Czech University of Life Sciences Prague

Faculty of Environmental Science

Department of Applied Ecology

DIPLOMA THESIS

The application of biochar in green infrastructure used for greywater treatment: mitigation of organic micropollutants

Author: Bc. Anna Šabršulová

Supervisor: Dr. Eng. Adam Sochacki

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The application of biochar in green infrastructure used for greywater treatment: mitigation of organic micropollutants

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Objectives of thesis

The goal of this thesis is to characterize the interactions of various types of biochar (source, pyrolysis temperature) with contaminants that may occur in wastewaters treated in gren infrastructure facilities.

Methodology

The methodology will be based on batch and column test in which biochar will be exposed to various types o solutions containing contaminants typical of grey water or surface runoff (detergents, pesticides, pharmaceuticals etc.)

The proposed extent of the thesis

60

Keywords

biochar; adsorption; pharmaceuticals; pesticides; green infrastructure

Recommended information sources

Fidel, R. B., Laird, D. A., & Spokas, K. A. (2018). Sorption of ammonium and nitrate to biochars is electrostatic and pH-dependent. Scientific reports, 8(1), 17627.

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The Diploma Thesis Supervisor

Adam Jan Sochacki

Supervising department

Department of Applied Ecology

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prof. Ing. Jan Vymazal, CSc.

Head of department

Electronic approval: 6. 11. 2019

prof. RNDr. Vladimír Bejček, CSc.

Dean

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Declaration

I declare that I have worked on my diploma thesis titled "The application of biochar in green infrastructure used for greywater treatment: mitigation of organic micropollutants" by myself and I have used only the sources mentioned at the end of the thesis. As the author of the diploma thesis, I declare that the thesis does not break copyrights of any their person.

In Prague ______________________________________

Acknowledgement

I want to sincerely thank to my friends and family for their encouragement throughout the past year and I would also like to express my deep appreciation and special thanks to my supervisor Dr. Eng. Adam Sochacki, for his guidance, patience and support during the entire period of my work on this thesis.

The application of biochar in green infrastructure used for greywater treatment: mitigation of organic micropollutants

Abstract

This study focuses on sorption of three commonly occurring greywater organic micropollutants (diclofenac, methylparaben and benzotriazole) on spruce and *Typha* biochar (produced at 350˚C and 600˚C, each). To find equilibration time and conduct Langmuir and Freundlich adsorption isotherm models, time dependent sorption processes and batch tests were performed for each pollutant and biochar. The results provide comparison of biochars sorption capacity. Spruce biochar, which was produced at high pyrolysis temperature, exhibited the maximum sorption capacity among all the studied biochars. Consequently, affinity towards this spruce biochar has been studied likewise. Methylparaben showed the greatest affinity for spruce biochar and was closely followed by benzotriazole. Diclofenac revealed the lowest attraction to spruce biochar. Results in this study are strongly related to physicochemical characteristics of chosen micropollutants and biochar. The adsorption process was significantly dependent on concentrations of C, O and the major biochar macroelements. Because of biochar good sorption ability, its application in green infrastructures and associated nature-based solutions consisting of green roofs, green walls or constructed wetlands, could help mitigate the amount of organic micropollutants in greywaters and improve wastewater management in cities and rural areas. The study outcomes reflected and supported suggested solution for biochar implementation in green infrastructures as greywater treatment.

Keywords: biochar, greywater, pharmaceuticals, green infrastructures, adsorption, green roofs

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List of abbreviations

AC	Activated carbon
BOD	Biological oxygen demand
BTR	Benzotriazole
CEC	Contaminant of emerging concern
COD	Chemical oxygen demand
CW	Constructed wetlands
DCF	Diclofenac
GHG	Greenhouse gas
GI	Green infrastructure
GW	Greywater
HPLC	High performance liquid chromatography
HTT	Highest treatment temperature
LECA	Lightweight expanded clay aggregate
MPB	Methylparaben
NBS	Nature-based solution
PPCPs	Pharmaceuticals and personal care products
TOC	Total organic carbon
TP	Transformation product
TSS	Total suspended solids
WSP	Waste stabilization ponds
WWTP	Wastewater treatment plant

1 Introduction

1.1 Motivation

Pollution along with its negative effects alter the air and soil quality, causing harm in urban developments in connection to elevated sound effects and excessive light, and lastly, results in adverse impacts in the aquatic environment (Robinson et al., 2006).

Humans extensively burn fossil fuels, cut trees and use aerosols, this way they on daily basis contribute to higher concentration of greenhouse gases (GHG) in the atmosphere. The higher concentration of GHG causes increase in temperature and overall climate change connected with it. The climate change is responsible for severe droughts surrounding our planet and for floods associated with glacier melting and dry soil. Every year our planet experiences less and less water reserves and complications with water supply. Water scarcity affects billions of people throughout the year. 2.7 billion people experience water shortage problems at least one month during a year (WWF 2020). In 2016, approximately 70% of the global population was living under the condition of moderate to severe water scarcity (Mekonnen and Hoekstra 2016), hence it is necessary to take care of the freshwater resources.

There are many institutions in the world working on solutions for saving the freshwater resources. Not only they try to create systems that would mitigate water consumption, but they also try to improve water treatment methods (Sahni 2012). Most of the centralized wastewater treatment plants (WWTPs) in cities filter wastewater coming from households, rainwater runoff from streets, water from multiple industries and agricultural water, and return it relatively clean back into water bodies. The main goal of municipal WWTPs is to reduce the concentration of nutrients such as nitrogen and phosphorus from the incoming wastewater. However, a wide range of pharmaceutical compounds for instance analgesics/anti-inflammatory drugs, antibiotics or psychiatric drugs, face difficulties with their removal from municipal WWTPs. Consequently, these pollutants end up in high concentrations in treated effluent waters and water bodies. Without great dilution capacity of receiving waters and photodegradation of pharmaceuticals, pollutants can initiate a possible threat to the aquatic environment and also humans (Al Aukidy et al. 2012).

New improved wastewater treatment methods separate wastewater sources into blackwater (with toilet discharge) and greywater (without toilet discharge) (Opher and Friedler 2016), and use some type of adsorbent such as activated carbon or biochar that adsorbs the unwanted contaminants and prevent surface water from contamination (Downie et al., 2009). Greywater often contains different pollutants than blackwater, as it comes from kitchen and bathroom, and the toilet discharge is left out (Butkovskyi et al. 2015). By treating greywater separately, there is a much higher chance for pollutants reduction and treated greywater can be also reused for toilet flushing or irrigation.

Biochar, as a carbon rich product, meets all the requirements to be a good pollutant adsorbent, and has been widely used across the world. Its application has been observed in agriculture, as it helps the water retention in soil and crop yield, and mitigates the effect of pesticides and usage of fertilizers (Gisi et al. 2017; Woolf et al. 2010). It has been also implemented in wastewater management projects for a treatment of rainwater and greywater. It can be implemented in nature-based solutions such as constructed wetlands or green roofs, where it helps to reduce the concentration of nutrients in the influent wastewater or rainwater (Kasak et al. 2018; Kuoppamäki and Lehvävirta 2016). Biochar application in green roofs has not been studied very deeply, but its potential to diminish organic micropollutants (Piscitelli et al. 2018) from greywater is sufficiently high to focus this research on mitigation of three organic micropollutants, commonly appearing in greywaters, via sorption on biochar, which can applied into green infrastructures.

1.2 Problem statement and knowledge gaps

The following knowledge gaps regarding the application of biochar for the removal of organic micropollutants have been identified based on the literature study:

1. The knowledge about the elimination of organic micropollutants from wastewaters using biochar is relatively decent, however, not enough research concentrating on their abatement from greywater using biochar as filtration material has been done. Greywater organic micropollutants as well as biochar are relatively new to wastewater management and their physicochemical characteristics are studied intensively, yet the information gap is still substantial.

2. Green infrastructures facilities in cities are getting increasingly common, because they can reduce the pollution (air, water, noise) heat island effects, and can offer other environmental and aesthetic benefits. Green roofs and walls are efficient in removing nutrients and heavy metals from greywater and urban runoff, and biochar implementation only improves this removal (Fowdar *et al.*, 2017; Piscitelli *et al.*, 2018). However, green roofs with biochar as a substrate amendment have not been widely used for a treatment of greywater organic micropollutants, as this type of treatment is very young.

3. Biochar can be produced from various types of biomass, ranging from wood to leaves and manure, and the extent of pyrolysis temperatures under which biochar can be created is also very voluminous. Such distinctions in source material and pyrolysis temperature can cause organic micropollutants to have less effective removal from greywater, since predominantly physicochemical characteristics of biochar influence micropollutants abatement from greywater. Further research about biochar characteristics is needed, since its development and application become more popular.

1.3 Hypothesis and objectives

The hypothesis of this thesis is:

Biochar is a porous, carbon rich product with unique characteristics, which can help with the adsorption of organic micropollutants commonly occurring in greywater. Biochar good sorption capacity and potential for storing carbon and mitigation of climate change can be beneficial for its implementation in nature-based solution, where is able to operate as an amendment for greywater treatment.

The objectives of this thesis are:

1. To evaluate the adsorption capacity of four types of biochar produced from spruce and *Typha* biomass under low and high manufacturing temperatures, based on adsorption processes involving three organic micropollutants diclofenac, methylparaben and benzotriazole. The aim is to find biochar with the highest sorption potential, which could be used for greywater treatment in nature-based solutions and examine how characteristics of each type of biochar affects their adsorption capacity.

2. To assess the magnitude of adsorption affinity of chosen greywater organic micropollutants via batch experiments and compare it with one another according to micropollutants and biochar physicochemical properties and according to level of pH during batch experiment. The aim is to identify a micropollutant, which concentration will most likely be maximally reduced from greywater by the adsorption on biochar with the highest adsorption capacity.

1.4 Methodology and structure of the thesis

This thesis reports the results of a laboratory-scale experiment dedicated to sorption of selected greywater micropollutants on various types of biochar. This thesis is divided into two main parts: the goals and hypotheses and literature overview (chapters 1-4) and the experimental part with discussion of the results and conclusion (chapters 5-8).

The first chapter of this thesis consists of an introduction, which tries to briefly describe current environmental problems concerning wastewater pollution caused by greywater organic contaminants and plausible solutions for their mitigation from greywater using biochar and green infrastructures.

The second, third and fourth chapter of this thesis cover the literature review. The second chapter discusses physicochemical characteristics of greywater from different sources, commonly occurring organic greywater micropollutants and different pathways of greywater contamination by organic pollutants. The second chapter also reviews various wastewater and greywater treatment methods and assesses their efficiency. The focus on the third chapter are nature-based solutions. Green walls, constructed wetlands and green roofs are in this chapter described as wastewater treatment solutions copying natural processes with the potential to be applied in cities and rural areas and able to treat wastewater of various sources. The fourth chapter introduces biochar as filtration material and define its production, physicochemical characteristics and a wide range of its sorption specifics. The chapter also explore biochar as a filtration material in various nature-based solutions and discusses its option for bioregeneration.

The methodology of the experiment is outlined in the fifth chapter and it is expounding the knowledge from the literature review. It comprises of detailed description of material as well as of a process of determination of equilibration time and adsorption isotherm for all chosen micropollutants. The results and discussion are presented in the sixth and seventh chapter, respectively. Chapters elaborate on the experimental part of the thesis and clarify equilibration time, adsorption capacity, adsorption affinity and pH dependency of chosen organic pollutants on biochar. The eighth chapter summarizes research findings and proposes treatment solutions, which could be feasible for the wastewater management and could contribute to sustainable development.

2 Greywater characteristics and treatment methods

2.1 Greywater characteristics

Greywater (GW) is defined as urban wastewater without any input from toilets, therefore it generally includes wastewater sources from baths, showers, hand basins, washing machines, kitchen sinks and dishwashers (Halalsheh et al. 2008; Jefferson et al. 2004). It contains residues from cleaning and washing processes, which are nutrients, organic matter, pathogens, micropollutants and heavy metals. Among the chemicals that might be detected in GW are pharmaceuticals, cosmetics, insect repellents, fragrances or food additives (Turner et al. 2019). GW represents 50-70% of total consumed water and as a consequence of high pollutants input contains only about 30% of organic fraction (Fountoulakis et al. 2016).

GW varies in the pollutant and nutrient content, but also in the physicochemical characteristics. Among the most important GW physicochemical parameters are chemical oxygen demand (COD) reflecting a number of chemical reactions of organic substances consuming free oxygen in water, biological oxygen demand (BOD), which represents biological oxidation of organic compounds in the presence of molecular oxygen, total suspended solids (TSS) and total organic carbon (TOC). GW has higher COD than BOD, the difference is caused by the presence of organic compounds in GW. High COD/BOD ratio usually indicates existence of detergents, shower products and pharmaceticals in GW and absence of organic matter typical for black water (BW) coming from toilets (Al-Gheeti *et al.*, 2019a). However, the range of COD/BOD ratio in GW varies. GW with high COD/BOD ratio presents higher COD soluble fraction and unlike GW with low COD/BOD ratio, which are characterized by the presence of organic matter such as biodegradable food particles, has lower biodegradability (Noutsopoulos et al. 2018). Table 1 shows parameters defining GW quality based on the household source. Concentrations displayed in this table are only approximate numbers taken from selection of authors.

Laundry GW contains high concentrations of N, P, sodium and surfactants. Products used for laundering such as powdered detergent are known for their high salt and phosphorus content. GW containing such products can be harmful to the soil and aquatic environment when not being properly treated (Meinzinger and Oldenburg 2009).

Laundry GW also shows higher concentrations of organic carbon, COD and BOD, which are multiple times higher than the one from bathroom. Higher concentration of BOD makes laundry GW more biodegradable. The occurrence of organic carbon is mainly attributed to presence of detergents and to fecal contamination from washing of children clothes (Meinzinger and Oldenburg 2009; Noutsopoulos et al. 2018).

Bathroom GW contains large quantity of soaps, shampoos and other cleaning products such as toothpastes or detergents, which are being used on everyday basis in shower or handbasin. The concentration of organic carbon is low in this source of GW (Noutsopoulos et al. 2018). The usage of soaps, shampoos and oral hygiene products belongs to one of the highest among all products (Eriksson et al. 2003).

Kitchen GW contains out of all sources the highest number of pollutants. It contains residues of cleaning products, food particles and oils, thus it is full of bacteria and shows the highest biologic activity and concentration of TSS. For example kitchens in the United States use very often waste grinders, and therefore increase the amount of organic waste in the GW (Meinzinger and Oldenburg 2009). Occurrence of drinks and food generally increases the concentration of organic carbon in the GW (Noutsopoulos et al. 2018). Kitchen sink water and dish water is a great place for microbial growth. Grease particles and food residues are full of nutrients, which can be very suitable for pathogen activity (Gisi *et al.*, 2015; Al-Gheeti *et al.*, 2019a).

Table 1 Quality of greywater from different household sources

	Bathroom	**Kitchen**	**Laundry**
mg/l			
COD	77-633	518-1780	340-1815
BOD	26-300	96-831	96-1363
TSS	7-207	229-319	147-169
TOC	11	26	30
TN	3.6-6.4	6.5-74	6-21
TP	0.28-0.779	0.12	0.1->101

References: Eriksson *et al.*, 2003; Gross et al., 2007; Meinzinger and Oldenburg, 2009; Donner *et al.*, 2010; Katukiza *et al.*, 2014; Fountoulakis *et al.*, 2016; Noutsopoulos *et al.*, 2018

The contaminants and physicochemical characteristics usually vary among GW sources. The volume and the quality of GW significantly depend on people's behavior, living standards, activities, income and the type of a facility, where the GW is produced and its size. For example a family house, an elementary school or a hotel will differ in the amount and content of GW that has been produced in a one day (Sahni 2012), and so will different countries. For this reason, parameters defining GW such COD or BOD fluctuate and can be fundamentally altered in different households (Donner et al. 2010; Noutsopoulos et al. 2018)

2.2 Organic pollutants occurring in greywater

Pollutants are substances introduced into the environment showing negative effects. There are many types of pollutants with harmful impacts, yet pharmaceutical compounds and personal care products (PPCPs), biocides or industrial chemicals belong to a group of organic pollutants threatening the aquatic environment and human health (Liu and Wong 2013). PPCPs form a group of emerging contaminants occurring in GW in higher amounts every year. Many of them serve to kill pathogens and organisms, thus they can be toxic when reaching the aquatic environment. Bioaccumulation of parent compound or its metabolite can also cause harm to water bodies and aquatic biota in them. The typical PPCPs found in GW are being used in cosmetics, medicine and contain antibiotics, disinfectants or antiseptics, their classification and common representatives are shown in Table 2. In recent years, there has been increased concern about organic pollutants originating mainly from human activities such as factories, power stations, transportation, agriculture and from normal daily use (Dey et al., 2019). Among organic pollutants detectable in GW sources, it is possible to name a broad range of fragrances and flavors such as menthol or eucalyptol, caffeine appearing in coffee, tea or soft drinks, preservatives such as parabens or citric acid, it is also possible to detect pesticides, which are used in lice shampoos (Eriksson et al. 2003).

Table 2

Classification of the most common organic micropollutants occurring in greywater

Group	Subgroup	Compounds
Pharmaceuticals	Antibiotics	Sulfamethoxazole
	Analgesics/anti-inflammatory drug	Ibuprofen
		Diclofenac
		Ketoprofen
		Naproxen
		Acetaminophen
	Antiepileptic drugs	Carbamazepine
	β-blockers	Propranolol
		Atenolol
Personal care products	Antimicrobial/fungal agents and Disinfectants	Triclosan
		Chlorophene
	Preservatives	Methylparaben
		Propylparaben
		Ethylparaben
	Fragrances	Menthol
		Hexadecanoic acid
		Squalene
	Emulsifiers	1-Hexadecanol
		Nonylphenol
	Surfactants	2-(Dodecyloxy)-ethanol
	Corrosion inhibitors	Benzotriazoles

References: Andersen et al. 2007; Eriksson et al. 2003; Hernandez-Leal et al. 2010; Turner et al. 2019; Zraunig et al. 2019

Marine and fresh waters represent the largest reservoir of organic pollutants (Thakur and Pathania 2019). Majority of pollutants will find the way how to enter surface waters mainly from WWTPs effluent releases, runoff from agricultural fields and roads, or atmospheric deposition (Hlavínek and Žižlavská 2018). A certain amount of these chemicals is also able to find the way back to humans. Chemicals are introduced back to the water cycle and via drinking water could cause health issues (Dey et al., 2019). The range of concentration of organic pollutants in waters is wide. Some pharmaceuticals or corrosion inhibitor such as benzotriazole can be detected in effluent waters of WWTPs in μg/L, however, some organic pollutants are found in low ng/L. Variations in concentration are caused mainly by differences in consumption of substances of concern, pollutants removal rate in WWTP, by dilution factor of water bodies and by physical degradation (Gros et al., 2007; Al Aukidy *et al.*, 2012; Liu et al., 2017). The concentration of individual pollutants in water bodies is mostly lower and does not seem threatening, however, the combine effects and concentration of multiple types of pollutants can cause synergistic effects and be the source of damages to the environment, specifically aquatic life (Verlichci et al. 2017).

When the contaminated water enters the environment and starts making potential threats to the surrounding ecosystem, it can also cause damages to local flora. Nevertheless, aquatic organisms and potentially humans are more susceptible to adverse effects of PPCP than plants. In order to reach the targeted negative effect, the concentration of pollutants getting into contact with plants would have to be significantly higher, but such concentrations have not been observed in the environment (Verlichci et al. 2017).

Little is known about metabolites emerging from GW organic pollutants. The mixture of pollutants occurring in GW is able to react and therefore create new secondary chemical compounds known as transformation products (TP), which ecological toxicity and environmental fate is scarce and need further research (Turner et al. 2019). Due to the fact that TPs travel long distances from WWTPs, they can easily spread into surrounding water bodies, where they can be further degraded and transformed. Transformation is caused by many physical processes in water and WWTP such as photolysis, oxidation or ozonation induced by disinfection. An example of an organic micropollutant, which can be transformed in the aquatic environment by physical processes is diclofenac known for its photo-transformation secondary products, which are formed in water when exposed to direct sunlight or UV-light (Michael et al. 2014).

GW pollutants can be also transformed via microbial activity, in that case it is called biotransformation. This process is more environmentally friendly as it operates near neutral pH. Microorganisms can produce a wide range of enzymes in a very short time (Hegazy et al. 2015). Biotransformation occurs mainly during biological treatment of GW. It can be direct, which is a biotransformation where microorganisms use pollutants as the source of energy or, as in in case of diclofenac, it can be co-metabolic, which is biotransformation of a compound without using it as an energy source and instead gaining energy from more easily degradable compounds. During biotransformation, several transformation products with different environmental fate are formed as well. Most of them are mineralized and are not detectable in the treated wastewater after a period of time, however, some of them are stable and can cause potential threats to the aquatic environment, thus they need more attention (Quintana et al., 2005). As an example of some TPs, it can me mentioned *p*-benzoquinoneimine as a major TP of diclofenac with its low degradative potential (Michael et al. 2014) or not very stable naproxen metabolite O-desmethyl-naproxen (Quintana et al., 2005).

As it was mentioned above, GW organic pollutants can be of different groups and subgroups and can be detected in effluent waters of WWTP in different concentration based on variety of factors. Table 3 lists three commonly occurring GW organic compounds diclofenac, methylparaben and benzotriazole along with their acid dissociation constant (pKa) and octanol-water partition coefficient ($logK_{ow}$). The pKa indicates the strength of the acid in a solution. A lower pKa signifies a stronger acid (Schaller 2019). The $logK_{ow}$ shows the hydrophobicity of the pollutant and its ability to partition in the aquatic environment. It is important indicator of bioaccumulation and toxicity of organic compounds. A lower $logK_{ow}$ indicated higher hydrophilicity of pollutants and vice versa, therefore organic pollutants with higher $logK_{ow}$ have tendency to adsorb more easily to organic matter in soils or sediments due to their hydrophobic character (Cumming and Riicker 2017; Kah et al. 2017). Organic micropollutants mentioned in Table 3 are also included in the experimental part of this thesis and their detailed characteristics are individually described in chapters 2.2.1, 2.2.2 and 2.2.3.

2.2.1 Diclofenac

Diclofenac (DCF) belongs to non-opioid analgesics. It is known as an anti-inflammatory drug which helps to reduce inflammation, symptoms of cold, flu or pain such as headache, dental pain, backache or muscular pain. It can be used orally in forms of tablets, but it has also its own dermal equivalent such as gel or liquid (Hlavínek and Žižlavská 2018). The well-known anti-inflammatory drug, which is used to reduce body pain and inflammation is called Voltaren and it is a high contributor of diclofenac in GWs (TGA 2014). Several studies observed high concentration of DCF in WWTP effluent waters ranging from 120 ng/L to 5.1 µg/L (Gros et al., 2007; Stülten *et al.*, 2008; Letzel et al., 2009). It was found that DCF usually prevail throughout a season with potential increase of diseases and consequently higher consumption of this anti-inflammatory drug (Letzel et al., 2009). Even though WWTP waters also include black water coming from toilets, and thus DCF which has been used orally, DCF dermal application plays a greater role in the pollution of aquatic environment. Human skin is able to absorb only 5 to 10% of the active ingredient from the product, thus most of the compound ends up in a sewer by washing off liquid and gel-based products (Heberer and Feldmann 2005). DCF is an organic compound, which is poorly biodegradable. It is very persistent in the water and its most convenient way of abatement is photodegradation (Letzel et al., 2009).

2.2.2 Methylparaben

Methylparaben (MTP) belongs to a group called parabens which is used mainly in cosmetic and preservative products, but it can be also found in blueberries or alcohol beverages. Products containing MTP often comprise of shampoos, make-up, shaving products, deodorants and a lot of other goods from self-care cosmetics (FDA 2008). The level of toxicity and irrigation is usually low, therefore it is safely added into eye liners, mascaras or eye shadows (ACME-HARDESTY 2020). Along with other preservatives, parabens are added into cosmetic products to prevent growth of molds, yeasts, microorganisms and fungi (FDA 2008).

Together with other PPCPs, it is frequently found in GWs as a result of application of self-care cosmetics on human skin. In Copenhagen, MTP was detected in influent GW from showers and hand basins in concentration of 6.9 to 9.7 µg/L (Andersen et al. 2007). However, such high concentrations are not always typical for all types of GW sources. Hernandez-Leal *et al.* (2010) study has demonstrated that concentration of MTP in influent GW can be much lower. Due to dilution with kitchen and laundry GW, where the occurrence of MTP is usually scarce, influent GW can contain MTP in concentration under the limit of quantification. As a Thailand research confirmed, MTP can be also found in surface water as a consequence of uncontrolled discharge of sewage by local residents (Juksu et al. 2019).

2.2.3 Benzotriazole

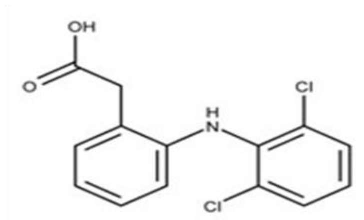
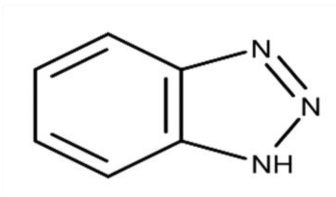
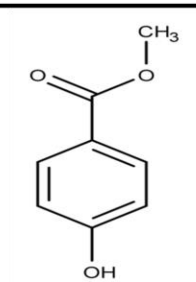
The use of benzotriazole (BTR) is very broad. It is possible to find it in cleaning products or dishwasher tablets and powders as corrosion inhibitor (Janna et al. 2011), it is also a part of aircraft anti-icing/de-icing fluids (ADAF), anti-freezing products, coating products and industrial cooling systems (Kiss and Fries 2009).

The occurrence of BTR in GW is caused by using this substance in households mainly in bathrooms and laundry rooms or it was also found outside of household in surface runoff at airports. There are more than a few pathways for BTR to reach GW and possibly water bodies. It has been found that the detection rate of benzotriazole in textile material made for infants is 15%, with printed boy's bodysuits having maximum concentration of 14 µg/g of BTR. Washing of textile material containing BTR with high concentration can release pollutant into wastewaters and cause potential threats to the aquatic life (Liu et al., 2017). In Berlin effluent wastewater, the BTR was detected in concentration of 9.6 µg/L when used mainly as corrosion inhibitor. Products with addition of BTR as a corrosion inhibitor are widely used in households and generate pollution to the surrounding environment (Weiss and Reemtsma 2005). BTR is also considered to be a part of point source pollution as it occurs in surface runoff at airports. Surface of an airplane is coated with ADAF and these substances are removed during the airplane movement on a runway and during its takeoff, thus they are becoming a part of airport runoff (Kiss and Fries 2009).

BTR is very stable in aquatic conditions particularly with presence of soil and has especially negative effect on plants. It is able to initiate structural changes, inhibit elongation or cause death to the plants (Wu et al. 1998). BTR biodegradability is very limited and it is considered as a long-term persistent substance with the potential to reach drinking water (Weiss and Reemtsma 2005).

Table 3

Characteristics of chosen organic micropollutants, Name of the substance, Structure, CAS number, function, dissociation constant and octanol partition coefficient

Substance	Structural Formula	CAS	Function	pKa	logKow
Diclofenac		15307-86-5	Non-opioid analgesic, anti-inflammatory drug	4.14	4.51
Methylparaben		99-76-3	Preservative, antifungal agent	8.5	1.96
Benzotriazole		95-14-7	Corrosion inhibitor, anti-freezing agent, lubricant	8.37	1.34

References: Gross et al. 2007; HSDB 2020a; HSDB 2020b; ECHA 2020

2.2.4 Mitigation measures

Before thinking about GW treatment and its reuse, it is crucial to mitigate the water use inside households and other buildings or to consider alternative sources of water. The water usage is possible to reduce with plumbing fixtures and implementation of new technologies, which can help to control toilets, urinals and showerheads. New installations as dual flushing or electronic faucets will save money and set the boundaries for protection of the environment before the next step is taken (Sahni 2012).

Mitigation measures are important to include into water management. The total consumption of fresh water in the Czech Republic in 2016 was 131.2 liters (per person/day), with Prague having the highest water consumption of the whole country (eAgri 2017). According to European Environmental Agency (EEA) data from Eurostat, there are many countries in EU with much higher water consumption than the Czech Republic. Mostly southern countries have higher water usage as they focus on agriculture and suffer from drought. Unlike in central Europe, where the water usage has decreasing tendency the last couple of years, there is no trend in terms of water consumption in the southern Europe. Between 1990-2017 the water usage fluctuated and in 2015 the water consumption was actually the highest with the focus on agriculture, forestry and fishing (EEA 2020). Global warming and scarce water resources make water management challenging. For that reason, there should be more project focused on GW reuse and improvement of the overall water consumption.

2.3 Wastewater treatment

2.3.1 Conventional Methods

Conventional treatments are designed to recycle wastewater coming from pavements, household's sewage or several industries. It removes solids, organic matter, nitrate, phosphate and pathogens (Buttiglieri and Knepper 2008). WWTP technologies commonly use primary, secondary and tertiary treatments. There are many steps and processes within WWTP, usually it involves sedimentation, filtration, coagulation, disinfection. (Gisi et al. 2017).

Primary treatment takes place in sedimentation tanks and its aim is to reduce BOD level in wastewater. Most of the solids settle down to the bottom of the tank and less dense material such as detergents from laundry water remain on the surface, where they are collected before the next treatment takes place.

Secondary treatment focuses on removing dissolved and suspended organic matter from the liquid part of the sedimentation tank (Wurochekke et al. 2019). The removal is usually performed by bacteria in aerobic conditions, thus it is usually called biological treatment (Buttiglieri and Knepper 2008).

Tertiary treatment improves the overall quality of effluent water. It is very crucial as it removes nutrients such as N and P out of the water. Different methods of filtration and disinfection are applied in this process before the final treated water is discharged into the environment. Tertiary treatment involves processes such as nitrification, denitrification for N removal or chemical precipitation for P removal (Buttiglieri and Knepper 2008). N or P are two very problematic macro elements and they should be properly removed from the wastewater before discharging into water bodies. P if not well removed can cause eutrophic condition to the water, especially if the level of P in the water body is already increased (Wurochekke et al. 2019).

Efficiency of conventional treatment is high, but the removal of emerging contaminants especially PPCPs is very low. If there is an option of reusing the treated wastewater for household or agricultural practices, new additional treatment must be added in order to eliminate occurring contaminants. WWTPs belongs to the biggest contributors of contaminants of emerging concern (CEC) in the water environment. In 2016, 84.7% of the whole population in the Czech Republic was connected to the centralized sewerage system and 97.3% of the discharged wastewater was treated (eAgri 2017). Without further treatment and CEC reduction, emerging contaminants will stop being only a concern to human health and become a legitimate problem for people. The additional treatment may consist of membrane separation such as nanofiltration or reverse osmosis, it may include UV radiation and ozonation. Each treatment has a different effect depending on the contaminant’s physical and chemical characteristics. (Rizzo et al. 2019).

As an example of such additional treatment, Switzerland included into their conventional wastewater treatment a supplementary step containing ozonation. The Swiss water protection goal was to abate the amount of micropollutants at least by 80%. This method was tested out on 43 relevant micropollutants. The biological conventional method with activated sludge was able to eliminate several micropollutants, but at least half of the micropollutants still remained in the wastewater. The addition of certain ozone doses helped with the removal of almost all 43 substances by 80% and more. The removal efficiency of benzotriazole increased from 64% to 94% when the biological treatment was followed by ozonation (Salhi et al. 2018).

2.3.2 Nonconventional methods

As it was already stated in Chapter 2.3.1, due to the physicochemical characteristics of emerging contaminants, wastewater that is being treated through conventional methods often needs an additional treatment. Even though the efficiency of conventional treatments is high, occurrence of new emerging contaminants and their secondary metabolites in wastewater limits the amount of produced clean water. The main goal of WWTP is to reduce N and P concentration and not to reduce micropollutants. Many non-conventional methods are designed to treat wastewater with good adsorptive material or plants implementation and increase the overall efficiency of conventional treatment systems.

Waste stabilization ponds

Waste stabilization ponds (WSP) belong to non-conventional extensive wastewater treatment made for small agglomerations, where usual number of inhabitants is under 1000. They are large and shallow and treat wastewater via natural processes. The Czech Republic owns over 25 extensive stabilizations ponds (Felberova, Kucera, and Mlejnska 2007). WSP are of three types, anaerobic, facultative and aerobic. Anaerobic and facultative ponds are valuable in BOD removal unlike aerobic ponds, which are designed for pathogen removal. Anaerobic, facultative and aerobic ponds are usually connected as water goes from one pond to another until cleaned.

Anaerobic ponds often treat wastewater with high organic load. The removal of BOD is the highest at neutral pH and temperature around 20˚C. Anaerobic ponds are able to abate up to 60% of biological oxygen demand.

Facultative ponds clean either untreated wastewater or already treated wastewater coming from anaerobic ponds or septic tanks. The process of BOD removal is longer than in anaerobic ponds. Facultative ponds convert into algae full ponds overtime, which help them with up to 90% BOD removal via algae photosynthesis.

Aerobic ponds follow the facultative ponds and they main function is to remove pathogens. They are very well oxygenated and contain a lot of algae. The ponds can still reduce the amount of BOD, but primarily they significantly reduce the number of fecal bacteria. The removal highly depends on temperature, light, pH and oxygen in the pond (Kayombo et al. 2004).

Anaerobic filter

Another non-conventional treatment are anaerobic filters. This method is good especially for households or facilities able to recycle their own wastewater or in areas with higher water demand. From the economic perspective anaerobic filters are highly efficient, they need no electrical power, filtration media are cheap, and they do not require many skills. The system is composed of a septic tank, where all small particles have time to settle, aerobic and anaerobic filter with wide range of gravel for efficient pollutant removal and storage tank, where the treated water is stored. The gravel also includes bacteria transferring the organic material into raw material, CO_2 and methane. Treated water is best for irrigation purposes, water is clear of color, impurities and odorless (Ghawi 2019).

2.3.3 Greywater treatment methods

BW has slightly different characteristic than GW. Pharmaceuticals such as paracetamol or naproxen are intended for oral use, so they are present in BW in higher concentrations than personal care products. Inversely, diclofenac as an anti-inflammatory drug which should be applied directly on skin is detected in black water in very small concentrations, but its presence in GW is immense (Butkovskyi et al. 2015). Unequal distribution of pharmaceuticals in BW and GW indicates their different routes. One option how to increase the efficiency of their abatement is to separate BW and GW sources and treat the water individually.

There are several methods for the treatment of GW, which differ in complexity and the level of treatment. Since, the policies and regulations do not correspond across the world, Specific guidelines allow countries to treat their GW in different manner and therefore there is no universal way how to use GW systems and treatment methods (Sahni 2012). In some developing countries there are no policies and regulations controlling free GW discharging into the environment. Polluting water bodies with GW can result in adverse effects on the aquatic environment and further environmental damage (Noman et al. 2019). Fig. 1. illustrates the route of pollutants from the GW source to human in the natural environmental. When GW treatment and discharge are not properly done, pollutants start to accumulate in agricultural land and crops, causing problems to the water environment and potentially to human body (Al-Gheethi *et al.*, 2019b). Even though the Czech Republic is one of the most developed countries in the world, there are no specific regulations on how to treat GW.

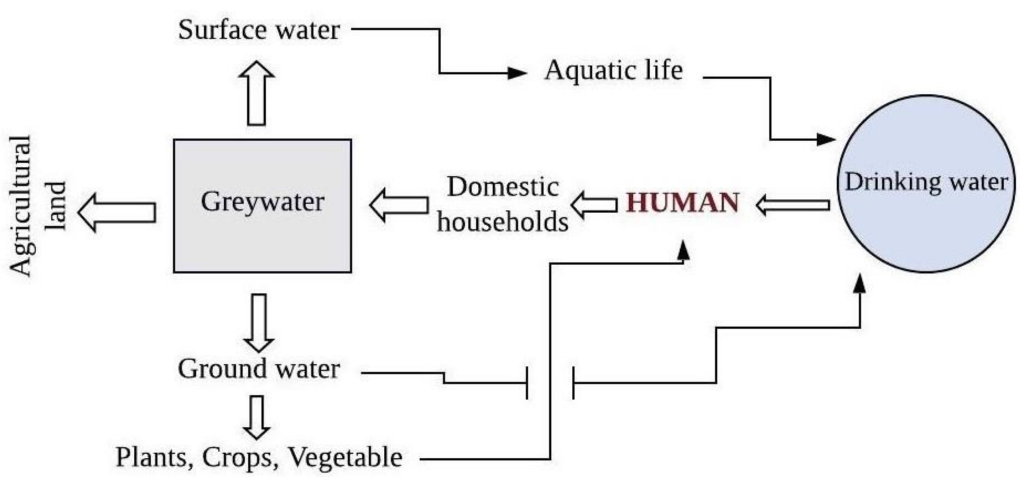


Fig. 1. Route of pollutants from GW to human, Diagram inspired by Al-Gheethi et al., 2019b

There are several mechanisms how to treat GW. They usually involve physical, chemical and biological treatment consisting of settling, filtration, adsorption, aeration, precipitation, aerobic/anaerobic digestion, and disinfection (Donner et al. 2010). The first treatment is of physical character and consists mainly in coarse sand and soil filtration, and its primary purpose is the same as in the municipal WWTP, to remove pathogens and suspended solids from the GW. Given the fact that kitchen GW is full of grease and organics, other adsorption material such as peat or charcoal has been successfully used for the physical treatment. Chemical treatment is the second process and its goal is to eliminate P, N and heavy metals, and thus to improve the overall GW quality (Wurochekke et al. 2016).

One of the GW treatment systems is rotating biological contractor (RBC) consisting of GW storage tank, rotating biological contractor, where the influent GW flows, settling tank, possible sand filtration and disinfection unit with UV light. RBC based treatments have low maintenance and are cost effective. The removal efficiency for TSS, BOD and TKN is 94.8%, 95.9% and 74.3% (Abdel-Kader 2013).

Membrane bioreactors belong to attractive GW treatment systems. They can treat GW from the entire urban residential buildings, yet they can be used as an on-site treatment for single households. The submerged membrane bioreactor (SMBR) consist of flat plate membrane and bioreactor with space for GW coming inside using gravity forces. The whole treatment assembly is aerated at the base of the membrane and controlled by pump and float switch system. For increased effectiveness, UV lamp is installed and helping with additional GW disinfection. SMBR is an efficient treatment method able to reduce the COD, TSS, TN, TP and anionic surfactants levels with removal efficiency of 87%, 92%, 40%, 69% and 80%, respectively (Fountoulakis et al. 2016).

Another type of GW treatment mainly used for decentralized treatments is a modification of recycling vertical flow constructed wetland, named recycled vertical flow bioreactor (RVFB). Both systems can efficiently treat domestic GW, which can be subsequently used for non-potable purposes. RVFB system includes treatment and reservoir container placed on the top of each other. The treatment container contains filling material such as peat, crushed limestones and dolomite, to help GW filtration.

Once GW reaches the reservoir container it is recirculated back to the treatment container for increased performance of the filtration process. In the end of the process treated GW is pumped out of the system. The removal efficiency of COD, TSS, TP, N-NO_2, and anionic surfactants is 85%, 95%, 75%, 95% and 99%, respectively (Gross et al., 2007).

A study conducted in Israel compared several hypothetical urban GW management policies. Treatments varied depending on level of centralization and urban reuse. Two of the testing treatments involve source separation of domestic wastewater. GW is in the first treatment collected from all building units and then locally treated and reused for toilet flushing or gardening. In the second treatment, GW is collected, recycled and then reused separately at each building. As a treatment option Rotating Biological Contractor system followed by filtration and disinfection was chosen. One of the big advantages of both treatments is the low energy demand in comparison to centralized WWTP. GW does not travel long distance, therefore there is less energy required for pumping. Because of the shorter distance, there is also reduced leakage into the surrounding environment and less contamination from piping (Opher and Friedler 2016).

Decentralized GW treatments are getting more popular as they offer separation of wastewater sources. GW reuse for toilet flushing is a good solution for families as it can save thousands of gallons per year (Sahni 2012). Treated GW can be also used for agricultural irrigation, fire protection or watering golf courses and green areas in cities. GW management belongs to a low-cost water source. It recycles important nutrients and avoids the application of fertilizers, therefore its more environmentally safe and increases the agricultural production (Gisi et al. 2017). Efficient application of reused GW in agricultural and urban areas supports the conservation of natural resources and contributes to sustainable water management and its development (Kaposztasova et al., 2014).

The above mentioned GW treatment technologies are effective in improving the GW quality and using it for non-potable purposes, however there are several other options how to treat GW. Nature-based solutions (NBS) are being introduced with the intention to manage precipitation and provide water resources, reduce air, noise and water pollution, mitigate the urban heat and they can be also used as an on-site treatment for GW (WWAP 2018).

3 Green infrastructures as a part of wastewater treatment

Another popular part of water management helping to improve wastewater pollution and water cycle in cities are green infrastructures. It is a network of natural or semi natural areas, river or lakes aiming to connect, conserve and protect villages, towns and natural ecosystem functions (Benedict and Mcmahon 2001). Green infrastructure (GI) contribute to the economic and environmental sector and evaluate its benefits in a wider range. Created green areas are able to positively affect the property markets, encourage people to use more sustainable way of transportation and maintain safe places for recreation. The individual assets of GI provide variety of functions and benefits such as increasing biodiversity, mitigating pollution, reducing urban heat or improving the aesthetic value of urban areas. Among GI assets it is possible to find managed coastal zones, business and wetland parks, green roofs and street boulevards, attenuation ponds or orchards (Cole, McPhearson, and Herzog 2017).

The term “green infrastructure” is very broad, it describes green environment with the focus on protection, conservation and sustainability, however the main goal of this thesis is abatement of organic micropollutants occurring in GW, therefore the natural based solutions (NBS) can be introduced as a cost-effective part of GIs with the potential to improve water management (Nesshöver et al. 2017). NBSs can be applied in urban areas or landscape of bigger scale. They copy natural processes, help to improve human settlements, sanitation services and water-related risks. Their main advantage is the promotion of sustainable natural resource use, recycling and effective reduction of water treatment costs (WWAP 2018). The population in cities increases every year as well as the living conditions are getting worse, because of air pollution. This is one of the reasons why the introduction of NBS into cities could provide ecosystem services by creating green areas with habitats for new species. There are many types of NBS used for wastewater such as constructed wetlands, green walls, green roofs or drainage basins and all of them are suitable for urban settings (Andersson et al., 2017; WWAP, 2018; Stagakis et al., 2019).

The wastewater found in urban areas is of several sources. It can be either rainwater or urban runoff which is characterized by pollution from the air and streets. This type of wastewater has very often due to the lack of green areas in cities trouble with infiltration, and therefore overloads sewage systems and it is released into water courses. The second type of wastewater is BW and GW characterized by pollutants such as PPCPs, nutrients, organic matter, heavy metals and also DCF, MTP and BTR which are studied and described in this thesis. Wastewater containing BW and GW is also going into the sewage systems and further into a centralized WWTP unless treated differently (Raček and Havlínek 2019). Rainwater, runoff, BW and GW can all be treated with NBS in urban areas. The treatment can diminish the amount of organic and inorganic pollutants occurring in wastewaters, improve water retention in cities as well as the overall natural water cycle (WWAP 2018). Each type of wastewater needs slightly different solution based on its physicochemical characteristics. Luckily, effective adaptive management can be applied for each type of NBSs (Nesshöver et al. 2017), thus special wastewater characteristics does not affect quality of water filtration.

A study conducted in Italy compared 3 different types of wastewater treatment solutions in cities. The first solution consisted only from poplar trees representing a treatment situation of "doing nothing", the second solution involved conventional treatment so called grey infrastructure consisting of underground storage tank, from which the water can be pumped to the WWTP and a retention pond determined to store excessive rainfall water. The last solution comprised of NBS with multiple types of constructed wetlands, retention ponds, buffer tank for flood events and green open spaces. When comparing all three solutions, the poplar trees solution was certainly valuable from the biodiversity point of view, but it did not help with water management in the city. When comparing grey infrastructure and NBS, NBS performed slightly better, especially from the viewpoint of pollutants abatement. NBS supports wildlife, help to evolve new green spaces, natural habitats and improve recreation. Even though the NBS is more expensive than grey infrastructures or poplar trees, an ex post multi-criteria analysis identified NBS as the best alternative with the most benefits for stakeholders (Liquete et al. 2016).

3.1 Green Walls

As the population density in cities grows, there is a higher number of green areas offering people time to relax and manage water sources in a more sustainable way. Green walls belong to NBS helping to enhance water availability, reduce urban pollution and bring nature's potential into cities (WWAP 2018).

Buildings in cities are made of conventional material, which might be protective, but does not offer the same environmental service as the plants on the building would do. Most of the time, stone walls heat up from the sun and increase the overall temperature in the air. On the contrary, green walls, consisting of plants, sequester carbon from the atmosphere and produce oxygen via photosynthesis, when the sunlight hits the vegetative surface. A green wall is a great air conditioner as it controls humidity by its evaporation function. It provides habitat to various birds and bats species and increases the overall biodiversity. Plants are able to regulate the temperature of surrounding environment and also the temperature of their body, therefore green walls have a great potential for implementation in big cities, where they enhance the aesthetics, help the pollution and cool down the air (Andersson et al., 2017). There are also a few disadvantages related to green walls. They need to be applied on temperature resistant material, if the substrate or vegetation dries out, there is a potential risk of fire, therefore they require a special care of professional gardeners as a part of maintenance service (UNaLab 2019).

It is possible to distinguish two categories of green walls. The first category is a climbing facade. Plants in climbing facades grow from the ground, where they require high quality soil. They naturally climb up and cover the wall and the climbing frame, which construction is usually located next to the wall. Climbing facades need a lot of moisture, plants rely on natural water cycle and it takes them many years to cover the entire wall. The second category practicing controlled cultivation is a facade bound system, which uses special panels along the wall for plant support, irrigation and nutrient supply, to improve the overall performance (UNaLab 2019).

Green walls help with the reduction of BOD, emerging contaminants, TSS, N and P from GW, but it is necessary they are properly designed. *Carex appressa* is a grass-like plant with high potential to abate N from GW, however, the removal efficiency can vary at certain temperature and watering conditions (Fowdar et al. 2017). For this reason, it is essential to select combination of substrate, plants fitting the seasonal changes and GW characteristics.

3.2 Constructed wetlands

Constructed wetlands (CW) are a system of plants and microorganisms integrated into the water environment, which can be used as a type of non-conventional wastewater treatment. It is an example of NBS trying to utilize the natural function and biodiversity of wetlands, so it can treat surface water containing variety of contaminants (Stagakis et al., 2019). CW are able to treat stormwater and wastewater coming from urban areas, agricultural wastewater and also industrial wastewater. It can also treat water coming from effluent stream of primary or secondary treatment of WWTP as this water contains micropollutants as well. The treated water is often collected and used for irrigation purposes (DuPoldt et al. 1996).

The CW beds are usually filled some gravel, sand, rock, organic material and they are planted with vegetation. Substrate is very often saturated with water causing oxygen-poor condition, defining growth of only certain plant species. Both, higher plants and algae plays an important role in vegetation of CW. Plants are non-woody, their roots are submerged in the substrate and the upper part of the body is emerging from the water. A good example of aquatic plants that are placed into the CW system are cattails (*Typha spp*.), common reed (*Phragrnites*) or bulrushes (*Scirpus*).

There are also many types of CW in terms of flow. They can have free water surface flow reminding open natural marshes, subsurface flow or it can be combined.

· **Horizontal Subsurface Flow (HSSF):** CW with HSSF are typical with water flow coming horizontally under the gravel bed surface from the inlet to the outlet of the system planted with the typical wetland vegetation (Stagakis et al., 2019).

· **Vertical Flow (VF):** CW involving VF usually contains sand and gravel beds. Water is treated as it flows from the top through the plant roots to the bottom of the system, where is drained out (Stagakis et al., 2019).

The subsurface flow is preferred for GW treatment, because there are better chances to avoid health risks connected with water contamination (DuPoldt et al. 1996; Gisi et al. 2015). Removing contaminants from wastewater is highly efficient in summer when biodegradable processes dominate. Each pollutant has special characteristics, thus this method is not suitable for all of them. According to a study conducted in Portugal, the concentration of carbamazepine removed from wastewater is much higher in beds planted with Typha spp. than in unplanted beds. The removal efficiency can be even more improved by presence of light expanded soil aggregates (LECA) served as a solid matrix (Dordio et al. 2010). Discharged water always has to meet certain criteria in terms of quality, however if they are not met, vegetation and soil can be replaced with a different type able to increase the removal efficiency, or the filtration time can be extended (Stagakis et al,, 2019).

3.3 Green roofs

Green roofs are manmade vegetative structures on the top of buildings in cities and towns minimizing the adverse effects of urbanization. They are getting more common as they have the benefits of thermal, noise and fire isolation, and they are also very valuable from the aesthetic perspective (Gisi et al. 2017). If they are properly designed and installed, they can be used as roof terraces, roof gardens, heliports or car parks. Among above mentioned benefits, green roofs can be also contributory in wastewater management, an increase of biodiversity and in providing energy efficient urban habitat.

During the rainfall event, green roofs can store water due to the implemented substrate with adsorptive characteristics. They are heavily planted with vegetation providing shade, which has a beneficial cooling effect. Plants also help to reduce carbon in the air and transpire water, therefore, along with the substrate, they contribute to energy conservation and storm-water management. The last couple of years, green roofs have been also used for wastewater, GW and rainwater filtration. With the right adsorbent, they are able to reduce the amount of nutrients and pollutants occurring in the incoming water. Treated water is a great source for flushing or irrigation (Kuoppamäki and Lehvävirta 2016; Piscitelli et al. 2018). Every green roof needs to meet some environmental standard such as hygiene, health, noise or environmental protection, and their follow up controls should be determined within the planning process (Raji et al., 2015; Šenfeldr *et al.*, 2019).

It is possible to distinguish three types of green roofs. In Table 4 there is possible to observe different characteristics of intensive, semi-intensive and extensive green roofs. The table shows the level of maintenance, irrigation processes, usage, vegetation type, and economical perspective of a particular green roof.

(1) Intensive green roofs: they usually require high maintenance and subsurface irrigation of planted vegetation. The depth of the substrate is about 30 cm and it is accommodating many plants, shrubs and small tress. Intensive green roofs are similar to roof gardens in ancient world. They are found in the wealthier areas, where they decorate hotels and expensive houses and where they need high investments and high-quality management (Oberndorfer *et al.*, 2007; Raji et al., 2015)

(2) Semi-intensive green roofs: The substrate layer in this roof is about 15 to 30 cm deep. This type of green roof is good for walking. Planted vegetation such as herbs and shrubs are not high maintenance and do not require irrigation activity (Raji et al., 2015; Šenfeldr *et al.*, 2019)

(3) Extensive green roofs: A layer of the substrate is approximately 20 cm, which is slightly thinner than in intensive green roofs. There is no irrigation involved, therefore the planted vegetation also differs. It usually includes plants able to resist dry and wet conditions. A typical example of vegetation for extensive green roof are moss, herbs, sedums and low maintenance plants. Extensive green roofs require less plant care and management as the vegetation consist of low maintenance species (Oberndorfer *et al.*, 2007; Raji et al., 2015; Šenfeldr *et al.*, 2019)

Not only there are more than one option to choose from when considering building a green roof, but there are also multiple factors affecting the function of green roofs. Factor such as type or density of vegetation, respiration and transpiration processes among plants, water content, substrate, climate factors, they all have an impact on green roof's performance (Raji et al. 2015). Extremely high temperature in summer or very low temperature in wintertime might limit the plant growth of certain species, thus it is important to select the best vegetation able to serve all functions of the green roof. Unfortunately, there are no best plant species suitable for green roofs. Bryophytes and algae can play an important role as facilitators of vascular plants, and underground plants could be significant in terms of mycorrhizae and its symbiotic association. Any vegetation can be a good fit, when it is able to meet all the green roof requirements and resist extreme weather conditions (Oberndorfer et al. 2007).

Besides vegetation, substrate is one the most important feature in green roofs as well. It defines its function as it forms the base for vegetation and a filter for water. The green roof substrate should be porous and contain some organic and inorganic material. The inorganic portion is usually higher in content than the organic one (Oberndorfer et al. 2007). As an example of organic material in green roof substrate can be mentioned coco-peat, known for its higher sorption capacity being able to prevent leaching. The inorganic content of the substrate can involve LECA, sand or vermiculite, which can improve water holding capacity (WHC) of the roof. Green roofs are found on the top of buildings and are exposed to extreme weather conditions such as drought or strong rainfall, thus it is important to have substrate with high water holding capacity able to store water in such weather (Vijayaraghavan and Badavane 2017). Another example of substrate component are poultry manure and sawdust. Both ingredients represent relatively affordable options with high WHC. They can improve the growth of vegetation, thus also the carbon sequestration and filtration abilities (Grassi et al., 2017).

Table 4

Main characteristic of extensive, semi intensive and intensive green roofs

	Maintenance	Irrigation	Plants	Height	Costs	Use
Extensive Roofs	Low	No	Moss, Sedum, Herbs, Grasses	6-20 cm	Low	Ecological Protection Layer
Semi-Intensive Roofs	Periodically	Periodically	Grass, Herbs, Shrubs	12-25 cm	Middle	Designed Green Roofs
Intensive Roofs	High	Regularly	Lawn, Perennials, Shrubs, Trees	15-40 cm and more	High	Park Like Garden

References: Raji et al. 2015

4 Biochar in wastewater management

One option how to reduce the concentration of organic contaminants in GW and how to make it less susceptible to any type of health risks is to use an adsorbent. For the purpose of this thesis, carbonized biomass called biochar was chosen as a potential sorbent. Biochar is environmentally safe and has the potential for further implementation in green projects focusing on pollutants abatement.

More than one definition can be used to characterize biochar, but The International Biochar Initiative has agreed on a common definition for biochar:

"*Biochar is a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment. Biochar can be used as a product itself or as an ingredient within a blended product, with a range of applications as an agent for soil improvement, improved resource use efficiency, remediation and/or protection against particular environmental pollution, and as an avenue for greenhouse gas (GHG) mitigation"* (IBI 2015).

4.1 Biochar production

Biochar is a carbon-rich product made from material of biological origin such as wood, manure, rendering waste or leaves (Mc Carl et al. 2009). It is produced under a wide range of conditions, therefore its characteristics and chemical properties are unique and vary (J. Amonette and Joseph 2009). Even though the characteristics of every type of biochar slightly differ, the major elements are the same, only with different proportions. Fibrous biomass consists mainly of cellulose, hemicellulose, lignin with small amount of organic material such as fats, fatty acids, phytosterols and inorganic minerals among them are nitrogen, phosphorous, potassium, sulphur, chlorine or some transition metals (Brown 2009). Parameters as heating rate, the highest treatment temperature (HTT), reaction residence time, pre-treatment activities and post-treatment activities, can all change biochar physical and chemical properties (Downie et al. 2009).

The most typical production is pyrolysis, irreversible thermochemical decomposition, a process of heating carbon in a closed container under oxygen starved conditions, however, a variety of other thermal degradation processes can be used to make biochar including hydrothermal conversion, torrefaction, gasification and various permutations (J. Amonette and Joseph 2009). Pyrolysis is possible to classify into two categories, where the first one is fast pyrolysis characterized by its fast heating time lasting less than 10 seconds and temperature between 400˚C and 550˚C. The second category is slow pyrolysis, which uses lower temperature and slower heating time. Biomass is being processed from 30 minutes up to several hours. Slow pyrolysis is characterized by higher and lower biochar yields (Mc Carl et al. 2009). Biochar is a result of solid phase reactions, where the volatilized biomass leaves behind primary biochar. During pyrolysis, there are some additional products created on the top of biochar such as gas or condensable vapors, which produce non soluble tars and pyroligneous acid. All additional products are present in a different quantity depending on the biomass composition and pyrolysis condition (Brown 2009).

As it was mentioned biochar is derived from several feedstock materials. Each material is unique and sets the characteristics for future biochar. The thesis will focus on two types of biomass. The first biomass is hard wood (spruce) and the second one is a wetland plant (*Typha*).

4.2 Biochar characteristics

The origin of biochar is connected to areas in Amazon Basin, where is incorporated in Terra preta soil. Terra preta soil are highly fertile, productive and sustainable Amazonian dark earth. It helps sequestering atmospheric carbon dioxide and keeps it in the soil for a long time (J. E. Amonette and Joseph 2009). Civilizations in Southern American started to use biochar as a soil amendment for efficient agriculture more than 10 000 years ago. Organic carbon can improve soil WHC and nutrient availability (Groot et al., 2016).

Biochar can be applied in agriculture as a soil amendment, in water management for water purification or it can be used for gas cleaning, metallurgical industries and cooking (Mc Carl et al. 2009). Its properties and production are very similar to charcoal, but there are some differences necessary to distinguish. Both materials are produced by pyrolysis, however, charcoal is produced from animal and vegetable matter in special kilns made for heating, and as a material it is used as a fuel (J. Amonette and Joseph 2009). Because biochar has the ability to store C in soil, and it can improve its condition and productivity, it is produced specifically for soil application. More C in soil usually results in increased plant growth and enhanced removal of CO_2 from the atmosphere, which helps mitigate climate change (Woolf et al., 2010). Application of biochar in soil has several valuable outcomes positively affecting agricultural economics. Due to its longevity, biochar can remain in soil for a very long time and it does not need to be applied annually like manure. This is one of the reasons, why soils with biochar addition avoid accumulation of heavy metals and other contaminants, which are otherwise applied regularly (Lehmann and Joseph 2009). Nowadays, its application is not only in soil, but also in water and other parts of the environment, where it adsorbs pollutants from its surroundings and improve the current state of the polluted area (J. Amonette and Joseph 2009; Brown 2009).

Biochar is also often compared to activated carbon (AC) which is another form of charcoal. The difference between the two products is their energy demand during production and adsorption, and GHG emission resulting from adsorption. AC has significantly higher energy demand during production, which multiple times exceeds biochars energy demand, however, spent AC is typically regenerated and reused, thus its energy demand can be lowered. The energy demand during adsorption has also greater values for AC than for biochar. In terms of gas production, biochar has much lower GHG emission production in comparison to AC, mainly due to its ability to sequester carbon (Alhashimi and Aktas 2018). Wood biochar is able to sequester 130% of carbon emission from WWTPs, which substantially contributes to climate change mitigation. Their adsorption capacity is very similar and depends on type of feedstock. When testing the removal efficiency of sulfamethoxazole, wood-derived biochar required twice as much adsorbent mass than powdered activated carbon, thus it can bring some uncertainty in terms its dosage and disposal (Thompson et al. 2016). The average price of biochar and activated carbon is estimated to be $5.6 and $5, respectively, suggesting there is no significant price difference between the two products, and the final price depends more on the type of contaminant being removed. Biochar represents a new cost-effective option with a good adsorption capacity, however its characteristics and future implementation must be further studied (Alhashimi and Aktas 2018).

4.3 The function of pyrolysis temperature in sorption processes

There are several physical and chemical characteristics influencing biochar and one of them is pyrolysis temperature. It is able to change biochar structure and properties in many ways. With increasing pyrolysis temperature, the overall yield, oxygen (O) and hydrogen (H) content decrease in plant derived biochar. On the contrary ash and C content rises, suggesting a high decrease in the total H/C atomic ratio. Ash content in biochar is higher, because of volatilization processes during pyrolysis (Kloss et al. 2012). When biochar loses its volatile compounds, the only structures remaining are mostly aromatic C-structures, causing in most cases the absence of negative surface charges such as -OH or -COOH (Novak et al. 2009).

Not only chemical properties, but also physical properties are affected by changing temperature during pyrolysis. Biochar's surface area generally increases as the heating process gives a rise to nano-pores, meso-pores and macro-pores in its structure. Pores are an essential part of adsorption process as they get filled with water and pollutants. Surface area can expand until the pyrolysis temperature reaches the temperature at which surface deformation occurs. Temperature deformation results in subsequent surface damages and decrease in surface area (Downie et al., 2009). Chen *et al.* (2019) in his study observed that pristine biochar pyrolyzed at 400˚C has its surface area 4.05-4.35 m^2/g. When the pyrolysis temperature in that experiment was raised to 800˚C, the structure of the biochar changed and the pores inside expanded and increased the surface area to 49.6 m^2/g. However, the effect of highly elevated pyrolysis temperature (900˚C) decreased the surface area to 39.7 m^2/g, The findings about the decrease in surface area under extremely high temperatures are in accordance with study of Brown *et al.* (2006), where biochar samples were pyrolyzed under various temperatures. The range of temperatures was between 450˚C and 1000˚C and the biochar maximum surface area was measured at 750˚C. Higher temperature causes the pores to seal off or in some cases due to rapid carbonization and gas evolution to crack, and dramatically decrease the biochar surface area.

4.4 The function of biochar pH in sorption processes

Not only that biochar pH can modify pollutants sorption on biochar, but it can also change the sorption processes in relation to production temperature and the type of the feedstock material. pH of biochar in aqueous solution vary rapidly, therefore certain types of wooden biochar with high pH can be used as an efficient liming material in agricultural (Kloss et al. 2012).

There are many factors influencing the sorption of pollutants on biochar and most of them are also in interrelation. The initial pH level of biochar can be in a range from 2 to 10 and each level has the potential to influence the sorption process differently (Kong et al. 2017). Fidel et al. (2018) found in his research that NH_4^- sorption is significantly improved with increased pH. Nevertheless, increased pH was not the only cause of the enhanced sorption, because decreasing pyrolysis temperature played simultaneously an important role. On the contrary, NO_3^- acted completely differently. Its sorption to biochar increased with decreased pH and higher pyrolysis temperature. Another example included an organic micropollutant. The effect of pH on sulfadiazine varied and changed its adsorption process. Its adsorption on biochar significantly decreased with pH rising from 2-3, then in remained stable at pH 3-6 and again decreased with further increasing pH (He et al. 2019). The pH level is different for every biochar, therefore, when adding a pollutant to a solution, it is necessary to find the perfect pH level, when the removal efficiency of the pollutant is the highest.

4.5 Adsorption of water pollutants on biochar

4.5.1 Adsorption processes

Because biochar has the ability to reduce the amount of pollutants in the environment, it is important to define the mechanism of adsorption for each contaminant as there are more than one. Adsorption can be divided into physical and chemical bonding, where the physical bonding is usually less strong. Adsorption kinetics is very dependent on physicochemical properties of chosen pollutant and biochar. The biochar maximum adsorption capacity for any pollutant is determined by porosity and pore structure, surface area and chemical structure (Brown et al. 2006). Sorption mechanism can be achieved via electrostatic interaction, van der Waals interactions, H-bonding, hydrophobic interaction or π- π electron donor acceptor interaction. Variety factors and chemical or physical reactions are able to affect the final abatement of contaminants from the environment. Temperature belongs to the most studied factors influencing the adsorption processes, therefore during most experiments, the temperature is set at a certain value (Li et al. 2018; Patiha et al. 2016).

One of the most common adsorption processes is electrostatic interaction. The most important aspect within this type of sorption is the presence of surface charges on the selected biochar. Different ionizable functional groups on the surface of biochar allows biochar to create variety of surface charges. The capacity of the adsorption is affected by many factors such as pH in the medium or by ionic strength. A change in the pH can cause dissociation of functional groups and a change in the overall adsorption capacity (Bernal et al. 2019). Electrostatic interactions can be distinguished into anion exchange and cation exchange. Anion exchange is an interaction between positively charged sorbents and negatively charged sorbates and cation exchange interaction happens between negatively charged sorbents and positively charged sorbates. Cation exchange interaction is typical for biochars as they usually carry negative charges. (Kah et al. 2017).

Another representative sorption process in hydrogen bonding. This type of adsorption belongs to stronger physical forces. Biochar containing oxygen organic groups, which increase the polarity of its surface, can act as a strong binding center for various organic contaminants. Aromatic surface of biochar is very hydrophobic and allows formation of hydrogen bond between certain organic contaminant and oxygen-containing organic group. Hydrogen bonding adsorption mechanism was, for example, detected between Perchlorate (ClO_4^-) and biochar without any surface charges (Fang et al. 2014).

There are several adsorption mechanisms related to biochar and each one of them depends on physicochemical properties of specific biochar and pollutant. The biochar's feedstock material, pyrolysis temperature and residence time, strongly influence the final adsorption mechanism (Ahmad et al. 2014).

4.5.2 Adsorption isotherms

Sorption of pollutants to biochar is usually described by the sorption affinity. Pollutant will get in touch with the sorbent (biochar) and starts to fill its pores and attach to its surface area. Each biochar has different affinity to the variety of pollutants, thus the time, when the pollutant is fully sorbed fluctuate. If the pollutant is in touch with the biochar sorbent long enough, an equilibrium between the sorbed pollutant and the pollutant in a solution is established. Every contaminant reaches the equilibrium at different time depending on biochar's and the contaminant's physicochemical properties (Kong et al. 2017; Smernik 2009).

A relationship between concentration of the sorbed pollutant and concentration of the pollutant in a solution in equilibrium is described by an adsorption isotherm. Several adsorption isotherms are used to describe the adsorption process of pollutants on biochar. The most often used isotherm models are those of Langmuir and Freundlich, which are described by specific non-linear equations. Each adsorption model is slightly different and has unique aspects and features, thus it is necessary to take those into consideration when deciding which model will be the best fit (Kong et al. 2017). Non-linear adsorption isotherms are usually more descriptive, therefore are more used in adsorption studies.

Langmuir isotherm: Langmuir isotherm is a surface based non-linear model, which is built on monolayer and finite adsorption, where the adsorbed neighboring molecules do not interact. The equation for Langmuir isotherm is as follows:

$$q_{s}= \frac{X_m b C_{eq}}{1 + bC_{eq}} \qquad (1)$$

q_s represents the concentration of a pollutant sorbed at the time of equilibrium (in mg/g), C_{eq} stands for the concentration of a pollutant in a solution at the time of equilibrium (in mg/L). X_m is the Langmuir monolayer maximum adsorption capacity and b is a constant related to the energy of adsorption (Belhachemi and Addoun 2011).

Freundlich isotherm: Freundlich isotherm is another non-linear adsorption model based on multilayer, heterogenous adsorption sites. The equation for Freundlich isotherm is given as follows:

$$q_s = k{C_{eq}}^{\frac{1}{n}} \qquad (2)$$

Where q_s stands for the for the concentration of a pollutant sorbed at the time of equilibrium (in mg/g) and C_{eq} is the concentration of a pollutant remaining in the solution at the equilibrium. k is a Freundlich constant describing the adsorption capacity of the adsorbent and n is a Freundlich heterogeneity factor, indicating the heterogeneity of the adsorbent and adsorption intensity (Belhachemi and Addoun 2011).

4.6 Biochar application in wastewater treatments

As it was already declared in the Chapter 4.2, biochar is not only a beneficial soil amendment positively affecting agriculture, but it is also used in different sectors of the environment. In 2009, it was for the first time applied in wastewater treatment system as a possible alternative adsorbent. Its distinct physical characteristics like porosity, high cation exchange capacity, surface area, texture, structure, define its ability to adsorb variety of water pollutants (Downie et al. 2009).

As an ingredient, biochar started to be incorporated into wastewater eco-treatment systems. An example of such systems is constructed wetlands. As an adsorbent it helps remediate polluted water and remove contaminants for instance metals, organic compounds, and also nutrients such as N and P (Orcid and Orcid 2019). In most cases, the ability of biochar to adsorb nutrients could be considered as bad and not efficient as they get removed from the environment. However, in areas of potential N and P losses and consequently potential eutrophication, biochar could be very beneficial as an adsorbent of the leaching nutrients and it could mitigate their impact (Major et al. 2009). In a study investigating wastewater treatment via horizontal subsurface flow CW containing only gravel as a media and gravel supplemented with biochar and *Canna* sp,, respectively, COD, TN and TP removal efficiency was compared. The CW supplemented with biochar was more effective and the minimum concentration of COD, TN and TP after the treatment was 53.5, 38.3 and 9.6 mg/L, respectively in comparison to CW with gravel media, where final minimum concentration of COD, TN and TP was 134.4, 63.7, and 15.8 mg/L, respectively (Gupta et al.,2016). Implementation of biochar into constructed wetlands could help mitigate the effect of eutrophication in water bodies as the wastewater has high influent of nutrients. It could be also a potential solution for abatement of organic micropollutants and other pharmaceutical contaminants occurring in wastewaters. In a study conducted in China, bamboo biochar was used for adsorption of fluoroquinolone antibiotic, which is frequently found in wastewaters. Fluoroquinolone adsorption affinity to biochar was significant and most of the antibiotic was adsorbed within a one hour (Wang et al. 2015). Another antibiotic sulfamethoxazole is also widely used and therefore its occurrence in wastewaters is quite substantial. Biochar was able to reduce its concentration as well, however, adsorption on biochar was concentration and pH dependent (Zheng et al. 2013). Experiments with antibiotics were carried out to obtain information on potential future low cost wastewater treatments.

Another sphere of biochar implementation are decentralized filters in households or buildings. In Ethiopia, a research including biochar and laundry wastewater has been conducted. Ethiopia, as a country with higher water demand and pollution seeks for alternative wastewater treatments that could improve the current water situation. The aim of the research was to create a filtration system treating laundry wastewater that has been collected from the local university. The filters consisted of crushed stone sand, biochar and teff straw, followed by each other. Because of biochar's high adsorption capacity, the removal efficiency was high in this system. It helped remove pollutants and reduce COD and BOD in laundry wastewater. The reused water has a great potential for gardening or flushing and it can be a great source for reducing water demand in the country (Yaseen et al. 2019).

As it was written in previous paragraphs, biochar can be implemented in several wastewater treatment systems. It can be applied in non-conventional treatment systems or NBS, and it can reduce the amount of nutrients and micropollutants in the incoming wastewater.

4.7 Biochar in green roofs

Special focus is given to green roofs in this work. As it was mentioned it Chapter 3.3, green roofs belong to NBS able to treat GW collected from buildings. They are considered as an on-site treatment with an aesthetic value. The treated water can be thereafter used for non-potable purposes such as toilet flushing or irrigation. Biochar started to be incorporated into green roofs as a filter since its addition can increase WHC and plant available water of the green roof substrate by 52% and 36 %, respectively and help the overall water retention in green roof (Farrell et al. 2016). The implementation of biochar in green roofs does not usually focuses on treatment of GW and organic micropollutants, more frequently biochar characteristics help to treat rainwater and mitigate the concentration of nutrients occurring in it. It also reduces the concentration of heavy metals and inorganic compounds from wastewaters (Gisi et al. 2017).

In a study conducted in Helsinki, biochar was used as a sorbent for P and N abatement from green roof runoff. Nutrient leaching causing water pollution was diminished by implementing biochar into the green roof. Biochar was able to reduce the annual load of TN and TP from green roofs when combined with substrate and planted vegetation and it was considered as a possible solution for the future improvement of water pollution (Kuoppamäki and Lehvävirta 2016). In China, green roof substrate with an addition of biochar helped significantly decrease the concentration of TN and COD in urban runoff in comparison to commercial green roof substrate (Qianqian et al. 2019).

Biochar in a green roof has also been used for an elimination of heavy metals and phenanthrene (an organic micropollutant) occurring in urban runoff, from impermeable surfaces and precipitation. Biochar as a substrate amendment helped with water retention and improved plant growth and filtering abilities of the green roof. The organic micropollutant phenanthrene was almost completely reduced in green roofs supplemented with biochar, suggesting biochar high potential for removal of organic pollutants. Phenanthrene adsorption on substrate with biochar and biochar/peat addition was much higher in comparison to its adsorption on substrate with volcanic rock. When comparing 6 heavy metals likely to occur in urban runoff or precipitation, biochar paired with peat also showed better adsorption abilities than volcanic rock, reducing 5 heavy metals with higher efficiency. Different types of biochar vary in porosity and adsorption capacity and can therefore have specific removal efficiency of heavy metals and organic pollutants. Consequently, it is necessary to design green roofs with special biochar mixtures, which are likely to eliminate pollutants of the treatment concern (Piscitelli et al. 2018).

There are no studies focusing on biochar in green roofs and its possibility to treat GW, however, all the above mentioned examples of its implementation indicate that biochar will have high potential for application in green roofs, and mitigation of GW pollution or other environmental risks, caused by organic micropollutants. Its implementation will mainly depend on the exact place where biochar is situated, the purpose of the future recycled GW and the inevitable biochar residues outcome (Turner et al. 2019).

4.8 Regeneration of biochar

Although there are no articles concerning the possibility of biochar regeneration, a few potential solutions how to remediate the amount of used biochar in green infrastructures still exist. Much more information is known about regeneration of AC, which has almost the same physical and chemical parameters as biochar. As well as biochar, AC is used for adsorption of organic and inorganic water micropollutants. However, as it was stated in Chapter 4.2, AC emits more CO_2 into the atmosphere than biochar, thus in order to be environmentally friendly and cost effective, it needs to be properly regenerated for its reuse (Alhashimi and Aktas 2018).

Among methods included in AC regeneration are listed thermal, hydrothermal, steam, microwave, chemical or electrochemical regeneration (Gamal et al. 2018). Thermal regeneration is effective, but higher amount of heat energy is needed for kiln processes. Chemical regeneration uses redox or acid base reactions for disrupting adsorption equilibrium as a method of AC recovery (Nath and Bhakhar 2011). Electrochemical regeneration uses a electrochemical batch reactor comprising of anode and cathode, and submerged electrode in electrolytes. This regeneration process was applied for granular activated carbon saturated with DCF. The maximum regeneration efficiency was gained when applying 20mA cm^{-2} for 5 hours. AC capacity was regenerated with 87% effectiveness (Alvarez-pugliese et al. 2019). According to Sühnholz et al. (2018), a hydrothermal treatment is also highly effective regeneration method for AC. In his research most of the pollutants were degraded from adsorption sites and the AC adsorption capacity was renewed.

The more cost-effective mechanism of regeneration, which can be also easily applied in households and does not require high management skills is stimulation of microbial growth on AC (Gamal et al. 2018). The abatement of pollutants can then happen through adsorption and biodegradation. Microbial growth will also help with the AC recovery. The process in which microorganisms use organic carbon as a source of energy and reduce the amount of sorbed pollutants from AC is called bioregeneration. The sorbed pollutants are removed from the AC adsorption sites via biodegradation due to the biological growth on AC. Bioregeneration remediates activated carbon and increases its adsorption capacity, but it also simultaneously degrades sorbed organic micropollutants (Nath and Bhakhar 2011). The bioregeneration is defined by microbial kinetics and adsorption characteristics of pollutants (Speitel and DiGiano 1987). Microorganisms need to have certain conditions such as optimum temperature, pH or dissolved oxygen level for efficient bioregeneration.

Although bioregeneration of AC is not well discussed Speitel and DiGiano (1987) described biodegradation of phenol from granulated activated carbon as a four phase process of microbial acclimation, rapid bioregeneration due to microbial growth, slow decrease of microbial activity and a period of low constant bioregeneration. Phenol concentration in AC after the bioregeneration rapidly decreased, suggesting its high biodegradability (Speitel and DiGiano 1987).

As previously mentioned in Chapter 4.2, biochar is considered as closely related to AC. Its application in NBS such as green roofs can also increase plant water availability and support growth of roof plants. It significantly increases the richness of total microbes by stimulating the growth of fungi, eukaryotes and anaerobes. The positive microbial activity is mainly caused by indirect effects on soil microbial biomass by improving soil abiotic factors such as N, soil pH, porosity, WHC and soil temperature (Chen et al. 2018). Such conditions could help the achievement of bioregeneration process and the biodegradation of micropollutants from biochar adsorption sites. Bioregeneration of biochar could extend its lifetime and create a cost efficient substrate amendment suitable for GW treatment in NBS. However, biochar properties as well as GW pollutants vary substantially and different behavior of microbial communities in terms of biodegradation rate was observed as well (Speitel and DiGiano 1987), therefore bioregeneration needs further research.

5 Methodology of the experiment

5.1 Material description

5.1.1 Biochar

Biochar samples for this research were obtained from the Czech Academy of Sciences. The fraction of biochar was chosen to be 0.2-0.6 mm and it was obtained by sieving. In order to compare biochars and their adsorption capacities, biochars were produced from two different feedstock biomass and under different pyrolysis temperature. Two biochar samples were produced from spruce biomass and two biochar samples were produced from wetland plant biomass (*Typha*). To distinguish the effect of pyrolysis temperature on biochars, low (350˚C) and high (600˚C) pyrolysis temperature were used for each type of biochar: The Table 5 presents symbols and total porosity for each biochar sample according to chosen feedstock material and temperature.

Table 5

Symbol, material, temperature and total porosity of biochar samples used in the experiment

Symbol	Material	Temperature	Total porosity
BCHSL	Spruce biomass	Low (350˚C)	121 mm^3liq/g
BCHSH	Spruce biomass	High (600˚C)	443 mm^3liq/g
BCHTL	Typha	Low (350˚C)	5 mm^3liq/g
BCHTH	Typha	High (600˚C)	62 mm^3liq/g

Typha and spruce biochars vary also in the concentration of basic elements in their biomass. Table 6 presents the elemental composition of chosen biochars along with their ash content, H/C and O/C ratio. Biochar produced from *Typha* contains higher concentration of inorganic compounds than biochar produced from wood-derived biomass. BCHTL contains Ca, Mg, K, Na, and P in concentrations of 38.6, 6.6, 59.4, 9.1, and 4.9 g/kg, respectively and BCHTH holds the same elements in concentration of 58.5, 9.9, 100, 15.5, and 8.3 g/kg, respectively. The concentration of Ca, Mg, K, Na, and P in BCHSL is much lower and equals to 3.4, 0.3, 1.0, 0.2 and 0.3 g/kg, respectively and in BCHSH Ca, Mg, K and P concentration is equal to 16.4, 2.85, 3.9 and 0.89, respectively. The carbon content is increasing with charring temperature changing the H/C, O/C and ash content in biochar samples, in spruce biochar more significantly that in *Typha* biochar.

Table 6

Biochar elemental composition, atomic ratio, ash content

	g/kg							% weight	
	Ca	**Mg**	**Na**	**K**	**P**	**H/C**	**O/C**	**Ash**	**C**
BCHTL	38.6	6.6	9.1	59.4	4.9	0.53	0.18	26.4	55.4
BCHTH	58.5	9.9	15.5	100	8.3	0.4	0.3	40.8	40.2
BCHSL	3.4	0.3	0.2	1	0.3	0.4	0.27	1.4	70.5
BCHSH	16.4	2.85		3.9	0.89	0.125	0.008	10.6	87

5.1.2 Organic micropollutants

Three organic micropollutants diclofenac (DCF), methylparaben (MTP) and benzotriazole (BTR) were selected for this study as representatives of compounds that commonly occur in GW, as it was mentioned in Chapter 2.2. Their characteristics including structural formula, CAS number, pKa, pH and $\log K_{ow}$ are listed in Table 3. Analytical standards of DCF (in the form of diclofenac sodium salt, purity 100%; product number: D6899), MTP (purity ≥ 99.0%; product number: H5501) and BTR (purity 99%, product number: B11400) were purchased from Sigma Aldrich (Czech Republic). Acetonitrile Honeywell CHROMASOLV™, gradient grade for HPLC, min. 99.9% was purchased from P-LAB (Czech Republic).

5.2 Analysis of water samples

High-performance liquid chromatography coupled with diode array detector (UltiMate 3000 system; Thermo Scientific Dionex) was used for quantification of DCF, MPB and BTR during all the tests. Prior to the analysis all the samples were filtered using using 0.22 µm polyethersulfone syringe filters Rotilabo (Carl Roth).

The chromatographic separation was performed using C18 Hypersil™ Gold column (250 mm × 4.6 mm; pore size: 5 µm) (Thermo Scientific, Pragolab, Czech Republic). The compounds were analyzed by separate methods. The mobile phase was a mixture of acetonitrile and 0.01 M ammonium formate-formic acid buffer (pH=3.33), in a volumetric ratio 40:60 (v/v) for MPB, 70:30 (v/v) for DCF and 30:70 (v/v) for BTR. During the analysis an isocratic flow rate of 1.0 mL/min was used. The retention time (RT) of MTP was 6.1±0.1 min and 5.5±0.1 min and 4.99±0.1 min for DCF and BTR, respectively. The limit of quantification (LOQ) of MTP, DCF and BTR was equal to 0.05 mg/L. It was established as the first lowest calibration point of their calibration curves (linear regression, R2> 0.99). The calculated value of "signal to noise" ratio (S/N) in the case of both investigated compounds was greater than 10. The limits of detection (LOD) of MPB, DCF and BTR were defined for S/N at the level of 3 and they were equal to 0.01 mg/L. The analyses of DCF were performed and confirmed at two different wavelengths, i.e., 277 nm and 283 nm. The analyses of MPB were performed and confirmed at 255 nm and 270 nm, and the analyses of BTR was confirmed at 273 nm. The data was evaluated by means of Dionex Chromeleon™ 7.2 software.

5.3 Sorption experiments

5.3.1 Determination of equilibration time

In order to find the sorption equilibrium of micropollutants (sorbate), a solution containing biochar and a small amount of sorbate had to be prepared for each type of biochar and micropollutant. Prepared solutions were shaken on a horizontal lab shaker for a given reaction time, filtered and analyzed in HPLC.

The solutions were prepared in 100 ml glass reagent bottles. Concentration of 0.1 g of BCHTL, BCHTH, BCHSL and BCHSH was weighed, inserted into reagent bottles and mixed with micropollutants stock solutions. The DCF, MTP and BTR stock solutions of 11.8, 9.582 and 100.05 mg/L, respectively were prepared by water dilution and by adding 1M of $CaCl_2$.

Stock solutions were properly shaken and inserted into glass reagent bottles filled with biochar samples. All samples were properly closed, tagged, wrapped in paper to protect micropollutants from photooxidation, and placed on a horizontal lab shaker for a specific number of hours. Each reagent bottle represented a different time interval. DCF samples were shaken for (1, 3, 5, 10, 25, 55, 79 hours), MTP samples were shaken for (1, 7, 22, 28, 49, 120, 144 hours) and BTR samples were on the horizontal lab shaker for (2.5, 4.5, 23 ¾ 76 ¾ and 124 ¼ hours). Two glass reagent bottles were added for each pollutant to symbolized control samples without micropollutant and biochar addition.

After a given interval, DCF, MTP and BTR samples were removed from the horizontal lab shaker. They were filtered using a 0.22 µm polyethersulfone syringe filters Rotilabo (Carl Roth) into 15ml test tubes, where the level of pH was measured. Approximately 1 ml of each sample was pipetted into small glass vial bottles. They were properly closed, tagged and inserted into HPLC system, where the concentration of micropollutants in the solution was measured.

To obtain the equilibration time, the results from HPLC were used for a graph establishment. Graphs were created by plotting the time intervals of our experiment and the C/C_0 value. C/C_0 value was computed as the concentration of DCF, MTP and BTR (mg/L) in BCHTL, BCHTH, BCHSL and BCHSH at every time interval, divided by their initial concentration in the stock solution. Final graphs were used for the equilibration time estimation.

5.3.2 Determination of adsorption isotherms

To conduct an adsorption isotherm, which is associated with equilibration concentration and a concentration of the contaminant in the liquid solution, batch adsorption tests for each of the selected organic micropollutant and biochar type were performed, and Langmuir equation (Eq.1) and Freundlich equation (Eq.2) were applied to conduct non-linear regressions.

For the DCF, MTP and BTR batch sorption experiment, 24 hours as an equilibration time was chosen based on the results from the equilibrium sorption experiments.

The batch experiment was performed in 100ml glass reagent bottles. For each of the pollutant a 100 mg/L concentration stock solution was prepared. From the initial stock solution, 100, 83, 67, 50, 25, 20, 10, 5, and 2 mg/L concentration were made by sequential dilution and inserted into 11, 100 ml volumetric flasks, with the last two representing control samples without biochar (100mg/L) and micropollutant addition, respectively. All volumetric flasks were well shaken and 80ml of the solution was poured into 11, 100ml glass reagent bottles. As the next step, 0.08 g of BCHTL was weighed and carefully added into the diluted DCF, MTP and BTR samples. Bottles were properly closed, tagged and wrapped in paper to protect micropollutants from photooxidation. Samples were placed on the horizontal lab shaker and shaken for 24 hours.

After 24 hours, samples were unwrapped, open, filtered using 0.22 µm polyethersulfone syringe filters Rotilabo (Carl Roth) and pipetted into 15ml test tubes for pH measurement. Approximately 1 ml of each sample was pipetted into a small glass vial bottle. Samples were diluted when needed. All vial bottles were properly closed, tagged and inserted into HPLC system, where the concentration of micropollutant in equilibrium could be measured. The whole experiment was repeated with BCHTH, BCHSL and BCHSH biochar.

For adsorption isotherms linear regression analysis was chosen at first to find the best fit isotherm and it was followed up with non-linear regression, as they can be more precise in terms of errors. The attention was paid mainly to Langmuir and Freundlich non-linear adsorption isotherm.

DCF, MTP and BTR adsorption isotherm were established in Statistica program using results from HPLC. A spreadsheet has been created in Microsoft Excel. The sheet contained weight (g), concentration of DCF, MTP and BTR in equilibrium Ceq (mg/L), concentration of DCF, MTP and BTR in a solution before the sorption process (mg/L), weight of sorbed DCF, MTP and BTR (mg) and weight of sorbed DCF, MTP and BTR (mg/g) for each of the 9 samples (control samples not included).The Langmuir and Freundlich non-linear regressions for DCF, MTP and BTR have been created using a method of least square for each type of biochar. The parameters X_m, b, k and n of Langmuir and Freundlich equations were estimated in Statistica program using Levenberg-Marquardt non-linear estimation method. Parameters along with the coefficient of determination are further specified in Table 7. After estimating the parameters of Langmuir and Freundlich equation, 95% confidence interval was used for creation of Langmuir and Freundlich non-linear isotherms for each biochar type representing the adsorption process. DCF, MTP and BTR Langmuir and Freundlich non-linear isotherm are visible in the Appendix of this work.

6 Results

6.1 Equilibration time

Diclofenac

DCF equilibration time is visible in the graph in Fig. 2. The graph compares pollutant C/C_0 value in time in different biochar solutions. C/C_0 value represents the amount of micropollutant in the solution at certain time and its decreasing tendency signifies increasing sorbing process.

After 79 hours, the value of C/C_0 for DCF in BCHTL was equal to 0.502, which makes it the highest out of all biochars. DCF in BCHTH had much lower C/C_0 value, when after 79 hours it was equal to 0.06. The value of C/C_0 for DCF in BCHSL and BCHSH after 79 hours was equal to 0.0013 and 0, respectively. The C/C_0 value in BCHSH was also equal to 0 after 25 hours, suggesting BCHSH best sorption capacity.

DCF in spruce and *Typha* biochar samples had slightly different C/C_0 values in time, which resulted in differences in the time of equilibrium. 24 hours equilibration time was subsequently chosen for DCF as an appropriate time for batch adsorption process.

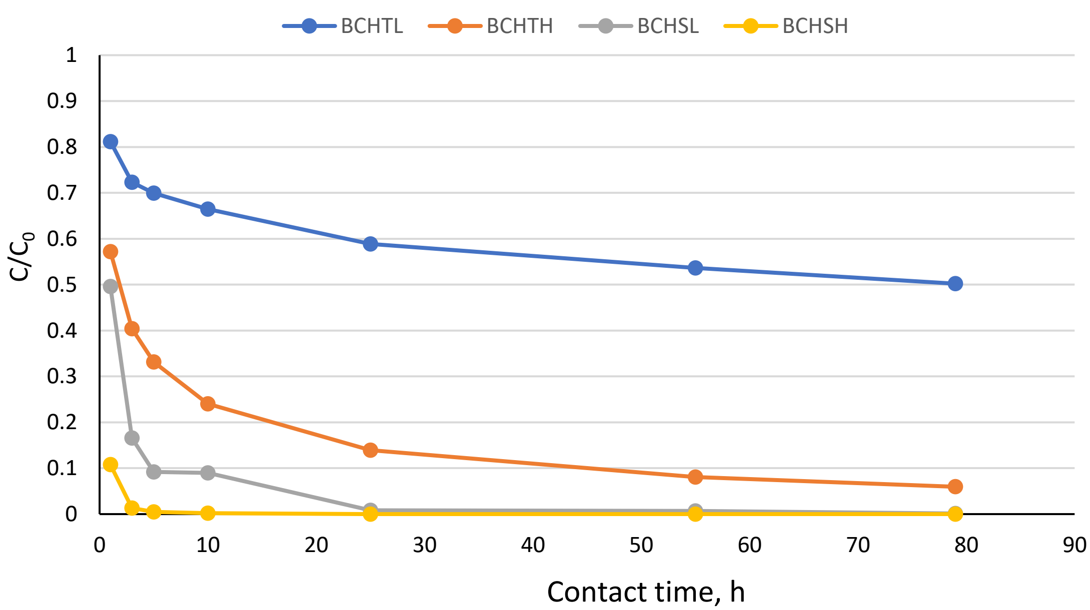


Fig. 2 Effect of contact time on DCF adsorption on biochars: BCHTL, BCHTH, BCHSL and BCHSH

Methylparaben

MTP equilibration time is presented in Fig. 3. The concentration of MTB in BCHTL was slowly decreasing over the 6 days until it reached C/C_0 of 0.044. MTB in BCHTH showed similar behavior as in BCHTL, but the C/C_0 value after 144 hours was equal to 0.039. Adsorption of MTB on spruce biochar was much faster. In BCHSL the concentration of MTP was reduced from the solution with the final C/C_0 value of 0.024 after 144 hours. In the BCHSH, the C/C_0 value was after 144 hours equal to 0 as well as after 28 hours, confirming BCHSH high adsorption capacity.

The MTP equilibration time shows similar results as the DCF equilibration time. BCHTL and BCHTH C/C_0 values tend to slowly decrease over a long period of time. This trend was perhaps caused by lower concentration of micropollutant in the solution. The MTP equilibration time was also estimated to 24 hours.

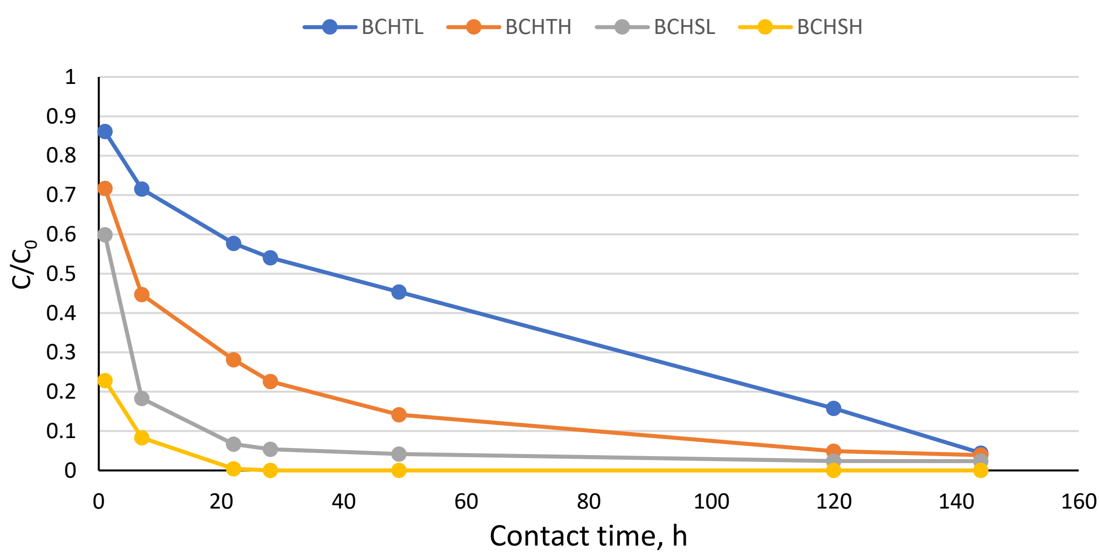


Fig. 3 Effect of contact time on MTP adsorption on biochars: BCHTL, BCHTH, BCHSL and BCHSH

Benzotriazole

As a consequence of low concentration of DCF and MTP in a stock solution and therefore their quick sorption on BCHSL and BCHSH in two previous sorption experiments, concentration of BTR stock solution was increased to 100 mg/L. BTR equilibration time is possible to observe in Fig. 4.The sorption process of MTP in BCHTL and BCHTH solution was very slow. The C/C_0 value was slowly decreasing after until 122 hours it reached a value of 0.77 and 0.73 for BCHTL and BCHTH, respectively. MTP C/C_0 values in BCHSL solution showed faster sorbing process. C/C_0 value of 0.71 was reached already after 4 ¼ hours and the final C/C_0 value of 0.42 was reached at the end of the experiment after 122 hours. The concentration of MTP in BCHSH was decreasing the fastest. The C/C_0 value after 2.5 hours was equal to 0.36 and after 124 ¼ to 0.14.

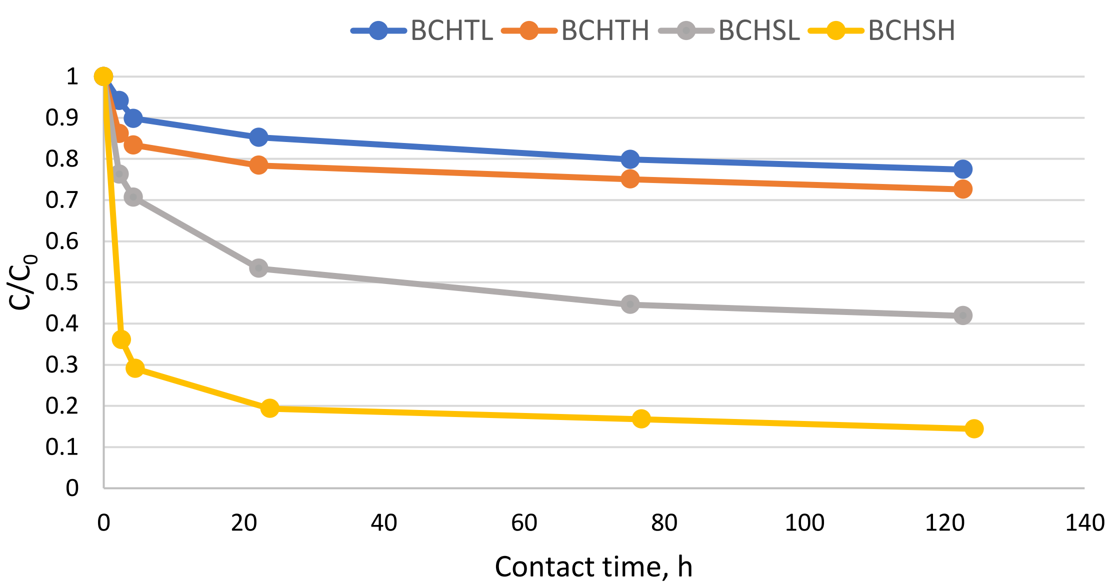


Fig. 4 Effect of contact time on BTR adsorption on biochars: BCHTL, BCHTH, BCHSL and BCHSH

6.2 Comparison of biochar adsorption capacity

The comparison of DCF adsorption process within each biochar solution is visible in Fig. 5. During the batch experiment, BCHSH showed the best adsorption capacity while the BCHTL showed the lowest capacity. The maximum concentration of DCF sorbed on BCHSH, BCHSL, BCHTH and BCHTL was equal to 49, 42.2, 13.87 and 1.54 mg/g, respectively. DCF adsorption efficiency had an overall increasing tendency with increased DCF concentration in the solution, except 3 decreasing trends in BCHTL solution and 1 decreasing activity in BCHTH solution. Decreasing tendency might has been a result of desorption. If these trends persist, additional tests such as increasing the concentration of micropollutant in the solution could improve the results. DCF also showed enhanced sorption on BCHSL at its higher concentration in a solution at the time of equilibrium. Increased sorption could have been a consequence of correlation between decreased pH of the solution and DCF pKa. Due to hydrophobic reactions, DCF can occur in undissociated form and with decreased solubility. Decreasing pH can cause DCF precipitation and thus its increased sorption on BCHSL, however further tests are needed for verification.

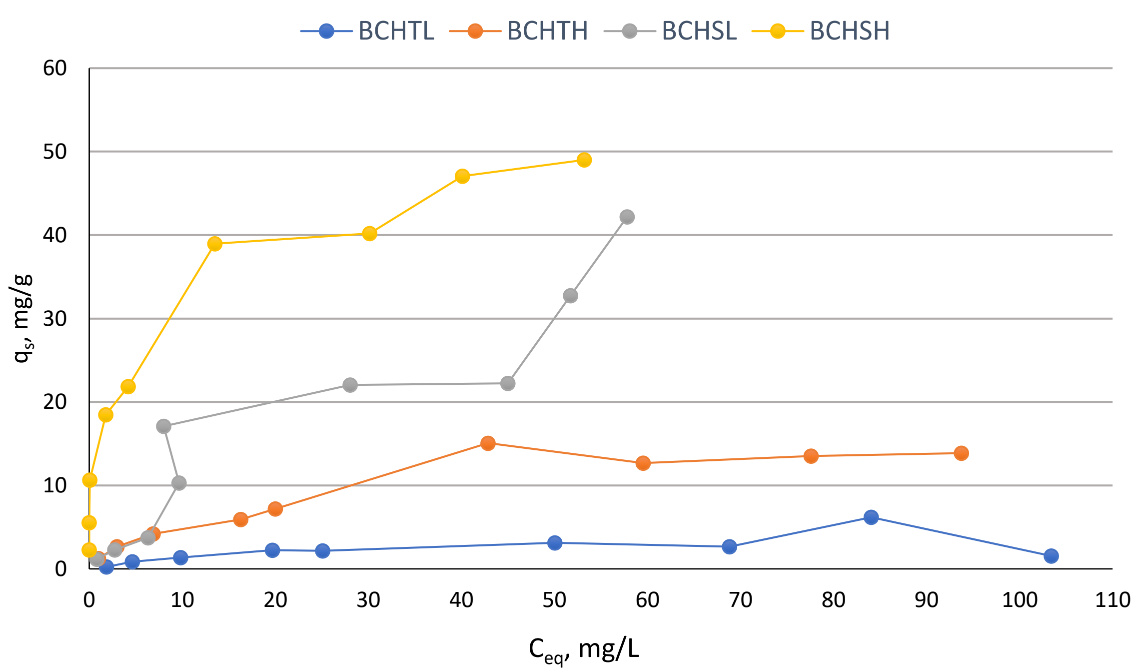


Fig. 5 DCF Adsorption comparison between BCHTL, BHCTH, BCHSL and BCHSH

The comparison of MTP adsorption processes within each biochar solution is visible in the Fig. 6. The adsorption of MTP to biochar is analogous to the DCF. Biochar made from spruce biomass at high temperature had the best adsorption capacity and was able to sorbed the highest concentration of MTP from the solution. The maximum concentration of MTP reduced from the BCHSH, BCHSL, BCHTH and BCHTL solution was 81.22, 45.75, 30.27 and 12.66 mg/g, respectively. Likewise, in DCF sorption process, MTP registered decreasing sorption tendency in BCHTL and BCHTH biochar solution in the end of the batch experiment. Decreasing trend could be caused by desorption processes in the solution and additional tests might improve the outcomes.

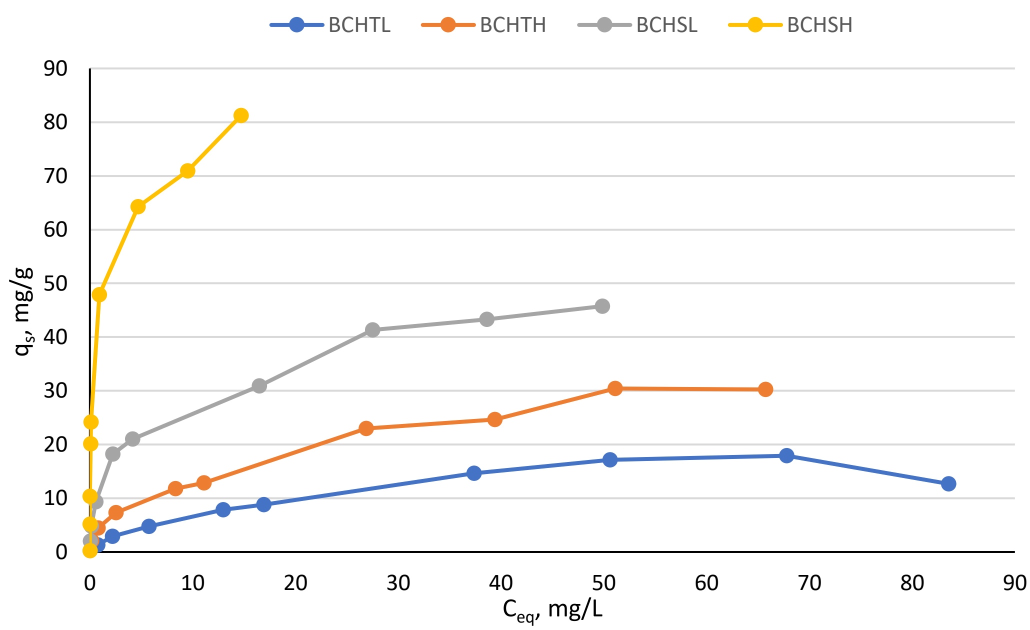


Fig. 6 MTP adsorption on biochars BCHTL, BCHTH, BCHSL and BCHSH

Lastly, the comparison of BTR adsorption processes between BCHTL, BCHTH, BCHSL and BCHSH is shown in Fig. 7. The sorption tendency is very comparable to DCF and MTP. The best adsorption capacity showed spruce biochar produced under high pyrolysis temperature (BCHSH) and was followed by BCHSL, BCHTH and BCHTL, respectively. The maximum concentration of BTR sorbed to BCHSH, BCHSL, BCHTH and BCHTL was equal to 79.87, 47.41, 25.77 and 13.08 mg/g, respectively.

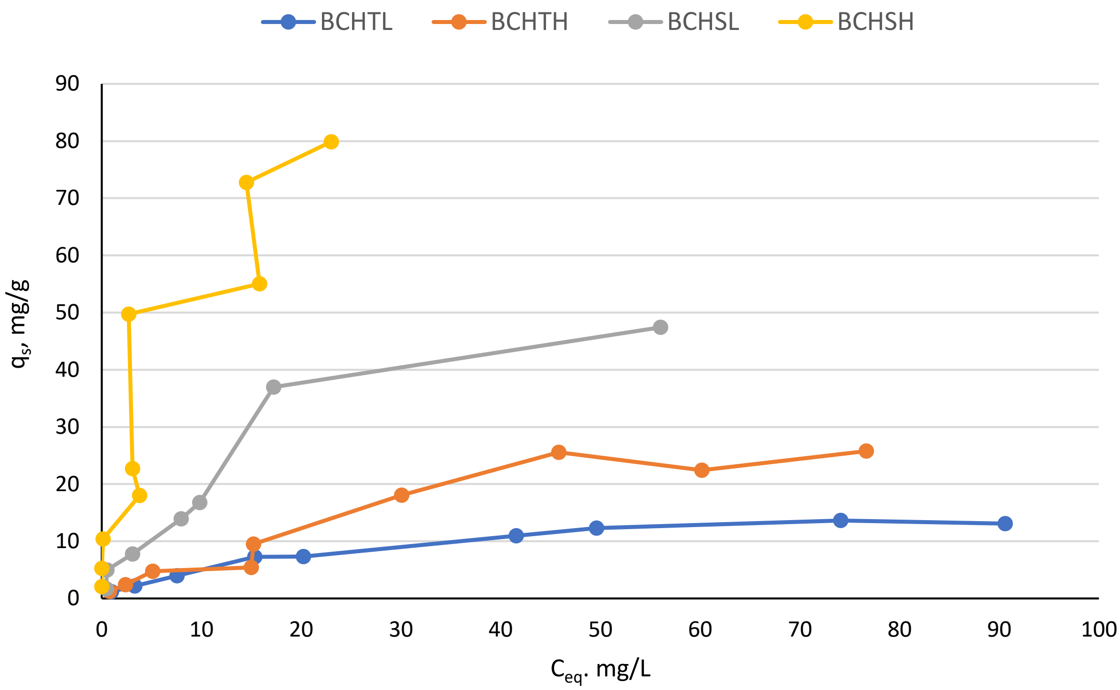


Fig. 7 BTR adsorption on biochars BCHTL, BCHTH, BCHSL and BCHSH

6.3 Micropollutants affinity for BCHSH

Because BCHSH was biochar with the highest adsorption capacity, a comparison of DCF, MTP and BTR assessing the adsorption affinity to BCHSH was established. The comparison is visible in Fig. 8. The comparison shows relatively good sorption of DCF. BCHSH was able to reduce DCF by 49.00 mg/g, however, DCF belongs to micropollutants with lower affinity to BCHSH. BTR showed much better affinity to BCHSH in the experiment. The concentration of BTR sorbed to BCHSH was equal to 79.870 mg/g, which was almost 30 mg/g more than DCF, and lastly the concentration of MTP sorbed to BCHSH was 81.22 mg/g, which made MTP a micropollutant with the best affinity to BCHSH.

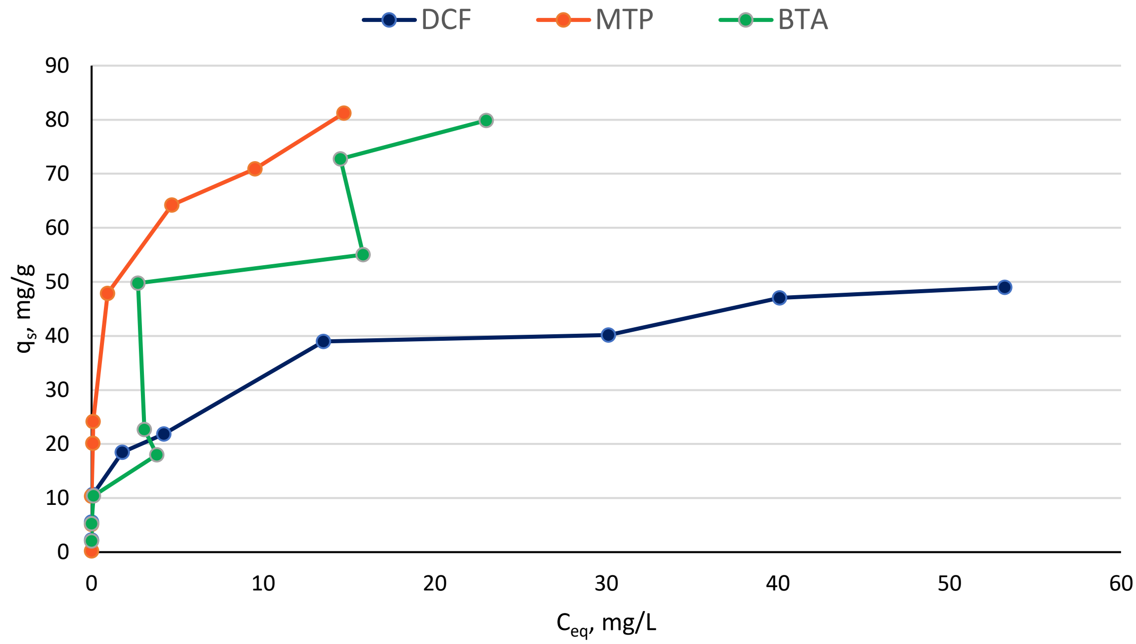


Fig. 8 Comparison of DCF, MTP and BTR sorption affinity to BCHSH

6.4 Adsorption isotherm

The parameters describing the DCF, MTP and BTR adsorption isotherm are shown in Table 6. The table contains partition/distribution coefficient (K_d) for DCF, MTP and BTR along with its coefficient of determination and X_m, b, k, n and R^2 parameters for non-linear Langmuir and Freundlich equation. All parameters are shown for DCF, MTP and BTR. The best model fit was determined based on the value of R^2. The higher the coefficient of determination is, the better fit for a certain model it makes. DCF showed very high and similar R^2 results in BCHTL, BCHSL and BCHSH for both non-linear models symbolizing their good fit, however, the better fit would have Freundlich isotherm model. In BCHTH, DCF preferred Langmuir nonlinear isotherm model. The MTP coefficient of determination showed the highest value for Freundlich non-linear isotherm model in BCHTH, BCHSL and BCHSH and in BCHTL it had better fit for Langmuir one. When comparing BTR R^2 results, micropollutant preferred non-linear Langmuir model in the BCHTL and BCHSL and non-linear Freundlich model. in BCHTH and BCHSH.

The K_d coefficient signifies the micropollutants reduction from the solution and varies across all biochars. It was increasing for all micropollutant from BCHTL, BCHTH, BCHSL, and BCHSH, respectively. The highest K_d values were found for MTP, BTR and DCF in BCHSH, respectively, which corresponds with their adsorption affinity. The K_d values were equal to 6.73 (L/g), 3.95 (L/g) and 1.15 (L/g), respectively. The lowest K_d was detected for DCF in BCHTL with a value of 0.04 (L/g), followed by BTR and DCF in BCHTL and BCHTH with its K_d value of 0.19 (L/g) and 0.19 (L/g), respectively. The meaning of the Langmuir and Freundlich parameters is described in the Chapter 4.5. The X_m appeared to have increasing trend from BCHTL, BCHTH, BCHSL to BCHSH for all 3 micropollutants. The only exception was visible for DCF in BCHSL, where the value of X_m (71.75 mg/g) exceeded BCHSH. The k constant showed increasing tendency for all 3 micropollutants in each type of biochar as well. The value of the constant was the lowest in BCHTL and reached the highest value in BCHSH.

Table 7

Parameter of Freundlich and Langmuir non-linear regression for DCF, MTP and BTR in each type of biochar solution. Kd coefficient and it coefficient of determination for DCF, MTP and BTR

		Linear		Non-Linear					
				Langmuir			Freundlich		
		K_d (L/g)	**R^2**	**b** (L/mg)	**X_m** (mg/g)	**R^2**	**k** (L/g)	**n**	**R^2**
DCF	BCHTL	0.043	0.139	0.053	4.2	0.701	0.242	1.479	0.896
	BCHTH	0.193	0.561	0.041	18.4	0.964	1.945	2.194	0.947
	BCHSL	0.666	0.867	0.017	71.4	0.944	2.029	1.408	0.95
	BCHSH	1.145	0.455	0.239	50.3	0.965	17.049	3.728	0.984
MTP	BCHTL	0.248	0.412	0.059	19.8	0.953	2.796	2.417	0.925
	BCHTH	0.574	0.727	0.053	39.1	0.985	4.686	2.18	0.994
	BCHSL	1.14	0.573	0.229	46.2	0.981	12.303	2.899	0.995
	BCHSH	6.728	0.434	3.602	73.2	0.964	43.476	4.285	0.991
BTR	BCHTL	0.191	0.582	0.043	17.3	0.995	1.848	2.179	0.981
	BCHTH	0.408	0.833	0.018	46.6	0.969	1.721	1.555	0.960
	BCHSL	0.998	0.668	0.044	68.9	0.972	5.783	1.868	0.957
	BCHSH	3.953	0.689	0.134	98.8	0.914	18.341	2.177	0.926

6.5 pH of solutions after batch experiments

The results of pH measurements from the batch experiment are visible in the graph in Fig. 9. The pH measurements were made for all chosen organic micropollutants, but the graph shows only MTP as all results were very similar. The graph includes pH mean, median, minimum and maximum pH values. The mean pH value for the samples before the batch experiment was 5.86. The pH has changed after adding biochar and shaking samples for 24 hours. The mean pH value for BCHTL, BCHTH, BCHSL and BCHSH after the 24 hours batch experiment was 7.58, 8.93, 4.56, and 8.33, respectively.

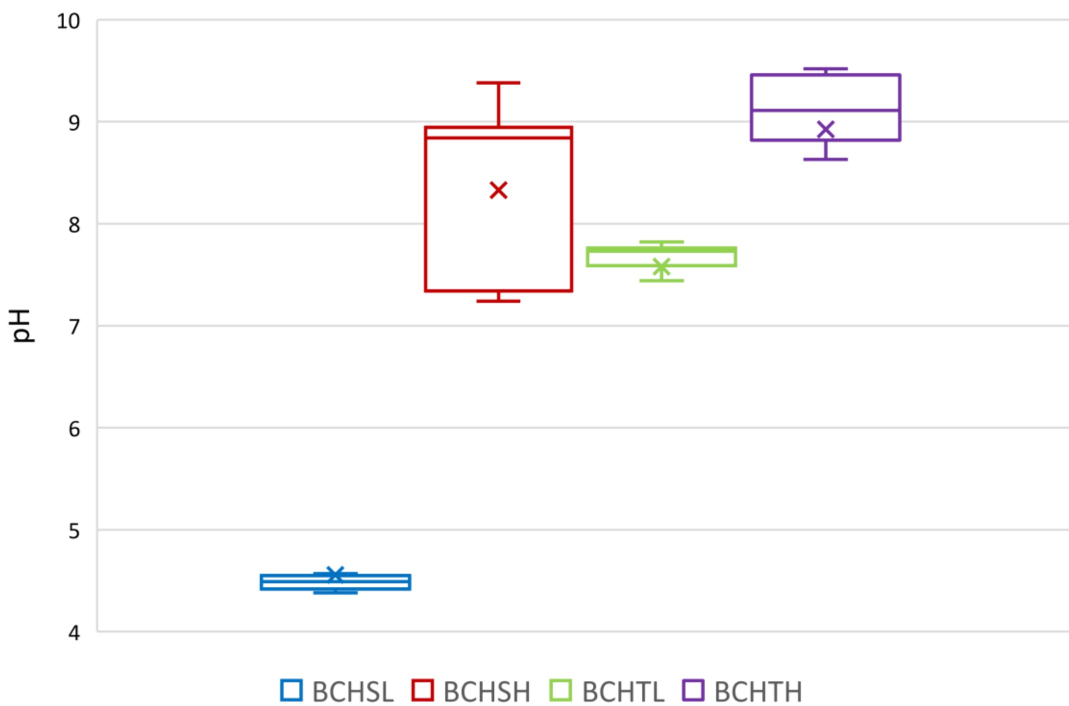


Fig. 9 pH values of the solution after batch experiment, including mean, median, minimum and maximum value

7 Discussion

7.1 Equilibration time

The time of equilibrium for DCF, MTP and BTR was estimated for 24 hours. Finding the equilibrium for micropollutants sorbed on biochars was challenging as the sorption process for DCF and MTP was very fast for spruce biochar samples and had slow decreasing tendency for *Typha* biochar samples. The spruce biochar proved to be a very efficient adsorbent in comparison to the *Typha* biochar, therefore the decision to increase BTR concentration in stock solution in the last equilibrium sorption experiment, helped with equilibrium time estimation. Higher concentration of micropollutant in the stock solution made the equilibration time of 24 hours more visible, and thus for the future research could be applied for all samples.

7.2 Comparison of biochar adsorption capacity

When comparing the adsorption capacity of all biochar types, the spruce biochar produced at 600˚C showed the highest adsorption capacity for all studied micropollutants DCF, MTP and BTR. Biochar produced from wood biomass under high pyrolysis temperature has high potential for storing C. The biomass is getting highly carbonized and the number of aromatic circles increases along with the increasing pyrolysis temperature (Zheng et al. 2013). Due to the higher carbon content in its biomass, wood-derived biochar has the capacity to sorb organic pollutants (Domingues et al. 2017). In the Table 6, it is visible how the carbon content of spruce biochar increased with higher pyrolysis temperature. Its ability to sorb organic pollutants therefore increased accordingly. Consequently, implying the higher C content, the H/C and O/C ratio in BCHSH was due to the high temperature also extremely low and demonstrated much better sorption capacity. These results are in accordance with Li *et al.*, 2013, in his study the H/C and O/C ratio was also decreased by increased charring temperature, which was associated with dehydration and creation of aromatic structures. As an example of biochar dehydration, it can be mentioned spruce biochar H/C ratio after low temperature and high pyrolysis temperature. The H/C ratio in spruce biochar produced at 350˚C was 0.4 and decreased after undergoing pyrolysis at 600˚C to 0.125.

Biochar is porous material and it enlarges its porosity and surface area with increased level of carbonization (Zheng et al. 2013). When comparing each type of biochar in our experiment, BCHSH showed the highest volume of micro-, meso- and macropores in its structure. The major difference was noticeable when comparing the total pore volume in spruce and *Typha* biochars with BCHTL having 5.0 mm^3liq/g and BCHSH having 443 mm^3liq/g of total pore volume. The increased porosity also corresponds with surface area. BCHSH showed the highest enlargement in surface area up to 564 m^2/g, which is substantially higher than the other biochar samples. Pores are a necessary part of adsorption process, as they make the space for pollutant adsorption. Increasing temperature changes the biochar pores structure and also pyrogenic nanoporosity, which is the internal porosity produced at higher temperatures. Pyrogenic nanoporosity extends with higher temperature and is mostly responsible for sorption of pollutants. (Gray et al. 2014). The impacts of increased biochar carbon content and porosity are visible on the higher K_d value of MTP in BCHSH shown in Table 7. K_d value describes the proportion of substances in solid phase versus proportion of substances in liquid phase of the solution, when the system is in equilibrium. Increased K_d values symbolizes improved micropollutant abatement from an aqueous solution, thus better sorption capacity of the sorbent (Styszko 2016; Žižlavská and Hlavínek, 2020).

In all experiments BCHTL and BCHTH showed slightly different results in comparison to spruce biochar. Their equilibration time and adsorption isotherm parameters differed, and adsorption capacity was much lower. The carbon content of BCHTL and BCHTH was 55.4% and 40.2% of the initial weight, respectively. It is usual that biochar produced from wetland plants has less carbon content and aromatic structures are not formed so frequently, thus *Typha* biochars can be better for sorption of inorganic pollutants such as NH_4^+, Cd^{2+} or $PO4^{3+}$ (Ahmad et al. 2014; Cui et al. 2016).

Based on the results of DCF, MTP and BTR sorption on all types of biochar, BCHSH was chosen to be the biochar for the micropollutants affinity comparison.

7.3 Micropollutants affinity for BCHSH

MTP and BTR were micropollutants with the highest affinity to BCHSH in the experiment. This was supported by the value of Freundlich constant (k) and the Langmuir monolayer maximum adsorption capacity (X_m), which usually corresponds with the adsorption affinity to some degree (Belhachemi and Addoun 2011). For all studied micropollutants in batch experiments, the k reached the highest value of 43.78 and 73.2 L/g and X_m reached the highest value of 18.34 and 98.8 mg/g for MTP and BTR in BCHSH, respectively. The value of Freundlich constant was also in accordance with the Freundlich heterogeneity factor (n), which indicates the extent of sorption activity. Adsorption is considered as favorable when $n > 1$ and increases with higher n value as a result of formation of new sorption sites (Sreńscek-Nazzal et al. 2016). Based on the n parameter, MTP had the highest amount of sorption sites on BCHSH. Although DCF affinity to BCHSH was the lowest, its certain parameters such as Freundlich constant were comparable to BTR parameters and in case of Freundlich heterogeneity factor they were even greater. The reduced DCF affinity was possibly caused by DCF low pKa value in comparison to pH level after batch sorption experiment. The pH level increase can affect the adsorption processes due to changes in ionization and diminish the pollutants affinity to sorbent (Wiśniewska et al. 2014).

The MTP and BTR increased affinity to BCHSH was also confirmed by the partition coefficient K_d showing a value of 6.73 L/g for MTP and a value of 3.95 L/g for BTR in BCHSH. According to Zheng et al. (2013), the K_d value and hence the adsorption is pH dependent and sorption process can dominate at different pH levels. The results of this study showed similar pH levels during batch experiments for both pollutants and since the acid dissociation constant of MTP and BTR is very similar, without any further research it is not possible to conclude the specific reasons for MTP higher K_d value in BCHSH.

The BTR and MTP increased affinity to spruce biochar can be considered as beneficial as the occurrence of these pollutants in treated wastewater is high. According to Janna *et al.* (2011), the concentration of BTR in surface waters in UK is immense and it could lead to the occurrence of this substance in drinking water. In a study conducted in Barcelona that analyzed the occurrence of BTR in rivers, and influent and effluent streams of WWTP, it was found that removing processes in WWTP are not very efficient, in fact in certain WWTPs it is only 27%. The reasons behind the low efficiency of BTR removal from wastewater is the low $\log K_{ow}$ causing problems with its adsorption onto the suspended particulate matter during the treatment process, and also formation of new and more stable transformation compounds (Molins-delgado et al. 2017). MTP presence in waters can be also high. In fresh waters in part of Nigeria, MTP was detected in concentrations up to 1.66 μg/L. High levels were caused mainly by inefficient pollutant removal and by several pharmaceutical companies located nearby (Folarin et al. 2019).

PPCPs are released into the environment from a variety of point and non-point sources, but usually the majority comes from wastewater. As it was stated in Chapter 1, there is lack of information about specific GW and wastewater treatments with the potential to reduce the amount of organic micropollutants in it MTP and BTR higher affinity to spruce biochar could represent new technologies of organic micropollutants removal from wastewaters and mitigation of their occurrence in the aquatic environment.

7.4 Adsorption isotherm

The results showed multiple options for adsorption isotherm fit, however, non-linear Freundlich isotherm model was more common among all micropollutants. Nonlinear models have a uniform error of distribution and follow the results of batch experiment more precisely (Kumar 2006). All micropollutants with preferred isotherm fit for Freundlich non-linear model are not able to show the highest adsorption capacity of biochar, because this model does not allow its calculation. On the contrary, because of monolayer adsorption, Langmuir non-linear isotherm model is capable of showing this highest peak of adsorption capacity (Bernal et al. 2019). This difference is also visible when looking at the non-linear isotherms in the Appendix. of this work, where the non-linear Langmuir isotherms have more curved shape than the non-linear Freundlich isotherm.

7.5 pH of solutions after batch experiments

As it was mentioned in Chapter 4.3 and Chapter 4.4, the ash content in biochars pyrolyzed at higher temperatures increases, causing possible increase in pH and enabling the usage of biochar as liming material in agriculture. BCHSH and BCHTH shows this pH increase in our experiment confirming the higher ash content, when the ash content in *Typha* biochar changes from 26.4% to 40.8 % of the original weight and in spruce biochar from 1.4% to 10.6% of original weight. The results from Kloss *et al.* (2012) study shows that increased ash content in biochar under higher pyrolysis temperature is caused mainly by volatilization coupled with enrichment of inorganic compounds.

On the contrary the lower pH level in BCHSL can be caused by lower biochar manufacturing temperature and also by lower concentration of inorganic compounds (Ca, Na, Mg). Inorganic compounds are usually the source of the ash in biochars. Perez-Mercado *et al.* (2018) confirmed that spruce biochar can contain lower concentration of elements such as Na, Mg, K, Ca, Fe, P. The decreased concentration of Ca, Mg, K, Na, and P (3.4, 0.3, 1.0, 0.2 and 0.3 g/kg, respectively) in BCHSL was also detected in this study, therefore the ash content and pH level in BCHSL were lower. Another explanation for the low pH in BCHSL can be presence of aliphatic O-alkylated structures, which would normally be lost by the increased temperature and reformed into aromatic groups causing higher pH level (Li et al. 2013). BCHTL, with its average pH level 7.58, was biochar produced at lower temperature, however, it contained higher concentrations of minerals Ca, K and Mg, therefore the decrease in pH was not so significant (Domingues et al. 2017). Biochar produced from wetland plants has usually higher pH, therefore it can be used as liming material in agriculture and improve the soil productivity. Biochars derived from aquatic plants have also higher mineral content, specifically K, than any other biochars (Cui et al. 2016).

Our experiment did not involve any pH adjustments, for that reason it was not possible to say how much the adsorption affinity changes with different level of pH. However, studies conducted in different countries showed, that pH is able to affect the sorption efficiency of inorganic and organic pollutants. Change of pH modifies the charge on the sorbent and the micropollutant due to the presence of ionizable chemical groups. Different pH levels change the level of cationic fraction, which is in most cases responsible for the adsorption process (Fidel et al., 2018; Bernal *et al.*, 2019; He *et al.*, 2019).

8 Conclusions and outlook

The practical part of this work assessed the adsorption of diclofenac, methylparaben and benzotriazole on spruce and *Typha* biochar. The equilibrium time for all chosen organic micropollutants was estimated for 24 hours, even though the spruce biochar appeared to have higher sorption capacity and micropollutants were adsorbed in a shorter period of time than in the *Typha* biochar. The biochar with the highest adsorption capacity was spruce biochar produced at higher pyrolysis temperature. The adsorption capacity of other biochars was decreasing from BCHSL, BCHTH and BCHTL, respectively. BCHSH was able to adsorb the highest concentrations of micropollutants, hence it showed the best potential for its incorporation into substrates treating GW.

When comparing the adsorption affinity of diclofenac, methylparaben and benzotriazole to the biochar with highest adsorption capacity (BCHSH), DCF exhibited the lowest adsorption affinity, on the contrary MTP and BTR were attracted to BCHSH significantly more. Based on the comparison of K_d coefficient, the greatest amount of MTP concentration was reduced from the stock solution followed by BTR and DCF, respectively. MTP and BTR were chosen for this study as they represent organic micropollutants commonly occurring in GW. Their high affinity to spruce biochar could help their abatement from GW as these pollutants have difficulties with their removal in conventional WWTPs.

Physicochemical properties of biochar and micropollutants are one of the main reasons of their different adsorption capacities and rates. The pH levels were measured before and after batch experiments and showed different levels for biochars produced at high and low temperature, and also for different biochar feedstock as they contain different macroelements. Such differences play important role in designing GW treatment and need further research.

Based on coefficient of determination majority of micropollutants in our research preferred Freundlich isotherm model and only a few of them had better fit for Langmuir isotherm model. Biochar surface is a porous material and it has also heterogenous surface, where multiple adsorption sites can be formed. Because the Langmuir model is based on assumption that monomolecular layer of noninteracting molecules of pollutant is formed on the biochar surface, the Freundlich model, which is described as adsorption of pollutant on heterogenous surface, where each adsorption site is having different energy and rate (Latour 2015), is much better fit and can show the adsorption process more accurately.

The results of this thesis showed that spruce biochar produced under high charring temperature can mitigate the concentration of organic micropollutants MTP and BTR, typically occurring in GW, the most out of all studied biochar. High porosity and carbon content make biochar convenient for implementation into substrates suitable for NBS, where it can potentially treat GW containing these pollutants.

Implementation of biochar into green roofs substrates could help treat GW in universities, industrial buildings, but also households, where the separation of wastewater sources helps the efficient water usage. Treated GW could be thereafter used for non-potable purposed such as flushing or irrigation of campus park and other green areas.

Biochar could be used for the removal of multiple types of organic pollutants, however, it is important to mention that physical and chemical characteristics of biochar and pollutants play a major role in their removal from GW. GW also contains more than one organic micropollutant, thus the biochar application into the green roofs should not be underestimated as biochar can change adsorption affinity for different pollutants based on variety of factors. The type of biochar should be always considered in relation to the site and pollutants appearing in the GW at the current location. Green infrastructures with biochar addition could be a major supplement to wastewater management and help the sustainable development in cities and rural areas.

Although, this study showed interesting results in terms of biochar and its potential to be implemented into green infrastructures and adsorb organic micropollutants. Further research is necessary to address the remaining knowledge gaps and to make biochar a cost-effective product easily applicable for any kind of water treatment.

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