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Sorption potential of sludge biochar for the removal of acetaminophen and carbamazepine from water

Sarah Charlotte Minos-Stensrud
Water and Environmental Technology

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Abstract

Increasing presence and levels of pharmaceuticals are detected in water bodies, along with growing concern about their impact on aquatic and human life. Currently, different water treatment studies focus on removing contaminants from water, and sorption has become an effective strategy for removing emerging contaminants. Carbonaceous products like activated carbon (AC) and biochar are prominent sorbents, due to their effective adsorption properties. Studies on the potential of biochar, in particular sewage sludge biochar (SBC), as an alternative to activated carbon, have sparked great interest among scientists and industries to develop a sustainable, low-cost, and environmentally friendly sorbent.

This thesis investigates the potential of sewage sludge biochar as an adsorbent for the removal of the pharmaceuticals acetaminophen (ACET) and carbamazepine (CBZ) from water. Preliminary experiments were carried out to find the optimal sorbent dose and contact time. Sorption studies were conducted to obtain the maximum adsorption capacity of the pharmaceuticals, comparing sludge biochar to activated carbon.

In the preliminary experiments, the optimal sorbent dose with the highest removal efficiency was found to be 3.3 g/L. The contact time was decided on 7 days, due to time limitations, although CBZ reached equilibrium within 4 days. The sorption study results showed that AC is highly effective in removing pharmaceuticals, and SBC is a promising sorbent. With a contact time of 7 days, sorbent dose of 3.3 g/L, and initial concentration of 5 mg/L, SBC removed 58% of ACET and 55% of CBZ. In comparison, AC removed 89% of ACET and 82% of CBZ, and proved the most effective of the two sorbents. This can be attributed to the higher surface area, lower particle size, and finer aggregates of AC compared to SBC. However, as SBC is a more sustainable, cost-effective, and environmentally friendly sorbent, it might be a good alternative to AC for the removal of ACET and CBZ. In the sorption study, the maximum adsorption capacity of SBC in removing ACET was obtained at 21.46 mg/g for the concentration range of 5-500 mg/L.

Sammendrag

I vannforekomster oppdages det en økende tilstedeværelse og høyere nivåer av legemidler, noe som har ført til økende bekymring for deres påvirkning på mennesker, dyr og økosystemer. Nå retter forskningen seg mot ulike metoder for å rense vannet, og sorpsjon anses som en effektiv strategi for å fjerne bekymringsfulle forurensningsstoffer som legemidler. Karbon-rike materialer som aktivt kull (AC) og biokull er fremtredende sorbenter på grunn av deres effektive adsorpsjonsegenskaper. Forskning på potensialet til biokull, spesielt biokull produsert fra avløpsslam (SBC), som et alternativ til aktivt kull, har vakt stor interesse blant forskere og industri for å utvikle en bærekraftig, kostnadseffektiv og miljøvennlig sorbent.

Formålet med denne masteroppgaven er å undersøke potensialet til biokull produsert fra avløpsslam som adsorbent av to utvalgte legemidler, acetaminophen (ACET) og karbamazepin (CBZ), fra vann. Innledende eksperimenter ble utført for å finne optimal mengde sorbent og kontakttid. Deretter ble det gjennomført sorpsjonsstudier for å bestemme maksimal adsorpsjonskapasitet av legemidlene, ved å sammenligne slambiokull og aktivt kull.

I de innledende eksperimentene ble den optimale dosen ved høyest fjerningseffektivitet funnet å være 3.3 g/L. Kontakttiden ble satt til 7 dager, på grunn av tidsbegrensninger, selv om CBZ nådde likevekt innen 4 dager. Sorpsjonsstudien viste at AC er svært effektiv i fjerning av legemidler, og SBC er en lovende adsorbent. Med en kontakttid på 7 dager, en sorbentdose på 3.3 g/L og en innledende konsentrasjon på 5 mg/L, fjernet SBC 58% av ACET og 55% av CBZ. AC fjernet 89% av ACET og 82% av CBZ, og viste seg å være mest effektiv av de to sorbentene. Dette kan tilskrives det større overflatearealet og den mindre partikkelstørrelsen til AC sammenlignet med SBC. Et større overflateareal indikerer høyere fjerningseffektivitet og adsorpsjonshastighet på grunn av et økt antall sorpsjonssider på overflaten til adsorbenten. Imidlertid, ettersom SBC er en mer bærekraftig, kostnadseffektivt og miljøvennlig adsorbent, kan den være et godt alternativ for fjerning av ACET og CBZ. I sorpsjonsstudien ble den maksimale adsorpsjonskapasiteten til SBC i fjerning av ACET oppnådd ved 21.46 mg/g for konsentrasjonsområdet 5-500 mg/L.

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List of Acronyms

AC	Activated carbon
ACET	Acetaminophen
AOPs	Advanced oxidation processes
ASP	Activated sludge process
CBZ	Carbamazepine
CECs	Contaminants of emerging concern
CMs	Carbonaceous material
DI	Deionized
DWTPs	Drinking water treatment plants
EDA	Electron donor-acceptor
FTIR	Fourier-transform infrared spectrometry
LC-MS/MS	Liquid chromatography tandem mass spectroscopy
MBR	Membrane bioreactor
NMBU	Norwegian University of Life Sciences
PPCPs	Pharmaceuticals and personal care products
SA	Surface area
SBC	Sludge biochar
SDG	Sustainable development goals
TGA	Thermogravimetric analysis
UV/Vis	Ultraviolet-visible
WWTPs	Wastewater treatment plants

1. Introduction

Water is an essential resource for the support of all forms of life on earth and access to safe water and adequate sanitation are basic human rights. However, water resources around the world face various pressures that can strain their availability (physical and economical) and quality, like population growth, climate change, agricultural demands, urbanization, industrialization, ecosystem degradation, pollution, and water quality degradation as some examples. As the world's population increases, so does the drinking water demand, wastewater generation, and the need for sewage sludge handling, along with a growing agricultural demand as more food is needed. Furthermore, increased agricultural, medical, and industrial activities have led to the release of dangerous pollutants into drinking water, groundwater, surface water, and seawater (Hojjati-Najafabadi et al., 2022). It is, therefore, crucial to ensure clean and safe water supplies and access to adequate sanitation (Sustainable development goals, SDG6) for human well-being, food security, and sustainable ecosystem services. This requires addressing the holistic water context including improved water use efficiency in the context of responsible consumption and production pattern (SDG12), improving water quality including treatment and reuse of wastewater to reduce water stress, for protecting and restoring water related ecosystems. There is an increasing concern that this valuable resource is continuously being strained by toxic water pollutants from different sources.

Water pollutants are substances or contaminants that are present in water bodies, and have the potential to harm the environment, human health, and aquatic ecosystems. The pollutants can originate from various sources, including industrial activities, agriculture, urban runoff, and domestic waste. Some common water pollutants are chemical pollutants, nutrients, microorganisms, and plastics. Chemical pollutants, such as heavy metals, pesticides, fertilizers, pharmaceuticals, industrial chemicals, petroleum products, and solvents, can have toxic effects on aquatic organisms and can contaminate drinking water sources (Madhav et al., 2020). Excess nutrients, particularly nitrogen and phosphorous, can lead to eutrophication, depleting oxygen levels and causing harm to aquatic ecosystems. Microbial pollution, including bacteria, viruses, and protozoa, can contaminate water sources and risk human health.

Contaminants of Emerging Concern (CECs), also called emerging contaminants, are substances that are not traditionally monitored or regulated in water systems but are increasingly recognized as potential threats to human and animal health and the environment (Tang et al., 2020; Raghav et al., 2013). These contaminants have gained attention due to their widespread presence, persistence, and potential adverse effects. Endocrine-disrupting compounds, pharmaceuticals, per- and polyfluoroalkyl substances, microplastics, flame retardants, nanomaterials, pesticide metabolites, and synthetic chemicals are some examples of CECs (Tang et al., 2020; Raghav et al., 2013).

Pharmaceuticals and personal care products (PPCPs) have been acknowledged in recent years as contaminants of emerging concern because of their persistent presence in aquatic environments and their effect on environmental, animal, and human health (Yang et al., 2017). A PPCP is any product for medical and personal care of humans and animals. For the past 30 years, PPCPs have increasingly been targeted as a safety issue (Schumock et al., 2014). PPCPs find many ways to enter the environment; domestic wastewater, hospital discharges, wastewater treatment plants (WWTPs), drinking water treatment plants (DWTPs), general water treatment plants, aquaculture facilities, runoff from fields into surface water, runoff from soil through animal farming and manure applications, and improper manufacturer disposal (Price et al., 2010; Boxall et al., 2012). Generally, hospital disposals have a higher concentration of pharmaceuticals than domestic wastewater (Kosma et al., 2010; Oliveira et al., 2015).

PPCPs are existing in groundwater, surface water, drinking water, and wastewater with concentrations of parts-per-trillion (ng/L) to parts-per-billion (µg/L) (Dai et al., 2015). Because the concentrations are relatively low, the removal efficiency of PPCPs in WWTPs tends to be low as well (Behera et al., 2011), but also because of secondary treatment systems that are commonly used today. Secondary treatment systems, like activated sludge processes, are designed to remove organic matter and suspended solids and are not designed to target PPCP removal. Hence, the primary source of releasing PPCPs into the aquatic environment is identified as the WWTPs (Focazio et al., 2008; Padhye et al., 2014). Even though the released PPCPs are relatively low in concentration in WWTPs and DWTPs, ranging between ng/L and µg/L, the residues may impact animal and human health and have unknown long-term effects (Boxall et al., 2012). Pharmaceuticals are designed to create a pharmacological response at low doses, making low doses of environmental concern (OECD, 2019). Many of the PPCPs behave like endocrine disruptors, which are chemicals that may interfere with the hormonal system, affecting humans and wildlife (EU, 2023). For instance, bioaccumulation in fish and other aquatic creatures happens with certain PPCPs, which can lead to unexpected results. One study shows that persistent exposure to estrogenic pollutants in water leads to enlarged fish livers (Gunnarsson et al., 2009). Another study reveals negative

reproduction impacts and histopathological changes in zebrafish, due to single and mixed PPCP residues (Galus et al., 2013a; Galus et al., 2013b). Brodin et al. (2013) reported that an anxiolytic drug (oxazepam) in surface water change fish behavior, with ecological and evolutionary consequences.

PPCPs can also enter and accumulate in food chains through effluent discharge and reuse of treated wastewater for agricultural reasons (Rajapaksha et al., 2014). The residues have been found in the human food chain, with fruit, vegetables, and drinking water, revealing its impact on human health and adverse effects on our ecosystems (Hernando et al., 2006; Carmona et al., 2014). Even though most individual PPCPs have a low risk to human health, the accumulated effect of PPCPs can be dangerous to humans. In a study done by The Environmental Working Group of the United States, EWG (2008), 16 hazardous chemicals were found, including synthetic musk, 2-benzenedicarboxylic salt, and Triclosan present in 20 girls aged 14-19 years old, all the girls in the survey, due to the use of cosmetic products (Yang et al., 2017). The United States Environmental Protection Agency found antibiotics, antimicrobials, estrogenic steroids, and antiepileptic drugs in US water sources (EWG, 2009), making their way to humans and animals (Yang et al., 2017).

Regulations regarding PPCPs vary across different countries and regions, and there are ongoing concerns about their effectiveness as contaminants are continuously released into the environment (OECD, 2019). The current regulatory frameworks for PPCPs often focus on their safety and efficacy for human use, with less emphasis on their potential environmental impact during manufacturing, use, and disposal. In addition, the fast pace of pharmaceutical and personal care product innovation often outpaces the regulatory response, making it challenging for regulatory agencies to keep up with the influx of new substances and their potential environmental implications. As an example, around 88% of human pharmaceuticals do not have environmental toxicity data (OECD, 2019), showing the lack of standardized testing for evaluating the potential ecological risks.

The conventional wastewater treatment facilities are not designed and equipped with advanced treatment technologies capable of removing PPCPs effectively, resulting in their discharge into rivers, lakes, and other water bodies. As the PPCPs are released, limited monitoring and surveillance programs exist to track the occurrence and levels of PPCPs in water systems, which hinder the assessment of their environmental impact and the implementation of effective mitigation measures. However, there are source control measures being taken against the release of CECs in the world today. The United States has national regulations on how to dispose of dangerous pharmaceutical waste in the health sector. Germany has developed an environmental checklist for reducing

the use and release of veterinary pharmaceuticals into the environment. Sweden has a "Wise list" of recommended common pharmaceuticals where the environmental impact is included, as some examples. (OECD, 2019)

New strategies for wastewater treatment are now being developed as the wastewater discharge permit requirements are becoming more stringent. In these new strategies integration of technologies for removal of contaminants of emerging concern are most encouraged. The presence of a wide variety of pollutant compounds with different characteristics calls for integrated treatment for pollutant removal methods that are not only effective but also technologically and economically feasible. For the last few decades, adsorption technology has gained importance in the removal of CECs especially for PPCPs. Emerging contaminants can be removed due to physical and chemical interactions between the sorbent and sorbate. Several types of sorbents have demonstrated good potential for the removal of contaminants from water, and in particular, carbonaceous materials are recognized with good sorbent properties. Biochar is a carbon-rich material produced through the pyrolysis, thermal-chemical treatment, of organic waste. It has a porous structure, and large surface area, and can be derived from a variety of sources, including sewage sludge. Sewage sludge handling and disposal is a great challenge today, as it increases due to population growth, and as it contains various toxic compounds (Ihsanullah et al., 2022). Sludge discharge into the environment can cause great ecological and health risks (Ihsanullah et al., 2022). Alternatively, through pyrolysis, sewage sludge can be transformed in an environmentally friendly and cost-effective technique, into various value-added products like biofuels or biochar (Jellali et al., 2021; Ihsanullah et al., 2022). Sewage sludge biochar reduces the cost of sludge disposal, and can work as an adsorbent to remove toxic contaminants from water (Gopinath et al., 2021), which is a focus in this thesis. Hence, utilizing sewage sludge biochar as an adsorbent for water pollutants offers a sustainable, efficient, cost-effective, and environmentally friendly solution for addressing water contamination issues, benefiting both the environment and human well-being.

2. Objectives, motivation, and thesis outline

There is a need for innovative solutions to remove emerging contaminants from water. In order to contribute to this challenge, I am very interested to study the use of sewage sludge biochar as an alternative, low-cost, and environmentally friendly adsorbent, to remove unwanted pharmaceuticals from water.

In a previous NMBU master thesis that evaluated sewage sludge biochar for removal of pharmaceuticals and personal care products in treated greywater, Kalheim (2022) reported equally good removal efficiency of sewage sludge biochar and activated carbon for the sorption of pharmaceuticals and personal care products with the concentration of 1 mg/L. Acetaminophen, carbamazepine and diclofenac were removed by 99% (Kalheim, 2022). However, the maximum sorption capacity was not reached, as the initial concentration tested was only 1 mg/L for each pharmaceutical and personal care product, and further studies were needed.

Aim of thesis

The main objective of this thesis is to evaluate sewage sludge biochar as a potential sorbent for the removal of two pharmaceuticals from water; acetaminophen and carbamazepine. This will be done through preliminary experiments and sorption studies. In the preliminary experiments, the aim is to find the optimal sorbent dose and contact time, and sludge biochar will be the main sorbent, due to time limitations. In the sorption studies, the goal is to determine the maximum adsorption capacity for two sorbents, activated carbon and sludge biochar, for the removal of acetaminophen and carbamazepine. The measurement method used will be UV/Vis, to quantify the pharmaceuticals in water, which is a fast, available, and cost-effective analysis method for this purpose. The following research questions are central in this thesis, and will be discussed in greater detail in chapter 5.

Research question I *How well does sludge biochar work as a sorbent for the removal of acetaminophen and carbamazepine from water?*

Research question II *To what extent can sludge biochar replace activated carbon as a low-cost sorbent for the removal of acetaminophen and carbamazepine?*

Outline of thesis

In chapter 3, relevant background about pharmaceuticals, their removal from wastewater with chemical, biological, and physical processes, the adsorption process, and different adsorbents, will be presented. Chapter 4 explains the preparation of materials used in the experiments, both sorbates and sorbents, and gives an overview of all the conducted experiments in the thesis. Additionally, in chapter 4, the validation of the analysis method UV/Vis is described, along with different equations and models that are used to examine the data. Chapter 5 presents the results and discussion from the method validation, preliminary experiments, and the sorption study. It also includes isotherm studies to describe the adsorption removal mechanisms. In chapter 6 a conclusion is given, and chapter 7 presents future work.

3. Background

In this chapter, the most relevant information regarding pharmaceuticals, their removal methods from water with a specific focus on sorption, and different sorbents will be presented. Adsorption properties will be explained at the end of the chapter.

3.1 Pharmaceuticals

Pharmaceuticals are crucial for human and animal health. The consumption and production of pharmaceuticals significantly increased in the last 20 years (OECD, 2023). OECD (2023) reported the consumption of medicines from 2000 to 2020, displaying a variety of countries around the world, including Norway, where different pharmaceuticals like anti-hypertensives, lipid-modifying agents, anti-diabetics, and anti-depressants have remarkably expanded in consumption. Pharmaceuticals are increasingly recognized as contaminants of emerging concern to the environment and human health because of their rising occurrence in aquatic environments. Studies have shown that psychiatric drugs change fish behavior; endocrine-disrupting pharmaceuticals increase the risk of breast or prostate cancer in humans and can cause reproduction toxicity in fish; and antibiotics are connected to antimicrobial resistance which already is a global health crisis (OECD, 2019).

Pharmaceuticals can be divided into the categories of analgesics and anti-inflammatory drugs, anticonvulsants, lipid regulators, antibiotics, β-blockers, and nervous stimulants (Luo et al., 2014). Studies suggest that pharmaceutical concentration in wastewater correlates well with their production and consumption. For example, analgesics and anti-inflammatory drugs, also called painkillers, like acetaminophen, ibuprofen, and naproxen, are non-prescription medicine and some of the most widely used. Kasprzyk-Hordern et al. (2009) found high concentrations (> 10 μg/L) of acetaminophen, tramadol, and codein in wastewater in Wales, which could be explained by the high distribution of these pharmaceuticals.

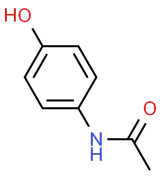
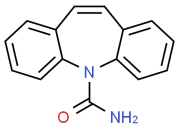
Not only over-the-counter drugs are persistent in aquatic environments. Luo et al. (2014) reported that carbamazepine, sulfamethoxazole, caffeine, and triclosan were commonly

detected compounds in surface water and wastewater, with high influent and effluent concentrations. Furthermore, carbamazepine was observed in drinking water in Ontario, Canada, with a concentration exceeding 600 ng/L, more than 10 times higher than other compounds, which could be explained by its high persistency (Kleywegt et al., 2011).

A study done by Carlsson et al. (2020) on pharmaceuticals in the northern environment showed that paracetamol is one of the most commonly used pharmaceuticals in Sweden, Norway, and Iceland. In 2021, paracetamol was the most used drug in Norway by 683 thousand individuals (Statista, 2023). However, 98% of paracetamol is metabolized in humans before excretion. Hence, other pharmaceuticals like codein, valsartan, naproxen, tramadol, and metformin, among others, are compounds that are mostly released into the aquatic environment in the investigated Nordic countries (Carlsson et al., 2020). Haikonen et al. (2017) measured released pharmaceuticals from WWTPs in Sweden, where diclofenac, metoprolol, oxazepam, and carbamazepine were amongst the highest released ($>$ 640 ng/L).

The focus of this thesis is two pharmaceuticals; acetaminophen (ACET) and carbamazepine (CBZ). These pharmaceuticals were selected because of their common worldwide usage, varying properties, challenging removal, different removal efficiency in WWTPs, and persistent presence and detection in aquatic environments. The properties of the selected pharmaceuticals are found in Table 3.1.

Table 3.1: Acetaminophen and carbamazepine properties

	Acetaminophen	Carbamazepine
Brand name	Paracetamol	Tegretol
CAS ID	103-90-2	298-46-4
Usage	Analgesic, antipyretic drug	Analgesic, antiepileptic
Molecular structure		
Molecular formula	$C_8H_9NO_2$	$C_{15}H_{12}N_2O$
Molecular weight (g/mol)	151.2	236.3
log K_{ow}	0.46	1.51-2.45
Solubility water 25 °C (mg/L)	14,000	18

References ACET: (ChemSpider, 2023b; NCBI, 2023a)
References CBZ: (ChemSpider, 2023a; NCBI, 2023b; Scheytt et al., 2005a; Scheytt et al., 2005b; Zhang et al., 2008)

3.1.1 Acetaminophen

Acetaminophen, also known as Paracetamol, is a non-opioid analgesic and antipyretic agent used for pain and fever treatment. ACET is one of the most common and widely used painkillers and is a non-prescription drug (NCBI, 2022), as mentioned before.

Shown in Table 3.1, ACETs octanol-water partition coefficient is low (log $K_{ow} < 1$), indicating a higher affinity for water compared to octanol (organic solvent). This suggests that ACET is hydrophilic and more likely to dissolve in water than in an organic solvent. This is expressing good solubility in water, also confirmed by the solubility factor of 14,000 mg/L. At the same time, ACET is showing persistence in aquatic environments, from ng/L to µg/L, which can be explained by a constant discharge from many pathways.

Despite being one of the most popular painkillers, ACET was only detected in <10% of the effluents from WWTPs, and not detected in rivers downstream in Germany (Heberer, 2002). In addition, ACET was only detected in 17% of all samples from 142 streams in the US in 2002, with the maximum concentration of 10 μg/L (Kolpin et al., 2002). This can be explained by the properties of ACET as it is easily degradable in some treatment processes and is therefore effectively removed in WWTPs (Heberer, 2002). In addition, even as acetaminophen is one of the most used pharmaceuticals in the Northern investigated countries, it metabolized by 98% to glucuronic acid and sulfuric acid in humans before excretion (Carlsson et al., 2020). However, there is not enough knowledge on WWTP efficiency on metabolites, or how the metabolites affect the aquatic ecosystem (Carlsson et al., 2020).

3.1.2 Carbamazepine

Carbamazepine, also called Tegretol, is a medication indicated for epilepsy, trigeminal neuralgia, and bipolar disorder, which is widely prescribed (NCBI, 2023c). Zhang et al. (2008) reported the CBZ estimated consumption worldwide of 1014 tons. About 72% of CBZ is absorbed by the human body, while the rest 28% is excreted unchanged through the feces (RxList, 2023). Absorbed CBZ is metabolized primarily by the liver, into several different metabolites, and discharged through urine (Zhang et al., 2008). Therefore, a higher concentration of CBZ metabolites may be observed in water bodies. CBZ is flushed with wastewater to the WWTPs, along with other pollutants, and Zhang et al. (2008) reported the removal efficiency of CBZ mostly below 10%, finding CBZ to be a persistent pharmaceutical.

CBZ has frequently been detected in aquatic environments. Several studies have indicated the presence of CBZ in the effluent wastewater treatment plants and water bodies including surface water, groundwater, and drinking water at concentrations ranging from 820 to 6300 ng/L (Zhang et al., 2008). CBZ has been detected in several surface water at various concentrations; in Berlin (1075 ng/L), in Detroit River (0.3-0.8 ng/L), and in Jamaica Bay, New York (5-35 ng/L) (Heberer, 2002; Hua et al., 2006; Benotti and Brownawell, 2007). The US Geological Survey discovered 60 ng/L in water and 41.6 ng/mg in sediments when looking at 44 rivers across the United States (Zhang et al., 2008). WWTP effluents around the world, in Europe, the USA, Canada, Japan, and South Korea contained CBZ in hundreds of nanograms per liter (Zhang et al., 2008). If WWTP effluents are used for groundwater recharging, then the presence of CBZ in groundwater would increase in those regions (Zhang et al., 2008). CBZ was found with concentrations of 43.2 and 13.9 ng/L in drinking water wells in the Mediterranean region (Zhang et al., 2008). Carbamazepine's presence is worldwide, as Zhang et al. (2008) states that concentrations in µg/L range are detected in surface waters in Austria, Finland, France, Germany, Switzerland, Canada, and in WWTP effluents in Austria, Denmark, Finland, France, Germany, Italy, Spain, Sweden, Switzerland, Canada, and South Korea.

Shown in Table 3.1, CBZ octanol-water partition coefficient is relatively high (ranging between 1.51-2.45) compared to ACET, expressing lower solubility in water. This is also shown by the solubility (mg/L) of CBZ compared to ACET, where 14,000 mg of ACET can dissolve in 1 L of water compared to 18 mg of CBZ, expressing that CBZ is more hydrophobic. These are some of the properties of CBZ that make it proposed as an anthropogenic marker in water bodies, indicating human activity and an influence on the environment (Clara et al., 2004). In a study, Clara et al. (2004) showed that carbamazepine was not degraded or retained in wastewater treatment plants, showing very persistent properties that resulted in aquatic environmental presence. As CBZ is often found in water bodies, concern about its potential impacts on aquatic organisms has increased. In a study done by Qiang et al. (2016) it was revealed that carbamazepine disturbed the normal growth and development of exposed zebrafish embryos and larvae. With the exposure of 1 μg/L, the neutral-related genes of zebrafish embryos and larvae were disrupted (Qiang et al., 2016).

3.2 Removal of pharmaceuticals in water

Pharmaceuticals have very different physical and chemical properties. To remove them from water, processes such as chemical, biological, and physical processes, can be used.

3.2.1 Chemical processes

Chemical processes that have been used to remove pharmaceuticals from water are advanced oxidation processes (AOPs), including UV oxidation, ozonation, and Fenton oxidation processes (Zhang et al., 2022). One of the most widely used and studied AOP for pharmaceutical removal is ozonation (O_3), though when it is used it is combined with other pretreatment processes in WWTPs (Lee et al., 2012). Im et al. (2012) reported significant influenced CBZ by O_3, however the removal was enhanced with increasing H_2O_2 concentration up to a certain level.

Other promising chemical treatments for pharmaceuticals are Fenton oxidation processes (Zhang et al., 2022). They operate similarly to ozonation, where oxidizing hydroxyl species contribute to the degradation of organic pollutants (Bokare and Choi, 2014). In addition, the hydroxyl species are more easily generated from Fenton processes than ozonation, proving more promising than ozonation on the removal of pharmaceuticals. In a study, Dai et al. (2012) reported the degradation of carbamazepine by five different oxidation processes where UV/Fenton proved the most efficient (86.9%) and Fenton alone less efficient (67.8%) but with the lowest cost. For the degradation of acetaminophen de Luna et al. (2013) reported complete degradation within 24 h by Fenton-like reactions, enhanced by decreasing pH or increasing H_2O_2 concentrations.

UV oxidation is another chemical process, which through photodegradation destroys chemical bonds of organic pollutants, though low efficiency on degrading organic structures (Zhang et al., 2022). However, in combination with H_2O_2, UV can eliminate toxic organic compounds from wastewater (Lai et al., 2017).

The downsides of the chemical processes are energy consumption for UV, cost, acquisition, transportation, and storage for O_3 and H_2O_2, among others (Bagheri and Mohseni, 2015). In addition, by-products may be formed by using chemical oxidation processes, with higher water solubility, which again needs to be removed, but can be harder to remove (Yang et al., 2016). In a study done by Kosjek et al. (2009), CBZ was removed by 99.8% after 30 minutes of UV irradiation, however, it was shown that several transformation products were produced, where the organic compound acridine was the most produced. In a study, Hübner et al. (2014) looked at the removal of carbamazepine and its transformation products, reporting that 90% of CBZ was removed and 50-60% of the initial CBZ was detected as transformation products, at a specific ozone dose.

3.2.2 Biological processes

Biological processes such as the activated sludge process (ASP) and membrane bioreactor (MBR) can be used to remove pharmaceuticals. In the ASP the oxidation of carbonaceous biological matter, nitrogenous matter, and nutrients occurs. Microorganisms in the system degrade organics and remove nutrients in the presence of oxygen. Chen et al. (2015) reported rapid removal of fenoprofen (55-90%), ketoprofen (77-94%), and naproxen (46-90%) by ASP, though other pharmaceuticals like carbamazepine and diclofenac were persistent and not removed. One main disadvantage of the ASP is the disposal of sludge and the residue of pollutants in the sludge. As around 50% of treated sludge in the European Union is applied as a fertilizer on soil, thus environmental contamination is a big challenge (Martin et al., 2015).

An MBR is another biological process, where membrane processes like microfiltration or ultrafiltration are combined with a suspended growth bioreactor (Mutamim et al., 2012). Carbamazepine was reported removed by 68% under near-anoxic operation, but under aerobic conditions only 12% was removed, with a loading of 750 μg/Ld (Hai et al., 2011). A challenge for MBR, as for membrane processes, is membrane fouling.

3.2.3 Physical processes

Physical processes that have been tested on pharmaceutical removal are sedimentation, membrane filtration, and sorption. Sedimentation is a traditional water treatment process using gravity to remove suspended solids from water. For removing pharmaceuticals, the effect is low, because of the high solubility and hydrophilicity of many pharmaceuticals (Luo et al., 2014; Yang et al., 2017).

Membrane technology is used today to control micropollutants in water and wastewater treatment, in addition to applications within water reuse (Schäfer et al., 2011). The removal efficiency depends on size exclusion, sorption onto the membranes, and charge repulsion, among others (Yoon et al., 2006). Pressure-driven membrane filtration processes, like nanofiltration and reverse osmosis, are more suitable for removing pharmaceuticals water, compared to more porous processes like microfiltration and ultrafiltration that cannot hold back the micropollutants (Schäfer et al., 2011). The membrane efficiency is also related to the pharmaceutical molecular weight and hydrophobicity (Garcia-Ivars et al., 2017). As acetaminophen is hydrophilic and has a lower molecular weight than some membranes it would not be kept from going through the membrane and only removed by 30%-40% in a nanofiltration process (Garcia-Ivars et al., 2017). In addition, membrane technology struggles with the problem of fouling, which often hinder including membranes as a treatment step in WWTPs (Rodriguez et al., 2016). Membrane fouling happens when particles accumulate on the membrane

surface and block the membrane pores, resulting in reduced process performance and membrane lifespan, increased operational costs, compromised water quality, and the need for intensive monitoring and management.

Sorption occurs when sorbents, such as activated carbon and biochar, are present in water and wastewater treatment systems (Van Wieren et al., 2012). Sorption behavior can also happen in conventional WWTPs, with the biological activated sludge processes (Ebele et al., 2017). The effective removal of pharmaceuticals by sludge varies due to the physical-chemical properties of pharmaceuticals. Nevertheless, adsorption has revealed great potential for removal (Xu et al., 2017), and will further be described below.

Adsorption is a process by which molecules or particles from gas/liquid adhere to the surface of a solid/liquid material. In adsorption, the adsorbate (the substance being adsorbed) accumulates on the surface of the adsorbent (the material on which adsorption occurs) due to attractive forces between the two. (Rudzinski and Everett, 2012). Sorption and adsorption, and sorbent and adsorbent will be alternatively used in this thesis. Adsorption is typically classified into two main types; physisorption (physical adsorption) and chemisorption (chemical adsorption). Physisorption involves intermolecular forces between the adsorbate and the adsorbent, also known as van der Waals forces (Agboola and Benson, 2021). The binding force caused by intermolecular forces is weak and the adsorption heat is low, though with a fast rate of adsorption and desorption (Agboola and Benson, 2021). Physisorption is usually reversible, with adsorbate molecules easily desorbing from the surface. Chemisorption happens when electrons are transferred, exchanged, or shared between adsorbate and adsorbent, involving stronger chemical bonds such as covalent or ionic bonds (Agboola and Benson, 2021). Chemisorption is often more difficult to reverse and requires more energy to desorb the adsorbate.

The process of adsorption starts with diffusion, where the adsorbate molecule moves from the bulk phase (gas or liquid) to the surface of the adsorbent. When the adsorbate molecule reaches the surface of the adsorbent, they interact through various forces such as van der Waals forces, electrostatic interactions, hydrogen bonding, or chemical bonding. The forces and interactions cause the adsorbate to adhere to the adsorbent surface and form a layer. To quantify the amount of adsorbate onto the adsorbent, the process is often described at the equilibrium by certain equations. The equations are called isotherms, where Langmuir and Freundlich are the most common, and this is explained further in subsection 4.5.1.

3.3 Carbonaceous materials

Carbonaceous materials (CMs) refer to materials with a high content of carbon, which has been noticed due to its distinct properties such as large surface area, developed pore structure, and functional groups with unique sorption abilities (Ahmad et al., 2014). CMs include activated carbon, carbon nanotubes, graphene, mesoporous carbons, and biochar. In this thesis, activated carbon and biochar are the tested CMs, and will be presented further.

3.3.1 Activated carbon

Activated carbon (AC) is a highly porous carbon material with a large surface area, that is commonly applied to remove many different dissolved organic substances from the liquid phase, such as pharmaceuticals. AC can be produced from organic matter with high carbon content, such as wood, coal, or coconut shells. Yahya et al. (2015) showed that waste materials that are difficult to dispose of can be made into activated carbon. The application of AC in conventional wastewater treatment can be relatively effective in removing different pharmaceuticals and personal care products. In a large-scale study in a WWTP using powdered AC done by Mailler et al. (2015), several pharmaceuticals and personal care products were removed with varying removal effects. For example; ibuprofen, paracetamol, and estrone were removed by less than 60%, diclofenac and naproxen were removed moderately (60-80%) and carbamazepine and trimethoprim were effectively removed (>80%) (Mailler et al., 2015). In a treatment system, activated carbon can be added as an improvement step, increasing the removal efficiency of the system.

Compared to the chemical treatment AOPs, AC adsorption does not produce any undesired by-products.

3.3.2 Biochar

Biochar is a carbon-rich solid material derived from organic materials, such as wood, agricultural waste, industrial organic by-products, or other biomass (Tan et al., 2015). It is produced through pyrolysis, a thermal decomposition process of organic materials at high temperatures under the complete or partial absence of oxygen (Klinar, 2016; Tan et al., 2015).

In recent years, biochar produced from sewage sludge has gained attention for several reasons. Sewage sludge biochar (SBC) reduces the risk related to sludge disposal, which is an increasing challenge as the world's population is growing, and it can function as an excellent adsorbent of pharmaceuticals in water (Ihsanullah et al., 2022). Biochar has

high cost-effectiveness, as the feedstock cost is low, and it is an available product regardless of season (Barquilha and Braga, 2021). Hence, biochar made from sewage sludge is one step closer to more economical and sustainable water treatment technologies and it contributes to resource recovery.

Furthermore, biochar production is one technology that can contribute to the control and decrease of greenhouse gas emissions (Pahunang et al., 2021). When sewage sludge, or other carbon-rich materials, are pyrolyzed into biochar the organic carbon is in a stable form and will stay that way for long periods, removing it from the carbon cycle and preventing its release (Mašek et al., 2013). Biochar is also used as an effective soil fertilizer, which has an indirect effect on climate change as the atmospheric carbon is kept in the soil, in addition to contributing to food security (Laird, 2008). As biochar can be produced from different feedstocks, the environmental challenges caused by agricultural and animal-waste disposal, among others, can be reduced by reusing the waste and turning it into a product instead (Qambrani et al., 2017).

Biochar, in general, can be an alternative to other carbonaceous materials as an adsorbent, due to its low-cost, environmentally friendly production and unique properties. Namely, a developed pore structure, various functional groups, and a relatively high specific surface area make biochar an outstanding adsorbent (Ahmad et al., 2014). Biochars' characteristics depend on the feedstock material and the pyrolysis conditions (pyrolysis temperature, residence time, and heating rate). For instance, it is reported that surface area and pore volume increase, and that oxygen-containing functional groups decrease with increasing pyrolysis temperature, which affects the adsorption process in different ways (Salem and Yakoot, 2016).

There are several methods for "activation" of the biochar where the surface is modified, including steam activation, heat treatment, and acid and alkali modification (Ahmed et al., 2016). Modified biochars have shown higher sorption capacities of pharmaceuticals compared to original biochars. For example, adsorption of sulfamethazine onto steam-activated biochar proved 55% more effective than for inactivated biochar, due to more sorption sites and oxygen-containing functional groups (Rajapaksha et al., 2015).

3.3.3 Properties of CMs

The removal of pharmaceuticals by CMs is mainly due to the sorption process, which depends on the surface properties of CMs, the physical-chemical properties of pharmaceuticals, and the environmental conditions as the sorption is happening (Zhang et al., 2022). The primary mechanisms for removal include pore-filling, partition, electrostatic attraction, hydrophobic interaction, $\pi - \pi$ electron donor-acceptor interaction, Lewis acid-base interactions, and hydrogen bonding (Zhang et al., 2022).

Specific surface area and pore size

A large specific surface area (SA) usually means higher sorption capacity for a sorbent, as the number of available sorption sites increases. For biochar, the surface area increase as the pyrolysis temperature increase (Ahmed et al., 2016). In addition, there are other modification techniques to increase the surface area of CMs, where new pores are created and inaccessible pores are opened (Bhatnagar et al., 2013; Ahmed et al., 2016). For example, steam activation, heat treatment, acid or alkali treatment, ozonation, microwave stimulation, and salt impregnation, are some techniques (Zhang et al., 2022). However, excessive use of certain techniques can work against its purpose, whereas excessive acid modification reduced the specific area by fracturing and collapsing pore structure (Zhang et al., 2017).

Scientists have reported that the largest specific surface area does not always show the highest sorption capacity, suggesting that the sorption process is a symbiosis of several other factors in addition to SA (Zhang et al., 2022).

The sorbent pore size is another factor affecting the sorption process significantly. There are different types of pores; micropores (pore diameter < 2 nm) provide sorption sites, mesopores (2 nm $<$ pore diameter < 50 nm) and macropores (pore diameter > 50 nm) behave as diffusion channels that shorten the sorption time (Liu et al., 2014). In a study done by Ncibi and Sillanpää (2017), the sorption process favored porosity over a larger surface area when adsorbing carbamazepine and dorzolamide, indicating that meso and macropores are more prominent in that sorption process than micropores. The pore structure can be identified with a scanning electron microscope.

Surface functional group

The surface chemical groups are another key factor affecting the sorption of pharmaceuticals. It is the feedstock materials, activation methods, and carbonization temperature that give the number and type of surface groups (Ahmed et al., 2016).

Heteroatoms, including hydrogen, oxygen, nitrogen, and halogen atoms, play a crucial role in determining the surface chemistry of organic molecules such as carbon materials (Zhang et al., 2022). The most common and important groups for CMs composed of heteroatoms are the oxygen-containing groups, which have different acidity, alkalinity, and neutrality (Shen et al., 2008). Some examples of functional groups are carboxyl groups (-COOH), hydroxyl groups (-OH), and carbonyl groups (C=O) (Zhang et al., 2022).

If there is an increase of oxygen-containing functional groups on carbonaceous materials, the sorption of pharmaceuticals containing amino, carbon-carbon double bonds, benzene, or other electron donors, will increase due to increased electron-donor-acceptor (EDA) interactions (Zhang et al., 2022). For example, if a biochar is modified by methanol, increasing hydroxyl functional groups, the sorption of tetracycline onto the biochar will increase due to $\pi - \pi$ EDA interactions Jing et al. (2014). A $\pi - \pi$ EDA interaction is when an electron-rich molecule donates an electron to the electron-poor acceptor, creating a specific non-covalent force, which can happen between CMs and pharmaceuticals. Oxygen on the surface of a CM can also affect the hydrogen bonding between a CM and a pharmaceutical, where an increase results in greater hydrogen bonding as pharmaceutical benzene rings act as hydrogen bond donor (Czech, 2016).

3.3.4 Challenges and research gaps with CMs

While carbonaceous materials are widely used as adsorbents due to their high surface area, porosity, and chemical properties, they do have some challenges and limitations. For example, a big question is what to do with a loaded adsorbent after it is used.

Hence, the regeneration of CMs is an important topic when discussing the real application of CMs as adsorbents, considering the cost, reuse, and recycling of a loaded adsorbent. There are several regeneration techniques for sorbents like thermal regeneration, chemical and solvent regeneration, microwave, ultrasonic, electrochemical, microbial, and humid air oxidation methods (Ahmed et al., 2016). Thermal regeneration methods are the most used on loaded sorbents, including pyrolysis, pyrolysis-gasification, and gasification (Ahmed et al., 2016). However, the regeneration process may not completely restore sorbents' original adsorption capacity. Yanyan et al. (2018) observed that sorption performance by carbon nanotubes of acetaminophen decreased successively after being regenerated thermally four times. He et al. (2021) found that bimetallic modified sewage sludge biochar had high adsorption of diclofenac (95.7%) after the first regeneration round, but then decreased to 78.2% in the second cycle.

Research on the potential of biochar, and other CMs, as an adsorbent has been done using batch tests and trials, which is insufficient data for full-scale process operation (Ihsanullah et al., 2022). To include adsorption as a step in wastewater treatment or other water treatments, continuous flow experiments and scaled-up pilots are needed (Ihsanullah et al., 2022).

Ihsanullah et al. (2022) states that research shows the adsorption of only single pollutants, like acetaminophen only, in fabricated aquatic solutions. To assess biochar's potential, it would be important to test real wastewater with several coexisting pollutants. The adsorption performance of biochar is likely to be affected by the presence of other species, as intermolecular interactions and competition occur (Shin et al., 2021).

As other adsorbents are "activated" and modified to increase their adsorption performance, so should technologies on surface modification of biochar be focused on. Regeneration data, like the amount of regeneration cycles correlated with adsorption efficiency, is lacking for sewage sludge biochar (Ihsanullah et al., 2022).

4. Materials and methods

This chapter describes the preparation of sorbates and sorbents that will be used in the experiments. In addition, a description of the conducted experiments, the preliminary experiments and the sorption study, is given. The data achieved from the experiments need to be analyzed, and UV/Vis is used for this purpose in this thesis. Therefore, method validation is done for UV/Vis and presented here. Many of the results need further examination, which is done by several different equations, which will be presented at the end of this chapter. Furthermore, all instruments and equipment used in this thesis are listed in Table F.1.

4.1 Preparation of sorbates

The pharmaceuticals used in this experiment, acetaminophen and carbamazepine, were purchased from Merck (Darmstadt, Germany) for a previous master's thesis work at NMBU in 2022, and used in this thesis as they were all intact. Stock solutions of both pharmaceutical compounds were prepared from their powder form by diluting in deionized water and in methanol for ACET and CBZ, respectively. The stock solutions are shown in Table 4.1.

Table 4.1: Pharmaceutical stock solution

Pharmaceutical	Dissolvent	Concentration (g/L)
ACET	Deionized water	1, 10
CBZ	Methanol	1, 10

In the preliminary experiments, four different concentrations were tested. Their dilutions are shown in Table 4.2

Table 4.2: Concentrations for preliminary experiments

Concentration (mg/L)	Pharmaceutical	Stock solution (g/L)	Pharmaceutical solution (mL)	DI water (mL)	Total volume (mL)
2	ACET/CBZ	1	4	1996	2000
4	ACET/CBZ	1	8	1992	2000
5	ACET/CBZ	1	10	1990	2000
20	ACET/CBZ	10	4	1996	2000

For the sorption study, nine different concentrations were tested and prepared. Their dilutions are shown in Table 4.3

Table 4.3: Concentrations for the sorption study

Pharmaceutical	Stock solution (g/L)	Pharmaceutical solution (mL)	DI water (mL)	Total volume (mL)	Concentration (mg/L)
ACET/CBZ	1	2.5	497.5	500	5
ACET/CBZ	1	12.5	487.5	500	25
ACET/CBZ	10	2.5	497.5	500	50
ACET/CBZ	10	3.75	496.25	500	75
ACET/CBZ	10	5	495	500	100
ACET/CBZ	10	7.5	492.5	500	150
ACET/CBZ	10	10	490	500	200
ACET/CBZ	10	20	480	500	400
ACET/CBZ	10	25	475	500	500

4.2 Preparation of sorbents

In this section, the preparation of the two sorbents; sludge biochar and activated carbon, is explained.

4.2.1 Sludge biochar

The biochar used in the experiments was taken from Scanship AS at Lindum AS (Drammen, Norway). The biochar feedstock material was sewage sludge-biosolids; solid digestate sources from a biogas plant in Drammen that handles sludge. To prepare the

biosolids for pyrolyzing, it was dried to a moisture content of >90% and pelletized into 8 mm pellets in diameter. The pyrolysis process was carried out in a pyrolysis session, using a 20-minute retention time and a temperature of 600 degrees Celsius.

To compare the performance of the same sludge biochar with results from previous master's thesis (Kalheim, 2022) it was decided in the beginning that the particle size of the SBC was to be 1-2 mm. The biochar was therefore crushed in a mortar and sieved with a 2 mm mesh sieve followed by a 1 mm mesh sieve to collect the 1-2 mm SBC. In 2021, as part of her master's thesis, Dizhora characterized SBC produced from the same feedstock, at the same temperature, and by the same company (Lindum AS). The characterization of the SBC used in this master thesis is mainly based on the information from the characterization done by (Dzihora, 2021).

In 2022, the same biochar and activated carbon samples used in this thesis were sent to Eurofins for analysis, where the results are shown in the table Table 4.4. Due to the time limitations of this thesis, only surface area will be discussed in the results and discussions in chapter 5. However, the rest of the parameters are presented with the purpose of reproducing the experiments and results in this thesis.

Table 4.4: SBC and AC properties from Eurofins analysis

Sample	Surface area (m2/g)	C (%)	H (%)	Ash/550 (%)	Moisture (%)
Raw SBC	40	10.50	0.11	88.01	0.10
Washed SBC	97	13.21	0.17	76.60	1.83
Washed AC	2340	80.32	0.33	0.23	12.58

Sample	pH	Moisture/105	Volatiles/900	Ash/750	Fixed C
Raw SBC	8.81	1.18	4.95	91.54	3.51
Washed SBC	7.32	2.18	9.08	74.14	16.77
Washed AC	7.74	24.40	8.30	2.64	89.06

4.2.2 Activated carbon

It was decided to use an already purchased activated carbon from Watts (North Andover, MA, USA) as it was available and had been tested in a previous master thesis. It was purchased from Eco Water (Drøbak, Norway).

The AC was used as a reference to be compared with the sludge biochar performance, as well as with results from Kalheim's master thesis (Kalheim, 2022). The production

size of the AC was 0.5-1.4 mm, and therefore a smaller size than the SBC. The AC was sieved with a 1 mm mesh sieve followed by a 0.5 mm mesh sieve to collect the 0.5-1 mm AC. Properties regarding the used AC are found in Table 4.4.

4.2.3 Sorbent experimental preparation

Figure 4.1 shows the steps for the preparation of the sorbent materials. The two sorbents were further prepared similarly for later experiments. The sorbents were washed to remove ash and gain a stable pH. In the test run, shown in Appendix A, washing ratios 1:20 and 1:10 solid-to-liquid were tested at 165 rpm in a horizontal shaker. Both washing ratios showed a relatively clear liquid after the test run, and it was decided to go with the largest ratio to produce more washed sorbent material.

In the process, 25 g sorbent was added to a 250 ml bottle with 250 ml DI water. To use the 16 spaces on the horizontal shaker, 8 bottles with SBC and 8 with AC were prepared. Before measuring the initial pH, the bottles were shaken by hand. After the pH measurement, the bottles were secured on the shaker at a speed of 165 rpm. After 24 hours the pH was measured again, followed by changing the water in the bottles two times and measuring the pH after the wash. This washing procedure was executed after 24, 48, 72, and 168 hours. The washing of the sorbents ended after 168 hours as the washing water was clear and the pH was stable. An overview of all pH measurements during the washing of sorbents is shown in Appendix A. The washed sorbent materials were added to aluminum cups and kept in the drying cabinet for 3 days at 105 °C to dry. After drying, the sorbents were kept in their cups and stored in a desiccator.

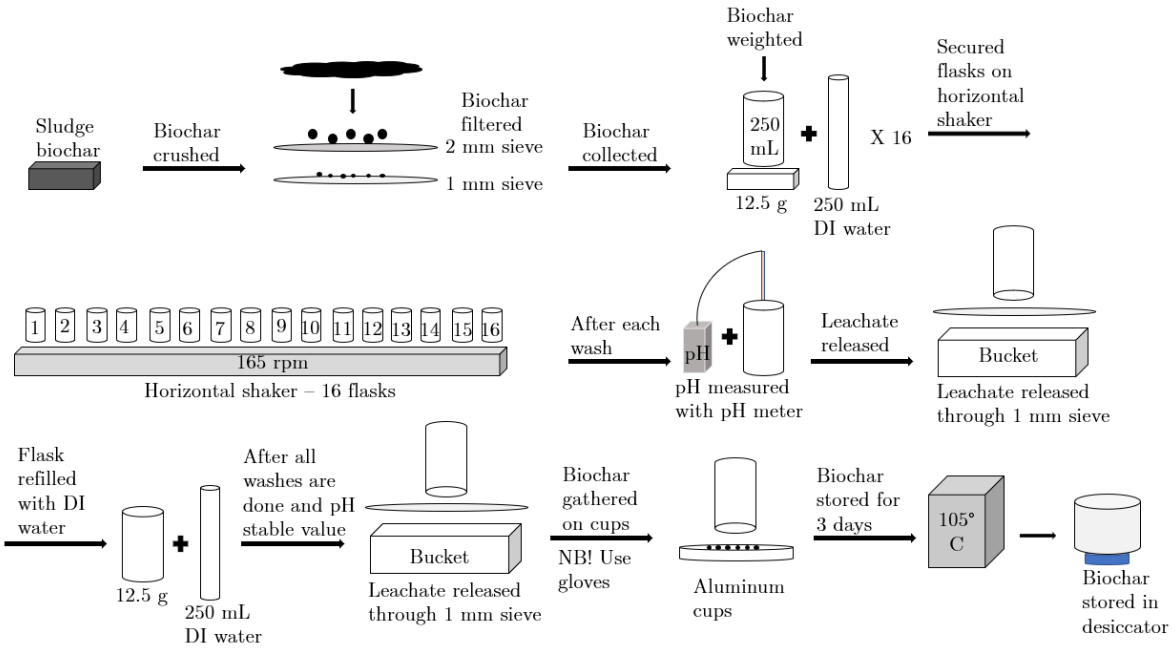


Figure 4.1: Preparation of sorbents

4.3 Description of conducted experiments

In this section, a description of the conducted experiments is given. It includes the analysis via UV/Vis, the preliminary experiments with sorbent dose and equilibrium time, and the sorption study for finding the maximum adsorption capacity of the sorbents.

4.3.1 Analysis of pharmaceuticals via UV/Vis

When analyzing samples with a UV/Vis Spectrophotometer, the method sat some limits to conducted experiments, i.e. the concentrations to be detected in the UV/Vis. For each stock solution used in an experiment, a standard curve based on that stock solution was made. When making the standard curve for different compounds, such as ACET and CBZ, it is shown that concentrations in the range of 0.5-25 mg/L are stable and have a linear fit. Outside this range, there is instability and uncertainty due to Lambert-Beer law limitations (Mäntele and Deniz, 2017). Therefore, it was chosen to set 25 mg/L as an upper limit for analyzed concentrations. All concentrations above were diluted to fit in the range. The analysis of a pharmaceutical was done at a certain wavelength. For acetaminophen, the wavelength was set to 241 nm, and for carbamazepine, it was fixed to 283 nm.

4.3.2 Preliminary experiments

The first conducted experiments were done to determine the sorbent dose and the equilibrium time of the sorbents. The sorbent dose is the amount of sorbent mass in g added in one liter. The equilibrium time is the time when the sorbents are saturated with sorbates.

The sorbent dose varies greatly in the literature between 0.1 g/L and 100 g/L (Zhou et al., 2022; Patel et al., 2021; Chen et al., 2017; Ahmed and Hameed, 2020; Ncibi and Sillanpää, 2017). In the preliminary experiments ratios 1, 2, 3.3, 3.6, 5, 10, and 25 g/L were tested. The tests are shown in Table 4.5.

The preparation of the preliminary experiments is shown in Figure 4.2. Solutions with a specific concentration of the compound were prepared and added to their respective bottles. Each pharmaceutical had three replicates with SBC, three with AC, and two blanks with only pharmaceutical solution. The blanks are important to control the concentration of the pharmaceutical during the experiments. In addition, one replicate with SBC in deionized water and one replicate with AC in deionized water was prepared, to blank in the Spectrophotometer when analyzing. All bottles were secured on the horizontal shaker and shaken at a speed of 165 rpm.

Table 4.5: Overview of preliminary experiments

Test	Sorbate	Sorbent	Dose (g/L)	Sorbent dose (g)	Volume (mL)	Concentration (mg/L)
1	ACET/CBZ	SBC	1	0.25	250	20
2	ACET/CBZ	SBC	1	0.25	250	2
5	ACET/CBZ	SBC	2	0.5	250	4
5	ACET/CBZ	SBC	2	0.5	250	20
8	ACET/CBZ	SBC	3.3	0.83	250	20
7	ACET	SBC/AC	3.6	0.9	250	20
6	ACET	SBC/AC	5	1.25	250	20
4	ACET/CBZ	SBC	10	2.5	250	5
4	ACET/CBZ	SBC	10	2.5	250	20
3	ACET/CBZ	SBC	25	6.25	250	2

It was decided that samples were to be taken at twelve time steps: initial 0, 1, 2, 4, 8, 24, 48, 72, 96, 120, 144, and 168 hours for analysis with UV/Vis. At timesteps initial, 48, 72, and 168 hours additional samples were taken for analysis with LC-MS/MS, to compare with the results from UV/Vis. All the samples needed to be representative when they were taken out. Therefore, less than 15% of the total volume was extracted. At every timestep, the shaker was stopped, and a sample was taken. This was done through a 10 mL NORM-JECT Luer Lock syringe with a 0.2 µm PFTE Membrane syringe filter. The syringe filter needed to be activated by 1 drop of methanol. The analysis with UV/Vis Spectrophotometer was to be done immediately after sampling to secure a stable concentration, and the samples for LC-MS/MS were frozen down for later analysis.

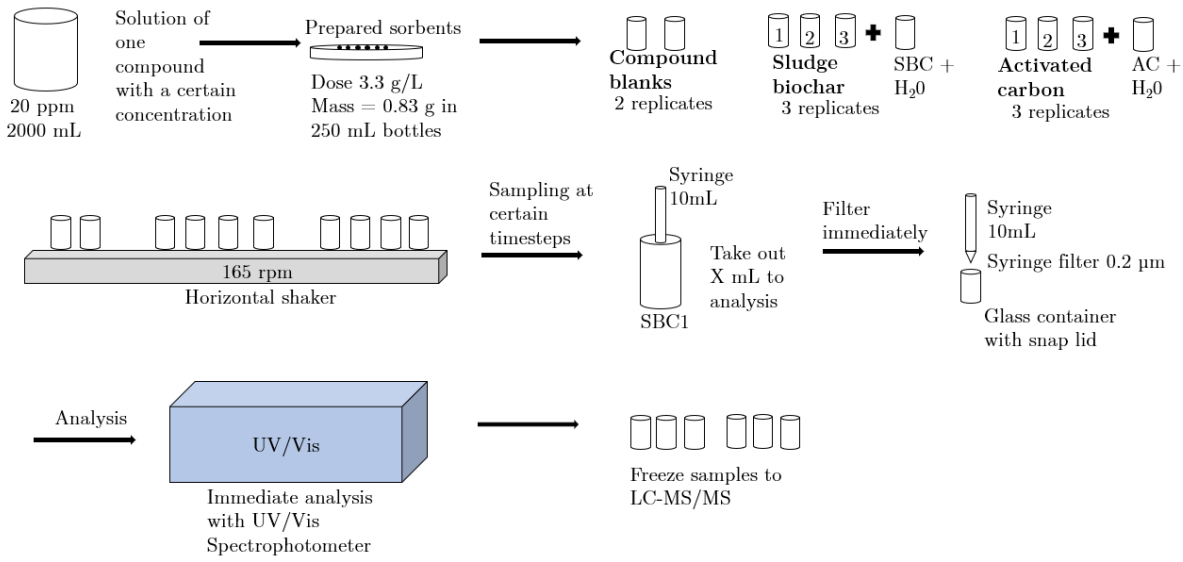


Figure 4.2: Preparation and conduction of the preliminary experiments. Example with initial concentration of 20 mg/L and sorbent dose 3.3 g/L

4.3.3 Sorption study

The next set of experiments was the sorption studies with the goal of finding the sorbent materials' maximum adsorption capacity. From the preliminary experiments, the solid-to-liquid ratio was decided to be 1:300, hence the adsorbent of dose 3.3 g/L, and the experimental contact time was determined to be 7 days (168 hours).

The sorption study was to be tested for SBC and AC at the same time, starting with 6 different concentrations for both ACET and CBZ in the range of 5-200 mg/L. After the first test, new and higher concentrations needed to be tested, and an overview of all concentrations and tests are shown in Table 4.6.

Table 4.6: Overview of the sorption study

Test	Pharmaceutical	Sorbent dose (g/L)	Concentration (mg/L)
1	ACET	3.3	5, 25, 50, 75, 100, 200
2	CBZ	3.3	5, 25, 50, 75, 100, 200
3	ACET	3.3	150, 400, 500
4	ACET	3.3	25, 100, 200, 300, 400
5	CBZ	5	5, 25, 50, 75, 100

The steps of the sorption study are shown in Figure 4.3. In each experiment, there were three replicates with SBC, three with AC, and two blanks for each concentration. The blank samples were necessary to recognize that the concentration was the same for the whole experiment, to compare with the initial concentration. In addition, one replicate with SBC and deionized water, and one replicate with AC and deionized water were prepared, to blank in the Spectrophotometer when analyzing.

A sample of the initial concentration was taken before adding the sorbent dose to each replicate with sorbate concentration. Other sampling points were at 48 and 168 hours, where the latter was the determined contact time. At all sampling points, two replicate samples were frozen for later LC-MS/MS analysis, and one replicate was taken to analysis with UV/Vis immediately after sampling. After the sorption material was added to the replicates, all replicates were secured on the horizontal shaker at a speed of 165 rpm. pH was measured in two replicates, for SBC, AC, and blanks, at all timesteps.

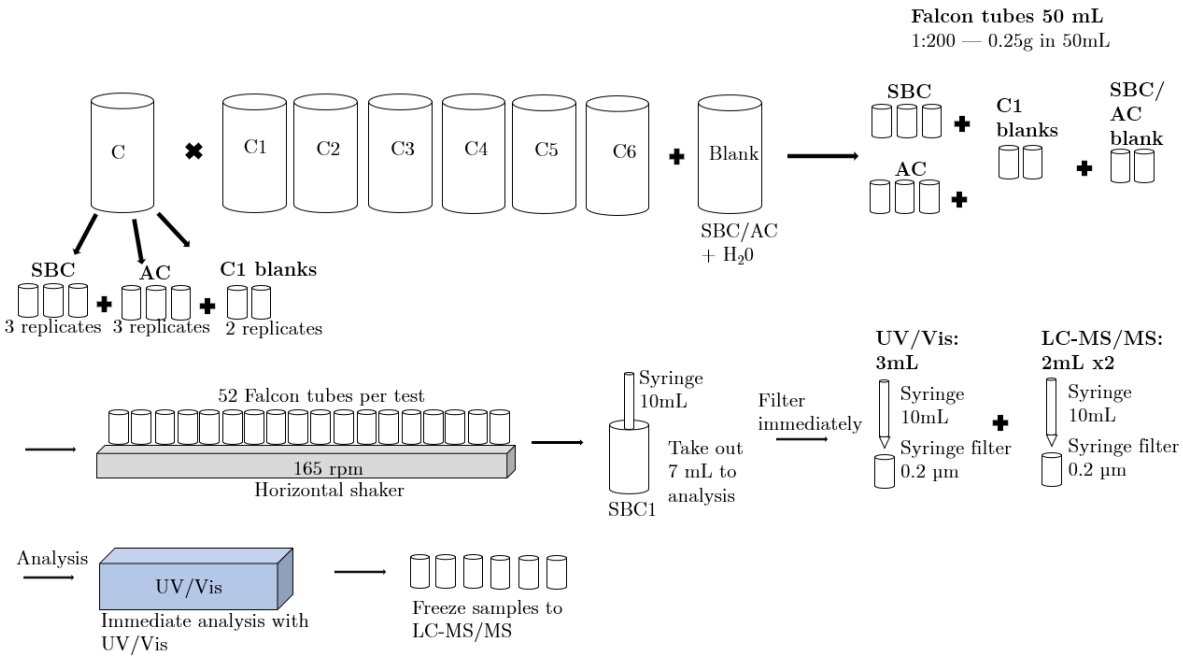


Figure 4.3: Preparation and conduction of the sorption study with acetaminophen and carbamazepine

4.4 Analytical methods

In this section, the analytical method validation of UV/Vis is presented.

4.4.1 UV/Vis - Analytical method validation

The instrument used to analyze samples was a UV/Vis Spectrophotometer with 10 mm Quartz Cuvettes, connected to a computer with UV/Vis software. For the intermediate precision study, a different UV/Vis machine was used, HORIBA Aqualog (Horiba, 2023). The measurements were also done in 10 mm quartz cells.

Specificity and selectivity

After preparation of CBZ and ACET stock solutions in methanol and distilled water respectively, different aliquots were prepared in a series of concentrations ranging from 0.25 to 25 mg/L. ACET and CBZ solutions were also prepared in two different sludge biochar leachates. The solutions for ACET and CBZ were scanned in the range of 400 to 210 nm, and 400 to 250 nm respectively.

Accuracy

Accuracy was determined by making different levels of pharmaceutical concentrations; lower concentration, intermediate concentration and higher concentration, within the

range tested in the sorption study (5-500 mg/L). The concentrations were prepared from an independent stock solution and analyzed (n=9).

To calculate C_t (mg/L), total drug concentration measured after standard addition, shown in Table 4.7, equations Equation 4.1, Equation 4.2 and Equation 4.3 are used. C_s (mg/L) is the drug concentration of 20 mg/L, M_s (mg) is the corresponding mass for C_s, and V_s (mL) is the corresponding volume for C_s. C_a (mg/L) is the drug concentration of 10 mg/L added to the formulation, M_a (mg) is the corresponding mass for C_a, and V_a (mL) is the corresponding volume for C_a.

$$M_s(mg) = V_s(mL) \cdot \frac{C_s(mg/L)}{1000} \tag{4.1}$$

$$M_a(mg) = V_a(mL) \cdot \frac{C_a(mg/L)}{1000} \tag{4.2}$$

$$C_t(mg/L) = \frac{1000 \cdot (M_s + M_a)(mg)}{V(mL)} \tag{4.3}$$

The calculated values in Table 4.7 are shown by the example below, with 4.4, 4.5 and 4.6. To calculate C_s, example 4.4 is shown. In 1000 mL there is 20 mg. Hence, in 2 mL there is 0.04 mg.

$$C_s(mg) = 2mL \cdot \frac{20mg/L}{1000} = 0.04mg \tag{4.4}$$

To calculate C_a, example 4.5 is shown. In 1000 mL there is 10 mg. Thus, in 1 mL there is 0.01 mg.

$$C_a(mg) = 1mL \cdot \frac{10mg/L}{1000} = 0.01mg \tag{4.5}$$

To calculate the concentration of C_t with C_s and C_a, shown by example 4.6.

$$C_t(mg) = \frac{1000 \cdot (0.04 + 0.01)mg/L}{5mL} = 10mg/L \tag{4.6}$$

The method is shown in Table 4.7.

Table 4.7: Accuracy method. Each compound test contains 3 replicates each

	ACET 1	ACET 2	ACET 3	CBZ 1	CBZ 2	CBZ 3
C_s = 20 mg/L (mL)	2	2	2	2	2	2
C_a = 10 mg/L (mL)	1	2	3	1	2	3
H_2O (mL)	2	1	-	2	1	-
Total volume (mL)	5	5	5	5	5	5
C_t (mg/L)	10	12	14	10	12	14

Precision

Precision was determined by studying inter-day, intra-day, inter-instrument and inter-person variations. The same procedure was repeated for all variations, namely minimum of 5 replicates of the same concentration were diluted from the same stock solution.

For testing inter-day variations, the same concentrations with 9 replicates were diluted and analyzed on Tuesday 28^{th} of February and Thursday 2^{nd} of March. Intra-day variations were tested with the same concentration and 5 replicates within the same day, Thursday 2^{nd} of March. For inter-day and intra-day variations, two different people carried out the experiments and the results were compared. The UV/Vis Spectrophotometer was compared with HORIBA Aqualog (Horiba, 2023) and the results were compared. Each pharmaceutical was tested at one concentration and with three replicates.

Linearity

To determine the linearity, several separate series of solutions have been conducted, through making the standard curve. Every time a new stock solution was made, a new standard curve was made. This happened several times during the experiments.

When analyzing a sample using the created standard curve, two replicates of the dilutions of 5 and 10 mg/L were made on that specific date to control if the standard curve was valid for the results. For both pharmaceuticals, there was linearity between 0.5 and 25 mg/L. Outside of this range, the equation needs to be extrapolated and values are more uncertain.

Limit of detection and quantification

After making several standard curves and checking their accuracy, stability, and representativity, it was shown that we had linearity between 0.1 and 1.2 adsorbance.

LC-MS/MS - Method validation

Samples were analyzed with UV/Vis and sent to the Faculty of Veterinary Medicine at the Norwegian University of Life Sciences for validation with LC-MS/MS. The validation report and the analysis with LC-MS/MS were written and executed by Stine Göransson Aanrud in the Toxicology group at the Veterinary Faculty at NMBU. The validation report and the LC-MS/MS results are found in Appendix B.

4.5 Data analysis

To examine the data attained from the different experiments, different equations were needed. Adsorption capacity, removal efficiency, solid-to-liquid ratio along with different isotherm model equations are given below.

Adsorption capacity

To calculate the adsorption capacity Equation 4.7 was used.

$$q_e = \frac{C_i - C_e}{m} \cdot V \tag{4.7}$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, C_i (mg/L) is initial concentration, C_e (mg/L) is equilibrium concentration, m (g) is weight of sorbent and V (L) is volume of sorbate.

Pharmaceutical removal efficiency of sorbent

The equation for pharmaceutical removal is given by Equation 4.8.

$$pharmaceutical\ removal\ efficiency = \frac{C_i - C_e}{C_i} \cdot 100\% \tag{4.8}$$

Where C_i (mg/L) is the initial concentration and C_e (mg/L) is the equilibrium concentration.

Solid-to-liquid ratio

The solid-to-liquid ratio is calculated by Equation 4.9

$$ratio = \frac{m}{V} \tag{4.9}$$

Where m is the mass of sorbent (g) and V is volume of sorbate (mL).

4.5.1 Modelling

To understand the mechanisms of adsorption, isotherm models have been used.

The **Langmuir** adsorption isotherm was initially created to explain the adsorption of gas onto activated carbon in the solid phase, but has commonly been used to compare the performance of different bio-sorbents (Langmuir, 1916). Langmuir is an empirical model that assumes monolayer adsorption on a homogeneous uniform surface with a finite number of definite sites (Vijayaraghavan et al., 2006). The Langmuir graph is identified by a flat region, a saturation point of equilibrium, beyond which no more adsorptions can occur once a molecule occupies a site (Allen et al., 2004).

The Langmuir equation is given by

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{4.10}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg) and C_e is the concentration of sorbate in equilibrium (mg/L).

The separation factor (R_L) acquired from the Langmuir constant "K_L", where C_0 is the initial concentration and K_L is the Langmuir constant is shown by

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{4.11}$$

R_L is a dimensionless constant, defined by Hall et al. (1966), indicating the isotherm shape where $R_L > 1$ is unfavourable, $R_L = 1$ is linear, $R_L = 0$ is irreversible and $0 < R_L < 1$ is favourable.

The **Freundlich** adsorption isotherm model is another commonly used isotherm. Where Langmuir describes monolayer adsorption, Freundlich describes multilayer adsorption on heterogeneous non-uniform surfaces (Adamson, Gast, et al., 1967).

The Freundlich equation is given by

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \tag{4.12}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_F is the Freundlich isotherm constant related to adsorption capacity, C_e is the concentration of sorbate in equilibrium (mg/L) and n is a correction factor related to adsorption intensity.

Another isotherm model is **Redlich-Petersons (R-P)**, a hybrid between Langmuir and Freundlich isotherm models, which include three parameters into an empirical equation (Redlich and Peterson, 1959). At high concentrations, the R-P approaches the Freundlich isotherm model and at low concentrations the Langmuir.

The Redlich-Petersons equation is given by

$$q_e = \frac{K_{RP} \cdot C_e}{1 + a_{RP} \cdot C_e^g} \tag{4.13}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_{RP} (L/g) and a_{RP} (L/mg) are Redlich-Peterson isotherm constant, C_e is the concentration of sorbate in equilibrium (mg/L) and g is the Redlich-Peterson isotherm exponent.

Sips (Sips, 1948) is a hybrid of Langmuir and Freundlich equations that allows for accurate predictions of heterogeneous adsorption systems (Gunay et al., 2007). At high concentrations it predicts monolayer adsorption in relation to Langmuir isotherm model, and at low concentrations it reduces to Freundlich isotherm. The equation parameters are mainly influenced by operating conditions such as pH, temperature, and concentration (Pérez-Marín et al., 2007).

The equation is expressed by

$$q_e = \frac{K_s \cdot C_e^{\beta_S}}{1 + a_S \cdot C_e^{\beta_S}} \tag{4.14}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_s (L/g) and a_S (L/mg) are the Sips isotherm model constants (L/g), C_e is the concentration of sorbate in equilibrium (mg/L), and β_S the Sips isotherm model exponent.

Toth (Toth, 1971) isotherm model is another empirical equation, which can be useful in describing heterogeneous adsorption systems with low and high concentrations.

The Toth equation is expressed by

$$q_e = \frac{K_T \cdot C_e}{(a_T + C_e)^{\frac{1}{t}}} \tag{4.15}$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g), C_e is the concentration of sorbate in equilibrium (mg/L) and K_T (mg/g), a_T (L/mg) and t are Toth isotherm constants.

5. Results and discussion

This chapter includes the method validation analysis, properties of the sorbents, results from the preliminary experiments, and the sorption study. In addition, the experimental results are modeled and shown in this chapter, along with adsorption removal mechanisms explaining what could be happening in the adsorption process.

5.1 Method validation analysis

The UV/Vis method for analysis of ACET and CBZ is validated for various parameters such as specificity and selectivity, accuracy, precision, linearity, and limit of detection. In addition, a correlation between the dataset of UV/Vis and LC-MS/MS is presented.

5.1.1 UV/Vis

Specificity and selectivity

After ACET and CBZ were prepared in solutions and scanned, the λmax for ACET solution was found to be 241 nm in Figure 5.1 and for CBZ solution 284 nm shown in Figure 5.2. Similar results were reported in Aljuboury (2017), where λmax for ACET was found to be 243 nm. For CBZ, Mawazi et al. (2019) found the selected wavelength to be 286 nm, and Padma et al. (2019) and Borse and Mulgund (2015) found it to be 284 nm.

According to the Lambert-Beer law, which describes the relationship between the concentration of a solute in a solution and the amount of light absorbed by the solution, the absorbance of light (A) in a solution is directly proportional to the concentration (c) of the absorbing solute and the path length (d) that the light travels through the solution (Swinehart, 1962). Mathematically, the law is expressed by $A = \epsilon \cdot c \cdot d$ (Mäntele and Deniz, 2017). This is shown in Figure 5.1 and Figure 5.2 whereas the concentration of ACET and CBZ increases, the absorbance of light also increases.

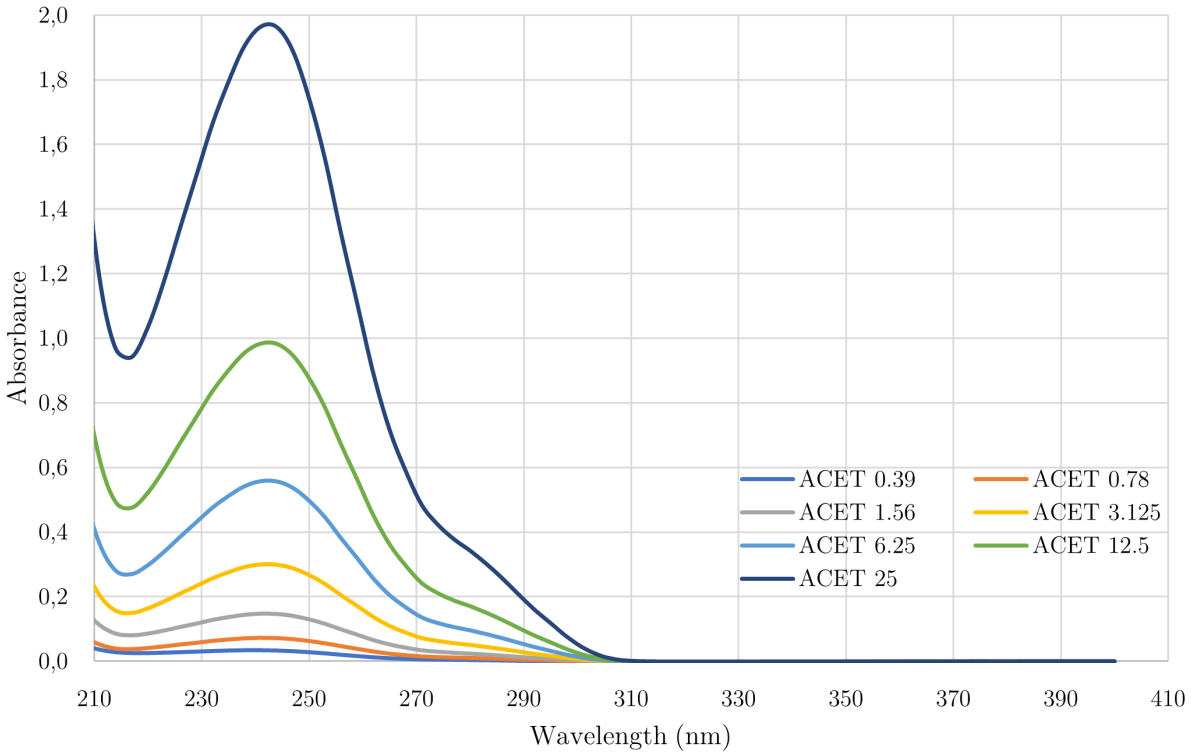


Figure 5.1: UV/Vis spectra of acetaminophen

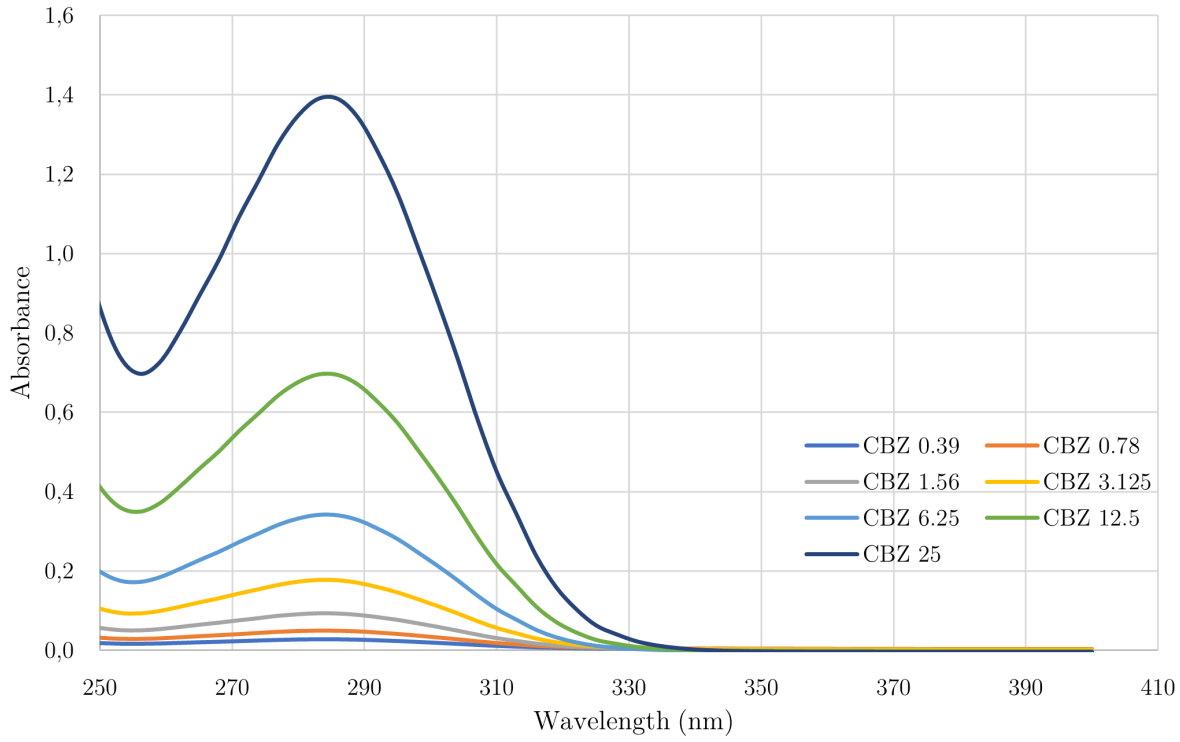


Figure 5.2: UV/Vis spectra of carbamazepine

It is also shown that leachate from the sludge biochar affected the absorbance and needed to be corrected for, shown in Figure 5.3 and Figure 5.4. This was done by zeroing the Spectrophotometer with the respective sorption media every time before analyzing.

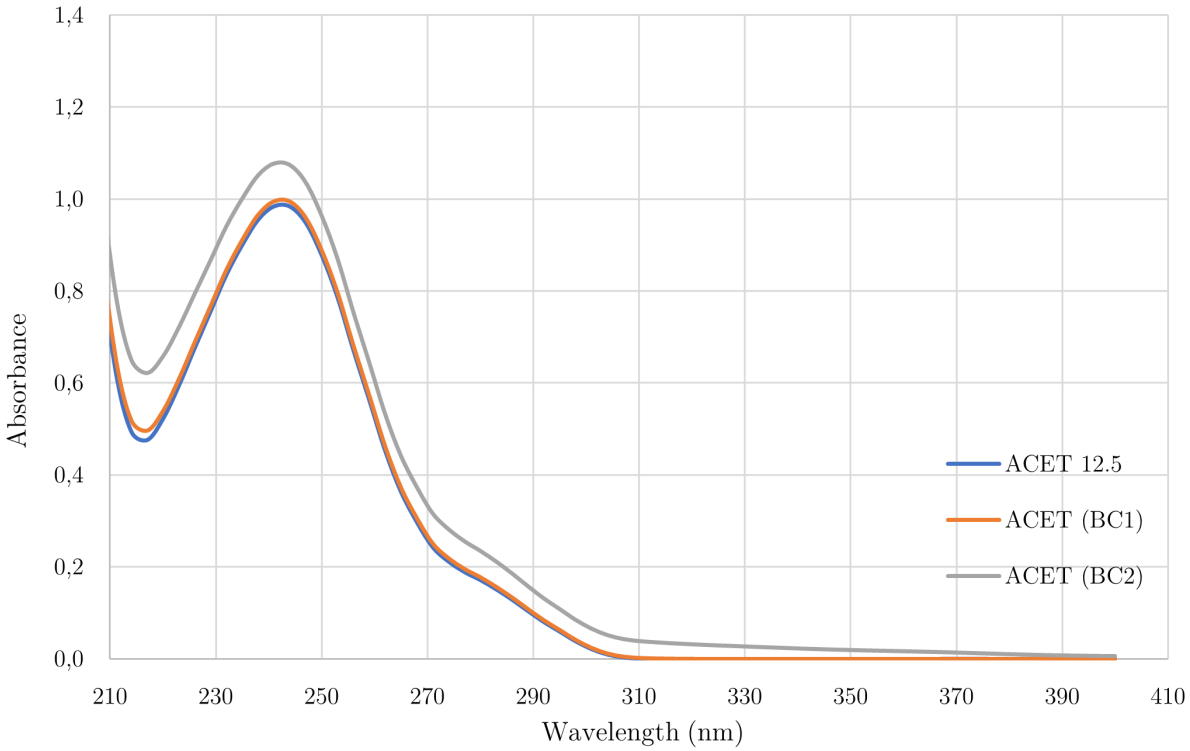


Figure 5.3: Spectra of ACET diluted in water and two biochar leachates

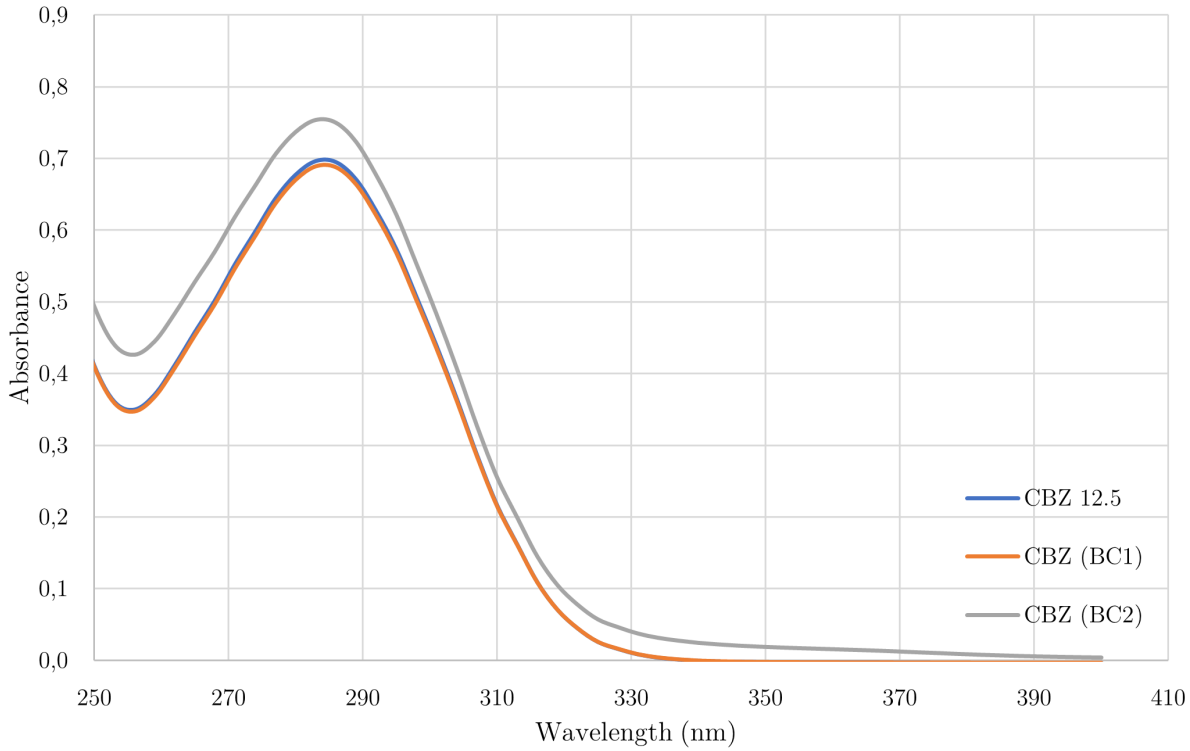


Figure 5.4: Spectra of CBZ diluted in water and two biochar leachates

Accuracy

The results from the accuracy tests are shown in Table 5.1. The standard deviation for all the tests is relatively low, indicating a smaller variation related to the mean value, suggesting a greater uniformity of the dataset. However, CBZ has a somewhat higher relative standard deviation, exhibiting higher variability than ACET.

Table 5.1: Accuracy test results

Compound C_t	Predicted concentration (mg/L)			Accuracy (%)
	Range	Mean ± S.D.	% R.S.D	
Acetaminophen				
A 1 (10 mg/L)	10.219-10.251	10.239 ± 0.0017	0.17	-2.33
A 2 (12 mg/L)	12.162-12.198	12.177 ± 0.0015	0.15	-1.45
A 3 (14 mg/L)	14.351-14.358	14.355 ± 0.0002	0.02	-2.47
Carbamazepine				
C 1 (10 mg/L)	10.173.10.200	10.188 ± 0.0014	0.14	-1.85
C 2 (12 mg/L)	11.992-12.033	11.997 ± 0.0029	0.29	0.03
C 3 (14 mg/L)	14.033-14.075	14.059 ± 0.0016	0.16	-0.42

Accuracy is given in % relative error = [100*(predicted concentration-mean concentration)/mean concentration].

Precision

Precision testing involved inter-day, intra-day, and intra-instrument testing, and the results are shown in Table 5.2. In the inter-day testing, it is shown that day 1 had a higher standard deviation compared to day 2, which can be explained by human error. It also shows that acetaminophen is more stable with a lower standard deviation than carbamazepine. One explanation for this might be that CBZ is diluted in methanol which could have partly evaporated. Results from the intra-day testing show a similar standard deviation for each compound, but like the inter-day testing, a high deviation for CBZ. The intra-instrument testing shows a higher deviation in Table 5.2 for Horiba aqualog UV/Vis Spectrophotometer than for UV/Vis.

Table 5.2: Precision test results

Compound	Inter-day % R.S.D (n=9)		Intra-day % R.S.D (n=5)		Intra-instrument % R.S.D (n=3)
	Day 1	Day 2	Morning	Evening	
Agnieszka					
A – 10 mg/L	2.88	0.65	0.65	0.53	1.27
C – 10 mg/L	2.77	1.95	1.95	1.61	5.21
Sarah					
A – 10 mg/L	1.49	0.58	0.58	0.73	
C – 10 mg/L	2.50	2.65	2.65	4.98	

Linearity

The validation of the results for the two compounds was achieved using regression statistics between the respective absorbance versus concentrations. The calibration curves for the two compounds were linear with correlation coefficients R^2 of 0.9999 and 0.9996 for ACET (Figure 5.5) and CBZ (Figure 5.6), respectively. The high correlation coefficient indicates a strong linear relationship between the two variables.

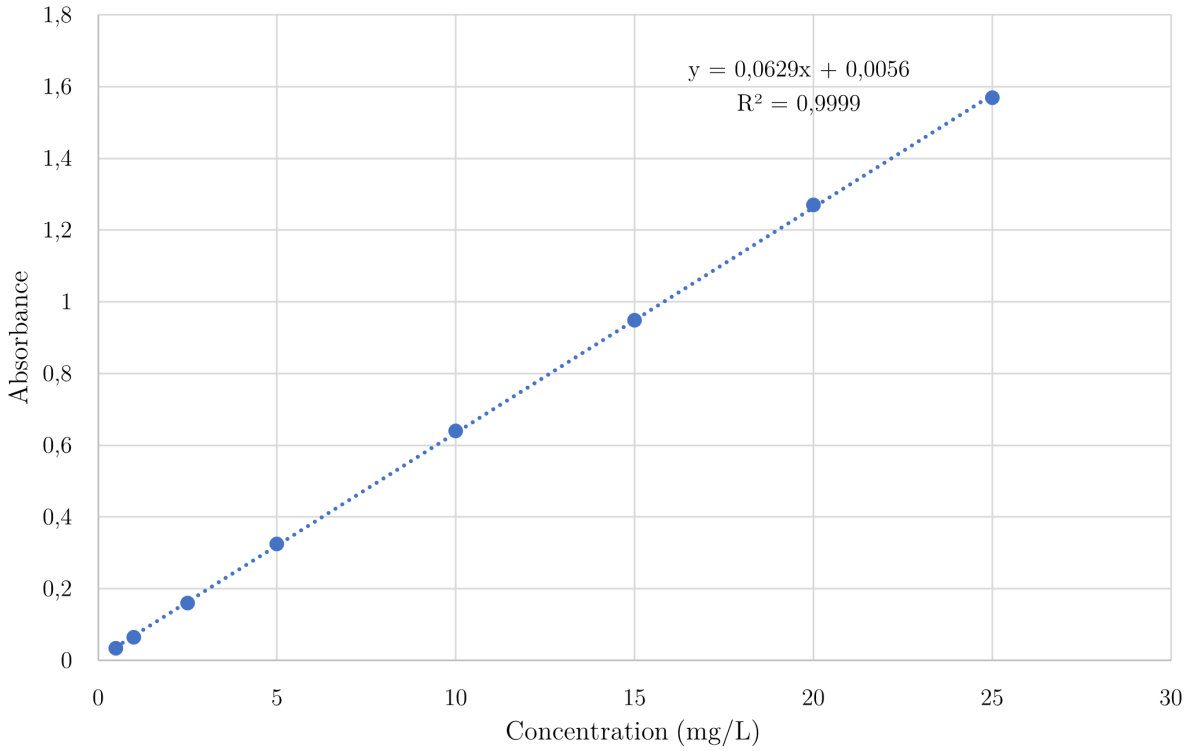


Figure 5.5: Standard curve for ACET (23.3.23)

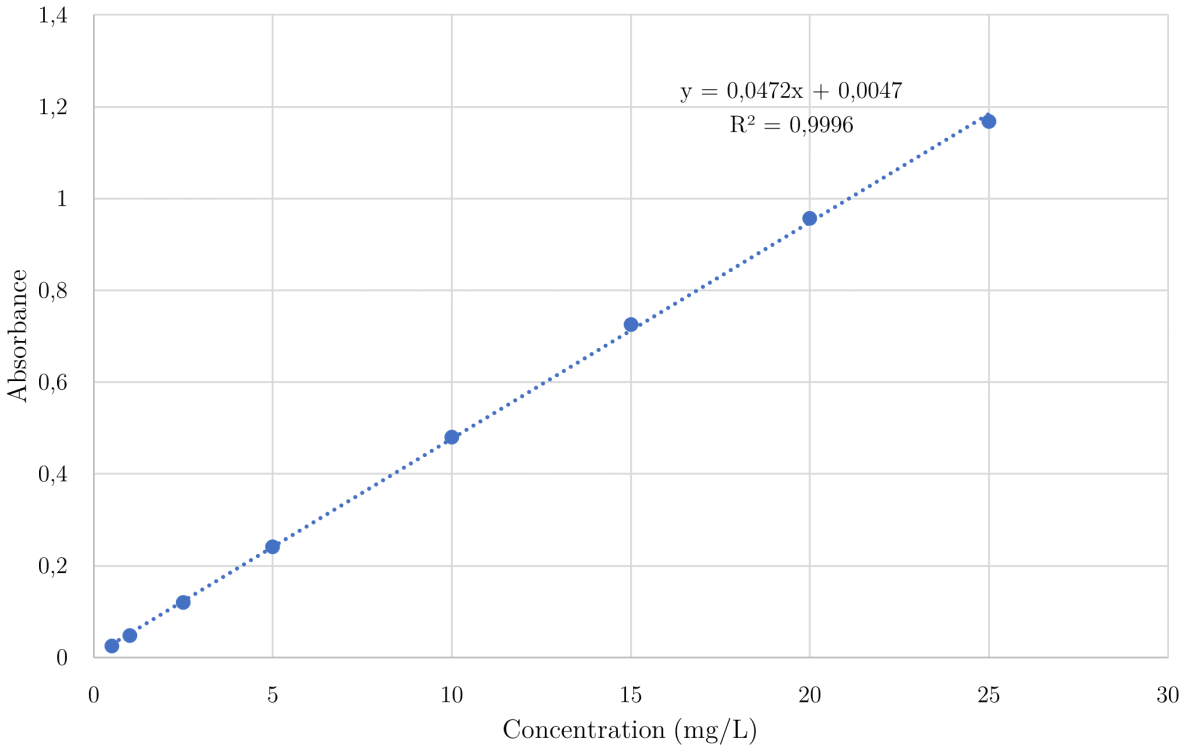


Figure 5.6: Standard curve for CBZ (13.3.23)

5.1.2 UV/Vis compared to LC-MS/MS

Samples from the sorption study were analyzed with UV/Vis immediately after sampling. Part of the sample was frozen for later and analyzed with LC-MS/MS by Stine Göransson Aanrud in the Toxicology group at the Veterinary Faculty at NMBU. The results from samples analyzed with UV/Vis compared to results from LC-MS/MS are illustrated in Table 5.3, and shown in detail in UV/Vis compared with LC-MS/MS.

To understand the difference between the two results, it was decided to find the relationship between them by creating a factor Δ, shown with Equation 5.1.

$$\Delta = \frac{UV/Vis\ concentration}{LC-MS/MS\ concentration} \tag{5.1}$$

The first Δ in Table 5.3 is calculated by using Equation 5.1, and is shown in example 5.2

$$\Delta = \frac{5.5534(mg/L)}{4.082(mg/L)} = 1.36 \tag{5.2}$$

Table 5.3: Comparing UV/Vis and LC-MS/MS results

Pharmaceuticals	Stock solution	Sample name	UV/Vis (mg/L)	LC-MS/MS (mg/L)	Δ
Preliminary experiments					
ACET	A1	14 A SBC2	5.5534	4.082	1.36
		5 A AC2	21.4565	15.411	1.39
		15 A SBC3	6.5517	4.269	1.53
ACET	A2	26 A SBC2	19.9307	14.373	1.39
		50 A SBC2	0.6056	0.384	1.58
		37 A SBC1	4.3548	2.666	1.63
CBZ	C1	40 C SBC1	4.0873	3.836	1.07
		30 C SBC3	19.8295	15.684	1.26
		47 C SBC2	2.7817	1.793	1.55
Sorption study					
ACET	A2	111 A C1 AC3	0.5083	0.459	1.11
		114 A C2 SBC1	13.4323	9.354	1.44
		127 A C3 AC3	6.7409	4.129	1.63
ACET	A3	270 A C8 AC1	95.4766	81.565	1.17
		281 A C9 B1	502.5848	386.266	1.30
		261 A C7 SBC3	114.3780	80.004	1.43
ACET	A4	299 A C2 AC1	14.6741	14.753	0.99
		304 A C3 SBC1	157.6948	120.591	1.31
		316 A C4 AC2	101.1924	65.152	1.55
CBZ	C2	344 C C2 AC1	7.8375	7.539	1.04
		358 C C4 SBC2	57.0208	46.004	1.24
		247 C C5 B2	102.2708	65.331	1.57

The results in Table 5.3 are grouped per stock solution with three replicates, showing the minimum and maximum Δ per stock solution and a random within that range. For example, for stock solution A1, the Δ ranges from 1.36 to 1.53 for all the results analyzed with UV/Vis and LC-MS/MS.

Figure 5.7 and Figure 5.8 visualize the comparison between LC-MS/MS and UV/Vis results for the preliminary experiments and the sorption study in Table 5.3, respectively. Though there are variations in values, because of instrument or methodology variations, for example, they are highly correlated with $R^2 = 0.9914$ for the preliminary experiments and $R^2 = 0.9964$ for the sorption study. This shows that UV/Vis is a simple, fast, robust, effective, inexpensive, and accurate method for the quantification analysis of acetaminophen and carbamazepine.

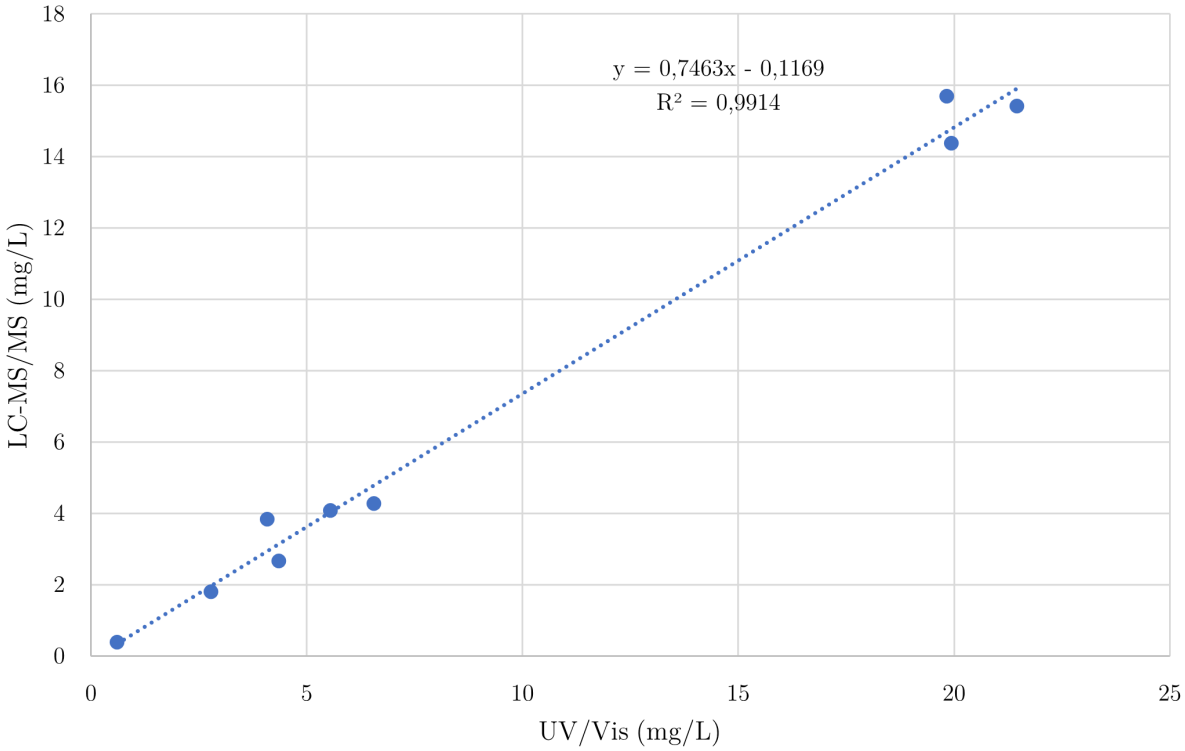


Figure 5.7: LC-MS/MS vs. UV/Vis for the preliminary experiments

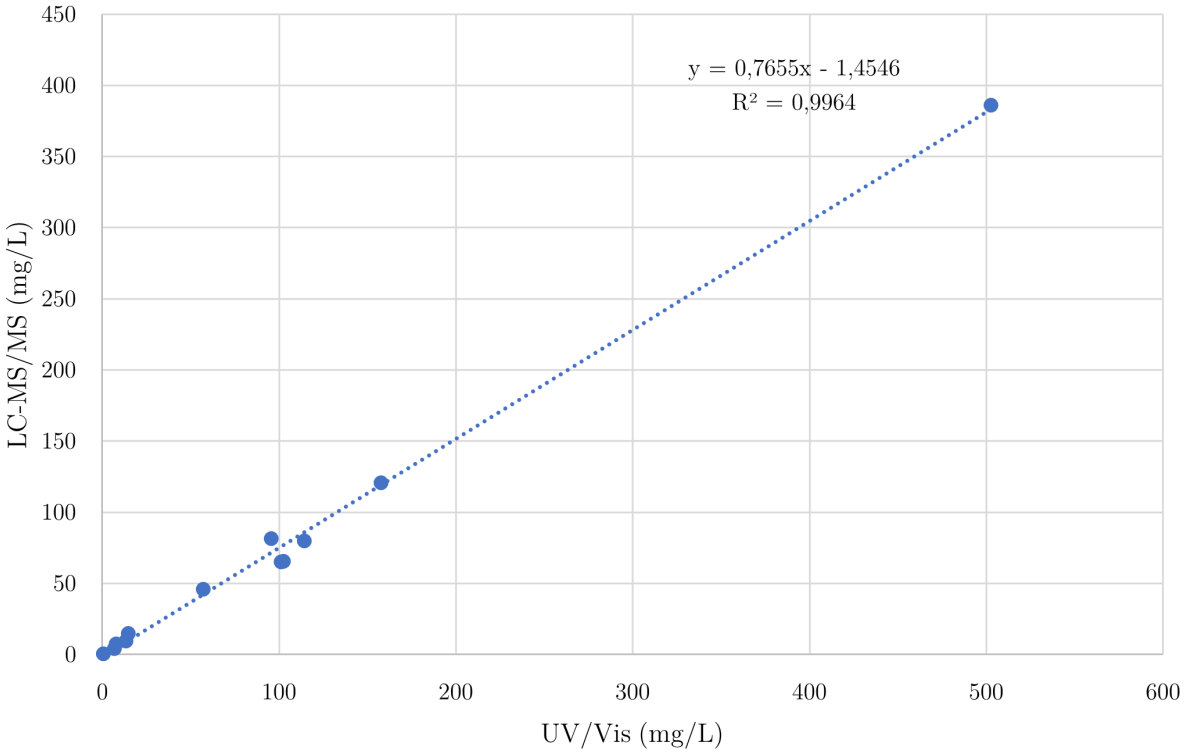


Figure 5.8: LC-MS/MS vs. UV/Vis for the sorption study

There can be many reasons for the difference in concentration values between LC-MS/MS and UV/Vis, where LC-MS/MS values are lower. Of the 282 samples sent for analysis with LC-MS/MS, 200 of them were diluted, which could be one possible reason for the difference. However, it does not explain the last 82 samples, and why they also have the same factor difference.

Another reason could be the use of different stock solutions when creating standard curves for pharmaceuticals, for UV/Vis and LC-MS/MS analysis. This might be the main reason for the difference. Every time a new stock solution is made, a new standard curve needs to be made, to find the right correlation between absorbance and concentration, in the UV/Vis analysis. This was done multiple times for the UV/Vis analysis, as a new stock solution needed to be made before several experiments. For LC-MS/MS only one main stock solution for each pharmaceutical was used, and this was different than the ones used for UV/Vis. In addition, the samples prepared for LC-MS/MS were first frozen for a period of time and then thawed when analyzed in the LC-MS/MS. This process of freezing and thawing could have influenced the results as well.

The aspect of human differences is also important. Three different people were involved in the analysis as Agnieszka made the stock solutions, Sarah made the standard curves, did the experiments and sampling, and the analysis in the UV/Vis, and Stine diluted samples, added internal standard, and analyzed in the LC-MS/MS. Personal differences and errors might have affected the results. However, what matters when comparing LC-MS/MS and UV/Vis is that there exists a high correlation between the datasets. The results presented further in this thesis are from analysis with UV/Vis.

5.2 Preliminary experiments

In the preliminary experiments, two main parameters were tested: sludge biochar adsorbent dose and equilibrium time. For the sorption study experiments, these parameters were significant to establish beforehand.

5.2.1 Adsorbent dose

The results of the preliminary experiments for sludge biochar dose, where a range 1-10 g/L was tested for the same initial concentration (20 mg/L), are shown for acetaminophen in Figure 5.9 and for carbamazepine in Figure 5.10. As shown in the figures, the doses 1 g/L and 2 g/L were too low, as the adsorption rate was low and slow, in addition to a low pharmaceutical removal. On the other hand, with an adsorbent dose of 10 and 5 g/L, the whole concentration was adsorbed in total, and relatively quickly. The optimal dose was expected to be somewhere between 2-5 g/L and a test with 3.3 g/L was therefore conducted. The goal of the preliminary experiments was to gain a flattening of the curve after a significant part of the initial concentration of 20 mg/L was adsorbed, but to the point where the sorption had stopped, and the value could be detected and quantified. In addition, the lowest possible biochar dose was the aim, taking cost into consideration.

Although most of the tests were performed for both acetaminophen and carbamazepine, one adsorbent dose was not tested for carbamazepine (5 g/L) due to practical issues and time limitations. During testing, it was assumed that acetaminophen would represent the two pharmaceuticals in the same way.

Figure 5.11 shows the effect of the sludge biochar adsorbent dose on the removal efficiency of ACET and CBZ. As the dose increase, the removal efficiency increase. It is shown in the figure that low doses reveal low removal, and a higher dose shows higher removal. In the figure, the top data point, 3.3 g/L, is the optimal dose, which shows high removal efficiency in the graph, as a higher dose does not affect the removal efficiency further.

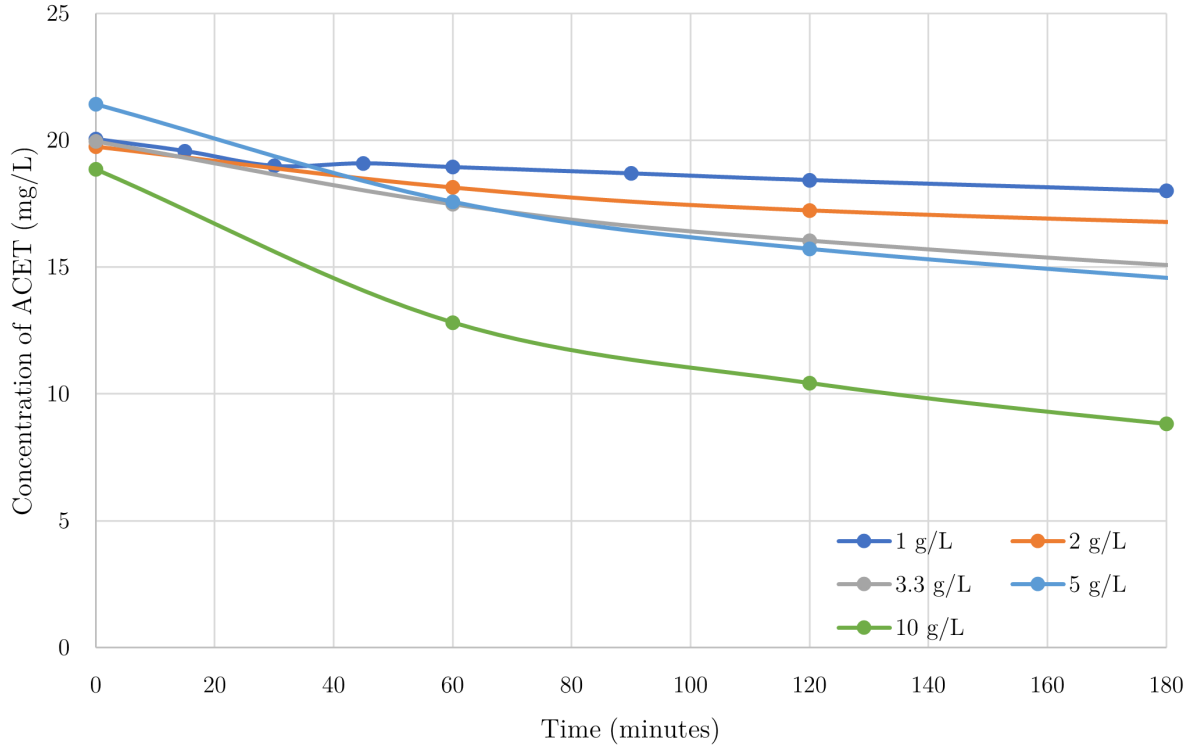


Figure 5.9: SBC adsorbent dose for ACET

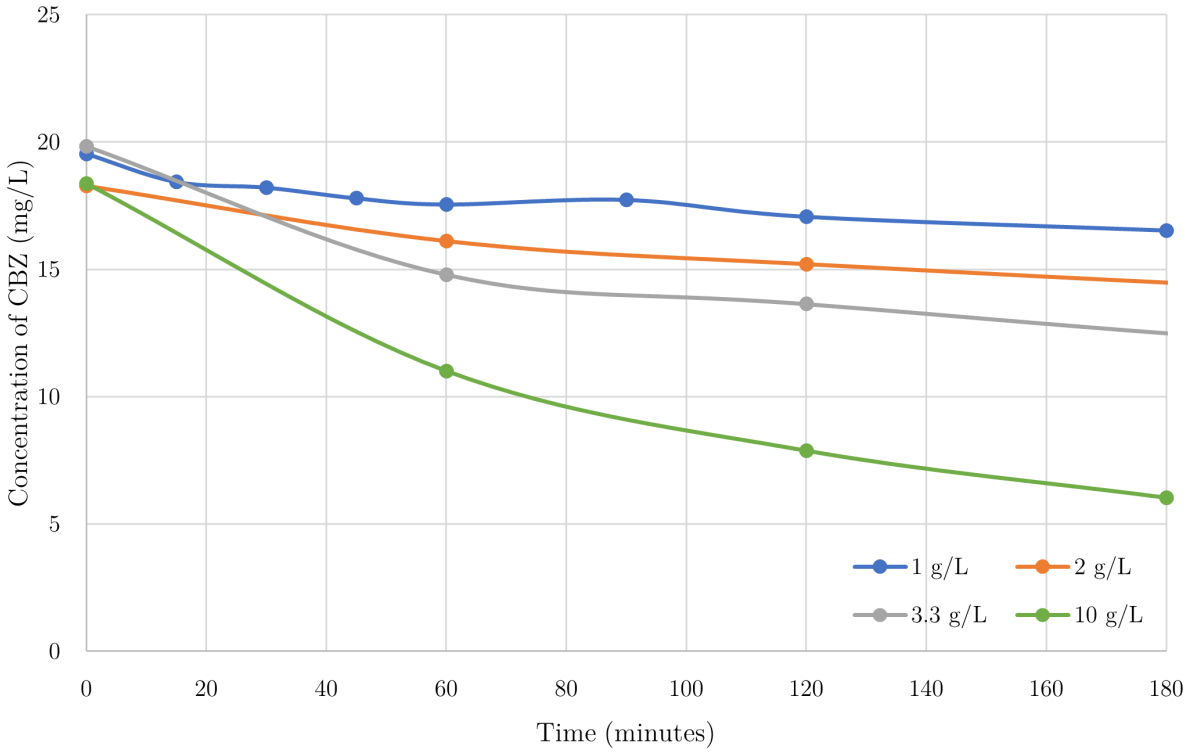


Figure 5.10: SBC adsorbent dose for CBZ

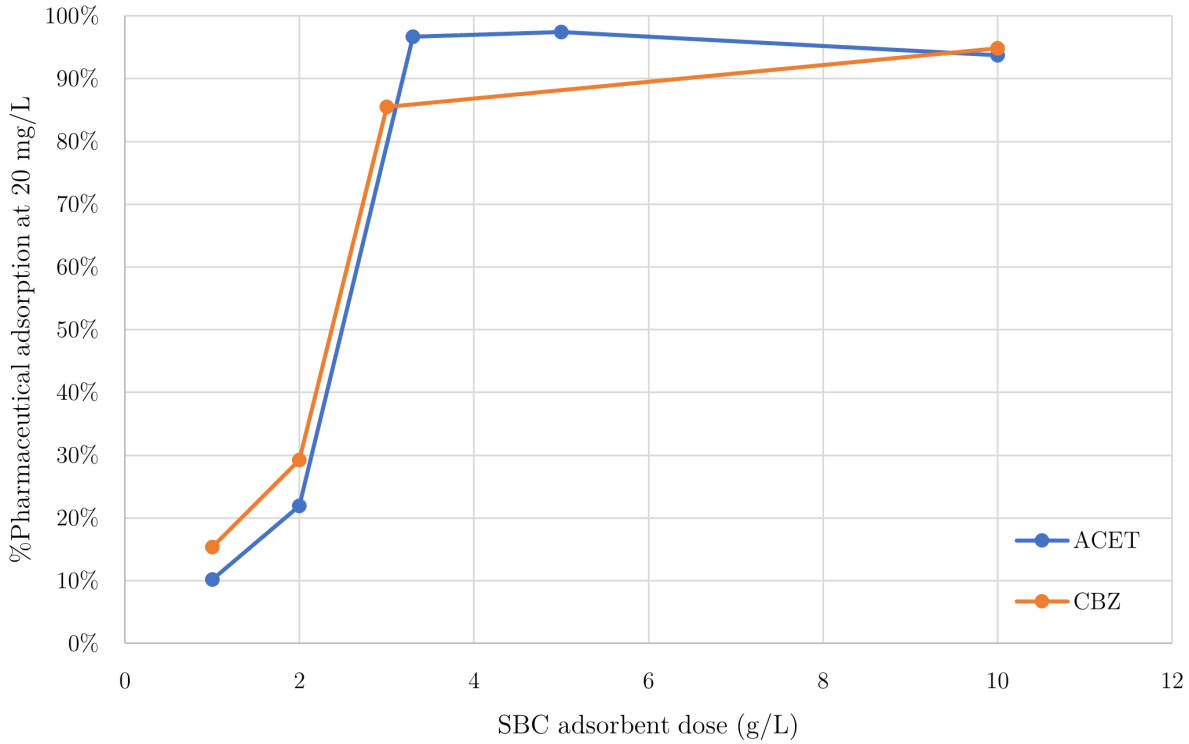


Figure 5.11: Effect of adsorbent dose on ACET (blue) and CBZ (orange)

In Figure 5.12 and Figure 5.13 the effect of SBC adsorbent dose is shown regarding the removal efficiency of ACET and CBZ, respectively. When increasing the adsorbent dose, the percentage of removal increases. This can be attributed to the increase in the number of adsorption sites owing to the increase in mass and, thus, in the surface area of the adsorbent. As shown in the figures, a higher sorbent dose in the preliminary experiments lead to faster adsorption, as the number of available sorption sites increased. Sludge biochar is behaving similarly when adsorbing ACET and CBZ, considering the adsorption rate. However, higher removal efficiency is achieved when adsorbing ACET compared to CBZ at the initial concentration of 20 mg/L and with the sorbent dose of 3.3 g/L. The adsorbent dose needs to be high enough so that the removal efficiency rate is high but at the same time be the lowest possible dose when considering the sorbent cost. In addition, in the preliminary experiments, a concentration at the end of the adsorption needed to be detected, indicating that a too high adsorbent dose would adsorb the whole concentration leaving it outside the range of detection.

All preliminary test results are found in Appendix C, shown in Figure C.1, Figure C.2. SBC was tested for other concentrations than 20 mg/L, which is shown in Figure C.3. Limited sorbent dose testing was done with AC, which is found in Figure C.4.

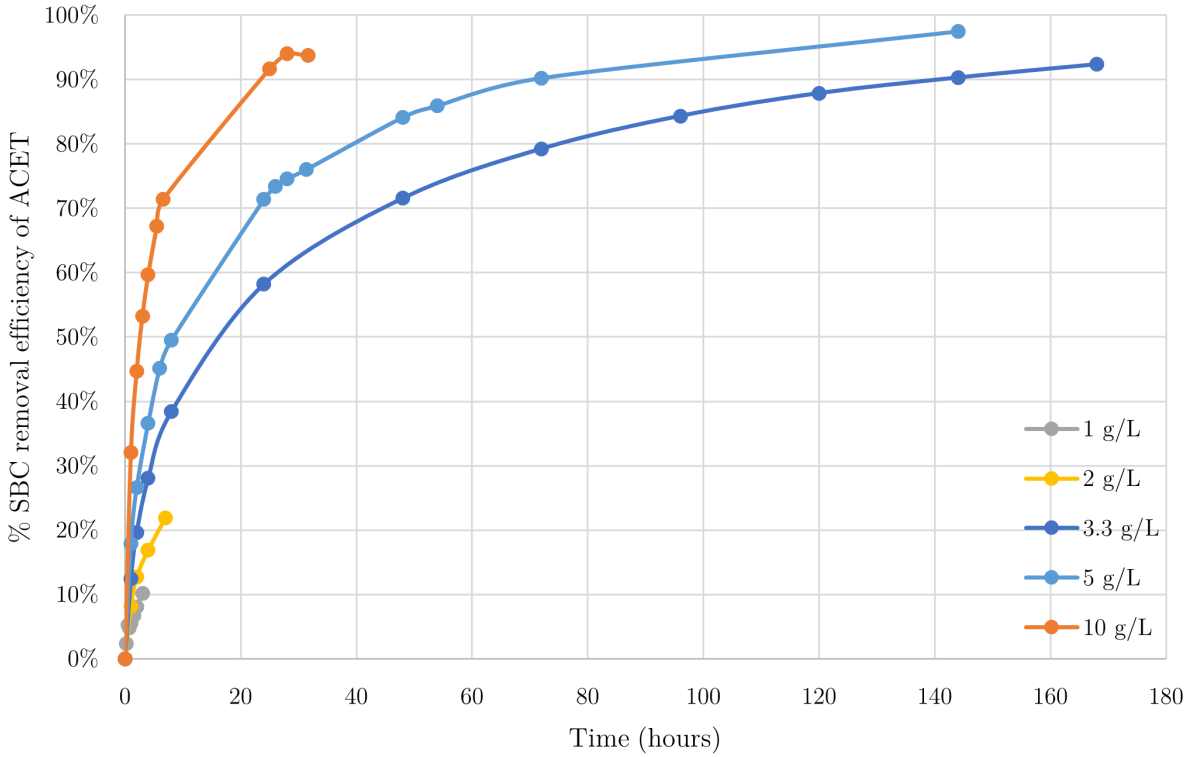


Figure 5.12: Effect of SBC adsorbent dose on removal efficiency of ACET

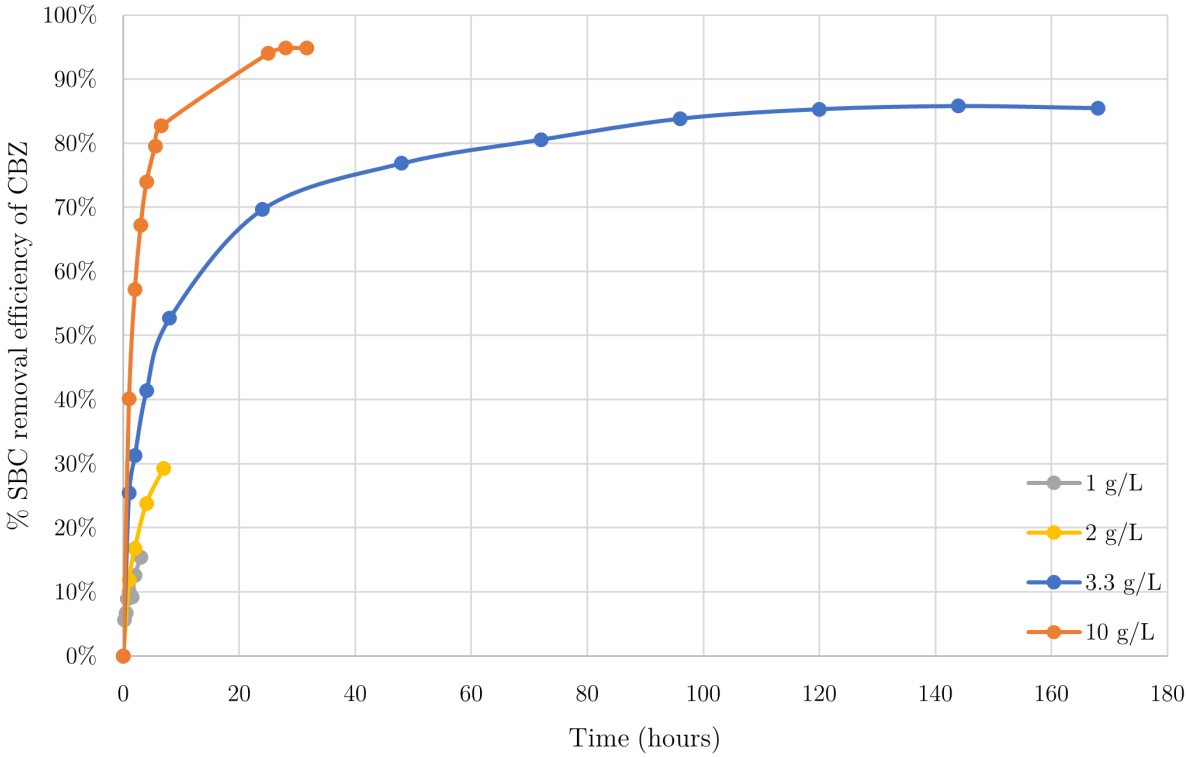


Figure 5.13: Effect of SBC adsorbent dose on removal efficiency of CBZ

5.2.2 Equilibrium time

For the equilibrium time experiment, only sludge biochar was tested due to the main focus of this thesis and time limitations. The sorbent dose of 3.3 g/L of sludge biochar was chosen, the contact time was decided on 168 hours (7 days) and the initial concentration was 20 mg/L. The results, in Figure 5.14, show that acetaminophen decreased rapidly from 0 to 24 hours where half of the initial concentration was adsorbed by the sludge biochar. After 24 hours, the curve flattens out as the adsorption slows down. After 7 days 92% (18.4 mg/L) of the initial concentration of ACET was adsorbed by the sludge biochar and the curve was flattening out but still decreasing. Based on the values taken every 24 hours from the 48 hours measurement, the rate of adsorption could be calculated. The calculated equilibrium values show that the adsorption continues for 5 days after ended contact time of 7 days.

CBZ has an even more rapidly decreasing concentration within the first 24 hours, compared to ACET. After 6 days (144 hours) the concentration of CBZ is 2.8 mg/L, which is the same value as the day after (168 hours). Furthermore, the concentrations at 96, 120, 144, and 168 hours are more or less the same, which indicates that CBZ reached equilibrium within 4 days (96 hours) (Figure 5.14, Figure 5.15).

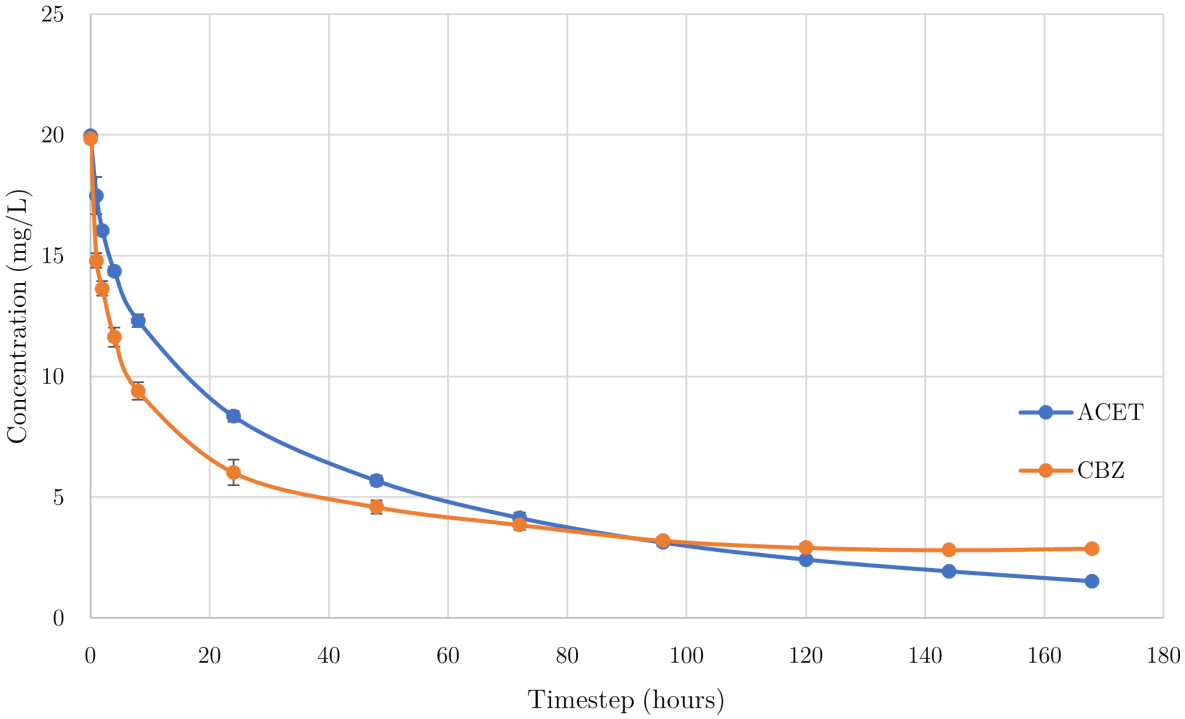


Figure 5.14: Equilibrium time for dose 3.3 g/L of sludge biochar with ACET (blue) and CBZ (orange). Average ± S.D., n=3

The rapid decrease of the ACET and CBZ concentration in the initial timesteps may be attributed to the presence of a larger number of free sites on the SBC surface. However, when the contact time is increased, the available adsorption sites become saturated while increasing the repulsion between the ACET/CBZ molecules in the liquid phase and on the surface of the SBC, and the ACET/CBZ adsorption consequently decreases until it attains a constant adsorption capacity, thus confirming that the process has reached its equilibrium.

It was decided that the experimental contact time used for the sorption study would be 7 days, although CBZ reached equilibrium within 4 days. For ACET it is still unknown, as the calculated expected data showed the concentration still going down after 12 days, found in Appendix C. It is important to mention that after 168 hours the absorbance for ACET was 0.0956, which is below the limit of 0.1. We have a higher uncertainty with values below 0.1, giving another reason for stopping the experiment after 7 days. In addition, due to time limitations, the contact time could not be longer than 7 days for the sorption study. The experimental contact time decision for sorption of CBZ on SBC can also be visualized by Figure 5.15, where an increase in contact time for CBZ did not show any significant change in adsorption efficiency after 96 hours.

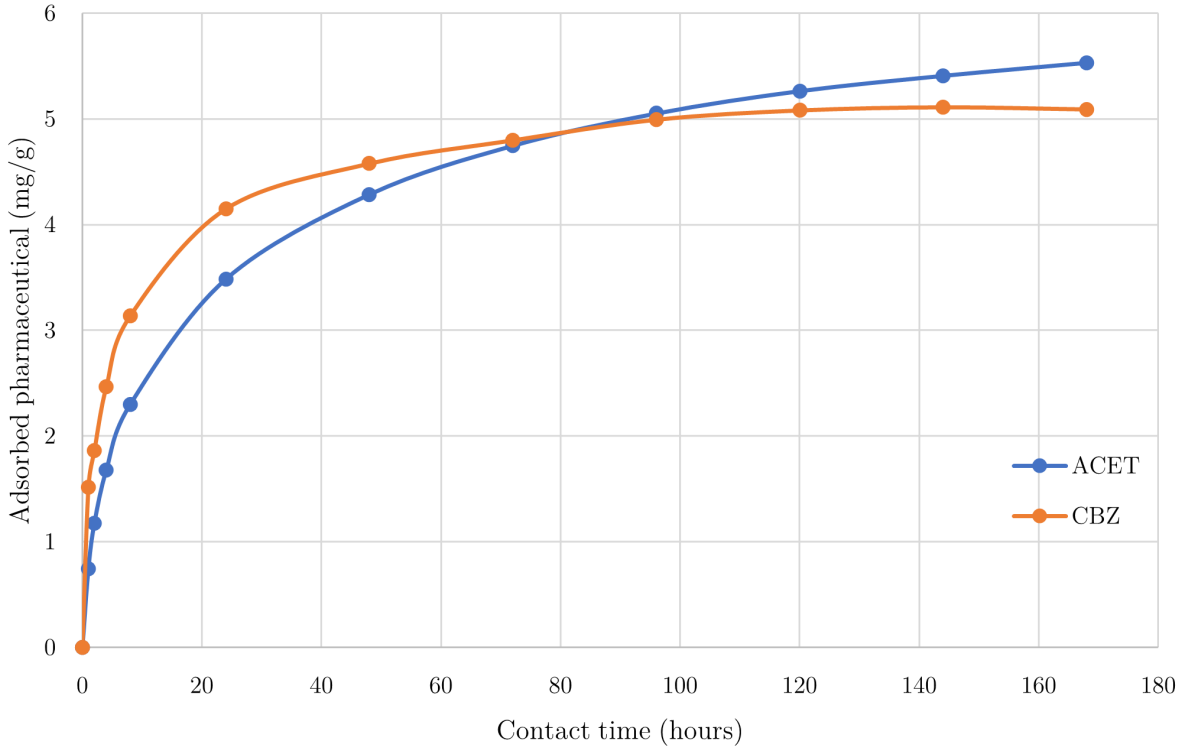


Figure 5.15: Effect of contact time on adsorption capacity of SBC (mg/g) with ACET (blue) and CBZ (orange)

5.3 Sorption study

After preliminary experiments, the sorption study was conducted with the decided adsorbent dose of 3.3 g/L and an experimental contact time of 7 days (168 hours).

5.3.1 Adsorption capacity

In this section, the adsorption capacity of sludge biochar and activated carbon for the two different pharmaceuticals are presented; acetaminophen and carbamazepine respectively.

Acetaminophen

The sorption study of acetaminophen with sludge biochar and activated carbon was conducted with initial concentrations in the range of 5-500 mg/L. Results are shown in Figure 5.16 for both sorbents. Sludge biochar has reached a maximum adsorption capacity of 21.46 mg/g, as the curve has flattened out. Activated carbon is still adsorbing with initial concentrations of 400 and 500 mg/L, and has not reached the maximum adsorption capacity for ACET. All the results from the sorption study for acetaminophen are found in Appendix C shown in Figure C.5 for SBC and Figure C.7 for AC.

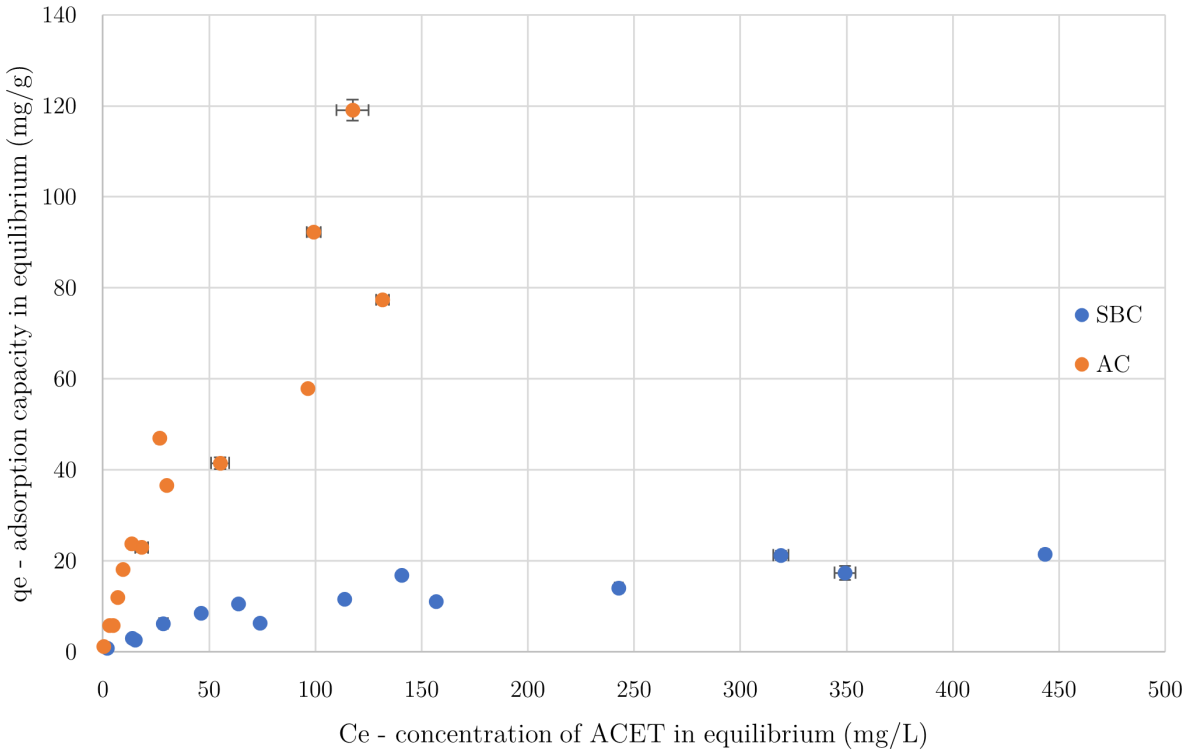


Figure 5.16: Adsorption capacity for SBC (blue) and AC (orange) of ACET. Average ± S.D., n=3

Carbamazepine

Sorption study tests were conducted for carbamazepine, and the results are shown in Figure 5.17. Carbamazepine precipitates over a certain concentration when it is diluted in water, which in this experiment was 100 mg/L, and the samples from 200 mg/L are not included in the results, but the solubility issue of CBZ is shown in Appendix C. This is also the reason why higher concentrations could not be tested, and the sorbent limit needed to be conducted with a lower sorbent dose. Here 2 g/L was decided, but results show it was not low enough and behaved very similarly to 3.3 g/L. Due to time limitations, more sorption study experiments with lower adsorbent doses were not conducted.

As the maximum adsorption capacity for CBZ is concerned, Figure 5.17 indicates that it was not reached for SBC or AC, even though the adsorption rate has slowed down for the higher concentrations for SBC. All the results from the sorption study for carbamazepine are found in Appendix C shown in Figure C.6 for SBC and Figure C.8 for AC.

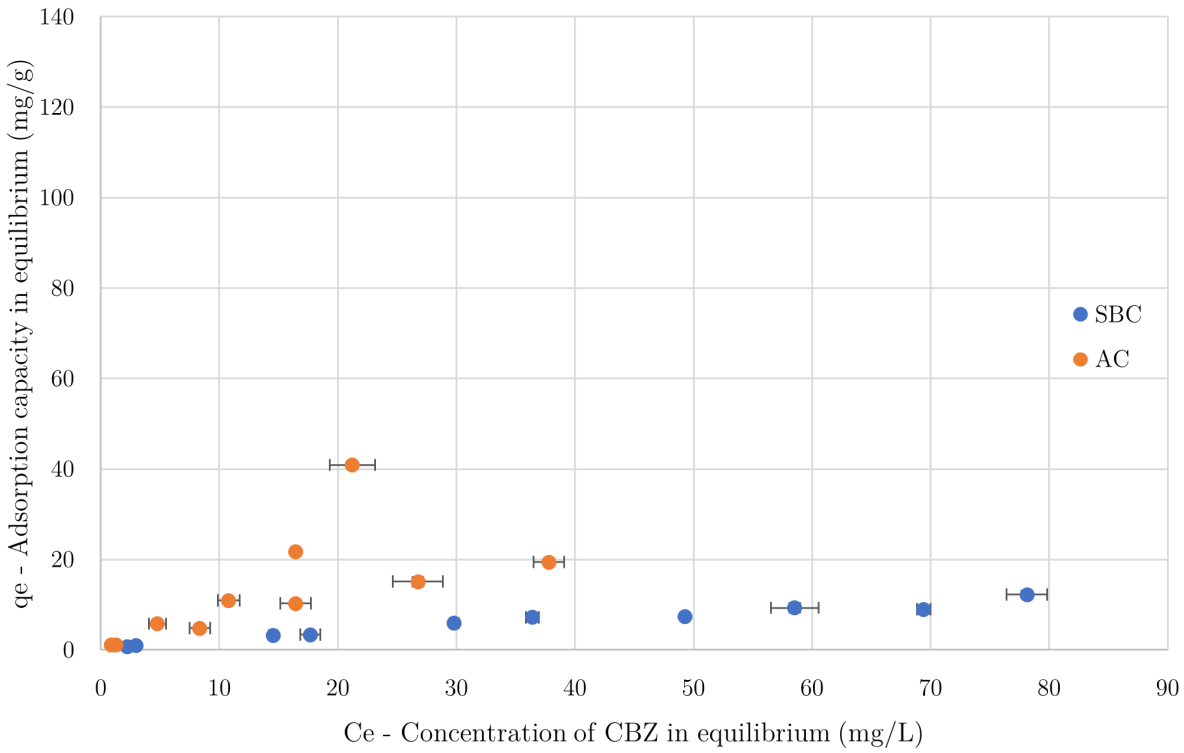


Figure 5.17: Adsorption capacity for SBC (blue) and AC (orange) of CBZ. Average ± S.D., n=3

5.3.2 Removal efficiency difference between SBC and AC

Factors influencing the adsorption of pharmaceuticals onto SBC and AC are particle size distribution, specific surface area, and surface chemistry of the sorbent with different functional groups, among others. These will be discussed more in detail under subsection 5.4.2. As adsorbent dose, pH and temperature affect the adsorption of pharmaceuticals, so does the initial concentration of the sorbates.

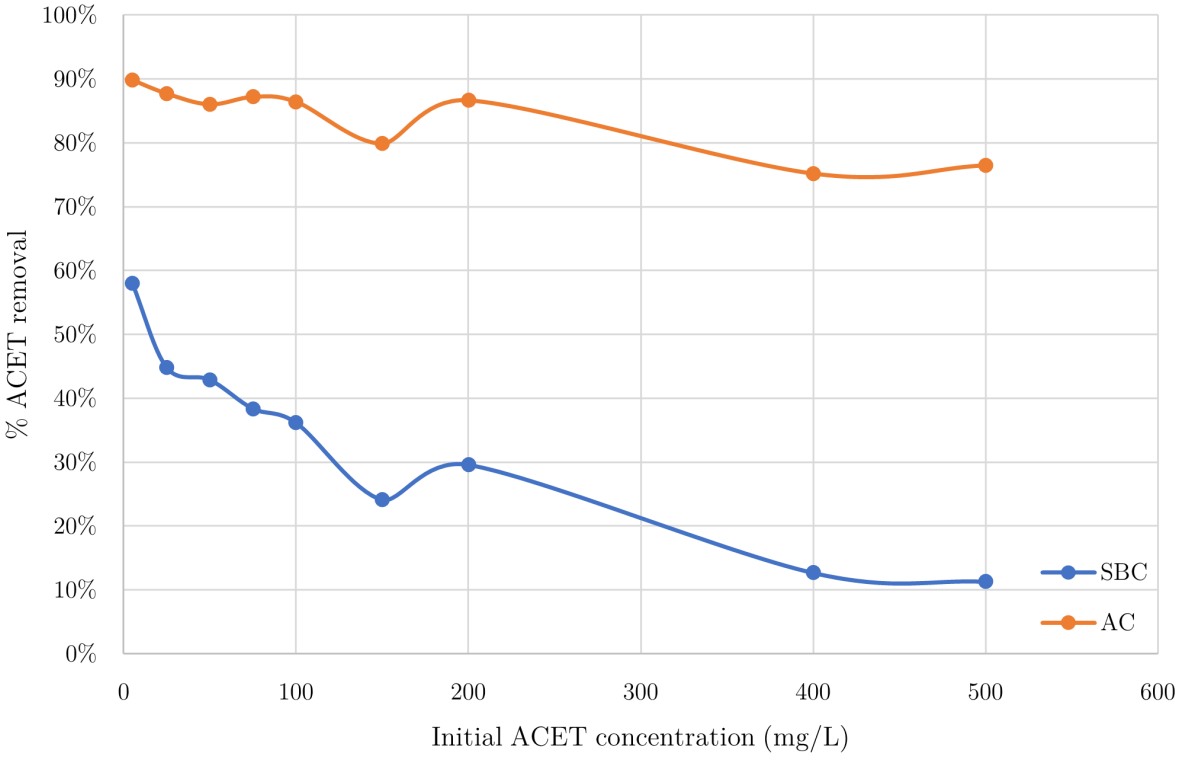


Figure 5.18: Effect of initial concentration of ACET on removal efficiency with SBC (blue) and AC (orange)

The effect of the initial concentrations of the sorbates is shown in Figure 5.18 for acetaminophen and in Figure 5.19 for carbamazepine. The figures visualize a higher percentage of ACET and CBZ removal by AC than SBC. The AC removal efficiency for ACET ranges from ca 75% for higher concentrations to about 90% for lower concentrations. Although a lower and sharper drop than AC, the SBC showed removal efficiency between 60% and 30% for initial concentrations between 5 to 200 mg/L and only about 10% at high initial concentrations (400 and 500 mg/L). The removal for CBZ is also stable at about 80% for AC and between 55% and 30% for SBC with initial concentrations between 5 to 100 mg/L. The lower surface area and coarser aggregates of SBC might be a reason for lower adsorption efficiency in general, compared to AC.

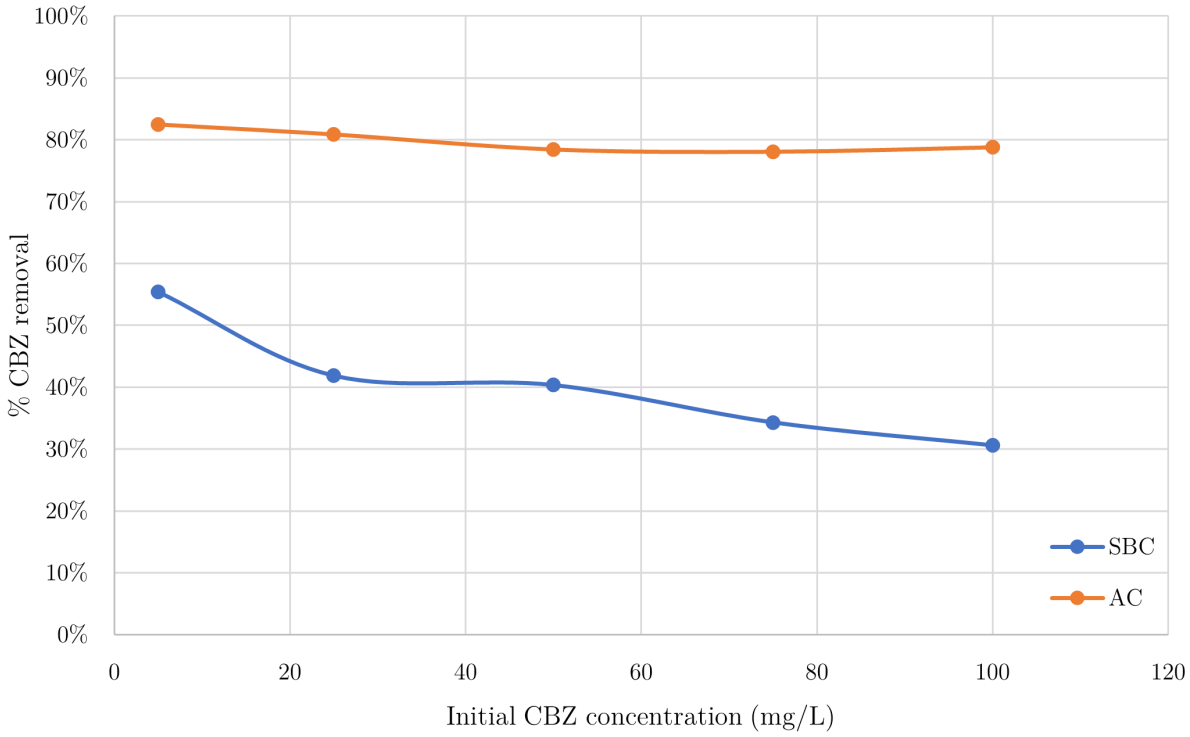


Figure 5.19: Effect of initial concentration of CBZ on removal efficiency with SBC (blue) and AC (orange)

In Figure 5.20 and Figure 5.21 it is shown that the amount of ACET and CBZ adsorbed onto activated carbon increases with higher initial concentrations. There are more sites on the surface of the activated carbon particles, as the surface area of AC is high and higher than SBC. For SBC there is an increase of adsorbed ACET up to 200 mg/L, and then it flattens out. This indicates that there are no more available sites for the sorbates. Compared to AC, the rate is low.

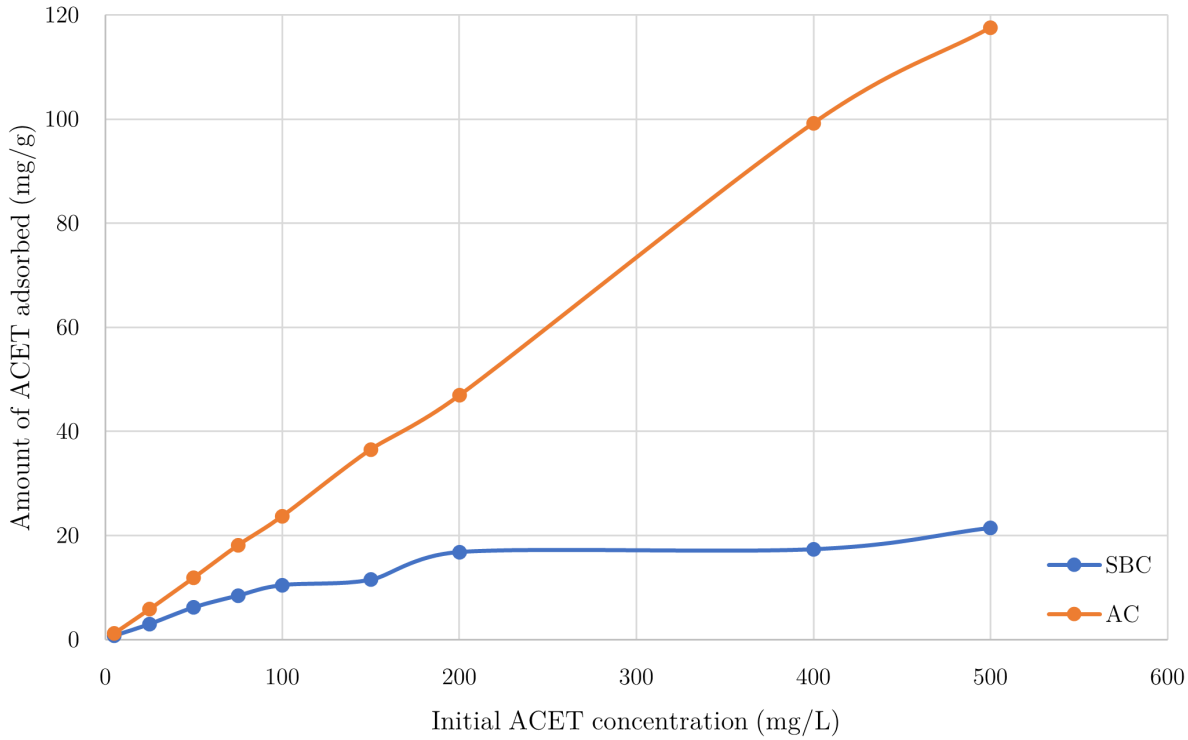


Figure 5.20: Effect of initial concentration of ACET on adsorption capacity with SBC (blue) and AC (orange)

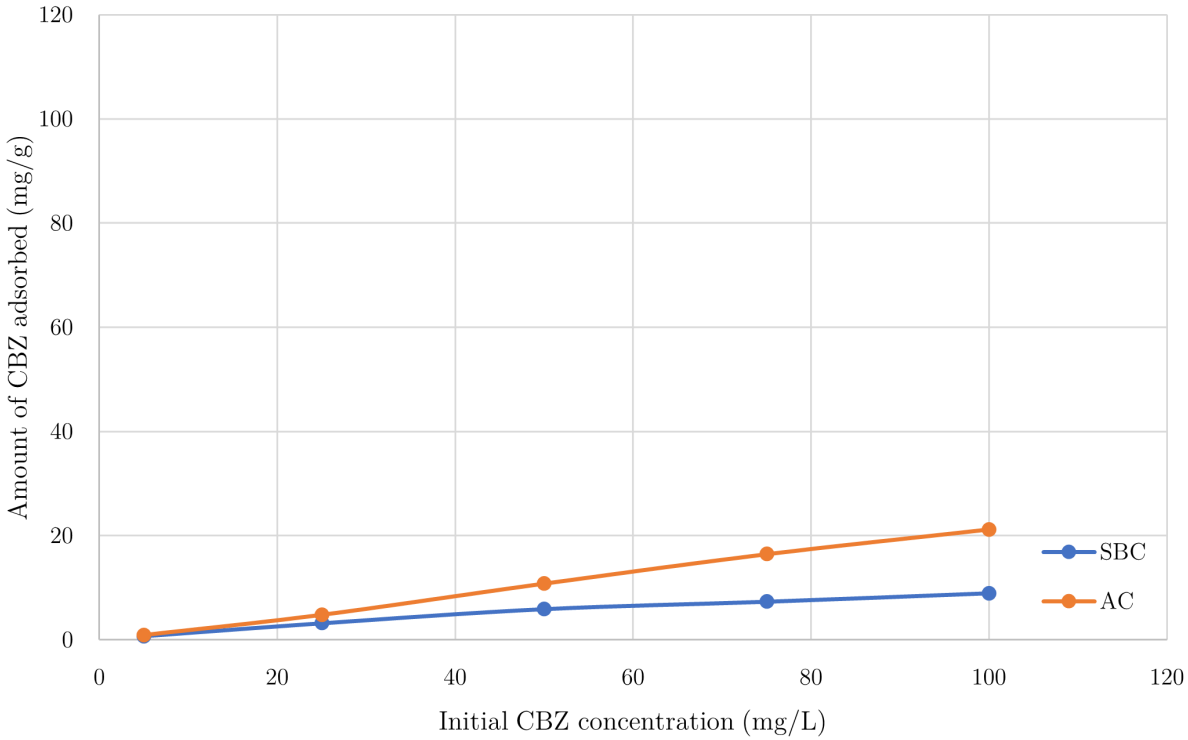


Figure 5.21: Effect of initial concentration of CBZ on adsorption capacity with SBC (blue) and AC (orange)

5.4 Adsorption mechanisms

5.4.1 Isotherm studies

To better understand the mechanisms of adsorption of ACET and CBZ onto SBC and AC, the adsorption results from the sorption studies were fitted to various isotherm models.

Sludge biochar

The regression coefficient (R^2) exhibits a high correlation for all five models in Table 5.4 and Table 5.5 for acetaminophen, and carbamazepine, $R^2 > 0.90$ and $R^2 > 0.97$ respectively. High correlation with more than one isotherm model suggests both homogeneous monolayer, multilayer, and heterogeneous sorption processes occur at the same time. Kumar et al. (2019) reports this simultaneous adsorption process in their research, where ciprofloxacin and acetaminophen are sorbed onto banana peel biochars.

Comparing the two sorbates fitting to isotherm models show that carbamazepine fits better with all the models, as R^2 is higher than for acetaminophen. ACET reached the maximum adsorption capacity, but with scattered data points. CBZ did not reach maximum adsorption capacity because tests with higher concentrations could not be followed through, but the data points are following the same curve.

With the isotherm model Langmuir, q_{max} is estimated, which for ACET is 25.767 mg/g and CBZ is 27.296 mg/g. The modeled q_{max} for both pharmaceuticals are close in value. The experimental maximum adsorption capacity revealed 21.46 mg/g for ACET, which is close to the modeled value of 25.767 mg/g. The maximum adsorption capacity was not reached for CBZ, as the curve was still increasing. The maximum experimental value for CBZ in the sorption study was 12.25 mg/g, and based on the trend and curve it is possible that it would reach the modeled value of 27.296 mg/g at maximum adsorption capacity. However, the equilibrium was not reached, and the modeled value should be treated as an estimate.

The separation factor (R_L) indicates the isotherm shape. All R_L values were $0 < R_L < 1$, demonstrating favorable ACET and CBZ adsorption onto sludge biochar. This is shown in Appendix D in Figure D.1. In the Freundlich isotherm model, it is shown that the adsorption process for both ACET and CBZ to sludge biochar is favorable as $\frac{1}{n}$ is between 0 and 1. All Freundlich exponent "n" values are higher than 1 in Table 5.4, supporting the sorption favorability (Tran et al., 2017).

For the isotherm model Redlich-Peterson, the parameter g indicates how the data points lean towards Langmuir or Freundlich, as it is a hybrid model. For ACET the value g is closer to 1 compared to CBZ, indicating that the adsorption for ACET leans more towards Langmuir than CBZ. The R-P model provides a more accurate description of adsorption behavior as it takes into account both monolayer and multilayer adsorption.

The Toth isotherm model describes adsorption over a wide range of concentrations, which is relevant for the data points where the initial concentrations range from 5-500 mg/L. The model takes into account the heterogeneity of the sorbent material by the parameter t. For t close to 1, Toth becomes Langmuir. ACET is closer to 1 than CBZ, repeating the inclining towards Langmuir as in the R-P model. Larger deviations from 1, like for CBZ, indicate that the adsorption system is more heterogeneous.

Table 5.4: Isotherm parameters for Langmuir and Freundlich for SBC

	Langmuir			Freundlich			
	R^2	K_L	q_{max}	R^2	K_F	n	1/n
ACET	0.896	0.008	25.767	0.901	1.123	2.060	0.485
CBZ	0.965	0.009	27.296	0.967	0.449	1.353	0.739

Table 5.5: Isotherm parameters for Redlich-Peterson, Sips and Toth for SBC

	Redlich-Peterson				Sips			
	R^2	K_{RP}	a_{RP}	g	R^2	K_s	a_S	β_S
ACET	0.907	0.455	0.145	0.670	0.905	0.659	0.014	0.667
CBZ	0.968	1.135	1.776	0.311	0.967	0.449	0.000	0.739

	Toth			
	R^2	K_T	a_T	t
ACET	0.907	2.009	17.891	1.638
CBZ	0.968	0.477	1.291	3.645

The experimental data for sludge biochar and acetaminophen fitting to the different isotherm models are visualized in Figure 5.22. In Figure 5.23 sludge biochar and carbamazepine are shown.

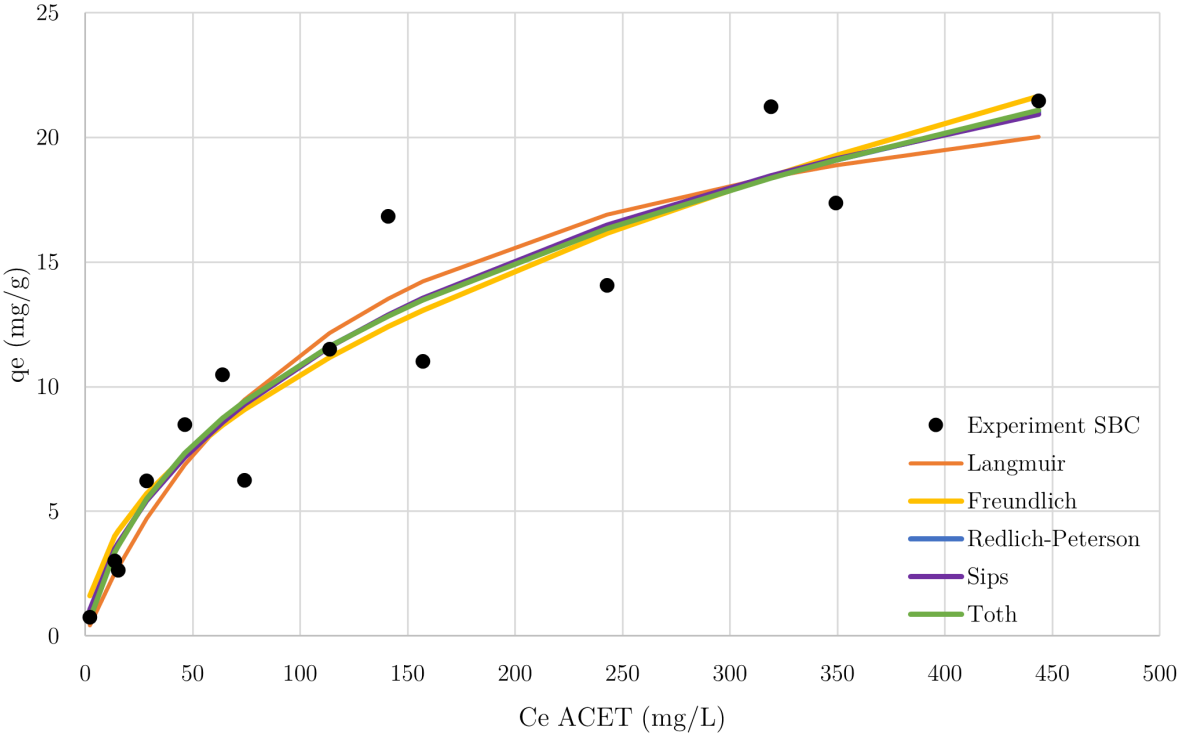


Figure 5.22: Isotherm models visualized for SBC regarding ACET

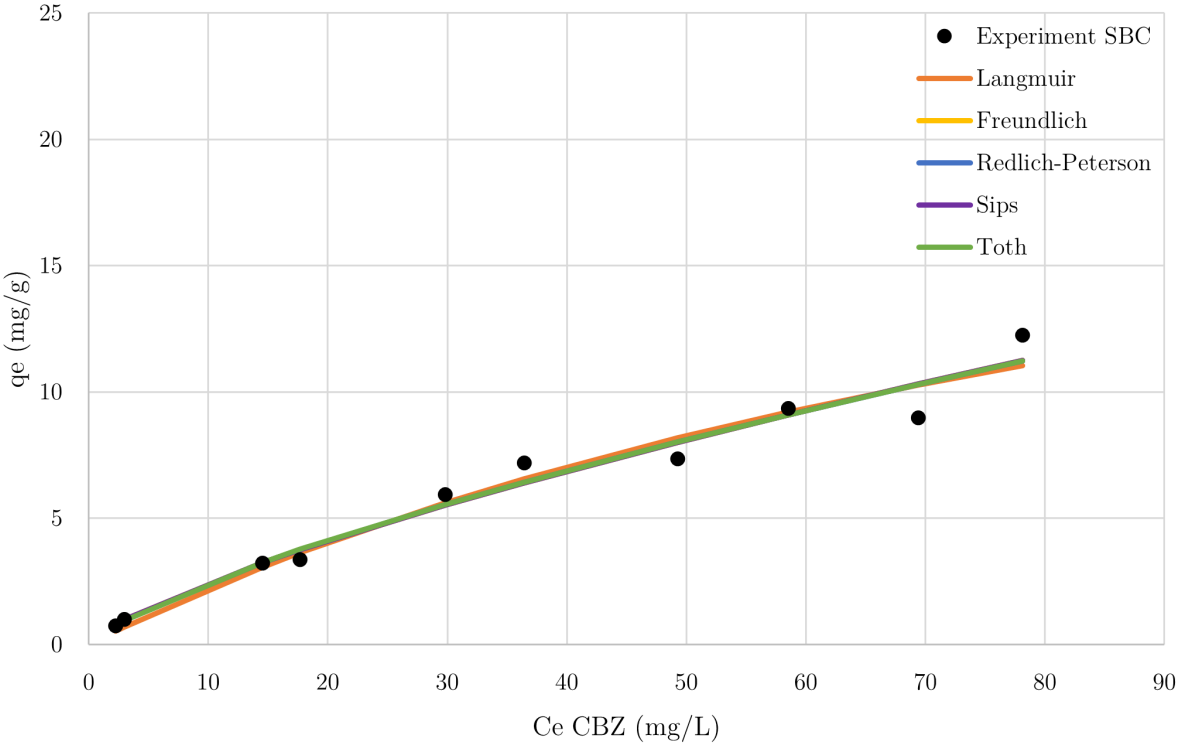


Figure 5.23: Isotherm models visualized for SBC regarding CBZ

Activated carbon

The data for activated carbon were fitted to isotherm models and the parameters are shown in Table 5.6 and Table 5.7. The activated carbon could be loaded way more than it was, as the data show a linear fit, visualized in Figure 5.24 for ACET. The regression coefficient regarding ACET is above 0.86, but as the equilibrium was not reached, more studies are needed. The regression coefficient regarding carbamazepine is low, between 0.37 and 0.6, with even more uncertainties, which is why the visualization of the isotherm models is placed in the Appendix D and found in Figure D.2. Activated carbon did not reach the maximum adsorption capacity for either pharmaceutical, and the isotherm models are inconclusive.

Table 5.6: Isotherm parameters for Langmuir and Freundlich for AC

	Langmuir			Freundlich			
	R^2	K_L	q_{max}	R^2	K_F	n	1/n
ACET	0.861	0.010	165.547	0.865	3.721	1.501	0.666
CBZ	0.374	0.000	3.39E+05	0.470	3.041	1.690	0.592

Table 5.7: Isotherm parameters for Redlich-Peterson, Sips and Toth for AC

	Redlich-Peterson				Sips			
	R^2	K_{RP}	a_{RP}	g	R^2	K_s	a_S	β_S
ACET	0.866	4.838	0.679	0.435	0.865	3.452	0.003	0.701
CBZ	0.600	1.215	0.000	4.625	0.578	0.000	0.000	4.443

	Toth			
	R^2	K_T	a_T	t
ACET	0.866	4.634	4.211	2.648
CBZ	0.531	2.70E+16	24.641	0.145

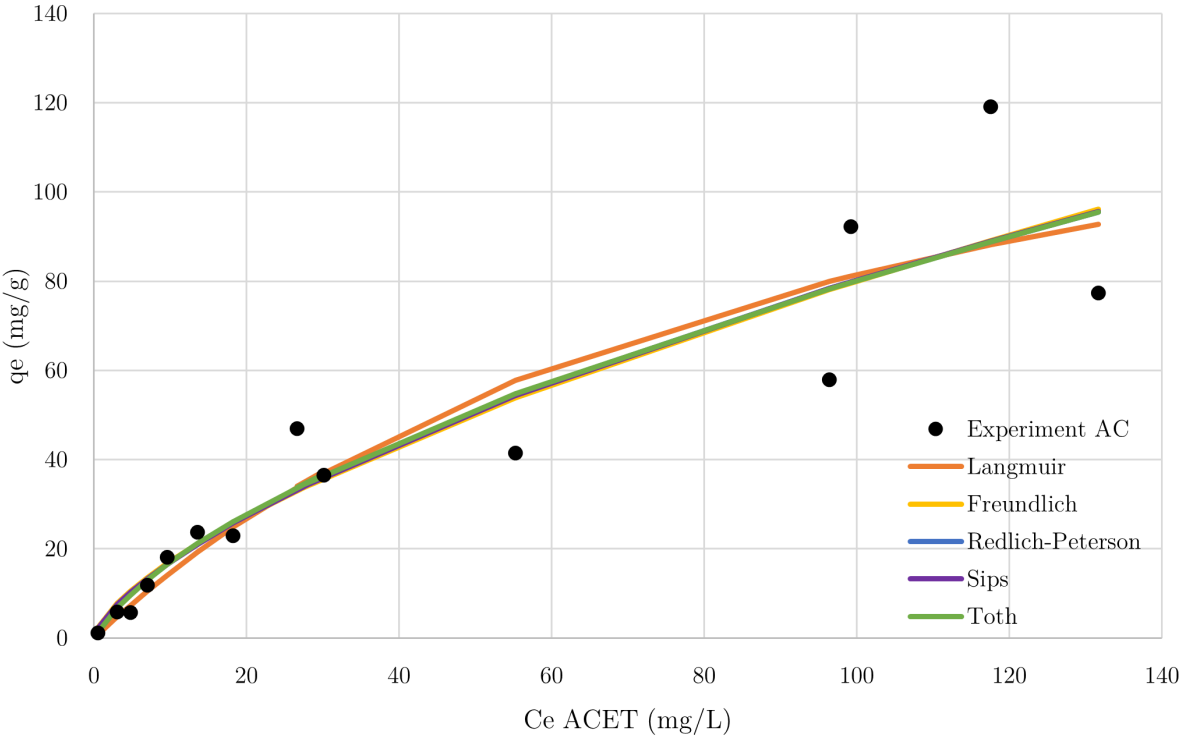


Figure 5.24: Isotherm models visualized for AC regarding ACET

5.4.2 Removal mechanisms

The removal of acetaminophen and carbamazepine by sludge biochar and activated carbon can occur by several possible adsorption mechanisms, physical and chemical. The mechanisms depend on the properties of sorbents and sorbates. Characterization of the sorbents before and after experiments were not done in this thesis work. However, the adsorption results can be elaborated based on literature review, which the discussion below is based on.

Specific surface area and pore size

The surface area of the sorbent plays an important role in the adsorption of organic contaminants, such as acetaminophen and carbamazepine (Patel et al., 2021). Generally, the increase of surface area, combined with the particle size reduction, increases pharmaceutical adsorption capacity (Ahmad et al., 2012) due to a higher number of adsorption sites on the surface of the adsorbent. The specific surface area of sludge biochar and activated carbon are shown in Table 4.4, where analysis was done by Eurofins. The surface area (2340 m^2/g) in AC was superior to the values for SBC, 97 m^2/g, respectively. Here, the specific surface area seems to play an important role in adsorbing the pharmaceuticals, as AC, with a larger SA than SBC has a higher removal efficiency than SBC.

The total pore volume, average pore diameter, and micropore volume were not analyzed in this thesis work, though it had been characterized for the same sludge biochar in another master thesis. Dzihora (2021) reported that the sludge biochar from Lindum had all kinds of pore sizes, but was low in micropore volume. Commercial AC generally contains micropores, while SBC contains more mesopores (Chen et al., 2014). Micropores provide the sorption sites and the larger pores often occur as diffusion pathways. It can be an advantage for SBC to contain a variety of pore sizes, as organic contaminants are diverse and come in many different sizes.

In a study done by Chen et al. (2017), carbamazepine was removed more effectively due to a relatively large specific surface area, large pore volume, and a mesoporous structure in activated biochar derived from pomelo peel. A large pore volume provides many active sites for the organic contaminant, and the mesoporous structure makes the transport of molecules accessible through diffusion pathways.

Generally, the high specific surface area, in addition to the typical microporous structure, benefits the physical adsorption of pharmaceuticals onto AC as many sorption sites are made available. The specific surface area for sludge biochar is smaller, along with larger pore sizes, revealing reduced adsorption of pharmaceuticals compared to activated carbon.

Particle size

In this thesis, the focus has been on sludge biochar as a practical and cost-effective sorbent material. The particle size was decided to be 1-2 mm because it can be practically handled and would avoid further crushing to a smaller size. The sludge biochar was compared to activated carbon that already exists on the market, but with a smaller size. It would be interesting to see if SBC, with a larger particle size, could be exchanged with AC as an effective sorbent material.

With a larger particle size, it would reduce the cost of crushing, sieving, and washing before use as a sorbent. Smaller particle sizes are also generally more difficult to handle because they are smaller. A larger part of small sizes is also lost in e. g. transport and use when handling.

It is evident that the results for sludge biochar are different than for activated carbon, as is shown in the results for the sorption study. Activated carbon has a much higher sorption capacity than sludge biochar, and the initial concentrations tested for both sorbents were not high enough for AC to reach the maximum adsorption capacity. This is somewhat expected as the particle size is smaller, and the specific surface area is higher shown in Table 4.4. Sludge biochar is not more effective than activated carbon with the particle size used in this thesis.

Hydrophobic interaction

Hydrophobic interaction can play an important role in the adsorption of pharmaceuticals onto sorbents. The octanol-water distribution coefficient (K_{ow}) can be used to predict the hydrophobic interactions between a sorbate and sorbent, where a high K_{ow} means high hydrophobic interaction. In Table 3.1, K_{ow} is shown for acetaminophen and carbamazepine, with their values 0.46 and 1.51-2.45 respectively. Acetaminophen is fairly hydrophilic and would rather stay in the water solution. The weak hydrophobic interactions can therefore not explain the high sorption capacity in the sorption study results alone. Carbamazepine is highly hydrophobic and is likely to be adsorbed via hydrophobic interactions, which could be one of the mechanisms for CBZ sorption onto the sorbents. It could also explain why the modeled q_{max} is higher for CBZ than for ACET. Jung et al. (2013) reported hydrophobic interactions as one of the main mechanisms for the adsorption of CBZ onto loblolly pine chips-derived biochar.

Hydrogen bonding

Hydrogen bonding is another possible adsorption removal mechanism for pharmaceuticals. Hydrogen bonds may form between functional groups (-COOH, -OH, -NH_2) of aromatic compounds and biochar (Chen et al., 2017). Chen et al. (2017) reported hydrogen bonding as one of the main mechanisms for the adsorption of carbamazepine by pomelo peel activated biochar where the increase of pH solution, resulting in a reduced concentration of H^+, made hydrogen bond donor groups on CBZ interact with hydrogen bonding acceptors or π-donors on the biochar. In previous studies done by Boudrahem et al. (2017), it was reported that proton acceptor groups (such as –OH and –C=O) in acetaminophen molecules can have strong hydrogen-bonding interactions with biochar.

$\pi - \pi$ interactions

Another possible adsorption removal mechanism is $\pi - \pi$ interactions, which is a key mechanism for the adsorption of aromatic compounds (Kang et al., 2022). The interaction exists between an electron-poor and an electron-rich compound, called a $\pi - \pi$ electron donor-acceptor (Chen et al., 2017).

In Kang et al. (2022), it is reported that $\pi - \pi$ interactions are one of the main removal mechanisms of acetaminophen adsorbed onto biochar as acetaminophen has hydroxyl and amide groups that are power electron donors and can act as a π-donor. This is reported also for Patel et al. (2021), where acetaminophen is sorbed onto banana peel biochars, and $\pi - \pi$ interactions between sorbent regions and ACET can play an important role in the overall adsorption.

$\pi - \pi$ interactions are also reported to be one of the most important adsorption mechanisms for the removal of carbamazepine onto pomelo peel activated biochar (Chen et al., 2017). The biochar in the study is a strong π-donor due to π electron donor groups, and the CBZ act as a π-electron acceptor because of the electron withdrawing capacity of the amide group.

Electrostatic interaction

Electrostatic interaction is another plausible adsorption removal mechanism of pharmaceuticals onto sorbents and is the interaction between oppositely charged ions. Kang et al. (2022) reported that electrostatic interactions occurred when ionized molecules of acetaminophen were transferred to the charged adsorbent surface. Nevertheless, the interaction is lower when the surface net charge on the biochar is zero (Kang et al., 2022).

Experiments with pH adjustments during adsorption were not executed in the thesis work. The pH during the whole experimental period, or the point of zero charge was not tested. However, the pH measurements for all replicates during the sorption study at time zero and at the contact time at 7 days are found in Appendix C. For sludge biochar, the pH solution for ACET and CBZ was around pH 7. For activated carbon, the pH was increased for both sorbate solutions around pH 9. The increase in pH reduces H+ ions and results in a more negatively charged solution where the sorbates interact with the negative surface charge of the sorbents. Hence, for activated carbon, hydrogen-bonding, and electrostatic interaction could be happening and possibly explain why AC has higher removal efficiency than SBC, even though it is not possible to conclude.

5.5 Uncertainties in experiments

In all conducted experiments, there are several uncertainties that need to be accounted for and mentioned.

Pipette

Acceptable error is between 1-2% shown in Figure F.1, which means that all values gained in experiments contain uncertainty because of the pipette, if it was used.

Dilutions

All dilutions are affected by pipette, stock solution, and human error. Acetaminophen has shown to be stable, from low to high concentrations. Carbamazepine is diluted from a stock solution in methanol that partly evaporated, which often results in a lower concentration than planned.

Machines and instruments

All instruments used have their internal instrument error. The analytical balance used, Balance SMB425i-C (WVRI611-3549), has 0.1-1% uncertainty shown in Figure F.2. The pH meter used, SOP pH-meter – pH20 VWR, showed stabilizing issues during the experiments.

Human error

There are several factors in being human that affect laboratory work. For instance, incorrect measurements, mislabeling or misidentification of samples, failure to follow the experimental protocol, improper use or calibration of equipment, data entry errors or transcriptional mistakes, and interpersonal communication with supervisors are some important factors. In addition, the daily feeling, specifically if it is feeling tired or stressed, affects laboratory and research work.

5.6 Future recommendations

After conducting several experiments, preliminary experiments and sorption studies, there are many parameters that may have affected the results in different ways. Firstly, sludge biochar and activated carbon are not uniform and homogeneous materials, but heterogeneous, which greatly affected the result. Their particle form is varying, which greatly affects the homogeneity of the samples.

Secondly, biochar dose connected to initial concentrations needs to be considered. As carbamazepine precipitated over 100 mg/L, higher concentrations could not be tested and compared to acetaminophen. In the future, a lower sorbent dose should be tested, to test the limits of the sorbent, and to achieve a higher adsorption capacity for sludge biochar in adsorbing carbamazepine. In addition, a lower dose and/or higher concentrations need to be tested for activated carbon, as its limits were not reached at all for either pharmaceutical.

Thirdly, these experiments were done on a small scale with small amounts of biochar. The error becomes large when the scale is small. In the future, it would be important to do experiments with higher volumes to compensate for the heterogeneous nature of biochar. In general, the experiments should be executed on a larger scale, to compare to a real water treatment plant.

6. Conclusions

The main goal of this thesis has been to explore the potential of sewage sludge biochar as an adsorbent for removing the pharmaceuticals acetaminophen and carbamazepine from water. In addition, sludge biochar has been compared with activated carbon, to see if it can substitute an effective sorbent already on the market. This has been done through preliminary experiments, with finding adsorbent dose and equilibrium time, and sorption studies, with the goal of finding the maximum adsorption capacity of ACET and CBZ.

For all experiments, the measurement method UV/Vis was used, which was validated by LC-MS/MS. Highly correlated values were found for analysis with both preliminary experiments and the sorption study, comparing UV/Vis and LC-MS/MS. This indicates that UV/Vis can be used as a simple, effective, fast, and cost-effective method for the quantification analysis of acetaminophen and carbamazepine in water.

In the preliminary experiments, only sludge biochar was tested, due to time limitations and the primary objective of this thesis. The adsorbent doses 1-10 g/L, for the same initial concentration (20 mg/L) were tested. As the dose increased, the removal efficiency and the rate of adsorption increased. This can be attributed to the increase in number of adsorption sites owing to the increase in mass and thus surface area of the adsorbent. The optimal dose was found to be 3.3 g/L, where a higher dose did not affect the removal efficiency of ACET and CBZ further. The contact time was tested for sorbent dose 3.3 g/L. After 24 hours, a rapid decrease of concentration was found for both pharmaceuticals, before the curves flattened out. The rapid decrease may have been caused by a large number of free sites on the SBC surface, and as the contact time increase, the sites become saturated. Within 4 days, SBC sorption of CBZ reached equilibrium, while the sorption of ACET continued even after 7 days. Due to time limitations, no further testing was done and the experimental contact time for the sorption study was decided on 7 days.

In the sorption study, both activated carbon and sludge biochar was used to find the maximum adsorption capacity of acetaminophen and carbamazepine. The results

showed that activated carbon is highly effective in removing the chosen pharmaceuticals, and sludge biochar is a promising sorbent for removing acetaminophen and carbamazepine. With a contact time of 7 days, for sorbent dose of 3.3 g/L, and initial concentration of 5 mg/L, sludge biochar removed 58% of acetaminophen and 55% of carbamazepine. In comparison, activated carbon removed 89% of acetaminophen and 82% of carbamazepine.

In the sorption study, it was revealed that the data for sludge biochar fit well with all the isotherm models tested; Langmuir, Freundlich, Redlich-Peterson, Sips, and Toth, with $R^2 > 0.90$ for acetaminophen and $R^2 > 0.97$ for carbamazepine. This indicates that homogeneous monolayer, multilayer, and heterogeneous sorption processes are possibly happening simultaneously. In addition, the isotherm models with the highest R^2 were Redlich-Peterson and Toth, indicating physical and chemical adsorption, in addition to taking the heterogeneity of the sorbent into account.

The sorption study was conducted with a concentration range of 5-500 mg/L. The maximum adsorption capacity was reached for sludge biochar adsorption of acetaminophen, with the q_{max} of 21.46 mg/g. Through the Langmuir isotherm model, a modeled q_{max} showed 25.77 mg/g, being close in value to the experimented value. For carbamazepine, the maximum adsorption capacity was not reached due to solubility issues during the sorption study. Carbamazepine precipitated over 100 mg/L, and higher initial concentrations could not be tested. The experimental q_{max} for CBZ was 12.25 mg/g, quite far from the modeled q_{max} value of 27.30 mg/g. However, if higher concentrations would have been tested, it is reasonable to believe it would reach the modeled value as the adsorption curve is flattening out in the sorption study. In addition, CBZ has a higher K_{ow} value than ACET, indicating higher hydrophobic interactions. This could be an explanation of why the modeled q_{max} for CBZ is higher than ACET.

Activated carbon did not reach maximum adsorption capacity during the sorption studies, for either of the pharmaceuticals, as the tested initial concentrations were not high enough. The sorption study data were fitted to isotherm models, but the models were inconclusive. More studies are needed to determine the maximum adsorption capacity and removal mechanisms of activated carbon. However, activated carbon has a much higher removal efficiency when adsorbing ACET and CBZ compared to sludge biochar. This could be explained by the higher surface area, lower particle size, and finer aggregates for AC compared to SBC. Physical adsorption, where a high surface area creates more adsorption sites, could be one of the main reasons why the adsorption is higher for AC than SBC. In addition, the pH of AC is higher (pH 9) compared to SBC (pH 7) during sorption, resulting in a more negatively charged surface where electrostatic interaction may have occurred.

In conclusion, the results revealed that sludge biochar is a potential sorbent for the removal of acetaminophen and carbamazepine, as about 50-60 % of 5 mg/L were removed in the sorption study. Compared to activated carbon, which is much more effective with the removal of 80-90% of 5 mg/L, sludge biochar is less effective. However, there are many advantages with using SBC instead of AC as SBC is a more sustainable, cost-effective, and environmentally friendly sorbent.

7. Future work

To further understand the adsorption mechanisms of the sorbents, different sorbent properties should be analyzed. For instance, scanning electron microscope and transmission electron microscope helps understand sorbent morphology, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy provide knowledge on surface chemistry and Thermogravimetric analysis (TGA) support understanding of thermal stability of the sorbent. In this thesis, FTIR and TGA were conducted during an academic visit to Agroscope where the methodology and results are given in Appendix E. Unfortunately, due to time limitations and experience limitations, detailed explanations regarding the results are not given. However, in future studies, it would be important to provide information regarding such analysis and experiments.

To allow for a more realistic evaluation of biochar's performance as a sorbent, full-scale testing, preferably with real wastewater, would be important. Batch tests and lab-scale experiments may not fully capture the complexities and variations in a treatment plant, taking into account flow rates, variations in water quality, and system dynamics. Furthermore, studies should focus on multi-component pollutants, handling real effluents from industrial sectors and municipal treatment systems. With a mixture of coexisting pharmaceuticals and other pollutants, the adsorbent would be evaluated on their target of the adsorbates, and measures could be taken on the specificity of the adsorbent.

In order to increase biochar performance, like AC, several things can be done to "activate" the surface, like washing with acid, alkaline, activating with steam, or heat treatment like pyrolysis. More research would have to be done, to understand more of the limits of sludge biochar.

Future studies should also focus on the regeneration of biochar, to consider the cost, reuse, and recycling of loaded biochar. In addition, the treatment of waste gas or waste solvents, from the regeneration processes, along with the waste CMs after adsorption should be carefully considered, to avoid any potential secondary environmental risks (Zhang et al., 2022).

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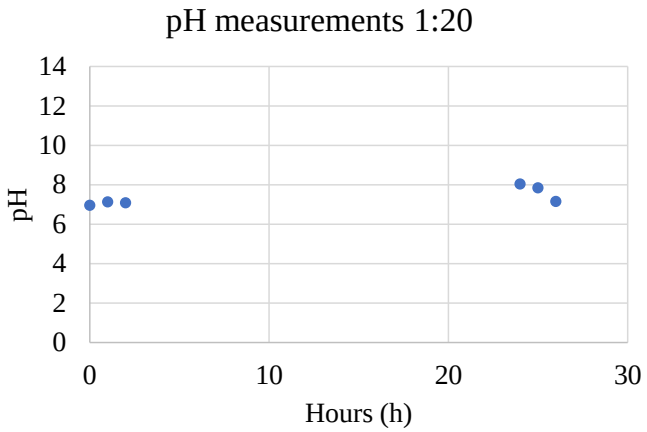
Appendix A. Methodology

Test run washing sorbents

Date 4-5th of January

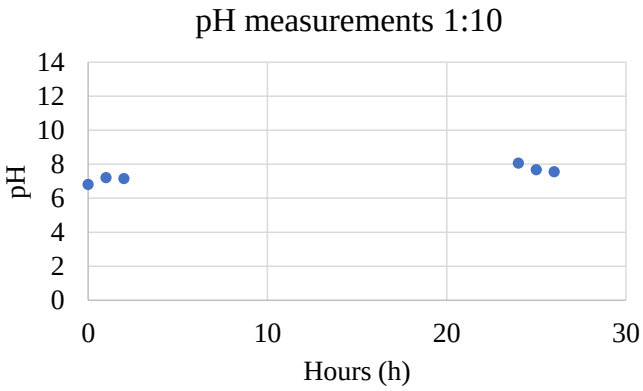
Ratio **1:20**
Mass (g) **12.5 g**

Hours	Start	1	2	24 pre	24 post	26
	0	1	2	24	25	26
pH	6,96	7,13	7,08	8,03	7,84	7,15



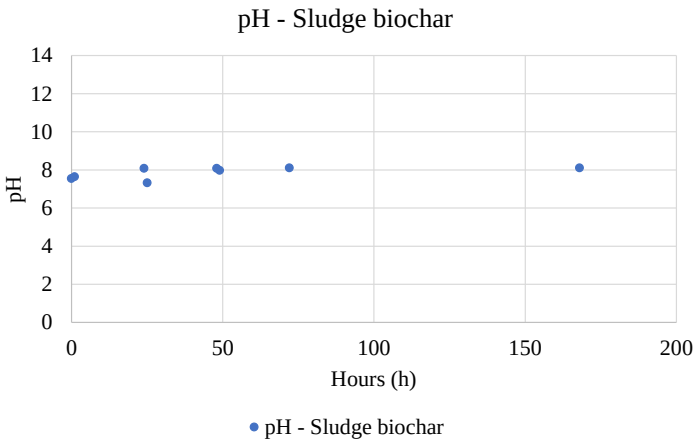
Ratio **1:10**
Mass (g) **25 g**

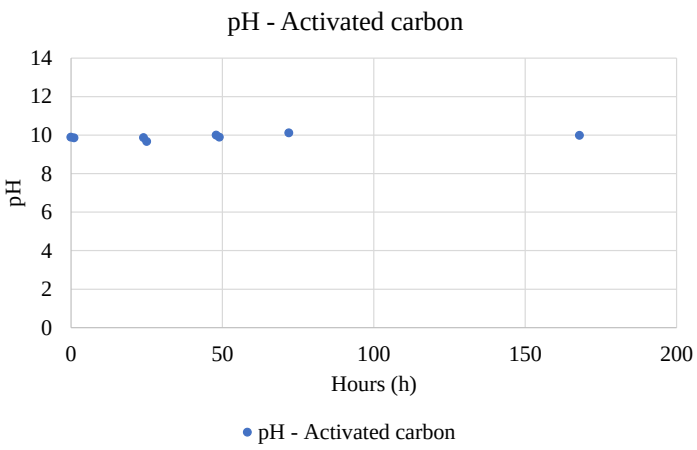
Hours	Start	1	2	24 pre	24 post	26
	0	1	2	24	25	26
pH	6,8	7,2	7,14	8,05	7,66	7,54



pH measurement during washing of sorbents

				09.jan	09.jan	10.jan	10.jan	11.jan	11.jan	12.jan	16.jan
				Day 1	Day 1	Day 2	Day 2	Day 3	Day 3	Day 4	Day 4
Bottles #	**Mass (g)**	**V (mL)**	**Ratio**	**pH start**	**pH 1h**	**pH 24 h pre**	**pH 24h post**	**pH 48h pre**	**pH 48h post**	**pH 72h**	**pH 168h**
Sludge biochar				13:00	14:00	13:00	14:00	13:00	14:00	13:00	09:00
1	25	250	1:10	7,55	7,61	8,06	7,10	7,84	7,80	8,08	8,11
2	25			7,67	7,71	8,11	7,26	8,15	8,08	8,09	8,09
3	25			7,53	7,81	8,10	7,27	8,07	8,03	8,07	8,08
4	25			7,44	7,65	8,07	7,32	8,11	7,98	8,13	8,15
5	25			7,56	7,66	8,05	7,34	7,96	7,76	8,11	8,12
6	25			7,51	7,59	8,08	7,32	8,04	7,93	8,05	8,08
7	25			7,49	7,61	8,10	7,44	8,10	8,06	8,12	8,16
8	25			7,55	7,63	8,00	7,35	8,07	7,96	8,11	8,07
SUM SBC	200										
Average				**7,54**	**7,64**	**8,08**	**7,32**	**8,07**	**7,97**	**8,10**	**8,1**
Hours (h)				0	1	24	25	48	49	72	168
Activated carbon											
9	25			9,91	9,88	9,92	9,80	10,03	9,90	10,06	9,98
10	25			9,85	9,83	9,78	9,60	9,97	9,85	10,01	9,96
11	25			9,89	9,82	9,87	9,78	9,98	9,86	10,10	9,97
12	25			9,88	9,86	9,88	9,65	10,02	9,95	10,13	9,99
13	25			9,90	9,83	9,84	9,62	10,00	9,81	10,12	9,97
14	25			9,87	9,86	9,91	9,73	9,97	9,94	10,10	9,95
15	25			9,88	9,86	9,85	9,63	9,98	9,91	10,11	9,97
16	25			9,87	9,83	9,83	9,66	10,00	9,81	10,08	9,95
SUM AC	200										
Average				**9,88**	**9,85**	**9,86**	**9,66**	**9,99**	**9,88**	**10,10**	**9,97**
Hours (h)				0	1	24	25	48	49	72	168


pH - Sludge biochar
14
12
10
8
6
4
2
0
pH
0
50
100
150
200
Hours (h)
pH - Sludge biochar


pH - Activated carbon
14
12
10
8
6
4
2
0
pH
0
50
100
150
200
Hours (h)
pH - Activated carbon

Appendix B. Results LC-MS/MS

Samples from the preliminary experiments and the sorption study were analyzed with UV/Vis and sent to the Faculty of Veterinary Medicine at NMBU for validation with LC-MS/MS. The validation report and the analysis with LC-MS/MS were written and executed by Stine Göransson Aanrud in the Toxicology group at the Veterinary Faculty. In this appendix, the validation report is attached, followed by the results from LC-MS/MS analysis. To validate the results from UV/Vis, which this thesis is based on, it was important to include validation of the UV/Vis method with LC-MS/MS results, in addition to validating the LC-MS/MS results.

Validation rapport SiEUGreen Project

1. Introduction

The Resource Recovery Research Group at RealTek at NMBU, by Nazli Pelin Kocatürk Schumacher, have ordered analysis of three compounds in water samples. The compounds are Acetaminophen, Carbamazepine and Diclofenac. The order is on 500 samples, and within these 500 samples are about 50 samples to complete a validation of the three compounds. The results of the validation and of the samples can be included in the Master Thesis of Sarah Charlotte Minos-Stensrud.

The validation is done according to the "SiEUGreen validation plan" and this report summarizes the results for presentation to the Resource Recovery Research Group.

The validation was planned and executed during February and March 2023 by Stine Göransson Aanrud.

2. Instrumentation

The validation and the analysis of the samples was conducted on an Agilent 1290 Infinity II Ultra-High Pressure Liquid Chromatograph (UHPLC) (Agilent Technologies, Waldbronn, Germany) combined with an Agilent 6495 Triple Quadrupole Mass Spectrometer (Agilent Technologies, Santa Clara, CA, USA) with an Agilent Jet Stream Electrospray Ion Source. The analysis was done using multiple reaction monitoring (MRM). For instrument control, optimization and quantification, The Agilent MassHunter software (V 10.1/Build 10.1.67) was used.

3. Method

LC parameters:

Injection volume: 2,0 µL

Needle wash: 60 seconds with 50:50 Acetonitrile:water

Mobile phase A: 0,1% formic acid in water

Mobile phase B: 100% Acetonitrile

Flow: 0,4 mL/min

Column oven: 30 °C

Table 1: Mobile phase program

Time (min)	B (%)
0,0	0
0,5	0
3,0	100
4,0	100
4,1	0
6,6	0

Ion Source parameters

Gas Temp: 140 °C

Gas Flow: 16 L/min

Nebulizer: 30 psi

Sheath Gas Temp: 300 °C

Sheath Gas flow: 12 L/min

Hight Pressure RF: 190 V

Low pressure RF: 140 V

Capillary: 2500 V

Nozzle Voltage: 100 V

MS parameters

Table 2: MS parameters of Acetominophen, Carbamazepine and Diclofenac

Compound	Precursor ion	Product Ion (Quant)	Qualifier Ion 1	Qualifier Ion 2	Collision Energy (CE) for Quant	Retention Time (RT) in min	Cell Accelerator Voltage (CAV)
Acetominophen	152,1	110,1	93,0	65,1	17	1,64	3
Acetominophen D4	156,1	114,1	Internal standard		17	1,64	5
Carbamazepine	237,1	179,1	194,1		41	2,35	4
Carbamazepine 13C6	243,1	185,1	Internal standard		43	2,35	4
Diclofenac	296,0	214,0	249,9	278,0	41	2,89	5
Diclofenac 13C6	302,0	220,1	Internal standard		41	2,89	5

4. Results of the validation

The results from the validation are presented in the Table 3-4:

Table 3: Validation results part 1

Compounds		Acetominophen		Carbamazepine		Diclofenac	
Parameter	Level	%	CV%	%	CV%	%	CV%
Accuracy	50 ng/mL	99	2,3	100	1,7	95	2,3
	500 ng/mL	94	0,66	97	0,84	91	0,64
	5000 ng/mL	102	0,037	99	0,037	97	0,038
Recovery	50 ng/mL	98	1,2	98	0,83	98	1,2
	500 ng/mL	99	3,5	101	4,3	98	3,5
	5000 ng/mL	99	1,8	100	1,9	98	2
Repeatability	50 ng/mL		1,2		3,5		1,8
	500 ng/mL		0,8		4,3		1,9
	5000 ng/mL		1,2		3,5		2
Efficiency of Extraction Method	50 ng/mL	97		96		94	
	500 ng/mL	98		99		98	
	5000 ng/mL	96		97		96	

Table 4: Validation results part 2

Compounds		Acetominophen	Carbamazepine	Diclofenac
Calibration Curve	Type	Linear	Linear	Linear
	Weight	1/X^2	None	1/X
	Origin	Force	Force	Force
	R^2	0,999	0,9999	0,9999
	Range	2-10 000 ng/mL	1-10 000 ng/mL	30-10 000 ng/mL
Confidence interval of intercept includes 0		Yes	Yes	Yes
Retensjon time drift		0,0006 min	-0,0018 min	0,000001 min
Carry Over: % of lowest standard (10 ng/mL)	Sample 1	2,09	5,9	59,83
	Sample 2	0,93	2,09	17,62
	LOD	0,25 ng/mL	0,25 ng/mL	10 ng/mL
	LOQ	2 ng/mL	1 ng/mL	30 ng/mL
Matrix effect compared to type 1 water from VET	H2O (From RealTek)	100,8	99,6	102,8
	H2O+AC	96,4	94,5	96
	H2O+SBC	96,7	95,1	97,1

Detection limits

The method Limit of detection (LOD) and method Limit of Quantification (LOQ) were determined by calculating expected LOD and LOQ from the calibration curve according to ICH guidelines, spiked matrix samples based on these results were injected 6 times from the same vial and the Relative Standard Deviation (RSD) was calculated on the area. LOD should have an RSD lower than 17% and LOQ lower than 5%.

Recovery, repeatability, and accuracy

Recovery was calculated according to equation 1, where *signal (I)STD* refers to the actual signal level and *conc* refers to the expected signal level. *Sample* refers to the six replicates at each level, *blank* refers to a sample with no added STDs or ISTDs. The *cal* sample (n = 1) was the level of the calibration curve prepared to the same level.

$$Recovery\ (\%) = \sum_{i=1}^{n=6} \frac{\left(\frac{signal\ STD\ (sample)_i - signal\ (blank)}{signal\ ISTD(sample)_i - signal\ ISTD(blank)}\right) * conc(cal)}{\frac{signal\ STD\ (cal)}{signal\ ISTD(cal)} * conc(sample)} * \frac{100}{n} \qquad \text{(eq. 1)}$$

Repeatability is reported as the relative coefficient of variation (CV%) of the six samples at the three levels according to equation 2 and 3, where x is the calculated concentration of the samples and N is six.

$$\sigma = \sqrt{\frac{1}{N-1}\ \sum_{i=1}^{N}(x_i - \bar{x})^2} \qquad \text{(eq. 2)}$$

$$CV\% = \frac{\sigma}{\bar{x}} * 100\% \qquad \text{(eq. 3)}$$

Accuracy was calculated as the average difference between calculated concentration and expected concentration for each of the six samples in the three levels and are reported in % of expected concentration (equation 4). The relative coefficient of variation (CV%) was calculated and are reported in the results as well (Table S7).

$$Accuracy\ (\%) = \sum_{i=1}^{n=6} signal\ STD(matrix)_i - conc(sample) * 100\% \ / \ n \qquad \text{(eq. 4)}$$

Matrix effect and Efficiency of Extraction method.

Matrix effect was calculated in the three different matrices delivered from RealTek, H2O, H2O+AC and H2O+SBC.

$$ME\ (\%) = \left[\frac{(\overline{MM_S} - MM_0)}{(\overline{MS_S} - MS_0)} - 1\right] * 100 \qquad \text{(eq. 5)}$$

Efficiency of the extraction method (EEM) was calculated in the same manner as recovery (equation 1), except that the signal of the ISTDs were not included.

$$EEM\ (\%) = \sum_{i=1}^{n=6} \frac{(signal\ (matrix)_i - signal(blank)) * conc(solvent)}{signal(solvent) * conc(matrix)} * \frac{100}{n} \qquad \text{(eq. 6)}$$

5. Assessment of the validation

All three compounds were validated with success.

Detection limits

An RSD lower than 17% and 5% was accomplished for all three compounds but carry over can also affect the detection and quantification limits. For Diclofenac, the carry over was above the controlled LOD, so the LOD and LOQ were adjusted to account for any possible carry over from high concentration samples.

Matrix matched calibration curve

The validation showed matrix effects between 95 and 103 %, for all matrices compared to water, so it was decided to not use a matrix matched calibration curve.

Internal standards

Even though the sample preparation is very simple, the validation was done using internal standards. There is no earlier point where it is possible to add internal standards, because the samples need to be filtered straight after being collected, to stop the effect of the added matrix. The same matrices could carry away unknown amounts of internal standards, so adding before filtration is not a good option. After the filtration the samples are simply added internal standards during a dilution step, and then they are ready for analysis.

The need to add internal standards was very apparent. The calibration curve covers a wide range, and without the internal standards, the saturation of the system makes the calibration curves become non-linear. So the need to add internal standard is tested during this validation, and should be adhered in further experiments.

This validation report was written by:

Stine Göransson Aanrud
Head Engineer at the Veterinary Faculty at NMBU

11.05.2023

Results from LC-MS/MS analysis

Analyzed by Stine Göransson Aanrud

	Acetaminophen	Carbamazepine
1	15546	<LOQ
2	15269	<LOD
3	15518	<LOD
4	15463	<LOD
5	15411	<LOD
6	15320	<LOD
7	8022	<LOD
8	7346	<LOD
9	7903	<LOD
10	18	<LOD
11	8	<LOD
12	15	<LOD
13	4577	<LOD
14	4082	<LOD
15	4269	<LOD
16	<LOQ	<LOD
17	<LOQ	<LOD
18	<LOQ	<LOD
19	1622	<LOD
20	1329	<LOD
21	1415	<LOD
22	<LOD	<LOD
23	<LOD	<LOD
24	<LOD	<LOD
25	14098	<LOD
26	14373	<LOD
27	14070	<LOD
28	<LOD	16247
29	<LOD	15440
30	<LOD	15684
31	3987	<LOD
32	3733	<LOD
33	3945	<LOD
34	<LOD	4442
35	<LOD	3457
36	<LOD	3498
37	2666	<LOD
38	2727	<LOD

	Acetaminophen	Carbamazepine
<LOD	0,25 ng/mL	0,25 ng/mL
<LOQ	2 ng/mL	1 ng/mL

Alle verdier er i ng/mL

39	2858	<LOD
40	<LOD	3836
41	<LOD	2835
42	<LOD	2962
43	1064	<LOD
44	972	<LOD
45	1036	<LOD
46	<LOD	2338
47	<LOD	1793
48	<LOD	2252
49	430	<LOD
50	384	<LOD
51	425	<LOD
B52	3629	<LOD
B53	18221	<LOD
B54	35904	<LOD
B55	54242	<LOD
B56	71263	<LOD
B57	141309	<LOD
106	1538	<LOD
107	1621	<LOD
108	1448	<LOD
109	437	<LOD
110	406	<LOD
111	459	<LOD
112	3559	<LOD
113	3473	<LOD
114	9354	<LOD
115	9547	<LOD
116	9758	<LOD
117	2250	<LOD
118	2009	<LOD
119	2528	<LOD
120	18012	<LOD
121	17724	<LOD
122	20546	<LOD
123	23109	<LOD
124	20373	<LOD
125	5518	<LOD
126	5365	<LOD
127	4129	<LOD
128	34703	<LOD

129	35266	<LOQ
130	32249	<LOD
131	34529	<LOD
132	33705	<LOD
133	7169	<LOD
134	6922	<LOD
135	7559	<LOD
136	52807	<LOD
137	51874	<LOD
138	44521	<LOD
139	47386	<LOD
140	48003	<LOD
141	9334	<LOD
142	8986	<LOD
143	10765	<LOD
144	71508	<LOD
145	69986	<LOD
146	102469	<LOD
147	103004	<LOD
148	103002	<LOD
149	18464	<LOD
150	17453	<LOD
151	23425	<LOD
152	141223	<LOD
153	137019	<LOD

154	<LOD	4002
155	<LOD	21565
156	<LOD	40933
157	<LOD	62003
158	<LOD	74198
159	<LOD	135885
208	<LOD	1602
209	<LOD	1627
210	<LOD	1813
211	<LOD	676
212	<LOD	584
213	<LOD	654
214	<LOD	3976
215	<LOD	3683
216	<LOD	11231
217	<LOD	10985

218	<LOD	10768
219	<LOD	3976
220	<LOD	3518
221	<LOD	4038
222	<LOD	20619
223	<LOD	19742
224	<LOD	23028
225	<LOD	23073
226	<LOD	23384
227	<LOD	716
228	<LOD	8398
229	<LOD	8943
230	<LOD	40414
231	<LOD	39879
232	<LOD	36674
233	<LOD	38206
234	<LOD	41522
235	<LOD	13368
236	<LOD	9867
237	<LOD	14438
238	<LOD	59672
239	<LOD	60932
240	<LOD	55683
241	<LOD	57533
242	<LOD	52053
243	<LOD	13572
244	<LOD	15606
245	<LOD	20730
246	<LOD	79090
247	<LOD	65331
248	<LOD	86399
249	<LOD	82640
250	<LOD	92364
251	<LOD	37818
252	<LOD	38805
253	<LOD	46682
254	<LOD	89201
255	<LOD	89244
256	109607	<LOD
257	312265	<LOD
258	373475	<LOD
259	80514	<LOD

260	81088	<LOD
261	80004	<LOD
262	23114	<LOD
263	22445	<LOD
264	21504	<LOD
265	109633	<LOD
266	110937	<LOD
267	259561	<LOD
268	261415	<LOD
269	261992	<LOD
270	81565	<LOD
271	86275	<LOD
272	85933	<LOD
273	301979	<LOD
274	301262	<LOD
275	325204	<LOD
276	327238	<LOD
277	338509	<LOD
278	95647	<LOD
279	105308	<LOD
280	86901	<LOD
281	386266	<LOD
282	383963	<LOD

283	18743	<LOD
284	74296	<LOD
285	154593	<LOD
286	228166	<LOD
287	321989	<LOD
288	12043	<LOD
289	12094	<LOD
290	11863	<LOD
291	4182	<LOD
292	4023	<LOD
293	4147	<LOD
294	19610	<LOD
295	18877	<LOD
296	59130	<LOD
297	54714	<LOD
298	57735	<LOD
299	14753	<LOD
300	18771	<LOD

301	18096	<LOD
302	70567	<LOD
303	73844	<LOD
304	120591	<LOD
305	122287	<LOD
306	114745	<LOD
307	49620	<LOD
308	46818	<LOD
309	42746	<LOD
310	152847	<LOD
311	150227	<LOD
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319	224830	<LOD
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322	262747	<LOD
323	108785	<LOD
324	96685	<LOD
325	106420	<LOD
326	302614	<LOD
327	311667	<LOD
328	<LOD	3601
329	<LOD	19122
330	<LOD	35468
331	<LOD	60949
332	<LOD	71540
333	<LOD	2105
334	<LOD	2260
335	<LOD	2234
336	<LOD	856
337	<LOD	1061
338	<LOD	959
339	<LOD	3591
340	<LOD	3597
341	<LOD	13702
342	<LOD	14550

343	<LOD	15734
344	<LOD	7539
345	<LOD	6304
346	<LOD	6328
347	<LOD	18571
348	<LOD	18206
349	<LOD	29238
350	<LOD	28412
351	<LOD	27646
352	<LOD	10842
353	<LOD	11916
354	<LOD	13294
355	<LOD	39548
356	<LOD	39392
357	<LOD	48331
358	<LOD	46004
359	<LOD	44708
360	<LOD	22918
361	<LOD	21443
362	<LOD	18208
363	<LOD	60992
364	<LOD	59625
365	<LOD	57672
366	<LOD	65351
367	<LOD	66719
368	<LOD	26518
369	<LOD	26254
370	<LOD	29997
371	<LOD	81707
372	<LOD	74415

Appendix C. Results UV/Vis

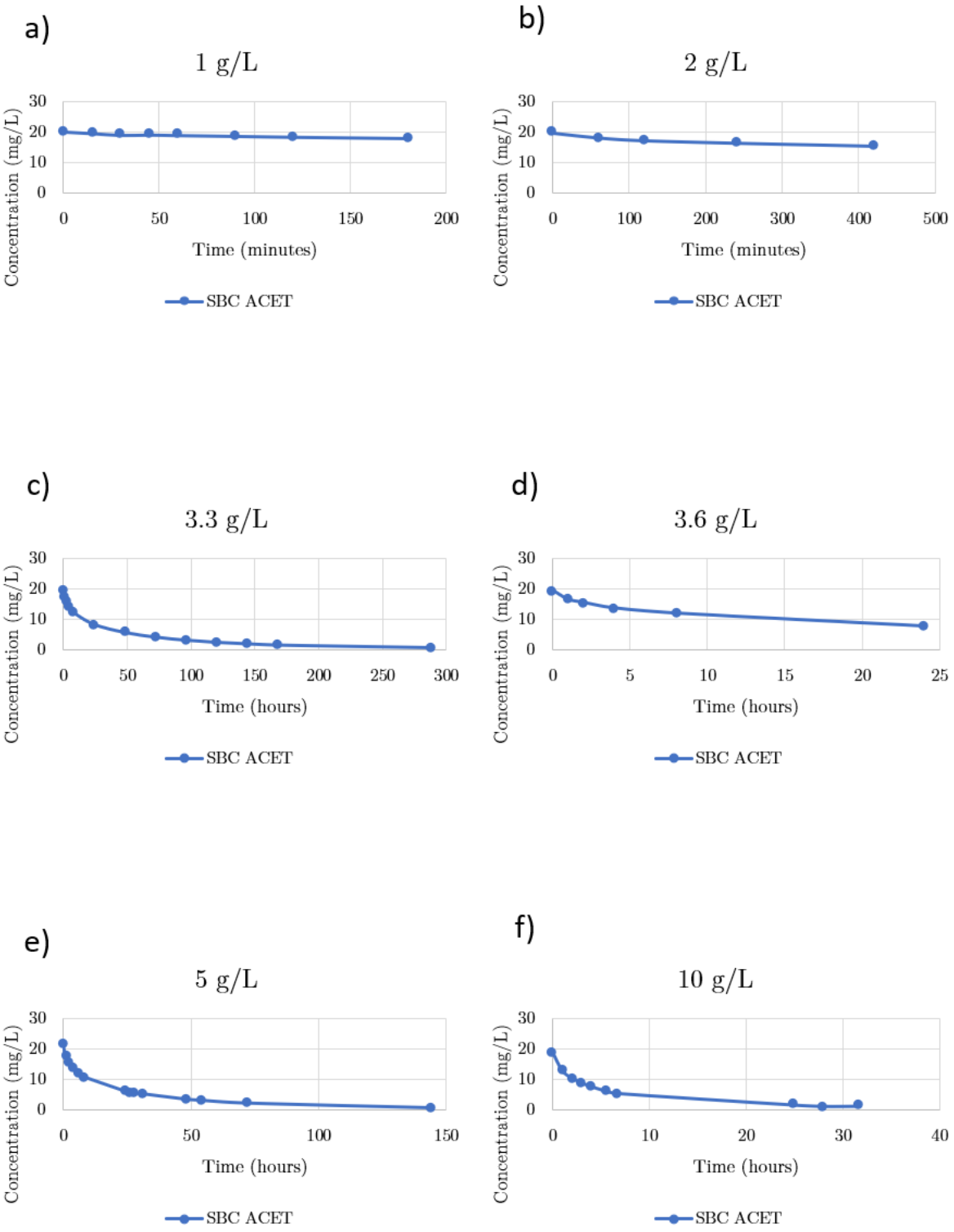


Figure C.1: SBC dosage for adsorption of 20 mg/L ACET

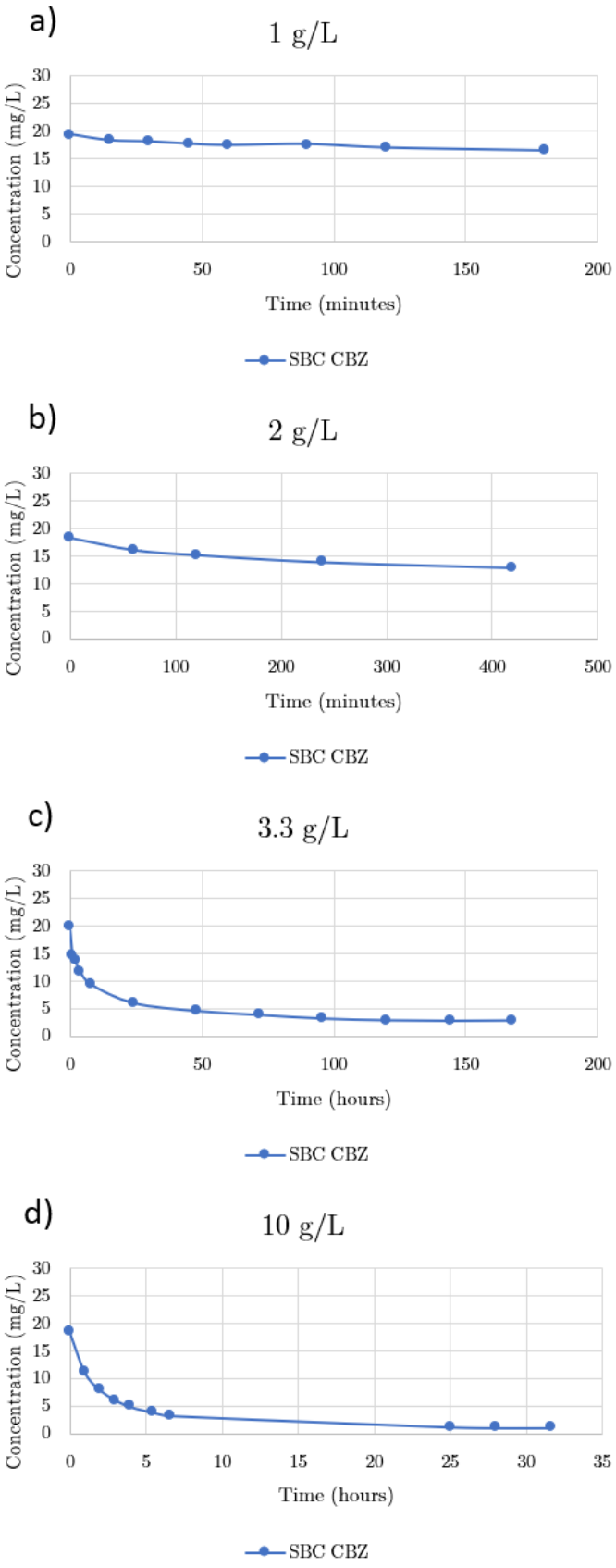


Figure C.2: SBC dosage for adsorption of 20 mg/L CBZ

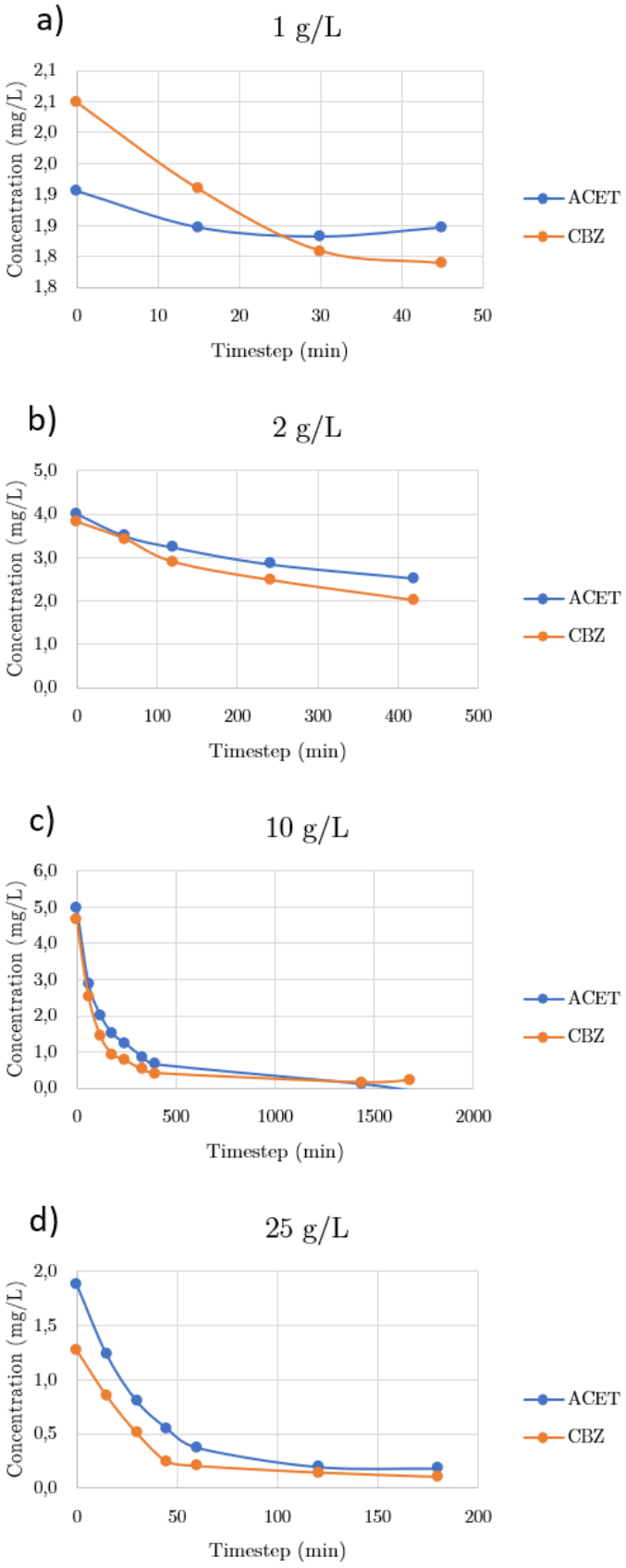


Figure C.3: Different doses with adsorption of lower concentrations

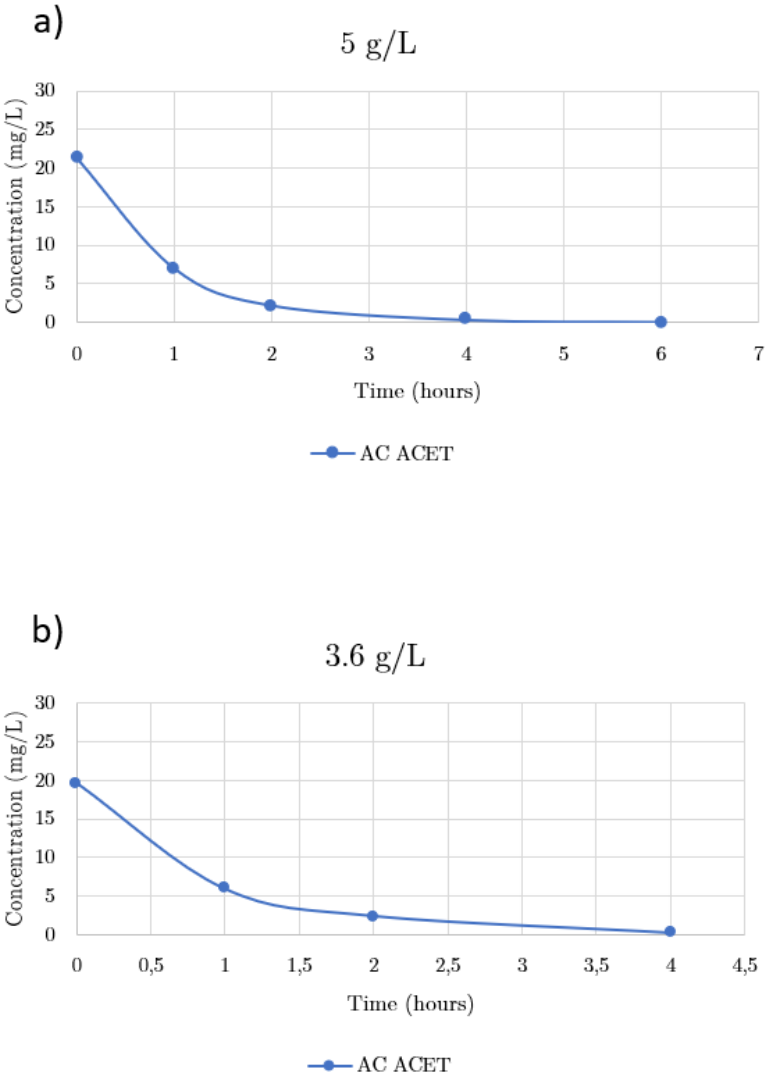


Figure C.4: AC dose for adsorption of 20 mg/L ACET

Equilibrium time - Acetaminophen
Expected values

Sludge biochar 3.3 g/L

Time (hours)	Absorbance	C_t - Concentration (	SD	%SD
0	1,213	19,958	0,057	0,286
1	1,062	17,479	0,763	4,366
2	0,975	16,041	0,130	0,813
4	0,873	14,361	0,183	1,274
8	0,748	12,295	0,267	2,171
24	0,509	8,345	0,226	2,712
48	0,347	5,679	0,211	3,719
72	0,254	4,142	0,210	5,060
96	0,192	3,124	0,148	4,728
120	0,150	2,419	0,111	4,576
144	0,120	1,936	0,119	6,151
168	0,096	1,526	0,091	5,963
192		1,255	$C_t = C_{t-1}+dC_t$	
216		1,062		
240		0,923		
264		0,853		
288		0,802		
288	0,043	0,662	0,049	7,435

Experimental values
Calculated values

Calculating the adsorption rate

Timestep	Every 24h	dC_t (mg/L)
48-72	0	1,537
72-96	1	1,018
96-120	2	0,705
120-144	3	0,483
144-168	4	0,410
168-192	5	0,271
192-216	6	0,193
216-240	7	0,138
240-264	8	0,099
264-288	9	0,071
288-312	10	0,050

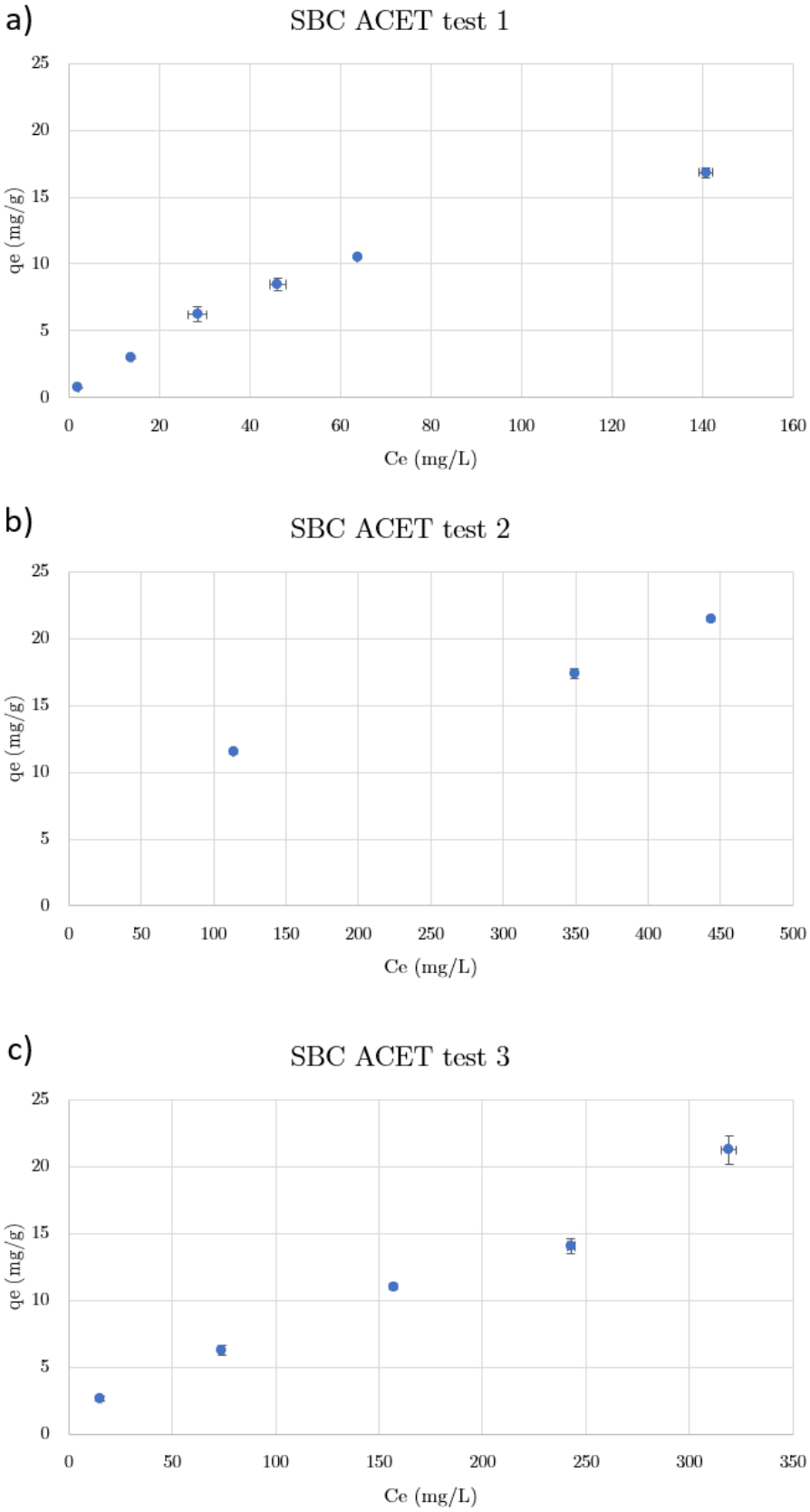


Figure C.5: Sorption study with SBC and ACET

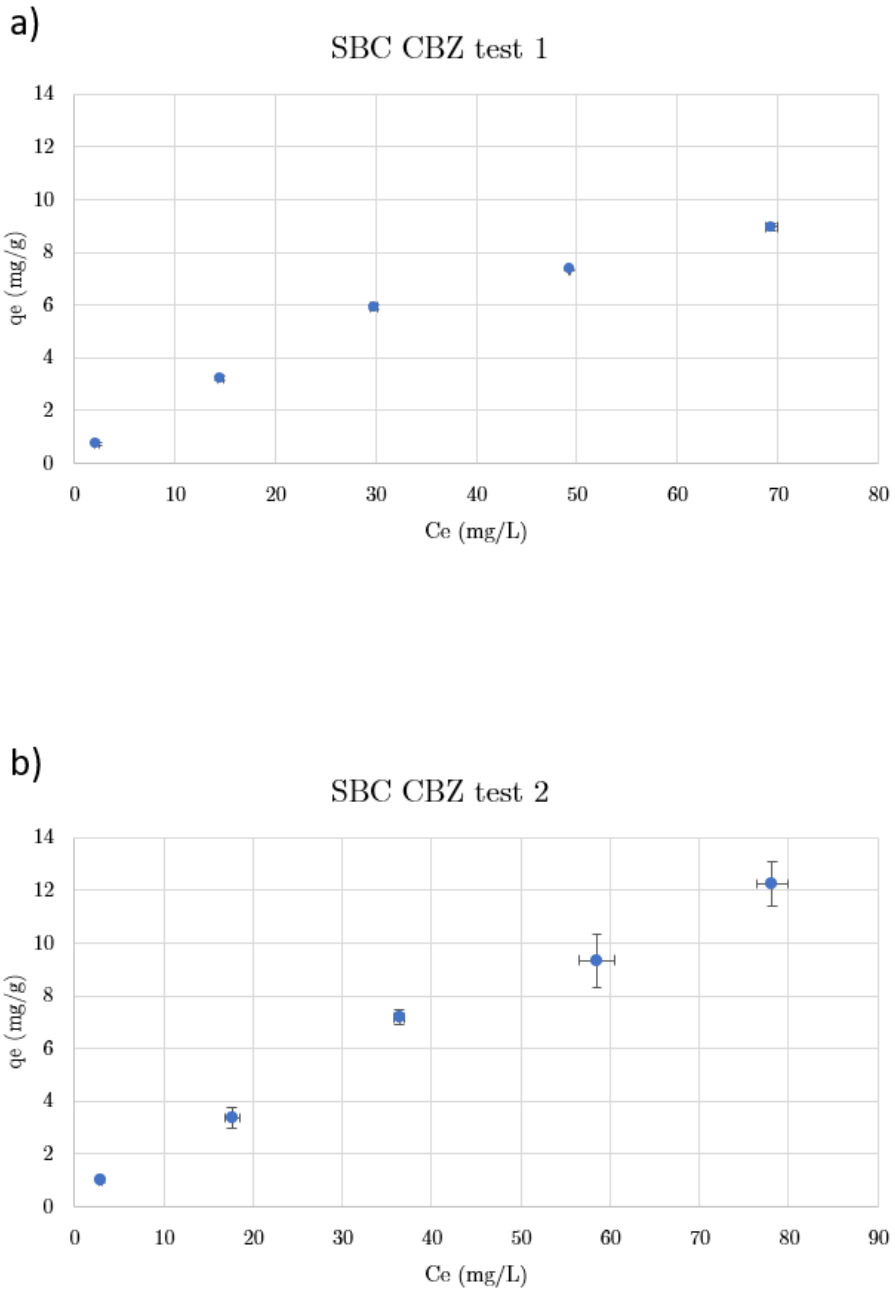


Figure C.6: Sorption study with SBC and CBZ

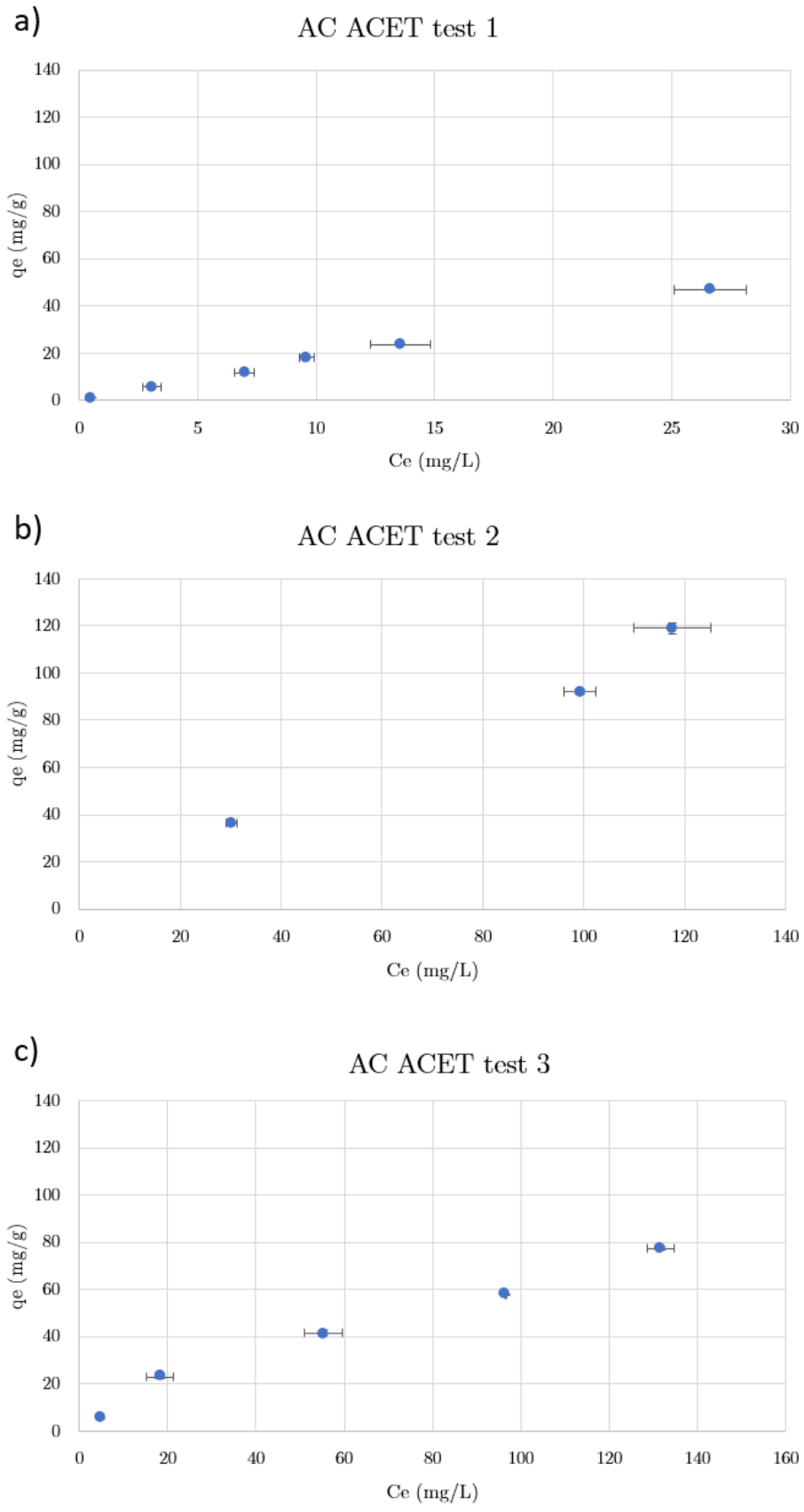
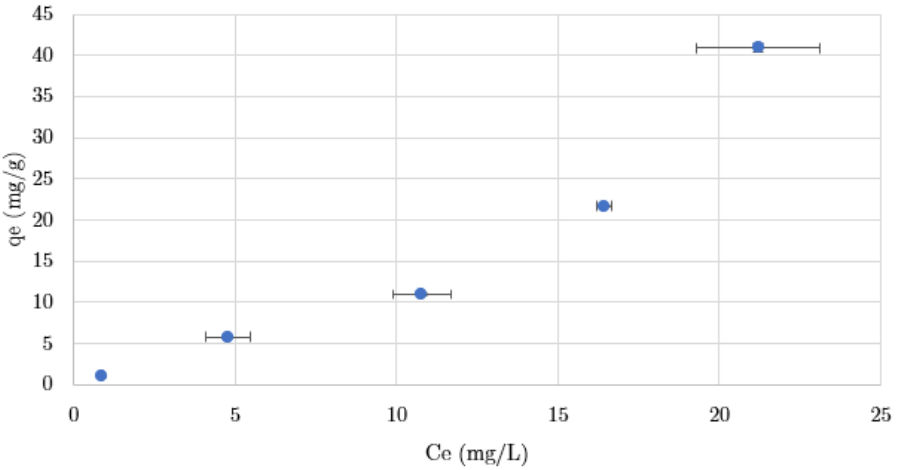


Figure C.7: Sorption study with AC and ACET

a)



b)

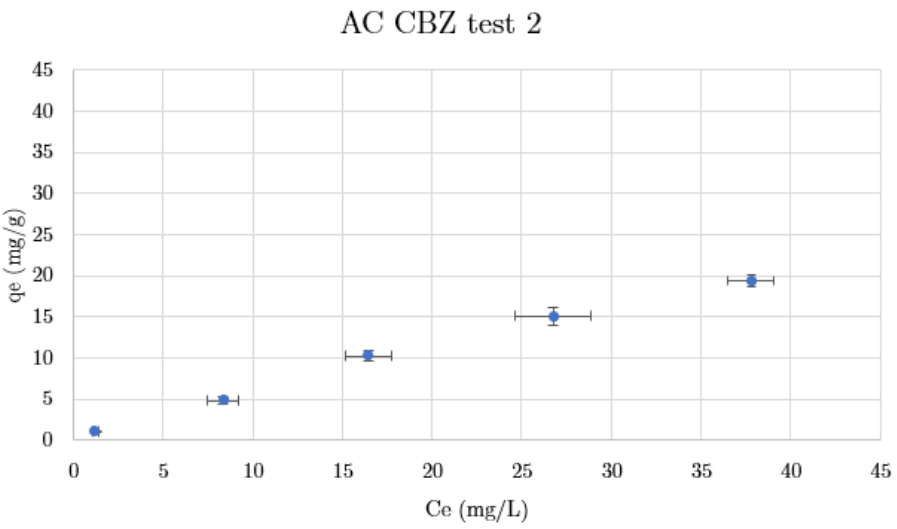


Figure C.8: Sorption study with AC and CBZ

pH during sorption study

		ACET		ACET blank		CBZ		CBZ blank		Sorbent blank	
	Initial C	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}
SBC	5	7,03	7,06	6,22	5,96	6,39	7,33	6,60	5,85	6,17	7,28
	25	5,96	6,71	5,96	6,04					6,64	7,40
	50	6,47	7,09	5,97	6,07	6,46	7,23	6,57	6,13	6,57	7,42
	100	6,15	7,07	5,61	5,78	6,48	7,33	6,42	6,05	6,22	7,28
	150	6,40	6,90	6,19	5,79					6,20	7,20
	200	6,07	7,05	5,94	6,04	6,29	7,34	6,28	5,92		
	300	6,44	7,10	6,20	6,11						
	400	6,40	7,12	6,33	6,03						
	500	6,34	7,22	6,42	6,04						

		ACET		ACET blank		CBZ		CBZ blank		Sorbent blank	
	Initial C	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}	pH_0	pH_{168}
AC	5	7,62	9,37	6,22	5,96	7,20	9,49	6,60	5,85	8,62	9,46
	25	7,26	9,48	5,96	6,04					7,55	9,46
	50	7,69	9,37	5,97	6,07	7,18	9,14	6,57	6,13	7,30	9,49
	100	7,53	9,02	5,61	5,78	7,20	9,41	6,42	6,05	7,20	9,58
	150	7,25	9,14	6,19	5,79					7,10	9,13
	200	7,39	8,81	5,94	6,04	7,08	9,43	6,28	5,92		
	300	7,27	8,26	6,20	6,11						
	400	7,14	8,61	6,33	6,03						
	500	7,23	8,23	6,42	6,04						

Solubility of carbamazepine

Taken from the sorption study

C = 100 mg/L	48h abs	48h diluted	48h C	Average	%SD	168h abs	168h diluted	168h C	Average	%SD
C C5 SBC1	0,415	8,629	86,292	87,319	0,011	0,332	6,908	69,083	69,410	0,81 %
C C5 SBC2	0,424	8,813	88,125			0,337	7,006	70,063		
C C5 SBC3	0,421	8,754	87,542			0,332	6,908	69,083		
C C5 AC1	0,312	6,490	64,896	65,375	0,063	0,168	3,483	17,417	21,222	20,97 %
C C5 AC2	0,296	6,150	61,500			0,194	4,027	20,135		
C C5 AC3	0,336	6,973	69,729			0,252	5,223	26,115		
C C5 B1	0,491	10,215	102,146	102,594	0,006	0,491	10,215	102,146	102,208	0,09 %
C C5 B2	0,495	10,304	103,042			0,492	10,227	102,271		

C6 = 200 mg/L	48h abs	48h diluted	48h C	Average	%SD	168h abs	168h diluted	168h C	Average	%SD
C C6 SBC1	0,682	14,190	141,896	139,507	0,015	0,578	12,029	120,292	119,035	1,24 %
C C6 SBC2	0,662	13,781	137,813			0,564	11,742	117,417		
C C6 SBC3	0,667	13,881	138,813			0,574	11,940	119,396		
C C6 AC1	0,513	10,669	106,688	109,917	0,026	0,445	9,244	46,219	51,222	13,17 %
C C6 AC2	0,534	11,098	110,979			0,467	9,710	48,552		
C C6 AC3	0,539	11,208	112,083			0,566	11,779	58,896		
C C6 B1	0,653	13,583	135,833	137,333	0,015	0,647	13,463	134,625	135,646	1,06 %
C C6 B2	0,667	13,883	138,833			0,657	13,667	136,667		

The blanks for carbamazepine concentration 200 mg/L changed, possibly precipitated

UV/Vis vs. LC-MS/MS

A = Acetaminophen
C = Carbamazepine
SBC = Sludge biochar
AC = Activated carbon

	Acetaminophen	Carbamazepine
<LOD	0,25 ng/mL	0,25 ng/mL
<LOQ	2 ng/mL	1 ng/mL

Number	Name	UV/VIS (mg/L)	LC-MS/MS (mg/L)	Δ
Preliminary experiments - Acetaminophen				
1	A SBC1	21,524	15,546	1,38
2	A SBC2	21,300	15,269	1,40
3	A SBC3	21,414	15,518	1,38
4	A AC1	21,245	15,463	1,37
5	A AC2	21,456	15,411	1,39
6	A AC3	21,447	15,32	1,40
7	A SBC1	11,163	8,022	1,39
8	A SBC2	10,325	7,346	1,41
9	A SBC3	10,970	7,903	1,39
10	A AC1	0,071	0,018	3,92
11	A AC2	0,011	0,008	1,44
12	A AC3	0,043	0,015	2,85
13	A SBC1	6,296	4,577	1,38
14	A SBC2	5,553	4,082	1,36
15	A SBC3	6,552	4,269	1,53
16	A AC1	Unknown, but low under 0.07	<LOQ	
17	A AC2	Unknown, but low under 0.07	<LOQ	
18	A AC3	Unknown, but low under 0.07	<LOQ	
19	A SBC1	2,223	1,622	1,37
20	A SBC2	1,949	1,329	1,47
21	A SBC3	2,120	1,415	1,50
22	A AC1	Unknown, but low under 0.07	<LOQ	
23	A AC2	Unknown, but low under 0.07	<LOQ	
24	A AC3	Unknown, but low under 0.07	<LOQ	
Preliminary experiments - Acetaminophen and Carbamazepine				
25	A SBC1	19,919	14,098	1,41
26	A SBC2	19,931	14,373	1,39
27	A SBC3	20,023	14,07	1,42
28	C SBC1	19,884	16,247	1,22
29	C SBC2	19,809	15,44	1,28
30	C SBC3	19,830	15,684	1,26
31	A SBC1	5,891	3,987	1,48
32	A SBC2	5,469	3,733	1,46
33	A SBC3	5,678	3,945	1,44
34	C SBC1	4,886	4,442	1,10
35	C SBC2	4,362	3,457	1,26
36	C SBC3	4,524	3,498	1,29
37	A SBC1	4,355	2,666	1,63
38	A SBC2	3,936	2,727	1,44
39	A SBC3	4,137	2,858	1,45
40	C SBC1	4,087	3,836	1,07
41	C SBC2	3,694	2,835	1,30
42	C SBC3	3,786	2,962	1,28
43	A SBC1	1,624	1,064	1,53

44	A SBC2	1,444	0,972	1,49
45	A SBC3	1,510	1,036	1,46
46	C SBC1	3,046	2,338	1,30
47	C SBC2	2,782	1,793	1,55
48	C SBC3	2,813	2,252	1,25
49	A SBC1	0,695	0,43	1,62
50	A SBC2	0,606	0,384	1,58
51	A SBC3	0,686	0,425	1,62

Sorption study - Acetaminophen

52	A C1	5,005	3,629	1,38
53	A C2	25,236	18,221	1,38
54	A C3	52,162	35,904	1,45
55	A C4	78,416	54,242	1,45
56	A C5	103,614	71,263	1,45
57	A C6	204,686	141,309	1,45
106	A C1 SBC1	2,152	1,538	1,40
107	A C1 SBC2	2,234	1,621	1,38
108	A C1 SBC3	1,914	1,448	1,32
109	A C1 AC1	0,493	0,437	1,13
110	A C1 AC2	0,520	0,406	1,28
111	A C1 AC3	0,508	0,459	1,11
112	A C1 B1	5,170	3,559	1,45
113	A C1 B2	5,206	3,473	1,50
114	A C2 SBC1	13,432	9,354	1,44
115	A C2 SBC2	14,028	9,547	1,47
116	A C2 SBC3	13,941	9,758	1,43
117	A C2 AC1	3,025	2,25	1,34
118	A C2 AC2	2,696	2,009	1,34
119	A C2 AC3	3,483	2,528	1,38
120	A C2 B1	25,417	18,012	1,41
121	A C2 B2	25,475	17,724	1,44
122	A C3 SBC1	28,564	20,546	1,39
123	A C3 SBC2	30,644	23,109	1,33
124	A C3 SBC3	26,452	20,373	1,30
125	A C3 AC1	7,467	5,518	1,35
126	A C3 AC2	6,741	5,365	1,26
127	A C3 AC3	6,741	4,129	1,63
128	A C3 B1	48,878	34,703	1,41
129	A C3 B2	48,927	35,266	1,39
130	A C4 SBC1	44,785	32,249	1,39
131	A C4 SBC2	48,168	34,529	1,40
132	A C4 SBC3	45,743	33,705	1,36
133	A C4 AC1	9,587	7,169	1,34
134	A C4 AC2	9,266	6,922	1,34
135	A C4 AC3	9,901	7,559	1,31
136	A C4 B1	74,125	52,807	1,40
137	A C4 B2	73,795	51,874	1,42
138	A C5 SBC1	63,993	44,521	1,44

139	A C5 SBC2	63,647	47,386	1,34
140	A C5 SBC3	63,845	48,003	1,33
141	A C5 AC1	13,226	9,334	1,42
142	A C5 AC2	12,483	8,986	1,39
143	A C5 AC3	14,967	10,765	1,39
144	A C5 B1	96,749	71,508	1,35
145	A C5 B2	97,228	69,986	1,39
146	A C6 SBC1	142,426	102,469	1,39
147	A C6 SBC2	140,182	103,004	1,36
148	A C6 SBC3	139,818	103,002	1,36
149	A C6 AC1	25,033	18,464	1,36
150	A C6 AC2	22,871	17,453	1,31
151	A C6 AC3	32,030	23,425	1,37
152	A C6 B1	191,700	141,223	1,36
153	A C6 B2	192,838	137,019	1,41

Sorption study - Carbamazepine

154	C C1	5,021	4,002	1,25
155	C C2	26,708	21,565	1,24
156	C C3	52,313	40,933	1,28
157	C C4	77,146	62,003	1,24
158	C C5	103,438	74,198	1,39
159	C C6	206,500	135,885	1,52
208	C C1 SBC1	2,163	1,602	1,35
209	C C1 SBC2	2,098	1,627	1,29
210	C C1 SBC3	2,421	1,813	1,34
211	C C1 AC1	0,917	0,676	1,36
212	C C1 AC2	0,831	0,584	1,42
213	C C1 AC3	0,879	0,654	1,34
214	C C1 B1	5,006	3,976	1,26
215	C C1 B2	5,023	3,683	1,36
216	C C2 SBC1	14,877	11,231	1,32
217	C C2 SBC2	14,429	10,985	1,31
218	C C2 SBC3	14,279	10,768	1,33
219	C C2 AC1	5,131	3,976	1,29
220	C C2 AC2	3,973	3,518	1,13
221	C C2 AC3	5,242	4,038	1,30
222	C C2 B1	26,979	20,619	1,31
223	C C2 B2	26,996	19,742	1,37
224	C C3 SBC1	29,458	23,028	1,28
225	C C3 SBC2	29,771	23,073	1,29
226	C C3 SBC3	30,229	23,384	1,29
227	C C3 AC1	9,490	0,716	13,25
228	C C3 AC2	10,771	8,398	1,28
229	C C3 AC3	12,104	8,943	1,35
230	C C3 B1	51,104	40,414	1,26
231	C C3 B2	51,500	39,879	1,29
232	C C4 SBC1	49,229	36,674	1,34
233	C C4 SBC2	49,292	38,206	1,29

234	C C4 SBC3	49,292	41,522	1,19
235	C C4 AC1	18,021	13,368	1,35
236	C C4 AC2	12,990	9,867	1,32
237	C C4 AC3	18,354	14,438	1,27
238	C C4 B1	76,167	59,672	1,28
239	C C4 B2	75,979	60,932	1,25
240	C C5 SBC1	69,083	55,683	1,24
241	C C5 SBC2	70,063	57,533	1,22
242	C C5 SBC3	69,083	52,053	1,33
243	C C5 AC1	17,417	13,572	1,28
244	C C5 AC2	20,135	15,606	1,29
245	C C5 AC3	26,115	20,73	1,26
246	C C5 B1	102,146	79,09	1,29
247	C C5 B2	102,271	65,331	1,57
248	C C6 SBC1	120,292	86,399	1,39
249	C C6 SBC2	117,417	82,64	1,42
250	C C6 SBC3	119,396	92,364	1,29
251	C C6 AC1	46,219	37,818	1,22
252	C C6 AC2	48,552	38,805	1,25
253	C C6 AC3	58,896	46,682	1,26
254	C C6 B1	134,625	89,201	1,51
255	C C6 B2	136,667	89,244	1,53

Sorption study - Acetaminophen

256	A C7	152,229	109,607	1,39
257	A C8	407,270	312,265	1,30
258	A C9	515,186	373,475	1,38
259	A C7 SBC1	112,439	80,514	1,40
260	A C7 SBC2	114,604	81,088	1,41
261	A C7 SBC3	114,378	80,004	1,43
262	A C7 AC1	30,824	23,114	1,33
263	A C7 AC2	30,646	22,445	1,37
264	A C7 AC3	29,031	21,504	1,35
265	A C7 B1	153,877	109,633	1,40
266	A C7 B2	153,393	110,937	1,38
267	A C8 SBC1	346,527	259,561	1,34
268	A C8 SBC2	355,089	261,415	1,36
269	A C8 SBC3	346,204	261,992	1,32
270	A C8 AC1	95,477	81,565	1,17
271	A C8 AC2	101,131	86,275	1,17
272	A C8 AC3	100,969	85,933	1,17
273	A C8 B1	401,616	301,979	1,33
274	A C8 B2	402,262	301,262	1,34
275	A C9 SBC1	445,396	325,204	1,37
276	A C9 SBC2	441,519	327,238	1,35
277	A C9 SBC3	443,619	338,509	1,31
278	A C9 AC1	116,963	95,647	1,22
279	A C9 AC2	129,402	105,308	1,23
280	A C9 AC3	106,139	86,901	1,22

281	A C9 B1	502,585	386,266	1,30
282	A C9 B2	502,423	383,963	1,31
Sorption study - Acetaminophen				
283	A C1	24,092	18,743	1,29
284	A C2	94,913	74,296	1,28
285	A C3	193,800	154,593	1,25
286	A C4	289,666	228,166	1,27
287	A C5	389,984	321,989	1,21
288	A C1 SBC1	15,787	12,043	1,31
289	A C1 SBC2	14,638	12,094	1,21
290	A C1 SBC3	15,374	11,863	1,30
291	A C1 AC1	4,866	4,182	1,16
292	A C1 AC2	4,668	4,023	1,16
293	A C1 AC3	4,782	4,147	1,15
294	A C1 B1	24,162	19,61	1,23
295	A C1 B2	24,541	18,877	1,30
296	A C2 SBC1	74,960	59,13	1,27
297	A C2 SBC2	72,496	54,714	1,32
298	A C2 SBC3	74,658	57,735	1,29
299	A C2 AC1	14,674	14,753	0,99
300	A C2 AC2	20,079	18,771	1,07
301	A C2 AC3	20,032	18,096	1,11
302	A C2 B1	100,159	70,567	1,42
303	A C2 B2	102,703	73,844	1,39
304	A C3 SBC1	157,695	120,591	1,31
305	A C3 SBC2	156,312	122,287	1,28
306	A C3 SBC3	156,995	114,745	1,37
307	A C3 AC1	58,283	49,62	1,17
308	A C3 AC2	57,122	46,818	1,22
309	A C3 AC3	50,334	42,746	1,18
310	A C3 B1	201,113	152,847	1,32
311	A C3 B2	202,226	150,227	1,35
312	A C4 SBC1	244,356	186,897	1,31
313	A C4 SBC2	243,084	196,004	1,24
314	A C4 SBC3	240,700	179,445	1,34
315	A C4 AC1	101,049	84,16	1,20
316	A C4 AC2	101,192	65,152	1,55
317	A C4 AC3	87,011	83,299	1,04
318	A C4 B1	296,979	238,819	1,24
319	A C4 B2	302,067	224,83	1,34
320	A C5 SBC1	301,431	272,377	1,11
321	A C5 SBC2	325,437	251,086	1,30
322	A C5 SBC3	330,366	262,747	1,26
323	A C5 AC1	137,758	108,785	1,27
324	A C5 AC2	123,593	96,685	1,28
325	A C5 AC3	133,593	106,42	1,26
326	A C5 B1	397,933	302,614	1,31
327	A C5 B2	400,954	311,667	1,29

Sorption study - Carbamazepine

328	C C1	4,958	3,601	1,38
329	C C2	24,415	19,122	1,28
330	C C3	50,771	35,468	1,43
331	C C4	77,208	60,949	1,27
332	C C5	102,625	71,54	1,43
333	C C1 SBC1	2,990	2,105	1,42
334	C C1 SBC2	3,104	2,26	1,37
335	C C1 SBC3	2,779	2,234	1,24
336	C C1 AC1	1,102	0,856	1,29
337	C C1 AC2	1,413	1,061	1,33
338	C C1 AC3	1,263	0,959	1,32
339	C C1 B1	4,931	3,591	1,37
340	C C1 B2	4,935	3,597	1,37
341	C C2 SBC1	16,879	13,702	1,23
342	C C2 SBC2	17,629	14,55	1,21
343	C C2 SBC3	18,521	15,734	1,18
344	C C2 AC1	7,838	7,539	1,04
345	C C2 AC2	7,846	6,304	1,24
346	C C2 AC3	9,377	6,328	1,48
347	C C2 B1	24,071	18,571	1,30
348	C C2 B2	24,021	18,206	1,32
349	C C3 SBC1	36,188	29,238	1,24
350	C C3 SBC2	37,042	28,412	1,30
351	C C3 SBC3	36,021	27,646	1,30
352	C C3 AC1	15,135	10,842	1,40
353	C C3 AC2	16,488	11,916	1,38
354	C C3 AC3	17,696	13,294	1,33
355	C C3 B1	49,542	39,548	1,25
356	C C3 B2	49,438	39,392	1,26
357	C C4 SBC1	60,833	48,331	1,26
358	C C4 SBC2	57,021	46,004	1,24
359	C C4 SBC3	57,750	44,708	1,29
360	C C4 AC1	28,750	22,918	1,25
361	C C4 AC2	24,563	21,443	1,15
362	C C4 AC3	26,938	18,208	1,48
363	C C4 B1	75,625	60,992	1,24
364	C C4 B2	75,667	59,625	1,27
365	C C5 SBC1	77,375	57,672	1,34
366	C C5 SBC2	76,938	65,351	1,18
367	C C5 SBC3	80,083	66,719	1,20
368	C C5 AC1	36,563	26,518	1,38
369	C C5 AC2	37,750	26,254	1,44
370	C C5 AC3	39,125	29,997	1,30
371	C C5 B1	100,063	81,707	1,22
372	C C5 B2	100,396	74,415	1,35

Total amount of samples 282

Appendix D. Isotherm models

The separation factor R_L

R=1	Linear
R=0	Irreversible
R_L>1	Unfavorable
0<R_L<1	Favorable

$R_L = 1/(1+K_L*C_0)$

SBC	ACET	SBC
K_L	0,00785	0,00869
Initial C_0	R_L	R_L
5	0,96223	0,95837
25	0,83593	0,82157
50	0,71810	0,69718
75	0,62939	0,60550
100	0,56019	0,53513
150	0,45921	0,43421
200	0,38907	0,36531
300	0,29803	
400	0,24152	
500	0,20302	

AC	ACET	CBZ
K_L	0,009689	2,39E-06
Initial C_0	R_L	R_L
5	0,95379	0,99999
25	0,80500	0,99994
50	0,67365	0,99988
75	0,57914	0,99982
100	0,50789	0,99976
150	0,40760	0,99964
200	0,34039	0,99952
300	0,25597	
400	0,20510	
500	0,17110	

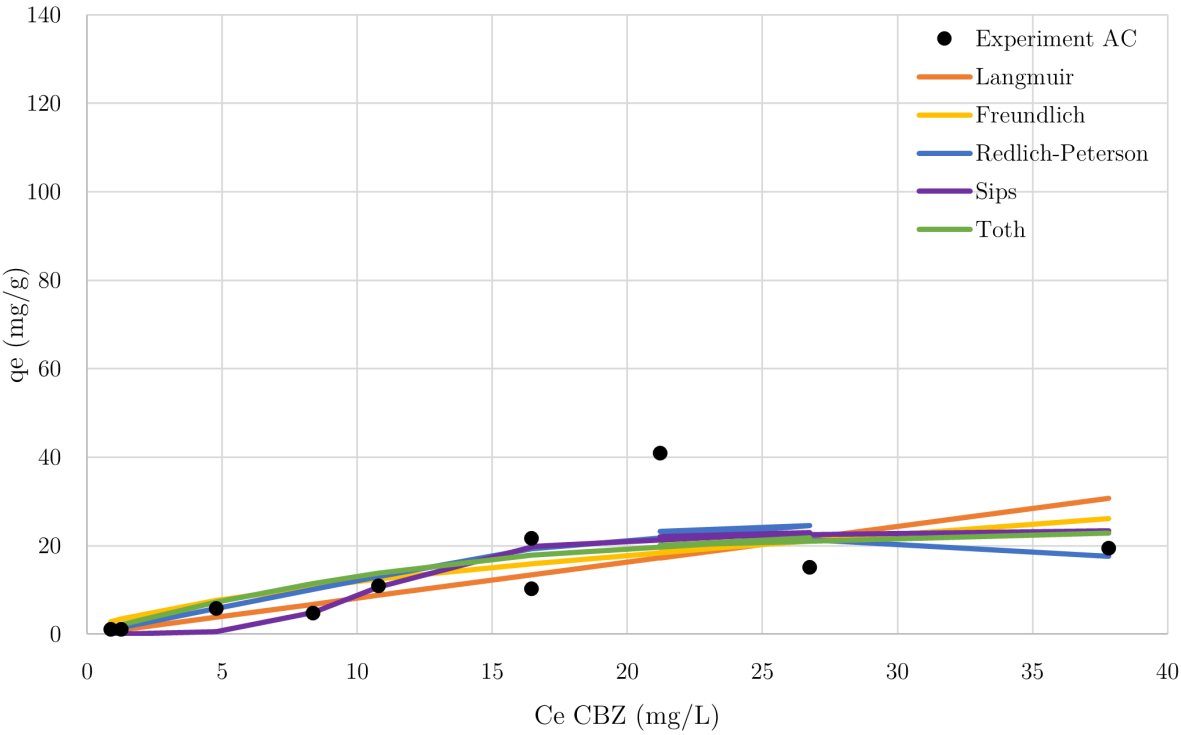


Figure D.2: Isotherm models visualized for AC CBZ

Appendix E. Analysis at Agroscope

E.1 Materials and methods

Two analysis methods were used during the academic visit to Agroscope (Zürich, Switzerland); Fourier Transform Infrared Spectroscopy and Thermogravimetric analysis. Samples were prepared beforehand at NMBU.

Sample prep

Sludge biochar and activated carbon samples, 18 in total, were taken to Agroscope. Washed SBC and AC were dried for 3 days at 105 °C and kept in a desiccator before being transferred to glass containers. Raw unwashed SBC and AC samples were kept in the original bag before being added to the containers. Some of the washed samples were ground in a mortar until powder before adding to glass containers. All pharmaceutical-loaded SBC and AC samples with pharmaceuticals were taken out of their Falcon tubes, kept in a heater for 6 hours at 30 °C, and stored overnight at room temperature before being added to glass containers.

An overview of samples taken to Agroscope is shown in Table E.1. For the loaded sorbent materials, low, medium, and high initial concentration samples were chosen, to cover the range of the conducted experiments.

Table E.1: Samples to Agroscope

Sorbent	Type	Concentration (mg/L)
SBC	Washed	
	Raw unwashed	
	Washed and grinded	
	Loaded ACET	25, 100, 400
	Loaded CBZ	5, 50, 100
AC	Washed	
	Raw unwashed	
	Washed and grinded	
	Loaded ACET	25, 100, 400
	Loaded CBZ	5, 50, 100

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy is a common infrared spectroscopy. Infrared radiation passes through a sample, some of the radiation is absorbed by the sample and some is transmitted (Merck, 2023a). The recorded signal is a spectrum representing molecular spectral fingerprints (Scientific, 2023). FTIR can be used to identify functional groups in a sample because different chemical structures produce different spectral fingerprints.

The FTIR instrument at Agroscope was cleaned with ethanol before use and between each sample analysis. A software was connected to the instrument to digitally convert the results. A thin layer of a sample was put on the instrument, covering a small circle on the instrument where IR radiation would pass through. The tip was turned down until there was a clicking sound, and the analysis lasted for about a minute, scanning the samples between 500 and 4000 nanometers. The result was exported in a CVS. file with absorbance in one column (y-axis) and nanometer (x-axis) in another. All samples in Table E.1 were analyzed.

Thermogravimetric analysis

Thermogravimetric analysis is a thermo-analytical technique that measures the mass of a sample as it is heated, cooled, or held at a constant temperature in a defined atmosphere. A thermobalance is used, which is an apparatus for weighing a sample continuously while it is being heated or cooled. The equipment provides quantitative and qualitative information about physical changes (loss and gain) in the sample in response to the current temperature, heating rate, and atmosphere (AuregaResearch, 2022). A sample is heated using nitrogen gas or dry compressed air. TGA can quantify the major constituents of a material, study decomposition and thermal stability, and be used as a secondary means of material identification.

For TGA analysis, only washed SBC and washed AC were analyzed, because of time limitations. The samples were ball milled at a frequency of 25 $\frac{1}{s}$ for 2 minutes, before being taken to TGA analysis. Two replicates of each sample were measured to 10 mg and added to containers that fitted in the TGA instrument. The instrument was connected to a nitrogen gas container and four different softwares for analysis. During the analysis, the samples were exposed to temperatures up to 700 °C.

E.2 Results and discussion

A short discussion around FTIR and TGA results obtained from the analysis at Agroscope is given in the subsections below.

E.2.1 FTIR

In the Figure E.1 washed SBC, and SBC loaded with 100 mg/L of ACET and CBZ is shown. In the area 1500-2000 nm there are peaks that are reduced with the loaded sample of CBZ and some with ACET, but that is present for washed SBC, suggesting the presence of surface functional groups in this area. There are more pulses, and an amplitude below 1600 nm, reflecting that CBZ affected the functional groups of washed SBC. However, it is difficult to interpret the results and conclude about the surface functional groups as the pulses are too crowded and difficult to separate.

A reason for the crowded and high number of peaks could be that the particles were aggregated. When turning the knob on the FTIR instrument down, to secure the sample, it crushed the sample as the particle size of SBC was 1-2 mm, and AC was 0.5-1 mm. Ball milling should have been used as sample prep for this analysis method.

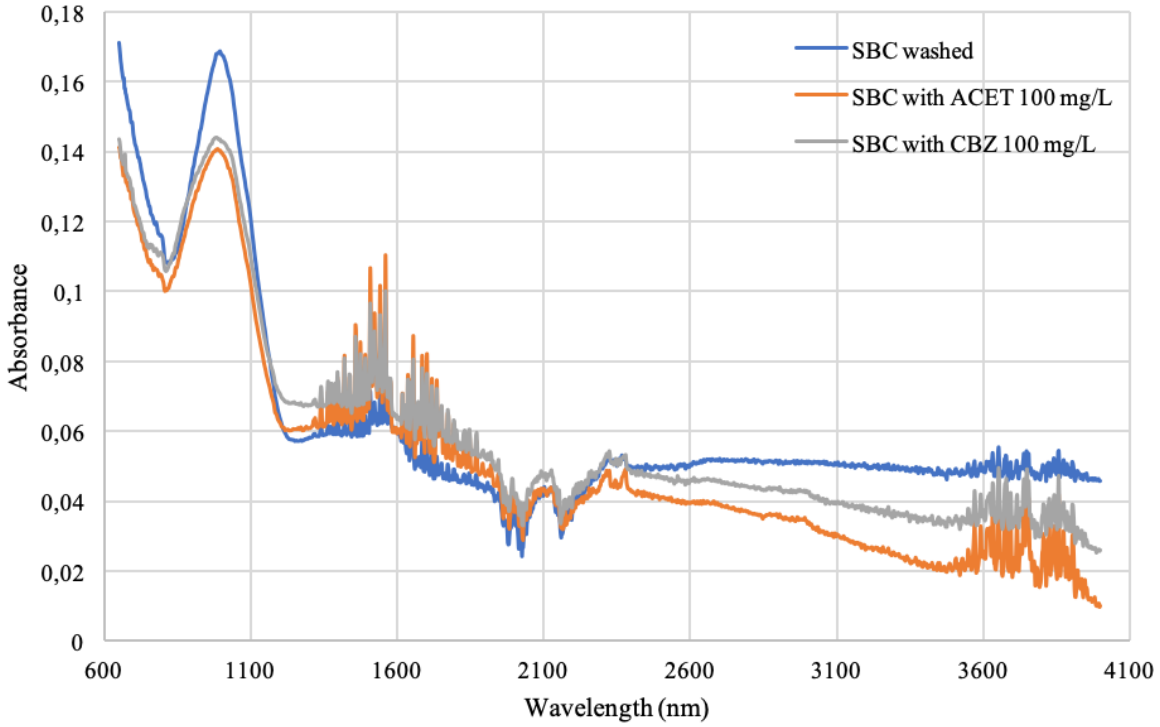


Figure E.1: FTIR analysis with SBC loaded with ACET and CBZ

E.2.2 TGA

Results from TGA analysis on sludge biochar are shown in Figure E.2 and Figure E.3, and on activated carbon are shown in Figure E.4 and Figure E.5.

The TG curve show change in mass with increase in temperature. Sludge biochar is stable until 400 degrees, then the mass drops sharply until 700 degrees as heat is absorbed. The weight loss of SBC is more than 10% as it reduces from 100% to 86% in Figure E.2 and to 88% in Figure E.3. For activated carbon, there is weight loss, although it is not significant. In both Figure E.4 and Figure E.5 the mass reduces from 100% to 93%.

All figures show that the sorbent material absorbs heat, as the differential scanning calorimeter curve swings upwards, and all processes are endothermic. Activated carbon has a higher peak value than sludge biochar.

When comparing the area of the calorific value, AC is smaller than SBC. This is compatible with the fact that AC is already "activated", and a way to activate is for example to pyrolyze again, reducing the mass. The slope for mass reduction is much sharper for SBC, in addition to total weight loss, because it has more mass to be reduced. The SBC has the potential of being activated, as there is much more of SBC mass left.

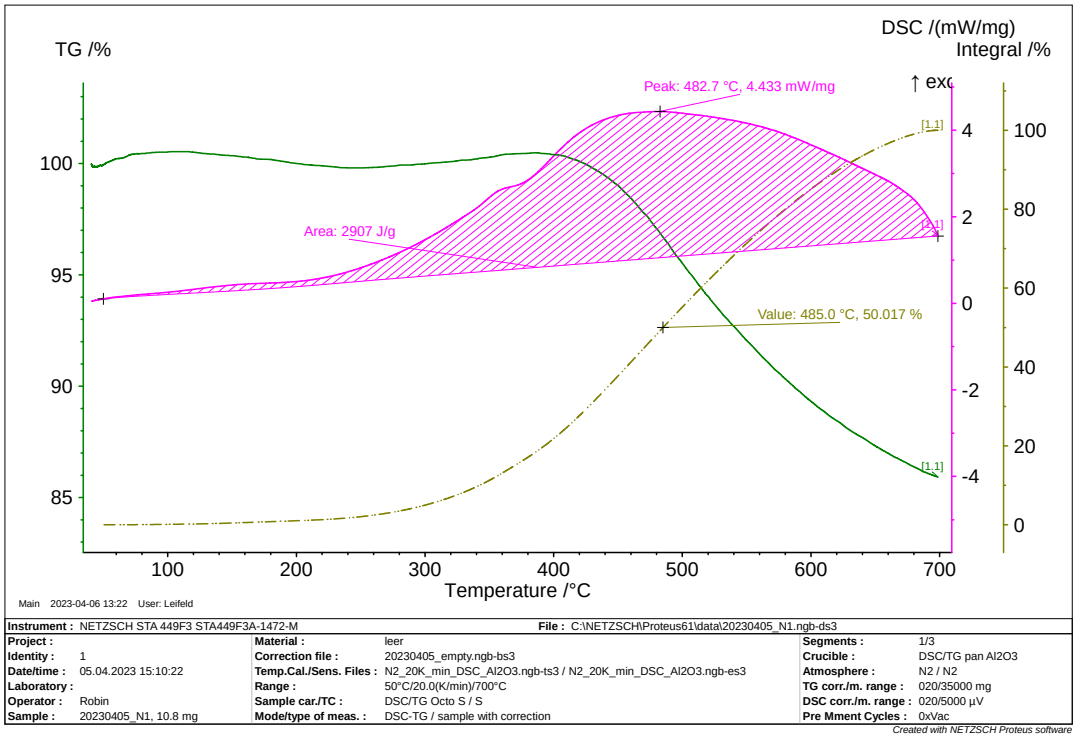


Figure E.2: TGA analysis of sludge biochar replicate 1

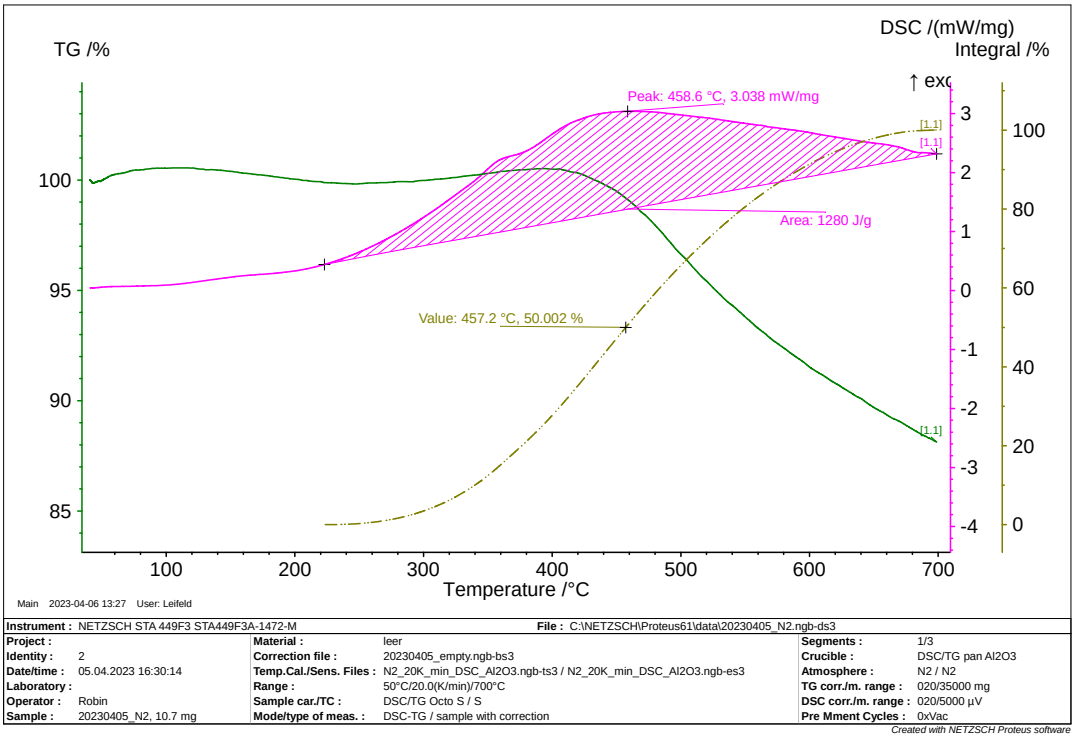


Figure E.3: TGA analysis of sludge biochar replicate 2

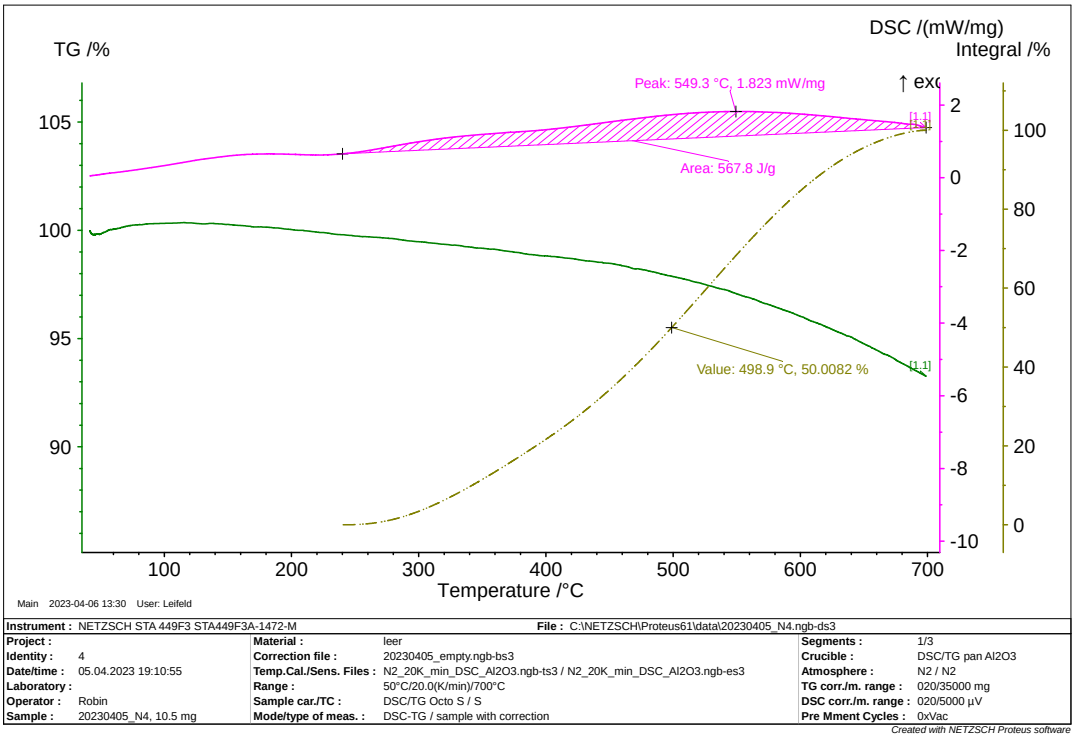


Figure E.4: TGA analysis of activated carbon replicate 1

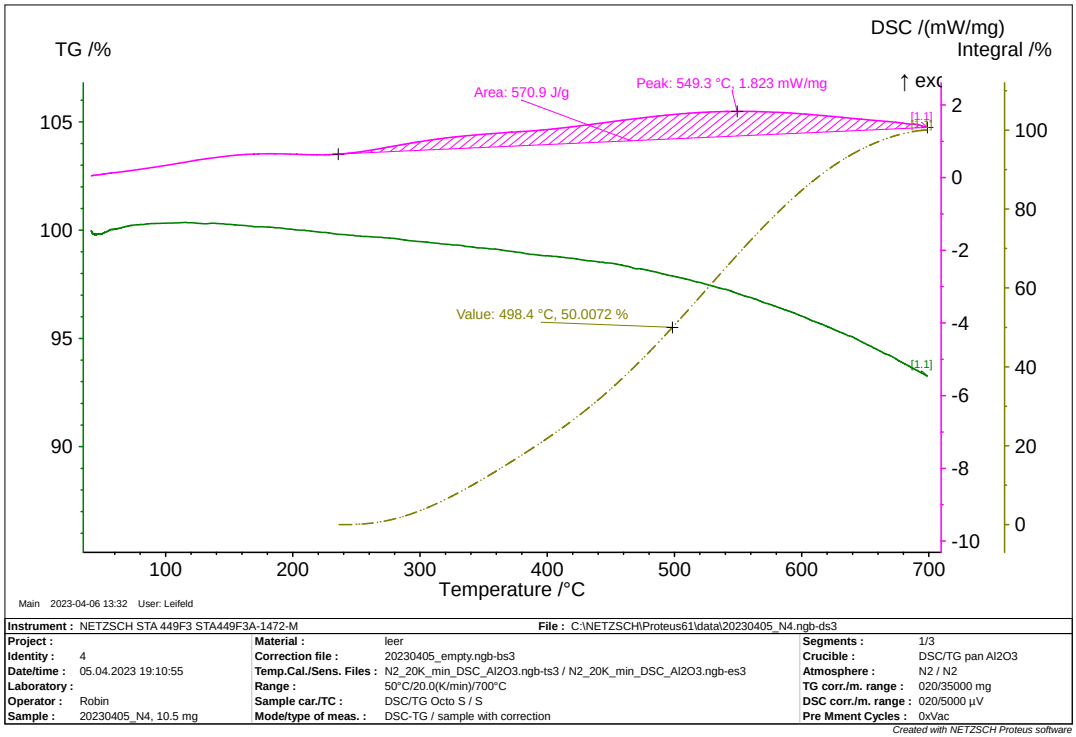


Figure E.5: TGA analysis of activated carbon replicate 1

Appendix F. Instruments and equipment

How to check if a pipette is working OK?

Pipet 5 times at lowest and highest volume on the balance and calculate the average value. of each

What is an acceptable error for you? This depends on what you are doing. An ok error is normally below 1 or 2 %.

For < 1 and 2 %, acceptable average volumes (grams) are as follows:

	10 mL	5 mL	1 mL	0.1 mL
+ 2 %	10.2	5.1	1.02	0.102
- 2 %	9.8	4.9	0.98	0.098
+ 1 %	10.1	5.05	1.01*	0.101
- 1 %	9.9	4.95	0.99*	0.099

For the blue pipetts you have to use the 5 decimal balance

*On the red pipettes (1-10 mL) the standard for calibration is error < 2 %

Remember to use room temperature DI water. You can correct the weight by multiplying with the Z factor: 18 °C =1.0025, 19 °C = 1.0027, 20 °C = 1.0029, 21 °C = 1.0031, 22 °C = 1.033 etc.

Figure F.1: Pipette uncertainty

Table F.1: Overview instrument and equipment

Instrument / equipment	Name	Information
Pharmaceutical 1: ACET	Acetaminophen	(Merck, 2023b)
Pharmaceutical 2: CBZ	Carbamazepine	(Merck, 2023c)
Sieves 0.5, 1 and 2 mm	Laboratory test sieve from Endecotts LTD (London, England)	
pH meter	Manual pH Meter, Handheld, pH20 VWR	
Horizontal shaker	PSU-20i, Multi-functional Orbital Shaker – Biosan	
UV/Vis Spectrophotometer	UV/Vis Spectrophotometer with Metaspec Pro Version 2.2.12.0720 software	Model: UV-T500PRO Spectrophotometer, Series No: AJ1701003
UV/Vis Horiba Spectroscopy	Horiba Scientific Aqualog – Spectroscopy with software	Model: Aqualog-UV-800. Series No: 0540U-1722-AL-800
LC-MS-MS	Agilent 1290 Infinity II Ultra-High Pressure Liquid Chromatograph (UHPLC) (Agilent Technologies, Waldbronn, Germany), Agilent 6495 Triple Quadrupole Mass Spectrometer (Agilent Technologies, Santa Clara, CA, USA) with an Agilent Jet Stream Electrospray Ion Source	
Analytical balance	Balance SMB425i-C (WVRI611-3549)	
Syringe	10mL SOFT-JECT Syringe from Henke-Sass Wolf	VWR: 613-2045 (VWR, 2023a)
Syringe filters 13mm	13mm Syringe Filter w/0.2 µm PFTE Membrane	VWR: 514-1275 (VWR, 2023e)
Syringe filters 25mm	25mm Syringe Filter w/0.2 µm PFTE Membrane	VWR: 516-7655 (VWR, 2023b)
Glass vials	1.5ml Short Thread Vial, ND9, 32x11-6mm, amber glass, 1st hydrol class, w/o, label/filling lines	VWR: 548-8013A (VWR, 2023d)
Screw caps for glass vials	Screw cap, ND9, short thread, openTop, PP, yellow, liner: red Rub/beige, PTFE, 1.0mm, 45° shore A	VRW: 548-3299A (VWR, 2023c)

Analytical balances

We have two balances:

SMB425i-C (WVRI611-3549)

VWRI611-2610

	SMB425i-C	VWRI611-2610
Min. weight (0.1 % uncertainty)	0.02 g (20 mg)	2 g (2000 mg)
Min. weight (1 % uncertainty)	0.002 g (2 mg)	0.2 g (200 mg)
Max. weight	42 g	210 g
Digits (smallest step possible to read)	0.00001 g (0.01 mg)	0.001 g (1 mg)

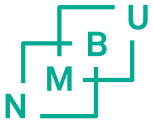
How to use an analytical balance:

- The doors of the balance should be kept closed when measuring. Open the doors as little as possible when placing your sample.
- The balance should be level (check that the air bubble is in the centre of the indicator) before each weighing.
- Always place your container in the middle of the weighing pan.
- Both your sample and the weighing container should be at **room temperature** when measuring.
- The container you use for weighing your sample should weigh as little as possible. This becomes very important when you are weighing very small amounts (mass) of sample.
- Wait until the * *appears*, before reading the results. Stability is then achieved.

The balances should always be kept clean. Clean up if you spill.

Video of how to use an analytical balance:

Figure F.2: Analytical balance



Norges miljø- og biovitenskapelige universitet
Noregs miljø- og biovitskapelege universitet
Norwegian University of Life Sciences

Postboks 5003
NO-1432 Ås
Norway