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Removal efficiency of multiple per- and polyfluoroalkyl substances (PFAS) in groundwater at a landfill using granular activated carbon (GAC) and anion exchange (AIX) column tests

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Abstract

Per- and polyfluorinated substances (PFAS) are used in many areas of application due to their many beneficial properties such as heat resistance, insulator and water- and oil repellent. PFAS containing products can often be found in landfills and their leachate. This study compares the two common treatment techniques granulated activated carbon (GAC) and anion exchange (AIX) for treating groundwater at a landfill site. The removal efficiencies of the PFAS found at the site were determined for both methods as well as the cost of treatment for removal efficiencies at 99, 95, 90, 85, 80 and 50 % for one cubic metre of groundwater. Twenty different PFAS were found and the removal efficiency of Σ PFAS ranged between 4 – 90 % for two stage GAC and 30 – 100% for AIX. Within the groups perfluoroalkyl carboxylic acid (PFCA) and perfluorosulfonic acid (PFSA), both methods were most efficient in removing long chains. PFSA generally had a higher removal efficiency than PFCA. The cost of removing PFAS was related to the removal efficiency. Since AIX had a higher removal efficiency the cost became lower, despite the filter media costing nearly seven times more than GAC's. The costs of removing PFCA and PFSA were 3.1 – 32 and 2.3 – 6.5 euros/m³ groundwater for removal of 50 – 99% using AIX. For GAC, the cost could not be calculated for 99 % removal since the removal efficiencies were too low for the Lin and Huang adsorption model to work. For 50 – 95% removal the costs for PFCA and PFSA were 2.9 – 23.1 and 2.8 – 6.9 euros/m³ groundwater.

Keywords: PFAS, granular activated carbon, anion exchange, removal efficiency, cost

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REFERAT

Per- och polyfluorerade ämnen (PFAS) används inom många områden på grund av deras fördelaktiga egenskaper som värmebeständighet, isolerande förmåga samt avvisande av vatten och olja. PFAS-innehållande produkter finns ofta i deponier och deras lakvatten. Denna studie jämför två välbeprövade behandlingsmetoder, granulärt aktivt kol (GAC) och anjonbyte (AIX), för att behandla PFAS-förorenat grundvatten vid en deponi. Borttagnings effektiviteten av de PFAS som fanns på platsen bestämdes för båda metoderna samt kostnaden för behandling med borttagnings effektivitet på 99, 95, 90, 85, 80 och 50 % för en kubikmeter grundvatten. Tjugo olika PFAS identifierades och borttagnings effektiviteten för summan av PFAS varierade mellan 4 – 90 % för två stegs GAC och 30 – 100 % för AIX. Inom grupperna perfluorerade karboxylsyror (PFCA) och perfluorerade sulfonsyror (PFSA) var båda metoderna mest effektiva för att avlägsna långa kedjor. PFSA hade generellt en högre borttagnings effektivitet än PFCA. Kostnaderna för att avlägsna PFAS var relaterade till hur effektivt ämnena kunde avlägsnas. Eftersom AIX hade en högre borttagnings effektivitet blev kostnaden lägre, trots att filtermediet kostade nästan sju gånger mer än GACs. Kostnaderna för att avlägsna PFCA och PFSA var 3,1 – 32 och 2,3 – 6,5 euro/m³ grundvatten för att avlägsna 50 – 99 % med AIX. För GAC kunde inte kostnaden på 99 % avlägsnande beräknas eftersom borttagnings effektivitet var för låg vid först provtagningspunkten för att kunna använda Lin och Huang's adsorptionsmodell. Vid 50 – 95 % avlägsnande var kostnaderna för PFCA och PFSA 2,9 – 23,1 respektive 2,8 – 6,9 euro/m³ grundvatten för GAC.

Nyckelord: PFAS, granulärt aktiverat kol, anjonbytare, borttagnings effektivitet, kostnader

PREFACE

This thesis is the final part of the program Environmental and Water Engineering at Uppsala University and Swedish University of Agricultural Science (SLU). The project was a collaboration between Uppsala Vatten och Avfall AB and SLU with Philip McCleaf from Uppsala Vatten och Avfall AB as supervisor and Lutz Ahrens from SLU's department of Aquatic Sciences and Assessments as subject reviewer. EU LIFE SOuRCE – LIFE20 ENV/ES/000880 was also part in making the thesis possible through its financial support.

I want to thank both Philip McCleaf and Lutz Ahrens for sharing their knowledge and making time for meetings and answering my questions the whole semester. Thanks for the quick and thorough feedback. I'd also like to thank Oscar Skirfors, PhD student at SLU's department of Aquatic Sciences and Assessments, who has helped me with the day to day work and always been supportive. Lastly, I'd like to thank all the people working at Hovgården who made me feel welcome and helped me.

Sara Ferndahl
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POPULÄRVETENSKAPLIG SAMMANFATTNING

Per- och polyfluorerade alkylsubstanser (PFAS) har fått alltmer uppmärksamhet på senare tid i och med sänkta gränsvärden och rättegångar om vem som ansvarar för spridning till dricksvatten. Det är ett ämne som har använts både inom industrisektorn och för privat bruk sedan 1940-talet. Exempel på användningsområden är brandskum, teflonpannor och impregnering av kläder. Anledningen till att PFAS har så många användningsområden är deras eftertraktade egenskaper såsom värmeresistens, isolerande samt vatten- och fettavstötande. Dess utbredda användning har resulterat i spridning till ytvatten, jord och grundvatten. En utsläppskälla är lakvatten från deponier, som ofta innehåller produkter med PFAS. Om lakvattnet läcker från deponin blir kan både den omkringliggande jorden och sedan grundvattnet bli förorenat.

Det har utvecklats ett flertal tekniker för att rena PFAS-förorenat vatten. Två av de vanligaste är granulärt aktiverat kol (GAC) och anjonbytare (AIX). GAC är behandlat kol som har de två viktiga egenskaperna att det är poröst och hydrofob, alltså vattenavvisande. Även PFAS har en hydrofob del och det skapar attraktion till GAC och gör att PFAS kan adsorbera på GAC:s ytor. AIX ser ut som små plastpärlor och dessa pärlor har negativa joner, även kallat anjoner, på sin yta. PFAS har utöver sin hydrofoba del en hydrofil del som består av en samling atomer vilka utgör en funktionell grupp. Den funktionella gruppen ger PFAS en negativ laddning och gör PFAS till en anjon. Vid avlägsning av PFAS med AIX byts anjonerna på AIX ut till PFAS:s funktionella grupp. Utöver jonbytet finns det även en hydrofob attraktion mellan AIX och PFAS hydrofoba del.

I den här studien undersöktes borttagningegraden av PFAS från grundvatten vid en avfallsdeponi med metoderna GAC och AIX. För GAC skedde avskiljning i två steg och vattnet gick igenom två GAC-filter medan vattnet bara gick igenom ett filter för AIX. Effektiviteten av de två metoderna jämfördes för de grupper av PFAS som hittades på platsen. Kostnadsskillnaden mellan de två metoderna undersöktes också för PFAS-grupperna perfluorerade karboxylsyror (PFCA) och perfluorerade sulfonsyror (PFSA).

Totalt upptäcktes 20 olika PFAS. Utöver grupperna PFCA och PFSA hittades även grupperna fluortelomerer (FTSA), perfluorsulfonamid (FOSA) och perfluoroktansulfonamid-ättiksyra (FOSAA). Avskiljningsgraden för summan av alla PFAS var 4 – 90 % för två stegs GAC och 30 – 100 % för AIX. Över lag hade AIX en högre borttagningsgrad för de olika PFAS. I ett tidigt stadium togs en större andel FOSA och FOSAA bort av GAC men sedan blev AIX mer effektiv. En gemensam trend för båda metoderna var att PFAS med längre kolkedjor var lättare att avlägsna. En förklaring till det var att långa kolkedjor blir mer hydrofoba. Det gjorde attraktionen till både GAC och AIX starkare. En annan trend var att PFSA var lättare att ta bort än PFCA. Skillnaden mellan de här två grupperna är den funktionella gruppen och PFSA:s hade större attraktion till GAC och AIX.

Kostnaden för AIX-filter var betydligt högre än för GAC med 10 080 euro/m³ filtermaterial respektive 1516 euro/m³ filtermaterial. Trots det blev reningskostnaderna för en kubikmeter vatten billigare med AIX. Vid kostnadsjämförelsen delades PFCA och PFSA in i långa och korta kedjor. Den högsta borttagningsgraden då kostnader kunde beräknas för alla grupper med både GAC och AIX var vid 95 %. Då kostade det 16,9 och 23,1 euro för långa respektive korta PFCA kedjor med GAC. Med AIX var kostnaderna 7,5 och 10,8 euro för långa respektive korta PFCA kedjor. För både GAC och AIX konstaterades det att de långa kedjorna var billigare att avskilja. I jämförelse med PFSA var kostnaderna högre för PFCA. För PFSA kostade det 5,8 och 6,9 euro för långa och korta kedjor med GAC samt 3,5 och 3,9 euro med AIX. Vid lägre borttagningsnivåer minskade priserna och det blev en lägre skillnad mellan de två metoderna. Anledningen till att AIX blev billigare var att borttagnings effektiviteten var högre och det samma gällde skillnad mellan korta och långa kedjor samt PFCA och PFSA.

GLOSSARY

AFFF - Aqueous film-forming foam
AIX - Anion exchanger
BV - Bed volume
DOC - Dissolved organic carbon
EBCT - Empty bed contact time
GAC - Granular activated carbon
MTZ - Mass transfer zone
MUR - Media usage rate
O&M - Operation and maintenance
PASF - Perfluoroalkane sulfonyl fluoride
PBT - Persistent, bioaccumulative and toxic substance
PFAS - Per- and poly-fluoroalkyl substances
PFAA - Perfluoroalkyl acids
PFBA - Perfluorobutanoic acid
PFBS - Perfluorobutanesulfonic acid
PFCA - Perfluoroalkyl carboxylic acid
PFDA - nonadecafluorodecanoic acid
PFDoDA /PFDoA - Perfluorododecanoic acid
PFDS - Perfluorodecanesulfonic acid
PFHpA - Perfluoroheptanoic acid
PFHpS - Perfluoroheptanesulfonic acid
PFHxA - undecafluorohexanoic acid
PFHxDA - Perfluorohexadecanoic acid
PFHxS - Perfluorohexanesulfonic acid
PFNA - Perfluorononan-1-oic acid
PFOA - Perfluorooctanoic acid
PFODA - Perfluorooctadecanoic acid
PFOS - Perfluorooctanesulfonic acid
PFPE - Perfluoroalkyl and polyfluoroalkyl ether carboxylic acids
PFPeS - Perfluoropolyethers
PFPeA - Perfluoropentanoic acid
PFSA - Perfluorosulfonic acid
PFTeDA - Perfluorotetradecanoic acid
PFTrDA - Perfluorotridecanoic acid
PFUnDA / PFUnA - Perfluoroundecanoic acid
REACH - Registration, Evaluation, Authorisation, and restriction of chemicals
WWTP - Wastewater treatment plant
6:2 FTOH - Fluorotelomer 6:2-alkohol
6:2 FTSA - 6:2-fluorotelomersulfonic acid
8:2 FTOH - Fluorotelomer 8:2-alkohol

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1. INTRODUCTION

Per- and poly-fluoroalkyl substances (PFAS) have been used since the 1940s and have a wide range of applications for industries and households. That is due to their useful properties such as being both water and fat repellent and having high stability (Androulakakis et al. 2022). However, these properties also make them persistent and bioaccumulative. During the last few decades, it has been discovered that several PFAS have adverse effects on both health and environment (OECD 2013). Since they have been used for many applications, it can also be found in waste facilities such as solid waste landfills (Coffin et al. 2023). Landfills release leachate which can leak to the groundwater. Modern landfills have a protective or impermeable layer in the bottom that prevents the leaking and collection of leachates (Ren 2022 et al.). Although precautions are taken to prevent leaking it still occurs sometimes which has happened at the landfill site Hovgården in Uppsala (Golder Associates 2004). Both the soil and groundwater have been contaminated with PFAS (Uppsala Vatten och Avfall AB 2023). This study will focus on treatment techniques of the groundwater at Hovgården, a landfill site in Uppsala, Sweden.

The landfill facility Hovgården is one of the sites used to evaluate a new combination of three treatment methods as a part of the EU LIFE SOuRCE Project. The aim of the LIFE SOuRCE project is to find a cost efficient remediation method for both long and short chain PFAS in comparison with conventional treatment methods. At Hovgården, the three methods used will be surface active foam fractionation followed by electrochemical oxidation for the concentrated foam and phytoremediation as an additional treatment for the short chain PFAS (LIFE SOuRCE n.d.). This study will focus on two commonly used techniques to remove PFAS (McCleaf et al., 2017), granular activated carbon (GAC) and anion exchange (AIX) filters.

1.1 AIM AND RESEARCH QUESTIONS

The aim of this study was to evaluate how well PFAS could be removed from the groundwater at Hovgården using either GAC or AIX. The study will also compare the treatment costs between the two methods. The following questions will be answered in the report.

- How efficient are two stage GAC filters for treatment of PFAS in groundwater at Hovgården?
- How efficient are AIX filters for treatment of PFAS in groundwater at Hovgården?
- What are the differences in efficiency for treatment of PFAS in the groundwater at Hovgården between GAC and AIX?
- What are the cost differences between using GAC and AIX filters?

2. BACKGROUND

2.1 PFAS

PFAS are a group of hydrocarbons where at least one of the hydrogen atoms has been exchanged with a fluorine atom. Hydrocarbons where all hydrogens have been exchanged for fluorine are called perfluoroalkyl substances and hydrocarbons with partly exchanged hydrogens are polyfluoroalkyl substances. There is no international agreement on the definition of PFAS. One definition commonly used in Sweden is the Organisation for Economic Co-operation and Development's (OECD) definition (Kemikalieinspektionen 2023a), "*PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS*" (Wang 2021).

PFAS has a vast area of use where some of the more commonly known applications are firefighting foam, impregnation of textiles and non-stick cooking pans. They have many desirable properties such as low friction, being a surface active agent, resistance to heat and chemical agents, fat and water repellent, and a good insulator (OECD 2013). Since the 1940s PFAS have been used for both industrial and consumer applications which has led to spreading in the environment. PFAS can be transported by water due to its hydrophilic properties and more volatile PFAS can also be transported by air (Ahrens 2011). It can therefore be found in most places, even as far as the Arctic (Giesy & Kannan 2001). Another reason for finding PFAS in remote places is that they are persistent. They are also found to be bioaccumulative and biomagnifying, meaning that they increase in the biomass over time and increase upwards in the food chain respectively. This is problematic since PFAS are classified as toxic substances and probably have adverse effects on both humans and animals (Kemikalieinspektionen 2023a). There is still not enough research for the different PFAS to determine the health effects. Although, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been shown to be toxic for reproduction and cause reduced humoral immune response for children. They are also suspected of being carcinogenic (OECD 2013).

2.1.1 Classification and properties of PFAS

PFAS are a large group of substances which can be divided into several groups and subgroups (Figure 1). They are usually divided into the two main groups of polymers and non-polymers (OECD 2013) where the polymers are large molecules made up of several smaller units (Britannica 2023). The polymeric PFAS is divided into three groups. The first one is fluoropolymers where the fluorine atoms are attached directly to the backbone which only consists of carbons, the second is side chained fluoropolymers where there are fluorinated side chains on the carbon backbone and the third is perfluoropolyether which have a backbone of both carbon and oxygen, but the fluorine is only attached to the carbons (OECD 2013).

Polymeric PFAS are precursors for non-polymeric PFAS because they can be broken down into smaller segments (Dixit 2021). Non-polymeric PFAS are smaller molecules and the backbone of carbon is attached to a functional group such as carboxylates or sulfonates (Buck et al. 2011). There are four groups of non-polymers, perfluoroalkyl acids (PFAA), perfluoroalkane sulfonyl fluoride (PASF), fluorotelomer-based products and lastly perfluoroalkyl and polyfluoroalkyl ether carboxylic acids (PFPE) (OECD 2013). The non-polymer PFAS are commonly mentioned as short chained and long chained. It is the number of carbons that determine whether it is a short or long chained PFAS. To classify as a long chained PFAS it must either be a perfluoroalkyl carboxylic acid (PFCA), with at least eight carbons or a perfluorosulfonic acid (PFSA) with at least six carbons. Both PFCA and PFSA are subgroups of the PFAA (Buck et al. 2011).

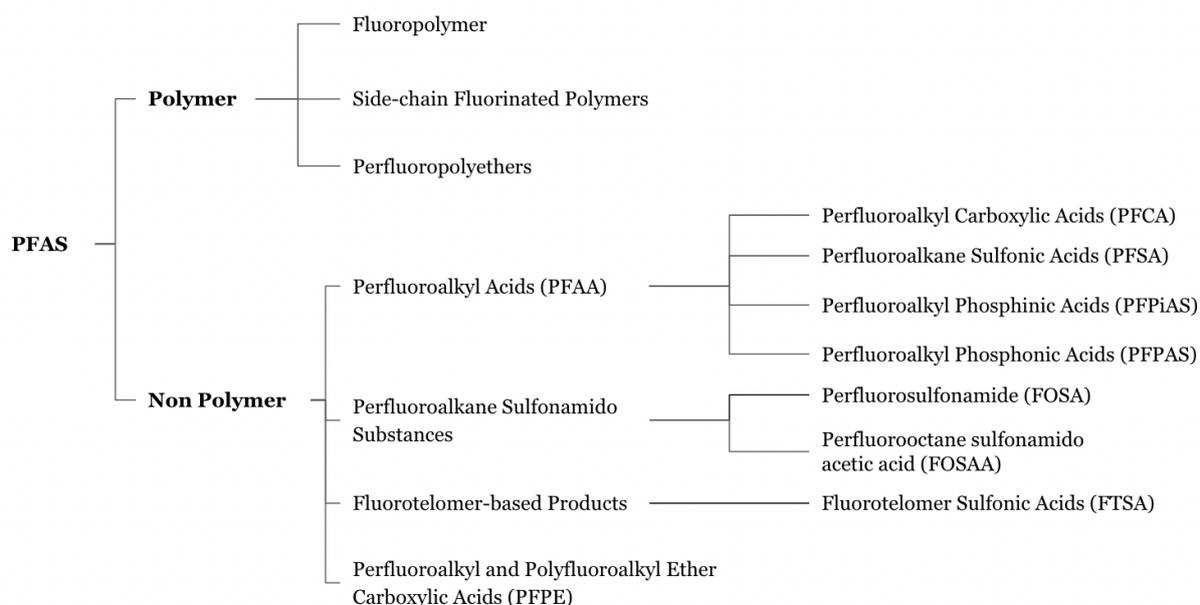


Figure 1. A family tree of the different groups and subgroups of PFAS (based on Buck et al. 2011, OECD 2013 and Knutsen et al. 2019).

It is their many beneficial properties that have made PFAS so common. The strong bond between fluorine and carbon is the reason for several of these properties. Fluorine is the strongest electronegative element and therefore draws the electrons of carbon closer. This is making the molecules strong and persistent (Leung et al. 2023). Because PFAS doesn't easily degrade, it accumulates over time in the environment, animals, and humans. Its bioaccumulative behaviour varies with its chain length where the shorter chain PFAS are more mobile whereas the longer chain PFAS tend to be more bioaccumulative (Kemikalieinspektionen 2023a). So, some of the longer chain PFAS fulfil the criteria of persistent, bioaccumulative and toxic substance (PBT). The fluorine-carbon bond together with the proportion and placement of the fluorine atoms also affects the surfactant properties. A surfactant has both a hydrophilic and hydrophobic part, making it possible for them to create a layer between polar and nonpolar substances. This is a useful property for many applications

including non-stick cooking pans and food packaging (Kancharla 2022; Buck et al. 2011). Another property due to the fluorine-carbon bond is its ionic behaviour. The negatively charged fluorine atoms and functional groups can attract positively charged particles. Because the functional group is negatively charged PFAS becomes an anion (Leung et al. 2023).

2.1.2 Sources of PFAS

Since PFAS have many areas of use it spreads to the environment from several sources. These sources can be divided into point and diffuse sources. A point source is clearly identifiable, whereas a diffuse source has an unclear origin. Diffuse PFAS sources can be caused by both consumer products and industrial activities. Atmospheric transportation and thereafter deposition is one diffuse source from industries. Other diffuse sources are precipitation, surface run-off and degradation of PFAS containing consumer products (Kurwadkar et al. 2022). Identified point sources for PFAS are industrial or manufacturing facilities, wastewater treatment plants (WWTPs), firefighting training sites and landfills (Kurwadkar et al. 2022). PFAS from industrial and manufacturing facilities leave the facilities through wastewater, solid waste, accidental leaks, air emissions and manufactured products (ITRC 2023). There are no manufacturing facilities in Sweden, so all the PFAS needed for products must be imported (Baresel et al. 2022). Some examples of industries that need PFAS for the production and final product are construction, cable and wiring, industrial surfactants, packaging products and surface treatment of textiles (ITRC 2023). The reason firefighting training sites are a point source of PFAS is because several firefighting foams contain PFAS. PFAS contributes to creating an aqueous film-forming foam (AFFF) between the burning material and the foam which allows the foam to spread and suffocate the fire (ITRC 2023). It has become one primary point source for surface water and groundwater (Kurwadkar et al. 2022). The most investigated point source for PFAS is WWTPs. They cause spreading of PFAS to surface and well water (Kurwadkar et al. 2022; Banzhaf et al. 2017). The amount and kind of PFAS that enters the environment from the WWTP depends on what the influent water contains and treatment methods within the WWTP. The spreading from landfills is depending on what kind of waste the landfill receives. It is likely for PFAS to end up at landfills since it's a way to handle hazardous waste. They may receive industrial waste, sludge from WWTP and PFAS-containing consumer products. The landfills produce leachate and this may leak and therefore contribute to spreading of PFAS into the environment (ITRC 2023).

2.1.3 Regulations

There are no regulations covering all different PFAS. In the EU, PFAS concentrations are regulated by Registration, Evaluation, Authorisation and restriction of chemicals (REACH) (ECHA 2023). When one kind of PFAS is restricted, another one soon replaces it. It is often replaced by a short chain PFAS which were believed to be less harmful. However, studies have shown that that is not the case (Nian et al. 2020).

There are several governmental bodies that provide threshold values and recommended values. The Geological Survey of Sweden (SGU) prescribes the threshold values for the groundwater,

but it is Vattenmyndigheten that decides the final value in Sweden. There are two threshold values for groundwater. The first one applies for PFAS 11 which includes perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), perfluorooctanesulfonic acid (PFOS), 6:2-fluorotelomersulfonic acid (6:2 FTSA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), undecafluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and nonadecafluorodecanoic acid (PFDA). The other one applies for PFAS 24 where PFHxS, PFOS, PFOA, PFNA, PFBS, PFHxA, PFBA, PFPeA, Perfluoropolyethers (PFPeS), PFDA, perfluorododecanoic acid (PFDoDA /PFDoA), perfluoroundecanoic acid (PFUnDA / PFUnA), PFHpA, perfluorotridecanoic acid (PFTrDA), perfluoroheptanesulfonic acid (PFHpS), perfluorodecanesulfonic acid (PFDS), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), HFPO-DA / Gen X, ADONA, fluorotelomer 6:2-alkohol (6:2 FTOH), fluorotelomer 8:2-alkohol (8:2 FTOH) and C6O4 are included. The PFAS 11 and PFAS 24 threshold values are 90 ng/L and 4,4 ng equivalents of PFOA/L respectively. The equivalents of PFOA are calculated for each substance in regard to its toxicity. There is also a recommendation to not exceed 45 ng PFOS/L (Kemikalieinspektionen 2023b). There is an additional regulation for PFOS from the Water Framework Directive where the average environmental quality standard for the sum of PFOS was set to 0.65 ng/L for inland surface water (Gobelius et al 2018). In Sweden this is implemented by the Swedish Agency Marine and Water Management (Kemikalieinspektionen 2023b).

Drinking water has its own criterions. In 2020 the EU adopted a new Drinking Water Directive with the limit value of 500 ng/L for the total of all PFAS and 100 ng/L for 20 specific PFAS. These values had to be implemented by all membership countries by 2023. In Sweden it was implemented by the Swedish Food Agency (Naturskyddsföreningen 2022). The limits will become stricter by 2026 with a reduced maximum allowed value for the four PFAS PFOA, PFNA, PFOS and PFHxS at 4 ng/L. The Swedish Food Agency has also set the value of 100 ng/L for 21 specific PFAS. PFAS 4 is included in PFAS 21 and additionally PFBA, PFPA, PFHxA, PFHpA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFBS, PFPS, PFHpS, PFNS, PFDS, PFUnDS, PFDoDS, PFTrDS and 6:2 FTS. These values will be legally binding by 2026 but until then they can be seen as a reference value for when improvements need to be made (Kemikalieinspektionen 2023b).

2.2 SITE DESCRIPTION - HOVGÅRDEN

Hovgården waste facility covers an area of 570 000 m². Today, the facility handles waste from several areas with their three main methods: sorting, landfill and temporary storage (Figure 2). There are two landfills, one active with non-hazardous waste and one inactive with hazardous waste. The inactive landfill stopped receiving hazardous waste in 2016 and the capping was finished in 2019 (Uppsala Vatten 2020). There is a treatment plant at the facility which is used to treat leachate from the landfill and surface run-off water from the facility area. After the treatment, the water is discharged into Hovgårdsbäcken which leads to Lissaån and Tomtaån

that discharges into the lake Funbosjön. The leachate contains higher concentrations of organic material, nitrogen, phosphorus, PFAS, chloride, sulphate and some metals compared to Funbosjön. The concentrations upstream the facility is however about the same as the concentrations in the lake (Ekhagen 2022).

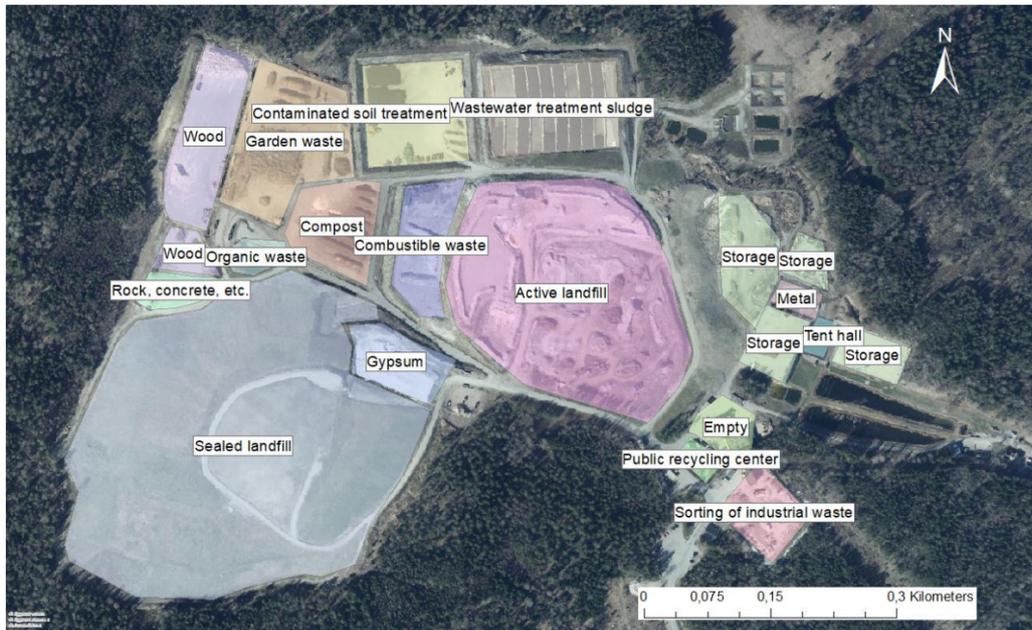


Figure 2. Overview of Hovgården waste facility (Uppsala Vatten och Avfall AB 2023).

2.2.1 Hydrology and groundwater chemistry

Investigations from 2004 concluded that the groundwater flow mainly went from the higher points in the area towards the landfills and the hydraulic gradient from the landfill had an eastern direction. In 1996 a barrier was built to prevent the leachate from spreading in the eastern direction of the landfill. However, when samples were taken in 2004 the results showed that the groundwater was affected east of the barrier. The groundwater still contained high levels of chloride and sodium. The reason was probably that the polluted groundwater was going under and on the side of the barrier (Golder Associates 2004).

From September 2022 until March 2023 several water chemistry parameters were measured as a part of the characterization report for the Life SOuRCE project. There were high concentrations of chloride, sulphate, and sodium. Their average concentrations were 1111, 740, and 935 mg/L respectively. Dissolved organic carbon (DOC) was also measured, and the average value was 34 mg/L (Uppsala Vatten och Avfall AB 2023).

2.2.2 PFAS in the groundwater at Hovgården

Both the soil and groundwater around the facility have been contaminated with PFAS. Most of the pollution is likely from the landfill leachate and storage areas. This was concluded after water from the drainages systems at the facility's different areas were analysed. The results showed that the PFAS concentrations were the highest in the drainage systems from the landfill

and storage area. The drainage water from the sludge storage area also contained PFAS but not as much. After measuring PFAS concentrations both downgradient and upgradient of the landfill the concentrations were found to be higher downgradient which indicates that the landfill's leachate is the main contribution to PFAS in the groundwater (Uppsala Vatten och Avfall AB 2023).

In 2023 PFAS levels were measured both upstream and downstream of the barrier. Twelve different types of PFAS were measured; PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFHxS, PFHpS, PFOS, 6:2 FTSA and PFPeS. The measurements were taken in eight wells, located both upstream and downstream of the barrier. They showed that the concentrations decreased downstream the barrier. There was a significant difference between the well located right before and right after the barrier. In all the eight wells the concentration for PFAS11 exceeded 18 ng/L which is a recommended lower value to change the trend. The criterion of 90 ng/L for the total of PFAS11 was also exceeded for all wells except the one located the furthest downstream the barrier. Of all the different PFAS, PFOA had the largest proportion with an average of 27% of all PFAS in the eight wells (Uppsala Vatten och Avfall AB 2023).

2.3 GRANULAR ACTIVATED CARBON (GAC)

GAC is one of the most studied methods for PFAS removal (McCleaf et al. 2017). The treatment is based on adsorption. There are two different types of adsorptions for activated carbon, physisorption and chemisorption. Physisorption is the main mechanism of adsorption for activated carbon and is a result of van der Waals forces (Chen et al. 2021). The van der Waals forces operate over a distance and therefore several layers of pollutants can be bound to the carbon. Physisorption is a reversible process meaning that the pollutants can desorb again. In water treatment, physisorption is the most common mechanism to remove adsorbates (Crittenden 2012a). With chemisorption a bond between the carbon and substances in the water is created. This is often an irreversible process and the pollutants stay adsorbed to the carbon since they share electrons (Crittenden 2012a).

Activated carbon is oleophilic, which means that it has affinity for oil (Patil et al. 2023). This creates a hydrophobic surface. Since PFAS has a hydrophobic part, it is attracted to the activated carbon and adsorbs on the surface. A larger surface increases the adsorption since there are more places for substances to adsorb (Chen et al. 2021). GAC is a porous material and this gives it a large surface area where the contaminants can adsorb. GAC's different pore sizes are good for different pollutants and the predominantly pore size depends on the material the GAC has been made of. For example, would GAC made of wood have more pores in macro size which makes it better for removal of larger organic pollutants whereas GAC made of coconut shells have more micro-pores which makes them better for smaller contaminants (Patil et al. 2013). Micropores have a diameter less than 2 nm and macropores have a diameter larger than 50 nm. Smaller pores normally give a larger surface area (Crittenden 2012a).

The hardness and particle size are important physical properties since it affects how much GAC may be lost during handling and reactivation. The losses are smaller for harder carbons since

they have a lower tendency to break apart and therefore lasts longer. The particle size relates to the head loss across the bed where smaller particles will result in a higher head loss (Crittenden 2012a). Head loss is loss of potential energy as it transforms into kinetic energy and is mainly caused by friction (Stewart 2018). When the GAC no longer removes the desired amount of pollutants it either needs to be changed or regenerated. In the regeneration the adsorbed substances are removed and thereafter the GAC can adsorb new pollutants (American Water Works Association n.d.).

GAC's removal rate depends on the characteristics of the pollutants, type of the carbon as well as of the water characteristics. The removal is generally less effective for short chain PFAS (Chen et al. 2021; McCleaf et al. 2017). The long chain PFAS such as PFOA and PFOS are more successfully removed. This is because the longer chains are more hydrophobic and therefore more likely to adsorb to the hydrophobic GAC (American Water Works Association n.d.). The preference for long chain PFAS can make the short chain PFAS desorb. This can result in higher concentrations in the effluent water compared to the influent water (Medina et al. 2022). At the start of removal with GAC the efficiency might be higher for the short chain PFAS but after an increased amount of bed volumes the efficiency will reduce due to desorption. Then some of the long chain PFAS can get a higher rate of adsorption since they bind to the sites where the short chain PFAS were previously adsorbed (McCleaf et al. 2017). There is a difference of adsorption efficiency for PFAS with the same chain length as well and it depends on the functional groups. PFSA are more efficiently removed by GAC than PFCA with the same chain length (Medina et al. 2022; Liu et al. 2022). For example, did PFOS which has eight carbons and is part of the PFSA have a higher adsorption rate than PFOA which also has eight carbons but is a part of the PFCA in a study by Medina et al (2022). A phenomenon that can increase the removal efficiency is formation of micelles or hemicells (Liu et al. 2022). This mainly happens for long chain PFAS since they have a stronger hydrophobic attraction to GAC and therefore reach the critical micelle concentration at the surface (Zaggia et al. 2016). The water matrix also affects the removal. The presence of dissolved organic carbon (DOC) will often affect the removal adversely since it also adsorbs to GAC. It can also clog the bed of GAC and prevent the water from running through (Chen et al. 2021). However, there are studies when the presence of DOC has improved the removal capacity of GAC (Siriwardena et al. 2019). This is because PFAS can have hydrophobic interactions with Hyaluronic acid (HA) which is a part of DOC. Depending on the type of GAC the influence of DOC varies. Different PFAS also react to the presence of DOC differently. For example, is DOC decreasing the adsorption on GAC for PFOS but increasing it for PFOA (Siriwardena et al. 2019). Another important water parameter is pH. A low pH will give GAC a more positively charged surface and therefore increase the attraction to the negatively charged PFAS (Siriwardena et al. 2019).

2.4 ANION EXCHANGE (AIX)

Ion exchange is a common method for treatment of drinking water and landfill leachate water. The principle is based on ions whose opposite charges attract each other and exchange of ions with the same charge. The anion exchange filter consists of a positively charged resin with functional groups attached (American Water Works Association n.d.). These resins are

copolymers which are created by linking a linear polymer to the ionic resin in a process called cross-linkage (Miller et al. 1981). The polymers can either be acrylic or styrenic (Dixit et al. 2021) Crosslinking is often done with divinylbenzene. Depending on how many times the resins have been crosslinked they can be divided into two groups, gel or macroporous resins. The gel resin has a crosslinking at 4-10 %. They have a higher water content and can both swell and shrink depending on their functional group. Because of its high water content, they are sensitive to drying since that would destroy their pore structure. An advantage with the gel resin is that the ion exchange rate is fast since it has an open matrix. The macroporous resins have a lower water content and can therefore keep their structure if they become dry. They have a higher percentage of crosslinking with divinylbenzene at 20-25 % (Crittenden 2012b). To give an everyday understanding of a resin they can be described as small porous plastic beads (Baresel et al. 2022). The resins have a functional group attached and it is the functional group that determines whether it is an anionic or cationic resin (Török et al. 2022). For the anion exchange, the functional groups are negatively charged. The pollutant anion can bind to the negatively charged functional group and replace its anion. When all the functional groups are full the resin needs to be regenerated to work. This is done by flushing the resins with a regeneration solution. Two commonly used solutions for anion exchangers are solutions with sodium hydroxide or sodium chloride (Malovanyy et al. 2023). Besides ion exchange with the functional group the anionic pollutants can also adsorb to the positively charged resin (American Water Works Association n.d.). These electrostatic interactions are two of the main mechanisms through which AIX works with PFAS. The other significant process is hydrophobic effects (Dixit et al. 2021).

To remove anions, an anion exchanger is used. There are two different types of anion exchangers, strong base exchange and weak base exchange. What differentiates these two are the functional groups attached. A normal group for the strong base exchanger is quaternary ammonium groups and for the weak base exchanger amine groups are common (Barbaro & Liguoir 2009). A difference between the strong base exchanger and weak base exchanger is that the former can exchange anions for a broader range of pH. The weak base exchanger normally needs a pH below 7 to function. They have regenerative and reuse capabilities in contrast to the strong base exchangers which are more physically and chemically stable (Dixit et al. 2021).

Since PFAS are negatively charged in aqueous solutions the ion exchangers used to remove the pollutants are anion exchangers. There are many different anion exchangers and some that have been developed to specifically remove PFAS, for example Purolite PFA694E and Lewatit TP108 (Baresel et al. 2022). When developing ion exchangers for specific pollutants one important property is selectivity. If the resins have a higher selectivity for a certain pollutant, it is more likely that that pollutant will be exchanged with the mobile ions on the resin. Selectivity depends on many different chemical and physical properties such as atomic number, pore size and functional groups. The pollutants properties will also influence the removal efficiency (Crittenden 2012b). For PFAS, the removal rate depends on the initial concentration of the pollutant and on the chain length of PFAS where a shorter chain gives less sorption (Baresel et al. 2022). The adsorption kinetics also depend on both the resin and PFAS properties.

Polystyrene resins with amino functional groups have been found to reach sorption equilibrium faster than polyacrylic resins with quaternary or tertiary amines as functional groups. This is probably because the polystyrene resin is more hydrophobic than the polyacrylic resin (Dixit et al. 2021; Liu & son 2021). Furthermore, the water matrix affects the removal capacity of PFAS. If there are other negatively charged ions in the water the treatment might be less effective. Sulphates, phosphate and nitrates are the strongest competing ions for removal (Dixit et al. 2021). The anion exchanger is also sensitive to organic material such as high levels of DOC and suspended material (Chen et al. 2021).

2.5 OPERATIONAL PARAMETERS FOR GAC AND AIX

There are two different ways to run a GAC or AIX. It can either be done in a complete mixing system or in a column system (Malovanyy et al. 2021). In this study column systems will be used. The column is packed with either the GAC or AIX media. As the water filters through the system the pollutants become sorbed to the filter. After a certain time period or contact time, which depends on the characteristics of the pollutants, type of the carbon as well as of the water type, the pollutants will break through the filter. To examine the capacity of the filters the tests are often run until the pollutants go completely through the filters and this is called “breakthrough” (Malovanyy et al. 2021).

Bed volume (BV) is one important parameter since it affects two other important parameters, empty bed contact time (EBCT) and hydraulic load (Malovanyy et al. 2021). The parameter BV is simply the volume of the filter in the column and consists of both the ion exchange resin/activated carbon and the volume between the particles called void volume (Miller et al. 1981; Malovanyy et al. 2021). The BV is dependent on the mass transfer zone (MTZ) which is the length of the filter needed to adsorb all the pollutants from the water. It is calculated according to equation 1 (Crittenden 2012a).

$$BV = A_C \cdot L = \frac{r \cdot t}{V_{ad}} \quad (1)$$

A_C = Cross sectional area of the cylinder

L = Length of the bed

r = flow rate, L/min

t = time, min

V_{ad} = volume of adsorbent material, L

EBCT is the time that the pollutant is in contact with the filter material. It can be calculated by dividing the volume of the bed occupied with the adsorbent by the flow rate (equation 2). A longer EBCT will result in a higher removal rate (Fundneider et al. 2021; Murrey et al. 2021). For GAC, EBCT ranges between 5-30 minutes (Crittenden 2012a). When using GAC to remove PFAS it is common with a contact time between 10-20 minutes (American Water Works Association 2019). However shorter EBCT have been used when studying the performance of

GAC (Murray 2021; McCleaf 2017). AIX often has a shorter EBCT and it ranges between 2-5 minutes for PFAS removal (American Water Works Association 2019; Chow 2022).

$$EBCT = \frac{V_{ad}}{Q} \quad (2)$$

V_{ad} = volume of bed occupied with the adsorbent, m³

Q = flow rate to adsorber, m³/h

To quantify the performance of GAC the parameter specific throughput is used. The specific throughput is defined as the volume passing through the filter until breakthrough divided by the mass of GAC (equation 3). Another way to quantify the performance is with media usage rate (MUR). Which is the inverse to specific throughput, (equation 4). When the EBCT increases the specific throughput will increase and the MUR will decrease. A higher specific throughput will result in lower operational and maintenance cost but will increase the capital cost since the filter material would not need to be exchanged as often but a larger volume would be needed (Crittenden 2012a).

$$Specific\ throughput = \frac{Q \cdot t}{M_{GAC}} \quad (3)$$

Q = flow rate to adsorber, m³/h

t = time to breakthrough, h

M_{GAC} = mass of GAC, kg

$$MUR = \frac{M_{GAC}}{Q \cdot t} \quad (4)$$

GAC needs to be backflushed regularly to not become clogged. In drinking water treatment plants this is often made with treated water (Chen 2021). When the filters have reached their maximum capacity, they need to either be changed or regenerated. Regeneration of GAC involves removal of the adsorbed molecules from the carbon surface by desorption. Some of these regeneration processes are adding acids/bases, carbon dioxide or organic solvents to make the pollutants desorb. Afterwards the solution with the pollutants needs to be taken care of (Crittenden 2012a). Regeneration of GAC can also be accomplished through heating in a process called thermal reactivation. During the treatment it is also possible to destroy some of the PFAS. However, the high temperatures needed to destroy PFAS can also ruin the structure of GAC and make it less efficient. In some cases, the efficiency can become better after thermal reactivation since it may open up additional pores and create additional adsorption sites (Sonmez Baghirzade et al. 2021). About 10 % of the GAC's mass is lost during the thermal treatment. Therefore, more material needs to be added after the process (Baresel et al. 2017).

To keep the PFAS removal efficient when using AIX, blockage needs to be prevented. The main reason for blockage is often the amount of total suspended solids. Other factors contributing to clogging are the amount of dissolved iron and manganese, growth of microbes

and total organic carbon (TOC). When solids build up in the filter the water running through will take the path of least resistance and no longer pass through the filter evenly distributed. This will cause a premature breakthrough. Build-up of solids is discovered by visually inspecting the filter and an increase in pressure drop. If the pressure drop first increases and thereafter decreases, it is an indication that the resin bed has changed. By adding a prefiltration system the anion exchange filter will last longer. Blockage can be rectified by backwashing. However, the backwashing may cause mixing of PFAS-loaded resin from the top of the bed with less used resin from the bottom of the bed and this can cause a premature breakthrough. Other factors affecting the capability to remove PFAS are oxidants and anions in the water. Oxidants will destroy the resins if they are in contact for longer periods and anions will compete with PFAS for the places on the resins (Purolite 2022).

Regeneration of AIX adapted for PFAS are challenging because of their high selectivity for PFAS. The best suited regeneration method varies depending on the resin and PFAS properties. Liu and Son (2021) studied the regeneration effect for different polystyrene resins crosslinked with divinylbenzene for multiple salts and methanol in different amounts. Chloride salt proved to work the best followed by bicarbonate and acetate salts. That conforms with the selectivity of strong anion exchange resins where the selectivity is the strongest for chloride (Liu & Son 2021). Sodium hydroxide (NaOH) is a commonly used and studied regenerant for ion exchange resins. However, it has mainly been used to remove natural organic carbon (NOM). It has not been efficient in removing PFAS on its own. Methanol is another regenerant that has proven to be the most efficient organic regenerant. However, they are not a good option for treating drinking water applications. Lastly, a combination of regenerants can be used (Dixit et al. 2021). Results from the study of Liu and Son (2021) concluded that resin specifically developed for PFAS are not suitable for regeneration since the rate of recovery is too low. Although the recovery for short chained PFAS was better and had a recovery rate varying between 80-94 % (Liu & Son 2021).

2.6 COSTS DIFFERENCES FOR AIX AND GAC

There are several parameters to take into consideration when estimating costs for AIX and GAC. Ellis et al. (2023) made a life cycle cost analysis where cost of the AIX/GAC media, solvents, treatment infrastructure, labour costs, service fees for transport and incineration was included. The costs of elements that would have been the same for the different treatment methods were excluded, such as electricity for pumping water (Ellis et al. 2023). Other studies have chosen to include the electricity for pumping (Franke et al. 2021). Several studies group the cost into operation and maintenance (O&M) costs. The parameters included are often media cost, transportation, disposal of media and analytical costs (Murray et al. 2021; Medina et al. 2022; Liu et al. 2022). One key factor of the O&M cost is the media replacement frequency. It contributes to the cost of media but also for reactivation or disposal costs (Medina et al. 2022). How often the media needs to be replaced depends on the threshold value or breakthrough

percentages considered. Examples of previously used breakthrough percentages are 10% (Liu et al. 2022; Murray et al 2021) 50% (Murray et al.) and 60% (Medina et al. 2022).

AIX is often found to be the cheaper alternative compared to GAC (Liu et al 2022; Ellis et al. 2023). The media for AIX can however be more expensive than GAC. In the study by Medina et al. (2022) the O&M costs were higher for AIX because of the higher price per kilo. When looking at the price per volume treated water instead, AIX was less expensive to use than GAC (Medina 2022). AIX becomes cheaper since it has a lower media usage rate (MUR) (Ellis et al. 2023; Franke et al. 2021). In the comparative study by Liu et al. (2022), the PFAS removal was 6-7 times higher using AIX on a mass basis. When comparing the removal efficiency for the same amount of water, the capability was similar for AIX and GAC (Liu et al. 2022). However, another study showed that the unit water costs were lower for AIX (Medina et a. 2022). A lower MUR makes it possible to use the media for a longer time before changeout which reduces the O&M costs. For Murray et al (2021) the change out period was about 16 times longer for AIX compared to GAC. Besides having a lower MUR, AIX also requires a shorter EBCT which reduces the O&M cost (Medina et al. 2022). In a life cycle cost analysis, it was suggested that GAC may prove more cost efficient for very stringent PFAS breakthrough criteria. The life cycle cost analysis was looking at both single use and regenerated AIX and GAC. Single use AIX proved to be the most cost efficient regarding capital costs, annual operation and cost per m³ treated water. It was followed by regenerated AIX, regenerated GAC, and lastly single use GAC (Ellis et al. 2023).

3. METHOD AND MATERIAL

3.1 FILTRASORB® 400

Filtrisorb® 400 is a granular activated carbon developed to treat ground and surface water. It is adapted for water containing higher levels of background total organic carbon and is made of bituminous coal. The bituminous coal is durable and can therefore endure backwashing without losing its adsorption properties (Calgon Carbon Corporation 2008). Properties and an illustration for Filtrisorb® 400 can be viewed in Table 1.

Table 1. Properties for Filtrisorb® 400 (Calgon Carbon Corporation 2008).

Property	Value	Illustration
Iodine Number, min.	1000 mg/g	
Abrasion Number, min.	75	
Moisture Content, as packed, max.	2%	
Effective Size	0.6-0.7 mm	
Uniformity Coefficient, max	1.9	
Trace Capacity Number, (min)	10 mg/cc	
Apparent Density	0.52 g/cc	
Mesh Size, US Sieve Series		
> 12 mesh (1.70 mm), max.	5 %	
< 40 mesh (0.425 mm), max.	4 %	

3.2 PUROFINE® PFA694E

Purofine® PFA694E is an anion exchange filter developed to treat PFAS. The polymers are polystyrene and they have been crosslinked with divinylbenzene. The functional group is complex amino (Purolite 2021). Properties and an illustration of Purofine® PFA694E can be found in Table 2.

Table 2. Properties for Purofine® PFA694E (Purofine 2021).

Property	Value/ Characteristic	Illustration
Polymer Structure	Polystyrene crosslinked with divinylbenzene	
Appearance	Spherical Beads	
Functional Group	Complex Amino	
Mean Diameter	675 ± 75 µm	
Uniformity Coefficient (max.)	1.3	
Specific Gravity	1.05	
Shipping Weight (approx.)	650 - 700 g/L	
Temperature Limit 100 °C	(212.0 °F) (Cl- form)	
Temperature Limit 60 °C	(140.0 °F) (OH- form)	

3.3 PREPARATION OF COLUMNS

The columns were made of transparent PVC. They were 205 cm long and had an inner diameter of 5.4 cm. At the bottom, a fine stainless steel mesh was placed to keep the GAC and AIX in the columns. The GAC used was regenerated and was therefore dried on a glass tray in the oven overnight at 35°C. Two of the columns were filled with 100 g of Filtrasorb® 400 and one was filled with 100 g of Purofine® PFA694E.

The columns were placed in a stand to keep them upright. The stands had one outlet for the water that had gone through the columns and one inlet that could be used for backwashing. The columns were placed 18 cm down, above the in- and outlet in the stand. This left a space for the water that would go through the columns and enabled the water to leave through the outlet without disturbing the packing of the media. The columns were rinsed with two litres of deionised water to pack the filter correctly. The GAC1 column was rinsed with additionally 1.2 litres of deionised water since it was leaking at first and had to be adjusted and thereafter rinsed again.

3.4 SET UP AND RUNNING OF COLUMNS

Figure 3 shows the setup of the three columns and Figure 4 shows how it looked in reality. They were set up next to each other at Hovgården. From water tank 1 (polyethylene), with the well water, two small tubing (marprene) went to a peristaltic pump (Watson Marlow) and then to either the AIX column or the GAC1 column. The two tubing were placed inside a small PVC pipe which was put in water tank 1. The pipe prevented the tubing from going out of the tank and the intake for the tubing could be placed above the bottom from the tank, thus preventing sediment from going into the tubing. A tubing (polyethylene) from GAC 1's outlet led to a bucket and a small tubing went from the bucket, passing through the pump and thereafter to GAC 2. The outlet at the bottom of the AIX and GAC 2 columns were attached to a tubing (polyethylene) which had its outlet above a PVC collection trough. The trough led water to water tank 2 where all the treated water was collected.

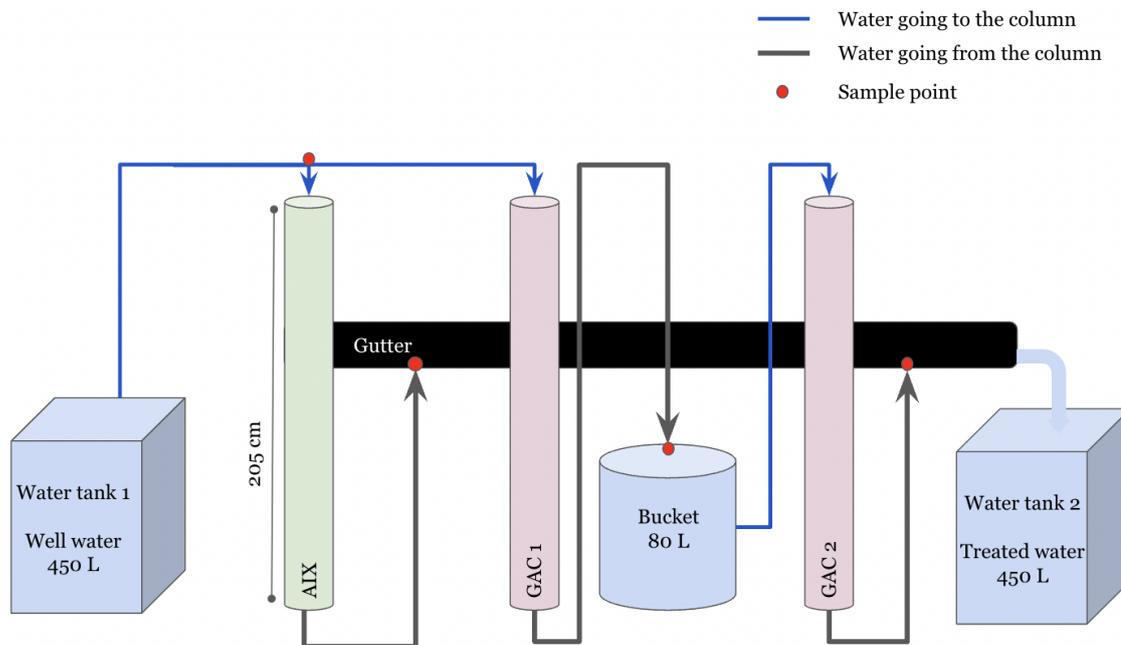


Figure 3. Setup of column tests with AIX and a two stage GAC.



Figure 4. Photo of the set up for the column test with AIX and two stage GAC.

To ensure that the water levels in the three columns would be approximately the same the atmospheric pressure had to be at the same level. For AIX and GAC2 this was adjusted with the height of the tubing outlet above the trough. To receive the same water height in GAC 1 the tubing from the outlet was first led to the same level as the outlet of the tubing from AIX and GAC2, thereafter to the bucket.

Before running water through the column, the peristaltic pump (Watson Marlow) was calibrated. The EBCTs were to be 5 minutes for GAC and 4.4 minutes for AIX which resulted in a flow of 40.4 mL/min. Since the flow would be 40.4 mL/min during the running of the columns three points around that value were used to calibrate the pump: 30 mL/min, 40 mL/min and 50 mL/min. The pump was set to 30 mL/min. Then 200 mL of water was pumped into a measuring cylinder and the time it took was measured. This was done for all three flows and every time the corresponding revolution per minute (rpm) for the flow was recorded. The measured flows were plotted against the recorded rpms and an equation for their relationship was obtained. Using the equation, the correct amount of rpm could be set on the pump.

A test run was made with tap water and screws around inlet, outlet and rubber seal were tightened until there were no leakages. The columns were filled with tap water until equilibrium in the water level was reached. After a week they were backwashed. This was done to remove air pockets, dirt and to pack the filters correctly. The pipe going in from the top was removed and a j-shaped tube with a rubber seal in the bent end was attached to the top of the column. The rubber seal was tightened so no water would leak during the backflushing. Thereafter tubing was attached to the inlet at the bottom of the column and the outlet was turned off. Tap water from a 10 litre tank was pumped through the tubing using the pump. The pump was first set to a low flow at 40 - 60 mL/min to ensure the filter didn't transport too far up in the column. The AIX column was backflushed at 222 mL/min and the GAC columns at 240 mL/min. Once the water had reached the top of the column they were flushed for five minutes. The j-shaped tube let the water out in the trough and the water was transported to water tank 2. After the flushing the pump was turned off, the inlet turned off and the outlet turned on again.

Once the columns were running, they were backwashed when the water level in the columns reached 170 cm. The AIX and GAC1 column were always backwashed at the same occasion. Every time samples were taken, the height was recorded to discover quicker rises in the water level. The water which had been treated and collected in water tank 2 was used for the back washing. The columns were first sparged with air for 10 minutes at 40.4 mL/min. Thereafter the treated water was pumped through the inlet at the bottom of the columns. Once the water level had reached the top of the columns the backwashing continued for 10 minutes. The water from the backwashing was collected in a separate container and pumped to the sewage system at site. The last time the backwashing was performed the flow was increased. Then the air

sparging went on for 10 minutes at 97 mL/min and the water was pumped at 168 mL/min for 30 minutes when the water was visibly cleaner.

Water tank 1 had to be refilled with groundwater every fourth day. The groundwater was taken from two wells downstream of the landfill. The first time the groundwater went through a 200 micron filter. However, the groundwater could not be pumped through the filter for the remaining refills. Therefore, the groundwater was pumped directly to water tank 1 without a filter thereafter. When water tank 1 was refilled, water tank 2 was emptied. A submersible pump (Cocraft) was placed in water tank 2 with tubing leading to the sewage system at site.

3.5 SAMPLING

Samples were taken at four points; the AIX's outlet, GAC1's outlet, GAC2's outlet and the inlet to AIX which was untreated groundwater (Figure 3). The samples from the three outlets were taken first so the water level and flows wouldn't be affected by taking water from the inlet. From each sample point three samples were taken. The first one was for groundwater parameters and was sampled in a 500 mL HDPE plastic bottle. Each PFAS sample was taken in two 100 mL HDPE plastic bottles each. Lastly a sample to analyse metals was taken in a 50 mL PP plastic tube. At every sample point pH and conductivity were also measured. The pH metre was calibrated once a week, on Mondays, except from the first sample since it was taken on a Thursday. When backwashing was needed, samples for groundwater parameters, PFAS and metals were taken for the backwashing water as well. The samples of the ground water and outflows from the three columns were always taken before the backwashing.

The first 18 days samples were taken every day except on weekends. Thereafter samples were taken twice a week, on Mondays and Thursdays to get even intervals. All samples were taken at the same time every day. The samples were stored in a fridge during the week and sent to Eurofins at the end of the week. It was only the samples from Mondays and Thursdays that were sent for analysis as well as the samples for the backwashing water. The other samples were collected in case additional data was needed.

3.6 REMOVAL EFFICIENCY

The removal efficiency for each PFAS was calculated according to equation 5, where C_{out} was the concentration after the water had gone through the column and $C_{groundwater}$ was the concentration in the groundwater. For each sample the amount of bed volumes that had run through the column was calculated. Thereafter breakthrough curves were plotted for each PFAS substance with an influent concentration above detection level. When the effluent concentration was below detection level, the half value of the detection level was used to calculate removal efficiency. This was done for AIX, GAC1 and GAC2.

$$Removal\ efficiency = 1 - \frac{C_{out}}{C_{groundwater}} \quad (5)$$

To compare different treatment goals for short respectively long chained PFAS within PFCA and PFSA an average of the treatment efficiency was calculated for each group.

3.7 COSTS

The cost analysis considered the costs of running the two stage GAC and AIX. This included media costs, number of BV until breakthrough and clogging of the filters. The treatment of the media after usage was also included. GAC was regenerated and AIX went to destruction. The cost for transport to regenerate or destroy the media was also taken into consideration. Parameters that were the same for both AIX and GAC were excluded since they did not contribute to the comparison between the two medias.

The column adsorption model (equation 6) by Lin and Huang (1999) was used to calculate the time and thereafter BV for each substance at the different removal efficiencies 99, 95, 90, 85, 80 and 50 %. τ and $1/k$ were obtained by plotting the time against $\ln(C/(C_0-C))$ from the measured values and making a linear trend line. The intercept with the y-axis and the slope of the line equals τ and $1/k$, respectively. To give the model a good fit the number of sample values were removed or added (Appendix B).

$$t = \tau + \frac{1}{k} \ln \frac{P}{(1-P)} \quad (6)$$

t = time (days)

τ = half saturation time (days)

k = column constant (days⁻¹)

P = fraction that passes through the column

To compare the cost of the two medias the cost of treating one cubic metre of water was calculated. Firstly, the material cost per cubic metre water was calculated according to equation 7. The media costs for GAC and AIX were provided by Uppsala Vatten AB in euros. Thereafter the regeneration and destruction cost per cubic metre water for GAC respectively AIX was calculated with equation 8. The regeneration cost for GAC was given from Uppsala Vatten AB in euros and a cost estimation for the destruction of AIX was from Fortum Waste Solutions AB. For GAC, the water that had passed through GAC1 and GAC2 was added together and the filters in both columns were included before using equation 7 and 8.

$$\text{Filter cost (euro/m}^3 \text{ water)} = \text{media cost (euro/m}^3 \text{ filter)} \cdot \frac{\text{filter in column(m}^3\text{)}}{\text{water that has passed through the filter(m}^3\text{)}} \quad (7)$$

$$\text{Destruction/regeneration cost (euro/m}^3 \text{ water)} = \text{destruction/regeneration cost (euro/m}^3 \text{ media)} \cdot \frac{\text{filter in column(m}^3\text{)}}{\text{water that has passed through the filter(m}^3\text{)}} \quad (8)$$

Since some of the GAC is lost during regeneration the cost of adding 10% for a cubic metre of water was calculated and lastly all costs were added.

The goal was to have a removal efficiency at 99% for long chain PFAS and 95% for short chain PFAS. The cost of treating one cubic metre of water was calculated for the removal rates at 99%, 95%, 90%, 85%, 80% and 50%. The costs were calculated separately for long and short chained PFAS within the groups PFCA and PFSA. How often backwashing was needed for the different columns was also taken into consideration but without looking at costs.

4. RESULT

4.1 WATER PARAMETERS FOR INFLUENT AND EFFLUENT WATER

Several of the water parameters measured before and after the filters did not show any difference in concentration. Chloride decreased from 920 mg/L to 860 mg/L after AIX and 880 mg/L after GAC1 the second day, otherwise the influent and effluent concentrations were nearly the same (Table C1, Appendix C). Fluoride and manganese had similar influent and effluent concentrations which ranged between 0.41 – 0.55 mg/L and 0.79 – 1.1 mg/L respectively. The sulphate concentration was similar for the influent and AIX's effluent, until AIX was backwashed (1 900 BV) and the concentration increased from 310 mg/L to 340 mg/L after the water had passed through the column. After 1 400 BV, the sulphate concentration was 340 mg/L in the ingoing water and 350 mg/L in the outgoing GAC1 and 360 mg/L in the outgoing GAC2. Thereafter (> 1 500 BV) the effluent concentrations from GAC1 and GAC2 remained higher or the same (320 – 360 mg/mL) as the influent (310 – 350 mg/mL). The full data set for chloride, fluoride, manganese, sulphate, pH and conductivity is shown in Table C1 in Appendix C.

The DOC concentrations decreased after all the columns compared to the influent water until 2 500 and 2 200 BV for AIX respectively GAC (Table 3). There was an increase of DOC from 40 mg/L for the influent water to 49 mg/L and 44 mg/L for AIX respectively GAC1 at 2 500 (AIX) and 2 200 (GAC1), thereafter the effluent concentrations were lower than the influent again. GAC2 was more efficient to remove DOC than AIX. The removal efficiency ranged between 10 – 72% with GAC2 and -23 – 43 % with AIX.

Table 3. Concentrations in mg/L of DOC for the untreated influent water and after the AIX, GAC1 and GAC2 column filters.

BV AIX / GAC	Day of the experiment	Influent	AIX	GAC1	GAC2	Backwash
300 / 200	1	40	23	26	11	-
600 / 500	2	41	29	31	21	-
1 500 / 1 400	5	42	35	35	28	-
1 900 / 1 700	6	-	-	-	-	37
2 500 / 2 200	8	40	49	44	33	-
3 800 / 3 400	12	38	35	35	30	33
4 700 / 4 200	15	28	26	27	25	-
6 000 / 5 300	19	31	30	29	27	-
7 000 / 6 500	22	33	32	31	28	-

The effluent iron concentrations (0.07 – 0.78 mg/L, 0.14 – 3.1 mg/L and 0.25 – 1.1 mg/L) were lower than the influent (0.49 – 23 mg/L) for the whole period (Table 4). GAC2 (0.66 mg/L) was more efficient at 1 500 / 1 400 BV, otherwise AIX was the most efficient. For the first 2

200 BV there was an improvement after GAC2 compared to GAC1 where concentrations after GAC1 were 1.2 – 3.1 mg/L and 0.66 – 1.1 mg/L after GAC2. Thereafter the concentrations became higher after GAC2 at BV 3 400 and 4 200. The concentrations after GAC1 were 0.19 and 0.14 mg/L whereas the concentrations after GAC2 were 0.25 and 0.44 mg/L. Then from 5 300 BV the concentrations became lower after GAC2 again with 0.29 – 0.38 mg/L after GAC2 and 1.1 – 1.2 mg/L after GAC1.

Table 4. Concentrations in mg/L of iron for the untreated influent water and after the AIX, GAC1 and GAC2.

BV	AIX / GAC	Day of the experiment	Influent	AIX	GAC1	GAC2	Backwash
300 / 200		1	6.6	0.36	3.1	1.1	-
600 / 500		2	5.5	0.57	2.3	1.1	-
1 500 / 1 400		5	1.5	0.78	1.2	0.66	
1 900 / 1 700		6	-	-	-	-	2.4
2 500 / 2 200		8	19	0.3	1	0.36	-
3 800 / 3 400		12	23	0.07	0.19	0.25	0.62
4 700 / 4 200		15	0.49	0.21	0.14	0.44	-
6 000 / 5 300		19	0.76	0.69	1.2	0.29	-
7 000 / 6 500		22	1.7	0.58	1.1	0.38	-

4.2 REMOVAL EFFICIENCY FOR PFAS USING GAC

At the first sampling point (200 BV) the removal efficiency for the sum of the 20 PFAS (Σ PFAS) was 52% after GAC1 and 90% after GAC2. This is shown in Figure 5 where the pink line was the result for GAC1 and the dark red line was the result for GAC2. Both columns showed a decrease in efficiency until the fourth sampling point (2 200 BV). GAC1 had a removal of -20% whereas GAC2 was at 4%. The removal efficiency increased after 2 200 BV and remained between 1–6% and 9–12% for GAC1 and GAC2 the last few days.

The removal efficiency decreased with increasing BV for GAC1 and GAC2 (Figure 6 and 7). At 2 200 BV there was a drop in removal efficiency for all PFCA and PFSA, thereafter it increased again. The short chain PFCA (PFBA, PEPeA, PFHxA, PFHpA and HPFHpA) and PFSA (PFBS, PFHxS, PFHpS and PFPeS) showed a lower removal rate than long chain PFCA (PFOA, PFNA and PFDA) and PFSA (PFOS). For GAC1, PFDA had a removal efficiency at 66% during the first sample point (200 BV) which was the highest out of the PFCA and it remains among the highest during the 21 days of sampling. All PFCA except PFDA had a negative removal efficiency at 2 200 BV (Figure 6).

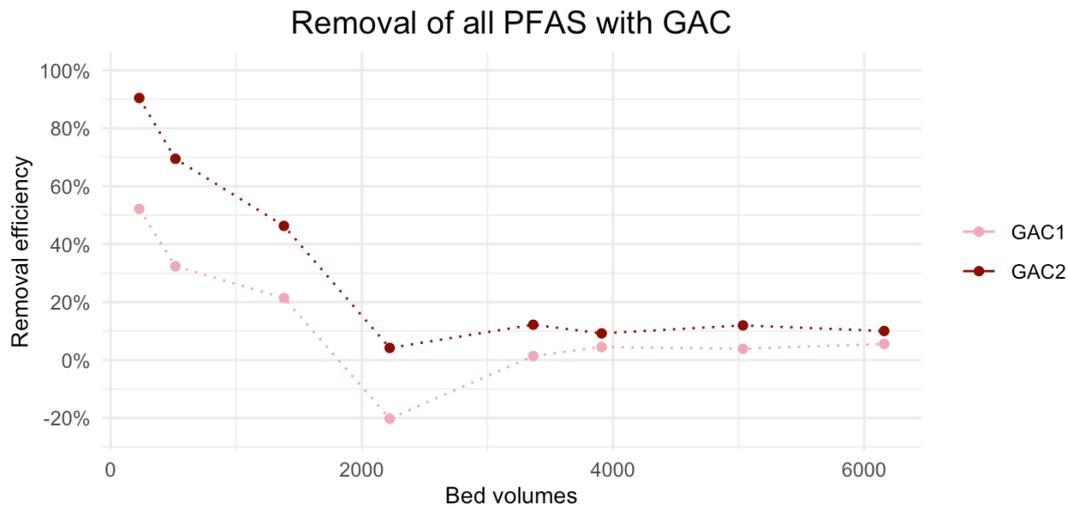


Figure 5. Removal efficiency for the sum of 20 PFAS found at Hovgården using two stage GAC.

PFOS had the highest removal rate for PFSA, starting at 79% and remained the highest until 6 200 BV (35%). PFBS had the lowest removal efficiency at 2 200 BV with -51%. The fluorotelomers 4:2 FTSA, 6:2 FTSA and 8:2 FTSA were all below 0% at 2 200 BV. At 3900 BV, FOSAA and MeFOSAA reached -127% and -120% respectively.

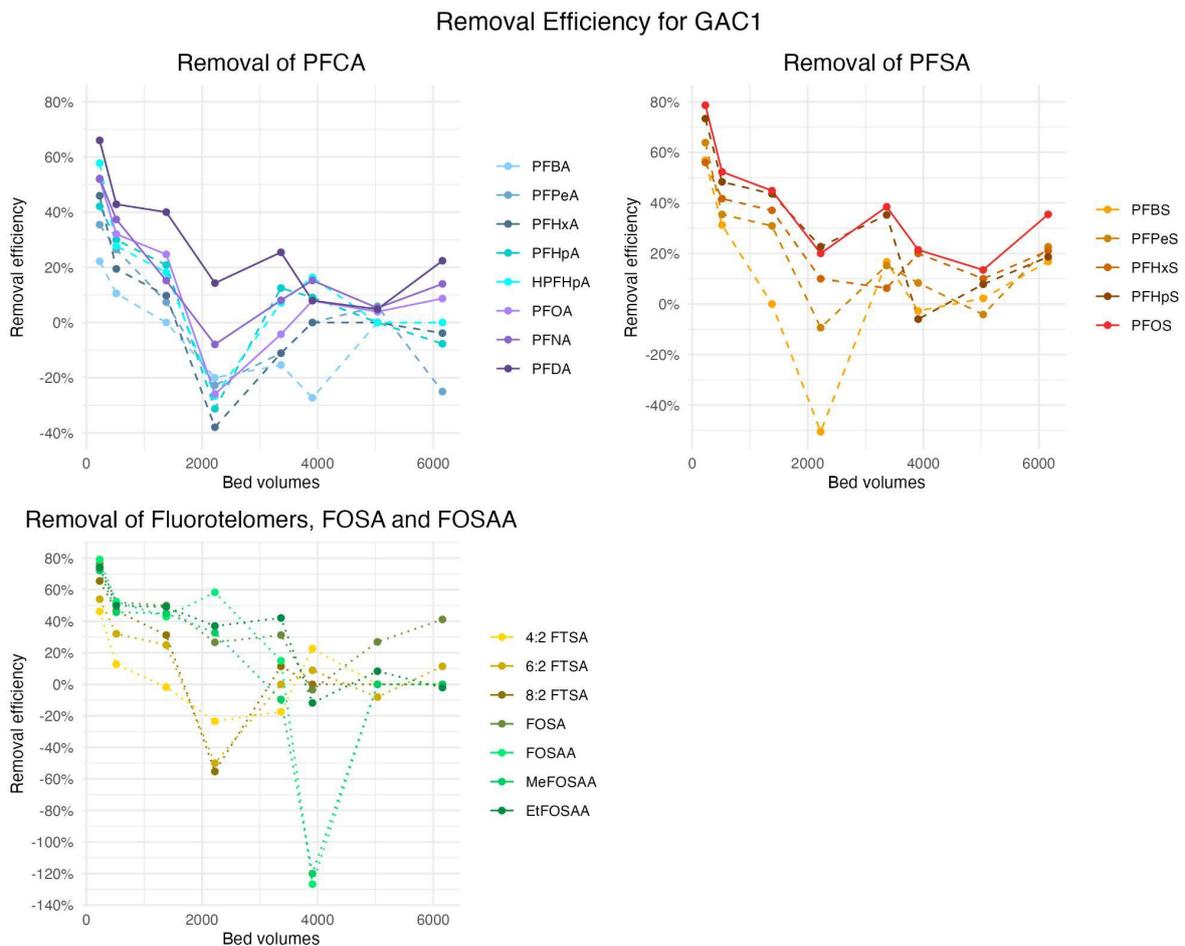


Figure 6. Removal efficiencies for PFAS after GAC1 during a 22 day long period. For PFCA and PFSA the dashed lines represent short chain and the solid lines represent long chain.

The removal efficiencies were overall higher in GAC2 compared to GAC1. All PFCA removal efficiencies were above 80% at the first sampling point (200 BV), except for PFBA. During the first 2 200 BV the short chain PFCA had a lower removal efficiency (-28 – 93%) than the long chain (4 – 95%), thereafter PFHpA (25%) and HPFHpA (14%) became higher than PFOA (9%) until BV 4 200 (Figure 7). PFDA had the highest removal percentage (24 – 93%), followed by PFNA (95 – 16%) and PFOA (92 – 4%). After 5 000 BV, there was an increase in removal efficiency for PFDA (39%), PFNA (26%) and PFOA (15%), whereas short chain PFCA decreased (-19 – 0%). PFSA were all above 95% removal at the first sample point (200 BV) and PFOS had a 99% removal rate. It had the highest percentage except at 3 300 BV where PFHpS was higher (68%). PFHpS (29%) was close to PFOS the whole time but after 5 000 PFOS increased more (42%). The other three short chain PFSA (PFBS, PFHxS and PFPeS) were constantly lower (97 – (-)18%). PFBS was the only one to go below 0% of the PFSA after 2 200 BV. The 4:2 FTSA, 6:2 FTSA and 8:2 FTSA were all below 0% at least one data point for GAC2. The FOSA and FOSAA never went below 0%. FOSA and EtFOSAA had their lowest removal efficiency at 38% and 27% respectively.

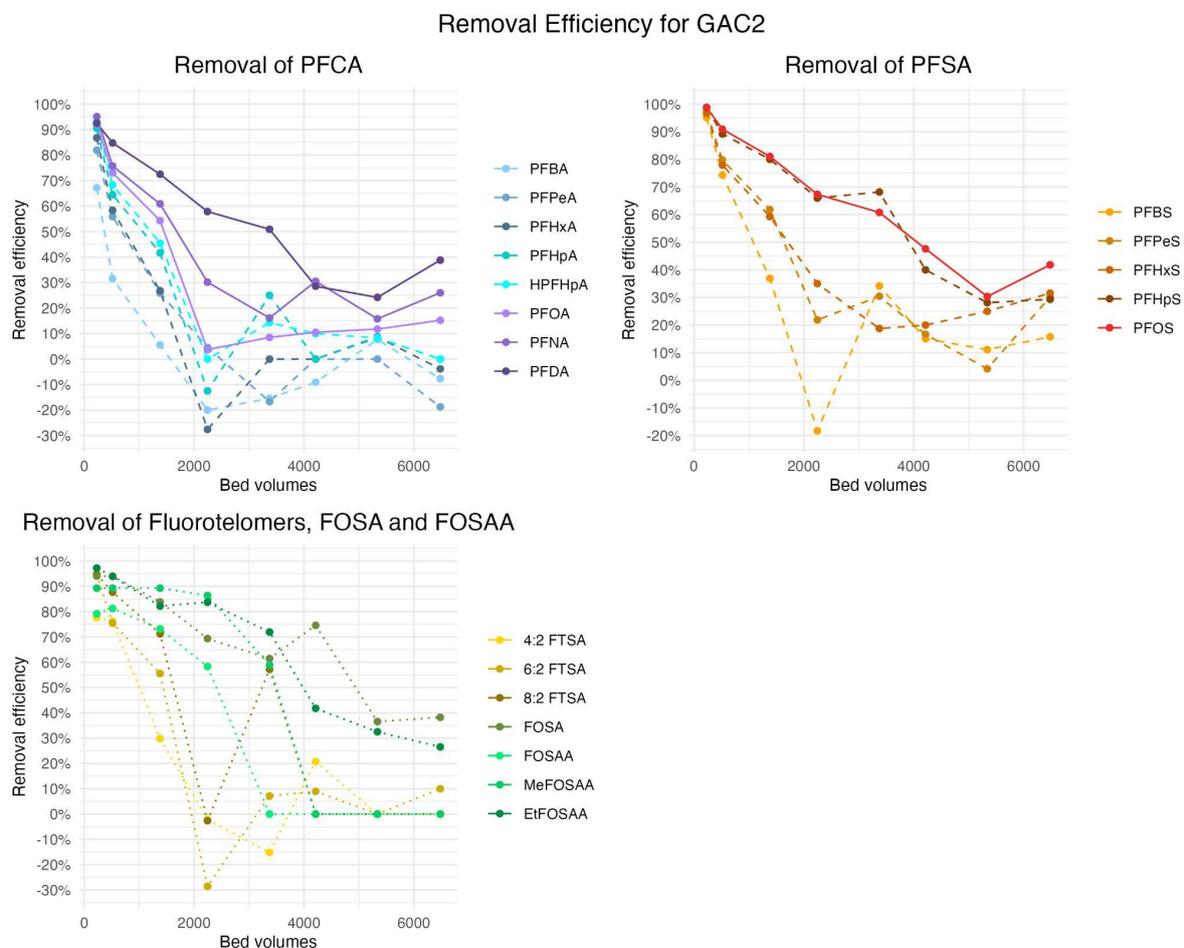


Figure 7. Removal efficiencies for PFAS after GAC2 during a 22 day long period. For PFCA and PFSA the dashed lines represent short chain and the solid lines represent long chain.

4.3 REMOVAL EFFICIENCY FOR PFAS USING AIX

The removal efficiency for the sum of the 20 different PFAS found at Hovgården was above 99% after 300 BV (Figure 8) using AIX. There was a decrease to 68 % for the sum of PFAS until 1 500 BV. Then the removal efficiency of sum PFAS decreased further to 30 % at 6 000 BV, and thereafter the removal rate increased to 52% at 7 000 BV.

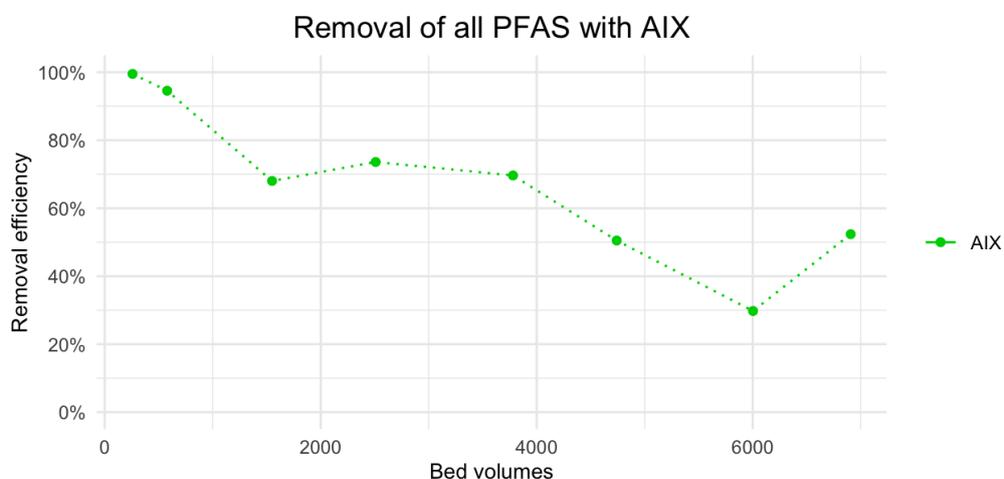


Figure 8. Removal efficiency for the sum of 20 PFAS found at Hovgården using AIX.

The removal efficiencies for each PFAS using AIX are shown in Figure 9. There were two drops in the data, one at 1500 BV and one at 6 000 BV. The long chain PFCA (PFOA, PFNA and PFDA) had a higher removal percentage than most of the short chain (PFBA, PEPeA, PFHxA, PFHpA and HPFHpA). The short chain HPFHpA (90, 89 and 38%) showed occasionally higher removal efficiencies than PFOA (88, 86 and 33%) at 2 500 BV, 3 800 BV and 6 000 BV, respectively. HPFHpA (93%) and PFHpA (100%) showed higher removal efficiencies than PFDA (93%) until 300 BV. Thereafter HPFHpA (89 – 90 %) was higher than PFDA (86 – 89%) during 2 500 – 3 800 BV. It was only PFBA (-23 %) and PEPeA (-13 %) that had a negative removal efficiency after 2 500 and 6 900 BV, respectively. The first 580 BV, which was equivalent to the first three days, all PFSA had a removal efficiency above 99%. PFBS had the lowest removal efficiency at 44%. Of the fluorotelomers, 6:2 FTSA had the highest removal efficiency starting above 99% at 300 BV and ending with 16% at 7 000 BV. 8:2 FTSA had a higher percentage 73 – 95% between 600 and 1 500 BV. FOSA started at 94% at 300 BV and had the lowest removal efficiency at 40% at 6 000 BV. Out of the FOSAA, EtFOSAA had the highest removal efficiency with 97% at 300 BV followed by MeFOSAA (89%) and FOSAA (79%).



Figure 9. Removal efficiencies for PFAS after AIX during a 22 day long period. For PFCA and PFSA the dashed lines represent short chain and the solid lines represent long chain.

4.4 DIFFERENCES IN REMOVAL EFFICIENCY BETWEEN GAC AND AIX

AIX had a general higher removal efficiency than GAC2 for the long and short chain PFCA during the sample period (Figure 10). The long chain PFCA removal efficiency was at 97% and 93% for AIX and GAC2, respectively in the beginning (300 and 200 BV). Until 1 500 (AIX) and 1 400 (GAC2) BV the efficiency decreased for both sorbents (76% and 63%, respectively), thereafter it increased for AIX to 90% at 2 500 BV and kept on decreasing for GAC2 to 17% at 5 300BV. The short chain PFCA had a decreasing removal efficiency using AIX during the whole test period (7 000 BV) while they decreased to -11% for GAC2 until 2 200 BV and thereafter increased to 7% (5 300 BV).

The removal efficiency was similar for the short and long chain PFSA when AIX was used. There was a bigger difference when GAC2 was used (Figure 10). Short and long chain PFSA were both above 99% at 300 BV using AIX. The long chain PFSA had a removal of 99% at 300 BV when two stage GAC2 was used, thereafter it decreased to 30% at 5 300 BV where it increased again. The removal efficiency for short chain PFSA was at 97% at 200 BV when GAC2 was used, thereafter it decreased with the lowest point at 17% at 5 300 BV.

The removal efficiencies followed each other closely for FOSAA during the whole experimental period. Until 2 200 BV, GAC2 showed higher removal for FOSAA (82%) than AIX (73%), thereafter AIX was more efficient with 14 – 80% until 7 000 BV when GAC2 showed 9 – 76% until 6 500 BV. FOSA had a similar pattern, but AIX became more effective between 1300 BV and 2 500 BV. For the FTSA, there was a decrease for both methods and AIX was always a few percentages higher.

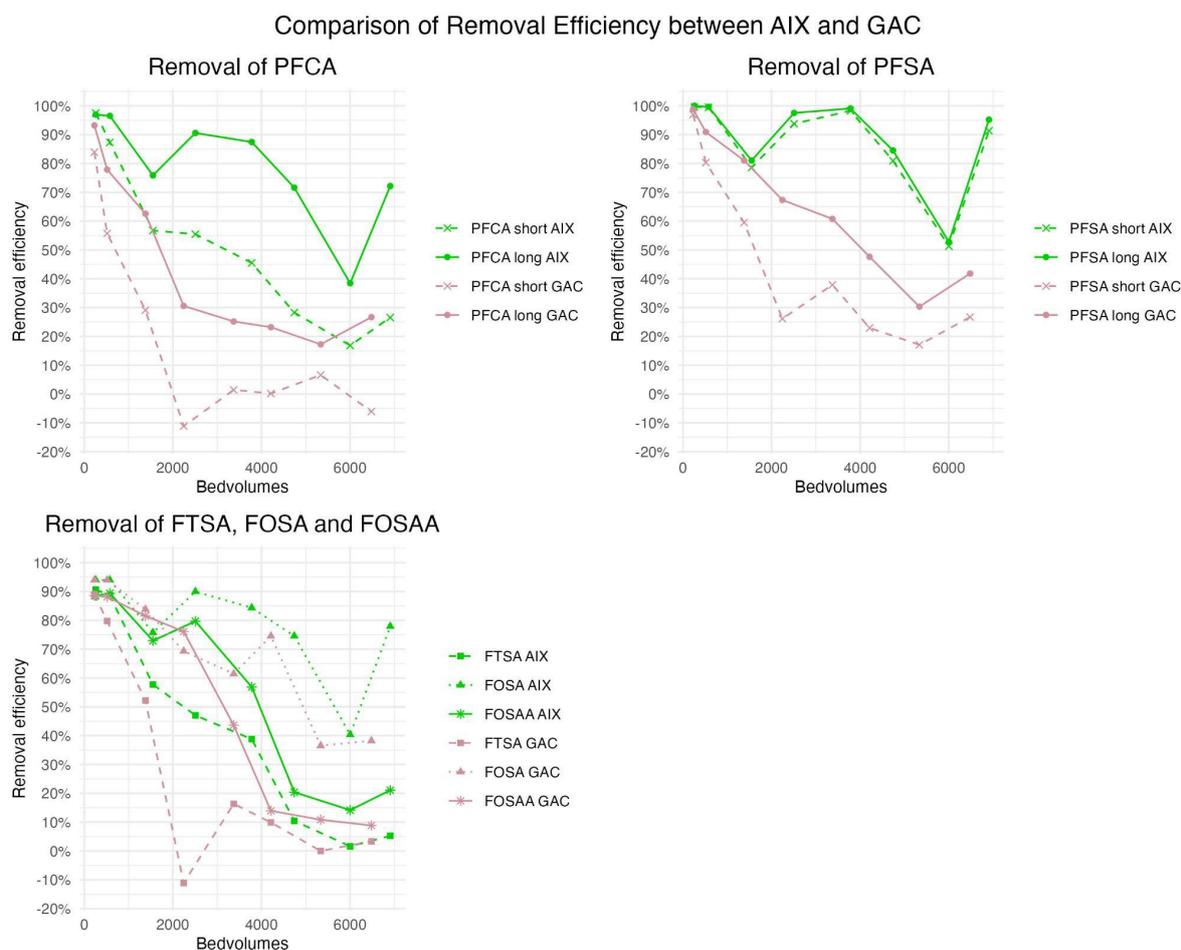


Figure 10. Comparison in removal efficiencies for PFAS when using either AIX or GAC. For PFCA and PFSA, the short chains are represented with dashed lines and the long chains with solid lines

Table 5 displays the total PFAS concentrations for influent water and the water treated after AIX, GAC1 and GAC2. The concentrations decreased the most for AIX and there was also a further decrease in GAC2 after GAC1. It was the same pattern for PFAS4 and PFAS11 (Table 6 and 7).

Table 5. Total PFAS concentrations for the 20 PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, HPFHpA, PFBS, PFHxS, PFHpS, PFOS, 4:2 FTSA, 6:2 FTS, 8:2 FTS, FOSA, PFPeS, EtFOSAA, FOSAA, MeFOSAA) found in the groundwater. All concentrations are in ng/L.

BV AIX / GAC	Day of the experiment	Influent	AIX	GAC1	GAC2
300 / 200	1	2860	14.2	1370	273
600 / 500	2	2880	157	1950	880
1 500 / 1 400	5	279	891	2190	1500
2 500 / 2 200	8	1910	504	2290	1830
3 800 / 3 400	12	1710	518	1680	1500
4 700 / 4 200	15	1340	661	1280	1210
6 000 / 5 300	19	1610	1130	1545	1420
7 000 / 6 500	22	1610	764	1520	1440

Table 6. PFAS4 (PFOA, PFNA, PFOS, PFHxS) concentrations in the groundwater. All concentrations are in ng/L.

BV AIX / GAC	Day of the experiment	Influent	AIX	GAC1	GAC2
300 / 200	1	1490	0.6	588	77
600 / 500	2	1470	16.6	886	305
1 500 / 1 400	5	1380	330	948	539
2 500 / 2 200	8	896	74.4	987	703
3 800 / 3 400	12	766	71.3	726	616
4 700 / 4 200	15	610	175	541	508
6 000 / 5 300	19	803	473	751	665
7 000 / 6 500	22	765	200	645	588

Table 7. PFAS11 (PFBS, PFHxS, PFOS, 6:2 FTSA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA) concentrations in the groundwater. All concentrations are in ng/L.

BV AIX / GAC	Day of the experiment	Influent	AIX	GAC1	GAC2
300 / 200	1	2750	12.9	1330	270
600 / 500	2	2780	155	1880	861
1 500 / 1 400	5	2650	866	2100	1450
2 500 / 2 200	8	1820	501	2210	1770
3 800 / 3 400	12	1640	516	1630	1460
4 700 / 4 200	15	1290	651	1230	1180
6 000 / 5 300	19	1550	1100	1490	1360
7 000 / 6 500	22	1540	758	1470	1400

4.5 COSTS OF GAC AND AIX

The cost for the AIX filter and its destruction was higher than for the GAC filter and its regeneration (Table 8).

Table 8. Cost of filter media and their regeneration or destruction.

	AIX	GAC
Cost of media (euro/m ³) Including transport to the facility	10080	1516
Regeneration cost (euro/m ³) Including transport from the facility	-	1179
Destruction cost (euro/m ³) Including transport from the facility	1239	-

The number of values used for the Lin and Huang model (1999) was adjusted for every PFAS so it would be a good fit to the sampled values. In Table B1 in Appendix B, the number of data points used to obtain τ and $1/k$ are displayed. The model did not fit for all the PFAS at every observed removal efficiency. PFDA and HPFHpA showed negative times for removal efficiency at 99% using AIX and they were therefore excluded from the average time for short and long chained PFCA. For GAC2, PFBS and all PFCA had a negative time at 99% removal efficiency and some had a negative time for lower removal efficiencies as well. All the modelled times that were excluded from the average times for long and short chained PFCA and PFSA are summarised in Table B1 in Appendix B. All the values excluded from the modelled times were also excluded in the cost calculations.

For the removal efficiency goals of 99%, 95%, 90%, 85%, 80% and 50% for PFAS the cost was lower when using AIX, except for long chain PFCA with 50% removal rate when AIX cost more (Figure 11). The cost difference between the methods decreased at a lower removal efficiency. For example, the cost for short chain PFSA at 99% removal efficiency was 30 euros/m³ for GAC and 6.5 euros/m³ for AIX which resulted in a cost difference of 23.5 euros/m³. At 50% removal efficiency the cost was reduced to 2.8 and 2.3 euros/m³ for GAC respectively AIX which resulted in a cost difference of 0.5 euros/m³. It was not possible to model the cost for removing PFCA with GAC at 99% removal since the adsorption model gave a negative time. The short chain PFCA cost more to remove than the long chain ones. For GAC the cost to remove the short chain PFCA was 4.7 – 23.1 euros/m³ whereas the long chain was 2.9 – 16.9 euros/m³. For AIX the cost was 3.3 – 32 euros/m³ for the short chain PFCA and 3.2 – 13.5 for the long chain PFCA. The cost difference between long and short chain PFCA was larger for GAC. It was overall a lower difference in cost to remove long and short chained PFCA and PFSA with AIX. When comparing the short chain PFCA and PFSA the cost was higher for PFCA. For GAC the costs were 4.7 – 23.1 and 2.8 – 6.9 euros/m³ for the removal efficiencies 95 – 50 % for PFCA and PFSA respectively. The costs using AIX were 3.3 – 32 and 2.3 – 6.5 euros/m³ for removal efficiencies 50 – 99% for PFCA and PFSA respectively. The

same trend appeared for long chain PFCA and PFSA, except at 50% removal efficiency. These costs were 2.9 – 16.9 (PFCA) and 3.9 – 5.8 (PFSA) euros/m³ for 50 –95% removal using GAC and using AIX 3.1 – 13.5 (PFCA) and 2.3 – 5.0 (PFSA) euro/m³ for 50 –99% removal efficiency. When removing PFSA the cost difference between long and short chain PFSA was apparent at 99% removal with a difference of 18 euros/m³ for GAC and 1.5 euros/m³ for AIX, where the short chain PFSA were more expensive to remove. At lower removal rates the price became more similar. Both the long and short chain PFSA cost 2.8 euros/m³ at 80% removal efficiency with AIX and with GAC it was only a difference of 0.1 euro/m³. Short chain PFSA remained more expensive to remove with AIX until 80% removal rate where the price became the same. For GAC the cost became lower for short chain PFSA at 80% and 50% removal efficiency. The short chain PFSA cost 3.8 and 2.8 euros/m³ whereas the long chain had a cost of 3.9 and 3 euros/m³ for 80% respectively 50% with GAC. All costs can be viewed in Appendix B, Table B2 and B3.

During the first two weeks the AIX and GAC1 column had to be backwashed every third or fourth day. Thereafter it was needed every second day. It was mainly AIX that exceeded the limit of 170 cm column height for backwashing. GAC2 needed backwashing three times during the 22 days that the experiment was running. All the water levels for the three columns can be viewed in Appendix D, Table D1.

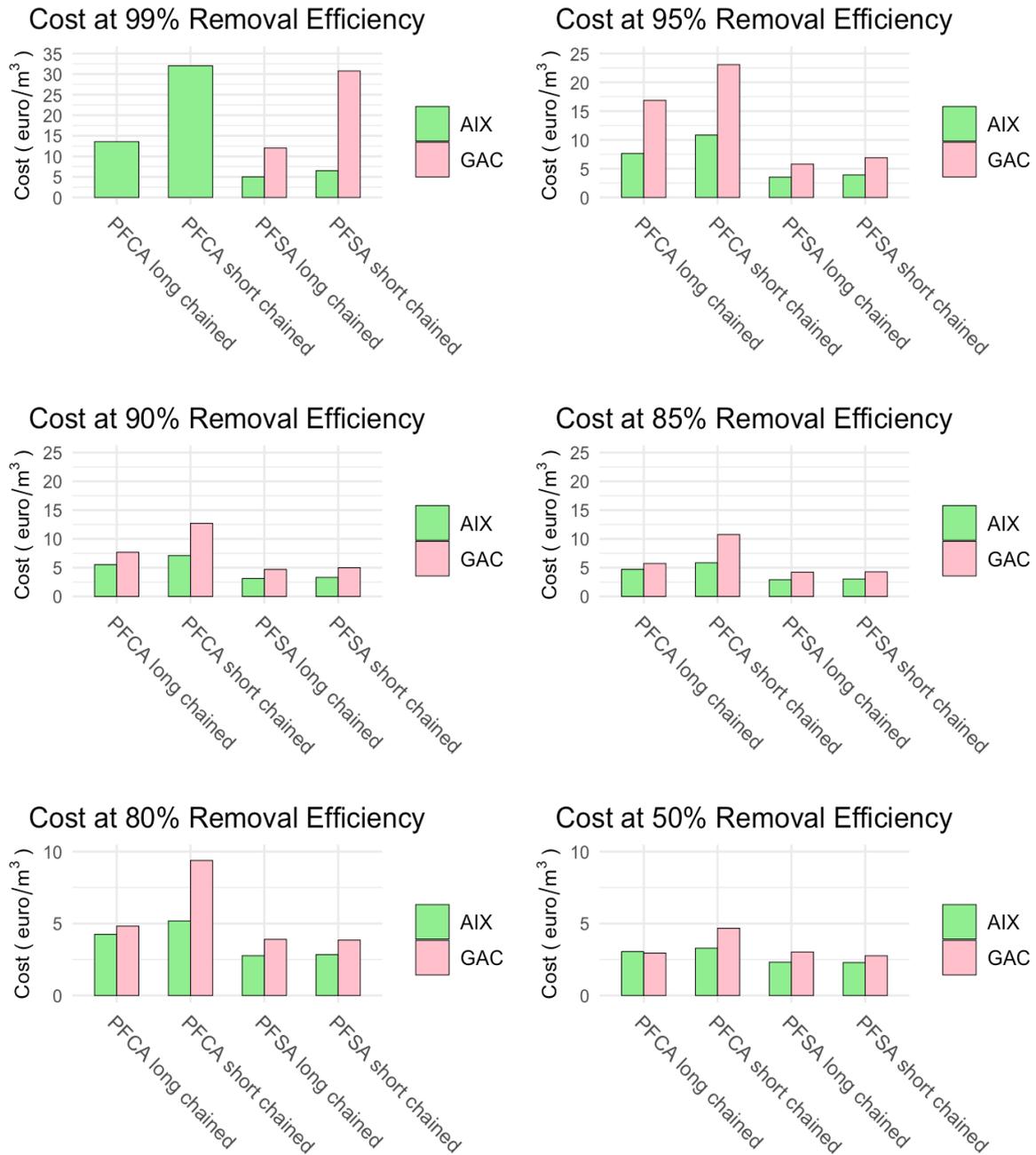


Figure 11. The cost to remove long and short chained PFCA and PFSA for the two treatment techniques AIX and two stage GAC. The cost for PFCA long chained and PFCA short chained were not calculable at 99% removal efficiency with GAC. All costs are calculated for treatment of one cubic metre of water.

5. DISCUSSION

5.2 REMOVAL EFFICIENCY WITH GAC

5.2.1 Changes in removal efficiency with GAC

After 200 BV the removal efficiency of Σ PFAS was 52% and 90% for GAC1 and GAC2, respectively with a decrease to -20% and 4% respectively, until 2 200 BV. After 2 200 BV the removal efficiency increased for both GAC columns (Figure 5). This happened again for long chain PFCA and all PFSA after 5 300 BV (Figure 6). Both increases occurred after backwashing (1 700 BV and 5 600 BV). The water in the columns got a brown colour after air sparging and backwashing which indicated that particles in the filter bed were removed. This could be seen every time the backwashing was done. One explanation for the improved removal efficiency was removal of particles, DOC and ions after backwashing, which increased the capacity of the GAC for removal of PFAS (Chen et al. 2021; Franke et al. 2019). They all had lower removal efficiency at 2 200 BV and the removal efficiency increased after the backwash (Table 3 and Table C1 in Appendix C). However, the measured concentrations of DOC in the backwashed water that were removed from the columns during the backwash at 5 600 BV did not show higher concentrations than the influent concentrations, so it is not certain that DOC was the main factor in reducing the removal efficiency at 2 200 BV. Iron on the other hand had a significantly higher concentration in the column's backwashed water at 94 mg/L compared to the influent concentrations at 0.76 mg/L which might have been one of the main substances blocking the GAC filter at both 2 200 and 5 300 BV. The blockage and creation of preferential flow paths in GAC would have decreased the removal efficiency since the water gets less contact with the GAC (Carbotecnia 2021; Frank et al. 2015). That would explain the increase in removal efficiency at both 2 200 and 5 300 BV. Calcium carbonate has previously been noted to cause clogging (Knappe et al. 1992; Lee et al. 2003). It was not measured in this study but would have been interesting to see if calcium carbonate was contributing to the clogging.

5.2.2 Negative removal efficiency with GAC

All columns had a negative removal efficiency for at least one kind of PFAS. The negative removal efficiency means that the concentration going out of the column was higher than the concentration going in. It mainly happened for short chain PFCA and PFSA since the long chain PFAS show a general stronger sorption compared to short chain PFAS. The presence of long chain PFAS and other compounds such as DOC will cause the short chain to desorb from the GAC and thereafter take the freed adsorption surface (Medina et al. 2022).

In GAC1 both short chain (PFBA, PEPeA, PFHxA, PFHpA, HPFHpA) and two long chain (PFOA, PFNA) PFCA showed a negative removal efficiency. It was only PFDA, which had the longest chain with nine perfluorocarbons, that kept a positive removal efficiency. After GAC2 it was only the short chained PFCA that desorbed. A reason why PFNA and PFOA did not desorb in GAC2 could have been the lower influent concentrations of PFDA and DOC and their stronger affinity to GAC than the short chain PFCA. Regarding the removal of PFSA, it

was the short chained PFBS and PFHpS that desorbed in GAC1. This can be explained since PFBS (C₄) and PFHpS (C₇) are among the shortest PFSA chains. However, PFHxS (C₆) kept the positive removal efficiency the whole time. The negative removal efficiency for PFHpS at 4 000 BV could be due to measurement errors since the influent (5 ng/L) and effluent (5.3 ng/L) concentrations at 4 000 BV were very similar. Therefore, could the measurement errors with a standard deviation of 0.8 for the influent concentration be the reason for the negative removal efficiency.

For GAC2 it was only the shortest chain, PFBS (C₄), that desorbed. FTSA showed a different behaviour where 6:2 FTSA had a higher desorption (-29%) than 4:2 FTSA (-2%) for the two GAC columns at 2 000 BV. It could have been caused by measurement and experimental uncertainties. FOSAA (> -127%) and MeFOSAA (> -120%) had similar negative removal efficiency at 4 000 BV in GAC1. It can be explained by the influent concentration being below the detection level at 0.3 ng/L. Since all values below detection were replaced by half of the detection limit, it is possible that the actual influent concentration was higher than 0.15 ng/L. Then the removal efficiency would still have been negative but closer to 0% which would have agreed with the two adjacent values.

5.2.3 Removal efficiency in comparison with treatment goal and regulations

It was desirable to have a removal efficiency of 99% for the long chain PFCA and PFSA. After passing through the second GAC column this was never achieved for any of the long chain PFCA (PFOA, PFNA, PFDA) after 200 BV. The goal was only reached for PFOS, a long chained PFSA at 200 BV. For the short chain PFCA and PFSA it was desirable with a removal efficiency of at least 95%. None of the short chain PFCA reached the goal. All the short chain PFSA exceeded 95% at 200 BV; PFBS (95 %), PFHxS (97 %) and PFHpS (99 %). According to the adsorption model they would remain above 95% until 300 BV (PFBS), 300 BV (PFHxS) and 700 BV (PFHpS). This did not agree with the measured data for PFHpS which had a removal efficiency of 89% at 516 BV.

The threshold value for PFAS11 in groundwater at 90 ng/L (Kemikalieinspektionen 2023b) was always exceeded after GAC1 and GAC2 which had their lowest PFAS11 concentration at 1331 ng/L and 270 ng/L, respectively, at 200 BV (Table 7). The recommendation of 45 ng/L PFOS was achieved after GAC2 at both 200 BV with concentration at 5.2 ng/L and 500 BV at 40 ng/L. A comparison with the drinking water criteria can also be interesting since groundwater can be a source of drinking water. Since 2022, there is a limiting value of 500 ng/L for \sum PFAS (Naturskyddsforeningen 2022) which was achieved after GAC2 at 200 BV. Thereafter was 500 ng/L for \sum PFAS exceeded. In 2026, there will be new limits applying and one of them is the threshold value at 4 ng/L PFOS4 (Kemikalieinspektionen 2023b). That was never reached with two stage GAC (Table 6).

There was a clear improved removal efficiency of PFAS comparing GAC1 and GAC2 (Tables 5, 6 and 7), although the improvement after GAC2 decreased over time. Having additional GAC columns could therefore be an option to reach the threshold values.

5.3 REMOVAL EFFICIENCY FOR AIX

5.3.1 Changes in removal efficiency with AIX

The removal efficiency for Σ PFAS was 100 % at 300 BV thereafter it decreased to 52% at 7 000 BV. After 1 500 and 6 000 BV the removal efficiency increased to 73% and 52% for sum PFAS, respectively (Figure 8). Both times the column had been backwashed. During the backwashing the water turned brown/red. The filter had been compacted during the running of the columns and was lumped together during the air sparging. By hitting the column, the lump was dissolved and air and water could flow through. It became harder to dissolve the lump over time. One likely reason for the improved removal efficiency was that particles and thus blockage was removed. It is often caused by suspended materials (Purolite 2022) and during the backwash it could be seen that suspended material was released from the filter since the column's water became a lot darker. Dissolved iron and manganese may also have contributed to the blockage (Purolite 2022). In this groundwater there were high levels of iron and AIX removed large parts of it (Table 4). A reason why backwashing at 1 500 BV gave such visible improvement in removal efficiency could be that the columns had been running six days without backwashing. Afterwards the backwashing was done every two or three days and should therefore not have gathered as much DOC, suspended material, iron or manganese. Blockage reduces the removal efficiency because it forces the water to take the preferential flow path of least resistance. This results in the media in contact with the water being saturated while the remaining media still has a high removal capacity (Purolite 2022). PFBA and PEPeA, two short chained PFCA, did not increase in removal efficiency in difference to the other PFCA and PFSA. It is probably due to their short chain length of three and four carbons respectively which agrees with the explanation in the study of McCleaf et al (2017). The reason it did not happen for PFSA with the same chain length is that their functional group sulfonate has a higher affinity to AIX than the carboxylic acid in PFCA (McCleaf et al. 2017; Medina et al. 2022; Liu et al. 2022). For MeFOSAA and EtFOSAA, the removal efficiency increased after 1 500 BV while FOSAA decreased. They have the same chain length, but the groups attached to the carbon backbone differ (Knutsen et al. 2019), therefore it was probably the attached groups that caused the different response after 1 500 BV. None of the fluorotelomers (4:2 FTSA, 6:2 FTSA, 8:2 FTSA) increased after 1 500 BV. These are polyfluorinated PFAS in difference to PFCA and PFSA, meaning that they have at least one carbon without a fluor attached. It reduces their hydrophobicity and gives them inferior hydrophobic interactions with AIX which is one of the main mechanisms in PFAS removal (Dixit et al. 2021). When the removal efficiency increased again after 6 000 BV, backwashing had been done with a higher flow rate (168 mL/min instead

of 40 mL/min). A larger volume of water passed through the column and brought the suspended material with the outflow.

Negative removal efficiencies only occurred for PFBA (C₃) and PEPeA (C₄) using AIX. The reason is that they had the shortest carbon chain and the functional group carboxylic acid which gave them lower affinity for AIX (Medina et al. 2022; McCleaf 2017).

5.3.2 Removal efficiency in comparison with treatment goal and regulations

The treatment goal was to have 99% removal efficiency for long chain PFCA and PFSA. For PFCA it was only achieved for PFOA (100%) at 300 BV (Figure 9). The only long chain PFSA, PFOS, was also at 100% removal efficiency at 300 BV and remained above 99% until 600 BV. The desirable removal efficiency for short chain PFCA and PFSA was 95%. Among the PFCA, HPFHpA never reached above 95% removal. The other four; PFBS (95 %), PFPeA (99 %), PFHxA (100 %) and PFHpA (100%) all reached the goal at 300 BV. PFHpA (97 %) remained above at 600 BV as well. The three short chain PFSA reached the goal until 600 BV: PFBS (100%), PFHxS (100 %) and PFHpS (99 %). After a decrease at 1 500 BV where the removal efficiency went below 95 % it increased again and PFBS (98 %), PFHxS (98 %) and PFHpS (98 %) remained above 95 % until 3 800 BV.

The groundwater threshold value of 90 ng/L for PFAS11 was maintained at 300 BV with 12.9 ng/L (Table 7). It thereafter exceeded 90 ng/L until 7 000 BV. Regarding the groundwater recommendation of 45 ng/L PFOS it was exceeded at 1 500 BV with the concentration of 55 ng/L. However, at 2 500 BV (3.7 ng/L) the concentration had decreased again and remained below 45 ng/L with the last sampled concentration at 5.3 ng/L. The drinking water criterion with 500 ng/L for Σ PFAS was kept until 600 BV (156.7 ng/L) (Table 5). For PFAS4 the new threshold value of 4 ng/L was only kept at 300 BV with concentration at 0.6 ng/L (Table 6).

5.4 DIFFERENCE IN REMOVAL EFFICIENCY BETWEEN GAC AND AIX

Both for the long and short chain PFCA and PFSA, AIX showed a higher removal efficiency than GAC for the whole test period (Figure 10). The backwash on the fifth day improved the removal efficiency for long chain PFCA and PFSA with AIX but not with GAC. The blockage in AIX was probably removed more efficiently. In Table 3, DOC concentrations were 49 mg/L for AIX, 44 mg/L for GAC1 and 33 mg/L for GAC2 at 2 500/2 200 BV. The higher effluent DOC concentration from AIX could be because it was less sorbed to the filter. GAC has previously been shown to be sensitive to blockage from DOC although this is also true for AIX (Chen et al. 2021). The two stage GAC was overall more efficient in removing DOC than AIX which could have caused a stronger competition with PFAS and blockage of the filter. Franke et al. (2019) had a similar result where GAC was more sensitive to organic matter. For some PFAS, DOC has contributed to a higher removal, so it does not always have an adverse effect (Siriwardena et al. 2019). It has also been noted that GAC and AIX are sensitive to iron and manganese since they clog the filters (Chen et al. 2021; Purolite 2022).

The removal efficiency improved for both GAC and AIX on day 18 (6 000 and 5 000 BV) for long chain PFCA and PFSA. The reason was probably because the backwashing was done with a higher flow rate and continued until the water in the columns looked clear. The main substance removed was iron. The removed water from the AIX column had a lower iron concentration but a steeper increase in removal efficiency after the backwashing compared to GAC (Figure 10). This could be because GAC was more sensitive to iron.

If the column test was run again, it would be recommended to use higher flows during the backwash from the beginning. That would probably have kept the removal efficiency higher for both GAC and AIX for a longer time. It would also be good to have a filter before the columns that could remove iron and suspended particles. This groundwater had a high iron concentration which impaired the removal efficiency. In water tank 1 where the untreated groundwater was kept, a layer of iron and particles gathered over time.

5.5 FIT FOR ADSORPTION MODEL

The adsorption showed a worse fit for GAC than AIX when looking at the higher removal rate of 99% and 95%. How well the model worked was related to the measured removal efficiencies. For example, the model gave a negative time for all PFCA at 99 % removal efficiency when GAC was used. They never had 99 % removal efficiency for any of the samples. The closest to 99 % removal efficiency was PFDA with 93 %. For AIX the model worked for all PFCA except for PFDA and HPFHpA which had removal efficiencies at 93 %. The other PFCA were all between 95 - 100% with AIX. Although the adsorption model gave negative times for several PFAS it generally gave times close to the sampling data when the modelled times became positive. More measured values during the first 48 hours would have improved the modelled times for removal efficiencies between 90 – 99 %. That could have made it possible to make two different modelled values for each PFAS, one where the removal efficiency was 95 – 99 % and another one for the lower removal efficiencies. This approach was used in McCleaf et al. (2017) with the Lin and Huang (1999) adsorption model.

To get a good fit for the adsorption, in comparison to the measured data, several data points were excluded. An explanation for the need of exclusion could be the backwashing which caused irregular increases in the removal efficiency. If the backwash had been done with a higher flow from the start it is possible that the removal efficiency would have shown a smoother trend.

5.6 COST OF TREATING PFAS WITH GAC AND AIX

The costs were overall lower for AIX than two stage GAC (Figure 11). That AIX cost less has been reported in previous studies as well (Liu et al 2022; Ellis et al. 2023). When Medina et al. (2022) studied the unit water cost they discovered that it was lower for AIX which it was in this study as well. This is because AIX maintained a higher removal efficiency for a longer time

than GAC. MUR was not calculated in this study but would have been a good parameter to explain which media could be used the longest. This was done by Ellis et al. (2023) and Franke et al. (2021) which both discovered that AIX had a lower MUR than GAC. AIX seemed to be more sensitive to blockage since it needed backwashing more often than the two GAC columns (Table 9). That would have resulted in more maintenance costs.

Both AIX and GAC cost less for removal of long chain PFCA and PFSA than their short chain counterparts since it was harder to remove the short chain PFCA and PFSA. It was the easiest to see for PFCA when the removal efficiency of short chains clearly was lower for both AIX and GAC. There was also a clear difference in cost with the short chain PFCA being more expensive to remove (Figure 11). The cost difference between long and short chain was bigger for GAC which is explained by the larger difference in removal efficiency of short and long chain.

How well the times were modelled using the Lin and Huang (1999) adsorption model affected the price calculations since those times were used to calculate the volume of water that had passed through the filters. When the model times became longer compared to the measured data points it resulted in lower cost. Sometimes the modelled times were both longer and shorter for the same PFAS but at different removal efficiencies. There was no clear pattern for which groups of PFAS the time was longer or shorter than the measured data.

Later on the results could be used to compare cost effectiveness for the combination of the three cleaning techniques in the EU LIFE SOuRCE project: surface active foam fractionation, electrochemical oxidation and phytoremediation (LIFE SOuRCE n.d.). To examine the efficiency of these newer methods they need to be compared to traditional methods such as GAC and AIX. However, if the costs from this study are used for comparison it needs to be taken into consideration that they would probably have been lower if the backwashing had been done with a higher flow from the beginning. Another way to lower the costs would probably be to have a filter that took away suspended particles and iron which clogged the filters.

6. CONCLUSION

The two stage GAC had its highest removal efficiency for Σ PFAS at 90 % after 200 BV. It was the most efficient in removing PFSA, especially the long chain PFOS which had a removal efficiency ranging from 30 % to 99 %. There were several PFAS that desorbed during the study, mainly short chain PFCA and FTSA. The lowest values after GAC2 were -29 % (6:2 FTSA) and -28 % (PFHxA).

AIX had its highest removal efficiency for Σ PFAS at 100 % after 300 BV. The individual PFAS with the highest removal rates at 300 BV were PFHxA, PFHpA, PFOA, PFBS, PFHxS, PFOS, 6:2 FTSA and PFPeS which all had a 100 % removal. It was only PFBA and PFPeA that desorbed and their removal efficiencies were -23 % and -13 %.

When comparing the two methods, AIX was the most efficient. There were two exceptions, one for FOSA where AIX became more efficient first after 1 300 BV and the other one was FOSAA where GAC2 had a higher removal efficiency during the first 2 200 BV. The range of Σ PFAS for AIX was 52 – 100% whereas it was lower for the two stage GAC with 4 – 90%. For both GAC and AIX there was a higher removal efficiency for long chain PFCA and PFSA compared to short chain which depended on the stronger hydrophobic interactions with GAC or AIX for the longer chains. For PFCA and PFSA with the same chain length, the removal efficiency was higher for PFSA with both GAC and AIX. The explanation was that the electrostatic interactions are stronger for the sulfonic than the carboxylic groups. The desorption was higher for GAC where all the short chain PFCA desorbed in comparison to only two PFCA with AIX. There was also a difference for the FTSA which desorbed in both GAC1 and GAC2 but not in AIX. One explanation for the lower removal efficiency with GAC could be that it is more sensitive to DOC and iron both because they adsorbed to GAC and because they clogged the filters.

Regarding the costs, AIX was cheaper than GAC for all the examined removal efficiencies with the exception at 50 % removal efficiency when AIX was more expensive. When comparing removal efficiencies of 50 – 95 % the cost for GAC and AIX were 2.8 –23.1 respectively 2.3 – 10.8 euro/m³ treated water. The cost differences between the two methods were bigger for the higher removal efficiencies which was explained with AIX being able to keep a higher removal efficiency for a longer time.

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APPENDIX A. CALCULATIONS OF THE COLUMNS' FLOW RATE

Common parameters

Diameter of columns = 5.4 cm

Radius of columns = 2.7 cm

Area of columns = $2.7^2\pi = 22.9 \text{ cm}^2$

EBCT = 5 min

GAC

Height of GAC = 8.8 cm

Volume of GAC = $8.8 \cdot 22.9 = 202 \text{ cm}^3$

$Q = \text{Volume of GAC} / \text{EBCT} = 202 / 5 = 40.4 \text{ cm}^3 / \text{min}$

AIX

Height of AIX = 7.8 cm

Volume of AIX = $7.8 \cdot 22.9 = 179 \text{ cm}^3$

$Q = \text{Volume of AIX} / \text{EBCT} = 179 / 5 = 35.8 \text{ cm}^3 / \text{min}$

APPENDIX B. INFORMATION ON THE ADSORPTION MODEL AND COSTS

Table B1. Number of data points used for the Lin and Huang adsorption model and which modelled times that had to be excluded from the average times for long and short chained PFCA and PFSA because they were negative. The N/A values are for PFAS are not included in the PFCA or PFSA group.

Substances	AIX Data points used	GAC Data points used	AIX At which removal efficiency the model time was excluded from calculations	GAC At which removal efficiency the model time was excluded from calculations
PFBA	2	2	-	99, 95, 90%
PFPeA	3	2	-	99, 95%
PFHxA	7	2	-	99%
PFHpA	7	2	-	99%
PFOA	7	2	-	99%
PFNA	7	2	-	99%
PFDA	2	2	99%	99%
HPFHpA	8	2	99%	-
PFBS	7	2	-	99%
PFHxS	7	2	-	-
PFHpS	7	3	-	-
PFOS	7	2	-	-
4:2 FTS	4	2	N/A	N/A
6:2 FTS	7	2	N/A	N/A
8:2 FTS	3	2	N/A	N/A
FOSA	4	2	N/A	N/A
PFPeS	7	2	N/A	N/A
EtFOSAA	6	2	N/A	N/A
FOSAA	4	4	N/A	N/A
MeFOSAA	7	5	N/A	N/A

Table B2. Cost in euro to remove long and short chain PFCA from one cubic metre of groundwater. N/A values appear when the Lin and Huang (1999) adsorption model could not be used to model a time.

Removal efficiency	AIX Long chain PFCA	GAC Long chain PFCA	AIX Short chain PFCA	GAC Short chain PFCA
99%	13.5	N/A	32.0	N/A
95%	7.6	16.9	10.8	23.1
90%	5.5	7.7	7.1	12.7
85%	4.7	5.7	5.9	10.8
80%	4.2	4.8	5.2	9.3
50%	3.1	2.9	3.3	4.7

N/A = Not Available

Table B3. Cost in euro to remove long and short chain PFSA from one cubic metre of groundwater. N/A values appear when the Lin and Huang (1999) adsorption model could not be used to model a time.

Removal efficiency	AIX Long chain PFSA	GAC Long chain PFSA	AIX Short chain PFSA	GAC Short chain PFSA
99%	5.0	12	6.5	30
95%	3.5	5.8	3.9	6.9
90%	3.1	4.7	3.3	5.0
85%	2.9	4.2	3.0	4.3
80%	2.8	3.9	2.8	3.8
50%	2.3	3.0	2.3	2.8

APPENDIX C. WATER PARAMETERS

Table C1. Concentration of chloride, sulphate, fluoride and manganese for the influent groundwater and the water after AIX, GAC1 and GAC2 columns. All concentrations are in mg/L.

BV AIX / GAC	Day of the experiment	Parameter	Influent	AIX	GAC1	GAC2	Backflush
Chloride							
300 / 200	1		920	930	920	910	
600 / 500	2		920	860	880	910	
1 500 / 1 400	5		890	880	900	900	
1 900 / 1 700	6						870
2 500 / 2 200	8		650	860	860	860	
3 800 / 3 400	12		630	640	640	630	630
4 700 / 4 200	15		470	460	440	470	
6 000 / 5 300	19		470	470	470	470	
7 000 / 6 500	22		510	510	510	510	
Sulphate							
300 / 200	1		370	370	370	370	
600 / 500	2		370	370	370	370	
1 500 / 1 400	5		340	340	350	360	
1 900 / 1 700	6						340
2 500 / 2 200	8		310	340	340	360	
3 800 / 3 400	12		320	320	330	320	330
4 700 / 4 200	15		310	320	320	320	
6 000 / 5 300	19		320	320	320	330	
7 000 / 6 500	22		350	360	350	350	
Fluoride							
300 / 200	1		0.44	0.44	0.45	0.44	
600 / 500	2		0.43	0.44	0.43	0.43	
1 500 / 1 400	5		0.42	0.43	0.41	0.46	
1 900 / 1 700	6						0.37

BV AIX / GAC	Day of the experiment	Parameter	Influent	AIX	GAC1	GAC2	Backflush
2 500 / 2 200	8		0.47	0.44	0.47	0.5	
3 800 / 3 400	12		0.47	0.5	0.51	0.53	0.49
4 700 / 4 200	15		0.51	0.54	0.53	0.54	
6 000 / 5 300	19		0.51	0.54	0.52	0.56	
7 000 / 6 500	22		0.53	0.54	0.54	0.55	
Manganese							
300 / 200	1		1.1	1.1	1.1	1	
600 / 500	2		1.1	1.1	1.1	1	
1 500 / 1 400	5		1.1	1.1	1.1	1.1	
1 900 / 1 700	6						1
2 500 / 2 200	8		0.96	1.1	1.1	1.1	
3 800 / 3 400	12		0.95	0.9	0.92	0.9	0.84
4 700 / 4 200	15		0.79	0.85	0.85	0.87	
6 000 / 5 300	19		0.92	0.91	0.92	0.93	
7 000 / 6 500	22		1	1	0.89	0.89	

Table C2. Measured pH and conductivity values for the influent groundwater and the water after AIX. GAC1 and GAC2 columns.

Day of the experiment	Column	pH	Conductivity (mS/cm)
1	IN	7.12	4.96
2		7.15	5.06
5		7.15	4.75
6		7.26	4.65
7		7.13	4.67
8		7.13	3.76
9		7.17	3.74

Day of the experiment	Column	pH	Conductivity (mS/cm)
12		7.26	3.58
13		7.1	3.05
14		7.21	2.97
15		7.32	2.98
16		7.18	3.06
19		7.2	3.04
22		7.21	3.16
<hr/>			
1	AIX	7.31	4.89
2		7.33	4.87
5		7.2	4.74
6		7.2	4.53
7		7.14	4.8
8		7.15	4.67
9		7.25	3.75
12		7.09	3.83
13		7.1	3.14
14		7.11	3.07
15		7.06	3.01
16		7.04	3.13
19		7.07	3.1
22		7.06	3.28
1	GAC1	7.29	4.92
2		7.29	4.88
5		7.25	4.86

Day of the experiment	Column	pH	Conductivity (mS/cm)
6		7.21	4.55
7		7.15	4.74
8		7.14	4.3
9		7.1	3.7
12		7.23	3.81
13		7.18	3.08
14		7.17	2.97
15		7.22	2.99
16		7.26	3.08
19		7.32	3.13
22		7.2	2.66
	GAC2		
1		7.43	4.86
2		7.43	4.85
5		7.38	4.79
6		7.07	4.53
7		7.23	4.73
8		7.27	4.74
9		7.31	3.84
12		7.39	3.79
13		7.31	3.35
14		7.25	3.06
15		7.24	3.05
16		7.18	3.07
19		7.17	2.9
22		7.19	3.26

APPENDIX D. WATER LEVELS AND BACKWASHING IN THE COLUMNS

Table D1. Recorded water levels in the AIX, GAC1 and GAC2 columns. The orange colour shows when backwashing was performed.

Day of experiment	AIX	GAC1	GAC2
2	131	92.5	114
5	149.5	122.4	119
6	184.5	134.6	125
7	134.5	122	125
8	144.5	124.5	136
9	185	151.5	144.5
12	185	119	138.5
13	145	116	150
14	170	130.5	187
15	147	110	114
16	184	120	141
19	171	119	115
21	187	112	131
22	132	112	137.5