain, Balasubramanian & Srinivasan, 2015).

In order to research plausible adsorbent manufacturing methods, the focus in this thesis is on the temperature range of 180-250°C. A reason for this is on the other hand a request of the mild treatment from UPM but also the temperature needs to be high enough to start hydrolysis. In addition, cellulose starts breaking at 180°C so this is why 200°C is seen as the most suitable temperature to begin with. The reaction of hydrothermal carbonization is exothermal and the main factors of hydrolysis are dehydration and decarboxylation (Funke & Ziegler, 2009).

The products and their ratio are illustrated in Figure 5. Even though lignin does not degrade completely in the HTC process it is considered as a compelling source of carbon. The liquid fraction contains many water soluble organic compounds and therefore it has a very high TOC content as seen later in Section 7.6 in Table VII. The amount of gases is minor and was not researched in this thesis.

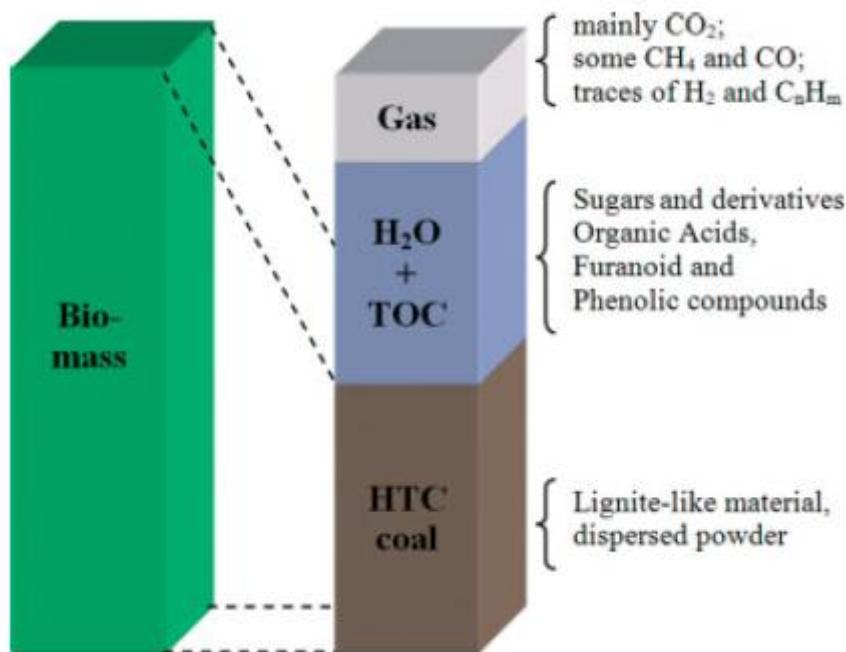


Figure 5. Ratio of products from HTC treated sludge (Funke & Ziegler, 2009).

Hydrothermal carbonization (HTC) is a mild yet effective process to convert biomass to carbon. HTC is similar to natural coalification where biomass is cleaved to carbon, oxygen, hydrogen and other compounds. To achieve carbonization, water and temperature (hydrothermal) are the crucial factors in the reaction. The reaction takes place in the enclosed space by autoclaves at 150-250°C degrees, which ensures that pressure will rise. The process can be cost-effective because there is no need for additional pumps and used temperatures are rather low. (Funke & Ziegler, 2009).

2.5 Current industrial applications

German company named SunCoal has patented HTC process, CarboREN, which homogenizes biomass to biocoal. Sources of biomass can be “green waste” from municipalities or organic waste from industrial processes. Products from process can be in form of granulate, powder or pellets. Plant design consists of totally automated loading and process is continuous. Biomass is crushed until particle size is <60 mm and during it impurities like sand and stones are removed. After this, leftovers from inorganic material are separated from biomass. In the feed the water content of biomass is 80% and it is pressurized

before entering the reactor. HTC is conducted in 200°C and 20 bars with few hour residence time. During the process the structure of biomass is decomposed and it separates from water which enables possibility of continuous process. Mechanical dehydration is used to reduce moisture content of slurry to 40-50%. Slurry is then thermally dried until <5% water content is achieved and cake is formed. (SunCoal, 2017).

AVA-CO₂ produces 8400 ton of biomass annually in Germany. Process design is batch process with two reactors where one reactor is used while another one is emptied. Both reactors have own flash tanks for cooling the product. HTC conditions are 220°C at 22 bar and heat is exchanged between the reactors. Liquid fraction is recycled in the process which allows carbon recovery up to 95% and as well as phosphorus recovery. AVA Biochem belongs to same concern where 5-HMF and 2,5-furandicarboxylic acid are recovered instead of carbon. (Avalon Industries, 2017, BusinessWire, 2010)

3 OTHER BIOMASS CONVERSION TECHNOLOGIES

Besides HTC, biomass can be converted by biological and thermal methods. Thermal conversion includes combustion, pyrolysis, liquefaction and gasification. At current state only thermal conversion methods are used in industrial applications to produce biochar for adsorption purposes. Biological conversion consists of anaerobic digestion and fermentation. (Mohan et al., 2014).

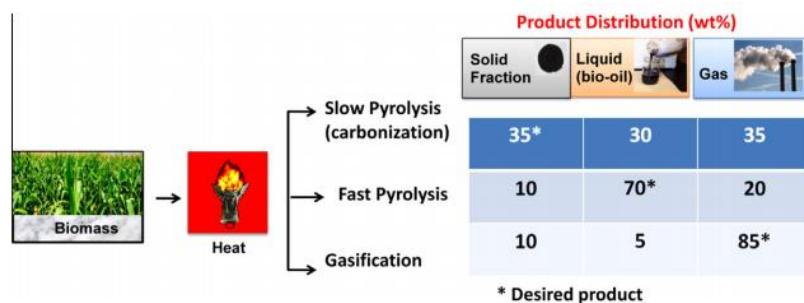


Figure 6. Three common biomass conversion technologies (Mohan et al., 2014).

Conventional or slow pyrolysis has been used over millenniums to create solid biochar. Biomass is heated under 500°C temperatures with absence of air. The heating rate is relatively small and reaction produces slowly solid carbon (char). Some fractions of liquids and gas are also produced by this method. State of fractions can be altered with temperature and residence time. Usually as temperature increases, yield of gaseous products increases. (Mohan et al., 2014).

When temperature is increased over 500°C degrees up to 1000°C, method is known as fast pyrolysis. Fast pyrolysis requires dry feedstock, which ensures fast heat transfer rate. Amount of oxygen fed to the process is very mild or none. The product formed is mostly liquid which reminds as oil and is often considered as bio-oil. (Mohan et al., 2014).

Biomass gasification is done with slightly higher temperatures than fast pyrolysis, but steam or air is fed into the process. This converts biomass to syngas in few seconds. Reaction rate is fast during combustion. Formed gas can be used on-site or purified for storage purposes.

Syngas is a mixture of hydrogen, carbon monoxide and carbon dioxide. With regulation of air reaction rate can be altered. (Mohan et al., 2014)

Biochemical conversion of biomass can produce various products, which usually are liquid fuels such as ethanol or biodiesel and gases (bio-syngas). Anaerobic digestion takes advantage of natural digestion, which occurs by the action of microorganisms. During this biomass decomposes to biogas and digestate that can be utilized for above mentioned products. Fermentation is a similar process as anaerobic digestion, but it occurs in a state where oxygen is not available. During this microorganisms consume biomass as source energy and convert biomass to products. (Zafar, 2018).

4 REACTIONS MECHANISMS AND PARAMETERS IN HTC

Reaction mechanism in the hydrothermal carbonization is exothermic reaction based on dehydration and decarboxylation. Water is acting as a solvent but also as catalyst that eases hydrolysis. Biomass is hydrolyzed to smaller components which form oligomers and monomers. Extracted products are eluted simultaneously and most of them are soluble with water. Therefore solute can contain many different compounds including carbon. However, reaction mechanism can be separated for few common phenomena that happens during the HTC treatment. These mechanisms are hydrolysis, dehydration, decarboxylation and polymerization. These are presented shortly below. Detailed breakdown of reaction mechanisms are discussed according to substances in HTC, meaning cellulose, lignin and hemicellulose reactions, which are the main components of the process in this case. (Funke & Ziegler, 2009). Reaction itself has been researched with a simple carbohydrate like glucose during the HTC treatment (Alatalo, 2016).

4.1 Hydrolysis

In general hydrolysis is a reaction where water reacts with substance and ends up into the product. Reaction releases energy and therefore is exothermic. Water molecules affect the compounds' anionic and cationic molecules creating a "cleaving" effect to the carbohydrate bonds. This breaks the bond leaving H₂O molecule to react with carbohydrate.

4.2 Dehydration

Dehydration means reaction where water is released, but chemical composition is not changed. This can be chemical reaction or physical process. Dehydration is important for coalification because it lowers the H/C and O/C ratios in the chemical compounds. (Funke & Ziegler, 2009).

4.3 Decarboxylation

In general, decarboxylation is a chemical reaction where carboxyl acid group reacts and it is replaced with hydrogen. When carboxyl group bond breaks carbon dioxide is formed. Exact decarboxylation mechanisms are still quite uncharted in HTC treatment especially with existence of water. Over 150°C carboxyl and carbonyl groups are degrading significantly which produces CO₂ and CO. Carbon dioxide is known to form more than other gases.

According to Funke & Ziegler (2009) increase of carbon dioxide can be explained by the elimination of carboxyl. This would mean that other mechanisms also participate in the process. Possible source of carbon dioxide is formic acid that is formed from cellulose during the HTC treatment. During hydrothermal conditions, formic acid also decomposes and produces carbon dioxide and water. Other sources can be CO₂ from the condensation reactions or cleavage of intramolecular bonds. Water could also operate as oxidizing agent but only when temperature is over 300°C. Then oxidized compounds could form carbon dioxide during thermal destruction.

4.4 Polymerization

Polymerization happens when monomers react together forming chain of polymers or three dimensional network. Polymerization requires energy for initiation. Monomers containing double bonds are most common for polymerization since after double bond breaks it forms enough free radicals that are active and monomers can react with each other.

4.5 Residence time

Residence time is important factor in HTC treatment. Higher residence keeps reaction stable and yields more HTC coal product. Polymerization, which is continuously happening during the treatment, is an important factor for creating coal. Small soluble compounds in the mixture precipitate with higher rate when the residence time is high, which explains the better yield. (Funke & Ziegler, 2009).

Apart from the reaction rate and yield, residence seem to be important factor in the cost-effectiveness. According to Funke & Ziegler (2009) some studies have noted that in some cases shorter HTC treatment time gives higher total value over increased residence time and therefore increased energy consumption. After all it is difficult to conclude which reaction mechanism determines the reaction rate. Diffusion in the biomass decomposition and condensation polymerization are probably the most important factors in the hydrothermal carbonization.

4.6 Temperature

According to Funke & Ziegler (2009) some kinetic models have been developed for HTC treatment which are often based on experimental data. Old model based on experiments is known as “rule-of-thumb” kinetic model which is presented below in equation (1). It is not systematically derived and it suggests HTC reactions to start at 170 °C even though it has been observed that first hydrothermal carbonization reactions are appearing at temperature 100°C.

$$P = t * 2^{\frac{(T-170)}{10}} \quad (1)$$

Where	P	reaction rate
	t	residence time
	T	temperature

Other model, equation (2), is based on the Arrhenius equation which is fitted for experimental data. Reaction rate is assumed as constant even though its dependent on pH and pressure.

$$P = 50 * t^{0.2} * e^{-\frac{3500}{T}} \quad (2)$$

Temperature is dominant parameter in HTC which can also be seen in both equations. It is still uncertain that can same carbonated material be obtained by altering residence time and

temperature with same reaction rate. Main influence of temperature is seen in the degradation of glucose whereas at 150°C it can take several hours and at 270°C dehydration can be achieved in few seconds. (Funke & Ziegler, 2009).

4.7 Pressure

Hydrothermal carbonization is done in the sealed autoclaves, which ensures the rising of pressure during heating. Pressure in reactor is isotropic because of water in the mixture. Solid particles are only affected by gravitational forces and convection during the heating in cases where stirrers are not used. Reaction pressure affects to the HTC treatment following LeChatelier's principle. At rising reaction pressure the equilibrium of reaction is moving towards liquid and solid phases when small molecules are reacted. (Funke & Ziegler, 2009).

It has been found that dehydration and decarboxylation reactions rate increases when pressure is increased. During lithostatic pressure, free space and solids density should be minimized. Effect is studied though its impact is quite small. (Funke & Ziegler, 2009).

4.8 Effect of pH

According to Funke & Ziegler (2009) many studies have noted that pH drops during the HTC reaction. It is proposed to arise from the formation of various organic acids. Identified acids are acetic, formic, lactic and levulinic acids. When considering sludge type adsorbents, acidic pH values are recommended. Adsorption efficiency is pH dependent to some extent (Alatalo, 2016). One benefit of acidic conditions is that it eases the hydrolysis of cellulose. Arrhenius acids catalyze the dehydration at high pH, which increases the liquefaction effect. Also, overall rate of reaction is improved with weak acids in the HTC treatment. Coalification in the nature is happening in the slightly acidic pH ranges. (Funke & Ziegler, 2009)

4.9 Loading

In this thesis loading refers to the ratio between biomass and water. The ratio is important factor in the hydrothermal treatment, for example biomass over surface of water does not carbonate. When amount of biomass is very low compared to water, biomass may dissolve completely leaving nearly zero residue. Doing the opposite leaves organic fractions as solid material during the treatment. It is known that higher concentration of glucose leads to higher concentration of solids precipitated during the HTC treatment. This increases the amount of monomers in the feed, which enhances polymerization. (Funke & Ziegler, 2009).

Residence time is somewhat dependent on the water/biomass ratio. However, when residence time is high enough, increasing biomass to water ratio does not increase monomers concentration in the liquid phase because solution equilibrium is obtained. Higher solid load increases concentrations, which speeds up the influence of polymerization which would then require lower residence time. (Funke & Ziegler, 2009).

When water is evaporated it can move the equilibrium towards the solid precipitation. Condensation of polymerization is increased, which increases the solid precipitation because of the removal of water in the process. Simultaneously higher solid load can change equilibrium because of the number of monomers in the solution that are relative to the amount of the feed used. This is due to the degradation of cellulose which is discussed in Section 5.4 cellulose. Another benefit is that during filtration, amount of wastewater is lower. This also lowers the loss of TOC amount, which can be considered as saved carbon (product). (Funke & Ziegler, 2009).

5 PULP AND PAPER PROCESS COMPOUNDS

Main components of the pulp and paper manufacturing process considering the HTC treatment are presented and discussed in this chapter. This contains short review about the tree types used by UPM in the pulp and paper processing and breakdown of the reactions of wood compounds. These compounds are cellulose, hemicellulose and lignin.

End-product, biochar, is powder like solid product that contains typically 60-70% of carbon after HTC treatment. Rest of it is mostly oxygen but also hydrogen. Other minor elements found are nitrogen and sulfur most likely from the waste treatment process.

5.1 Tree types used by UPM

Wood species in the industry are often divided to hard- and softwood. Hardwood trees are angiosperms trees, which means that their seeds are protected by casing. This generally consist most of the broad-leaved trees. Softwood trees belong gymnosperm group which means that their seeds are plain. Used softwood tree types in UPM Kaukas are spruce (*Picea abies*) and pine (*Pinus sylvestris*). Spruce and pine belong to the softwood category which covers most of the Pinophyta trees. The used hardwood tree by UPM is birch (*Betula*). (Kaukas, 2017)

UPM Kaukas Saha (saw) produces annually 510 000 m³ of pine and spruce timber. UPM Kaukas produces 740 000 t/a cellulose from spruce and birch. Cellulose from birch are most used for stickers, special papers and bio-composite material production. From ponophyta trees UPM manufactures 314 000 t/a MWC and LWC paper in a year. (Kaukas, 2017)

Difference between hardwood and softwood is mainly length of fibers in the trees. Wood composition varies a lot and this has its own effect in the hydrothermal treatment. Thorough reaction mechanisms are presented trough the main compounds.

5.2 Lignin

Lignin is one of the most abundant raw material that has many potential applications yet its use is problematic. Lignin is heterogeneous biopolymer that has complex structure which is why it is often burned as low-quality fuel. Pulp and paper industries produce 50 million tons of lignin annually as a side product that has great potential but low utilization. Depending on variety of trees they contain 20-35% of lignin in their wooden mass. (Chen & Wan, 2017).

Isolation of lignin is constant topic among the researchers. When considering pulp and paper industries, the key point is to separate lignin from cellulose and hemicellulose. Separation of lignin from its original sources is currently not possible without chemical modification. Most significant pulping processes are kraft and sulfite cooking. (Norgren & Edlund, 2014).

Currently two main methods are used in lignin separation. While lignin is kept as insoluble for mixture, cellulose and hemicellulose are hydrolyzed and solubilized. Alternative method is recovering lignin from liquor stream by dissolution. (Chen & Wan, 2017).

Lignin does not have defined primary structure or aromatic functionalities, which is why it is highly heterogenic. However, lignin has multiple identified repetitive compounds and it can be divided as polymerized composition of three monolignols; *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. (Norgren & Edlund, 2014). These monolignols are phytochemicals from biosynthesis of lignin and lignans. These monolignols are presented in Figure 7. (Chen & Wan, 2017).

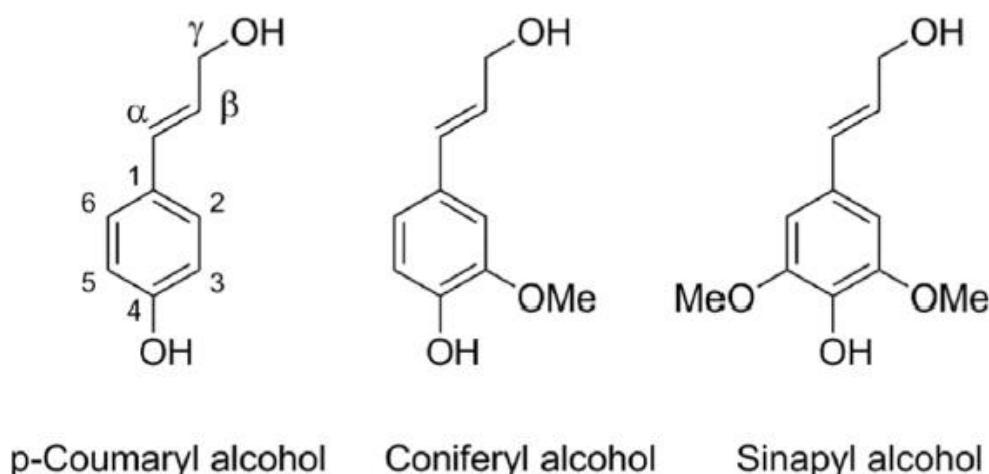


Figure 7. Most common monolignols in lignin. (Chen & Wan, 2017).

Because the lignin structure is complex, its products can be varied. Recent studies show that β -aryl ether (β -O-4) is the most common linkage in lignin. In the softwood half of the linkages are of this type. In the hard wood β -O-4-links incidence is around 60%. This is why the separation of lignin can be focused through linkages. β -O-4 linkages can be cleaved, as in organosolv lignin production, when lignin structure remains and product is pure. (Chen & Wan, 2017). Currently the HTC method is applied in the industry to process more valuable chemicals from lignin (Peterson et al., 2008).

5.3 Cellulose

Cellulose is the main component in the paper manufacturing process. Cellulose is long chained polysaccharide that consists of glucose compounds. These compounds are connected by glycosidic bonds known as b-(1-4)-glycosidic bond. Glycosidic bonds have strong intra- and intermolecular hydrogen bonds. Structure of cellulose is crystalline which makes it resistant to swelling in water. Hydrogen bond can be broken with HTC treatment at 180°C and upwards. This breaks crystalline structure and hydrolyzes the b-(1/4)-glycosidic bond resulting glucose monomers. However, it is impossible to predict completely how cellulose will behave during the HTC treatment. Cellulose can have different properties depending on its biological source. Properties can be affected by its physical and chemical structure. This is why degradation rates can vary a lot for cellulose. It

is noted that it can break down into the oligomers that some can hydrolyze and some cannot. (Peterson et al., 2008) Cellulose reaction mechanism is shown in Figure 8. and the detailed breakdown presented below.

According to Funke & Ziegler (2009) cellulose starts to degrade by following reaction (3):



Decarboxylation can only happen after water is forming. It is also noted that rate of dehydration is much higher than decarboxylation. This is explained by the elimination of hydroxyl groups. (Funke & Ziegler, 2009).

In hydrolysis water facilitates carbohydrates degradation. When water is autoionized, formed hydronium ions cleave to oxygen atoms and breaks the β -O-4 linkage in carbohydrates (Funke & Ziegler, 2009). This produces glucose but also various different oligomers like cellobiose, cellohexaose, cellopentaose, cellotetraose and cellotriose. These substances can isomerize to fructose. Decomposition of glucose and fructose creates monomers that can form various acids such as acetic, lactic, propenoic, levulinic and formic acids. This can be detected from the lowering pH during the HTC treatment. (Sevilla & Fuertes, 2009).

Formed oligomers are also hydrolyzed to monomers which follows dehydrating and fragmentation reactions. These reactions are also known as ring-opening polymerization. The products vary and are often soluble. Known products are 1,6-anhydroglucose, erythrose, various furfural-like compounds, 1,2,4-benzenetriol, acids and aldehydes. Decomposition of furfural-like compounds forms more acids and aldehydes, but also phenols. These can onwards polymerize or condensate. Simultaneously substances from the ring-opening are undergoing intramolecular dehydration and aldol condensation. The continuous dehydration reactions can create C=O groups while monomers are formatted. Also C=C bonds are plausible from keto-enol tautomerism or intramolecular dehydration. (Sevilla & Fuertes, 2009).

Aromatized substances can form clusters by the condensation. Concentration of aromatic clusters can reach critical supersaturation point when burst of nucleation happens. This makes molecules to grow towards surface due to diffusion. Molecules are then linked to the surface through reactive oxygen functionalities, like hydroxyl, carbonyl, carboxylic etc. groups. This makes quinone and ethers formation possible. Also this results that the surface of hydrochar contains high concentration of reactive oxygen groups. (Sevilla & Fuertes, 2009)

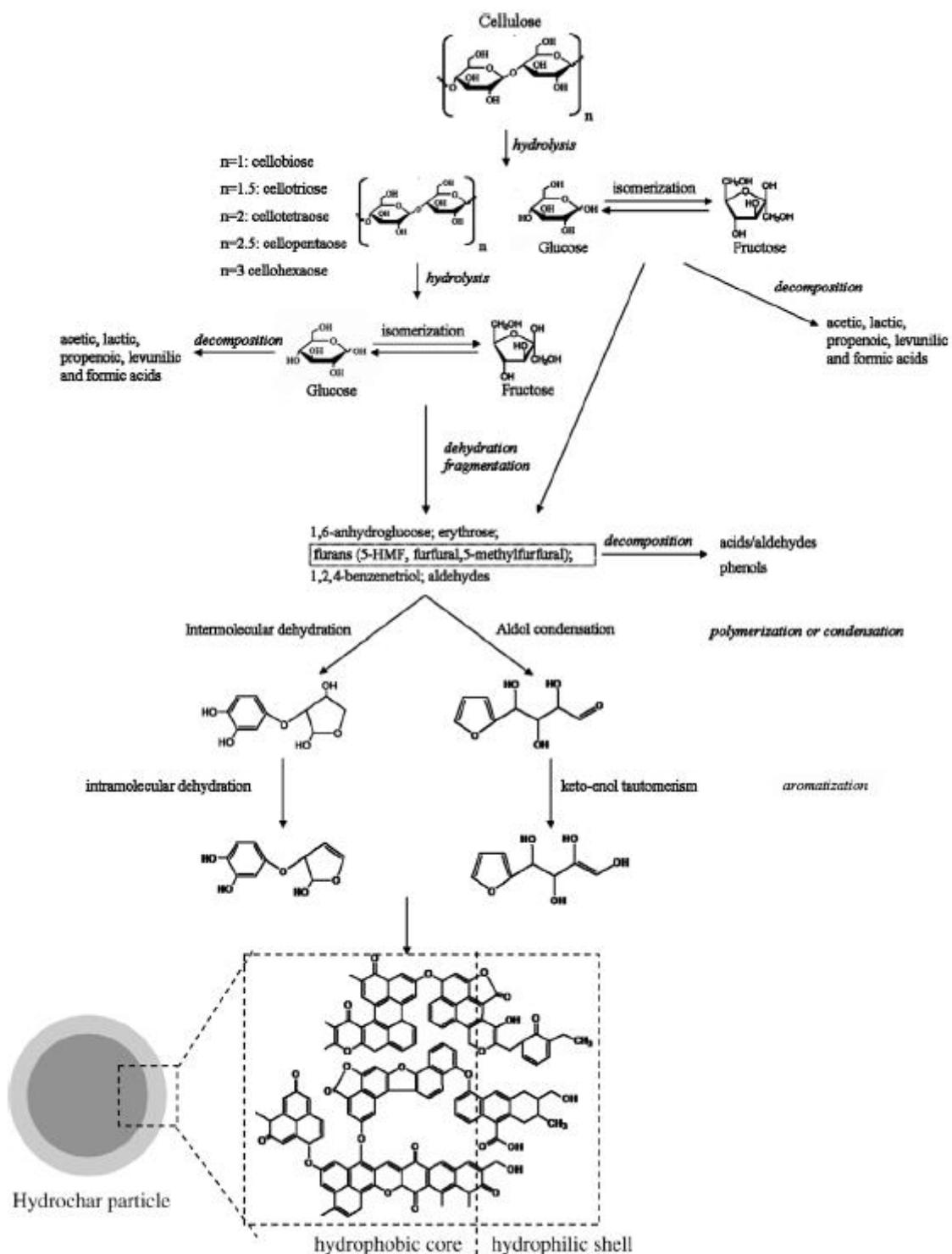


Figure 8. Formation and mechanism chain of cellulose carbonization.

5.4 Hemicellulose

Hemicellulose is a hetero-polysaccharide which is composed of sugar monomers including xylose, mannose, glucose, galactose. Amount of hemicellulose varies in wood but it is noted that a tree under physical stress has increased hemicellulose (D-galactose) content. Hemicellulose structure is typically $(C_5H_8O_4)_m$. Hemicellulose amount in biomass is typically 20-35 w-%. (Nizamuddin et al., 2017)

Hemicellulose is formed from D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid and D-galactopyranosyluronic acid and some minor other sugars (Nizamuddin et al., 2017).

Quantity of monomers can vary a lot depending on the biological source. Hemicellulose can include some other compounds that have side chains. Hemicellulose does not form crystalline structure like cellulose or lignin which is why it is more sensitive for hydrolysis and hydrothermal extraction. This is due to the lack of repeating $\beta-(1/4)$ -glycosidic bonds. (Peterson et al., 2008)

5.5 Other compounds

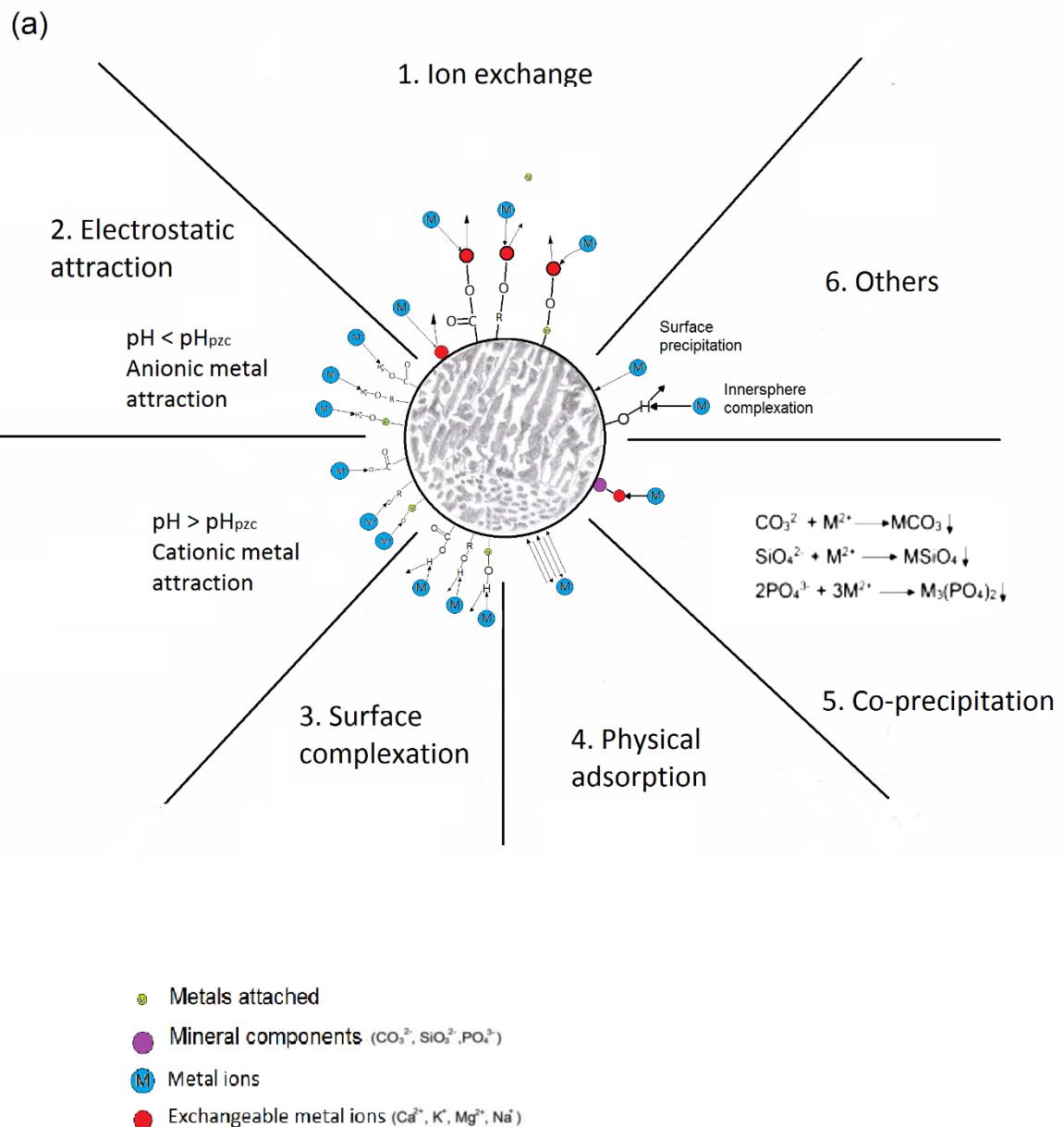
According to Nizamuddin et al. (2017) during hydrothermal conditions nitrogen in biomass is converted to N_2O . Phosphorus, chlorine and sulfur are oxidized and form their inorganic acids which are afterwards neutralized with addition of suitable base.

6 ADSORPTION

In the adsorption process matter is extracted from one phase and accumulated to the surface of another phase. Another phase, which acts as an adsorbing material, is called an adsorbent. Material that is adsorbed is adsorbate. Adsorption can be physical or chemical. (Repo, 2017)

In physical adsorption van der Waals interactions are significant. Also adsorbed molecules maintain their structure and they can form multiple layers. Process does not have activation energy and it is always reversible. In chemical adsorption adsorbent and adsorbate reacts among themselves and form chemical bonds between. This also changes molecules structure. Molecules are able to form only monolayers and reaction requires activation energy. Reactions can be irreversible depending on the reaction. (Repo, 2017)

The adsorption process begins with the diffusion of target compound (adsorbate) to the adsorbent surface. After this follows the migration of adsorbate into the pores of the adsorbent. When adsorption continues layers of adsorbate molecules are formed to the surface of the adsorbent. (Repo, 2017). Biochar has a large specific surface area, porous structure and it contains variable surface functional groups that make it promising substance to remove contaminants from the water with high efficiency. Biochar can be used to adsorb both heavy metals and organic pollutants. (Tan et al., 2014). Figure 9. shows the basic adsorption mechanisms that can occur on the surface on biocarbon and hydrocarbon as well. Various processes may happen simultaneously, which makes the detailed prediction of the surface reactions nearly impossible.



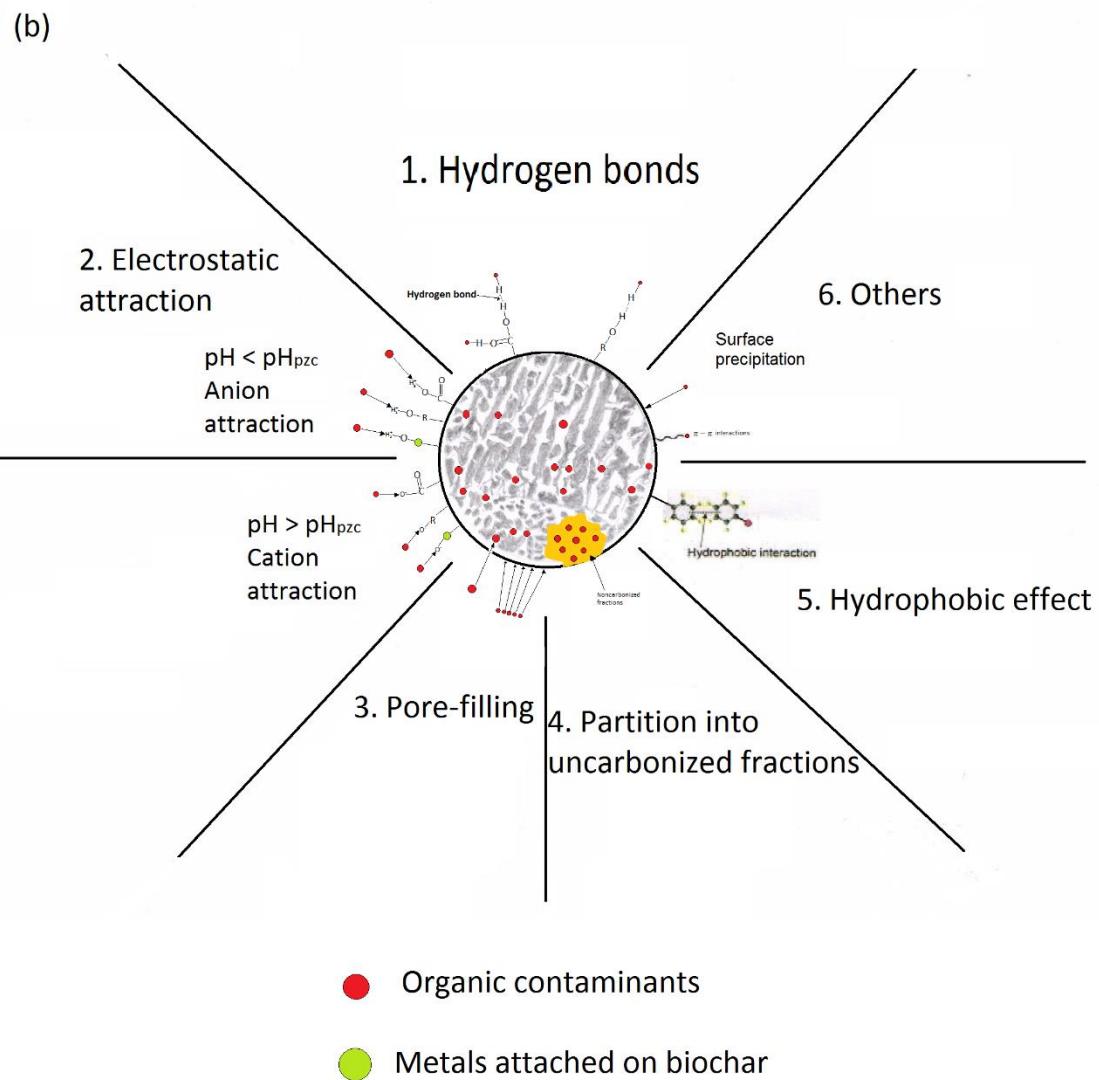


Figure 9. Possible adsorption mechanisms on the surface of biochar a) metal adsorption b) adsorption of organic contaminants (Modified from Tan et al., 2015).

The best way to compare the adsorption efficiencies of different carbon materials is to calculate their adsorption capacity or loading capacity as follows:

$$q_e = \frac{(C_i - C_e)}{m} V \quad (4)$$

Where	q_e	adsorption capacity at equilibrium
	C_i	initial adsorbate concentration
	C_e	adsorbate concentration at equilibrium
	m	mass of adsorbent
	V	volume of solution

The adsorption capacities of various carbonated materials are compared in Table I. Methylene blue is adsorbate which is considered as organic pollutant.

Table I. Hydrothermally carbonated materials adsorption performance. AC refers to activated carbon. References are from a) Alatalo, 2016, b) Xiaofei et al., 2015.

Feedstock	Hydrothermal temperature °C	Residence time	Synthesis information	q_e (mg/g)	Ref.
Palm date seed AC	200	5 h	NaOH activation	612	a
Hazelnut shell hydrochar	250	7.5 h	ZnCl ₂ activation 850°C	52	a
FruLi	180	16 h	Presence of salt	83	a
Eucalyptus	400	30 min		2.06	b
Kenaf fiber	1000	-	Pyrolysis	18.18	b
Palm bark	400	30 min		2.66	b

Adsorption capacity of few selected HTC-treated carbonates ranges between 2-80 mg/g, which is common range for them. Carbonated materials can be enhanced by activation for example using acids, but this requires processing. Activated carbons have higher adsorption capacity as it can be seen from carbonated palm date seeds. When comparing these adsorption capacities, it can be said that HTC-treatment is a promising technology in order to prepare novel adsorbents from biomass. Carbonated materials can be used for example in-situ water treatment applications.

7 EXPERIMENTAL PART AND RESULTS

This chapter contains detailed information of experiments that has been done during this project. Optimizing ranges of temperature and time during HTC treatment of each sludge type was important to recognize behavior and possibilities for further treatment. Sludge types were different from each other and therefore had various features. Therefore characterization of HTC treated sludge was highly important.

7.1 Hydrothermal carbonization

Various sludge types and materials which were mentioned in Section 1.1 were treated hydrothermally. Biosludge was already in firm liquid state and didn't require addition of water. For the other materials added water amount is mentioned in Table II. Sludge samples were placed to the reactors, which was sealed. Sizes of reactors were 200 mL. Reactors itself were placed in the autoclaves, which were sealed tight and autoclaves were placed in the oven at 150-260°C for 1-10 hours.

After hydrothermal carbonization solid fractions of products was filtrated three times with 50 ml volume of pure water. Products were then dried in the oven at 60°C for 5 hours. After drying carbonized materials were grinded as small as possible. The samples were stored in glass vials.

Sludge types differs from each other so much that various temperatures and retention times were required for optimization. According to Funke & Ziegler (2009) reactions need minimum 100°C degrees of temperature. However, to start substantial hydrolysis requires around 180°C degrees temperature. Table II contains information about the tested temperatures and retention times.

Table II. HTC conditions used for different sludge types.

Sludge type	Amount	Temperature [C]	Time [h]	Added water [ml]	Drying time [h]
Bio sludge	200 mL	200	10	-	5
Biosludge	200 mL	150	6	-	5
Biosludge	200 mL	200	5	-	5
Primary sludge	30 g	200	10	30	5
Primary sludge	30 g	200	15	60	5
Primary sludge	30 g	200	10	60	5
Primary sludge	30 g	200	10	30	5
Primary sludge	30 g	200	10	45	5
Primary sludge	30 g	200	10	60	5
Biosludge	100 mL	200	10	-	5
Biosludge	100 mL	200	5	-	5
Biosludge	200 mL	150	10	-	
BioPiva 100	25 g	200	10	25	5
BioPiva 100	20 g	150	5	40 mL	
BioPiva 100	20 g	150	10	40 mL	

To see difference between carbonated sludges after doing HTC treatment at higher temperatures, a series of HTC treatments was done for one sludge type at higher temperatures. Most promising one, biosludge, were used in this test. Temperatures that were used were 200, 220, 240 and 260°C and the effect of the washing procedure was tested. Adsorption and BET analysis were also performed to these samples.

Table III. HTC treatment parameters for sludge types used in adsorption isotherm and BET analysis.

Sludge type	Treatment notes	Temperature [C]	Time [h]	Drying time [h]
Biosludge		200	10	5
Biosludge		220	10	5
Biosludge		240	10	5
Biosludge		260	1	5
Biosludge		260	2	5
Biosludge		260	5	5
Biosludge	Carefully washed multiple times	200	5	5
Biosludge	Washed with 50% ethanol	200	10	5
Primary		200	10	5
BioPiva 100		200	10	5
Wooden Crust		200	10	5

7.2 Initial adsorption studies

Methylene blue (MB), which is an organic dye, is used as an indicator in the evaluation of activated carbon as adsorbent. In the solid form it is dark green powder or crystals but when it is in aqueous solution it dissociates to MB^+ cation and chloride ion. This solute strongly reflects blue color. (Qada, Allen & Walker. 2006). Methylene blue is slightly acidic and therefore works as cation.

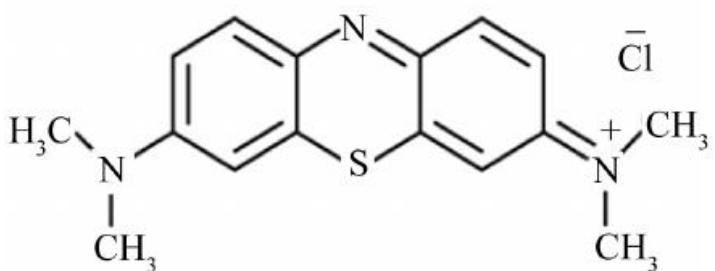


Figure 10. Structure of methylene blue. (Elmorsi, 2011)

Adsorption isotherms were made by batch experiments where 10 mg of adsorbents (carbonized sludge) were measured with 5 mL of water with a specified concentration of pollutant (methylene blue). These samples were held in a shaker for multiple hours until carbon was dispersed into the solution. In some cases heat was derived to the mixture to ease carbon dispersion. In addition, sample tubes were covered with foil to avoid methylene blue degradation with light. At the beginning, adsorbents were tested with 5, 10, 20, 40 and 60 ppm methylene blue concentrations or until MB was not adsorbed anymore. Carbon adsorbents were separated from the solution by filtering with $45\mu\text{m}$ polypropylene membrane filters connected to 10 mL syringes where mixtures were poured. Some residues of the carbon were seen in the measured filtrate in UV-vis spectrum.

The results of the first adsorption tests are presented in the Figure 11. Peak of lignin can be seen at ~ 280 nm and 200-250 nm peaks contain small carbohydrates and carbon. At 664 nm the peak of methylene blue can be observed. It should be noted that adsorption of methylene blue is dependent on the pH value of the solution. Effect of pH is more specifically discussed in Section 4.8.

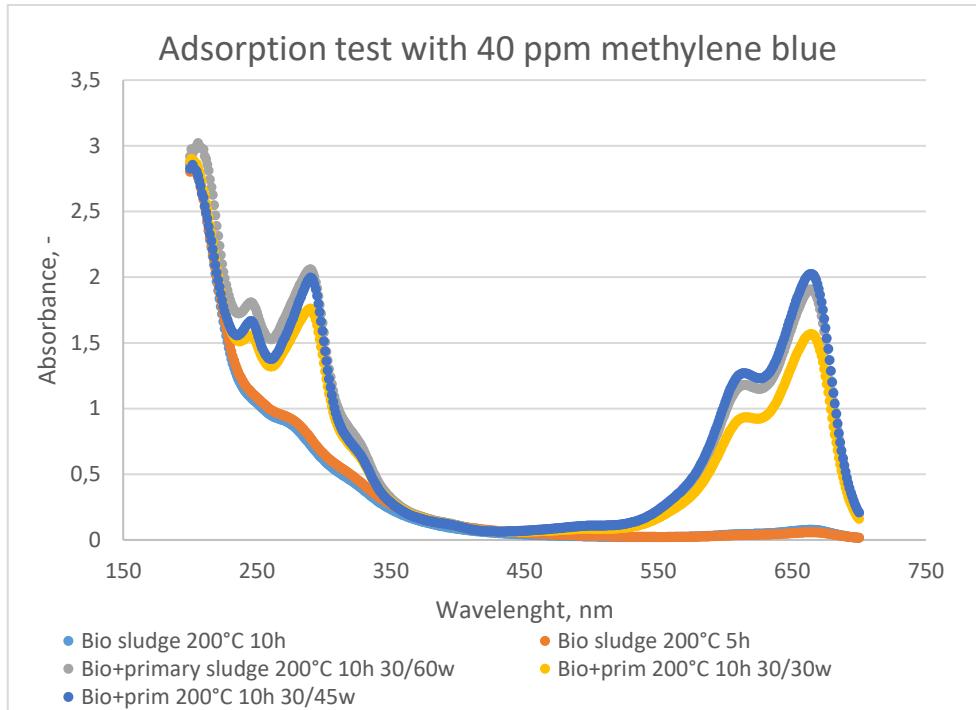


Figure 11. UV-VIS results after adsorption tests with 40 ppm methylene blue. Carbonized sludges are presented in the form of type, temperature, treatment time and mass/water rate in grams.

Typical UV spectra after adsorption tests are shown in Figures 11-12. Biosludges after 200°C HTC treatment adsorbed nearly all of the 40-ppm methylene blue and also MB with concentration of 60 ppm very well (Figure 12). However, primary sludge did not adsorb that much. Primary sludges' difference in adsorption between 45 grams and 60 grams of added water is quite small. However, 30/30 ratio did not seem to have enough water compared to other primary sludge tests.

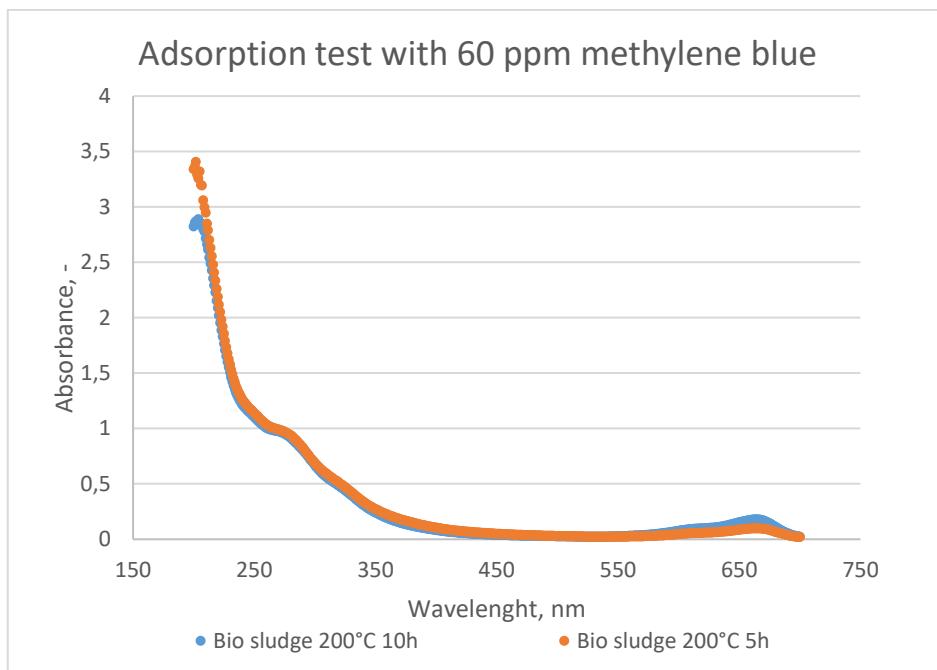


Figure 12. Adsorption analysis with MB concentration of 60 ppm.

7.3 Adsorption isotherms of carbonated sludges

Determining the loading capacities of the produced sludge-based carbons is the best way to compare the adsorption efficiencies of these novel materials. For these tests 10 mg of carbonated samples were measured to small tubes with 5 ml of methylene blue with various concentrations. Used methylene blue concentrations were 5, 10, 20, 40, 60, 80, 100, 120, 140 and 160 ppm depending on the estimated maximum loading values. In some cases carbonated materials required more grinding to achieve better homogenous powder. However, for example BioPiva 100 generated a tough surfaces, which were difficult to grind.

UV-VIS was used to scan absorbance between 660-680 nm to identify highest point of methylene blue peak and to calculate its concentration. Measured results are shown as points in adsorption isotherms presented below in Figures 13 and 14. Sips isotherm, which is based on Langmuir and Freundlich isotherms, is used to model adsorption capacity especially because it is suitable model for the heterogeneous adsorption processes. Model parameters can be used to describe the heterogeneity of the carbonated material.

According to Repo (2017) the Sips isotherm is presented by the following equation (5):

$$q_e = \frac{q_m(K_S C_e)^{n_s}}{1 + (K_S C_e)^{n_s}} \quad (5)$$

Where

q_m	modelled loading capacity
K_S	affinity constant
n_s	describes heterogeneity of surface

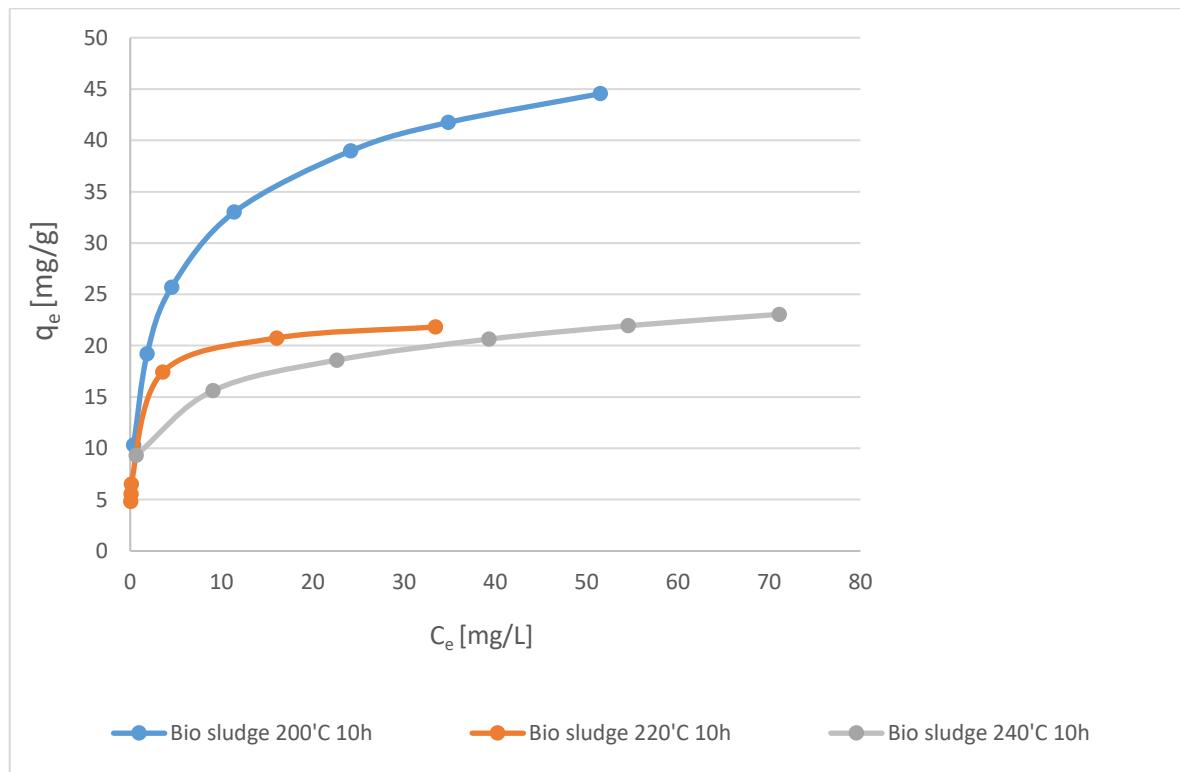


Figure 13. HTC treated biosludge loading capacity results. HTC conditions were 200, 220, 240 and degrees with 10 hour residence time.

As seen from Figure 13, the increasing temperature in the HTC treatment made the obtained carbon material less attractive for MB adsorption indicating that the proper functionalities are formed on the surface at relatively mild HTC conditions.

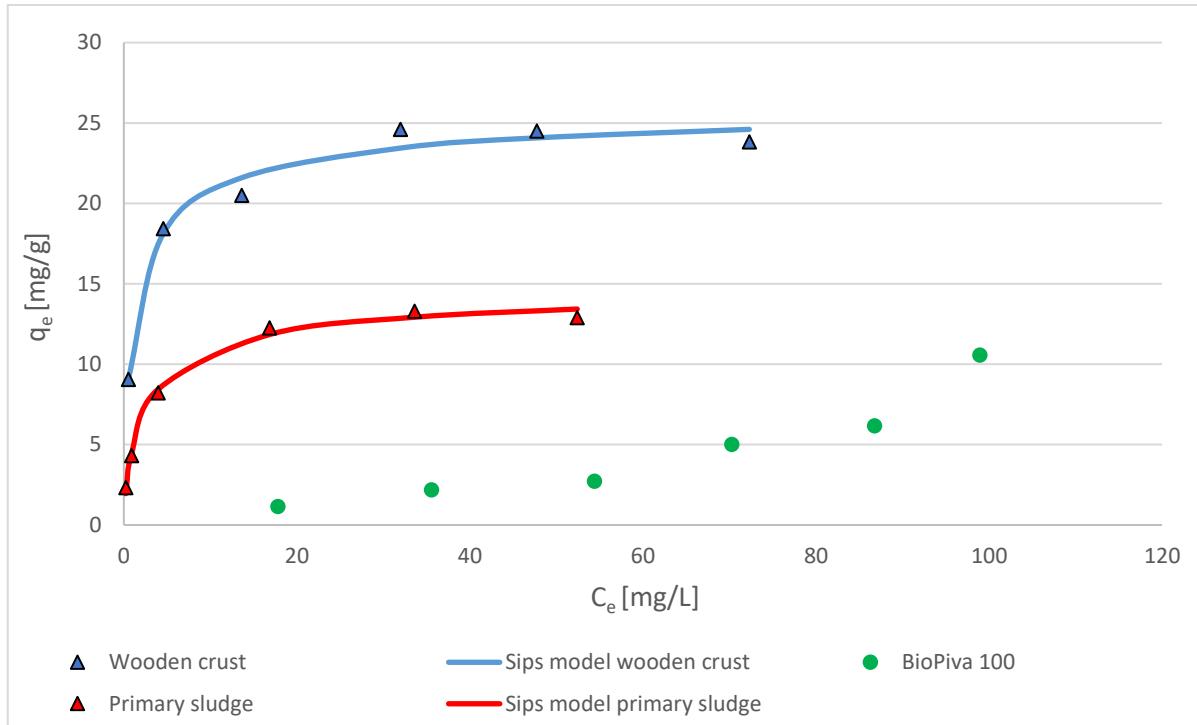


Figure 14. HTC treated primary sludge, wooden crust and BioPiva 100 loading capacity results. HTC conditions were 200°C degrees with 10 hour residence time.

Figure 14. shows that the adsorption capacities of the other sludge based carbon materials tested were not as good as in the case of biosludge. Carbonization of the biosludge clearly produced more attractive surface towards MB adsorption, which will be discussed more detailed during the next sections. The HTC treated BioPiva 100 did not perform well in the adsorption tests and the results were very inaccurate. Increasing adsorption capacity during increasing concentrations is discussed also later in this thesis.

A series of isotherm tests were done for the biosludges treated at 260°C with various treatment times which are presented in Figure 15. Treatment times were 1, 2 and 5 hours. Loading capacity results of HTC treated biosludge at 260°C for one hour were surprisingly high and the maximum capacity was around 60 mg/g. For 2 hour treatment the maximum loading capacity was around 35 mg/g and for the 5 hour treatment only around 16.5 mg/g.

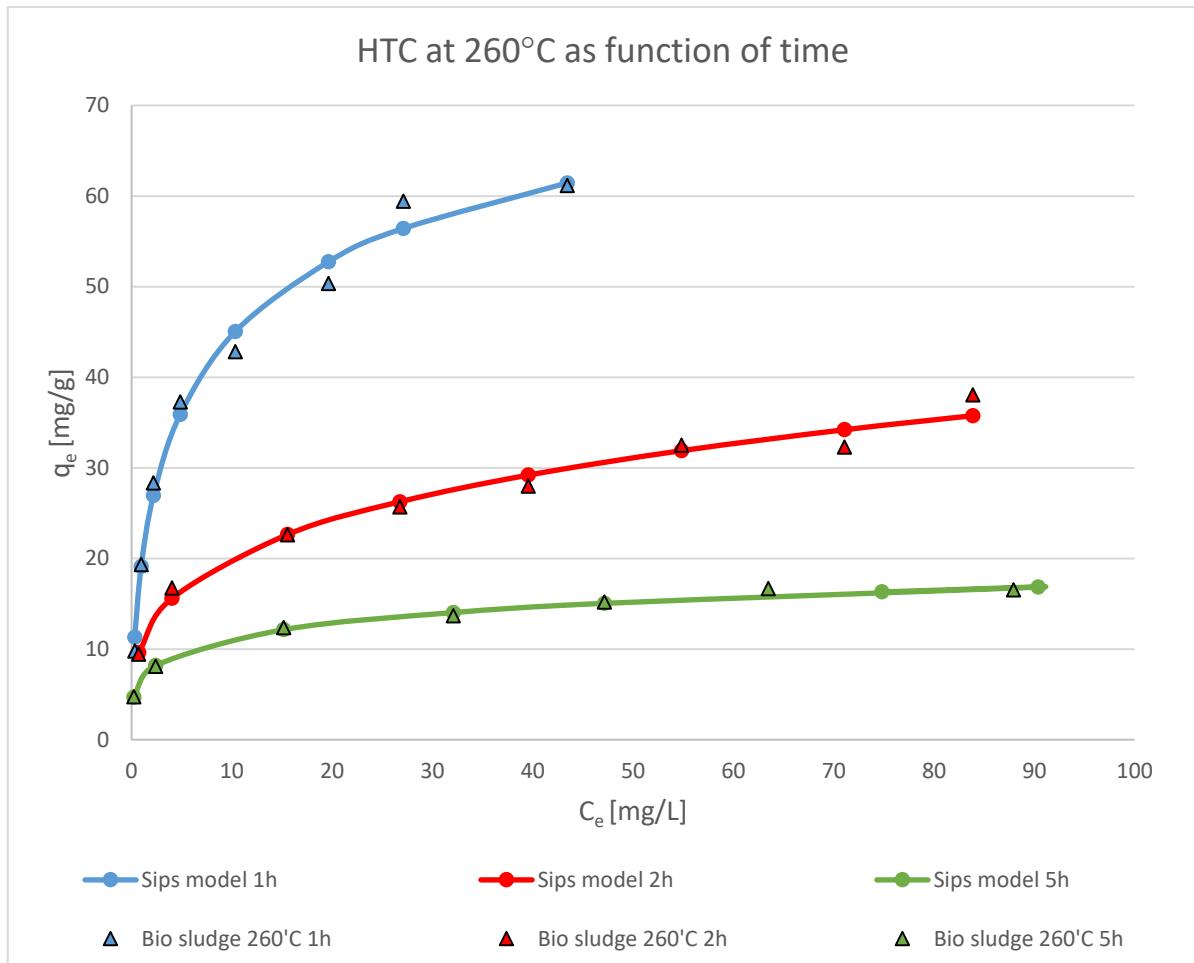


Figure 15. Hydrothermal carbonization of biosludge at 260°C where residence time is changed.

Some of the loading capacity results did not seem to achieve the equilibrium plateau and therefore the maximum loading capacity is difficult to determine. This may be due to incomplete equilibrium even though mixing was done overnight (12 hours or more) or most likely due to pH. During the loading capacity tests pH was not adjusted and this can affect to carbons' adsorption properties. When the methylene blue concentration is increased the pH of the solute decreases and this can increase the adsorption capacity. This affects to equilibrium balance and changes it towards higher loading capacity when maximum loading capacity is not completely achieved. However, results of loading capacities are greatly different from each other and therefore provide a great knowledge how the adsorption capacity is changing as a function of HTC temperature, resident time, and the type of the raw material.

7.3.1 Effect of washing

Washing of carbonated material during the filtration was researched to see if it has effect on the adsorption properties. “Well washed biosludge” was washed slowly while mixing it five times with 50 mL of pure water. Its hydrothermal treatment conditions were 5 hours in oven at 200°C. Another HTC biosludge was washed with 50% ethanol for several times. These results were compared to carbonated biosludge, which was treated for 10 hours at 200°C.

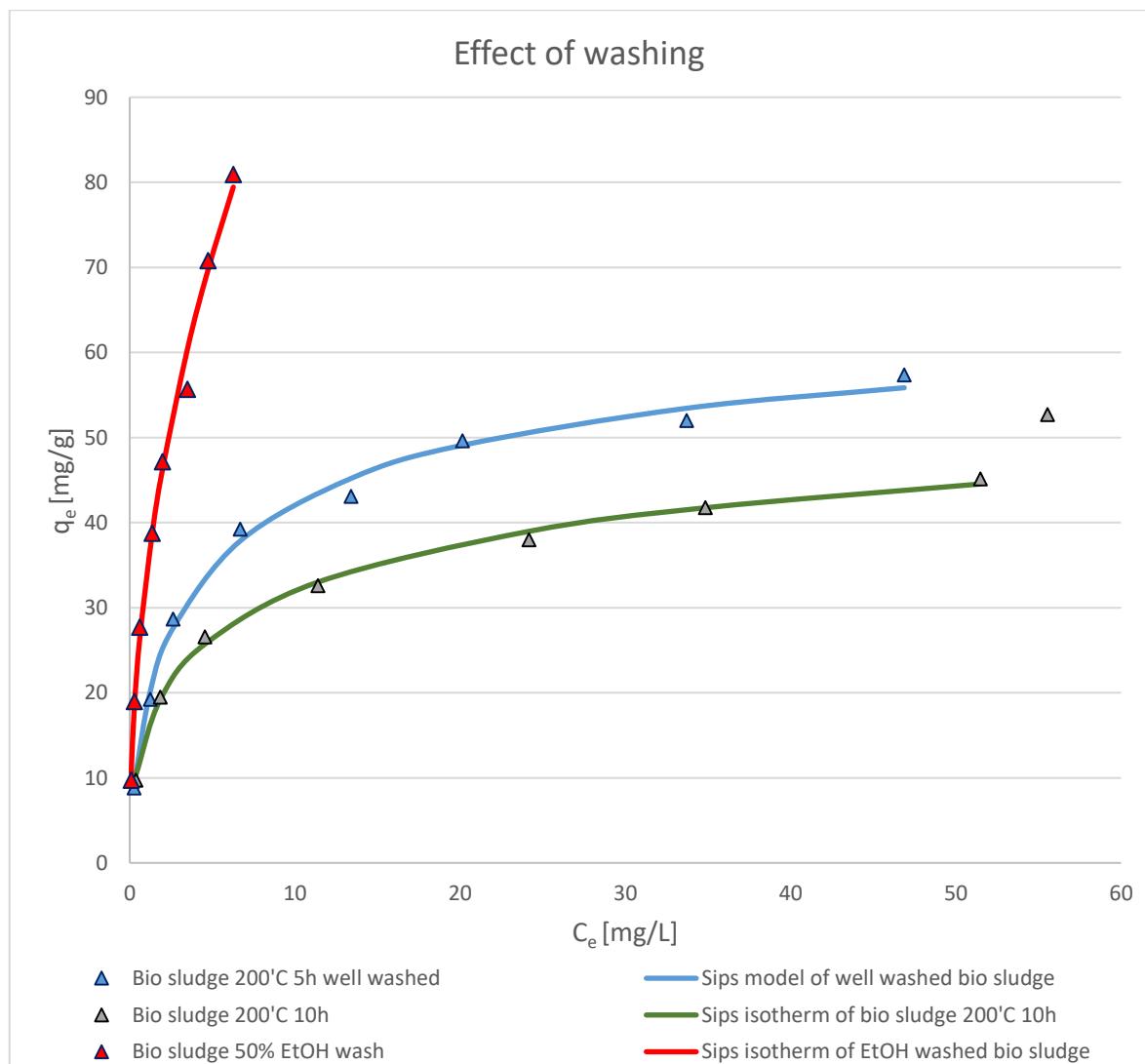


Figure 16. Biosludge was treated at 200°C for 10 or 5 hours. The carbon with 5 hour treatment was washed carefully using only water and with 10 hour treatment with 50% ethanol. These are compared to biosludge carbonized in 200°C for 10 hours.

Results shown in Figure 16. indicate clearly that washing with ethanol increases significantly the adsorption capacity. Ethanol can also remove small molecules and impurities from the carbon surface pores. Increasing “pore size” leaves more available pores for adsorption to occur. Ethanol also has activating surface properties where surface polarity of carbon molecules is increased and therefore carbon adsorption is increased. Maximum adsorption capacity for ethanol washed biosludge cannot be determined since it outranged all the other tested carbonated materials, but it was clearly over 80 mg/g. Interestingly, the well washed carbon performed better in the adsorption tests than in the same temperature treated biosludge even though it had lower treatment time. It was noted that adsorption capacity is lowering as treatment time is increasing and this is most likely due to same phenomena.

The Sips isotherm parameters are gathered in table below. As K_s is very small and most cases nearly zero, isotherm is basically reduced to the Freundlich isotherm meaning on the other hand highly heterogeneous surface processes seen also from the n_s values far from unity, and the shapes of the obtained isotherms not reaching the plateau.

Table IV. Sips isotherm parameters compiled from each modelled adsorption capacity experiment (q_m [mg/g], K_s [L/mg]).

Sludge type	Biosludge 200°C 10h	Biosludge 220°C 10h	Biosludge 240°C 10h	Biosludge 260°C 1h	Biosludge 260°C 2h	Biosludge 260°C 5h
q_m	64.90	24.40	233.39	86.93	654.11	40.82
K_s	0.09	1.50	0.00	0.11	0.00	0.00
n_s	0.50	0.55	0.21	0.56	0.28	0.28
Sludge type	Biosludge 200°C 5h water wash	Biosludge 200°C 10h ethanol wash	Wooden crust 200°C 10h	BioPiva 100200°C 3h	Primary sludge 200°C 10h	
q_m	69.07	3336.73	26.48	199.79	14.91	
K_s	0.20	0.00	0.72	0.00	0.36	
n_s	0.64	0.48	0.65	2.02	0.75	

7.4 BET analysis

Surface area and porosity analysis was done with Micrometrics TriStar II PLUS analysis device which is based on the Brunauer-Emmett-Teller theory. Sludge samples were degasified at 150°C for 5 hours after which the samples were given half an hour time to cool down before measuring their exact masses. Analysis were performed with 77.35 K bath temperature. The results are shown in Table V.

Table V. BET analysis of HTC treated sludge samples sludge samples.

Sludge sample	Temperature used in HTC treatment [°C]	Time used in HTC treatment [h]	BET Surface Area [m ² /g]	Average pore diameter [Å]
Biosludge	150	10	15.025	130.4
Biosludge	150	5	7.953	84.9
Biosludge	200	10	31.074	113.3
Biosludge	200	10	27.550	108.2
Biosludge	220	10	26.667	103.3
Biosludge	240	10	21.320	95.0
Biosludge	260	1	29.751	117.6
Biosludge	260	2	18.860	96.3
Biosludge	260	5	13.373	82.6
Biosludge 50% ethanol wash	200	10	40.673	116.9
Biosludge thorough wash with water	200	10	34.490	114.6
Primary sludge	200	10	7.9893	85.0
Primary sludge	200	10	33.3756	109.3
Primary sludge	200	10	6.313	87.1
Wooden crust	200	10	7.088	147.4
BioPiva 100	200	10	NAN	-

From Table V it can be noted that washing with 50% ethanol significantly increased the surface area. Washing thoroughly with water also increased the surface area when compared to other 200°C and 10 hour treated sludge samples. Besides increasing the surface area ethanol washing supposedly activated the surface molecules in carbon and therefore increased its adsorption capacity. Biosludge in overall gave the best surface area results compared to other carbonated materials. It seems that the surface area decreases as temperature increases while treatment time is short (1 hour). This can be seen in between the sets of carbonized biosludge with temperatures of 200, 220 and 260. The same phenomenon is seen when comparing results at the temperature of 260. Treatment durations were 1, 2 and 5 hours and surface area also lowered when the treatment time was increased.

Some variations in the results can be seen for example biosludge at 200°C for 10 hour treatment had 31.07 m²/g and 27.55 m²/g measured surface areas. This is quite common phenomena because biomass is not completely homogenous mixture.

Guangzhi et al. (2017) did experiments by producing carbon from camphor leaves with HTC at various temperatures between 180-300°C. Even though they researched CO₂ adsorption properties with sequential potassium hydroxide activation, they had similar findings as in this research project. Their BET surface area was increasing between 180-240°C as the temperature increased. After 240°C till 300°C the surface area lowered while temperature was increased. They explained phenomenon by different fractions of carbons in the solid-phase.

7.5 CHNS-O elemental analysis

Each HTC treated sludge type was analyzed by Thermo Scientific FLASH 2000 Elemental Analyzer CHNS-O analysis device. For determining carbon, hydrogen and nitrogen, 2.0 ± 0.4 mg of each sample was carefully balanced to a small tin foil. Measurements were done with Mettler Toledo XP6 micro balance. The samples were the same as used in the maximum loading capacity tests.

Table VI. CHNS-O-analysis results compiled. Nitrogen, carbon, hydrogen, sulphur and oxygen contents are presented as mass percentages.

Sludge sample	HTC circumstances	Nitrogen [%]	Carbon [%]	Hydrogen [%]	Sulphur [%]	Oxygen [%]
Biosludge	200°C, 10h	2.377	54.379	5.434	0.484	22.428
Biosludge	220°C, 10h	1.966	55.264	5.306	0.399	19.493
Biosludge	240°C, 10h	1.952	57.182	5.419	0.686	17.678
Biosludge	260°C, 1h	2.425	48.213	5.145	0.512	22.002
Biosludge	260°C, 2h	2.004	55.455	5.403	0.442	17.604
Biosludge	260°C, 5h	1.934	57.125	5.351	0.430	22.225
Biosludge	200°C, 5h Well washed	1.875	47.910	4.862	0.574	22.667
Biosludge	200°C, 10h 50% ethanol washing	2.062	52.848	5.369	0.743	28.423
Primary	200°C, 10h	1.832	45.292	4.942	0.148	28.432
Wooden crust	200°C, 10h	0.495	60.619	6.088	0.000	28.874
BioPiva 100	200°C, 3h	0.000	63.667	5.620	0.962	26.349

CHNS-O-analysis results are shown in Table VI. HTC treatment can be considered as a great treatment method since carbon w-% is high for all the sludge types. Increasing rate of carbon can be seen when the time and/or temperature is increased. At temperature of 260°C there is significant difference in carbon % between 1 hour and 2 hour treatment. When 5 hour treatment is taken into account carbon amount is still increasing yet carbon growth rate is decreasing which is a common phenomenon in the chemical reactions as reaction is moving towards equilibrium state. Between one and two hour treatment the carbon content increase was 7% while the difference in two and five hour treatment was 2%. Carbon mass increased as the used temperature increased. This can be seen in the biosludge series with 10 hour treatments when used temperatures were 200, 220 and 240. Difference in carbon w-% was

only few percentages, which is due to high reaction time. However, effect of temperature is still clear.

50% ethanol washed biosludge gave the best results in the adsorption tests. However, its carbon percentage is smaller than similarly treated carbonated materials but washed only with water. This is due to the properties of ethanol. Ethanol most likely activates the surface molecules and therefore creates more adsorption sites for MB. Washing does not seem to have impact on the elemental composition since well washed biosludge has the lowest carbon content. However, the well washed biosludge's treatment time was 5 hours so its carbon content is supposedly lowest. Also, it can be said that the adsorption capacity is not completely dependent on the carbon amount but rather influenced by surface functionalities and specific surface area.

The amount of nitrogen decreased as the time increased due to the nitrogen evaporation and transfer to the solution. All the sludge samples except wooden crust contained sulfur. This is most likely due to sludge treating process in UPM, which is presented in Section 2.3. Biosludge is neutralized by sulfuric acid if the solution is alkaline. Wooden crust and BioPiva 100 contained highest amounts of carbon after treatments, which is interesting. These substances were not that great in adsorption, but considering their compositions these could be viable in energy production.

7.6 TOC and COD analysis

TOC (Total organic carbon) and COD (Chemical oxygen demand) analysis were done for the liquid phases of sludges and for the wastewater samples. After HTC treatment sludges were filtrated and water phases were collected. HTC treatment parameters used for sludge treatments prior to TOC and COD analysis are shown in Table VII below. Wastewater samples were not treated in anyway except dilution. Used wastewater samples were alkali-, acidic- and refinery wastewater, which sources were discussed in Section 2.3.

Table VII. HTC treatment parameters for samples used in TOC and COD analysis.

Sludge sample	Temperature	Time	Sample size	Added water
Biosludge	200 °C	10 hour	200 mL	-
Primary sludge	200 °C	10 hour	25 g	Water 30 mL
Wooden crust	200 °C	10 hour	10 g	Water 40 mL
BioPiva 100	200 °C	1.5 hour	15 g	Water 40 mL

COD analysis were done by using HACH Lange LCK514 Chemical Oxygen Demand cuvettes. COD range of cuvettes were 100 – 2000 mg/L, therefore 1/20 dilutions were done for the samples. 2 ml of diluted samples were measured to cuvettes and treated 15 minutes in 170°C in HT200S High temperature thermostat. After cooling samples were shaken and measured in HACH Lange spectroscopy. Results of these tests are shown below in Table VIII.

Calibration curves for IC (inorganic carbon) and TC (Total Carbon) were made by calibration grade reagents. Range of TOC with this device was 1-100 mg/L. Samples, including sludges and wastewaters, were diluted by 1/25.

Table VIII. Results of COD and TOC analysis

Sludge sample	COD [mg/L]	TOC [mg/L]
Biosludge	11113	4020.0
Primary sludge	29163	14830.0
Wooden crust	21800	9820.0
BioPriva 100	10463	3307.5
Wastewater (alkali)	3075	1100.75
Wastewater (acidic)	920	423.25
Wastewater (to refinery)	1388	454.00

As Table VIII shows the COD and TOC amounts were significantly high. Based on the literature the liquid fractions arising from HTC processes contain various chemicals that can have a great value as well. When considering processing and sustainable development the liquid fraction should be definitely recycled and/or utilized. However, further studies related to this could not be included in this thesis.

7.7 FTIR analysis

Fourier Transform Infra-Red -analysis was done for each carbonated material. It was used to see differences in chemical bonds on the surfaces of carbons produced by various HTC treatments. Used analysis device was FTIR Vertex 70 BrukerCorp. with range of 400-4000 cm⁻¹. FTIR analysis were done for all the studied carbonated materials. Since the adsorption capacity and carbon content did not completely correlate each other FTIR can be used to give more explanations.

Most distinctive chemical bonds were characterized according to Alatalo (2016) and Wu et al. (2015). These are gathered and presented in Figure 17 with FTIR results from carbonated biosludge materials with diverse treatments. Between 3400-3300 cm⁻¹ O-H stretching, which comes from microcrystalline cellulose, can clearly be observed. Peaks at 2900 cm⁻¹ are from C-H stretching. Difference in the structures can be seen between low and high reaction duration times. When reaction time is low, microcrystalline cellulose can be seen in FTIR

images. Around 5 hour plus treatments microcrystalline cellulose has degraded. This also brings some new adsorption bands in the range of 1700 and 1600 cm⁻¹.

Wu et al. (2015) noticed three remarkable differences in their experiments dealing with hydrothermal carbonization of montmorillonite-hydrochar samples, which can also be seen in the following results. C-O stretching is seen at 1160-900 cm⁻¹ which is a result of glycosidic linkages between sugars. Also the amount of hydroxyl and carboxyl groups is lowering as the treatment time is increasing which can be seen as O-H stretching at 3400-3300. This is most likely due to hydrolysis and dehydration of cellulose which is carbonated. This can be seen when comparing biosludge treated at 260°C for 1 hour and 2 hour durations.

Aromatic rings are seen in 1600 cm⁻¹ as C=C bonds and also at 900-750 cm⁻¹ as C-H. Effect on these wavelengths is due to polymerization and aromatization process during hydrothermal carbonization. (Wu et al., 2015).

Aliphatic compounds such as ether and acids groups are seen in 3000-2800 cm⁻¹ (C-H). The aliphatic structures, ether structures, and acid groups are most likely formed with higher treatment times degrading C=O which contain carbonyls, quinones, esters and carboxyls in 1000-1460 cm⁻¹. These findings suggest that more carbonated material is produced as the reaction time is increasing. The same results were found from CHNS-O analysis by Wu et al. (2015).

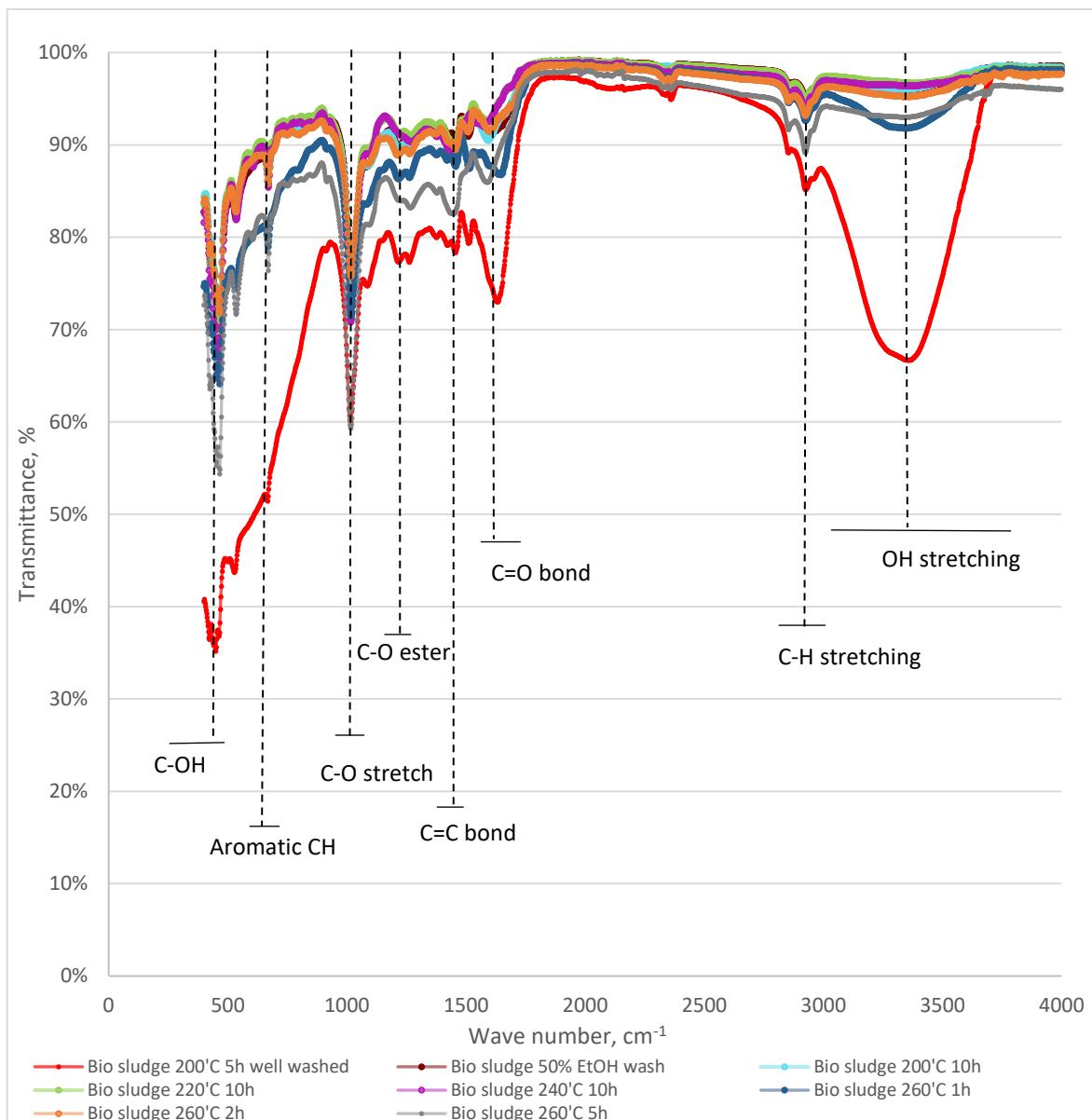


Figure 17. FTIR results of carbonated biosludge materials with various treatment methods and most significant molecule bonds gathered.

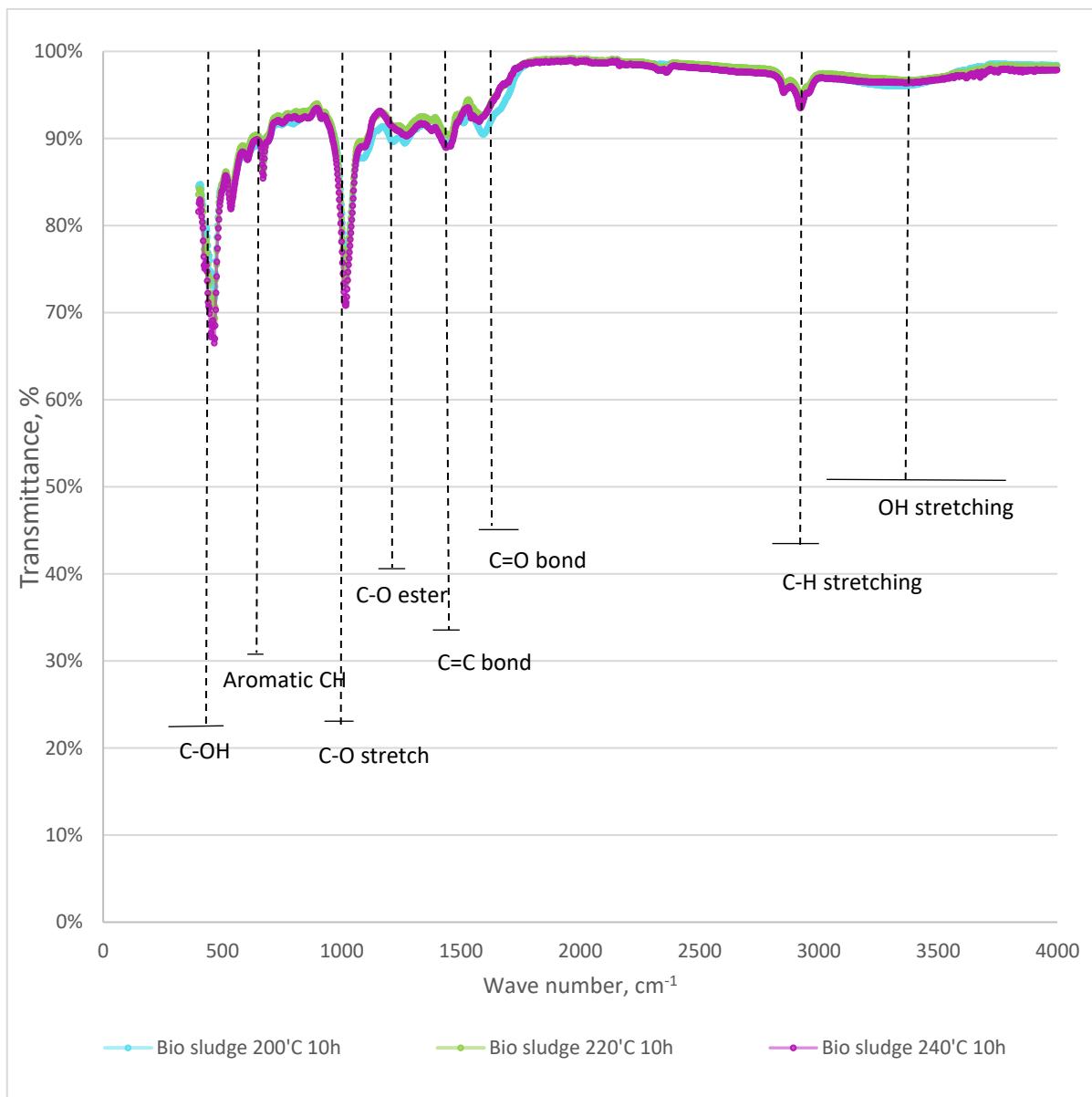


Figure 18. Biosludge was treated for 10 hours at 200 / 220 / 240 °C temperatures.

The effect of temperate is quite small when residence time is high enough, which can be seen from Figure 18. This is due to diminishing of the reaction rate when reaction has passed long enough. Compared to Figure 19. below the structure changes are more significant.

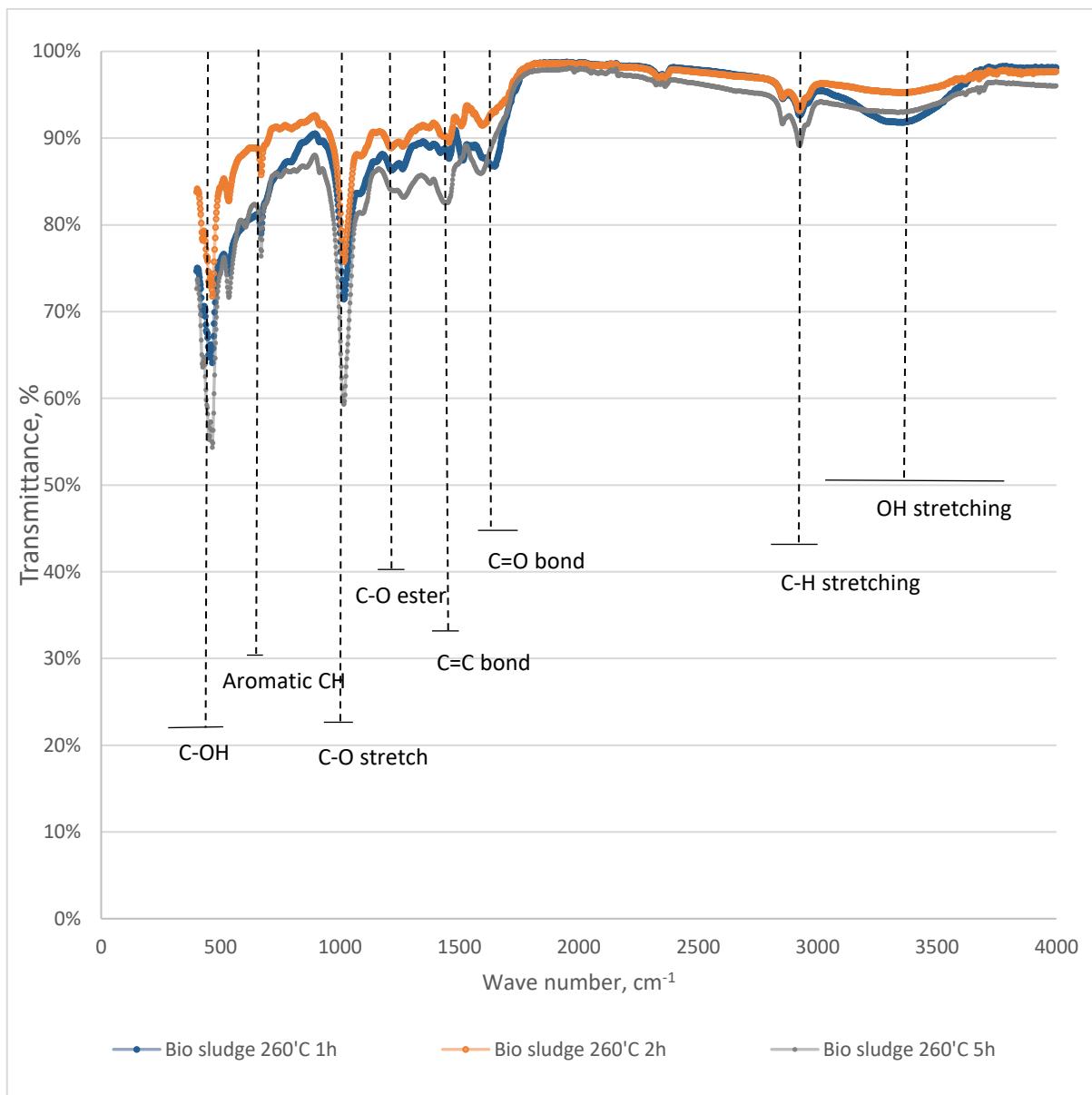


Figure 19. FTIR results as a function of time during hydrothermal treatment. Biosludge samples were treated at 260°C for 1, 2 and 5 hours.

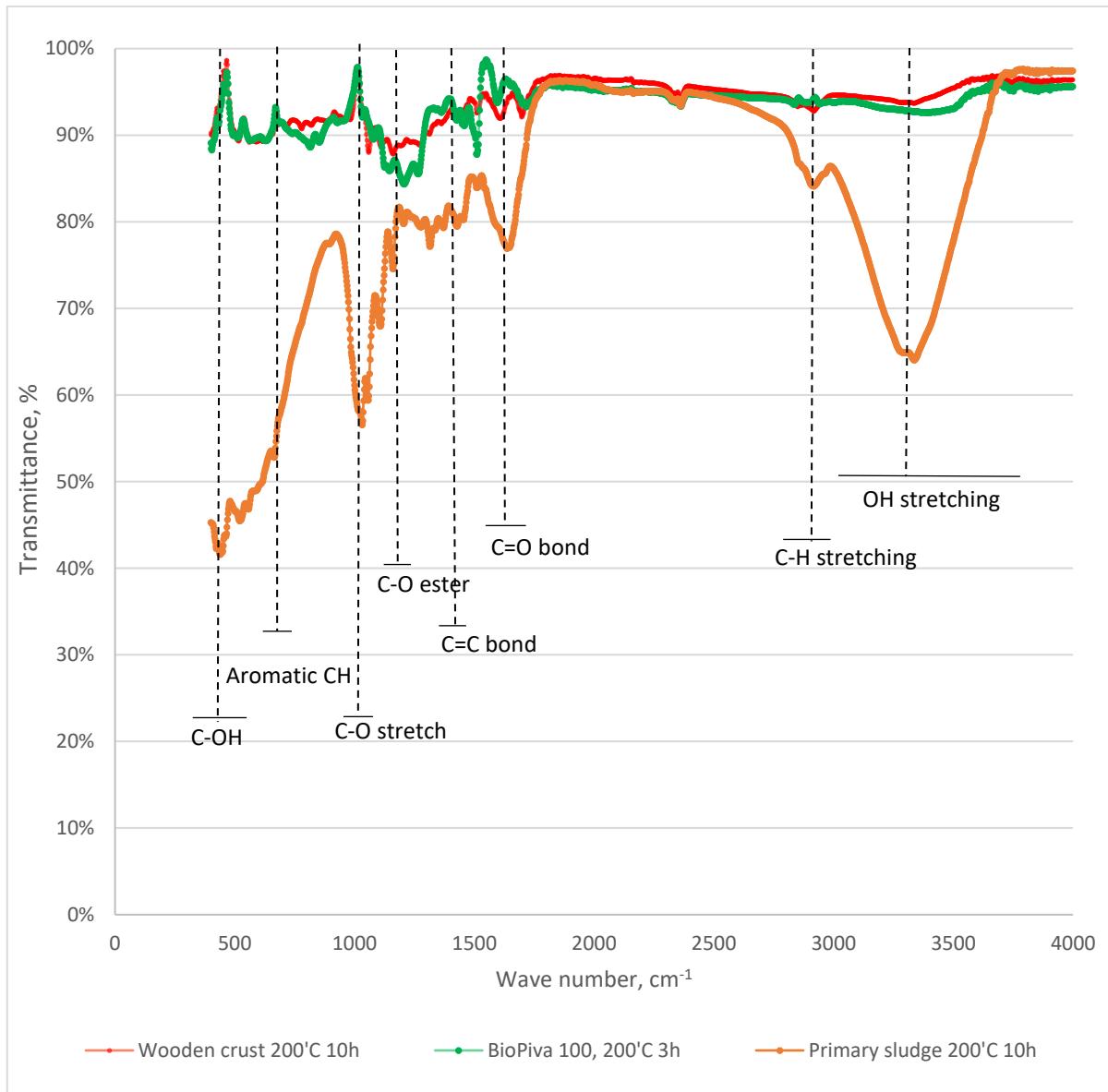


Figure 20. FTIR results of wooden crust, BioPiva 100 and primary sludge based carbonated materials.

Decarboxylation and volatilization of organic matter increases as the temperature increases. This can lower the carbon retention in the solid phase during HTC treatment. Besides this, functional groups are also significant factors in the adsorption properties. Diverse distribution of functional groups can increase the adsorption capacity and the surface area. As seen in Figure 19, biosludge with one-hour treatment contains OH stretching at 3400 cm^{-1} . As oxygen contains high ionization energy, it brings more intermolecular forces between the compounds. This can aid the methylene blue adsorption to the carbon as methylene blue was in cationic form (MB^+) during the adsorption experiments.

8 DISCUSSION AND CONCLUSIONS

Hydrothermal carbonization can be considered as a great carbonating method for biomass in several situations. Most promising situations are the cases where used biomass contains high amount of moisture. Water is used during the reaction and therefore drying is not needed. This can give economical advantage over other methods. HTC is also a carbon efficient process which is important considering the greenhouse gas emissions and “carbon economy”. Theoretically HTC reaction does not produce carbon emissions.

Process of hydrothermal carbonization can be manipulated with temperature, residence time, reactant concentrations, catalysts, and process conditions such as pressure. Hemicellulose degrading starts at around 180°C which is why lower temperatures are not considered. Higher temperature increases the reaction rate which lowers the required residence time. HTC during research was done by batch-processing and reactor was always sealed to ensure pressure in the reactor. Pressure increases the reaction rate following LeChaterlier’s principle.

Hydrothermal carbonization was found to be possible treatment method for pulp and paper industries biomass sources. It can be used to lower “fossil fuel economy” and increase sustainable development. Four various sources of biomass were used for the research in this thesis and carbonization of these materials was successfully implemented. These biomasses were named as biosludge, primary sludge, wooden crust and commercial kraft lignin, BioPiva 100. From these various types of sources biosludge gave the best performance and was researched the most. Biosludge was suitable to be treated with HTC method because it contained a great amount of water already.

Wooden crust and BioPiva 100 were troublesome substances to treat because of the hard structure. Even though the samples of wooden crust were grinded to small particles its dissolving qualities to the water were poor. This hindered the degradation of carbohydrates. Despite that the carbon based on the wooden crust performed quite well in the adsorption tests. On the other hand BioPiva 100 is kraft lignin powder, which does not degrade well during HTC treatment. After HTC treatment BioPiva still contained a hard surface. BioPiva

based carbon materials gave the worst results in the adsorption tests compared to others. In addition, BET surface analysis did not give any qualifying results for BioPiva.

From the economical aspect biosludge could be viable for HTC treatment due to its high water content. However, primary sludge from the process before drying could be also a very good option. Wooden crust could be considered because its current usage is only landfilling and it gave sufficient results from the adsorption experiments. It was also noted during the research that solid and liquid fractions are quite well separated after HTC treatment, but they start mixing together if they are not separated in short period of time.

Produced carbonated materials can be considered as successful treatment as for example 1 hour treated biosludge at 260°C achieved up to 60 mg/g capacity with only one hour treatment. When compared to other carbonated materials in Table I, result is great. At lower temperature, 200°C with 10 hour treatment, gave 45 mg/g adsorption capacity. This can also be considered as a good result. Interestingly, biosludge loading capacity results were lowering as temperature or time was increased. On the other hand, carbon content did increase as the time or temperature were increased based on the CHNS-O analysis presented in Table VI. However, carbon amount is not strictly indicating how good adsorbent the carbonated material is. When comparing CHNS-O results and adsorption results BioPiva 100 and wooden crust had most carbon, yet these gave the worst adsorption results.

Adsorption capacity is somewhat related to the oxygen content and specific surface area. In Table IX compiled results from HTC treated biosludge, where treatment time or temperature were increased, and their adsorption capacity results are presented. Oxygen content is taken from Table VI (CHNS-O-analysis) and surface area from Table V (BET surface area) and loading capacities from Figures 13 and 15 (adsorption isotherms). Colors are made to indicate whether the value is high (green), medium (yellow) or low (red) when comparing these series together. When both oxygen content and surface area were high the adsorption capacity was also high and vice versa. However, this is not directly proportional as 260°C, 2h series achieved 35 mg/g adsorption capacity with low/medium oxygen and surface area.

Table IX. Compiled results obtained with treated biosludge, where time or temperature were increased.

Sludge sample	Oxygen [%]	BET Surface Area [m ² /g]	Loading capacity [mg/g]
260°C, 1h	22.002	29.751	60
260°C, 2h	17.604	18.86	35
260°C, 5h	22.225	13.373	16,5
200°C, 10h	22.428	27.550	45
220°C, 10h	19.493	26.667	22
240°C, 10h	17.687	21.320	23

Carbon contains various complexity compounds and it is most likely that some of these compounds adsorb methylene blue but degrade as temperature is increased. FTIR analysis were done to see more structural information about the carbonated materials in order to explain the occurring phenomena. Carbon content can be seen increasing also as time increases when looking FTIR results since the amount of oxygen and carbon bonds are lowering as treatment time is higher. This is due to the amount of carbon in the solid-phase. Rate of forming gas fractions from decarboxylation and other organics are increasing as temperature increases. This can cause low retention of carbon in the solid phase, giving it a lower surface area.

When HTC residence is high enough carbonated materials are becoming very similar when looking FTIR analysis in Figure 18. However, from Figure 19 it can be seen that after one hour residence time the sample surface contains stretched OH functional groups. This can enhance methylene blue adsorption by increasing intermolecular interactions between the carbonated material and methylene blue as methylene blue was positively charged.

Pressure in HTC experiments were not adjusted but it was noted to have effect on the equilibrium state according to Le Chatelier's principle. The optimal residence time and temperature is trade-off with each other. Increasing temperature increases reaction rate which lowers required residence time and vice versa. Loading rate between biomass and water has its effect on the required residence time. Dehydration and decarboxylation were found to be key factors in the hydrothermal carbonization.

Effect of washing was compared between the biosludge sample treated at 200°C for 10 hours and the biosludge sample that was post-treated with 50% ethanol during washing. Washing with ethanol increased the surface area of carbonized material. Washing with 50% ethanol also increased the adsorption capacity. This roughly seems to lower the yield but improves greatly the quality of carbon. After hydrothermal carbonization of sludge, mixture can contain many tens of thousands of various compounds and hydrocarbons. When this mixture is washed with ethanol it most likely liquefies and removes the smallest compounds from the carbon surface. Therefore, even yield is lower, quality of carbon is enhanced. Yet, washing with water did not seem to have a significant impact on the adsorption capacity itself. Differences between the batches can be explained by the properties of ethanol and the residence time used in the HTC treatment.

Table X shows various carbonated materials and their treatment parameters which are same as presented Table I, but few results from this work are included. In Table XI surface area (BET) and CHNS-O elemental analysis results from these carbonated materials are presented. Produced carbonated materials from this work tend to have lower carbon content compared to other carbonated materials. However, treatment of this work was mild when comparing other treatment temperatures. Carbonated materials from Palm bark and Eucalyptus, which also had very mild treatment conditions, had still higher carbon composition. In the other hand, surface area from produced carbons from this work were higher, which is quite interesting. It can also be seen that generally activated carbonated materials have higher surface area than carbons without activation, which was expected.

Table X. Various carbonated materials HTC treatment information. References are from a), Alatalo, 2016, b) Xiaofei et al., 2015, c) this work.

Feedstock	Hydrothermal temperature °C	Residence time	Synthesis information	Ref.
Palm date seed AC	200	5 h	NaOH activation	a
Hazelnut shell hydrochar	250	7,5 h	ZnCl ₂ activation 850°C	a
FruLi	180	16 h	Presence of salt	a
Eucalyptus	400	30 min		b
Kenaf fiber	1000	-	Pyrolysis	b
Palm bark	400	30 min		b
Biosludge (a)	200	10 h		c
Biosludge (b)	260	1 h		c
Biosludge (c)	200	10 h	ethanol washed (activates carbons)	c

Table XI. Compiled results of various carbonated materials including few of this work. References are from a), Alatalo, 2016, b) Xiaofei et al., 2015, c) this work.

Feedstock	Surface area (BET) [m ² /g]	C [%]	H [%]	N [%]	S [%]	O [%]	Ref.
Palm date seed AC	1283.00	-	-	-	-	-	a
Hazelnut shell hydrochar	60.00	65.78	4.72	0.99	-	23.32	a
FruLi	431.00	70.20	5.40	-	-	-	a
Eucalyptus	10.35	77.80	5.38	0.41	0.06	18.30	b
Kenaf fiber	346.57	55.54	1.96	0.14	0.00	39.13	b
Palm bark	2.46	68.90	5.38	0.88	1.52	20.80	b
Biosludge (a)	29.75	54.38	5.43	2.38	0.48	22.43	c
Biosludge (b)	27.55	48.21	5.15	2.43	0.51	22.00	c
Biosludge (c)	40.67	52.85	5.37	2.06	0.74	28.42	c

Theory of hydrothermal carbonization was thoroughly considered and produced carbonated materials were shown to fulfill their expectations. As it was noted, adsorption capacity was lowering when treatment time was increased. Further research could be done by determining if practical adsorbent materials can be produced with even shorter treatment when the focus

would be on functional groups and their behavior during adsorption phenomena. Key factors for this would be determining how carbonated materials' functional groups affect the adsorbing organic compounds. More specific research is also needed for determining what kind of organic materials could be adsorbed. This could be obtained with very short required treatment times. Finally, there is still lack of research how the liquid phase formed during HTC could be better analyzed and utilized. Finding good solutions for this would enhance the recycling of sludge even further.

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