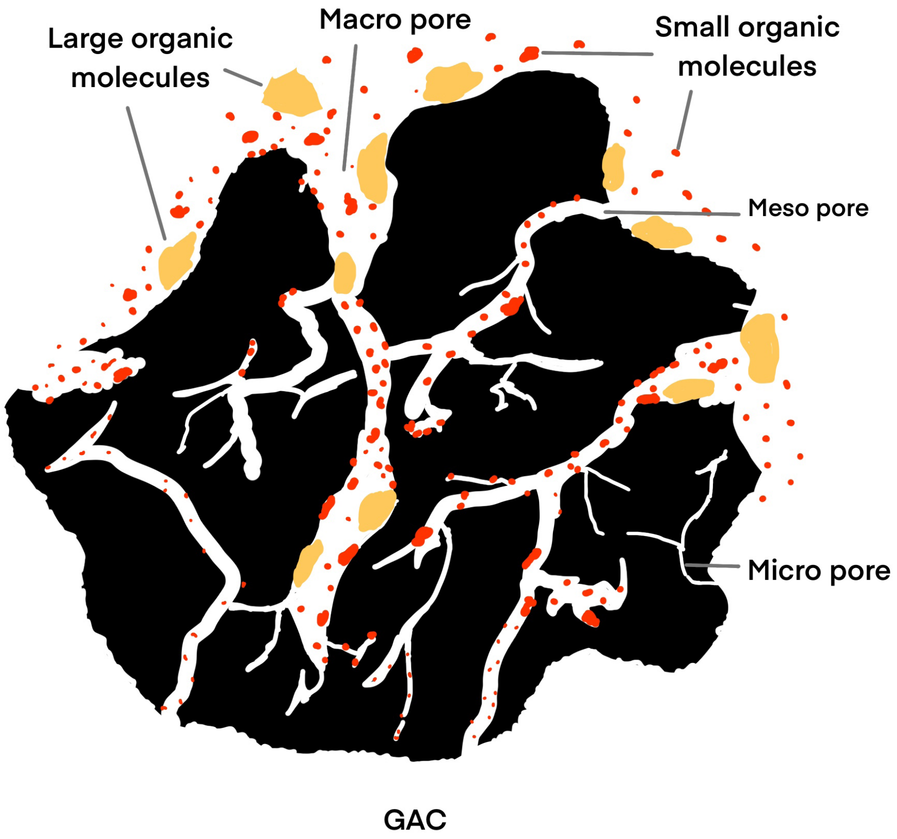
GAC filter Design Criteria for Wastewater Treatment for Removal of Organic Micropollutants

– A Literature Review



Bhargav Reddy Elavarthi

Water and Environmental Engineering
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by

Bhargav Reddy Elavarthi

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Water and Environmental Engineering
Department of Chemical Engineering
Lund University

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Supervisor: **Associate Professor Michael Cimbritz**
Co-supervisor: **Ph.D. Per Falås**
Examiner: **Associate Professor Åsa Davidsson**

Picture on front page:

Postal address
Box 124
SE-221 00 Lund, Sweden
Web address
http://www.lth.se/chemeng/

Visiting address
Kemicentrum
Naturvetarvägen 14
223 62 Lund, Sweden

Telephone
+46 46-222 82 85
+46 46-222 00 00

Preface

Firstly, I would like to thank my supervisor, Associate Professor Michael Cimbritz, whose expertise was crucial in formulating the research objectives and method. He has been highly supportive and helpful throughout my thesis and guided me through the right direction and helped me to successfully complete my dissertation.

I would also like to thank my Co-supervisor, Ph.D. Per Falås, for his valuable guidance throughout my thesis and for providing me with his insightful feedback. I would like to sincearly thank Anusha Muralidhar for her incredible support and encouragement throughout my Master's thesis. Also for her readability check on my thesis report.

Summary

Granular Activated Carbon (GAC) is nowadays suggested as a fourth (quaternary) treatment step at municipal wastewater treatment plants to remove certain chemicals and particularly organic micropollutants (OMPs). This work investigated the different factors that affect the performance of the GAC filter for the removal of micropollutants in a municipal wastewater treatment plant. This study is purely based on compiling data and analyzing different studies. Carbamazepine, diclofenac and sulfamethoxazole were chosen as breakthrough indicators. The comparisons were made by plotting bed volumes versus dissolved organic matter (DOC) and bed volumes versus empty bed contact time (EBCT) for a breakthrough criteria of 20%. A breakthrough occurs when the filter attains a breakpoint as saturation of OMPs, and the organic matter occurs. At that point, the filter cannot achieve the standard removal efficiency anymore. The pollutant concentration will then increase in the filter effluent after this breakpoint.

High pH makes the contaminants negatively charged, and activated carbon is also negatively charged, which causes repulsive force between the activated carbon surface and the OMPs. The increase in pH consequently decreases the adsorption of OMP's. The molecules are more stable at lower temperatures and tend to be adsorbed quickly. pH and temperature are essential for biological processes in the wastewater treatment plant. pH is recommended to be at a neutral phase of 6.5-7.5, and temperature is recommended at 20 – 35 ^{0}C. These conditions are perfect for organisms to thrive. Bitumen, lignite, coconut-based GAC did not show any significant difference in performance, which can be explained due to lack of data where characteristics of influent and pilot setups were diverse from the collected studies. EBCT is an essential factor for the removal of OMPs. Approximately 20 – 30 min is required for typical wastewater treatment and more than 30 min for physico-chemical where chemicals like coagulants and flocculants are used in wastewater treatment. Sulfamethoxazole showed higher resilience towards adsorption and required higher EBCT compared to carbamazepine, diclofenac.

SS and DOC play an essential role in predicting the bed life of the filter, where high DOC and SS can cause fouling (clogging of pores) through the accumulation of particulate matter by SS and buildup of biomass by DOC. The suspended solids content is recommended to be as low as possible, and DOC of less than 10mg/l is recommended for GAC filtration. The carbon usage rate for typical biological wastewater treatment is at 0.1 – 0.21 kg/m^3 due to less use of chemical treatment, and for physico-chemical treatment, it is 0.21-1.04 kg/m^3 where chemicals such as alum and iron salts are used for coagulation and flocculation to form flocs. Based on materials such as bitumen, lignite, and coconut, for US mesh size at 8x30, the effective grain size was found to be similar for all the materials at 1.25mm.

Keywords: micropollutants, activated carbon filtration, empty bed contact time (EBCT), pharmaceuticals, breakthrough curves, adsorption, PFOS and carbon use.

Popular Scientific Summary

Heading

Compilation of all the information on GAC filters and showing how parameters influence selection of design.

Main Text

Granular Activated Carbon (GAC) is nowadays suggested as a fourth (quaternary) treatment step at municipal wastewater treatment plants to remove certain chemicals and particularly organic micropollutants (OMPs). Wastewater contains many organic micropollutants that can affect the environment if not treated well. Also, the pollutants studied are not well regulated. But new standards regulating these pollutants are being investigated. From these studies, we have found that only a certain amount of concentration is allowed to be discharged from wastewater treatment plants and a standard was made.

We see an uprising in granular activated carbon as a treatment for the removal of organic micropollutants. This study shows how a GAC filter function and how to design it using the various parameters. These parameters may need to be understood to use as a design factor since some of the parameters are interdependent, explained in the study. The compiled data on these parameters and how they influence the functioning of the carbon filter is discussed in the study. The data collected undergoes meta-analysis where different values from all the papers for one parameter are compared.

This study shows that pre-treating the wastewater before it enters the GAC step is a crucial step as it determines the effectiveness and working life of the filter. We compared different pre-treatment steps to configure the most efficient and found that ozonation of wastewater is recommended. We see that ozonation helps oxidising compounds making them insoluble, and also helps in speeding up the biological processes.

There are multiple design papers and studies on the GAC filter, but very few explain the influence of parameters on the design selection. For example, we see that parameters are essential for designing the filter, but we don’t see many studies showing the correlation of these parameters. This study is purely based on compiling data and analysing this data from online sources (journals, reports, books, web articles). The findings were structured so that co-relations were made to understand the influence of design parameters on the GAC filter. These co-relations were made using specific micropollutants as the indicator compounds. However, few minor assumptions were made in this study. A table of compiled data was made using Microsoft Excel. When designing a large-scale granular activated filter for municipal wastewater treatment, this study will help the reader understand the parameters and give design values to work with.

Table of Contents

List of abbreviations

BV – Bed Volume

CBZ – Carbamazepine

CUR – Carbon Usage Rate

DCF – Diclofenac

DOC – Dissolved Organic Carbon

EBCT – Empty Bed Contact Time

EC – European Commission

EEA – European Environment Agency

EPA – Environmental Protection Agency

EQS – Environmental Quality Standards

EU – European Union

GAC – Granular Activated Carbon

GSD – Grain Size Distribution

MF – Microfilter

OMP – Organic Micropollutant

PFAS – Poly & Perfluoroalkyl Substances

SMX – Sulfamethoxazole

SS – Suspended Solids

TSS – Total Suspended Solids

UF - Ultrafilter

UWWTP – Urban Wastewater Treatment Plant

WWTP – Wastewater Treatment Plant

1 Introduction

Even with modern technology (reverse osmosis, nanotechnology, photocatalytic water purification), there is a limit on how easy it is to produce pure water due to sophistication and the high cost of operation filter technologies, but humans need water that is not likely to cause undesirable or adverse side effects (Siong et al., 2013). Safe water may contain some micropollutants, but it can still be drinkable within the regulated range. Granular activated carbon (GAC) is nowadays suggested as a fourth (quaternary) treatment step at municipal wastewater treatment plants(WWTP) to remove certain chemicals, particularly organic micropollutants (OMPs), from water.

WWTP in developing countries and countries with no laws on regulating the organic micropollutants in the effluent of treated waters is an existing problem (Rogowska et al., 2019). Since there are only a few regulated compounds, and the non-regulated ones are still being studied for better understanding. Even though few studies on non-regulated OMPs reside in wastewater parallel to regulated OMPs, the two can still be distinguished and measured. Numerous scientific works of literature and reports on non-regulated OMPs (Rogowska et al., 2019). Different outlooks and characteristics need to be considered for selecting appropriate technologies for treating various micropollutants since the implemented solution will have short and long-term effects on the resource-efficiency of a treatment plant in the future (Baresel et al., 2017). According to Baresel et al. (2017) "upgrading of the treatment plant for the additional removal of micropollutants should be integrated in a resource-efficient way" it should imply that when pretreated water flows through a GAC filter, saturation should not be achieved in an early stage due to the abundance of organic matter clogging the filters.

A great advantage of the GAC filter is that during carbon destruction/regeneration, no problematic decomposition products are generated, and micropollutants are destroyed. By choosing the right GAC based on size and origin, it can achieve maximum removal performance. Design selection includes developing criteria for GAC filtration units and their specifications based on various ranges gleaned from the compiled studies (shown in Appendix 1). There have been some studies (Rodriguez et al., 2015) giving design recommendations for the GAC filter, but few have a more comprehensive picture of how the design parameters influence it.

1.1 Objectives

The aim of this study is to investigate the different factors that affect the performance of GAC filters for the removal of micropollutants from a municipal wastewater treatment plant effluent. Also, this study will look at the questions below to find a suitable parameter range to achieve 80% or more removal efficiency through a GAC filter.

1. What is the importance of influent SS and DOC, and on what criteria? Which other parameters of the influent need to be considered?
2. Empty Bed Contact Time (EBCT) is considered a key parameter for designing a GAC filter. What ranges are suggested and why?
3. Which OMP's can be used as indicators for design?
4. What are the effects of pre-treatment processes on GAC filters?

2 Granular activated carbon filters.

Activated carbon (AC) filters have an essential role in a wastewater/drinking water treatment plant to remove certain chemicals, particularly OMPs. According to the United States, Environmental Protection Agency (EPA) activated is considered to be the best technology available to remove pollutants such as (EPA, 2018):

- taste, odour and colour
- natural organic materials
- disinfection by-products
- PFOS/PFOA
- Pesticides and heavy metals
- Endocrine-disrupting compounds

Activated carbon sources are from coal (anthracite, bituminous, lignite), coconut shells, peat and petroleum-based residues. According to Akhir, (2017) activated carbon is the most effective adsorbents for removing polluting substances in gases and liquids. Adsorption in activated carbon is due to its properties containing a sizeable surface-active area and a highly porous structure (Akhir, 2017). Activated carbons have varied surface characteristics and pore sizes distributions; these characteristics of activated carbon play an essential role in the adsorption of micropollutants in water (Ismadji and Bhatia, 2001). Higher surface area and pore volume will increase the adsorption of pollutants (Siong et al., 2013). According to Wvdhhr (2021)There are three steps in Activated carbon adsorption:

1. Adsorbate gets adsorbed onto the exterior of the carbon(adsorbent) granules

2. Adsorbate move into the carbon pores

3. Adsorbate is absorbed into the interior walls of carbon.

According to IUPAC(International Union of Pure Applied Chemistry), the pores within activated carbon are distinguished concerning pore size. Macropores have a larger than 50 nm diameter (nm = nanometre), mesopores have a diameter between 2-50 nm, and micropores range below 2 nm diameter here. As seen in Figure 1, most of the particles' pore structures follow this pattern: macropores are the large pores that open up from the surface of GAC and then branch out into mesopores and micropores. Micropores occupy about 90% of the inter-volume of GAC. GAC is made through physical activation involving oxidation and carbonization and chemical activation involving impregnating the carbon with a strong acid or a salt. Coconut shell or coal(lignite and bitumen) are used as base materials for activated carbon. Recently many studies on using various activated charcoals made from multiple materials are coming up. Even with all the different sources, the market is mainly occupied by coal and coconut shell based activated carbons. GAC comes in two forms it can either be irregular granules or extruded form. It has a large grain size compared to powdered activated carbon. The most popular GAC are the 12×40 (0.42 to 1.70mm) and 8×30 (0.6 to 2.36mm) US mesh sizes because they have a correct balance of size, contact area, and head loss characteristics for installing them in a fixed bed filter. US mesh size can be defined as the number of square openings in one square inch of a mesh screen. For example, a 8 mesh will have 8 openings while a 30 mesh will have 30 openings per square inch (ISO, 1990).

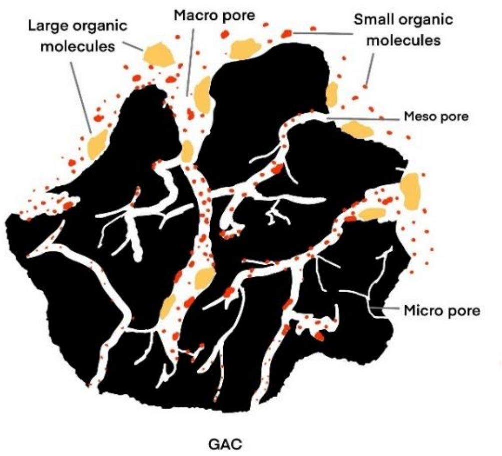


Figure 1: Pore structure within GAC showing macropore, mesopore and micropore

Two tests are conducted to check the pore volume of activated carbon: iodine and methylene blue number. An iodine number test is done where the amount of iodine adsorbed by the activated carbon indicates the pore volume (RD, GK and K, 2017). Iodine number is a measure of the micropore volume of the activated carbon and is usually equal to the total surface area of the activated carbon (RD, GK and K, 2017). Similar to the iodine number, the methylene blue number test is a measure of the mesopore volume.

Bituminous activated carbon is known to have larger surface area than lignite based carbon. Also bituminous carbon has a higher density than lignite carbon due to its densly packed micropore structure (John, 2020). Coconut shell-based AC has more micropores than bitumen, keeping it between bitumen and lignite (Schaeffer, 2008). Coconut Shell based AC is one of the most modern origin of activated carbon. It is environmently friendy and sustainable source of carbon over coal-based products, especially in acidification potential, and carbon footprint (Akhir, 2017). Some pollutants like nitrates and iron have less affinity towards carbon, due to which adsorption of such pollutants becomes difficult. Modifying GAC can help with better removal efficiencies for specific micropollutants since OMPs will have various breakthroughs and removal efficiencies depending on physical adsorption, electrostatic interactions and their relationship to the type of filter (Golovko et al., 2020).

2.1 Types of GAC filters

Currently, there are two types of granular activated carbon filters that are most often used for water filtration: fixed bed reactors and fluidized bed reactors, which can be seen in the section below.

2.1.1 Fixed bed reactors

The main focus in this study is fixed bed reactors which as shown in Figures 2 and 3. Figure 2 shows a traditional open media filter that runs on gravity, and Figure 3 shows a closed filter that uses mechanical pressure to push the water through the filter bed.

The advantages of fixed-bed rectors are:

- It can filter suspended solids

- More efficient in the removal of micropollutants

The disadvantages of fixed bed rectors are:

- High chances of clogging
- Possibilities of channelling where channelling refers to water entering the column will flow through the filter bed by the path that has the least resistance

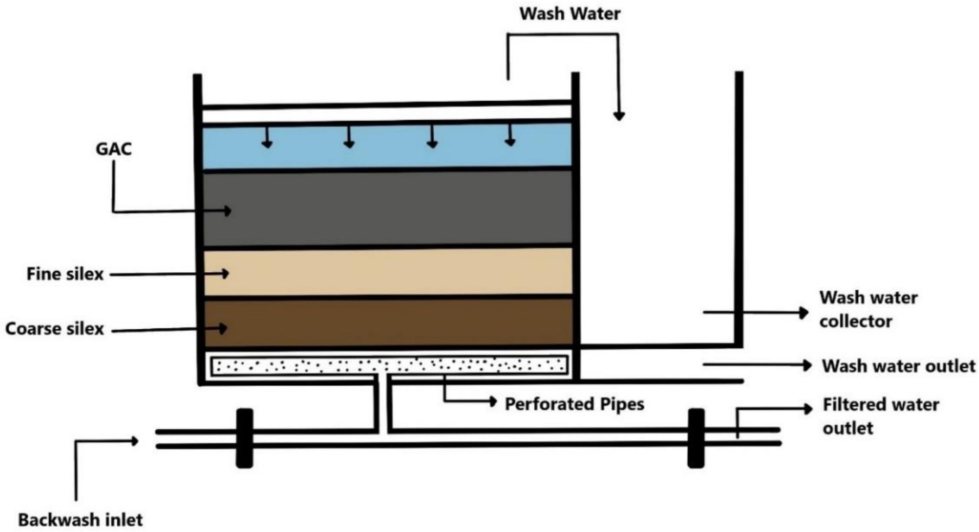


Figure 2: *Schematic diagram of gravity-based GAC filter system*

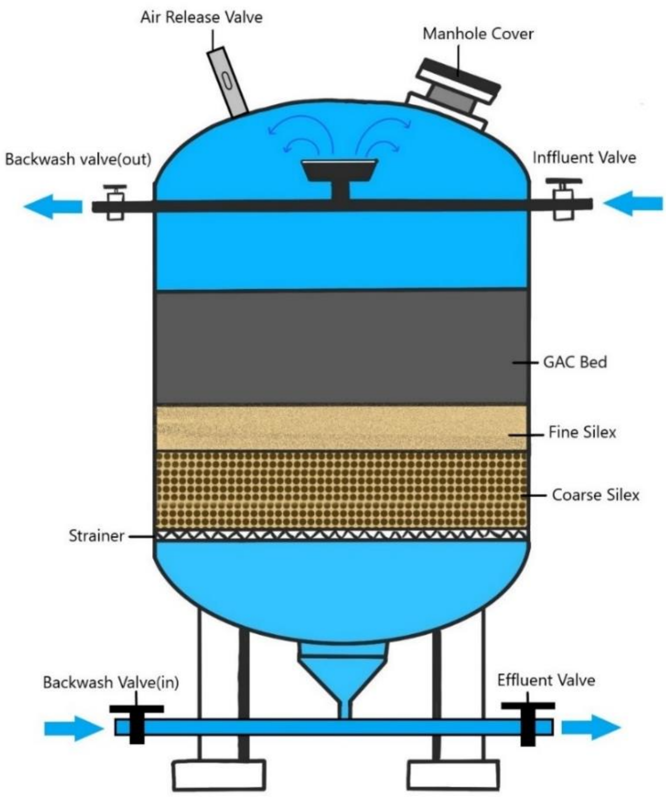


Figure 3: *Schematic diagram of a pressure-based GAC filter system*

2.1.2 Fluidized bed reactors

The information on fluidized bed reactors was taken from the study Cabrera et al. (2011). A fluidized bed consists of a reactor containing granulated activated carbon as an inert material. Fluidization in the reactor is achieved by two modes: a two-phase system (liquid injection) as seen in Figure 4 (a) or a three-phase system (liquid and gas injection), as seen in Figure 4(b). Once fluidized, each carbon grain provides a surface for biofilm formation.

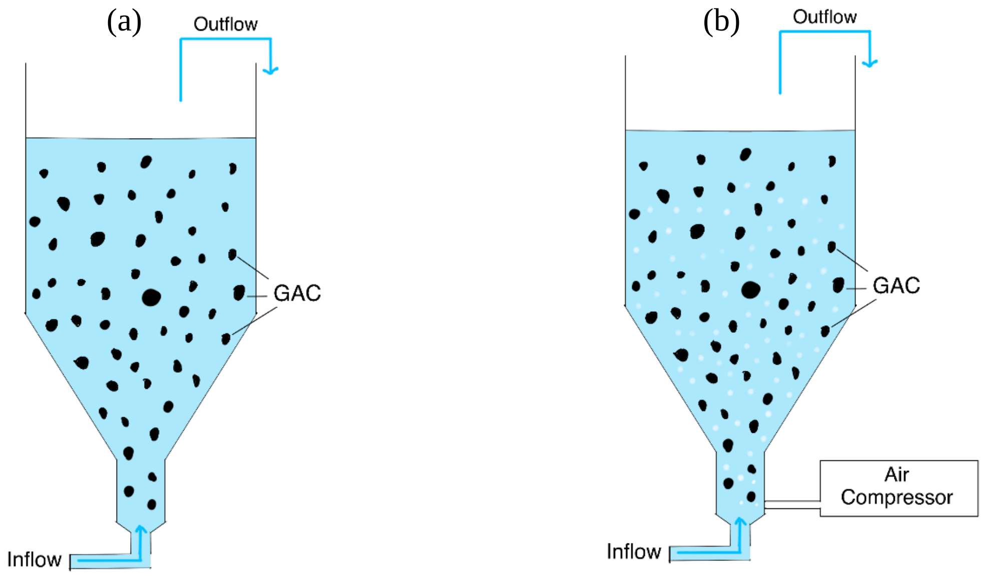


Figure 4: Schematic diagram of (a) two-phase system and (b) three-phase system fluidized bed reactors.

The advantages of fluidized bed rectors are:

- By Keeping the reactor aerobic, the emission of toxic compounds into the atmosphere can be avoided.
- High sludge retention time and small reactor size

The disadvantages of fluidized bed rectors are:

- Does not filter TSS
- Rigorous mixing in the fluidized bed rectors caused by the gas bubble motion can result in the shedding of the attached biofilm.
- It uses more energy than fixed bed reactors since it is pumped against gravity

2.2 Operation of GAC filter

Different processes are used in a wastewater/ drinking water treatment plant, depending on the targeted water quality, such as different combinations of pre-treatment steps with multimedia

GAC filters (Fundneider et al., 2020). Various filtering aids remove substances like small amounts of suspended matter (sand, mud and floccules from the coagulation process) in the pre-treatment process.

The complete treatment process is seen in Figure 5. The process focuses on the treatment plant having a GAC fixed bed reactor. Water is treated through primary treatment(grit removal and primary clarifier) and secondary treatment (activated sludge and secondary clarifier). The wastewater then moves to tertiary treatment (membrane filters, sand filters, and ozonation). In the tertiary treatment, only one of the treatments is used. When the wastewater flows into the pre-treatment process(tertiary treatment), the filtering material filters several undissolved substances simultaneously. The water flows through the filtering media, and particles are retained and deposited on the filtering medium. The same thing happens in the other tertiary treatment methods, except ozonation needs an additional filtration unit to remove suspended particles. The effluent from the tertiary treatment then enters into the column where activated carbon is used as a filtering medium. The water is then set at its specified flow rate so that the water is in contact with the filter bed for the required time. The activated carbon filter then adsorbs the odour, colour, chlorine and other organic pollutants when the water is allowed to rest in the filter bed. The silex layers help prevent GAC loss through the backwash process and the loss through the perforated pipes. When the backwashing process is needed, backwash valves are opened up, and pressurized water with air is pumped from under the bed. Backwashing will raise the bed and remove the attached particles that were clogging the pores. The back washed water is then recycled within the treatment plant. It is recommended to have more than two columns/filters in the filtration step to maintain redundancy during servicing/breakdown of any one column (Böhler et al., 2019).

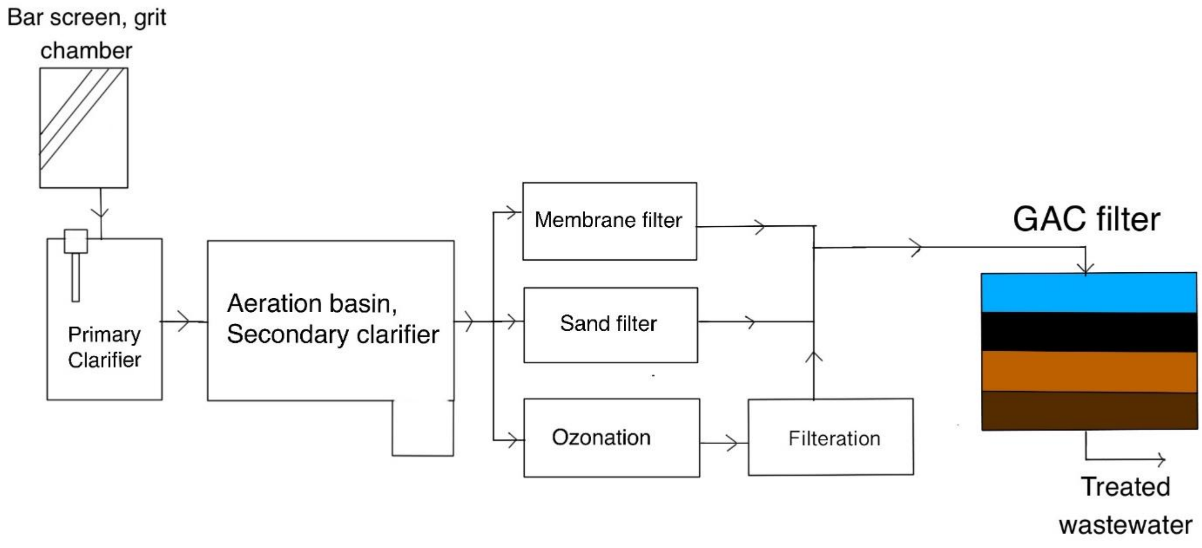


Figure 5: Schematic diagram of Municipal Wastewater Treatment Process

2.3 Essential Factors that affect the operation of GAC filter

Dissolved organic carbon (DOC) is typically mentioned as a critical parameter in understanding design and operation. It should generally be as low as possible in the water directed to the GAC filters. Breakthrough curve is an important tool to understand the efficiency of GAC filter. The breakthrough curves depend on the contact time, carbon use, DOC, total suspended solids (TSS) and concentrations of influent micropollutants (EPA, 2018).

The volume of the GAC particles plus the void volume makes up for the bed volume. When the liquid passes through the GAC filter bed with one complete cycle from the start of the filter bed in the column to leaving the filter, the bed gives one-bed volume. Empty bed contact time (EBCT) is an estimation of the time when influent water is in contact with the activated carbon bed in the filter column, assuming all water passes through the filter bed at the same velocity (URBANSAQUA, 2021). EBCT is directly related to removal efficiency, where short EBCT results in low removal efficiency and high EBCT is carbon demanding. Usually, 20-30min EBCT is required (Fundneider et al., 2020), but it may vary depending on the targeted micropollutants in the influent.

Longer breakthrough time may result in an increased number of bed volumes (BV) before replacement/regeneration of the filter is needed. Some contaminants require longer EBCT to adsorb compared to other pollutants under similar conditions. The influence of filter type, DOC, time of breakthrough, number of BV and EBCT is required to provide solid designs and reasonable cost estimates of the GAC filter system. However, different studies with different wastewaters and GAC filters are not always easily compared, as the influent characteristics vary. For example, a higher TSS or DOC content may reduce the number of BV reached before regeneration. Different concentrations of TSS and DOC may lead to a wide range of BV.

2.4 Influence of pre-treatment on GAC

When the wastewater enters the GAC used as a fourth step in municipal wastewater treatment, it has already gone through primary, chemical and biological treatment. When applying GAC filtration to surface waters, wastewater and groundwaters, fouling may occur (AMTA, 2010). Fouling refers to the when filter pores are clogged due to particulates like suspended solids, organic matter and biomass on the surface, or perhaps worst, among carbon pores. Unfortunately, the presence of organic substances and other solids can cause a decline in filter permeability (García, 2011). Usually, fouling happens within the GAC bed's upper layers and then works itself through the subsequent layers (AMTA, 2010). The adsorption effect of GAC on OMP's will reduce with increasing concentrations of influent DOC and organic matter (Salariarad, 2011).

When granular activated carbon filtration is involved, additional pre-treatment other than primary and secondary treatment may be necessary because it influences the influent concentrations for GAC. The first objective of pre-treatment is to create the feed water to the GAC filter compatible by treating the wastewater to have low concentrations that do not cause fouling. Pre-treatment is needed to extend the potency and lifetime of the GAC by minimizing concentrations of the inflowing particles and DOC (Da Silvaa, 2012).

When DOC concentrations are high in wastewater, rapid biomass growth will occur within the pores of GAC filters micro-organisms use DOC as nutrients. Microbial and organic fouling is perhaps the foremost common varieties of biofouling in the filter, making it harder to manage wastewater treatment. The microbial activity in GAC filters is sometimes considered valuable thanks to the extra removal of Natural organic matter from the inflow by biodegradation processes that lead to an extension of periods between regenerations. However, the sturdy attachment of micro-organism to GAC and poor backwashing efficiency increase dead and living biomass accumulation in GAC filters, leading to biomass-turnover processes. Increased temperatures will increase the growth of biomass. These processes can release compounds and micro-organisms, affecting the effluent water quality (Alaksandra, 2015). The benefits of microbial growth in the filter can be that having adequate pre-treatment (rapid sand filtration or dual-media filtration) might further improve the advantages of biological processes of GAC filters.

Pre-treatment for GAC comes in different types, and their effluent characteristics may vary, and their applications may come with advantages and disadvantages. Aspects of different kinds of pre-treatment processes are presented below.

2.4.1 Rapid sand filter/ rapid gravity filter

In a rapid sand filter, wastewater passes through granular materials, removing suspended particles and other impurities under gravity or pump pressure. The floc material is trapped between the sand particles. Flocs formed through coagulation achieved typically with alum or iron-based chemicals that cause particles to stick together by electrostatic and ionic forces (Tekerlekopoulou et al., 2020). Rapid sand filters are made up of coarse silex 0.5–1.0 mm in diameter with an effective size of 0.75mm. Once the filter has reached its filtration limits, it needs to be cleaned by backwashing, where the direction of water flow is reversed, and compressed air is added (Guastalli et al., 2013). High backwashing of the filter bed may result in loss of sand and wastage of water and energy (Ratatnayaka et al., 2009). Previous studies suggest that pre-ozonation is required to make a rapid sand filter into a biological process(Ivan, 2013). But irrespective of pre-oxygenation, biological processes happen in filters when there is a high filtration rate (low EBCT). Micro-organisms have less time to attach themselves to the carbon surface. As a result, such a filter favours bacterial species development that proliferates on readily available biodegradable organic matter, while complex organic compounds may not be removed biologically (Hammes et al., 2011).

2.4.2 Membrane filtration

Membrane filters maintain low turbidity values, which rejects almost 100% of algae contamination and a significant fraction of the bacterial content of the water, unlike the sand filters where there is some organic matter in the form of biomass/algae that enters the effluent after detachment from the media surface (Guastalli et al., 2013). Membrane filters have low SS in their effluent. As a pre-treatment step to the GAC filter, membrane filtration helps in reducing fouling chances and increase bed life. Membrane fouling can be a huge concern for reduction in removal efficiency. The decrease in removal efficiency can be overcome by introducing clean membrane stacks as replacements (Saltik et al., 2016).

Membrane filters generally require less space and chemicals than conventional pre-treatment systems such as flocculation and sand filters (Jeong et al., 2017). According to Košutić, (2002) the mechanism of membrane filtration technology in trap the micro-organisms in a two step combination (1) the effect of physico-chemical interactions between the membrane and micro-organisms (2) the filtering by using membrane porese as a sieve which can be constructed out of a wide range of synthetic materials and cloth-based materials. Membrane filtrations are classified based on their pore sizes and the materials used; these types are given below. When looking at the effectiveness of different membrane filters, the pore size plays an important role where the smaller the pore size better the removal efficiency. The membrane filter had turbidity levels lower than those obtained from conventional pre-treatment composed of a flotation unit followed by a dual media filter (DMF) (Guastalli et al., 2013). However, this, in turn, increases the energy required to pump the water through the filters, thus increasing energy demand. Also, smaller pore sizes increase the chances of fouling.

Nanofiltration - membrane process lies between ultrafiltration and reverses osmosis. The size of these nanopores forms a a very dense membrane structure with pore size less than 1 nm (Baker, 2012). It can separate organic matter and almost all of suspended solids of low molecular weight, but it comes with a very high cost for maintainence and construction.

Ultra-filtration (UF) - membrane separation falls between nanofiltration and microfiltration with a pore size range of 0.001- 5 µm (Rajindar, 2016). It helps with forming a gap between MF and NF to separate solids that may foul NF(Rajindar, 2016).

Microfiltration (MF) - Microfiltration membranes are generally of pore size between 0.1 and 10 µm, MF has the larger pore structure of the category (Pal, 2020). This membrane uses notably lower pressure compared to ultrafiltration and nanofiltration.

2.4.3 Ozonation

Ozonation is a chemical oxidation treatment technique used for wastewater treatment and used to disinfect drinking water based on the dosing of ozone(O_3) into wastewater. Ozone is one of the most potent oxidation agents (Chavoshani et al**.**, 2020. Hydroxyl radicals generated by concentrated ozone in water can reduce pharmaceuticals that are resistant to breaking down (Morone, 2019). Advantages are that it also rapidly reacts with biomass (bacteria, viruses and protozoa) over a wide range of pH. Disadvantages are that it is seen as a potential fire hazard (due to substantial oxygen concentrations), toxicity associated with ozone generation, by-products, and large amounts of energy required to produce O_3.

3 Effects of organic micropollutants on the environment

When using pharmaceuticals for human use and animal use through veterinaries, the medication compounds used will break down to form metabolites that are then excreted as body waste and faeces. The human and animal waste is transported to the wastewater treatment plant in that region. Therefore, the treatment process could also break down the drugs and their metabolites into different products. After treatment, WWTP will release these substances into the environment with the sewage sludge or the effluent (EEA, 2018). From the EU medical products regulation report (Grung M 2007), there is a need for environmental risk assessment for human and veterinary medications. However, environmental risks are taken into consideration solely inside the risk-benefit analyses for veterinary medicines. Risk-benefit analyses reflect tensions in priorities between the advantages of health care and the risks to water resources and ecosystems.

Besides total organic matter, TSS and nutrients, municipal and industrial wastewater contain a wide range of organic chemicals and inorganic chemicals. Flame retardants, phenols and dioxins are other contaminants that should be targeted (Baresel et al., 2017). Substances such as these are grouped as micropollutants. Humans subjected to repeated small doses of micropollutants that accumulate over time; health problems have been growing with the increase in drinking water contaminants, leading to immediate health effects and chronic health effects (Siong et al., 2013).

Poly- and perfluoroalkyl substances (PFAS) are widely used artificial organic chemical substances; they contain alkyl groups on which all or any of the hydrogen atoms have replaced with fluorine (Brussels, 2020). Perfluorinated acids include PFOA and PFOS which are made of carboxylic or sulfonic acids . The USA's Environmental protection agency (EPA) gave a health advisory limit of 70 ng/L for both compounds individually or combined concentrations of PFOA and PFOS for drinking water (Cordner et al., 2019). The new Directive 98/83 of the European Commission(EC) (to be adopted by the end of 2020) includes a limit value of 0.1 μg/L for a sum of 20 individual PFAS listed, as well as a limit value of 0.5 μg/L for total PFAS concentration for drinking water (Brussels, 2020).

In the past decade, water quality issues' political and social awareness has grown substantially in the European Union (EU). According to European Environment Agency (EEA), tracing back to the point sources for water pollution, it was found that sewage treatment plants, manufacturing industries, animal farms and agricultural-based industries were the key sources. According to River Basin Management Plans (RBMP) assessment (EEA, 2018), Europe's surface waters pollution is pointed towards urban wastewater treatment Plants as the significant point source of contamination.EU Water Framework Directive has included Carbamazepine and diclofenac in the monitoring list (Baresel et al, 2017). According to UBA 2017a (HRSG, 2017), from several monitoring sites in Germany, concentrations of several pharmaceuticals were compared with possible environmental quality standards. Environmental Quality Standards were exceeded for carbamazepine (an antiepileptic drug), Sulfamethoxazole (Antibiotic) and diclofenac (Analgesics/anti-inflammatories) (HRSG, 2017). This concern of exceeding quality standards has made many countries/organizations investigate and provide guidelines on the pollutant causing potential risk to human health and the environment due to the presence of micropollutants.

4 Materials and Methods

This study is purely based on compiling and analyzing data from online sources (journals, reports, books, web articles). The sources were searched by using the keywords: micropollutants, activated carbon filtration, empty bed contact time (EBCT), pharmaceuticals, breakthrough curves, adsorption, PFOS, micropollutants and carbon use. Findings/Data were structured so that co-relations were made to understand the influence of design parameters (EBCT, carbon use, DOC, TSS) on the GAC filter. Carbamazepine (CBZ), sulfamethoxazole (SMX), diclofenac (DCF) as the indicator compounds. Extraction of data was done based on analyzing literature seen under the subsection below.

4.1 Selection of literature, extraction of data and assessment.

The number of studies on removing micropollutants is limited, especially for granular activated carbon, as it is a new field of study in wastewater/ drinking water treatment. The collection of studies (literature, reports, journals) was taken based on the following criteria.

- This study focuses on fixed bed reactors and not on expanded/fluidized bed reactors. Since expanded bed reactors are used when there are a significant fraction of suspended particles, it does not act as a filter for SS but instead as target adsorption (Kennedy, 2005). The use of pre-treatment methods, which is a focus in this study, eliminates most of the incoming SS, so we use a fixed bed reactor.

- The study should show the DOC in the influent after the pre-treatment process. The data will help characterize the concentration of absorbable organic matter in tertiary effluents from municipal WWTPs. DOC is seen to compete with micropollutants for the available adsorption area on the GAC (Benstöm et al., 2017).

- The studies should have pre-treatment without any removal of micropollutants. When pre-treatment(ozonation and other oxidation treatments) involves pollutant removal, it is challenging to compare the performance of GAC. Compared to the GAC process, which has a pre-treatment step that does not remove micropollutant, the target pollutants might break down under pre-treatment processes and will not show any significance in performance comparison for the GAC step.

- To compare the results in the study, the pilot/full-scale tests should be done under constant conditions. Either one of the parameters (DOC, EBCT, Hydraulic loading) should be consistent throughout the experiment/test procedure in the selected study.

- GAC setup should have a pre-treatment to remove most of TSS. If GAC is subjected to wastewater without pre-treatment, it may get clogged with the flocs that come from the coagulation process—rendering it unusable before it reaches its potential.

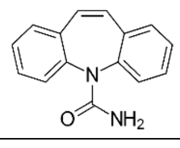
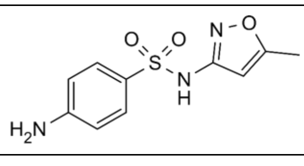
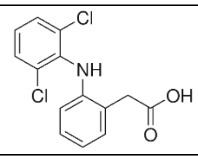
- They should consist of the following pollutants: SMX, CBZ, DCF, whose data is measured in the influent and effluent. The selection of the target pollutants is due to their ability to act as indicators for the breakthrough.

- The literature needs to have mentioned the bed volumes at breakthrough. Bed volumes help in comparing the performance of different GAC for EBCT and DOC.

4.2 Selection of micropollutants

The selection of OMP was made by finding the most common micropollutant that occurs in the WWTP effluents, and it needs to act as an indicator for a breakthrough. Carbamazepine (antiepileptic drug), sulfamethoxazole (antibiotic) and diclofenac (analgesics/anti-inflammatories) were selected as they showed high occurrences well above the detection limit in WWTP effluents and found in water source meant for drinking water production (WHO, 2012; Rogowska et al., 2019). The water partition coefficient represented by Log Kow it is a measure of solubility of a substance in water and oil. If the value of partition Log Kow value is higher than one, then it is less soluble in water and more soluble in oils. At Log Kow, lower than one its more soluble in water (Amézqueta et al., 2020). CBZ and DCF show a very high adsorbability due to their high log Kow value at 2.25 and 4.51 (Table 1). SMX shows moderate or low adsorbability due to low Log Kow at 0.89. Substances with high Log Kow values have a better adsorbability rate than the ones with low Log Kow value (Golovko et al., 2020). CBZ, DCF showed more than 90% removal and can be considered as late breakthrough indicators under optimum working conditions of GAC filters. Table 1 shows the physicochemical properties and the environmental and human-related effects for the selected compounds. Information on pollutant effects on human and the environment was taken (ECHA, 2021), and detailed information on CAS number, molecular formula, molecular weight, and log Kow value of the OMP reagents used is provided from another study (Gago-Ferrero et al., 2017).

Table 1: Physio-chemical properties of CBX, SMX and DCF

	Carbamazepine	**Sulfamethoxazole**	**Diclofenac**
Chemical Name	5H-dibenz[b,f]azepine-5-carboxamide (9.5.2)	4-Amino-N-(5-methyl-1,2-oxa-zol-3-yl)benzenesulfonamide	{2-[(2,6-Dichloro-phenyl)amino]phenyl}acetic acid
Molecular formula	$C_{15}H_{12}N_2O$	$C_{10}H_{11}N_3O_3S$	$C_{14}H_{11}C_{12}NO_2$
Molar mass (g/mol)	236.27	253	295
Acid dissociation constant (pKa)	15.96,-3.98	5.7, 1.6	4,-2
CAS no	298-46-4	723-46-6	15307-86-5
Water partition coefficient (log Kow)	2.25	0.89	5
Structural Formula			
Environmental and Human Effects	In humans, mental health effects, nausea, dizziness, reproductive toxicity. For aquatic life, it shows re-productive toxicity.	In humans, it causes cancer, se-rious eye irritation, genetic de-fects, skin irritation.	In humans, it causes damage to organs through prolonged or re-peated exposure and damaging fertility or the unborn child. It is also toxic to aquatic life on pro-longed exposure.

4.3 Breakthrough criteria

While there is no standard regulation on MP removal in the EU, 80% removal efficiency is being considered by a few countries such as Austria, Germany and the Netherlands (Benstoem et al., 2017), whereas Switzerland has already established 80% removal, which is defined by law (WPO, 2021). The definition of breakthrough is not well established due to different studies interpreting it in different ways. According to the presented requirement of 80% removal efficiency of GAC, breakthrough occurs when the filter attains a breakpoint as saturation through OMPs and matter (biomass, organic matter) occurs. The filter cannot attain the standard removal efficiency anymore, and the pollutant concentration will increase in the filter effluent after this breakpoint. This criterion shows that when the filter has a breakthrough, it does not meet the effluent concentration requirements of 80% removal. Plotting the standard effluent concentration (C/C_0) of an individual OMP against the output volume (e.g., in relevance to the bed volume), we can calculate a system-specific breakthrough curve shown in Figure 6. The form of the breakthrough curve depends on a similar factor affecting the utilization zone. In Figure 6, the breakthrough is outlined as a normalized effluent concentration of 0.2; in addition, the adsorbent is considered to be exhausted (reaching equilibrium) when the normalized effluent reaches a concentration of 0.95.

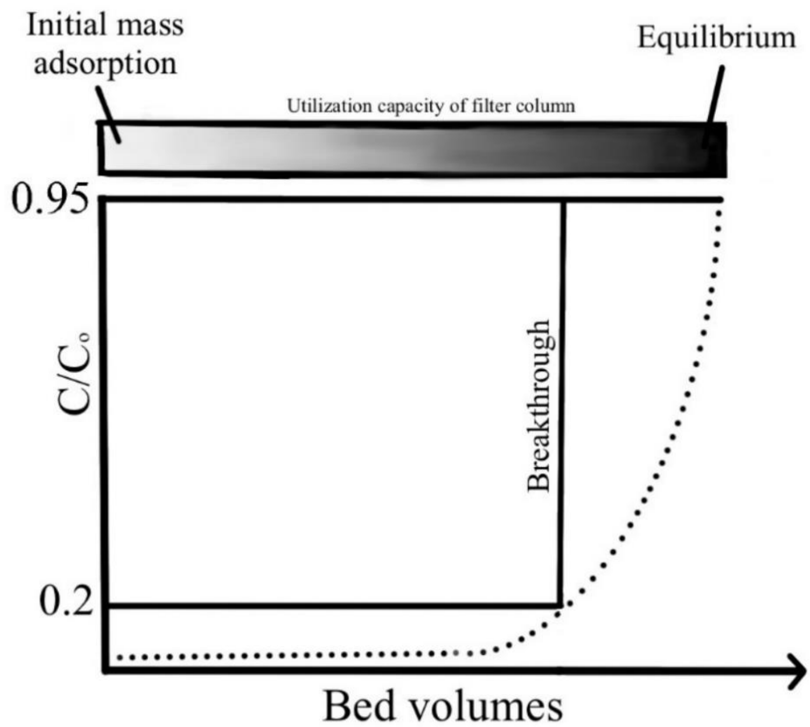


Figure 6: Schematic diagram for a breakthrough curve

4.4 Calculations of key parameters

When designing a GAC filter, the following parameters should be considered: EBCT, hydraulic loading rate, carbon use and bed depth (Benstoem et al., 2014). Also, GAC filters may be designed as up or downflow systems consisting of one or more vessels in series or parallel. The calculations of the given parameters will be shown in this section.

4.4.1 EBCT

Contact time is an essential parameter as it directly relates to the adsorption of OMP. It is the time taken for treating the water while it is in contact with the adsorber in a vessel. This is assuming that water is moving through the column at a constant velocity (Rodriguez et al., 2015). When calculating EBCT, we should either know the volume of the filter bed(m^3) or surface loading (m/h) or flow rate (m^3/h) or depth of filter bed(m) or all the parameters.

When bed volume and flow rate are given, then Equation (1) shows how to find EBCT.

$$EBCT = \frac{V_b}{Q} \tag{1}$$

Where V_b = Bed Volume (m^3)

Q = Flow rate (m^3/h)

It can also be given according to the following Equation (2) when the bed depth is known, and a hydraulic loading rate is given.

$$EBCT = \frac{L_b}{Q/A} \tag{2}$$

Where

L_b=depth of bed (m)

A= cross-sectional area of GAC bed (m^2)

Q/A=hydraulic loading rate (m/h)

Since GAC filters have void fractions in them, the contact time(t) is measured as

$$t = \frac{V_b \varepsilon_b}{Q} \tag{3}$$

Where $\boldsymbol{\varepsilon_b}$ Is the void fraction (Rodriguez et al., 2015).

4.4.2 Adsorption capacity

The adsorption capacity of GAC is defined as the mass of carbon used up to adsorb the mass of micropollutant. It can be derived by the following Equation (4) (Dwivedia et al., 2016).

$$q = \frac{V(C - C_o)}{m} \tag{4}$$

Where q = carbon use of the pollutant in mg/g

V = volume of the filter bed

C = influent concentration

C_0 = effluent Concentration

m = mass of GAC

4.4.3 Carbon usage rate (CUR)

CUR is defined as the mass of granular activated carbon required to treat the unit volume of wastewater (WW) until breakthrough, and the volume can be calculated using the breakthrough curve (Rodriguez et al., 2015).

$$CUR\ (mg/L\ or\ kg/m^3) = \frac{Mass\ of\ GAC\ in\ filter\ bed}{Volume\ treated\ until\ breakthrough} \tag{5}$$

4.4.4 Hydraulic loading rate

When the velocity of liquid moving in an a carbon bed along the cross-sectional area (A) and the depth of the bed (L), it is called hydraulic loading rate(H_L). As seen in Equation (6), the hydraulic loading rate is given as the flow of influent divided by the cross-sectional area of the Granular activated carbon bed (Rodriguez et al., 2015).

$$H_L = \frac{Q}{A} \tag{6}$$

Where H_L = hydraulic loading rate in m/h
A = Cross-sectional area of GAC bed in m^2.

5 Results and discussion

In this section, the analyzed data from a compilation of different studies will be shown in this section. We will see how the parameters (DOC, carbon use, EBCT and type of pre-treatment) taken in this study will influence GAC filtration efficiency. A design range will be considered based on the results showing effective grain size, EBCT, carbon use, and different pre-treatment processes. Analysis on DOC, EBCT and grain size distribution was taken from 23 studies summarized in Tables 1A,2A and 3A, from Appendix 1, for CBZ, SMX and DCF. The flow rate from the studies shows a wide range from 0.00014 on the pilot-scale to 1154 m^3/h in full-scale tests. Most of the studies with a lower flow rate were done in pilot-scale tests to assess the efficacy of GAC for the elimination of micropollutants.

5.1 Influence of DOC on Bed Volumes

Considering the treatment through GAC, which uses its adsorption capacity to remove the micropollutants, DOC and TSS are considered essential parameters to determine the practical life of the filter before breakthrough (Culp, 1983). To analyze the data on DOC influence, a plot of bed volumes versus DOC was made for all the studies and each micropollutant, as shown in Figures 7,9 and 11, each representing CBZ, SMX, DCF. The DOC values can be seen in Table 1A, 2A, and 3A , Appendix 1, and the data points are labelled according to their sourced studies. The concentration of DOC was evaluated in influent to GAC processes for all studies and detected in a range of 2 to 18 mg/L with an average of 9.11 mg/L.

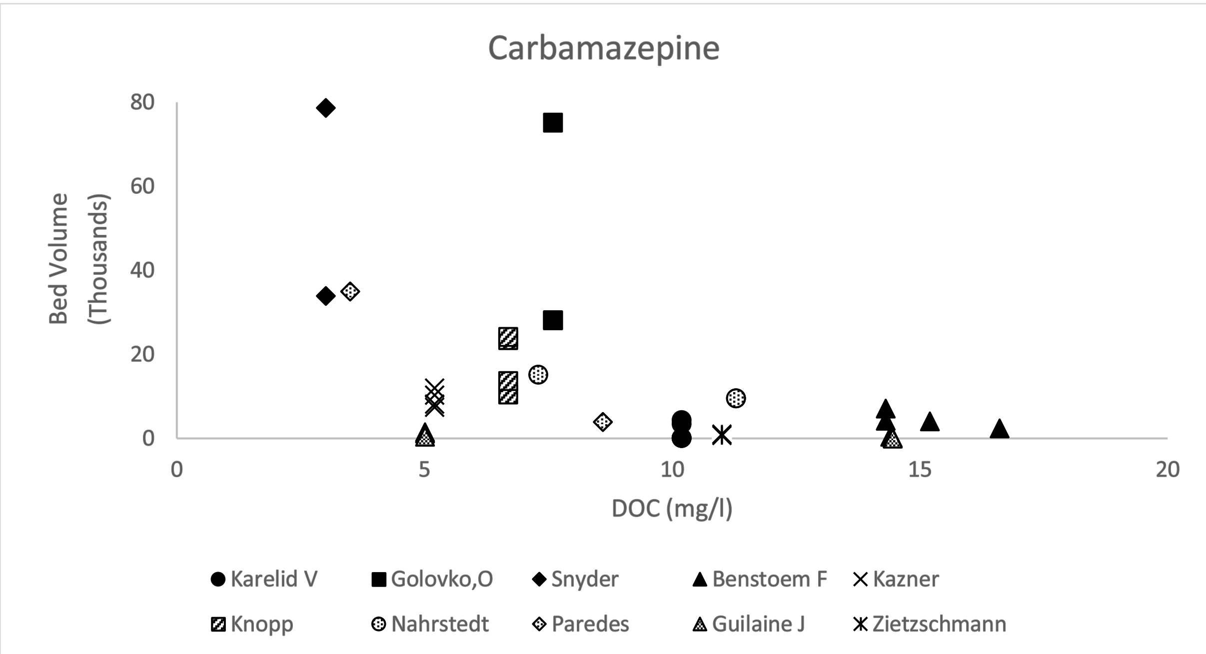


Figure 7: Treated BV as function of how DOC influences breakthrough of CBZ.

In Figure 7, the DOC versus bedvolumes for CBZ, the DOC range was from 2 to 16.6 mg/L with an average of 8.68 mg/L. DOC of 8.68mg/L comes well under the average DOC of 10mg/L influent concentration in a wastewater treatment plant. A trend for higher DOC leading to the breakthrough at lower bedvolumes is seen in Figure 7. Bar graphs of individual studies were made to show the effect of increasing DOC against bed volume, which is shown in Figure 8. These studies had at least two tests with different DOC characteristics in the influent water after pre-treatment. The rest of the parameters (EBCT, flow rate, and bed volume) remained similar.

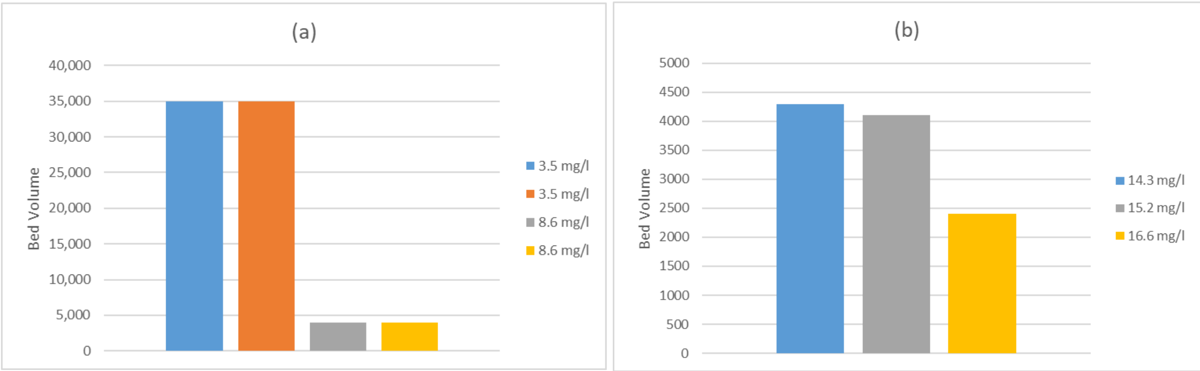


Figure 8: Treated number of BV as a function of DOC at a breakthrough of 20% for the studies (a) (Paredes 2018) and (b) (Benstom et al., 2014).

In Figure 8(a), at 3.5 mg/L DOC, the volume treated was 35,000, and at 8.6 mg/L, the volumes treated were 4000, and in (b) for DOC 14.3, 15.2, 16.6 mg/L, we see 4300, 4100, 2400 BV. The bar graph shows a considerable decline in bed volumes with an increase in DOC.

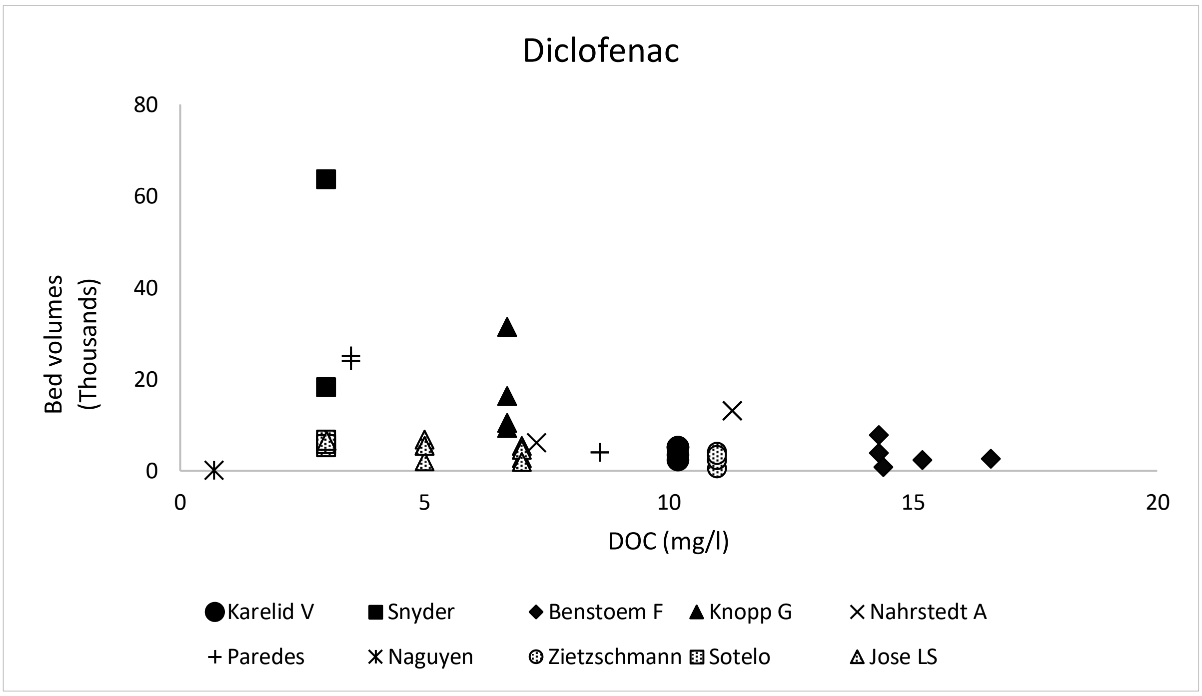


Figure 9: Treated BV as a function of how DOC influences breakthrough of DCF.

Figure 9, the DOC versus number of bedvolumes for DCF, the DOC range was from 2 to 16.6 mg/L with an average of 7.9 mg/L. DOC of 7.9mg/L comes well under the average DOC of 10mg/L influent concentration in a wastewater treatment plant. Like the graph in CBZ in DCF, a trend of increase in DOC reduces the BV treated. For Figure 10, the bar graphs are picked from the studies representing DCF.

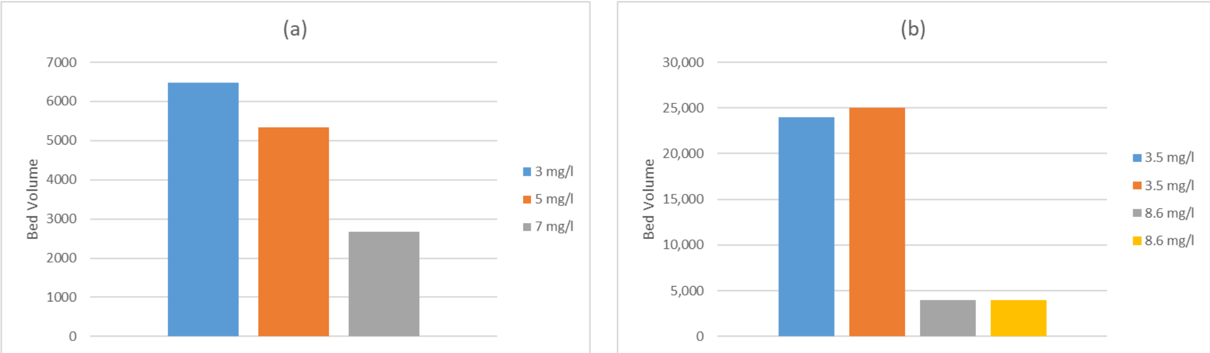


Figure 10: Treated number of BV as a function DOC at a breakthrough of 20% for the studies (a) (Sotelo 2014) *(b)* (Paredes 2018).

In Figure 10 (a) At 3, 5, and 7 mg/L DOC, the volume treated were 6476, 5332, 2666. (b) for DOC 3.5 mg/L we see 24,000 and 25,000 for 8.6mg/L it is 4000 BV treated.

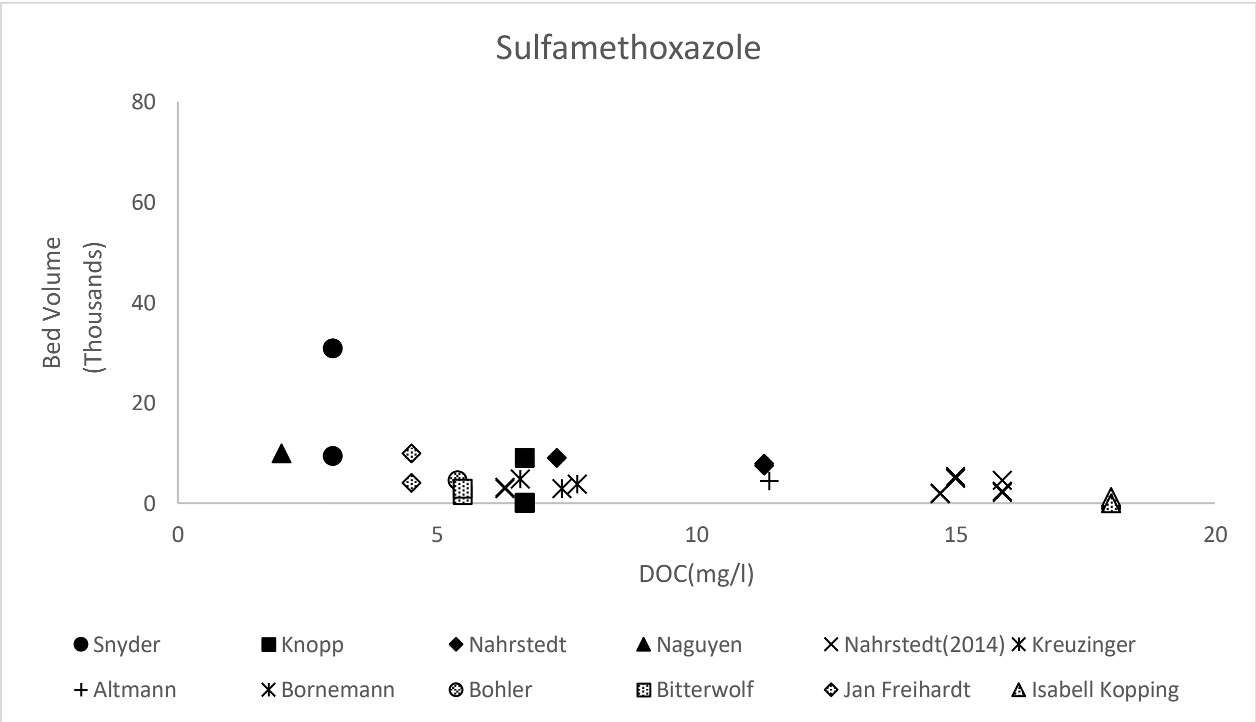


Figure 11: Treated BV as a function of how DOC influences breakthrough on of SMX.

In figure 11, the DOC versus bed volumes for SMX, the DOC range was from 2 to 18 mg/L with an average of 10.7 mg/L. DOC of 10.7mg/L comes closer to the average DOC of 10mg/L influent concentration in a wastewater treatment plant. Similar to the graph in CBZ, the graph in DCF shows that an increase in DOC reduces the BV treated. For Figure 12, the bar graphs are picked from the studies representing DCF. In Figure 10 (a), at 6.6, 7.7 mg/L DOC, the volumes treated were 4900 and 3800. In Figure 12 (b), the value for DOC 7.3 mg/L is 9,100. For 11.3 mg/L, the values are 7,900, and 7,500 BV treated.

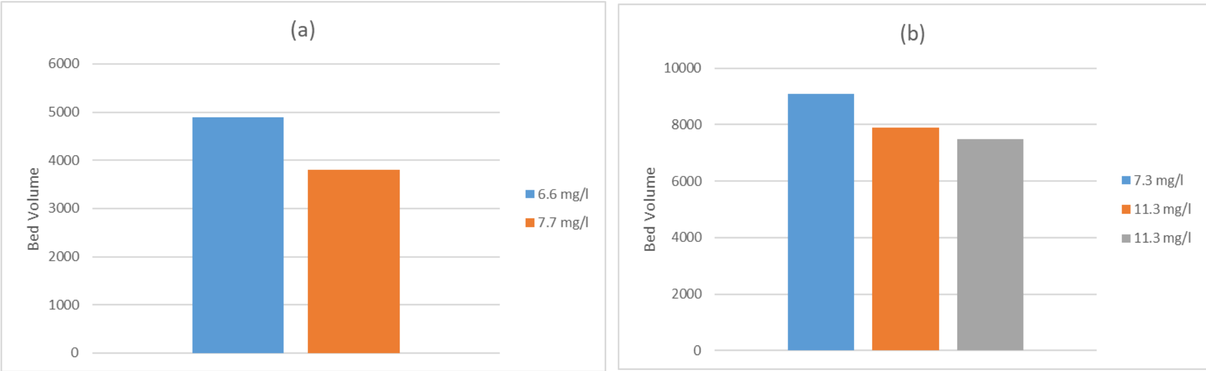


Figure 12: Treated number of BV as a function of DOC at a breakthrough of 20% for the studies (a)(Bornemann, 2015) (b) (Nahrstedt 2016).

When looking at the bar diagrams for carbamazepine, diclofenac and sulfamethoxazole, a consistent pattern of higher DOC leading to earlier breakthroughs under similar conditions is observed. High DOC content leads to faster exhaustion of GAC through fouling (Fundneider et al., 2020). GAC has the capacity to adsorb DOC at low concentrations. After GAC loses its capacity to adsorb, bioadsorption plays an important role where the micro-organisms that have attached to the external surface of GAC and macro-pores start organic biodegradation (Xing et al., 2008)

5.2 Grain size distribution based on GAC material

The grain size distribution (GSD) is chosen for CBZ, DCF and SMX based on what material was used, i.e., bituminous, lignite, and coconut shell activated carbons. The characteristics of activated carbon from 23 studies are summarised in Tables 1A,2A and 3A in Appendix 1. To find the effective grain size range, the data mentioned previously was used to create a graph for each OMP seen below in Figure 13,14 and 15. In this section, the effective grain size for each material (bituminous, lignite, and coconut shell) will be chosen. Since the grain sizes are shown in Tables 1A,2A and 3A in Appendix 1 are already the effective grain sizes from each study, the averages of these grain sizes will be represented as what could be the most common effective grain size available.

In Figure 13, the grain size range for bitumen is 0.7 – 1.6 mm for CBZ. Similarly, the range for lignite is 0.14 – 1.5 mm, but the range where the data points concentrate is selected due to insufficient data to show the range from 0.14 – 0.95 mm. Hence, the range at 0.95 – 1.5 mm for lignite is chosen. The grain size range for coconut is 0.8-1.5 mm, but the range of 0.8 – 1.35 mm is chosen due to insufficient data points, as mentioned previously for lignite. The effective grain size for bitumen, lignite and coconut is 1.27, 1.2, and 1 mm, respectively.

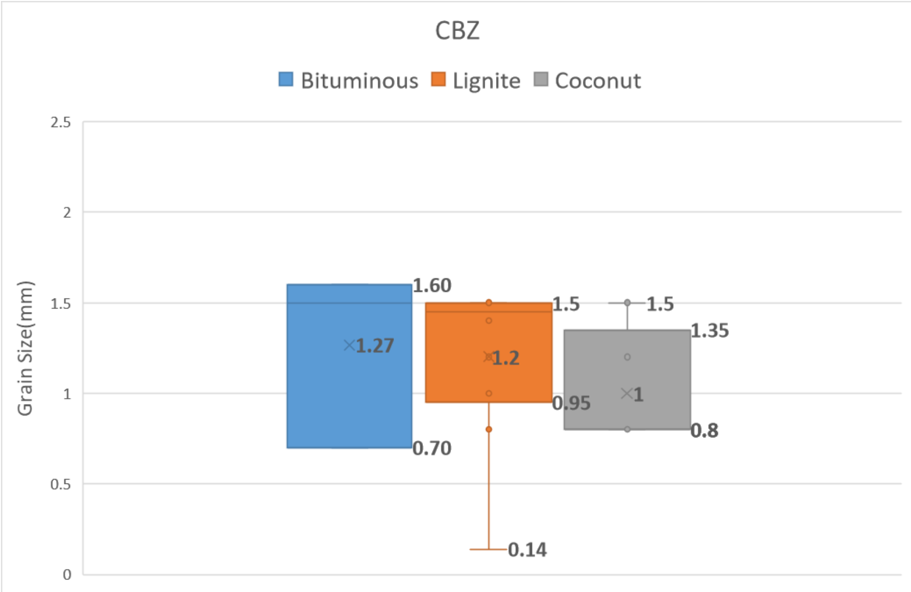


Figure 13: GSD of GAC based on the material (bituminous, lignite and coconut shell) for CBZ.

In Figure 14, the grain size range for bitumen is 0.6 – 1.5 mm, 1.1 – 1.55 mm for lignite, and 0.825-1.5 mm for coconut for DCF. Using the same method as for lignite in CBZ previously, the effective grain size for bitumen, lignite, and coconut is chosen as 0.98, 1.35, 1.25 mm, respectively.

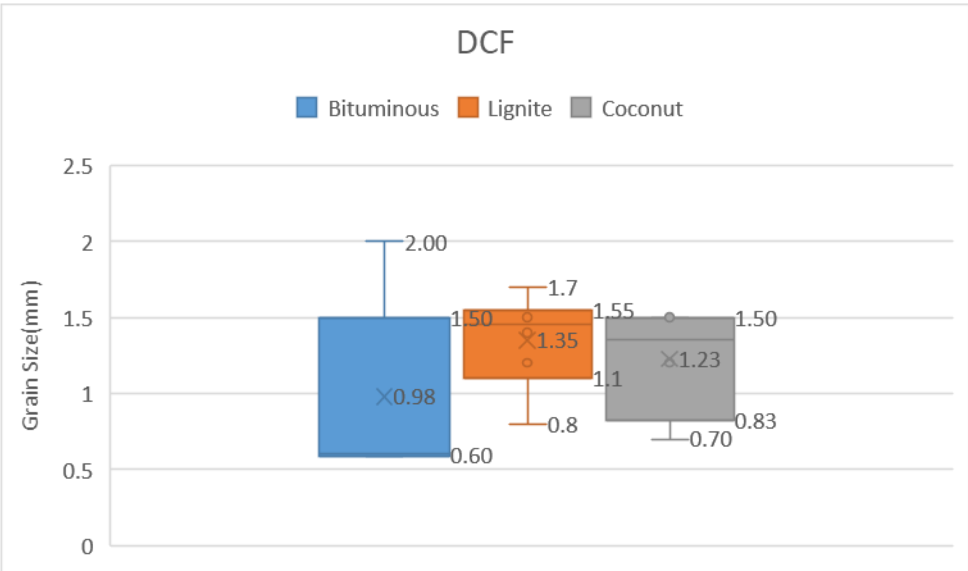


Figure 14: GSD of GAC based on the material (bituminous, lignite and coconut shell) for DCF

From the plot in Figure 15 for SMX, we see that the GSD range is between 0.85 - 1.8 mm for coconut. We do not see a range for lignite and bitumen because most of the grain size data points were limited for bitumen and lignite. So, we take 1.2 – 2.5mm for bitumen and 0.56 – 1.8mm for lignite. The effective grain size for bitumen, lignite, coconut is 1.5, 1.5, 1.37mm.

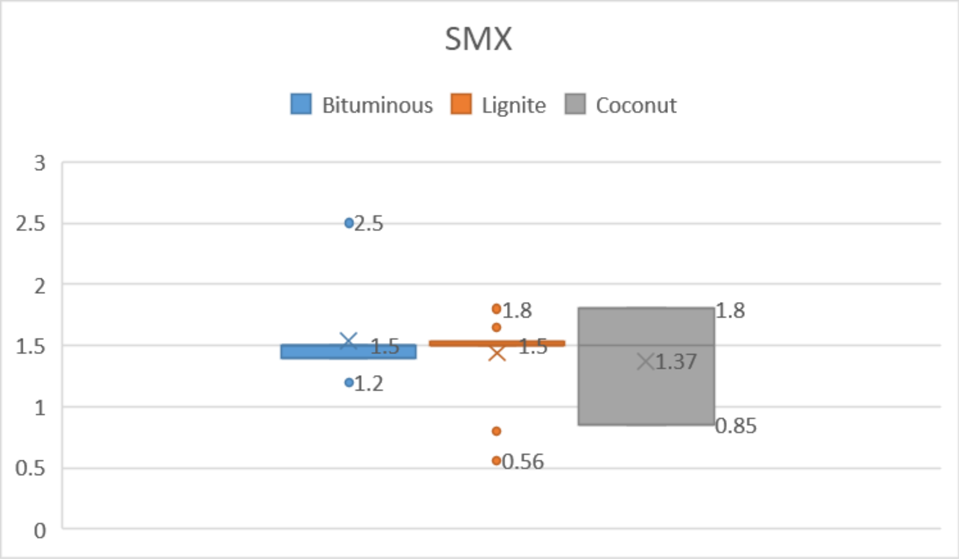


Figure 15: GSD of GAC based on the material (bituminous, lignite and coconut shell) for SMX.

Effective mean grain size distribution (EMGSD) for each material was calculated using the following method:

GSD of each MP for bituminous coal is chosen

CBZ = 0.7 – 1.6 mm

DCF = 0.6 – 1.5 mm

SMX = 1.2 – 2.5 mm

$$\textit{Effective mean grain size distribution (EMGSD)} = \frac{0.7 + 0.6 + 1.2}{3} \quad \text{to} \quad \frac{1.6 + 1.5 + 2.5}{3}$$

$$= 0.83 \text{ to } 1.86 \text{ mm}$$

Following the above method, the EMGSD of bituminous GAC is 0.83 - 1.86mm, lignite based GAC is 0.87 – 1.62mm, and coconut-based GAC is 0.825 - 1.55mm. This method was used for the simple classification of the grain size according to the raw material used. The mesh sizes under which this range of grain distribution can be served is given in table 6. Average effective grain sizes were calculated, and the mean effective grain sizes for bituminous coal, lignite, and coconut-based GAC was calculated to be 1.25 mm, 1.35 mm, and 1.2 mm, respectively. The effective ranges of all the materials are similar, with little difference suggesting that the recommended effective size for any type of GAC should be at 1.25 mm, which comes within the most commonly used US mesh 8x30. A few studies such as Freihardt et al. (2017), Benstoem et al. (2014) and Kopping et al. (2020) indicated that smaller grain size had better removal efficiencies compared to larger grain size due to smaller grains having more significant surface area compared to larger activated carbon grains. With fine GAC, a breakthrough occurred later, probably due to the shorter intraparticle diffusive path. Consequently, less GAC is required to treat the same wastewater volume when using fine GAC (Kopping et al., 2020).

5.3 Influence of EBCT on Breakthrough

EBCT is one of the most critical parameters in removing micropollutants, as it is directly related to the adsorption efficiency of GAC (Freihardt et al., 2017). Flow variations also result in the change of the EBCT, which in turn interferes with both adsorptive and biological removal. Longer EBCT gives more time for the contaminant to diffuse and absorb into the pores of GAC. Lower flows result in an increase in EBCT, whereas an increase in flow causes a decrease in EBCT. When comparing the data in this study, we see that finding a relationship, in general, is difficult due to the varying test procedures conducted in studies and varying influent characteristics. Studies show different results for treated bed volumes. However, there is a consistency where an increase in flow reduces EBCT and thereby increases the number of bed volumes. The increase in EBCT increases the removal of OMPs, as seen in the studies by Kopping et al. (2020) and Jaria et al. (2019). This can be explained by the amount of time required to get 80% removal as in Figures 16, 17, and 18. When one OMP requires more contact time than the others, the highest contact time is to be selected for the best removal efficiency of all the OMPs.

Figure 16 shows the influence of EBCT on bed volumes when the OMP CBZ is treated. This plot show data points from a compilation of 11 studies (Table 1A, Appendix 1). For CBZ, the average EBCT was 14.4 min. Though the averaged time does not represent any statistical significance, it gives a rough idea of how the micropollutant behaves within the given range of EBCT.

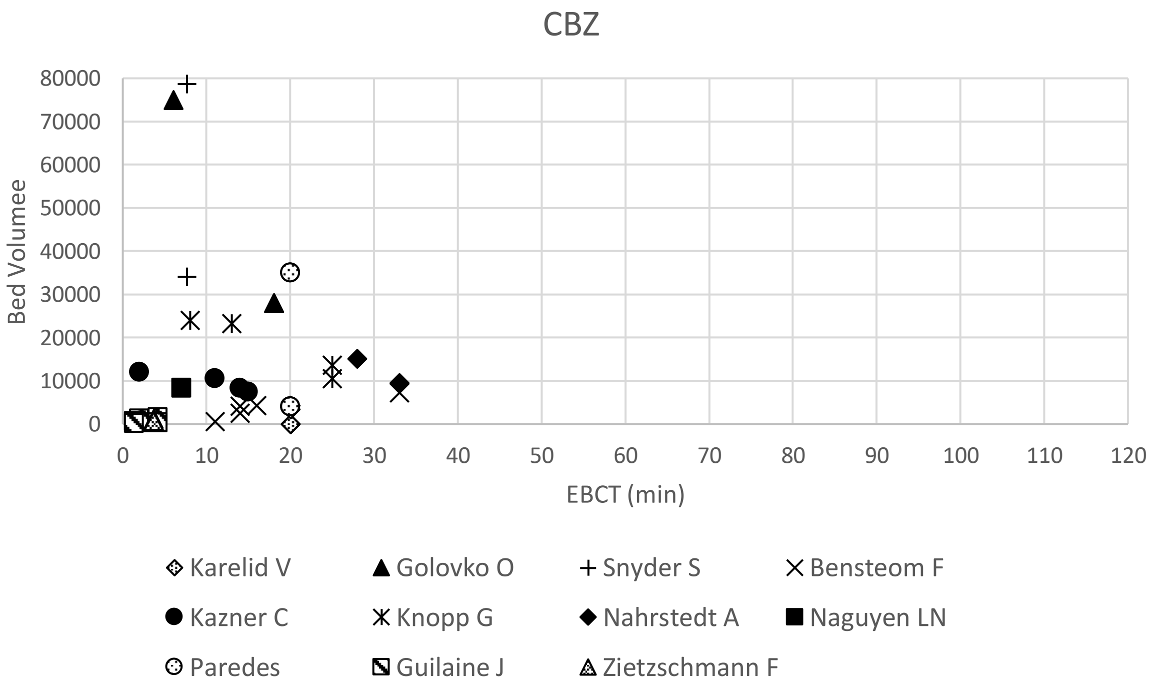


Figure 16: Influence of EBCT on bedvolumes for 20% breakthrough showing data points from each study for CBZ.

Figure 17 shows the influence of EBCT on bed volumes when DCF is treated. This plot shows data points from a compilation of 10 studies under Table 2A, Appendix 1. For DCF, the average EBCT was 12.3 min. This shows that DCF has the highest affinity towards activated carbon out of the three OMP selected for this study.

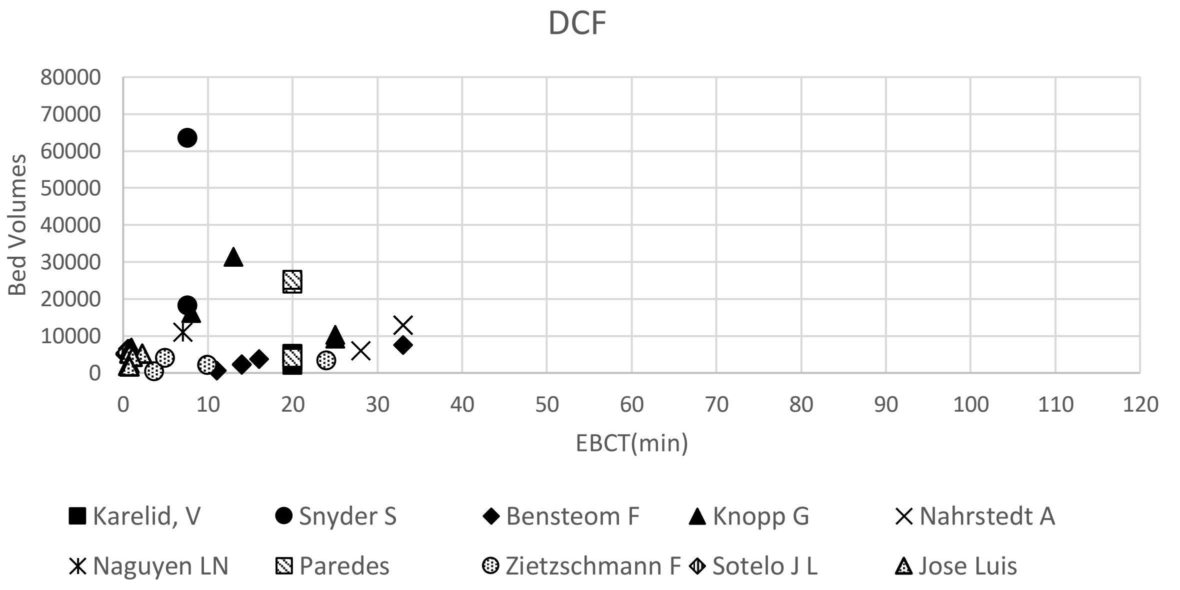


Figure 17: Influence of EBCT on bedvolumes for 20% breakthrough showing data points from each study for DCF.

Figure 18 shows the influence of EBCT on bed volumes when the OMP, SMX is treated. This plot shows data points from a compilation of 15 studies under Table 3A, Appendix 1.

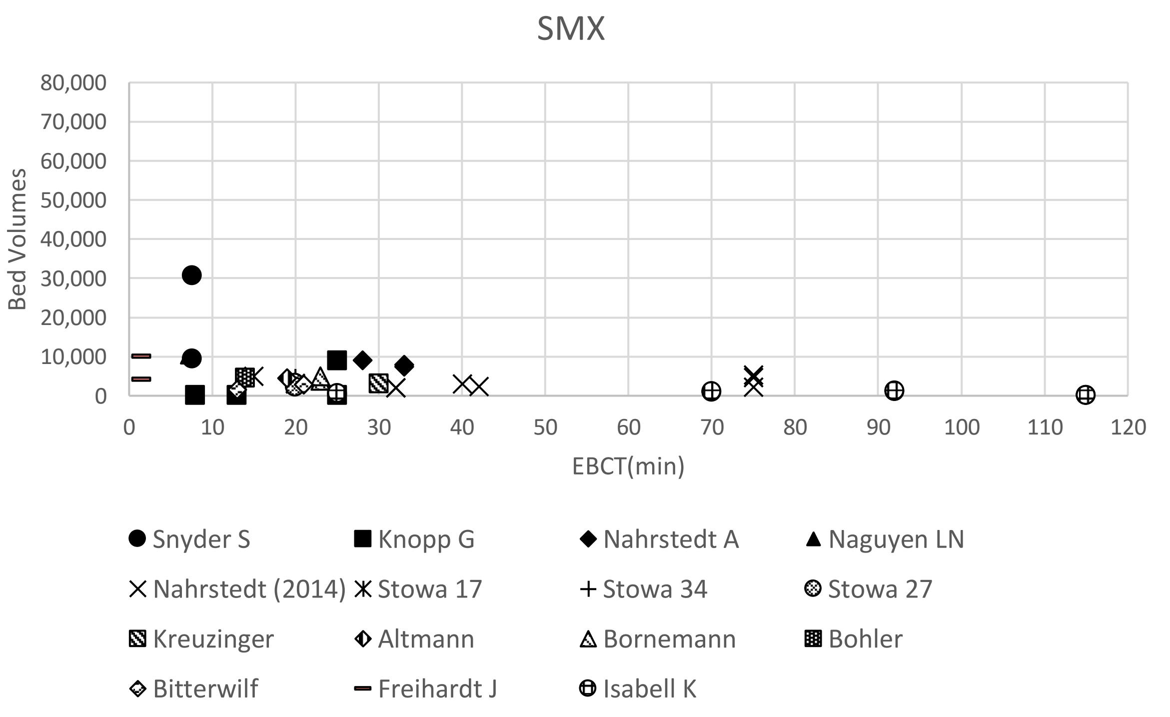


Figure 18: Influence of EBCT on bed volumes for 20% breakthrough showing data points from each study for DCF.

The EBCT range for sulfamethoxazole averaged at 35.2 min, showing that a more extended period of retention time for SMX is required to obtain the same removal efficiency as CBZ and DCF. The reason could be due to the low Log Kow of 0.89 for SMX and 2.25, 4.51 for CBZ and DCF, as seen in Table 1. Log Kow value refers to the octanol/water partition coefficient, where the lower the value, the more soluble the substance is in water (Golovko et al., 2020). The high solubility of SMX can be the reason for its low affinity towards adsorption. Longer EBCT time improves the reduction of DOC through biodegradation. The retention also positively affects particulate nutrients (phosphorous) since these are also reduced (Fundneider et al., 2018).

5.4 Influence of pre-treatment process

Due to how complex the nature of wastewaters is– WWTPs need to remove a wide variety of OMPs and other critical pollutants. Therefore, a process combination of filtration and adsorption or ozonation and adsorption is recommended (Fundneider et al., 2018). Table 2 is a data interpretation from Fundneider et al. (2018) and Guastalli et al. (2013), which shows the ratio of effluent and influent concentration (C/C_0, where C = effluent concentration, C_0 = influent concentration).

From the explanation above, it can be observed that the removal efficiencies are different depending on the combination of pre-treatment. Both sand filtration and membrane filtration showed that DCF is easily adsorbable, and SMX is the least adsorbed pollutant. As seen before in the previous section, the high Log Kow affects the adsorbability. However, SMX shows better degradation when treated with ozone. Dissolved organic matter highly contributes to the long-term biofouling (accumulation of biomass within the pores/structure while feeding DOC) of activated carbon filter (Guastalli et al., 2013). Hence a need for pre-treatment process to remove high concentration DOC is required. Pre-treating with ozone shows a higher DOC removal at 50% as compared to MF/UF at 20-30%. Ozone accelerates the biodegradation process of DOC by supplying micro-organisms with oxygen.

In Table 2, the highest micropollutant removal efficiency of pre-treatment processes without GAC as a follow-up process is seen in ozonation, followed by MF/UF filtration and sand filtration, respectively. Nevertheless, ozonation on its own cannot remove TSS without being paired with another filtration process.

Table 2: Comparsion of different treatment processes in terms of C/C_0 table interpreted from Fundneider (2018).

Process	CBZ	DCF	SMX	TSS	DOC
GAC	<0.05	<0.05	0.5-0.8	<0.2	>0.9
Sand Filter (SF)	>0.9	>0.9	>0.9	<0.05	>0.9
Ozonation (O_3)	<0.05	<0.05	<0.1	n.a	>0.8
Micro/ Ultra-filter (MF/UF)	0.8-0.9	>0.95	>0.95	<0.05	0.7 - 0.8
GAC+SF	<0.2	<0.05	0.5-0.7	<0.05	>0.8
GAC+O_3	<0.05	<0.05	<0.1	<0.05	0.5-0.6
GAC+MF/UF	<0.05	<0.05	0.5-0.8	<0.2	>0.9

The results demonstrate that higher BV can be achieved by combining GAC and filtration pre-treatments, and additional synergies concerning conventional parameters are possible. As a result, the effluent concentrations can be significantly reduced, and peaks of particulate matter can be avoided (overloaded secondary clarifier or poor settling characteristics of activated sludge). For a carbon filter to perform effectively, the feed water to the unit should be of uniform quality. When using MF or UF, the effluent concentration of SS is seen to be almost negligible. EPA (2000) suggests suspended solids concentrations less than 20 mg/l, but its recommended that the concentration of SS can be as low as possible. Comparing the pre-treatment processes in terms of economic efficiency also matters. Media filters have high reusability from backwashing, whereas Micro/Ultrafiltration membranes have a high initial cost. Expensive cleaning and regeneration is also required for membrane filters after fouling

5.5 Influence of pH and temperature

It is seen that most organics are less soluble and readily adsorbed at lower pH, and this phenomenon could be explained by an electrostatic repulsion effect between species in solution and activated carbon surface; as pH increases, removal of OMPs decreases. The influence of pH was studied, and it was observed that when pH became alkaline, the adsorption of OMPs reduced considerably. High pH makes the contaminants negatively charged, and activated carbon is also negatively charged, which causes repulsive force between AC surface and OMPs (Schreiber, 2005).

When the coagulation-flocculation process is used as a pre-treatment step for activated carbon adsorption, the alum (acidic in nature) affects the pH of the solution and the organic content of the influent to carbon columns (Semmens et al., 1986). Carbon use will decrease by adding an acidic medium to the influent. The service life of the activated carbon will also be extended by adding an acidic medium to the influent. This is because floccules formed by the use of the coagulant will be filtered, thus preventing fouling (Semmens et al., 1986). By adding an external acidic medium to the influent, the carbon use will decrease, and activated carbon service life will be extended because the organic content of the influent will be reduced by a higher coagulant dose (Semmens et al., 1986). Since pH is an important factor for biological processes, abnormal pH in biological treatment processes can reduce the rate of organic compound removal from the wastewater, which will affect the biochemical oxygen demand (BOD) concentrations. At pH range of 6 to 8 most micro-organisms thrive

Temperature plays a vital role in removing Dissolved Organic Micropollutants (DOM) since higher water temperatures decrease the solution viscosity and increase the adsorption capacity. Therefore, increased adsorption of DOM with increasing temperatures might be explained by entropic effects (Schreiber, 2005). The entropic effect can be explained as DOM forming larger molecules at lower temperatures and fall apart into smaller molecules at higher temperatures (Zhao and Ziming, 2020).Instead of one large molecule with access to a small surface area for binding, breaking down the large molecule into smaller molecules will allow it to access a larger GAC surface area. In this case, the average size of DOM molecules would decrease with increasing temperature, resulting in an increased accessible GAC surface area (Zhao and Ziming, 2020).

However, the adsorption amount and saturated adsorption decrease as the adsorption temperature increases, where lower temperatures favour adsorption (Chen et al., 2011). This can be explained with Le Chatelier's principle that when a system (Activated carbon) experiences disturbance, it will respond with a new equilibrium state. When the temperature has increased, the principal says that the molecules (OMP's) attached to the carbon surface will detach, which is called desorption. But the decrease in temperature can hinder biological processes by reducing the rate of biological reactions. Temperatures between 20-30^{0}C are considered optimum for biological processes such as activated sludge treatment and bio-reactors (Ji, Zhu, 2021). Controlling temperature is another hurdle due to most of the treatment procedures are exposed to external temperature. So, based on the climate conditions, the temperature in the treatment process is maintained.

5.6 Carbon usage rate for wastewater treatment

Carbon usage rate is an essential factor in calculating the mass of GAC required to treat a unit volume of WW until a breakthrough occurs. CUR can be calculated using Equation (5). Table 3 shows the CUR from two design reports (Rodríguez et al., 2015; EPA, 2000) and three studies on micropollutant removal Kårelid et al. (2017), Fundneider et al. (2020) and Altmann et al. (2016). Typical dosage rates for biological (activated sludge), the secondary effluent range at 0.1 – 0.23 kg/m^3 or the range can also be written as 100 – 230 mg/L.

Table 3: Carbon usage rate for municipal wastewater treatment plant.

Source	**CUR (kg/m^3)**
(Rodríguez, 2015)	0.12-0.23
	0.29 – 1.04[1]
(Fundneider, 2020)	0.105
(Kårelid, 2017)	0.1-0.18
(Altmann, 2016)	0.11
(EPA 2000)	0.08-0.21

CUR = Carbon Usage Rate

[1] = Physio-Chemical treatment

Physio-chemical treatment of wastewater focuses primarily on the separation of colloidal particles, and this is achieved through the addition of coagulants. Carbon use for physio-chemical treatment is 0.21 – 1.04 kg/m^3 due to the involvement of chemicals that modify the physical state of colloidal particles to stabilize and make them form flocs for settling and filtration process. An increase in the concentration of MP, DOC, SS in the influent requires an increased amount of carbon to remove that substance (Golovko, 2020). Depending on the chemical process (coagulation, ozonation, or chlorination) used, the wastewater characteristics (pH, alkalinity, organics, turbidity) can vary and affect the EBCT, causing variation in CUR.

5.7 Hydraulic Loading Rate and Bed Depth

The hydraulic loading rate is the most crucial factor as it determines EBCT in GAC filtration. Hydraulic loading rate can be calculated using Equation 6. Table 4A Appendix 1 shows that for an open-top GAC filter that is commonly used in municipal treatment plants, the bed depths may range from 1.5 -2.5 m. When more refined GAC is used, smaller bed depths are necessary for influents with high TSS concentrations (since surface adsorption and refined grains have higher surface area) and larger bed depths for low TSS concentrations (Böhler et al., 2019). The minimum bed depth of 1.5m can be related to the mass transfer zone within the initial layers of the GAC bed where adsorption occurs. At the very beginning of an adsorption process, the activated carbon layer at the top of the column encounters high concentrations of organic matter, and this area has the highest mass transfer speed. In mass transfer, the organic matter from the wastewater transfers onto the activated carbon surface. So applying a depth of 1.5 m will act as a reserve when the initial layers are used up. By taking contact time between 20-30 min and filter bed depths between 1.5-2.5 m, hydraulic loading rate is calculated between 3 – 7 m/h. When the plant is designed to operate at heavy loads, multiple filters are recommended for availability when one filter goes under maintenance and reactivation.

6 Design proposal

This section presents the typical design recommendations for GAC filtration based on material, grain size, and filter column design.

6.1 Selection of GAC

Table 4 shows the physical properties of GAC based on the material used (Bitumen, Lignite, Coconut). Iodine number can be defined as the amount of iodine adsorbed into GAC, giving it an estimation of the total pore volume available. According to Rajeshwar et al. (2019) Methylene blue number (MBN) can be defined as the amount of methylene blue dye which is adsorbed by 1.0 g of GAC.

Table 4: Properties of activated carbon-based on raw materials used.

Properties	Bitumen	Lignite	Coconut
Surface area(m^2/g)	900-1100	900-1200	1000-1100
Iodine number (mg/g)	900-1000	600-900	1000
density (Kg/m^3)	500-560	320-400	420-500
MBN(mg/g)	min 230	min 260	min 200

It can be observed that a higher iodine number gives better micropore volumes, which means that smaller organic molecules will be preferentially adsorbed. At the same time, higher MBN will show that the carbon has more mesopore volumes which adsorb medium-size molecules. In Table 4, we see that the coconut shell has a denser micropore structure and lignite has more mesopores.

Table 5: US mesh size and effective grain size of GAC based on material.

Material	Effective mesh size	Effective grain size (mm)
Bituminous	8 x 30	1.25
Lignite	8 x 30	1.35
Coconut shell	8 x 30	1.2

The effective US mesh size is selected as 8 x 30, as seen in Table 5. Here 8 x 30 effective Mesh size for granular activated carbon means that at least 93% of the granular carbon by weight are more significant than 30 Mesh which is 0.60mm, and granular carbon by weight is at least 90% smaller than 8 Mesh which is 2.36mm granule size (ISO, 1990).

6.2 Filter column design

Typical design recommendations are focused on municipal wastewater treatment plants. The ranges for the design criteria are given in Table 6 below.

Table 6: Typical Design values GAC filter column

Design criteria	Range	unit
EBCT		
Biological wastewater treatment	20 – 30	min
Physio chemical treatment	≥ 30	min
Carbon use		
Biological treatment of municipal wastewaters	0.1 – 0.21	kg/m^3
Physiochemical treatment of municipal wastewaters	0.21 – 1.04	kg/m^3
Hydraulic Loading		
Municipal wastewater treatment	3 - 7	m/h
GAC bed		
Depth	1.5 – 2.5	m
Silex Bed depth		
Fine silex	0.2 - 0.3	m
Coarse silex	0.3 – 0.45	m

Physio-chemical treatment is based on using chemicals such as coagulants and ozonation processes, where using such treatments gives additional chemical by-products that need to be treated. The biological treatment represents the activated sludge process and different bio-reactors.

7 Conclusions

To find relevant data on GAC filter performance in removing OMP's such as carbamazepine, diclofenac, and sulfamethoxazole in municipal wastewater treatment. A collection of 23 studies was selected from the available literature due to their focus on adsorption performance on OMP's. A breakthrough of 20% was assumed to understand and explain the influence of the parameters based on the results and the design criteria obtained, and the following conclusions are drawn.

- It was found that SS and DOC play an essential role in determining the lifetime of the GAC bed, where high DOC content leads to faster exhaustion of GAC and also increases CUR leading to an early breakthrough of CBZ, SMX, and DCF. High SS content in influent may result in early fouling of the first layers of the GAC bed. SS affects the design criteria through the selection of bed depth and the type of pre-treatment needed, and an SS and DOC content of less than 20 and 10mg/l is recommended in the influent of the GAC filter.

- Pre-treatment processes play a significant role in the effectiveness of the GAC filter. This study shows that pre-treatment controls the DOC (partially in the sand and membrane filtration) TSS that flows into the GAC filter.

- The EBCT is the main parameter for designing GAC filters for wastewater treatment. It is observed that EBCT mainly influences the breakthrough point of individual OMP's where SMX takes more than 30min compared to CBZ, DCF at less than 20min. EBCT also plays an essential role in the biological degradation of DOC. Increasing the EBCT leads to better removal of the micropollutants and better utilization of the GAC adsorption capacity. Approximately 20 – 30 min was suggested for typical wastewater treatment and more than 30 min for physio-chemical wastewater treatment.

8 Recommendations for future studies

To design a GAC there are many studies out there showing the design criteria, but few studies that give a clear understanding of why/how the parameters (EBCT, SS, DOC, pH, temperature, grain size, CUR, and bed depth) affect the selection of design criteria. We have obtained the answers to our objective mentioned for this study, but finding the data and analyzing it was challenging. For CBZ, bed volumes treated ranged from 42 – 78,00, and the adsorber breakthrough resulted in a wide variation of empty bed contact time. Better analysis and understanding can be obtained when there are more studies with the following conditions.

- Materials such as coconut, bitumen, lignite should be tested with equal volumes to compare each material with similar conditions.
- The test processes should have consistent EBCT and should be tested with 10,20,30,40min (since some MP's that are resilient need higher contact times). The flow rate or hydraulic loading should be consistent following the same conditions as EBCT. EBCT with the interval of 10 min was chosen since smaller intervals barely show variations in breakthrough time for individual micropollutants (CBZ, DCF compared to SMX).
- Pre-treatment is an essential factor in controlling the influent characteristics of the GAC filter. More tests should be done with various combinations (ozonation and sand filtration or ozonation and membrane filtration) to find the economic and qualitative efficiencies that can be studied.
- Spiked tests for DOC and SS to have a consistent solution to work within GAC experiments. Here DOC can be tested at 0-5mg/l, 5-10 mg/l, 10-15 mg/l simultaneously in three similar pilot test setups to get good breakthrough curves. The adsorption of micropollutants under lower and higher concentrations of DOC can be studied.
- The test should be done with each effective grain size distribution like 8 x 30 and 12 x 40. Doing so will give a better understanding of how grain size distribution will influence the effectiveness of removal.
- The test should include factors like temperature and pH due to some studies showing different results with temperature effect on adsorption.

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Appendix 1

***Table 1A**: Adsorber characteristics for Carbamazepine*

Sl. No	studies	DOC (mg/l)	EBCT(min)	Breakthrough at 20% (BV)	Pre-Treatment	Grain size(mm)
1	Kårelid, V.	10.2	20	4200	PT+SF	1.2
2	Kårelid, V	10.2	20	>5000	PT+SF	1.4
3	Kårelid, V	10.2	20	>5000	PT+SF	0.7
4	Kårelid, V	10.2	20	>5000	PT+SF	1.5
5	Kårelid, V	10.2	20	3300	PT+SF	1.6
6	Golovko, O	7.6	18	28,000	SC+SF	1
7	Golovko, O	7.6	18	28,000	SC+SF	0.7
8	Golovko, O	7.6	6	75000	SC+SF	0.7
9	Snyder, S	3	7.6	34,000	SC+SF	0.8
10	Snyder, S	3	7.6	78,600	SC+SF	1.2
11	Benstoem, F	14.4	11	500	SC	2
12	Benstoem, F	15.2	14	4100	SC	1.5
13	Benstoem, F	16.6	14	2400	SC	1.7
14	Benstoem, F	14.3	16	4300	SC+FF	1.5
15	Benstoem, F	14.3	33	7200	SC+FF	1.5
16	Kazner, C	5.2	2	12,000	SC+FF	1.5
17	Kazner, C	5.2	11	10,400	SC+FF	1.5
18	Kazner, C	5.2	14	8200	SC+FF	1.5
19	Kazner, C	5.2	15	7400	SC+FF	1.5
20	Knopp, G.	6.7	25	10,400	SC	1.7
21	Knopp, G.	6.7	25	13,600	SC+UF	1.7
22	Knopp, G.	6.7	13	23,200	SC+UF	1.8
23	Knopp, G.	6.7	8	24,000	SC+UF	1.8
24	Nahrstedt, A	11.3	33	9500	SC+FF	1.5
25	Nahrstedt, A	11.3	33	9500	SC+FF	1.5
26	Nahrstedt, A	7.3	28	15,000	SC+FF	1.5
27	Nguyen LN	2	7	8,300	SC	0.7
28	Paredes, Lidia & Alfonsín	3.5	20	>35,000	MF	1.5
29	Paredes, Lidia & Alfonsín	3.5	20	>35,000	MF	1.5
30	Paredes, Lidia & Alfonsín	8.6	20	4000	SF	1.5
31	Paredes, Lidia & Alfonsín	8.6	20	4000	SF	1.5
32	Guilaine Jaria	5	4.17	1495	MF	0.8
33	Guilaine Jaria	5	2.016	1185	MF	0.8
34	Guilaine Jaria	5	1.4	514	MF	0.8
35	Guilaine Jaria	14.45	4.17	172	MF	0.8
36	Guilaine Jaria	14.45	2.016	179	MF	0.8
37	Guilaine Jaria	14.45	1.4	42	MF	0.8
38	F. Zietzschmann	11	3.67	1071	MF	0.14
39	F. Zietzschmann	11	3.67	714	MF	0.14

Table 2A: *Adsorber characteristics for Diclofenac*

Sl. No	Studies	DOC (mg/l)	EBCT(min)	Breakthrough at 20% (BV)	Pre-Treatment	Grain size(mm)
1	Kårelid, V.	10.2	20	2100	PT+SF	1.2
2	Kårelid, V	10.2	20	5000	PT+SF	1.4
3	Kårelid, V	10.2	20	5000	PT+SF	0.7
4	Kårelid, V	10.2	20	5000	PT+SF	1.5
5	Kårelid, V	10.2	20	3200	PT+SF	1.6
6	Snyder, S	3	7.6	18,100	SC+SF	0.8
7	Snyder, S	3	7.6	63,400	SC+SF	1.2
8	Benstoem, F	14.4	11	700	SC	2
9	Benstoem, F	15.2	14	2300	SC	1.5
10	Benstoem, F	16.6	14	2500	SC	1.7
11	Benstoem, F	14.3	16	3800	SC+FF	1.5
12	Benstoem, F	14.3	33	7700	SC+FF	1.5
13	Knopp, G.	6.7	25	10,400	SC	1.7
14	Knopp, G.	6.7	25	9300	SC+UF	1.7
15	Knopp, G.	6.7	13	31,400	SC+UF	1.8
16	Knopp, G.	6.7	8	16,300	SC+UF	1.8
17	Nahrstedt, A	11.3	33	13,000	SC+FF	1.5
18	Nahrstedt, A	11.3	33	13,000	SC+FF	1.5
19	Nahrstedt, A	7.3	28	6000	SC+FF	1.5
20	Nguyen LN	2	7	11,000	SC	0.7
21	Paredes, Lidia & Alfonsín	3.5	20	24,000	MF	1.5
22	Paredes, Lidia & Alfonsín	3.5	20	25,000	MF	1.5
23	Paredes, Lidia & Alfonsín	8.6	20	4000	SF	1.5
24	Paredes, Lidia & Alfonsín	8.6	20	4000	SF	1.5
25	F. Zietzschmann	11	3.67	370	MF	0.14
26	F. Zietzschmann	11	10	2140	MF	0.14
27	F. Zietzschmann	11	10	2140	MF	0.14
28	F. Zietzschmann	11	5	3926	MF	0.25
29	F. Zietzschmann	11	24	3214	MF	0.25
30	J.L. Sotelo	3	0.55	6545	MF	0.6
31	J.L. Sotelo	3	0.22	5454	MF	0.6
32	J.L. Sotelo	3	0.22	4958	MF	0.6
33	J.L. Sotelo	3	0.33	5618	MF	0.6
34	José Luis Sotel	5	0.565	1991	MF	0.59
35	José Luis Sotel	5	0.75	5500	MF	0.59
36	José Luis Sotel	5	0.94	6781	MF	0.59
37	José Luis Sotel	3	0.75	6476	MF	0.59
38	José Luis Sotel	5	0.75	5332	MF	0.59
39	José Luis Sotel	7	0.75	2666	MF	0.59
40	José Luis Sotel	7	2.26	5309	MF	0.59
41	José Luis Sotel	7	1.131	4492	MF	0.59
42	José Luis Sotel	7	0.75	1845	MF	0.59

Table 3A: *Adsorber characteristics for Sulfamethozole*

Sl. No	studies	DOC (mg/l)	EBCT(min)	breakthrough at 20% (BV)	Pre-Treatment	grain size(mm)
1	Snyder, S	3	7.6	9,370	SC+SF	1
2	Snyder, S	3	7.6	30,700	SC+SF	1
3	Knopp, G.	6.7	25	<9600	SC	2
4	Knopp, G.	6.7	25	8900	SC+UF	2
5	Knopp, G.	6.7	13	>8200	SC+UF	2
6	Knopp, G.	6.7	8	>7400	SC+UF	2
7	Nahrstedt, A	11.3	33	7900	SC+FF	2
8	Nahrstedt, A	11.3	33	7500	SC+FF	2
9	Nahrstedt, A	7.3	28	9100	SC+FF	2
10	Naguyen LN	2	7	9,900	SC	1
11	Nahrstedt et al. (2014)	15	75	5300	SC+FD	2
12	Nahrstedt et al. (2014)	15	15	5000	SC+FD	2
13	Nahrstedt et al. (2014)	15.9	75	4600	SC+FD	2
14	Nahrstedt et al. (2014)	15.9	75	2200	SC+FD	2
15	Nahrstedt et al. (2014)	15.9	42	2400	SC+FD	2
16	Nahrstedt et al. (2014)	14.7	32	2100	SC	2
17	Nahrstedt et al. (2014)	14.7	32	1960	SC	2
18	Nahrstedt et al. (2014)	6.3	40	3000	SC+FF	2
19	Nahrstedt et al. (2014)	6.3	20	3200	SC+FF	2
20	STOWA No. 17 (2007)		20	3000	SC	2
21	STOWA No. 34 (2009)		20	4500	SC	3
22	STOWA No. 27 (2010)		20	3000	SC	2
23	STOWA No. 27 (2010)		20	3200	SC	2
24	STOWA No. 27 (2010)		20	2200	SC	2
25	Kreuzinger et al. (2015)	7.4	30	3000	SC	2
26	Altmann et al. (2016a)	11.4	19	4500	SC	2
27	Bornemann	7.7	23	3800	SC	1
28	Bornemann	6.6	23	4900	SC+FF	1
29	Bohler et al. (2017)	5.4	14	4500	SC	1
30	Bitterwolf et al. (2016)	5.5	13	1500	SC	2
31	Bitterwolf et al. (2016)	5.5	21	2800	SC	2
32	Jan Freihardt	4.5	1.5	4123	MF	2
33	Jan Freihardt	4.5	1.5	10000	MF	1
34	Isabell Kopping	18	25	176		1
35	Isabell Kopping	18	70	814		1
36	Isabell Kopping	18	92	1100		1
37	Isabell Kopping	18	115	>800		1
38	Isabell Kopping	18	25	588		2
39	Isabell Kopping	18	70	1038		2
40	Isabell Kopping	18	92	1280		2
41	Isabell Kopping	18	115	>1300		2

Table 4A: *Compiled data on bed depth and hydraulic loading from various studies.*

Source	Type of Treatment	Bed depth (m)	Hydraulic Loading (m/h)	Filter type
(Pablo Ures Rodríguez 2015)	General	3 - 9m	5 – 25	Closed top GAC filter
	Typical treatment	1.8 - 4	12	
	Tertiary treatment	3 - 10	7 – 16	
	Physio-chemical Treatment	2.7 - 11	6 – 15	
(Böhler M. 2019)	Water treatment	1.5 - 2.5	4 -7	open top GAC filter
(EPA 2000)	Water treatment	3 - 12	7 - 12.6	Closed top GAC filter
(DeSilva 2000)	Water treatment	1.5 - 2	3 - 5	open top GAC filter