

Sludge biochar as an adsorbent for pharmaceutical residues in wastewater

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Sludge biochar as an adsorbent for pharmaceutical residues in wastewater

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Picture on front page: Biochar. Obtained from AI-function from Canva.com (2024).

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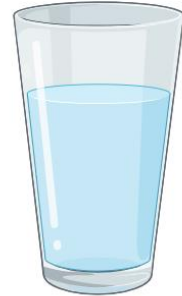
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Populärvetenskaplig sammanfattning –

Har kol renat vattnet i mitt glas?

Att ha rent vatten är en lyx vi i Sverige är vana vid men vad händer i avloppsreningsverken som gör vattnet så rent? Jo, bland annat kemikalier, bakterier och kol används för att rena vårt avloppsvatten. Tillsammans rensar de ut små och stora partiklar från vattnet. Det uppstår problem när små, stabila organiska ämnen som läkemedelsrester inte fångas i reningsstegen utan följer med ut i naturen via det rena vattnet eller slammet. Slam består av allt som rensas bort från avloppsvattnet och används ofta som gödsel i jordbruk.

På så sätt kan läkemedelsrester direkt nå ut i naturen vilket inte är miljövänligt och det är därför kol kommer in i vattenreningen. Kolet kan fånga organiska ämnen och stoppa deras spridning men det krävs en process som kallas aktivering för att kolet ska fånga in ämnena mer effektivt. Dessutom är kolet som används i reningen från fossila källor så för att göra rening med kol mer hållbar och miljövänlig undersöks möjligheten att skapa ett aktiverat kol från den hållbara källan slam. Det kolet kallas för aktiverat slambiokol och skapas från reningsverkens restprodukt avloppsvattenslam. Kan verkligen slambiokol användas för att rena vattnet från farliga ämnen som läkemedelsrester? Det är vad den här rapporten kommer svara på, i samarbete med Testbädd Ellinge. Efter aktiveringar av biokol från olika sorters slam i olika temperaturer och tider nalkades ett svar om slambiokolets potential. En aktivering på hög temperatur och kort tid gav ett aktiverat slambiokol som mycket riktigt renade avloppsvatten från organiska ämnen, såsom läkemedlet diklofenak. Kanske i framtiden får du istället fråga, har avloppsrester renat vattnet i mitt glas?



*Vattenglas. Från
Biorender.*

Sammanfattning

Den svenska avloppsvattenreningsprocessen består av flera olika steg som utnyttjar mekanisk, kemisk och biologisk rening för att avlägsna så mycket av ohälsosamma ämnen och organismer som möjligt från vattenomloppet. Avloppsvattenreningsprocesserna i Sverige saknar specifika reningsmetoder för vissa typer av organiskt material, såsom läkemedelsrester. Dessa mikroföroreningar bryts enbart delvis ned på avloppsreningsverken alternativt fångas upp i avloppsslam, som ofta används inom jordbruket som gödsel. På så sätt når miljöfarliga ämnen ekosystem och kan påverka organismer på negativa sätt. Mikroföroreningarna följer även med det utgående dricksvattnet, vilket innebär att kemikalierna kommer tillbaka till oss konsumenter. Därför finns det behov av att utöka avloppsreningen. Att använda aktivt kol är en effektiv metod för att rensa ut organiska föreningar då kolet har en utökad ytarea som bidrar till en ökad mängd av adsorptionsplatser som effektiviserar inbindningen av miljöfarliga ämnen. En negativ aspekt av att använda aktivt kol som reningsmetod är att källan som används för att producera det oftast är fossil. Genom att använda avloppsvattenslam för att producera aktiverat slambiokol återanvänds en icke-fossil källa för att förbättra livskvaliteten för människor likväl som för andra organismer som påverkas av spridningen av kemikalier från avloppsvatten. Om slam används som källa till aktiverat biokol i avloppsvattenrening skulle det inte endast begränsa spridningen av kemikalier ut i miljön utan även minska klimatpåverkan från avloppsrening och bidra till en cirkulär ekonomi i resursanvändningen.

Filter med aktiverat slambiokol kan implementeras i reningsprocessen för att ta bort organiska föroreningar från avloppsvatten. På så sätt adsorberas kemikalierna och tas bort från avloppsvattenflödet, vilket minimerar deras påverkan på miljö och liv. Att utnyttja restprodukt som avloppsvattenslam kan även vara till fördel för ekonomin då det kan minimera kostnaderna, både ur produktionsperspektiv likväl som transport. Därför är rening med aktivt slambiokol en metod som är värd att utforska. Dessutom är en uppdatering av direktivet kring avloppsvattenrening och hantering av läkemedelsrester på EU:s agenda och förväntas tillämpas under de närmsta åren. Därav finns det ett verkligt behov av att utveckla avloppsvattenrening, specifikt rening av läkemedelsrester. Användningen av aktivt kommersiellt kol är ett alternativ men för klimatet och ekonomins skull är slambiokol ett desto mer lockande alternativ.

I den här undersökningen var biokol, framtaget från avloppsvattenslam från 4 olika reningsverk, aktiverat genom pyrolys med olika förhållanden för att undersöka adsorptionsförmågan hos olika slambiokolspartiklar och finna de mest optimala förhållanden. Olika aktiveringstemperaturer (700, 800, 900 °C) och olika aktiveringstider (15 min, 30 min, 1 h, 2 h, 4 h) testades i en rad kombinationer för att kunna dra slutsatser om vilka förhållanden som ger högst aktiveringsgrad. För att mäta aktiveringsgraden mättes adsorptionen av olika organiska ämnen och nivån på adsorptionen kopplades direkt till graden av aktivering, en högre adsorbans tydde på att aktiveringen var av en högre grad. Adsorptionen av organiska föreningar mättes med UV-absorption och radioaktivitet från ¹⁴C-isotoper. I experimenten visade det sig att mindre partikelstorlekar, <0.425 μm, nådde en högre aktiverings-grad. En aktivering på högre temperaturer, 800–900 °C, behövde en kortare aktiverings-tid för att nå högre grader enligt adsorptionstesten via UV-absorbansen. Aktivering med lägre temperatur, 700 °C, krävde en längre tid för att nå samma nivå. Från absorptions-experimenten som gjordes under examensarbetet gav resultaten en kombination av aktiveringstemperatur och tid som uppnådde den mest optimala aktiveringen av de som undersöktes. Resultaten visade att en aktivering på 800 °C i 30 minuter bidrog till mest ökad adsorption av organiskt material. Även vid test med radioaktivt märkta kemikalier påvisades slambiokolet (800 °C, 30 min) ha den högsta adsorptionen.

Undersökningen resulterade i lovande resultat men utvecklingspotential finns ännu kvar för att finna aktivt slambiokol vars adsorptionsförmåga är mer lik det kommersiella kolet. Fördelarna med att utnyttja restprodukten avloppsvattenslam motiverar en fortsatt utveckling av aktivt slambiokol.

Abstract

The Swedish wastewater treatment processes consists of multiple steps including mechanical, chemical, and biological cleaning to remove as much of the unhealthy substances and organisms as possible from the water circulation. The wastewater treatment process in Sweden lacks specific removal methods for some types of organic material, such as pharmaceutical residues and other microcontaminants. These are only partly broken down by the wastewater treatment plants or taken up in wastewater sludge. The sludge is often used in agricultural practices as fertilizer and in that way, environmentally hazardous chemicals enter ecosystems and can affect the organisms in negative ways. Micropollutants also joins the effluent drinking water, which means the chemicals find their way back to us consumers. Therefore, there is a need to expand the wastewater treatment processes. The use active carbon is an efficient method to remove organic contaminants as the carbon has expanded surface area that contributes to an increase of adsorption sites which makes the binding of chemicals more efficient. A negative aspect of utilizing active carbon as a treatment method is that the source used to produce it often is fossil. By using wastewater sludge to produce activated sludge biochar, a non-fossil resource is reused to improve the life quality of humans as well as other organisms affected by the leaking of chemicals from wastewater. If sludge was utilized as activated sludge biochar in wastewater treatments, it would not only limit the leaking of chemicals into the environment but also diminish climate impact by wastewater treatment and contribute to a circular resource utilisation.

To remove organic chemical contaminants from the wastewater, filter with activated sludge biochar could be added to the wastewater treatment process. In this way the chemicals would be adsorbed and removed from the wastewater stream, minimising their impacts on environment and organisms. To use a residual product like wastewater sludge could benefit the economy as well as the environment as it could minimise the costs, from a production and transport point of view. Hence, a treatment step with activated sludge biochar is worth to investigate. Additionally, an update of the directive on wastewater treatment and handling of pharmaceutical residues is on the agenda of EU and is expected to be implemented in the upcoming years. Therefore, there is an actual need to improve the wastewater treatment, specifically the handling of pharmaceutical residues. The utilisation of commercial carbon is an alternative, but sludge biochar is the more attractive alternative, for the sake of the climate and economy.

In this experimental study, biochar obtained from wastewater sludge from 4 different wastewater treatment plants was activated through pyrolysis with different conditions to investigate the adsorption capacities of the different sludge biochar particles and to find the most optimal conditions. Different activation temperatures (700, 800, 900 °C) and different activation times (15 min, 30 min, 1 h, 2 h, 4 h) were tested in several combinations to be able to draw conclusions of which conditions give the highest level of activation. To measure the activity level, the adsorption of different organic substances was measured, and the level of adsorption was correlated to the level of activation, i.e. a higher adsorption degree was due to an activation of a higher level. Adsorption of organic material was measured by UV-absorption and scintillation counting of ¹⁴C isotopes. It was found smaller particles, <0.425 mm, reached a higher activation level. Activation of higher temperatures, 800-900 °C, required a shorter activation time to reach higher levels according to the adsorption test by UV-absorption. For activation with lower temperature, 700 °C, a longer time was required to reach similar levels as the higher temperatures. A conclusion on the most optimal combination of the activation temperatures and times that were tested could be drawn from the absorbance-experiments that was done in this thesis work. The results showed an activation in 800 °C for 30 minutes achieved the largest adsorption of organic material. It was shown also in the test with ¹⁴C-labelled chemical residues that the sludge biochar (800 °C, 30 min) had the highest adsorption degree.

The investigation showed promising results but there is still a potential for further development to discover an active sludge biochar with the adsorption capacity close to that of a commercial active carbon. The advantages to utilise the residual product wastewater sludge motivate for continuing the research on activated sludge biochar.

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1. Introduction

The circulation of water is a huge building block of sustainable and economically viable societies. When purifying wastewater, sludge is formed in significant amounts. As example, one treatment plant in Sweden, Ryaverket, produce 55 000 tonnes of sludge each year and it has previously been regarded as waste, with no value (Gryaab, 2024). A different perception of sludge has emerged in recent years, and it is today addressed as a useful resource. One of the reasons for its usefulness is the high ratio of nutrients, especially phosphorus. However, a lot of contaminants also exist in sludge.

Pharmaceuticals are excreted by the body through urine and faeces, meaning pharmaceutical molecules find their way to wastewater treatment plants (WWTPs), where they, in conventional WWTPs, are only partly degraded and therefore find their way to receiving waters (Hörsing *et al.*, 2014). Pharmaceutical residues continue to be active and therefore can have great impacts on ecosystems (Kayode-Afolayan *et al.*, 2022). Those residues that end up in the sludge can end up on agricultural fields and be absorbed by the plants (Zhang *et al.*, 2023). Some concerns that are caused by the leaking of pharmaceuticals is the spread of antibiotic resistance genetics and antibiotic resistant bacteria (Burzio *et al.*, 2022). Hence, there is cause and room for improvement for handling of sludge, apart from the significant amount that is produced each year.

To improve the efficiency of the wastewater treatment, an expansion of the processes is needed, and additional methods need to be implemented in a quaternary treatment. The quaternary treatment refers to technologies used to remove organic micropollutants which is not removed in earlier steps, such as pharmaceutical residues. In a study by Baresel *et al.*(2014) the removal of pharmaceutical residues by utilising granulated active carbon and ozone were compared, since these methods were of most relevance and interest. This is still the case today and the study showed the removal of pharmaceutical residues by active carbon was the most efficient. Since the late 1900s activated carbon has been used to improve the quality of drinking water in Western countries and has also been implemented in wastewater treatment in some cases (Alves *et al.*, 2021). To utilise the active carbon in the treatment processes, a common way is for the WWTPs to implement filter systems with granulated active carbon (GAC) (Baresel *et al.*, 2019). There is no law in Sweden regarding the removal of organic micropollutants from wastewater yet, although it is expected to be established once the EU Urban Wastewater Treatment directive (91/271/EEC) has been updated according to the proposal (2022/0345/COD) and implemented as it currently also does not address any criteria for pharmaceutical and organic material (91/271/EEC).

Activated carbon can “trap” organic materials through adsorption and can be used in different forms, granulated, or powdered. The powdered activated carbon (PAC) and GAC is conventionally used in the drinking water production; however, the production of the active carbon requires a lot of energy and resources (Baresel *et al.*, 2019), which makes it non-sustainable. By using residual products instead to generate activated carbon, the environmental impact is minimised. These residual products from biomass that can be used to produce biochar, which’s definition is char being produced from biomass. By using biomass as an alternative carbon source, the use of active carbon can be turned more sustainable (Alves *et al.*, 2021). Ozonation is another method to remove micropollutants from wastewater, and drinking water, as the natural, reactive compound degrades the pollutants and the compound itself has no negative impact on the environment as ozone easily degrades naturally (Remondino and Valdenassi, 2018). It is a technology often implemented in drinking water treatment, as well as wastewater treatment as it functions as a disinfectant with low environmental impact (Remondino and Valdenassi, 2018). However, ozonation does not fully degrade most of the micropollutants, which can form toxic metabolites, and an additional treatment step in the quaternary treatment is needed to obtain a greater degradation (Baresel *et al.*, 2019), such as activated biochar.

Biochar is typically produced via pyrolysis, which is a process where material is broken down into smaller molecules under high temperature conditions and absence of oxygen, due to thermochemical decomposition (Basu, 2018). Pyrolysis is a growing treatment method of sewage sludge and biochar produced from sludge in higher temperatures is suitable to use as adsorbents as the porosity is increased

(Agrafioti *et al.*, 2013). During pyrolysis, organic micropollutants in sludge are degraded, yet materials such as heavy metals are not removed (Agrafioti *et al.*, 2013). However, the leaking of those materials is reduced by pyrolysis as they become immobilized in the biochar (Agrafioti *et al.*, 2013). The biochar can be utilized as an adsorbent of organic materials in water purification that the prior steps were not successful in filtering out. However, the pyrolysis conditions for an optimized activation of biochar are not yet determined.

1.1 Aim

In this degree project, the aim was to determine the ability to adsorb organic pollutants, such as pharmaceuticals, of different sludge biochars in wastewater. Different activation temperatures, residual times and particle sizes were to be investigated to potentially find optimal physical activation-conditions for future usage. An evaluation of the chosen methods' practicality and accuracy was also part of the project.

2. Background

This section's purpose is to introduce the reader to the concepts that will be continuously discussed and put into consideration in this report. These concepts consist of a brief introduction of wastewater treatment, production and applications of active carbon, biochar, and activated sludge biochar, as well as parameters affecting the quality of the biochar.

2.1 Wastewater treatment

In today's society, there is an ongoing discussion of wastewater treatment and handling of wastewater sludge. As shown in Ryder (2017), the full potential of wastewater is not utilized. It can be utilized as water if treated properly, as wastewater contains various pollutants and contaminants. Heavy metals and organic micropollutants such as pharmaceuticals are some of the pollutants that wastewater needs to be disposed of. It also contains some nutrients, such as phosphorus and nitrogen, which can be applied in agricultural practices. The treatment of wastewater includes different unit processes, which are divided in levels called preliminary, primary, second primary, secondary, tertiary (Tchobanoglous *et al.*, 2003) and quaternary. In the preliminary treatment, larger objects are removed mechanically and in primary treatment, sedimentation is used to remove settleable materials from the wastewater (Tchobanoglous *et al.*, 2003). In the latter treatment steps, biological processes and chemicals are used to remove organic materials. The advanced step, tertiary treatment, utilise a combination of unit processes to remove the remaining constituents, such as further filtering and chemical disinfectants (Tchobanoglous *et al.*, 2003). Removal of micropollutants is in focus in the quaternary treatment, which can be done by adsorption by active carbon. In Figure 1, a general overview of the wastewater treatment including some of the treatment steps is shown. There are demands on, e.g., effluent levels of nitrogen and organic material in Sweden. In the regulations written by the state, there are clear maximum levels of yearly effluent flow of nitrogen from wastewater stated, as well as maximum chemical oxygen demand (COD), and biochemical oxygen demand within seven days (BOD₇) (SNFS 1994:7, 4-5§§). The demands on COD and BOD describe the regulation of organic materials, as they are measurement methods of the concentration of organic materials. However, the regulations do not provide demands on the effluent concentration of organic micropollutants, such as pharmaceutical residues yet. To reduce effluent micropollutants, quaternary treatment is needed, and it could be done via adsorption by either PAC or GAC, which has been proven to be more efficient than ozonation (Baresel *et al.*, 2019). GAC is utilised in a stationary filter column and is easier to regenerate than PAC, as PAC requires specific measures and internal circulation to achieve adsorption equilibrium (Kårelid *et al.*, 2017). A benefit of using PAC would be the faster adsorption due to a larger surface area, meaning a lower dose than that of GAC would be needed (Kårelid *et al.*, 2017).

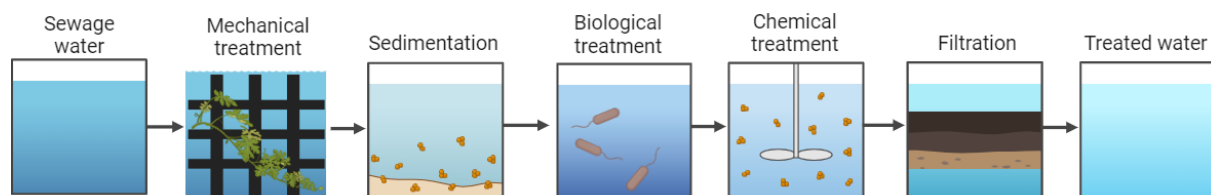


Figure 1. A general description of the wastewater treatment process, including mechanical cleaning where most of the larger particles is separated. In the biological cleansing step, bacteria are used to remove nitrogen and some of the organic material. Chemical treatment includes addition of compounds that cause contaminants to lump together (flocculation/coagulation). The flocs of contaminants then fall to the bottom in the sedimentation step and is separated from the water. The water then continues the treatment with a sand-bed that separates smaller particles from the water.

2.1.1 Sludge production

The sewage sludge from wastewater treatments is very heterogeneous and there are a variety of types of sludge, due to different water treatment technologies being applied in different areas (Betsholtz *et al.*, 2018). Wastewater can also have different properties and content, depending on the source (Betsholtz *et al.*, 2018). Hence, the wastewater source has a great impact on the composition of the sludge and its

properties (Betsholtz *et al.*, 2018). In the treatment process, two types of sludge are produced, primary and secondary sludge. They are derived from different parts of the conventional treatment process. Primary sludge is derived from the particles settled in the primary sedimentation and secondary sludge is obtained from a biological treatment step, where microorganisms are used (Demirbas *et al.*, 2017). The obtained sludge can then be stabilized through anaerobic digestion by microorganisms, which results in a sludge with lower carbon content than the original one and increased ratio of nutrients (Betsholtz *et al.*, 2018). Depending on which processes, e.g. anaerobic digestion, have been applied to the sludge, different properties can be obtained.

In the tertiary treatment, slurry formed by the chemicals is collected rather than a biomass, which is the case in the secondary treatment (Demirbas *et al.*, 2017). Organic materials are still present in the biological sludge and micropollutants, such as pharmaceuticals, are not completely eliminated in the primary, secondary, and tertiary treatment processes. After further treatment the sludge can be utilized as fertilizer in agriculture as it contains inorganic nutrients, such as nitrogen and phosphorus. However, due to containing micropollutants and heavy metals it is not harmless in a long-term perspective to use on land with crops, as the toxic material could be absorbed by the plants, accumulate or infiltrate ground water.

2.1.2 European Union's wastewater treatment directive

In European Union's Urban Wastewater Treatment directive (91/271/EEC) demands on the quality of the effluent water from wastewater treatment are stated and those determine the processes that are needed to achieve these quality requirements. There are also demands on feasibility of reusing sludge (91/271/EEC). However, specific demands on the content of micropollutants and pharmaceuticals, are currently missing and therefore, the directive is under revision and proposals have been made. According to the new proposal concerning Urban Wastewater Treatment (2022/0345/COD) the percentage of remaining organic micropollutants, such as pharmaceuticals, must be reduced by 80 % in the quaternary treatment in treatment plants for 150 000 people and more. Companies contributing to the outlet of these will be responsible for parts of the financing of reduction of the substances. There will also be a focus on the climate and an aim for emission-neutrality implemented in the new proposal. Demands for renewable energy in treatment plants for areas of 10 000 habitants or more will be stated in the updated directive (91/271/EEC).

2.1.3 Pharmaceuticals in the environment

In Swedish domestic wastewater, synthetic substances, such as oestrogenic compounds, have been found and been part of the effluent flow into water sources. According to a study by Larsson *et al.* (1999) the compounds have found their way into fish and affected their endocrine system. Oestrogenic compounds, which can be found in contraceptives, induces synthesis of a precursor to a protein found in the fish-egg yolk. Physiological functions of the fish are affected by the environmental oestrogens, which can accumulate in the organisms. These substances can also be found when sludge is used in agriculture, according to Larsson *et al.* (1999). Pharmaceuticals are often very stable and biologically active, making them a potential threat when reaching the environment (Larsson *et al.*, 1999). The concern for the presence of pharmaceuticals in the environment and their impacts have increased. When the environment is enduring long-term exposure of the water-soluble substances, even though the concentration may be low, organisms of different ecosystems may experience adverse effects and ecosystems could suffer great consequences. Pharmaceuticals in the environment may provide aquatic toxicity and raise resistance in pathogenic microorganisms, contributing to antibiotic resistance. They could have a direct effect on humans, as pharmaceutical substances are found in drinking waters. In terms of pharmaceutical residues present in water sources, Sweden has been reported as one of the leading nations and it poses a big concern for the human health (Kayode-Afolayan *et al.*, 2022).

2.1.4 Removal of organic micropollutants

During the wastewater treatment processes, the complete exclusion of pharmaceuticals is difficult to achieve, and they are often discharged into the effluent stream. Different routes for the spread of pharmaceutical residues are shown in Figure 2. To improve the purification of pharmaceuticals membrane

filtration and activated carbon are recommended as complimentary methods (Rakić *et al.*, 2015). Activated carbons are favourable for adsorption of pharmaceuticals due to large surface area and affinity to compounds in liquid phases. Adsorption of hormones and other compounds by activated carbon have been proved efficient. However, there is a need of disposal of activated carbon in powdered form after adsorption of pharmaceuticals, which contributes to the cost (Rakić *et al.*, 2015).

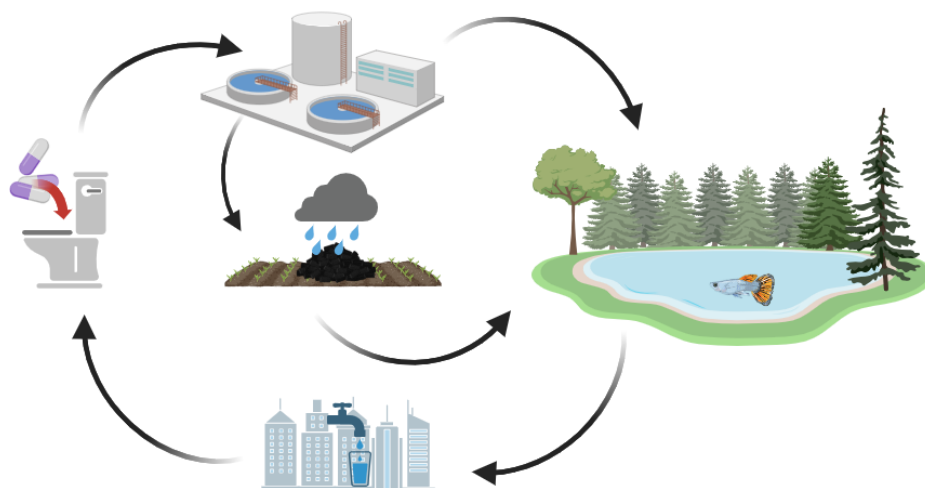


Figure 2. An overview of the different paths pharmaceuticals can spread via into ecosystems once they have entered the wastewater stream. One way is through sludge, containing pharmaceutical residues, being utilized in agricultural. Another way is through the effluent flow from WWTPs. Due to the residues' stability, they will not be degraded and through rainwater they can spread through nature to different water sources, as they are water soluble. The residues will join the effluent flow of water back into cities, closing the cycle.

2.2 Adsorption

The process called adsorption occurs when a molecule binds to a solid surface either by chemical interactions or physical forces. In that way the molecule is separated from fluid media it originated from. The molecule, which attaches to the surface, is called the adsorbate and the solid is the adsorbent. Only the surface of the adsorbent is involved in the process as the adsorbate does not diffuse into the solid, which would mean it was absorbed rather than adsorbed.

There are two types of adsorptions, physical and chemical (Artioli, 2008). The difference is that in physical adsorption, the adsorbate attaches to the adsorbent by physical forces, such as van der Waals forces, and in chemical adsorption the adhesion is due to chemical bonds (Artioli, 2008). In Figure 3, the difference between adsorption and absorption is shown.

In chemical adsorption, actual bonds are made, often covalent, and the enthalpy of the molecules decrease. As adsorption is spontaneous, the change of enthalpy is always negative, though activation energy is required. To describe the adsorption equilibriums, isotherm equations are utilized, Langmuir and Freundlich are some examples (Artioli, 2008). To find mathematic connections for the Langmuir expression, some assumptions are usually made; the adsorbate binds to specific binding sites on the adsorbent which provides appropriate conditions, and the adsorption sites can be saturated as it only

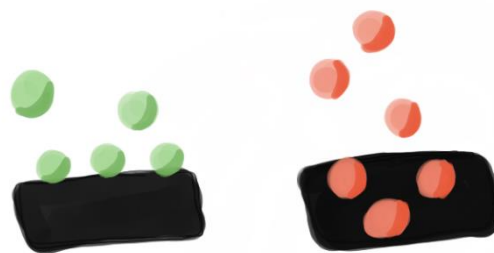


Figure 3. Adsorption is shown as the green particles merely attaches to the surface. The red particles diffuse into the material, hence are absorbed.

binds to one molecule at a time. Additionally, the energy in each binding site is equal for all sites and the adsorbed compound does not impact the adsorption of others. For Freundlich less empirical assumptions are made, such as adsorption is not limited to one molecule per site, meaning no saturation would occur. This limits the Freundlich isotherm to data of low adsorbate concentration because otherwise the equation would show unlimited adsorption by adsorbent, which is not accurate. They describe the amount of adsorbate that has attached to the adsorbent when the concentration in the fluid media is known. Temperature is one parameter that has a great influence on the adsorption capacity. Hence, the conditions must be isotherm when applying the equations. The reverse process, when the molecule is separated from the solid surface, is called desorption (Artioli, 2008). Adsorption can be utilized in different purifying processes or in general when separation of compounds is required. An example of this is wastewater treatment, where activated carbon is used as absorbent of pollutants (Hu and Xu, 2020).

2.3 Pyrolysis

Pyrolysis cause separation of organic products, which grants the product with different characteristics (Al-Haj Ibrahim, 2020). During the process, three different products are generated – char, bio-oil and gases. From the biomass both condensable and non-condensable gases are obtained, which are both separated from the solid product that is char. The condensable gas condenses during downstream processes, which includes cooling, and forms bio-oil. The gases produced, that are of non-condensable properties, are such as carbon dioxide, carbon monoxide, hydrogen, and methane gas. The chemical mechanisms that occur under pyrolysis is a degradation of hydrocarbon molecules into smaller molecules that are parts of one of the products. Traditionally, pyrolysis is utilized to produce bio-oil, though by reducing the speed and temperature of the process the generation of solid product is increased. In a study by Basu (2018) was it shown that the lower pyrolysis-temperature, the higher the char-yield. Another parameter that was shown to affect the pyrolysis outcome is the physical properties of the biomass. If the particle size is small, condensable gases are more easily released from biomass and the liquid-product yield increases. Bigger particle sizes limit the release as they have greater resistance, and the yield of solid char is greater. Through pyrolysis no harmful volatile gases are released to the atmosphere and a high yield of product is obtained, thus making pyrolysis a more beneficial technique to obtain biochar than simple combustion, for example (Basu, 2018a). Different kinds of pyrolysis exist, and they are called conventional, dry and wet. In the conventional pyrolysis, temperatures between 300-1000 °C is applied for more than an hour. The dry pyrolysis involves microwave, lower temperatures, and shorter time (Chen *et al.*, 2020).

2.4 Pyrolysis of sludge

Sludge has many applications, one of which is as a fertilizing agent in agriculture. Another process in which sludge can be utilized is the production of biochar. By pyrolysing sludge, the product sludge biochar is formed, see Figure 4. Depending on the parameters during the process, different characteristics of the biochar can be obtained, and the products are suitable for different functions. The parameters that affect the biochar are the temperature of the pyrolysis, the residence time of the product, the heating rate and the size of the product (Agrafioti *et al.*, 2013). It has been shown that biochar formed from sludge at low temperature pyrolysis had characteristics suitable for agricultural applications (Agrafioti *et al.*, 2013). Biochar produced in higher temperatures was more porous, thus more efficient for adsorbing pollutants in, e.g., soil (Agrafioti *et al.*, 2013) Due to being generated by carbon neutral biomass, sludge biochar, in comparison to coal, is the more environmental-friendly option. It can be used as fuel and in agriculture to improve the soil's properties (Basu, 2018). The surface area, porosity, and functional groups, such as minerals, contribute to biochar's capability to function as an adsorbent. The production of sludge biochar is also considered to be sustainable, even in large scale, as the emission of carbon dioxide is diminished due to waste products being harnessed in the process (Liu *et al.*, 2015). However, biochar obtained from different biomasses, such as agricultural waste,



Figure 4. Granulated sludge biochar.

has been reported to have a higher adsorption level of different heavy metals than sludge biochar (Zhao *et al.*, 2019). In another study, biochar prepared from cow dung was shown to be a more efficient adsorbent of organic pollutants than sludge biochar, as it had a larger surface area (Suárez *et al.*, 2021). The fact that biochars obtained from different sources have different properties, such as textural properties, affects the adsorption capacities (Suárez *et al.*, 2021). Alternatives to sludge biochar are, hence, available. Yet sludge biochar would be the alternative with the shortest transportation-route, if WWTP can utilise their self-produced sludge, which makes sludge biochar an attractive option.

A problem that could occur with the biochar during adsorption is limitations due to ash content as well as underdeveloped pores. This could be adjusted by pre-treatment, which could include washing with acid (Li *et al.*, 2020). With various carbon content, and a higher ash content, the properties of the derived sludge will impact the characteristics of the sludge-based activated biochar (Betsholtz *et al.*, 2018).

2.4.1 Properties of sludge biochar

From sewage sludge, biochar can be extracted through pyrolytic conversion. Different qualities and properties can be obtained depending on the pyrolysis parameters that are implemented, like temperature and residence time. In a study by Zhang *et al.* (2022) it was found that lower pyrolysis temperatures gave a larger yield of biochar, pyrolysis at 300 °C granted the largest yield. To obtain a large number of pores and largest surface area, a high pyrolysis temperature is required (Patel *et al.*, 2020). In pyrolysis, chemical impregnation with K_2CO_3 and H_3PO_4 could be applied to investigate the potential of increasing the surface area (Agrafioti *et al.*, 2013). It was found by Agrafioti *et al.* (2013) that chemical impregnation did not have a significant effect on the yield. The surface area increased when biochar was impregnated with K_2CO_3 , while H_3PO_4 was not as efficient in increasing the surface area. It was found by Zhang *et al.* (2022) that an increase of temperature also led to an increase of adsorption. The surface area increased and the formation of micro-and-mesopores expanded due to higher temperatures which contributed to aromaticity of the biochar. However, biochar consisting of a high amount of ash is not in favour for expansion of surface area (Agrafioti *et al.*, 2013).

The content of ash depends on the origin of the biochar, how it has been treated and produced. Heavy metals and other pollutants present in the wastewater is, during wastewater treatment, fixed into the sludge, which is the cause of the high concentration of it. Some of the heavy metals that are present are Pb, Cd and Cu. The formation of pores and enhanced surface area contribute to immobilization of these heavy metals, and hence, limit the leaking which reduces the spread of the contaminants (Agrafioti *et al.*, 2013). If ash is present, a higher pyrolysis temperature is required to obtain pores in the biochar (Patel *et al.*, 2020). Another factor that contributes to the reduction in leaking is the close to neutral pH of biochar as the solubility of the metals is reduced. Biochar also contains a lot of plant nutrients, due to being generated formed by sludge which contains minerals such as phosphorus and potassium. These compounds are still



Figure 5. A Schematic sketch of the circular usage of biochar. It begins at the wastewater treatment steps where biochar is obtained from sludge. Biochar can then be reused for wastewater treatment for an adsorption-step or applied in agricultural uses. By contributing to food and clean water, the cycle continues as cities contribute to more wastewater which will re-enter the cycle.

available when applied in, for example, soil fertilization, though a risk assessment need to be implemented to investigate the release of contaminants as well (Agrafioti *et al.*, 2013). By utilizing sewage sludge to obtain biochar, a sustainable resource is used, and a circular economy is promoted, see Figure 5. Other sources for biochar could be wood waste, agricultural waste, or cattle waste. Some alternative production methods to pyrolysis are gasification and carbonization. The produced biochar is porous, has a large surface area and an abundance of functional groups, as mentioned, which is useful for a variety of environmental amendment-areas (Gopinath *et al.*, 2021).

2.4.2 Parameters affecting the quality

The quality of the biochar is dependent on the conditions of the production process, pyrolysis, as well as the physicochemical properties of the sewage sludge, which is used as the feedstock. Among these properties the source and content of sludge is included, which is affected by the treatment processes (Chen *et al.*, 2020). These include primary treatment, which can be physical or chemical. In the physical treatment, particles are removed physically by filtration or sedimentation. In the chemical treatment, chemicals are added to flocculate contaminants. Anaerobic digestion could also be used. In this treatment microorganisms are utilized under anaerobic conditions to digest organic material. There is also the secondary treatment, where aerobic microbial digestion and biofilters are often utilised. The final treatment of sludges usually includes a dewatering process, where sludge is turned into a more solid product. Depending on the source of the sludge, the components and compositions can differ. This includes the nutritional composition of nitrogen and phosphorus content along with the number of pathogens and contaminants (Chen *et al.*, 2020). Biochar contains organic and inorganic materials; whose composition depends on the source of the biomass. The amount of ash could affect the adsorption efficiency of the activated biochar as it could block the pores—the source of biomass is the determining factor in this case also. Mian *et al.* (2023) state that during the carbonization of the biomass, in the generation process of biochar, organic materials are degraded up to 450 °C. After this point, rearrangement of molecules occurs which improves the stability of the biochar. Hence carbonization of sludge biochar should be done at temperatures at 450 °C and above.

Metal ions were found to be able to catalyse the formation of graphite structure of the biochar, which is an example of how the content of the feedstock can affect the quality of the product (Huang *et al.*, 2018). The type of pyrolysis affects the quality as well, as it can be either conventional, dry, or wet. These factors affect the leaching of pollutants and contaminants of the finished product (Chen *et al.*, 2020).

2.4.3 Pore size and distribution

The biochar produced from pyrolysis can then be utilized as adsorbent of organic material, at different efficiency levels depending on the particle sizes as already mentioned. The relationship between the particle size and the adsorption ability has not been investigated at a larger scale yet but it has been found that smaller particles of biochar has achieved increased adsorption in comparison to larger particles. This may be due to smaller particles tend to have a larger surface area and a larger amount of micropores in comparison to larger particles (Jin *et al.*, 2022). In an experiment of biochar's ability to adsorb the organic molecule trichloroethylene, Jin *et al.* (2022) concluded that particles of sizes 0-75 µm were superior in adsorption in comparison to particles of sizes between 75-150 µm (Jin *et al.*, 2022).

In another study by He *et al.* (2018), the physiochemical properties influence on the size was examined on biochar particles between 5-5000 µm. The source of the biochar was pine wood, and the conclusion of the functional groups' composition was that it showed no trends based on the particle size. In terms of the pore sizes and distribution, the pore sizes decreased with the particle size. The smaller particles had an increase of micropores, with a radius of 18-20 Å (He *et al.*, 2018). In activated carbon or biochar, different sizes of pores are present. These pores are called micropores, mesopores and macropores (Marsh and Rodríguez-Reinoso, 2006). Micropores are categorized as pores of sizes smaller than 2 nm, or 20 Å. Mesopores are of sizes between 2-50 nm, 20-500 Å, and macropores are larger than 50 nm, or 500 Å (Wu *et al.*, 2020). The different types of pores are shown in Table 1. It was found the most likely occurring pore size was inversely proportional to the particle size, as the average pore size decreased while the particle size increased, for the sizes 250-5000 µm. Due to differences of pore sizes and distribution, different sizes

of biochar particles could be more efficient in various applications such as agricultural practices or water treatment (He *et al.*, 2018).

Table 1. The different types of pores and their width, in diameter, in nanometer (nm) and ångström (Å).

Pore-classification	Size of diameter (nm)	Size of diameter (Å)
Micropore	< 2	< 20
Mesopore	2-50	20-500
Macropore	>50	> 500

The adsorption affinity of pores is affected by the size of the pore due to various factors. Among those is that in smaller pores the adsorbate has more points onto which to bind on the adsorption surface due to shorter distance between the surfaces. If the pore is too small, the adsorption is limited by size exclusion as the adsorbate cannot fit, which can occur when the adsorbate is bigger than 0.6 times the pore size (Li *et al.*, 2002). The pores are the epicenter for adsorption and therefore there is room for improvement of the porous architecture in sludge biochar to increase the microporosity as this would benefit the adsorption capacity (Mian *et al.*, 2023).

2.5 Activation of carbon

Active carbon can be derived from different materials, such as coconut shells, wood, and coal from mines. Different properties can be obtained, depending on what source is used and the parameters of the activation process. Those parameters are the temperature, the retention time, and the properties of the activating gas (National Research Council (US) Safe Drinking Water Committee, 1980). In the production process, two stages are involved in the physical activation: carbonization and activation. During carbonization, organic, volatile molecules are eliminated from the carbon particles, which occurs during heat with oxygen-limitations. For the activation stage, gas, such as CO₂, is added and the temperature increased. The activated carbon can then be obtained as a porous bio-based product (Tahir and Saad, 2021). The structure of the carbon is close to pure graphite, apart from more disorganized layers due to oxidation from the activation process. Vacancies are formed in the activated carbon and pores are formed. Micropores and macropores are some of the different kinds of pores formed. Out of the total surface area of the activated carbon particle, 90% or more are accounted for by micropores which contributes to adsorption (Mian *et al.*, 2023). In the water treatment process, activated carbon is utilized after sedimentation and coagulation. The carbon adsorbs material, such as organic molecules, and contaminants are removed from the water (National Research Council (US) Safe Drinking Water Committee, 1980). The pore structure determines the adsorption capacity as micropores can function as a physical barrier for particles, even though it contributes to large surface area. To avoid the size exclusion issue, the carbon can be activated which would open the pores up and widen them which would facilitate the diffusion of particles into the adsorption sites (Marsh & Rodríguez-Reinoso, 2006).

2.5.1 Physical activation

One of the possible ways to produce activated carbon includes physical activation, which utilizes gas as an activating agent. The gases used could be steam, carbon dioxide, air, or a combination of them. In a high temperature, porosities are shaped in the carbon particles (Miliotti *et al.*, 2020). Physical activation increases the porosity and surface area by introducing new binding sites. Additional active sites are also generated by the presence of oxygen, hydrogen, and nitrogen. Hence, functional groups of the surface are also formed due to binding heteroatoms (Marsh & Rodríguez-Reinoso, 2006). Physical activation is a two-step process, where the carbon first sustains charring and then undergoes activation where the porous structure is formed. Overall, physical activation avoids the usage of additives and hence, has less impurities in comparison to the chemical activation (Anto *et al.*, 2021). However, the most beneficial activation method so far has included chemicals and high amounts of energy, which is not beneficial economically wise nor sustainable. With other words, there is room to optimize the physical activation for it to out-perform the chemical activation. The challenge with physical activation is the risk of pores collapsing in conditions with excess of heat, which could occur at temperatures higher than 800 °C.

Nevertheless, the gas carbon dioxide contributes to improvement of pore morphology in physical activation. An activation temperature of 800 °C has been proven to be efficient and optimal temperature interval is between 800-1000 °C (Mian *et al.*, 2023).

2.5.2 Chemical activation

In the other production step of activated carbon, chemical activation is utilized. In this process, a reagent is added to the feedstock, which is the carbon. Common reagents are KOH, ZnCl₂ and H₃PO₄. This occurs in an inert atmosphere and in a temperature of hundreds of degrees, 300-800 °C (Miliotti *et al.*, 2020). This method is growing marketwise, for both organic and inorganic chemicals. The impregnation of the chemicals needs to be done carefully, as to not to block the pores, which can be checked with adsorption test. Depending on the chosen chemical different mechanisms will be implemented. H₃PO₄ increases the availability of internal surface area, which improves the adsorption capacity (Marsh & Rodríguez-Reinoso, 2006). Generally, the mechanism involves dehydration of the carbon, along with removal of low volatile chemicals. By removing volatile compounds, the formation of tar is reduced, and the carbon yield is increased, along with improved porosity. Chemical activation is a one-step process, and the choice of reagent depends on the chosen application of the carbon. If the adsorbate that it is supposed to adsorb is negatively or positively charged, the reagent should be alkaline or, respectively, acidic (Anto *et al.*, 2021).

2.5.3 Activation of sludge biochar

To increase the efficiency of adsorption in biochar, physical activation with CO₂ can be utilized as it expands the pore-formation and the pore structure. The gas CO₂ acts as an oxidizing agent at temperatures between 200 °C and 900 °C (Anto *et al.*, 2021). With increasing temperature, the reactivity of the gas increases and it has great affinity to biochar. Pores are formed through carbon dioxide being adsorbed on the surface after having broken its intramolecular bonds, forming oxide and carbon monoxide on the surface of the biochar. Surface oxide is then desorbed, or scavenged, which contributes to the formation of porous structure. The gasification of carbon monoxide is retarded, which reduces the emission into the atmosphere. In trials where oxygen and air were used as activating agents, a high porosity was difficult to achieve and due to exothermic reactions, the process temperature became harder to control (Anto *et al.*, 2021). Hence, CO₂ is the more beneficial choice of activating agent. The process of generating activated sludge biochar is shown as a simplified version in Figure 6.



Figure 6. Sewage sludge is carbonized into biochar. Biochar is then activated to increase the porosity, as shown in the magnifying glass.

As stated in earlier experiments, the optimal temperatures for activation is between 800-1000 °C (Mian *et al.*, 2023). In Colomba *et al.*'s (2022) earlier experiments a gas flow of CO₂ at 0.2 L/min was implemented, as this was found to achieve negligible flow of other product gases in the exit. CO₂ was also a preferred gas over steam, which could also contribute to physical activation, due to CO₂ being able to provide a larger surface area. It was also found that higher heating rates achieved a larger specific surface area of the activated biochar, while it did not affect the size of the pores. In their experiment it was also found that longer activation times caused shrinkage in porosity, which is not beneficial for activated biochar. A typical activation time that has been tested by them was that of 1 h. Appropriate time intervals to test are between 10 min and 2 h. The general process of the activation includes a heating stage with nitrogen gas,

then the activation stage at set temperature and gas flow of CO₂ for a set amount of time (Colomba *et al.*, 2022). Hence, there are numerous parameters to optimize.

2.5.4 Comparison between sludge biochar and activated carbon

By utilizing activated biochar instead of conventional activated carbon, many benefits would become unlocked. The carbon emission would be reduced, along with the atmospheric carbon. Due to this, climate change would be minimised. Additionally, the water quality would be improved as contaminants and pollutants are disposed of when including biochar in the purifying processes (Basu, 2018). Purely physiologically are the differences between biochar and activated carbon not significant as they are both porous carbon material, although biochar typically has a greater abundance of functional groups on the surface. Due to biochar's abundance of functional groups and porosity, the particles are suitable for adsorption of contaminants and pollutants, along with capturing CO₂ (Liu *et al.*, 2015).

Utilization of sludge biochar also provides economic advantages in comparison to commercial activated carbon. The cost of biochar production, through pyrolysis, is split between the feedstock, pyrolysis unit along with transportation and operational cost. Depending on the feedstock the total cost can vary significantly. In comparison to production of wood-based biochar, the sludge biochar production's net cost was valued much less, 46-60 \$/ton biochar compared to 293-382 \$/ton biochar (Gopinath *et al.*, 2021). In a large-scale production of sludge biochar, the net cost/ton biochar would be negative, i.e. it would bring a profit, while in medium scale production it would have a positive net cost around 50 \$/ton (Shackley *et al.*, 2011). This is the case for biochar produced by waste wood and agricultural waste as well (Shackley *et al.*, 2011). This shows one of the benefits of utilizing sewage sludge to generate biochar, apart from the disposal issue of sludge.

2.6 Organic materials

In this experiment, different organic materials will be utilized in adsorption measurements. These are affecting the environment in different ways as they enter through wastewater flows. The compounds that will be discussed are bisphenol A (BPA), diclofenac (DCF) and polyfluoroalkyl substances (PFAS).

2.6.1 Bisphenol A

Bisphenol A (BPA), see Figure 7, is a synthetically produced chemical which is present in different kinds of plastic products, such as food containers. It is a compound that is produced globally, and the yearly production is 700 000-800 000 tonnes (Paxéus, 2017). The material is hence produced in a large scale and the risk of it spreading into wastewater is significant. Therefore, the need for an efficient removal method is great. A study by Rybczyńska-Tkaczyk *et al.* (2023) states that the compound spreads into the environment through WWTP and exceeds the EU's set limit of 1500 ng/L of BPA in aquatic environment. Wastewater is classified as the most common source of BPA and it is difficult to remove by the conventional water treatment methods (Zielińska *et al.*, 2016). A reason as to why the wastewater treatment is not efficient in the removal of BPA is due to the substance's affinity to suspended solids and biofilm, as stated in the article by Zielińska *et al.* (2016). Due to the solids' ability to avoid removal in the biological treatment, the sorbed BPA can pass through the treatment steps. As the application areas of the substance is greatly varied, it is difficult to control the disposal of it. This increases the risk of the compound leaking into the environment, accumulate and cause toxic effects. These effects affect humans as well as other organisms and can be cytotoxic, neurotoxic, and carcinogenic (Rybczyńska-Tkaczyk *et al.*, 2023). In Sweden, reduction of BPA in WWTP occur through degradation in aerobic condition and transfer to sludge (Paxéus, 2017). Hence, the reported reduction is not a complete reduction as BPA still exist in the sludge and leaks into the environment from that. In total, only 50% of the total BPA in the wastewater is degraded, the rest is excluded via the effluent water flow or sludge (Paxéus, 2017).

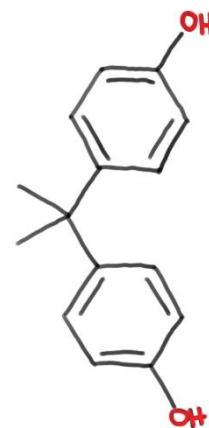


Figure 7. A sketch of the chemical structure of BPA.

2.6.2 Diclofenac

Diclofenac (DCF), see Figure 8, is a widely used anti-inflammatory pharmaceutical, acting as a painkiller, and the disposal of it is problematic due to being done incorrectly. Hence, it often joins the wastewater stream and WWTP lack efficient ways to remove the substance (Alessandretti *et al.*, 2021). In a review by Alessandretti *et al.* (2021) the toxicity of the compound is discussed, and it is stated to have toxic effects on multiple organisms, such as aquatic animals. They also discuss the potential in using adsorption to remove the substance. The toxic effects caused by the substance can occur in the metabolic pathways of the organisms, in organs, tissues or cellular levels. It can cause heightened mortality levels in, for example, aquatic life and have chronic effects. An example of a chronic effect is an effect on the egg growth, such as delayed hatching (Lonappan *et al.*, 2016). This can affect the local ecosystem as well as an ecosystem on a larger scale, due to continuous accumulation of the compound in different organisms. DCF can also react with other inorganic and organic contaminants and hence generate another sort of contaminating compound (Lonappan *et al.*, 2016). This makes it more difficult to trace the toxicity caused by the substance as other non-traced toxic effects can be caused by the compound, only in an undetected form. In Sweden, an exceedance of the level limit has occurred in 18 water sources and additionally 109 places are in risk of exceedance (Finsson, 2020). The occurrence of the compound in the water is therefore a significant problem of today's society. A large factor that has contributed to the spread is the fact that the pharmaceutical is applied as cream and hence washed out into the wastewater via showers or in similar situations. To control the amount of DCF that spreads out into the environment, the pharmaceuticals should be sold as prescription drug. Nonetheless, the removal of the pharmaceutical in wastewater treatment needs to be improved in order to control and limit the spreading into the environment.

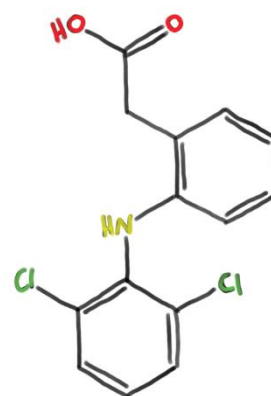


Figure 8. A sketch of the chemical structure of DCF.

2.6.3 Per- and Polyfluorinated alkyl substances

Built up by carbon and fluorine, per- and polyfluorinated alkyl substances (PFAS) are very stable molecules due to their carbon-fluorine bonds. One example of PFAS is perfluorooctanoic acid (PFOA), see Figure 9, which is the substance used in this project. There are major issues regarding PFAS spreading to the environment as they barely degrade in nature and can leak into soil, water, and air (NIEHS, 2024). They are substances that are used in different products, such as in fire extinguisher, cosmetics, and pans. One of the main routes into nature for PFAS is through WWTPs, via sludge or the effluent stream (Fredriksson *et al.*, 2022). If a more efficient removal step is added to the treatment, the amount of leaked PFAS would be reduced and it would be fewer negative impacts on the environment. Some of the negative impacts the chemicals would have in the environment is reduced growth of organisms and higher mortality rates (Sinclair *et al.*, 2020). An accumulation of PFAS can occur in plants and aquatic life due to the substances leaking into soil and water. Hence, when the PFAS reach humans, the intake of the chemicals is of high concentration due to their different routes into our system. Some of the toxic effects for humans are increased liver weight, altered immune response and cancer (Fenton *et al.*, 2020). In a study by Fredriksson *et al.* (2022), the occurrence of PFAS in the sludge of four different WWTPs were investigated. It was found the discharge of PFAS was between 1840-10 000 ng PFAS/day/person, depending on the region. EU's Drinking Water Directive (2017/0332/COD) has a limit of 5 000 ng/L of all PFAS. To control the outlet concentration of PFAS and limit the leaking, the wastewater treatment needs to be developed in order to increase the removal of PFAS.



Figure 9. A sketch of the chemical structure of a PFOA molecule.

3. Methods and materials

The experiments were set up to compare the adsorption capacities between different particle sizes, activation temperatures, residual times, and sludge biochar from different WWTPs. Different materials and methods were needed to accomplish this, which are described in the sections below.

3.1 Materials

For the performed experiments, the following materials were used;

1. Pyrolyser Trio™ Raddec International LTD equipped with the gear
2. Nitrogen (N₂), (g)
3. Carbon dioxide (CO₂), (g)
4. Sludge biochar
5. PAC NORIT® SAE SUPER Carbot
6. Sieves of different sizes
7. Containers
8. UV-spectrophotometer HACH DR 6000
9. Wastewater (Öresundsverket Helsingborg, Nykvarnsverket Linköping)
10. Scintillation liquid Hionic-Fluor™ PerkinElmer
11. ¹⁴C-labelled organic chemicals
12. Photosensor TriCarb 4910 TR PerkinElmer

Two different water sources were used in the experiment, as can be seen above. Different quality parameters were determined for each water, including dissolved organic carbon (DOC), chemical oxygen demand (COD), pH and ion content. These are presented in Table 2. These measurements were done by the lab-supervisor and another master thesis student, using ion chromatography (Metrohm 863 Compact Autosampler) and HACH DR 6000 spectrophotometer with HACH cuvette LCK 385 for DOC and LCK 314 for COD.

Table 2. The properties of the water from Öresundsverket and Nykvarnsverket.

Source	DOC (mg/L)	COD (mg/L)	pH	NH ₄ -N (mg/L)	NO ₂ ⁻ (mg/L)	NO ₃ ⁻ (mg/L)
Öresundsverket	7.6	24	7.8	1.1	0.24	5.1
Nykvarnsverket	15	34	7.0	6.0	0.16	6.7

3.2 Sludge biochar production

The sludge biochars studied were supplied by the company Aquagreen and produced at their two full-scale sludge pyrolysis plants in Denmark, see Figure 10. Hence, the production of the sludge biochars was not part of the experiment or method. An overview of the production has been included as a pre-step in the method to make information about the sludge biochar available. The following information was obtained from the supervisor's (VA Syd) mail-contact with AquaGreen.

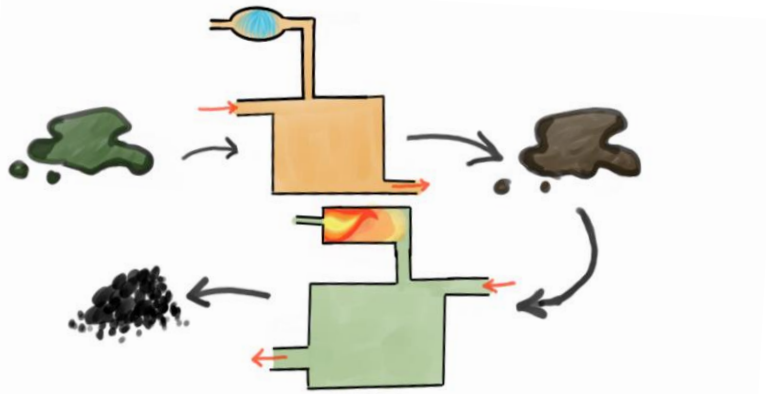


Figure 10. The flow chart of the carbonization-process performed by AquaGreen WWTPs. The inlet to steam drying section (orange) is wet biomass, and the outlet of the steam dryer is dry biomass, maximum drying temperature at 135 °C. Dry biomass enters the pyrolysisator (green), which carbonises the biomass to sludge biochar at a maximum temperature at 650 °C and residence time of 20 minutes. Sludge biochar is found in the outlet of the pyrolysisator. The original systematic figure is available in Appendix. Approval to include figure in report was given by AquaGreen (Wieth, 2024).

The sludges from the Søndersø, Højby, Nykøbing and Fårevejle WWTPs were pyrolysed in full-scale at Søndersø WWTP and Fårevejle WWTP (Højby, Nykøbing and Fårevejle) in maximum temperature 650 °C and a residence time of 20 min. The carbonization process followed the steps in the figure, which also includes the steam drying of the wet sludge.

3.3 Physical characterisation

First, the particle sizes being examined in the activation test had to be determined, which was done by employing a novel method. This method is explained in the following text.

As we had a surplus of samples from Søndersø WWTP, the biochar from there was used for the sieving. The samples were weighed, and the scale was tared for the sample container's weight, to subtract it from the total mass. Sieves with strainer holes of the mesh sizes 8 mm, 6.3 mm, 4.76 mm, 3.35 mm, 2 mm, 1 mm, 0.85 mm, 0.425 mm, 0.150 mm, 0.125 mm, and 0.075 mm was combined into a pile, or multiple, with the largest diameter at the top and the smallest at the bottom. A collection plate was placed at the bottom of each sieve pile. The sieving followed a program of 10 seconds of shaking, 5 seconds of slapping on each side and another 10 seconds of shaking. This method was set to treat all biochar the same, while, at the same time, obtain enough biochar of each sample for the activation. All the separated particle sizes were gathered in different containers and labelled.

3.3.1 Ratios between particle sizes

The amounts and ratio of the different particle sizes were determined by weighing the containers containing the different particles. The biochar particles were poured into another container and the original, empty container was weighed. The container-weight was subtracted from the total weight to obtain the weight of the mass of particles. The ratio of each particle size was determined in the original sample by dividing the total mass of a particle size with the total mass of the sample.

3.3.2 Biochar densities

The density of the biochar was determined, fractionated and un-fractionated. The masses of each particle size were transferred into a volume meter and the approximate volume achieved by the mass was noted. This was done for each collection of biochar size. When all separate particles have been measured, the volume of the unfractionated sample was measured by mixing the separate particles in a volume measure glass. With mass and volume known, the density of the un-fractionated biochar samples as well as the different particle sizes were calculated.

3.4 Activation

The Pyrolyser Trio™ Raddec International LTD, see Figure 11, was prepared by ensuring the gas tubes were airtight and water containers were filled with distilled water. The boats, see Figure 12, were weighed, and filled with 2 g of each sample before loaded into the pyrolyser. The pyrolyser was pre-set to an activation-program adjusted for the determined activation parameters. The heating-rate was set to 10 °C/min and the ingoing gas was 0.2 L/min of 1 bar N₂. When the temperature chosen for the activation was obtained, the gas was set to switch to 0.2 L/min of 1 bar CO₂ and the dwell-time was set for favoured time. During the cool-down, the gas-flow was set to switch back to N₂. To increase the efficiency of the cooldown, the fan was turned on and the chimney opened. The conclusions for the settings for the ingoing gas were drawn from an experiment by Colomba, Berruti and Briens (2022). The pyrolyser was run with an addition of samples from another master thesis-group, who were examining the adsorption capacities of activated biochar produced for lignin. As only one pyrolyser was available, cooperation with the instrument was required. This meant the activation process in this experiment also included a carbonization-step at temperatures between 400-600 °C for some samples, which should not affect the outcome as the biochar already has been carbonized.

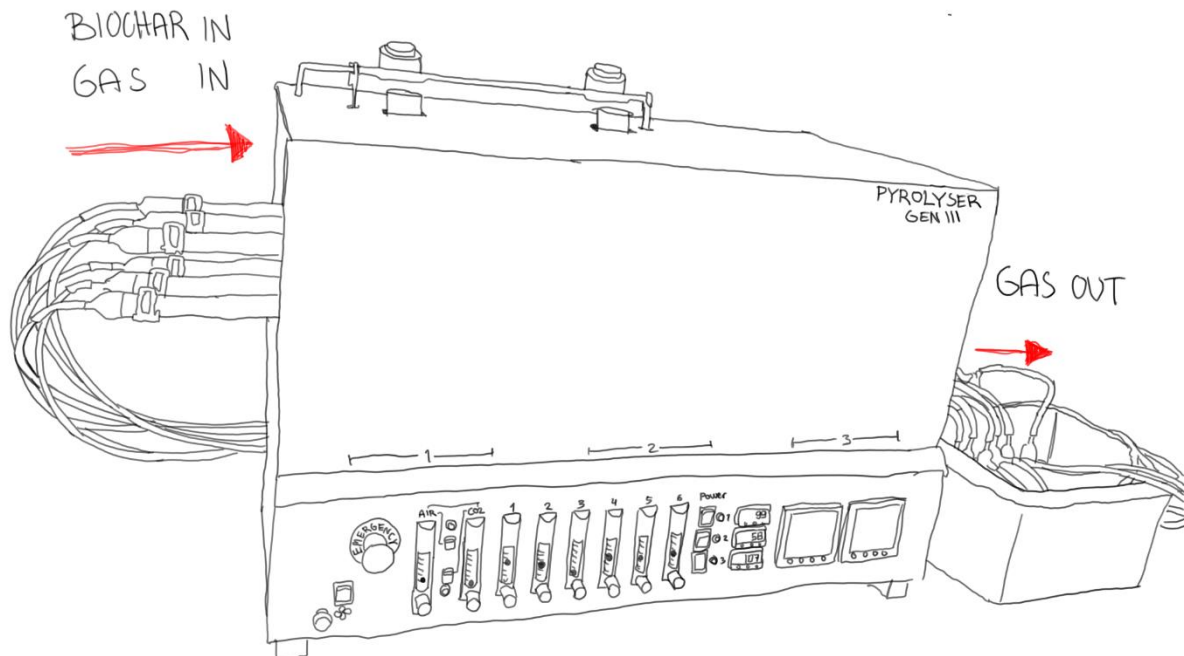


Figure 11. Pyrolyser Trio™ (Raddec International LTD) which was used for the activation process. The biochar was loaded into the “boats” that were put into the glass containers on the left, where also the input of gas occurred. Those were then put into the pyrolyser and on the right there is an outlet for gas. The outlet is connected to glass containers containing water, which are linked to a safe outlet for the gas. On top of the pyrolyser is the chimney, which was opened during the cooling stage. At the bottom of the pyrolyser is where the gas pressure and gas flow controllers are located, next to the display controls on the right.



Figure 12. The boat in which the biochar was loaded and put into the pyrolyser.

In this experiment, the activation temperature and particle size were in focus, as well as a comparison between activated biochars obtained from different water treatment plants. The time intervals being tested

were activation for 4h, 2h, 1h, 30 min and 15 min. This was based on reports of previous experiments that had found an appropriate time frame of 10 min to 2 h (Colomba *et al.*, 2022). In order to draw proper conclusions about the activation time, a more extreme time frame of 4 hours was also included. The temperatures to be tested were 600-900 °C, which was determined from reading conclusions of earlier experiments (Mian *et al.*, 2023). Temperatures outside the recommended interval was included to investigate if similar results could be achieved by lower temperature as this would be more energy efficient. After activation, the biochar samples were weighed and put into a labelled container, as illustrated in Figure 13.



Figure 13. The activated sludge biochar from the pyrolyser's boat being weighed and transferred to a container.

3.5 Adsorption measurements

The samples were prepared for the adsorption measurement by mixing solutions of 2 g biochar/mL. To make the solutions, 0.2 g of biochar of each size was weighed in an accurately marked 100 mL bottle. Then, 100 mL of distilled water was added into each bottle to obtain the set concentration. Each solution was put under magnetic stirring to obtain an as homogenous solution as possible and 2 mL of the solution was transferred into a 50 mL tube with 38 mL effluent wastewater. The wastewater had been filtered with a filter size of 45 μ m. A final concentration of 100 mg biochar/L was obtained. This was deemed to be an appropriate final concentration based on earlier trials in the experiment with a final concentration of 50 mg/L that had resulted in adsorption levels lower than 5% of the organic components, which made it difficult to draw accurate conclusions about optimal activation parameters. The biochar adsorbed organic material in the tubes with wastewater for 24 h on a shaker-tray set on 125 rpm. These steps are illustrated in Figure 14. Some samples were washed after 24 h of shaking and the washing was done by transferring 2 mL of 1 g/L biochar-solution to 50 mL tubes, adding an equal amount of distilled water into each tube and centrifuging them at 4000 rpm for 5 minutes. Some samples were centrifuged after the shaking, with a centrifugation program with a rpm of 4500 and centrifugation time of 10 min.

After the 24 h shaking, and washing/centrifugation for some samples, 15 mL of each sample was transferred into a 5 cm cuvette, through a 45 μ m filter, and put into an UV-spectrophotometer. The settings of the spectrophotometer were set to light of a wavelength at 254 nm since organic material absorbs light at that wavelength. A blank of distilled water was made before the sample measurements. A measurement of wastewater without biochar was also done to have the starting concentration of organic material. Then the absorbance of each sample was measured. The differences of absorbance between the non-treated wastewater and wastewater treated with difference kinds of biochar particles were put into a graph to visualize the reduction level of each activated biochar.

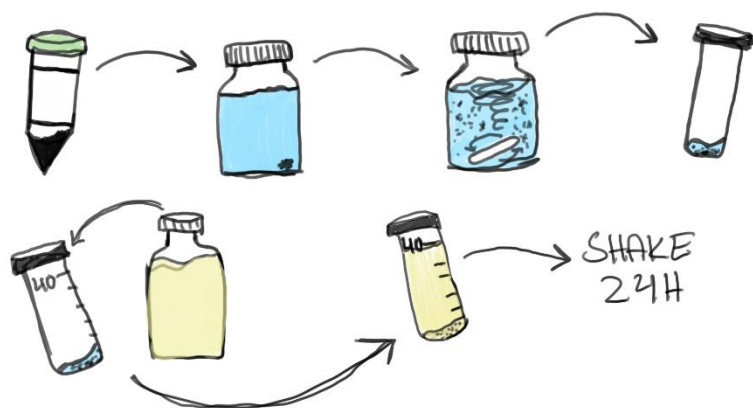


Figure 14. The steps needed to achieve the required concentration in the wastewater solution with activated biochar. Activated biochar was put into distilled water, marked as blue, to obtain a 2 g biochar/L solution. A magnetic stirrer was used to improve the homogeneity, as shown in step 3. Then 2 mL was transferred into another container, which was then filled up to 40 mL by wastewater, marked yellow in the figure to obtain the final concentration of 100 mg biochar/L wastewater. The wastewater-solution containing biochar was then put on a shaker for 24 h.

3.6 Systematic measurements

For the systematic adsorption tests, multiple containers were prepared. Eight different concentrations were investigated of chosen activated sludge biochar, the activated biochar from AquaGreen and commercial PAC. In total, the adsorption capacity of 11 different activated biochars were measured in concentrations of 10, 20, 30, 40, 60, 100, 150 and 200 mg/L. Wastewater from Öresundsverket was put through a 45 µm filter before 40 mL was added to each 50 mL container. The standard solutions with 100 mg activated sludge biochar/L from previous experiments were reused. Different volumes of these solutions were transferred to obtain the correct final concentrations. The determined transfer volumes are presented in Table 3.

Table 3. The transferred volumes of the standard solutions used to obtain the favoured final concentration. The distillation factor for each sample is included in the right column.

Transferred volume (mL)	Final concentration (mg/L)	Distillation factor
0.2	10	1.005
0.4	20	1.01
0.6	30	1.015
0.8	40	1.02
1.2	60	1.03
2	100	1.05
3	150	1.075
4	200	1.1

In the table, the distillation factor is included as this was used to calculate the absorbance of the samples with regard to the distillation caused by the transferred volume. Two containers with only filtered wastewater was also prepared. After addition of wastewater and standard solutions, the 90 containers were put for shaking for 72 h. When the samples had been taken out from the shaking board, the absorbance was measured by transferring 15 mL to a 5 cm cuvette which was put into a UV-spectrophotometer. The spectrophotometer was set to a wavelength of 254, as described in Method 3.5. The absorbance was noted, recalculated in regard to the distillation and then used to determine the reduction level of each

sample. The reduction was calculated in regard to the average absorbance of the two samples containing only filtered wastewater.

3.7 Adsorption test with ^{14}C labelled substances

In this part of the experiment the adsorption of three different chemicals, BPA, DFC and PFOA, was to be investigated. For these three different activated carbons was chosen, PAC and two different activated sludge biochar. For each adsorbent, the adsorption of each chemical was to be investigated in eight different concentrations. The concentrations of the biochar were the same as in the previous experiment, Method 3.6. Hence, seventy-two 50 mL containers were prepped with a solution of filtered wastewater, and chemical residues. The concentration for the solution of DCF was $0.529\ \mu\text{g/L}$, BPA $0.152\ \mu\text{g/L}$ and PFOA $0.753\ \mu\text{g/L}$. Addition of the sludge biochar and PAC solutions were done as according to Table 3 to achieve correct concentrations. For each organic chemical, solutions with only wastewater and the chemical in the mentioned concentrations were prepared in duplicates as references. In total, 78 containers were put on the shaking board for 72 h. After centrifugation at 4000 rpm for 10 minutes, 4 mL of the samples were transferred to 12 mL scintillation liquid, Hionic-FluorTM, and put into a photosensor (TriCarb 4910 TR) where the emitted light from the ionizing particles was measured. The analysis method to measure the concentrations of pharmaceutical residues in the study is scintillation counting of the activity of ^{14}C isotopes. In this technique, the number of emitted β -particles from ^{14}C -labeled residues is counted (Passmann *et al.*, 1956) and it is proportionate to the number of pharmaceutical residues dissolved in the solution. In the scintillator liquid a fluorescent material is present and emits light when it interacts with the radioactive β -particle released from a decayed ^{14}C -molecule (National Diagnostics, 2004). The energy from the ionizing radiation is absorbed by the fluorescent material which excites the atoms. When the excited electrons are returned to original state, the excitation energy is released in form of photons, which generates light that is detected and quantified by a photosensor. The measured unit is counts per minute (CPM) and it describes the number of occurring decay events (National Diagnostics, 2004). Pharmaceutical residues will be labelled with ^{14}C isotopes, and the dissolved substances will be quantified in the analysis technique. The reduction of ionizing particles in this project was correspondent to the amount of adsorbed chemical substance.

3.8 Summary of the experiments

In the table below, Table 4, is a summary of the different experiments that were studied in this master thesis in the order they are presented in Result and Discussion.

Table 4. Summary of the different experiments performed and discussed in this project.

Experiment number	1	2	3	4	5	6
Experiment	Physical Characterisation	Moisture content	Activated biochar yield	Adsorption capacities	Systematic test	Adsorption of organic chemicals

4. Results and Discussion

In this section, the results of the different experiments are presented and discussed. It is divided in different parts that focus on different segments of the experiment and different parameters of the activation process.

4.1 Physical characterisation

After sieving for all the particle sizes stated in Method 3.3, it was determined that 6.3 mm, 3.35 mm, 1 mm and 0.425 mm in diameter were appropriate particle sizes to examine in the activation-tests as these constituted a significant proportion of the available biochar particles and were suitable for the following measurements. In previous studies, smaller particle sizes have been proven to be more efficient in adsorption (Jin *et al.*, 2022). Larger particle sizes were included, though, to enable more accurate conclusions about the impact of the particle size. The results of the ratio for appropriate biochar particle fractions are presented in Figure 15. Three replicates were made to ensure the reliability for the Sønderlø samples, and the mean values of these measurements are included in the table. The detailed results from the replicate-measurements can be found in Appendix 2. The ratio of the fractions is in proportion to the total mass of the sample. Throughout the report, the different fractions will be referred to as 6.3, 3.35, 1, 0.425 and <0.425 mm. For each of these particles, everything larger than said diameter and smaller than the previous particle size is included in the fraction. E.g. in the sample from Sønderlø WWTP, the particles of 1 mm in diameter had the greatest ratio of all the fractioned samples, meaning the unfractionated sample had a majority of particles of this size, as shown in the table.

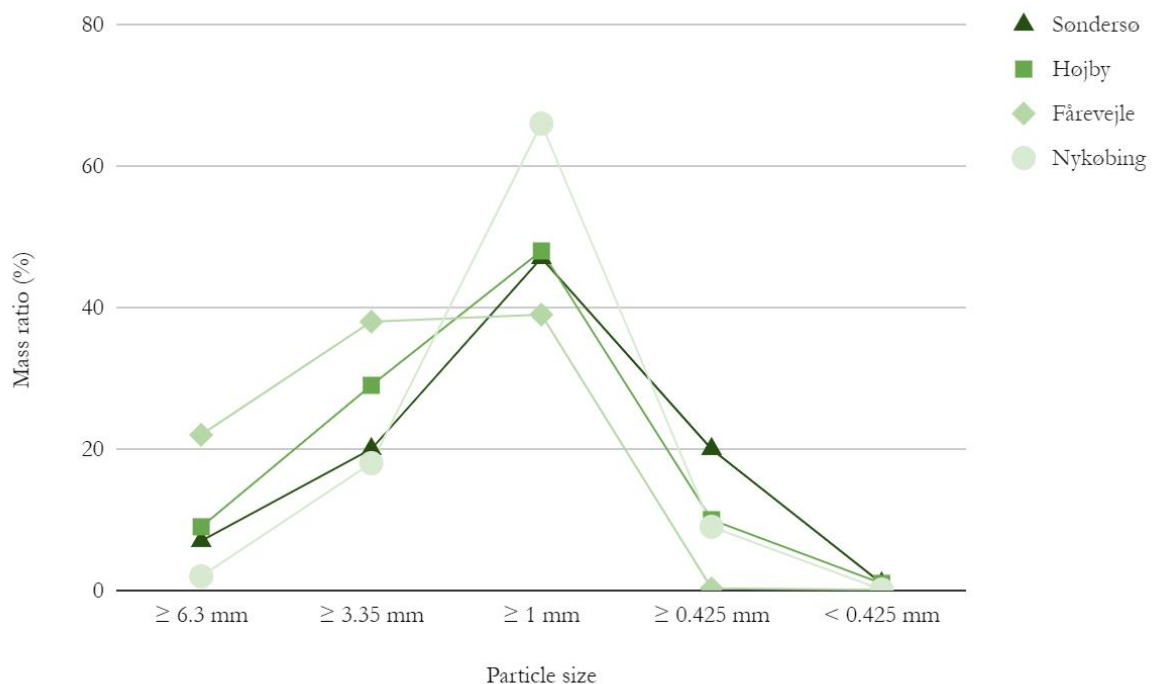


Figure 15. Ratio between the different particle sizes in comparison to the total mass of the unfractionated sample for the sludge biochar from the different wastewater treatment plant.

As shown in Figure 15, the measurements of the biochar from Højby had similar results as Sønderlø with a majority of particle size 1 mm. In comparison to Sønderlø though, it was richer in particles of sizes 3.35 mm and had less particles of diameter 0.425 mm. The sample from Fårevejle had, similarly to the other samples, a majority of particles of 1 mm, although the ratio of 3.35 mm particles was approximately the same. There was a higher presence of the larger particles, in comparison to the samples from Højby and

Søndersø. As can be seen in the ratio, the particles with a diameter of 1 mm are the vast majority for this sample as well. It is the sample richest in 1 mm, in comparison to the other samples. The ratio for particles of the diameter ≥ 6.3 mm is similar to Søndersø and Højby. With the aspect of particles with diameter of <0.425 mm, Nykøbing had a more similar result as Fårevejle. Similar to Fårevejle, Nykøbing also felt moister and dirt-like, although not as much as the previous sample source. Overall, most of the existing particle sizes of all the biochar samples were of a diameter between 3.35 and 1 mm.

In Figure 16, a concluded comparison of the densities of each sample is shown. From the figure, it can be seen the densities of the larger particles and unfractionated samples are relatively close while the variation increases for the smaller sizes. This is due to the amount of those being much smaller and therefore the precision of the weight and volume measurements had a significant reduction.

The densities of the mixed samples, i.e. the unfractionated, are quite similar between each biochar source, meaning the biochar compositions between the different sources are most probable alike. The exact density was however difficult to due to measuring of volumes of solids. Due to limited available equipment, the volume-measuring was done by transferring the particles into measuring glasses and hence, there was air pockets present affecting the results.

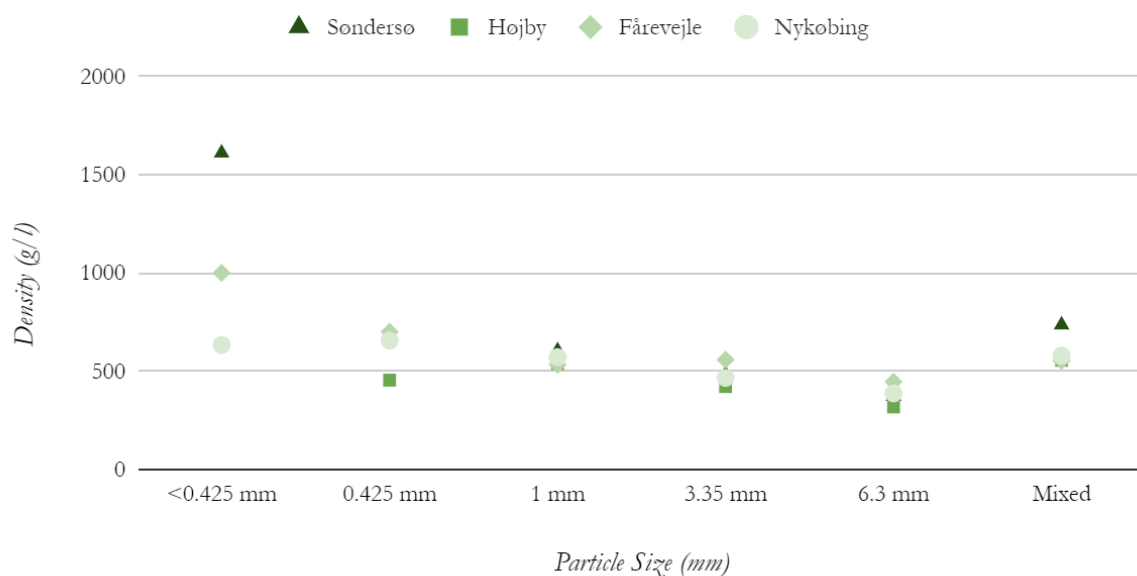


Figure 16. Comparisons of the densities between different particle sizes and wastewater plants. The results from Søndersø is represented by the triangles, Højby by the squares, Fårevejle by the diamond-shape and Nykøbing by the circle. The results coincide for most of the samples, except those of the particle size smaller than 0.425 mm in diameter.

The densities for the larger particles are similar between each wastewater plant source, while the smaller particles have a larger variation of density. As the density of the unfractionated samples were similar, the deviation between the different biochar sources of the smaller particles is most probably due to the available amount being a lot smaller, causing the measuring being of lesser precision. The variations of the density between the wastewater plants can be due to different moisture content and a varied composition of compounds, such as nutrients and contaminants.

4.2 Moisture content

The moisture content was measured in the biochar-samples from each wastewater plant in duplicates. The average moisture content for each source is presented in Figure 17 below.

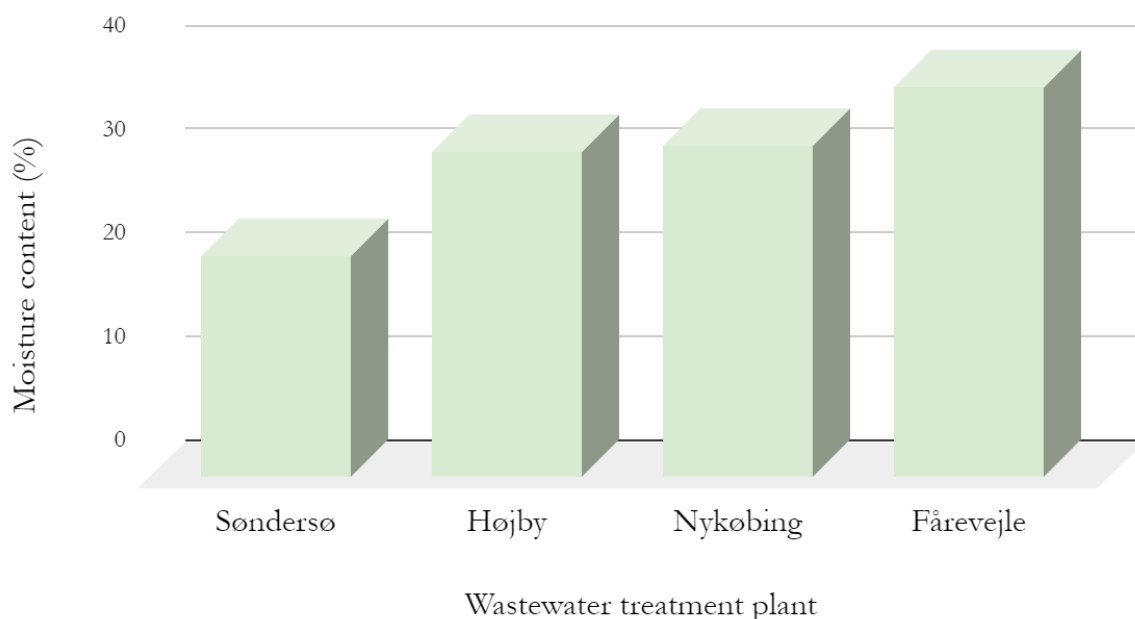


Figure 17. A visual representation of the average moisture content of each biochar sample.

As shown in the figure, the biochar-samples from Fårevejle had the greatest moisture-content. Nonetheless, each of the biochar samples had a rather high moisture content, varying between 21.4 % to 37.0 %. The water within the biochar was not expected to alter the activation as it evaporates at 100 °C, well before the activation temperature is reached. However, the composition of the compounds existing in the biochar, such as phosphorus and heavy metals, may still affect the pore formation and adsorption capacity of the activated biochar.

4.3 Biochar yield after activation

The mass loss after activation was also investigated, see the results in Figure 18. In the beginning of the experiment, activation with 800 °C for 1h was tested on most of the different biochar sources. It was found the mass decreased with approximately 40-60% for each particle, as shown in the figure below. The samples from Fårevejle were not activated due to the indication from the adsorption tests of the other biochar-samples that the activation parameters were not worth exploring further, which will be discussed further down. Since the moisture-content was determined to be maximum 37 %, and the mass loss after activation is above that for each sample, it can be concluded that more than only water has been removed in the activation process. Tar is one of the substances that is probably removed in the process as it decomposes in rising temperatures and hence, lowering the mass of the biochar (Zhao *et al.*, 2023).

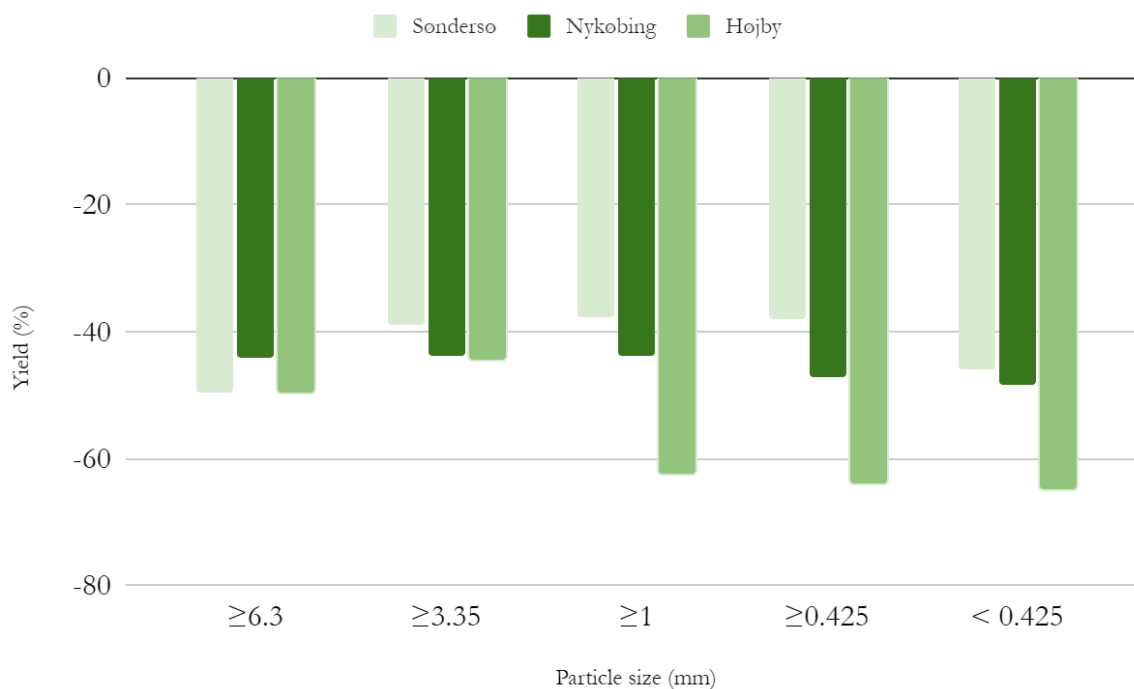


Figure 18. The mass loss after activation, in 800 °C for 1h, for each sample. Søndersø is represented by the light green stacks, Nykøbing by the dark green stacks and Højby by the medium green. Fårevejle is not included due to the experiment being partially paused as the activation did not result in particularly high adsorption-rates.

After activation, a silver and gray colour was observed on the surface of the carbon granules. A possible theory is that the visible grayness is due to ash coming to the surface as volatile compounds were excluded during the activation process. The presence of ash could affect the development of surface area, and hence the activation level (Agrafioti *et al.*, 2013a).

4.4 Adsorption capacities

After activating the samples, the adsorption was measured as described in Method 3.5. The adsorption of the wastewater was measured to be 1.065 in the 50 cm cuvette (21.3 for 1 m). The absorbance beyond the natural absorbance of wastewater was determined and then the reduction in percentage achieved by each particle size was calculated. These results are presented in Figure 19. The reduction value is comparable with the adsorption capacity, as a higher reduction indicates more efficient adsorption of the organic material. As can be seen in the figure, the particles of sizes < 0.425 mm had a higher adsorption capacity than those of diameter ≥ 0.425 mm. As the solutions with the larger particles, 1-6.3 mm, had a higher particle concentration (1 g/L instead of 100 mg/L), it is difficult to compare the adsorption capacity with the smaller particles as those solutions had a significantly lower particle concentration. However, as stated in the article by Jin *et al.* (2022), smaller particles have been reported to achieve a higher adsorption than larger ones. The adsorption for these samples, however, weren't optimal based on the figure below. In comparison of the reduction levels between un-activated and activated samples, the adsorption-capacities differ but not enough to be optimal for industrial use. However, there is a visible difference, meaning the activation process was functional to a certain extent as the activated samples had a measurably higher reduction level. Although, the activation process did not reach a high level with those parameters.

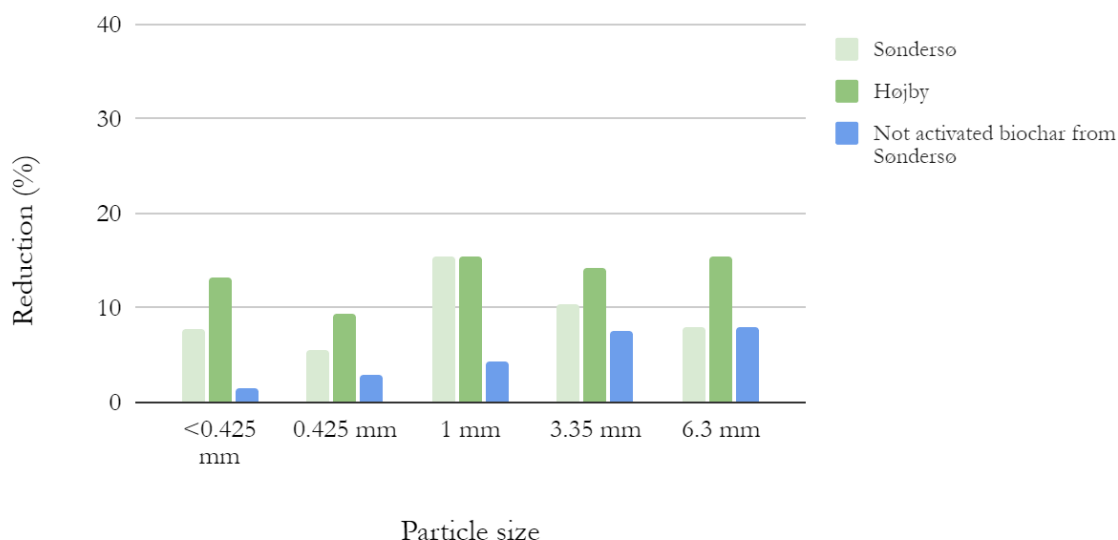


Figure 19. The adsorption-capacity of the different fractions of samples from Sønderø (light green) and Højby (green). The samples were activated in a temperature of 800 °C for 1 h. The blue stacks represent the adsorption-capacity of non-activated sludge biochar obtained from Sønderø. The reduction of organic material in wastewater was measured in solutions of 1 g biochar/L wastewater for particles of sizes 1, 3.35 and 6.3 mm. The smaller particles, between 1 and 0.425, and smaller than 0.425 mm, had a concentration of 100 mg biochar/L wastewater.

Hence, multiple parameters had to be tested to obtain a sufficient activation method which was done with the particles from Sønderø of the size 0.425 mm in diameter and those smaller than 0.425 mm. Parameters that were deemed interesting to test was temperature, residual time, gas flow and washing of the activated biochar. Also, the heating rate was included in these trials. The reduction of organic material in the wastewater by commercial activated carbon was included as a reference value. Both granulated and powdered activated carbon (GAC and PAC) were examined and the PAC had a greater reduction level than GAC, with 72.3% compared to 55.9%. This was expected as PAC reaches equilibrium faster due to being smaller, which is more favourable for a faster mass transport.

Activated biochar from AquaGreen was obtained and its adsorption was measured. From the available information of the activated AquaGreen biochar, it was stated the activation was done by steam. Unfortunately, further information was not available. Samples from AquaGreen was sieved to obtain particle sizes of 0.425 mm and smaller than that, to coincide with the other measurements. Trials of increased heating rate (50 °C/min) was included but it was noted the pyrolyser did not have the capacity for the high heating rate. The approximate practical heating rate was closer to 20 °C/min. Washing was done for the AquaGreen samples and the activated biochar with the activation temperature of 600 °C, CO₂ flow of 0.4 L/min and residual time of 1 h. An additional absorbance measurement was done of those samples, unwashed, although only for the particle size <0.425 mm. This was to be able to draw conclusion of the impact of adding a washing step. From the results, it was concluded the difference of the washing step was only marginally as the reduction differed with only a few percentage units. Therefore, washing was deemed an unnecessary step for determining parameters that provided an activated biochar with a reduction level of 30 %, as suggested by supervisors. The washing was included in the beginning as it contributes to reduction of ash, which can negatively impact the adsorption-capacity of the biochar as it prohibits the pore-formation (Mian *et al.*, 2023). However, as stated, the washing of ash had little effect. The most promising results for these trials are found in Figure 20 below. All the results can be found in Appendix.

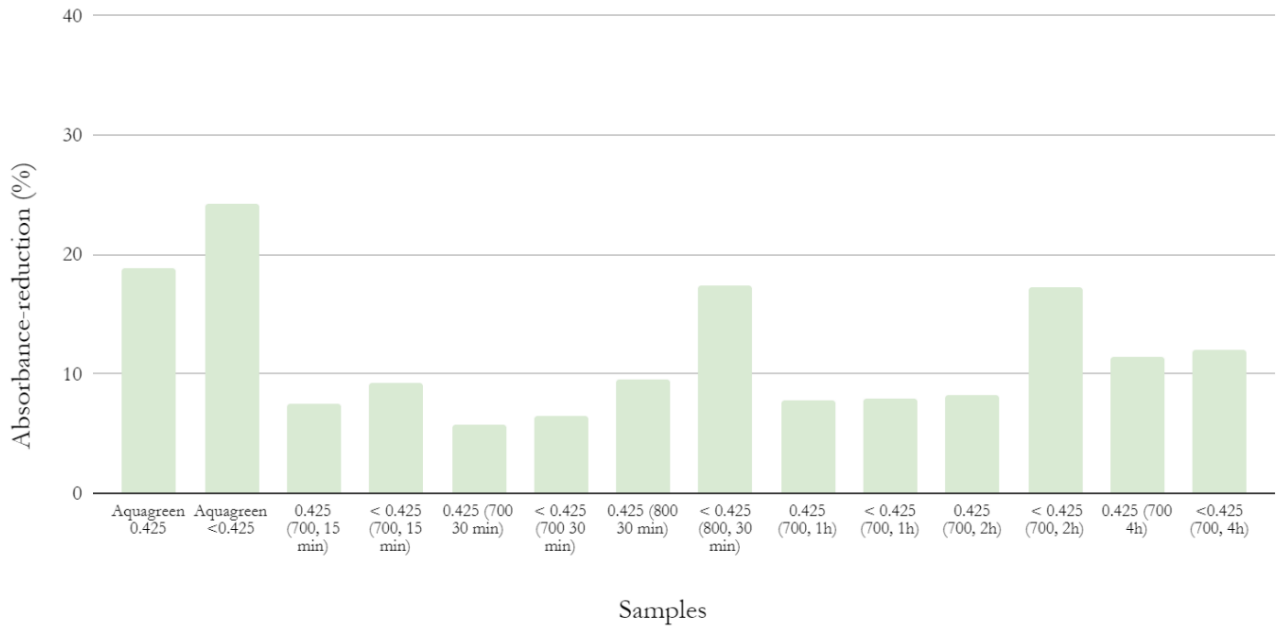


Figure 20. The reduction results of trials with different parameters. Here the concentrations of the particles bigger, equal, and smaller than 0.425 mm, yet not bigger than 1 mm, was 100 mg/L. All samples, except the samples from AquaGreen and the commercial carbon, are from Sonderso.

From the previous trials, it could be seen that biochar in particle sizes <0.425 mm and activation temperature of 700 °C and an activation time of 2 h achieved higher reduction than those of larger size and/or shorter activation time. At a higher temperature though, a short activation time resulted in the highest reduction level measured so far, which can be seen in the result for activation in 800 °C and 30 min. Therefore, the next trials focused on both longer and shorter activation times to determine which is more optimal for each temperature. Different activation times were tested for the temperatures 700, 800 and 900 °C, see Figure 21 below.

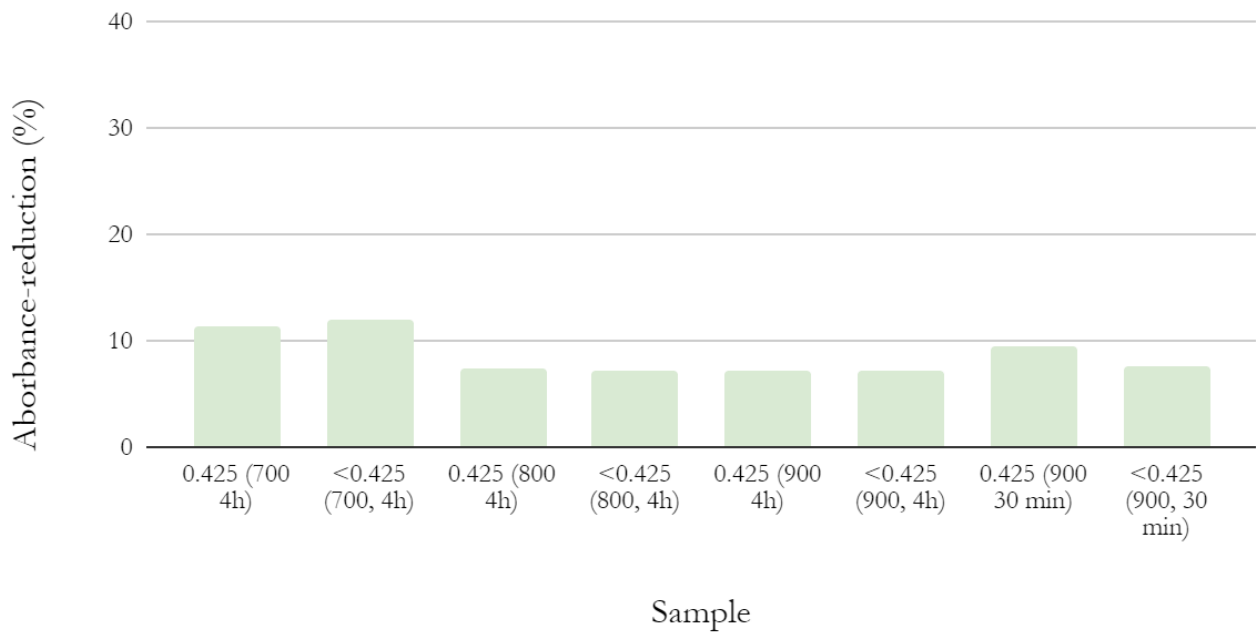


Figure 21. The reduction results of trials with different parameters. Here the concentrations of the particles bigger, equal, and smaller than 0.425 mm, yet not bigger than 1 mm, was 100 mg/L. All sample are from Sonderso.

As shown in these results, a lower temperature, like 700 °C, had a higher reduction level at the longer activation time of 4 h than the other temperatures at the same activation time. A reason for this could be that the excess of heat in the other trials caused the pores to collapse. In comparison between activation in 800 °C in 4 h respectively 30 min, it can be determined that the activation in shorter time for the higher temperature granted a higher reduction level as can be seen in the graph above, Figure 20. Due to the higher temperature, the pore formation, and hence the adsorption capacity, is probable to have had its measured optimum in lower activation times due to pores collapsing.

For the same Søndersø-samples as in the graph above, the adsorption was measured again after a centrifugation step, see Figure 22 below. As can be seen from Figure 22 when compared to the graph above, Figure 21, the adsorption capacity increased after centrifugation for all samples. Based on the improved results, it is probable that particles of biochar in the previous trials increased the absorbance in the measurements and hence contributed to a lower reduction rate.

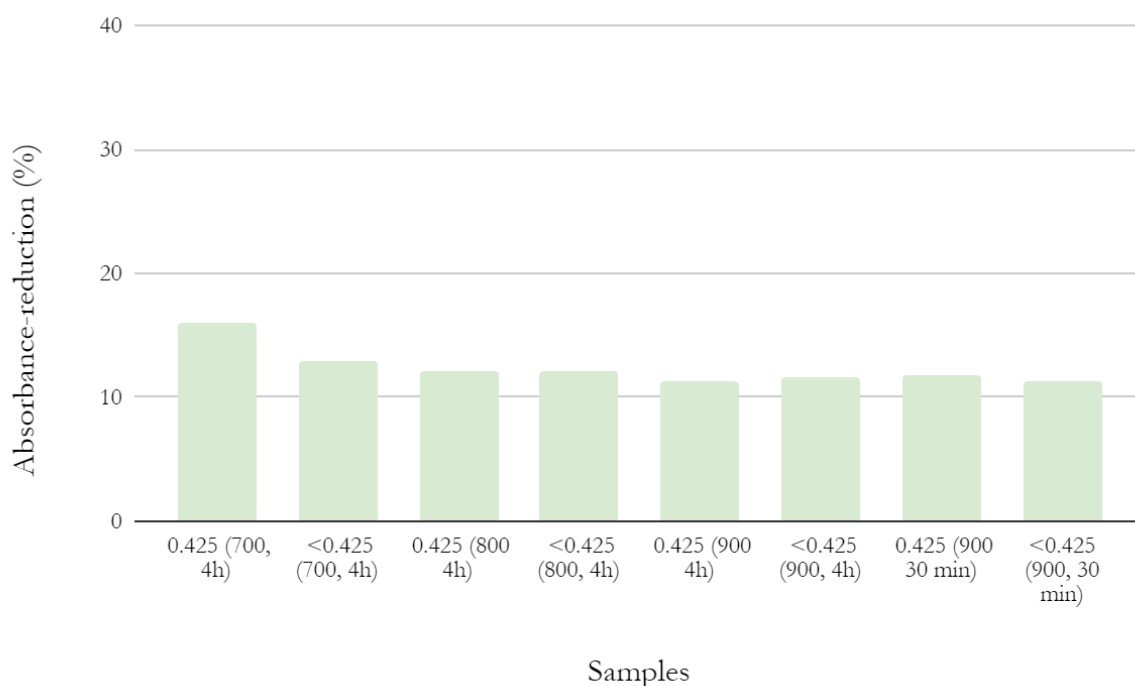


Figure 22. The reduction results of trials with different parameters. Here the concentrations of the particles bigger, equal and smaller than 0.425 mm, yet not bigger than 1 mm, was 100 mg/L. All samples are from Søndersø and they were centrifuged after the shaking to limit the amount of biochar particles present in the water phase.

4.5 Systematic adsorption measurements

The adsorption of organic material in the different concentrations of each sample were tested with an adsorption-time of 72 h and the trials were made with the particle sizes <0.425 mm. These trials were done with wastewater from Öresundsverket, while the previous experiments (4.1-4.4) were done with wastewater from Nykvarnsverket. To limit the impact on the adsorption measurement by the biochar particles present in the measured samples, the following samples were centrifuged, after the shaking-step. In this way, the particles were gathered at the bottom of the container and the risk of them being transferred to the adsorption test was minimised. The results for each activated sludge biochar at each concentration are shown in Figure 23 below.

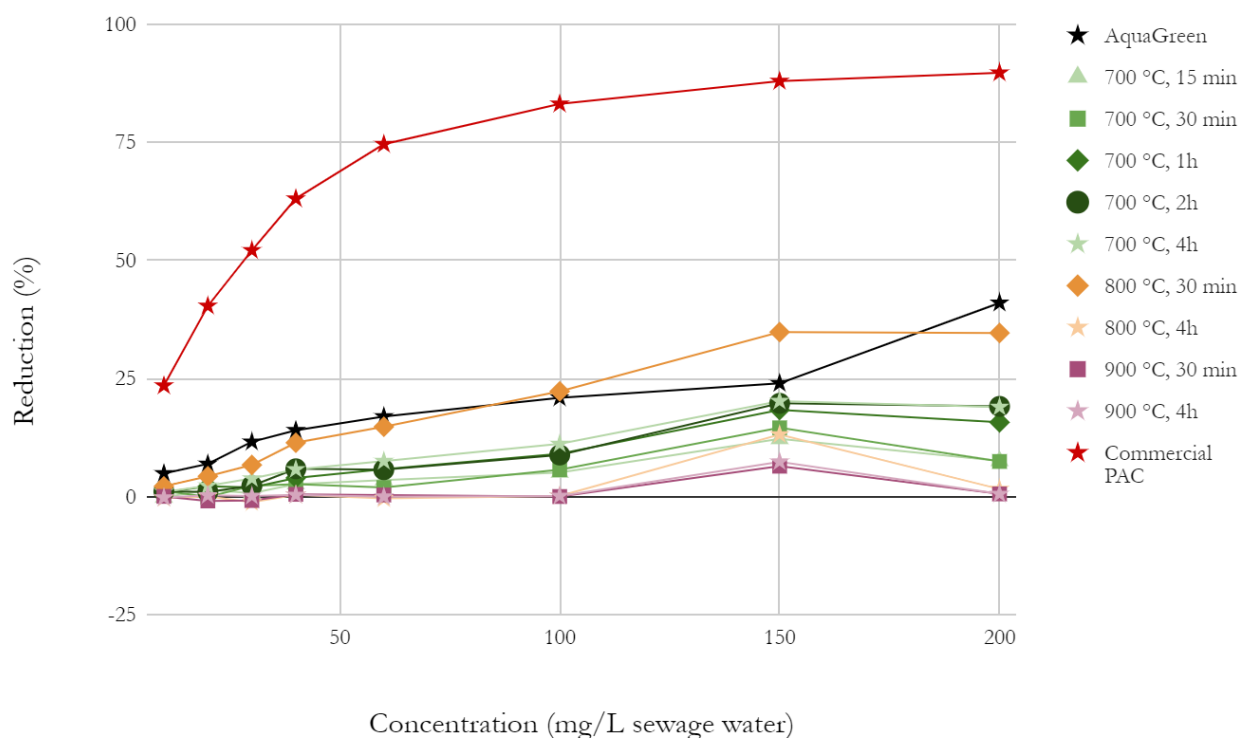


Figure 23. The results of the systematic adsorption measurements. Each sludge biochar that had been activated under a certain condition, which is shown at the right of the figure, have adsorbed organic material in wastewater from Öresundsverket for 72 h. The reduction compared to the original organic content in the wastewater is shown by the marked data points. Green coloured points have been activated in 700 °C, orange in 800 °C and purple is activation in 900 °C. Data points in the shape of a triangle have the activation time of 15 minutes, square 30 minutes, diamond 1 hour, circle 2 hours and star 4 hours. The commercial PAC has red colour and the star symbol. The activated sludge biochar obtained from AquaGreen is of the colour black and data points in the star symbol. The x-axis is the concentration (mg/L) of each activated biochar in the solution of wastewater and the y-axis is the reduction (%) for each concentration of each activated biochar.

As shown in the figure, the commercial PAC had the greatest reduction at all concentration-levels with a maximum of 89% at 200 mg/L. This was expected as a PAC, <0.100 mm, requires less time for equilibrium to set as the particles are significantly smaller and a faster mass transfer is possible. For the larger particles, <0.425 mm, of the sludge biochar a longer time is required to reach equilibrium. Based on the shape of the graphs, a state of equilibrium was achieved to some extent as they level out at the higher concentrations, meaning the adsorption sites were saturated. The activated sludge biochar from AquaGreen reached one of the highest measured reduction levels, levelling out at 41%. This was a reduction level similar to what was achieved by a sludge biochar with known activation conditions of 800 °C and 30 minutes, which was maximum reduction at 34 %. From the figure, it can be concluded that for a lower temperature at 700 °C, a longer activation time was more beneficial as the samples of shorter activation time show a poor reduction rate. The two highest reduction levels achieved by sludge biochar with an activation temperature at 700 °C were obtained at an activation time of 2 and 4 h, with a reduction around 19%. As the two different samples had a similar reduction level, it was shown the longer activation time had no significant benefit. From a perspective based on energy consumption, an activation of 700 °C and 2 h is therefore the more attractive choice. Based on the low reduction results of the activation at 900 °C, it can also be argued that the optimum temperature interval for activation of sludge biochar is below 900 °C and above 700 °C.

The samples with an activation temperature at 800 °C had two activation times, 30 min and 4 h. As can be seen in Figure 23, the sample of 800 °C and 4 h had a significantly lower reduction level than the sample of 800 °C and 30 min, with a maximum of 13 %. The 4 h-sample had a similar reduction level as the sludge biochar with the activation temperature of 900 °C, with a maximum of 6-7 %, meaning they had

similar adsorption capacities. An excess of heat could be the cause of the low adsorption, as the pores would collapse and the surface area would be reduced, leaving the sludge biochar with a low amount of adsorption sites. Hence, the different concentrations of the sludge biochar barely had any impact on the reduction levels as the adsorption capacity already was a significantly low. A lack of activation process is most probably what caused the low reduction of the samples of 700 °C and shorter activation times. Yet they obtained a higher reduction than that of the samples of higher temperatures, 800 °C 4 h, 900 °C 30 min, and 900 °C 4 hours. The activation times of 15 min and 30 min at the activation temperature at 700 °C had similar reduction results, with a maximum of 12-14 %. The lower reduction rates are due to the activation process not having enough time to increase the surface area and pore formation. An activation time of 1 hour for 700 °C proved to be more fruitful as it achieved a higher reduction level at multiple concentrations, yet it is not at the same level as an activation of either a higher temperature or longer activation time. Hence, the activation at 700 °C and 1 h was either of too low temperature or too short time to achieve a significant activation.

Based on the results in aspect of the different concentrations, the highest concentration of 200 mg/L seems to have obtained lower reduction levels than that of 150 mg/L for multiple samples. Due to the higher amount of biochar present in the sample, it generates a higher possibility of sludge biochar being transferred into the cuvette for absorbance measurements, which increases the content of organic material and hence increases the measured absorbance, which leads to a lower reduction. AquaGreen is the only sludge biochar which had a higher reduction level at 200 mg/L than 150 mg/L.

From these results it was shown that the most optimal reduction rates were obtained by an activation of 800 °C, 30 min and 700 °C, 2 h. Hence, these were the samples chosen for the next experiment, along with the commercial PAC, which is adsorption of pharmaceutical residues.

4.6 Adsorption of pharmaceutical residues

The results from the adsorption test of the different organic chemicals bisphenol A (BPA), diclofenac (DCF) and perfluorooctanoic acid (PFOA) are presented in Figure 24.

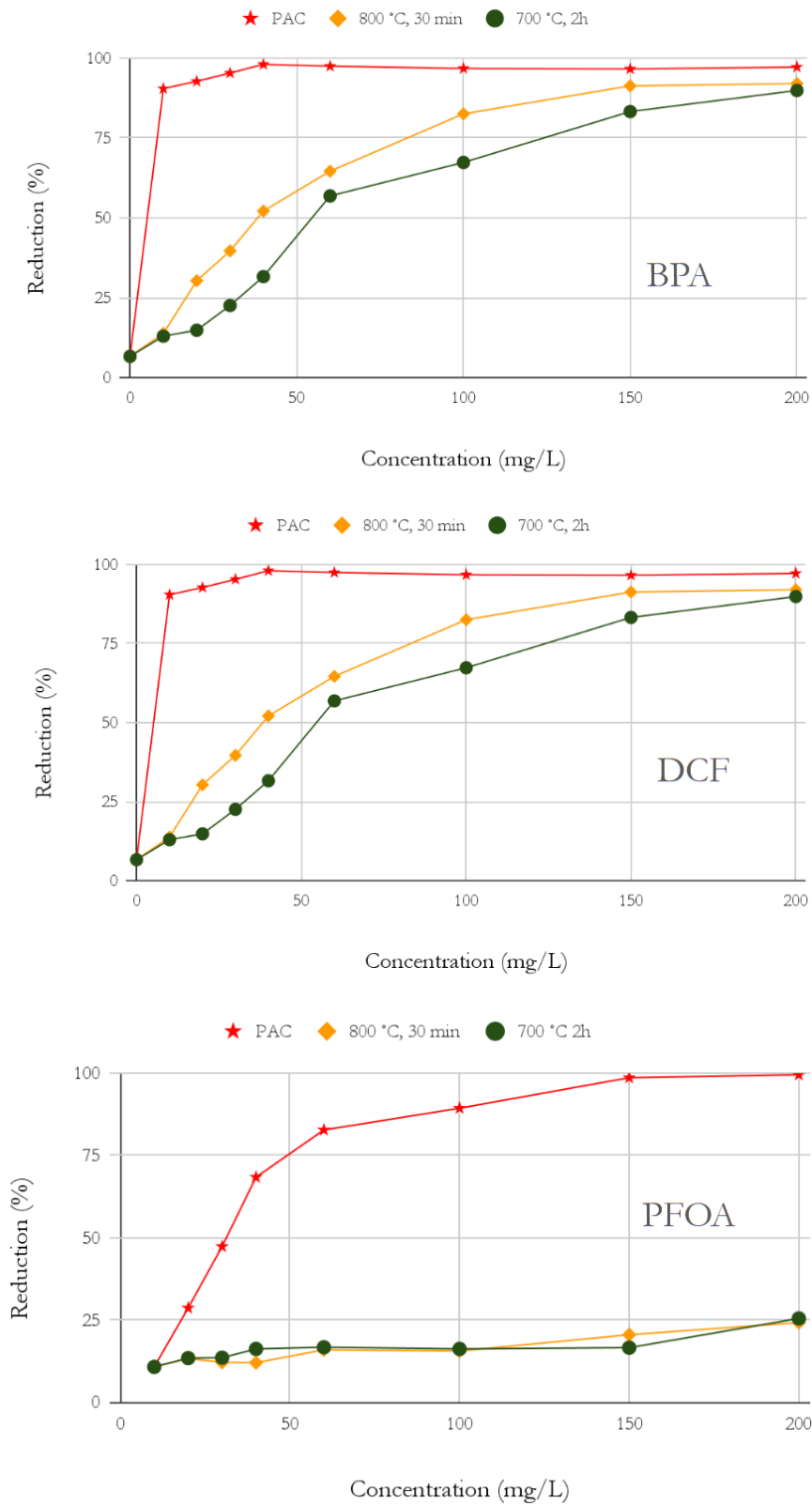


Figure 24. The reduction of pharmaceutical residues after 72 h by commercial PAC (red star) and sludge biochar activated at 800 °C, 30 min (orange diamond) and 700 °C, 2 h (green circle). The graph at the top-left represents the adsorption of BPA, the graph to the right represents the adsorption of DCF and the graph at the bottom-left PFOA. The y-axis is the reduction in %, i.e. the adsorbents' adsorption level of the pharmaceutical residues. The x-axis shows the concentrations of each adsorbent-particles in the solution.

The commercial PAC had the greatest adsorption of each substance in each particle concentration, which was to be expected based on earlier experiments (4.5). Biochar obtained from wastewater sludge has been proven to show adsorption capacities of BPA above 70% (Birrer *et al.*, 2021), which correlates with the results of the higher sludge biochar particle concentrations in this experiment. In another study, the adsorption level of DCF in bimetallic modified sludge biochar reached up to 95.7% and 78.2% (He *et al.*, 2021), which is similar to the results shown in Figure 24. As stated earlier, physical activation is to be preferred over chemical, such as bimetallic modification, as it utilises non-sustainable chemicals. Adsorption of DCF has been shown to be more dependent on the pH of the solution rather than the activation temperature of the biochar, with a peak of 135 mg adsorbed DCF/g sludge biochar at pH 3 (Czech *et al.*, 2021). Hence, adsorption tests with varying pH could be investigated to find optimal conditions for maximum reduction of pharmaceutical residues.

In the graphs of BPA and DCF, it can be seen that the sludge biochar with the activation conditions of 800 °C and 30 min had a greater adsorption level than that of the sludge biochar activated in 700 °C and 2 h. In the lower carbon concentrations in the graph DCF, a spike can be seen in the adsorption in 700 °C, 2h. This may be due to contamination in the solution, as carbon from another, better adsorbent could have been left in the lid. The same containers from the previous experiment were reused, which makes this a possible error. Adsorption of PFOA was low in each sludge biochar in comparison to PAC, which was expected. It has been shown there is a variable adsorption of PFOA in biochar as many factors determine the outcome, such as the pore size distribution and the number of surface functional groups (Wu *et al.*, 2022). The sludge biochar had larger particles and hence less micropores (Jin *et al.*, 2022). Micropores contribute to the adsorption efficiency and the functional groups could also contribute to increased adsorption efficiency, which explains why PAC was expected to be superior in adsorption of PFOA as sludge biochar and PAC differ in pore formation, functional groups, and particle size.

5. Conclusions

This project aimed to investigate the most optimal conditions of the following activation parameters:

- Temperature
- Time
- Particle size

Based on the different adsorption measurements it could be concluded that the shorter the activation time is, the higher the activation temperature should be to obtain most optimal adsorption as shown by the empiric results. This could be seen when comparing activation 700 °C, 30 min and 800 °C, 30 min as the latter one granted a greater adsorption in the particles smaller than 0.425 mm. The lower activation temperature of 700 °C achieved better results at longer activation times. It can also be concluded that smaller particles, those smaller than 0.425 mm, were more optimal for higher adsorption rates was drawn.

From the systematic adsorption measurements, it can be concluded that the activation of 800 °C and 30 minutes had the highest reduction level, followed by activation at 700 °C and 2, 4 h. The results suggest activation at 900 °C was of a too high temperature, possibly causing the adsorption sites to reduce. Activation at 800 °C and 4 hours had similar results, due to excess of heat. The difference between 2 h and 4 h activation at 700 °C was not large, based on the results in the graph, which means the activation time of 2 h is to be preferred due to lower energy consumption. From the adsorption test with ¹⁴C labelled chemicals, it could be concluded the biochar activated at 800 °C, 30 min was superior to 700 °C, 2h in adsorption of each chemical except PFOA. Both biochars were inferior to the PAC in adsorption of each chemical.

Based on the results from the physical characterisation of the sludge biochars obtained from the four different WWTPs, there was a majority of particles in the sizes between 3.35 and 1 mm in diameter. However, in the following adsorption measurements it was shown that smaller particles, those around 0.425 mm, had a higher adsorption level and were hence more beneficial in reduction of organic material in wastewater. For the sake of adsorption capacity, activated sludge biochar of a particle size smaller than 0.425 mm is recommended, although there seems to be a larger amount of biochar particle of size equal to or larger than 1 mm naturally.

As the physical characterisation of the sludge biochar from different sources showed, biochars from different sources consist of different compositions. In this experiment, the moisture content was in focus and the level of moisture in each biochar differed which was shown to affect the adsorption capacity. The results of the activation of sludge biochar from Sønderlø and Højby were compared, and it could be seen the samples from Højby in general had a higher adsorption capacity. These samples also had a larger moisture content. The conclusion drawn from this is that properties of the sludge biochar affect the outcome of the activation.

An evaluation of the chosen methods was also part of the aim, and it can be concluded that the analysis methods were efficient, although the sheer number of samples made the process intense. A better suited equipment would improve the efficacy as it would, for example, minimise the unnecessary steps of transferring samples into new containers. It was shown centrifugation had a positive impact on the adsorption capacity as it gathered the sludge biochar in the bottom of the container, minimising the contamination of the solutions transferred to the adsorption measurements.

6. Future recommendations

During the experiments, it was discovered the adsorption capacities of the different activated sludge biochars were much lower than anticipated based on earlier articles. Hence, to discover the activation optimum, more experiments are required. The results showed activation of particles <0.425 mm was most beneficial, though the biochar sources had a majority of particles with a diameter ≥ 1 mm. To obtain a larger number of particles <0.425 mm, the remainder of particles could be pulverised. For future trials, temperatures above 700 °C and lower than 900 °C are recommended. For the higher temperatures, shorter activation times are recommended and for the lower temperatures, longer time is recommended. In these trials, the gas flow and heating rate was kept consequent, yet it may be of interest to vary these to find an optimised activation technique. As discussed in the adsorption tests of the organic chemicals, an investigation of pH could also be of interest to optimise the adsorption of chemical residues. The accuracy of the method to determine density, moisture and particle size ratios was not determined, which could be done in future studies to compare properties of sludge biochar from different sources more accurately. An investigation of the components and properties of sludge biochar could be of interest in further studies to draw conclusions about their effect on the activation level.

In this experiment, there was not enough time to evaluate the properties of the different sludge biochars. To be able to draw conclusions about the quality of the activated biochar regarding its origin, examinations of the sludge's properties should be done. It was originally planned to utilise sludge biochar produced from Testbed Ellinge but due to delays this was not possible. For future trials, it would be recommended to use sludge biochar from Testbed Ellinge that is produced in known and controllable conditions, which also enables comparison between the properties of the wet sludge and the produced sludge biochar.

7. References

Front figure. AI-function at Canva. 2024. Närbild på biokol.

Figure 1, 2 and 5 obtained from Biorender.com

All other figures are designed by the author.

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Appendix

1. Biochar production system

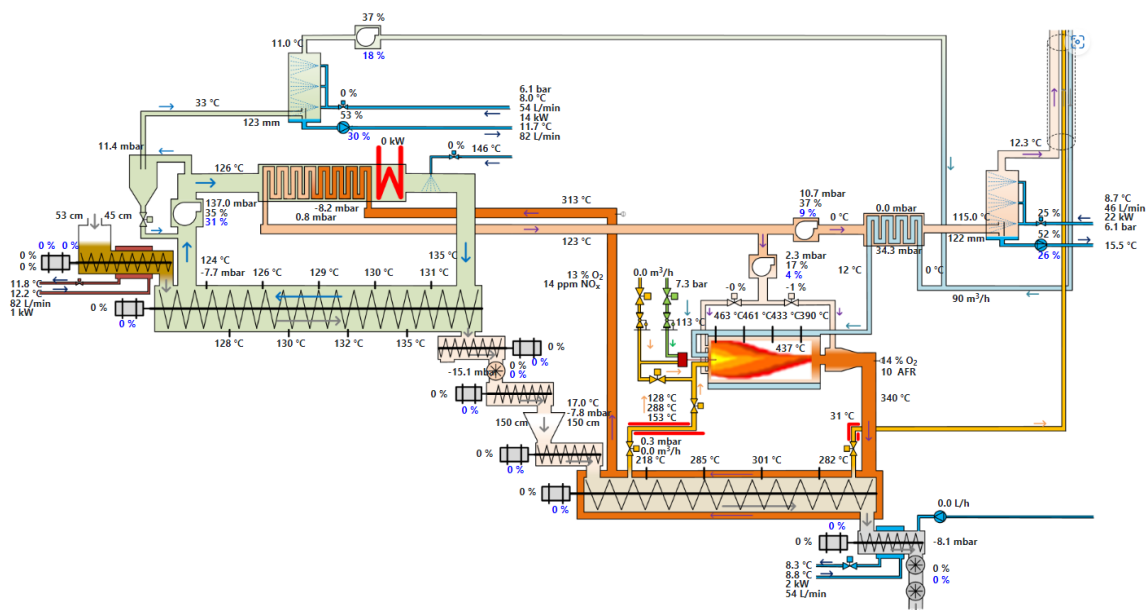


Figure A1. The detailed figure of the generation of sludge biochar. The green part describes the steam dryer section where dried biomass is produced and the orange part describes the conditions of the pyrolysis where the biochar is produced. Information was obtained by Wieth (2024).

2. Physical characterisation

Table A1. The density measurements for replicate 1 from Sønderso.

Sample	Mixed	> = 6.3 mm	> = 3.35 mm	> = 1 mm	> = 0.425 mm	< 0.425 mm
Mass (g)	154	11	31	73	31	2
Volume (mL)	210	29	65	120	45	1
Density (g/L)	735	373	484	604	694	1610
Ratio % (mass)	100	7	20	47	20	1

Table A2. The density measurements for replicate 2 from Sønderso.

Sample	Mixed	> = 6.3 mm	> = 3.35 mm	> = 1 mm	> = 0.425 mm	< 0.425 mm
Mass (g)	146	11	30	70	31	1
Volume (mL)	208	30	60	105	44	2
Density (g/L)	704	366	493	669	696	505
Ratio % (mass)	100	8	20	48	21	1

Table A3. The density measurements for replicate 3 from Sønderso.

Sample	Mixed	≥ 6.3 mm	≥ 3.35 mm	≥ 1 mm	≥ 0.425 mm	< 0.425 mm	
Mass (g)		151	15	32	70	30	1
Volume (mL)		220	37	63	105	48	1
Density (g/L)		688	401	514	667	615	810
Ratio % (mass)		100	10	21	46	20	1

Table A4. The mass and density measurements of Højby.

Sample	Mixed	≥ 6.3 mm	≥ 3.35 mm	≥ 1 mm	≥ 0.425 mm	< 0.425 mm
Mass (g)	122	11	36	58	13	1
Volume (mL)	220	34	85	110	28	2
Density (g/L)	555	318	422	531	454	635
Ratio % (mass)	100	9	29	48	10	1

Table A5. The mass and density measurements of Fårevejle.

Sample	Mixed	≥ 6.3 mm	≥ 3.35 mm	≥ 1 mm	≥ 0.425 mm	< 0.425 mm	
Mass (g)		122	27	46	47	0.35	0.10
Volume (mL)		220	60	82	88	0.50	0.10
Density(g/L)		553	446	558	533	700	1000
Ratio % (mass)		100	22	38	39	0.29	0.08

Table A6. The mass and density measurements for Nykøbing.

Sample	Mixed	≥ 6.3 mm	≥ 3.35 mm	≥ 1 mm	≥ 0.425 mm	< 0.425 mm	
Mass (g)		155	4	28	103	15	0.19
Volume (mL)		268	10	60	180	26	0.30
Density (g/L)		579	387	466	571	565	633
Ratio % (mass)		100	2	18	66	9	0.12

Ratio between fractions

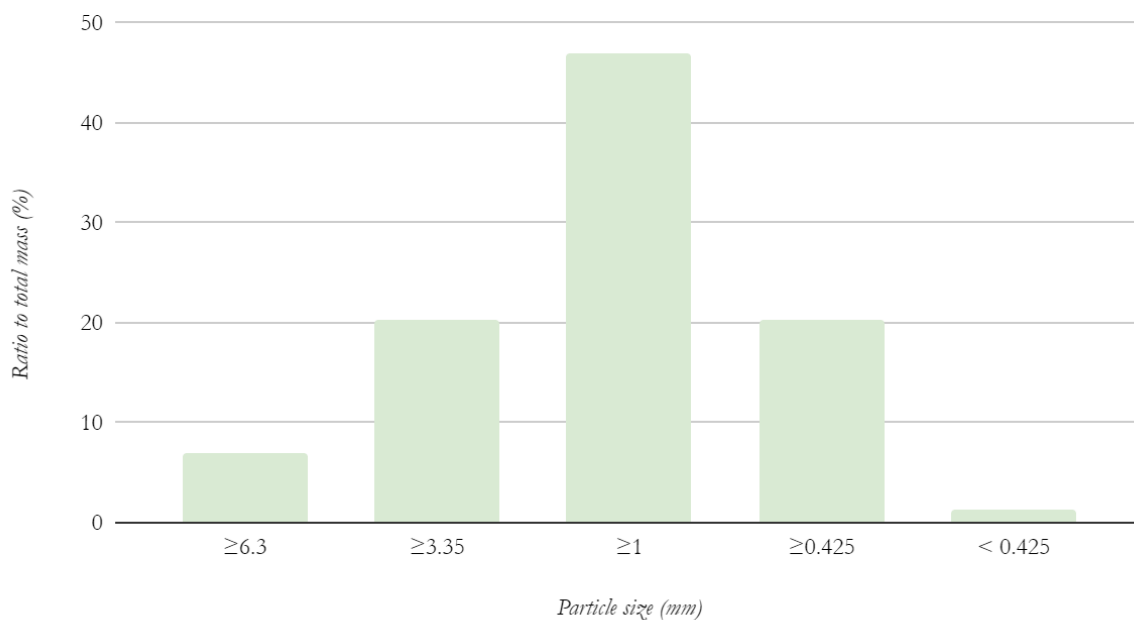


Figure A2. Concluded results of the ratio between particle sizes for the sample from Sønderlø.

3. Mass loss after activation

Table A7. The mass loss for each sludge source and samples of different particle sizes presented in percentage (%) for activation at 800° in 1h.

	Sludge biochar source	Particle size ≥ 6.3 mm	Particle size ≥ 3.35 mm	Particle size ≥ 1 mm	Particle size ≥ 0.425 mm	Particle size < 0.425 mm
Mass loss after activation (%)	Sønderlø	49.8	37.9	38.8	45.9	37.6
	Højby	49.5	62.5	44.6	64.0	64.9
	Fårevejle	54.5	-	-	-	-
	Nykøbing	44.1	44.0	43.7	47.2	48.3

4. Adsorption capacities

Comparison of reduction

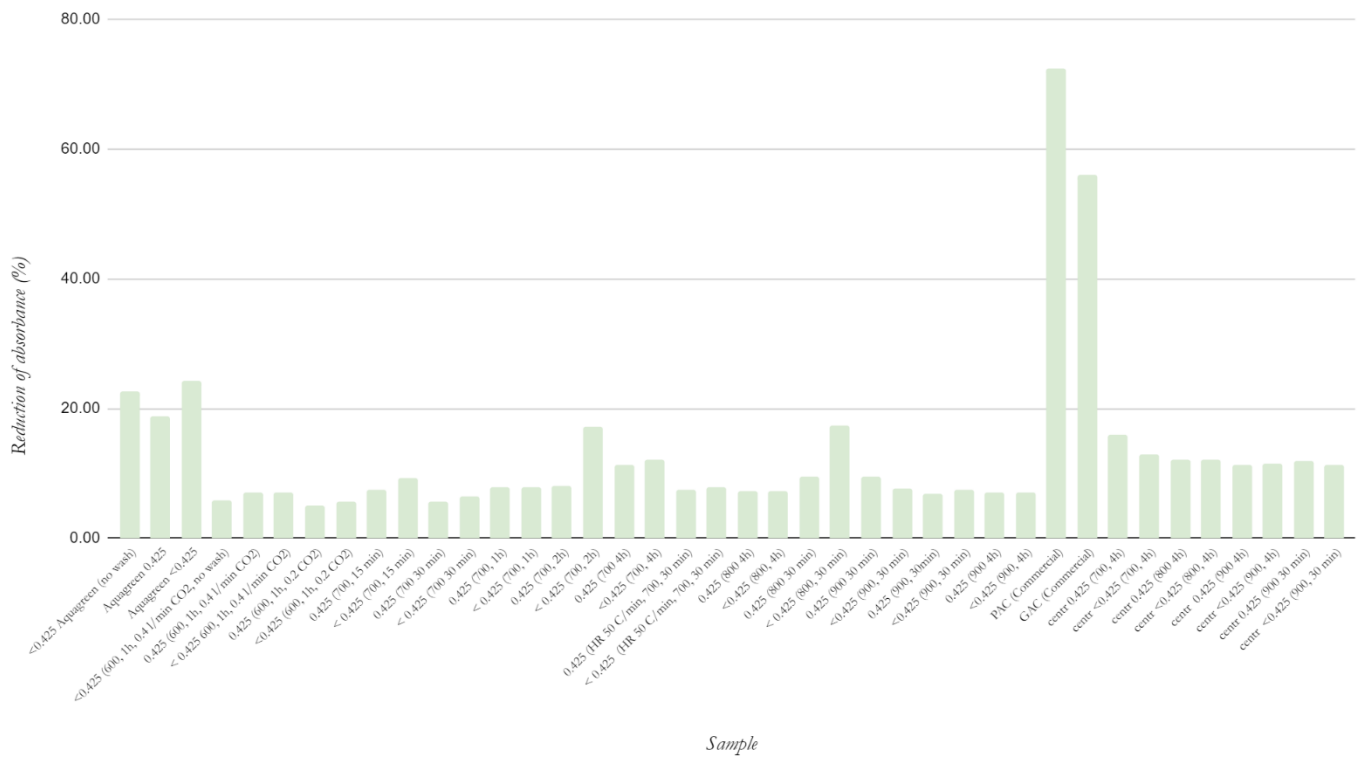


Figure A3. Concluded results from different activation trials with different parameters. The biochar source was Sønderø.

Reduction development over time

Activated (800 °C, 1h) biochar from Sønderø

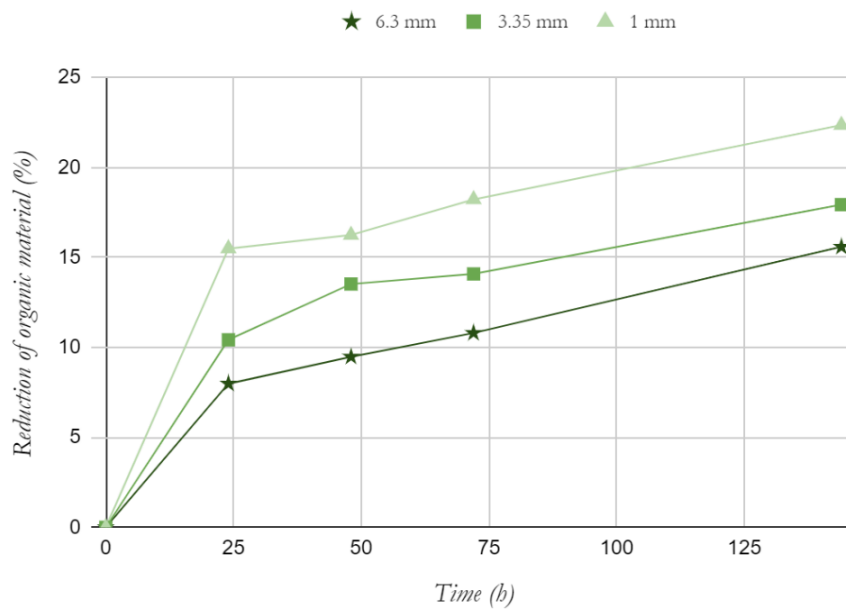


Figure A4. Study of how adsorption capacities change over time. These results are obtained from the particle sizes 1-6.3 mm from Søndersø.

Reduction development over time

Activated (800°C, 1h) biochar from Højby

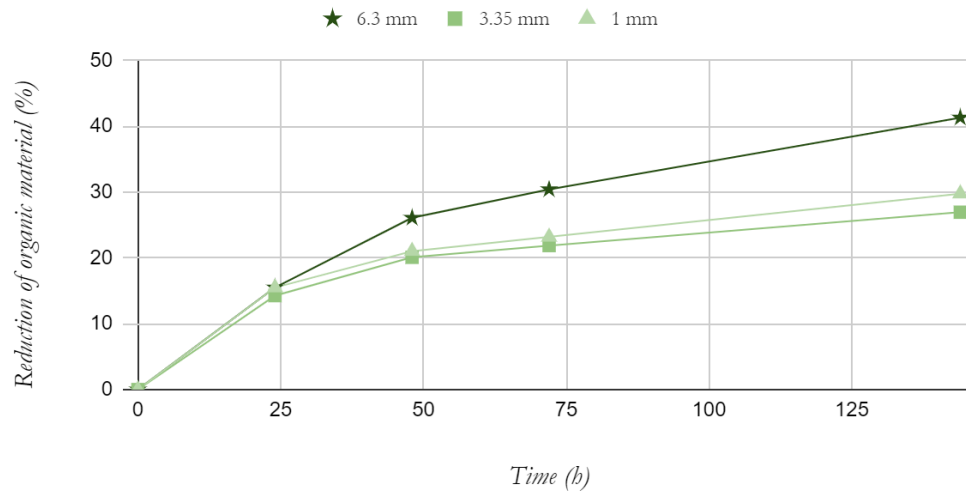


Figure A5. Study of how adsorption capacities change over time. These results are obtained from the particle sizes 1-6.3 mm from Højby.