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Effect of organic matrix on the adsorption of selected antibiotics and antiretroviral drugs from drinking water onto activated carbon

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Presence of natural organic matter (NOM) in surface waters is on the rise due to human activities. Along that, active pharmaceuticals ingredients, which are considered a threat as developing antibiotic resistance, are also detected in drinking water sources, particularly in less developed countries. Therefore, competitive treatment is required to make potable water from surface waters. Activated carbon (AC) filtration is a powerful tool in drinking water treatment because its ability to adsorb dissolved organic carbon (DOC) and specific micropollutants, such as pharmaceuticals. In this study, adsorption of methylene blue (MB), DOC and four pharmaceuticals; sulfamethoxazole (SMX), trimethoprim (TMP), lamivudine (3TC), and nevirapine (NVP) onto four ACs (two commercial, two wood- and peat-made AC under research and development (R&D)) was studied in batch experiments. Adsorption competition between selected pharmaceuticals (2.0–10.0 mg/l) and DOC (2.5–3.6 mg/l) was studied by spiking pharmaceuticals in coagulated water from local drinking water treatment plant (pH 7.2), corresponding the real treatment process. TOC analysis, high-performance size-exclusion chromatography (HPSEC) and liquid chromatography tandem mass spectrometry (LC-MS/MS) were used to analyze DOC and pharmaceutical contents. Langmuir and Freundlich isotherms were used to describe and calculate adsorption kinetics and capacities. Adsorption capacities of R&D wood and R&D peat for MB were 107.5 and 87.7 mg/g, respectively, while capacities of commercial ACs were 16.1 and 75.8 mg/g. Adsorption capacities of different ACs for DOC varied between 4.3 and 16.2 mg/g. In ultrapure MQ water, capacities varied between 10.8–29.1 mg/g for SMX, 4.0–29.7 mg/g for 3TC and 10.8–87.0 mg/g for NVP. Due to complete removal, adsorption capacity for TMP couldn't be determined. Presence of DOC in the matrix affected adsorption differently for each pharmaceutical. Capacities of ACs decreased 82 % for SMX at best, 59 % for 3TC at best and 80 % for NVP at best. Notable decrease in removal of TMP was also detected. Langmuir isotherm (monolayer adsorption) described better MB and pharmaceutical adsorptions, while Freundlich (multilayer) described better DOC adsorption. According to adsorption capacities and removal efficiencies, DOC really decreases adsorption of selected pharmaceuticals. Water solubility and pK_a constant of molecules, and pore size distribution and ash content of ACs appeared to have some influence on adsorption. Strong repulsion forces may have decreased the adsorption of compounds with low pK_a constant. Molecular sizes of molecules and pore size distribution of ACs made also difference between adsorption of some compounds. Further research of R&D products is needed with fixed-bed column tests. Compared to commercial ACs and literature, results indicate high potential of R&D products for use in water treatment process.

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Luonnollisen orgaanisen aineksen (NOM) määrä pintavesistöissä on kasvanut, minkä lisäksi niissä on havaittu ympäristölle haitallisia lääkeainejäämiä. Kun suuri osa Suomenkin juomavedestä on peräisin pintavesilähteistä, tulee sen puhdistamista kehittää kasvavien haitta-ainepitoisuuksien myötä. Aktiivihiilisuodatus on tehokas keino juomavedenpuhdistuksessa liuenneen orgaanisen hiilen (DOC) ja eri mikropollutanttien, kuten lääkeaineiden, poistossa. Tässä tutkimuksessa tutkittiin ravistelukokeiden avulla, miten erilaiset aktiivihiilet poistavat vedestä metyleenisineä (MB), DOC:tä ja neljää fysikaalis-kemiallisilta ominaisuuksiltaan erilaista lääkeainetta; sulfametoksatsolia (SMX), trimetopriimia (TMP), lamivudiinia (3TC) ja nevirapiinia (NVP). Käytössä oli kaksi kaupallista aktiivihiiltä ja kaksi kehitysvaiheessa olevaa, puusta (R&D puu) ja turpeesta (R&D turve) valmistettua aktiivihiiltä. Kokeissa tutkittiin myös, miten DOC:n (2,5–3,6 mg/l) läsnäolo vedessä vaikuttaa lääkeaineiden (2–10 mg/l) poistumiseen, lisäämällä lääkeaineet vedenpuhdistamolta saatuun kemiallisesti saostettuun veteen. DOC:n ja lääkeaineiden analysointiin käytettiin TOC-analyysiä, korkean erotuskyvyn kokoeksluusiokromatografiaa (HPSEC) ja massaspektrometriaa (LC-MS/MS). Langmuirin ja Freundlichin isotermejä käytettiin adsorptiomekanismien tutkimiseen ja adsorptiokapasiteettien laskemiseen. Adsorptiokapasiteetit R&D puulla ja R&D turpeella MB:lle olivat 107,5 ja 87,7 mg/g, ja kaupallisilla 16,1 ja 75,8 mg/g. Aktiivihiilten kapasiteetit DOC:lle vaihtelivat välillä 4,3–16,1 mg/g. Kapasiteetit ultrapuhtaassa vedessä oleville lääkeaineille vaihtelivat välillä 10,8–29,1 mg/g SMX:lle, 4,0–29,7 mg/g 3TC:lle ja 10,8–87,0 mg/g NVP:lle. Kapasiteettia TMP:lle ei voitu laskea sen täydellisen poistumisen vuoksi. DOC:n läsnäolo vedessä todella heikensi lääkeaineiden poistumista: aktiivihiilien adsorptiokapasiteetti SMX:lle laski enimmillään 82 %, 3TC:lle 59 % ja NVP:lle 80 %. Myös TMP:n kohdalla oli havaittavissa adsorption heikkenemistä. MB ja lääkeaineet adsorboituivat yhteen kerrokseen (Langmuir), DOC:n adsorboituessa useampaan kerrokseen aktiivihiilen pinnalle (Freundlich). Adsorptioon näytti vaikuttavan ainakin veden pH, yhdisteiden pK_a-arvo ja vesiliukoisuus, sekä aktiivihiilten tuhkapitoisuus ja huokoskokojakauma. Yhdisteiden pK_a arvot olivat TMP:tä lukuunottamatta alhaisia, joten niiden ja DOC-molekyylien toisiaan hylkivät negatiiviset pintavaraukset saattoivat heikentää adsorptiota. Molekyylikoot ja aktiivihiilten huokoskoot voivat toimia myös selittävinä tekijöinä DOC:n ja lääkeaineiden erilaisiin adsorptioihin. Tulosten mukaan tuotekehityksen alla olevat R&D-hiilet ovat täysin vertailukelpoisia kaupallisten, sekä muissa tutkimuksissa käytettyjen aktiivihiilten kanssa, minkä perusteella voidaan niiden katsoa soveltuvan juomaveden puhdistukseen. Jatkotutkimuksia kolonnikokeilla tarvitaan.

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ABBREVIATIONS

NOM	Natural organic matter
TOC	Total organic carbon
DOC	Dissolved organic carbon
AC	Activated carbon
GAC	Granular activated carbon
PAC	Powdered activated carbon
R&D	Coding for ACs under Research & Development
BET	Brunauer-Emmett-Teller theory serves as the basis for the measurement of the surface area of materials
HPLC	High-performance liquid chromatography
HPSEC	High-performance size exclusion chromatography
LC-MS	Liquid chromatography-mass spectrometry
MB	Methylene blue
TMP	Trimethoprim
SMX	Sulfamethoxazole
NVP	Nevirapine
3TC	Lamivudine
ARVD	Antiretroviral drug
MQ water	Ultrapure water
VW	Viitaniemi water, coagulated water containing 2.5–3.6 mg/l DOC
DBP	Disinfection by-product
UV-light	Ultraviolet light

1 INTRODUCTION

Surface waters, like lakes and rivers, are one of the main sources of drinking water, as well as the sink of wastewater, around the world. The use of groundwater would be more preferable, but aquifers are not present densely populated areas. Even though aquifers are present, population growth and urbanization have led to a situation where there is not enough groundwater locally for everyone. For example, there are large aquifers in Finland, but still about 39 % of drinking water comes from rivers and lakes, particularly in southern part of Finland (THL 2022). There is a higher demand of treating the surface waters to drinking water than relatively clean groundwater.

Surface waters are different around the world. In a boreal forest zone, surface waters are acidic, dark colored, and they contain lots of humus (Rantakari 2010). In these areas, climate is humid and the catchment areas are dominated by coniferous forests and peatlands (Rantakari 2010). Climate doesn't support complete decomposition, so the dead organic matter is accumulating on a soil surface. This natural organic matter (NOM) is the cause of the acidity and humus in these soils. High precipitation in these areas leads to surface runoff of water carrying NOM from catchment areas to the surface waters, causing the acidity and dark coloring (Rantakari 2010).

NOM causes problems in drinking water quality and treatment processes. In drinking water, NOM can cause unpleasant color, taste, odor of tapwater and increased the formation of sludge in treatment plants and toxic disinfection by-products (DBPs) (Matilainen *et al.* 2011; Beauchamp *et al.* 2018). NOM also enables the higher concentration of heavy metals and other toxic micropollutants by complexing them (Matilainen *et al.* 2011) as well as increased microbial growth in a drinking water distribution system (Lehtola *et al.* 2002).

Human land use and soil acidification have decreased the quality of surface waters with increased NOM content (Forsberg 1992; Eikebrokk *et al.* 2004; Korth *et al.* 2004; Fabris *et al.* 2008) and chemical contamination (Schwarzenbach *et al.* 2006). For example, the total organic carbon (TOC) content in Lake Päijänne, Finland, increased 18-47 %, depending on the measurement point, between 2000-2015 (Forsius *et al.* 2017). TOC content in lake Päijänne is probably caused by shorter snow cover and land use of catchment area, which increase the runoff. Along with health risks and aesthetic problems, increased NOM content can also increase the costs of water treatment due the higher need for coagulants and disinfectants (Eikebrokk *et al.* 2004). Man-made problems do not only relate to surface waters but also to groundwater supplies (Kløve *et al.* 2017).

Human population growth and increased amount and variety of used pharmaceuticals and personal care products have changed the sewage treatment or at least increased the monitoring of these levels. Most of the wastewater treatment processes are insufficient in the removal of many pharmaceuticals, because of their persistent structure and possible removal competition with NOM, for example (Andreozzi *et al.* 2003; Vieno *et al.* 2005, 2007b). These products will end up in environment and surface waters, from which they may end up in raw drinking water and human consumption. It is generally agreed that effects of pharmaceuticals in human body and environment are unlikely and harmful at least in third world countries(Ternes *et al.* 2005). One of the most emerging threats to public health around the globe is the developing antibiotic resistance of microbes. Antibiotic resistance can occur, if levels of antibiotic concentrations are not high enough to kill pathogens but to possibly catalyze the ability to resist antibiotics (Kümmerer 2003; Blair *et al.* 2015).

Activated carbon (AC) filtration is a common method in drinking water treatment for removal of organic matter and other pollutants as well as removal of unpleasant color, taste and odor. AC filtration is an efficient way to remove NOM molecules (Newcombe 1999; Schreiber *et al.* 2005; Matilainen *et al.* 2006b), and especially dissolved organic carbon DOC (particle size < 0.45 μm), because larger particles are

usually removed already in coagulation and flocculation. AC can be utilized for synthetic micropollutants, such as pharmaceuticals, self-care products and pesticides (Vieno *et al.* 2007b; Stuetz and Stephenson 2009; Zahoor 2013). AC is also used in the removal of industrial dyes, like methylene blue, which is the most common dye chemical globally and it is widely used as a reference compound to compare the adsorption capacities of different AC products (Rafatullah *et al.* 2010; Schirmer *et al.* 2011). There are also wide variety of other anthropogenic pollutants which can be removed potentially with this method (Schwarzenbach *et al.* 2006; Ullberg *et al.* 2021; Franke *et al.* 2021). Removal of micropollutants is usually challenging because of the several orders higher concentrations of organic matter. Excess amount of DOC molecules will occupy adsorption sites more likely and thus decrease the adsorption of less abundant micropollutants (Montgomery 1985; Pelekani and Snoeyink 1999; de Ridder *et al.* 2011). This adsorption competition is common issue in water treatment and more research in this area could help the removal of these micropollutants.

Methods for the removal of DOC and pharmaceuticals must be improved and adapted to changing conditions to reach even safer and cleaner water for everyone. In this empirical study, adsorption of DOC and pharmaceuticals onto four activated carbons was studied with batch experiments. Two commercial ACs and two ACs under research and development were compared. Adsorption capacities of these ACs for DOC were calculated, and the DOC content was characterized by molecular size and fluorescence using high-performance size exclusion chromatography (HPSEC) method. Adsorption capacities for four physiochemically different pharmaceuticals; sulfamethoxazole (SMX), trimethoprim (TMP), lamivudine (3TC) and nevirapine (NVP) were measured using the coupling of liquid chromatography and mass spectrometer (LC-MS/MS). Furthermore, adsorption competition between DOC and pharmaceuticals was studied by spiking pharmaceuticals in chemically treated water from Viitaniemi drinking water treatment plan. Langmuir and Freundlich isotherms were used to describe and calculate the adsorption mechanisms and capacities.

Research questions were: 1. What are the adsorption capacities of different ACs for reference compound methylene blue? 2. What are the adsorption capacities of different ACs for DOC? 3. What are the adsorption capacities of different ACs for selected pharmaceuticals without DOC? 4. Is there adsorption competition between DOC and pharmaceuticals, if they are present in same matrix? 5. What are the adsorption mechanisms of each compound?

2 BACKGROUND

2.1 Drinking water treatment in Finland

It is important to know the principles of drinking water treatment processes to understand why research work is needed and in which sectors it is must focus to achieve the targets that for example Finnish government has been set (National Drinking Water Degree 2015/1352/STM). For example, doing a development of adsorption processes, it is important to know that what kind of compounds or materials are already removed in previous processes in typical water treatment plants. This study is related to Finnish water treatment processes, which are optimized for acidic, dark colored and humus containing waters, which contains also anthropogenic compounds such as pharmaceuticals and personal care products. Abundant organic matter causes challenges to remove these anthropogenic compounds due to the competition of removal capacity.

Drinking water treatment in Finland is typically based on chemical coagulation, sedimentation/flotation, sand filtration, ozonization, activated carbon filtration, alkalining and post disinfection (HSY 2022). Chemical coagulation is an effective method for the removal of solid particles like organic matter, clay and algae. Coagulation is the most effective in removal of hydrophobic and high molar mass organic compounds (Matilainen et. al 2011). By adding coagulants such as iron-($Fe_2(SO_4)_3$) and aluminium sulphate ($Al_2(SO_4)_3$), negatively charged organic particles will lose their charge, which enables a possible agglomeration of particles.

However, colliding and thus agglomerating of particles may not occur without kinetic energy, which is implemented by blending the water slowly. This action is called flocculation. Agglomerated particles, flocs, are heavy enough to sink to the bottom of the pool. This sludge can be scraped off for disposal. Amount of coagulant and pH of the water are the most important factors of the coagulation process. (Parsons & Jefferson 2006).

Flocs can also be removed with air flotation. Flotation means removal of flocs by making the solid particles float rather than sink. Flocs are attached to air bubbles made at the bottom of the pool. When density of agglomerate of flocs and bubbles becomes lower than water, they are rising to the surface from which the sludge can be scraped off. Method is handy for removal of low-density material, which would sink rather slowly by using sedimentation. (Isoaho and Valve 1986).

After coagulation and clarification, water is typically filtered through a sand filter. Target is to remove particulate materials including residual particles, clays, silts, micro-organisms and precipitation of organics and metal ions, that were not removed in coagulation/flocculation/sedimentation (Parsons and Jefferson 2006). Filters can be cleaned with backwashing, where the water is back-pumped up through the filter bed.

One notable application of filtration is activated carbon filtration, which bases on adsorption processes. AC filtration is a very common method in drinking water treatment to remove pollutants, taste, odor and color from water by adsorbing the molecules onto its surface (Stuetz and Stephenson 2009). It is a very efficient way to remove natural organic matter (NOM) and its form of dissolved organic carbon (DOC, particle size < 0.45 µm) (Newcombe 1999; Schreiber *et al.* 2005; Matilainen *et al.* 2006b). In addition to natural origin compounds, AC filtration works also in the removal of synthetical, anthropogenic micropollutants, such as pharmaceuticals, personal care products, and pesticides (Vieno *et al.* 2007a; Zahoor 2013; Rodriguez *et al.* 2016; Rao *et al.* 2021). There can also be more micropollutants of wide variety which can be potentially removed by AC filtration (Schwarzenbach *et al.* 2006;

Ullberg *et al.* 2021; Franke *et al.* 2021). Adsorption processes and activated carbons are presented in more detail in Chapter 2.2.

Ozonation or some other oxidation method is used to remove unpleasant tastes and odors. Ozone is a very strong oxidizer, and it can break down very complex pollutants like pesticides or disinfectant by-products. Oxidizing effect is either based on very reactive oxygen radical, formed in a fission of ozone molecule, or selective oxidizing by the molecular ozone. Ozone is usually used before activated carbon filtration. Before activated carbon filtration, ozone eases removal of high molecular weight compounds by breaking them into smaller ones and making them more biodegradable and assimilable (Świetlik *et al.* 2004; Matilainen *et al.* 2006a). Ozonation supports the disinfection process, but its main purpose is the breaking of organic matter and removal of odor, taste, and color. Ozone doesn't leave any disinfectant residuals which would kill pathogens that appear after treatment. That is why there is a need for disinfectant with chlorine.

The main target of disinfecting drinking water is to inactivate or kill pathogens to prevent the spread of waterborne diseases. This diverse group of organisms includes bacterial, viral and protozoan species. There are typically two approaches to accomplish disinfection. On the first hand, chemical agents like chlorine or chloramines and its compounds, can be used. On the second hand, physical agents like UV-light or physical separation can be used. UV-light eliminates uneliminated bacteria coming from biofilms that are formed and leached for example from an activated carbon filter (Parsons and Jefferson 2006). Before releasing the water into a water supply system, acidity of water can be decreased with lime to prevent corrosion of water pipes.

2.2 Adsorption

Adsorption is a reaction where compound or particle (adsorbate) is adsorbed onto the interface between two bulk phases i.e. to the surface of adsorbent. In water treatment, adsorption is brought about the interactions between the solid, such as activated carbon, and the molecules in the aqueous phase. Adsorption mechanisms

can either be chemical (chemisorption) or physical (physisorption). In chemisorption, adsorbate molecules are linked to the surface of adsorbent with chemical bonds, such as covalent bond. There is a limited number of these available adsorption sites, so adsorption is confined to a monolayer (Figure 1). Physisorption in turn, occurs with the weak dispersion forces, such as van der Waals forces, between adsorbate and adsorbent. Adsorbates are not actually linked onto the surface of adsorbate, but opposite charges keep them close to each other. That is why physisorption allows a multilayer adsorption (Figure 1), so number of adsorbed molecules is not dependent on adsorption sites. A physisorbed molecule will keep its identity and original form when it is released from the surface of the adsorbent (desorption), but if chemisorbed molecules undergo desorption or dissociation, they lose their identities and can't be recovered. Breaking the chemical bonds, like for example in the regeneration of activated carbon, requires also more energy than the removal of the physisorbed compounds. (Rouquerol *et al.* 1999)
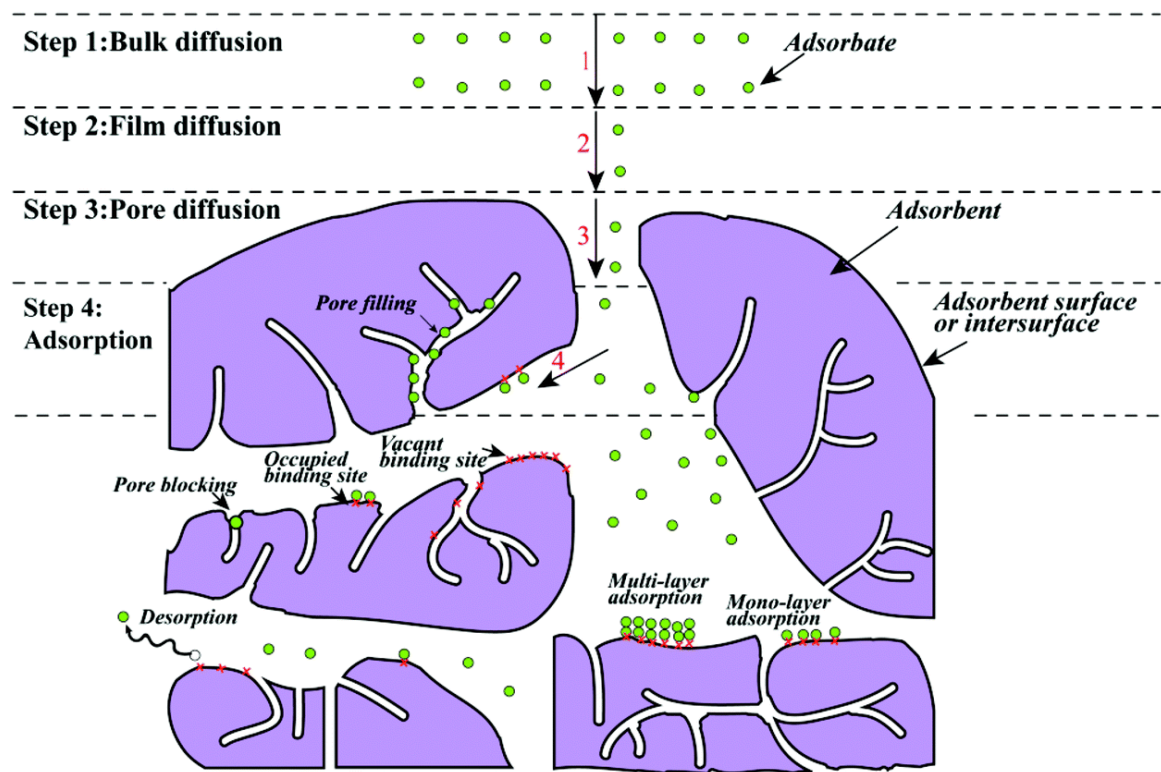

Figure 1. Adsorption process. Adapted from (Wang *et al.* 2020).

Adsorption process follows four phases. First, the adsorbate must travel to the liquid film surrounding the adsorbent. Second, adsorbate needs to get through that liquid film to get into the interstitial voids of adsorbate. Third, adsorbate must get to the solid phase of the adsorbate by diffusing through the voids and fourth, finally adsorb onto the surface of the adsorbent (Figure 1). Nature of the adsorbent and adsorbates affects all these phases and for example temperature, concentrations and pH determine the kinetics of the adsorption. (Parsons and Jefferson 2006). In many cases, one of the four steps can be viewed as a "rate-controlling step", which is the most resisting step in transport of adsorbate from bulk solution to adsorbent (Montgomery 1985). When this rate-controlling step is known, the adsorption process can be made the most effective by optimizing circumstances so that the resistance of this step is the smallest possible.

2.2.1 Activated carbon

One notable application of adsorption reactions is the use of activated carbon. Activated carbon is highly porous material with surface area of up to 1000 m^2/g (Stuetz and Stephenson 2009). It can be manufactured from wide variety of carbonaceous materials such as wood, coal, peat, coconut shells, plant leaves and seeds or organic wastes (Rafatullah *et al.* 2010). First step in AC manufacture is carbonization, a pyrolysis reaction, where non-carbon impurities are burn-off at high temperatures and absence of air, leaving a porous structure (Stuetz and Stephenson 2009). Activation of the surface is done by controlled oxidation at least in 800 °C temperature, giving the structure of micropores smaller than 10 nm, which are one of the most important factors in determination of the adsorption capacity (Stuetz and Stephenson 2009). Activation with oxygen produces also functional groups, which serve as an adsorption sites on the surface of activated carbon (Isoaho and Valve 1986). Activated carbon can be used in form of granulated activated carbon (GAC) (Figure 2) or in powdered activated carbon (PAC).
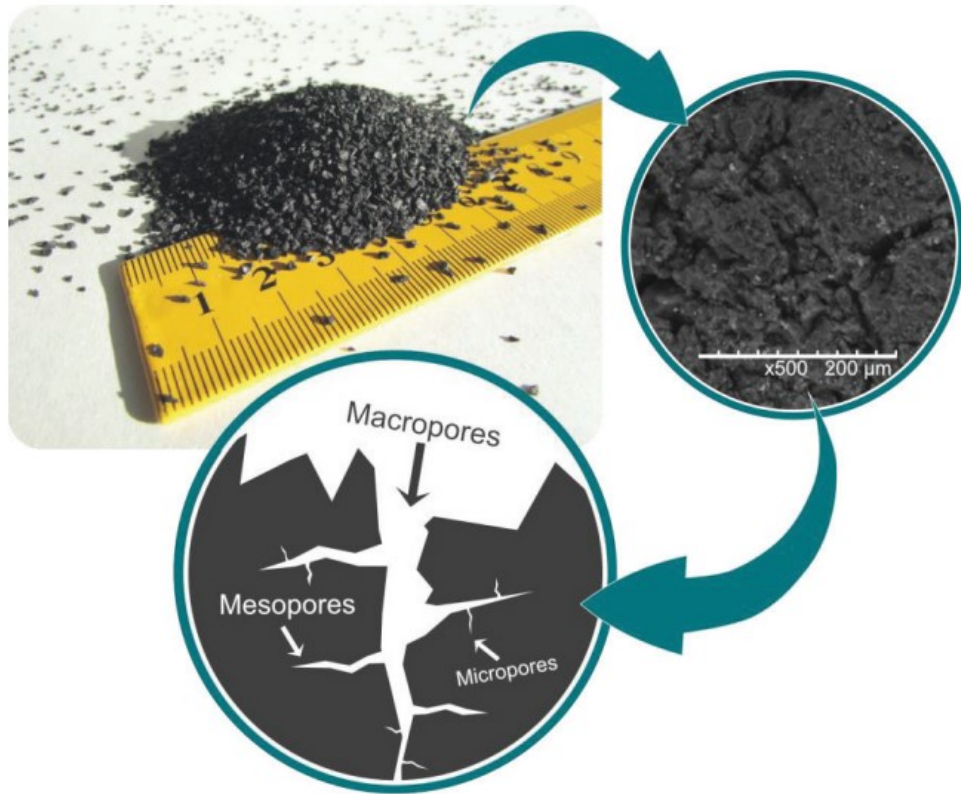
Figure 2. Illustration of granular activated carbon (CAG) including scanning electronic microscope image of GAC surface and illustration of pore size distribution. Adapted from (Ullberg *et al.* 2021).

In drinking water treatment, GAC can be used in deep bed contactors or in closed tanks. Water passes down through the AC so exhausting of AC begins from a top layer. This "exhaustion front" is the interface between exhausted carbon layer and fresh carbon below. An exhaustion front moves downwards during time and will eventually reach the bottom of the AC bed. This point is called "breakthrough", in which first target compounds are passing through the bed without getting adsorbed. When AC bed is exhausted or fouled, it can be cleaned by backwashing, where clean water is pumped backwards through the bed. Water will penetrate between AC particles, and the bed will expand 5-30 %. Backwashing recovers the adsorption capacity of exhausted AC, but it won't reach the original level, which is why backwashing can't be done forever. When effluent quality from backwashed AC filter can't reach the water quality standards, it is replaced or regenerated. In regeneration, matter on the surface of the AC is oxidized in high temperature and thus removed. It can also be pre-washed with acid. Regeneration is usually done

off-site and there are different methods for it. After regeneration, about 5-10 % of the AC is destroyed or lost during the process, which is replaced with virgin AC. Adsorption capacity will also decrease during the process. PAC in turn can be used for removal of temporary tastes and odors. Powdered AC is then captured by the sand filter. (Parsons and Jefferson 2006)

Physical and chemical properties of activated carbon and adsorbents determines if the adsorption happens and how fast it will be. Hardness and particle size are important properties especially for GAC, while filterability and bulk density are important for PAC. Losses in regeneration and breakdown of the particles in AC beds are smaller for harder carbons, which can reduce the costs of the process. Particle size in turn controls the bulk transport through the bed, because smaller size increases the surface area and availability of macropores. (Montgomery 1985)

Total specific surface area is one of the first things to measure from AC, and it can be investigated with BET method, which measures the volume of a monolayer nitrogen atoms on the surface of AC, and thus the surface area of the material. Adsorption capacity can't be evaluated by just specific surface area, because all the adsorbate might not fit in the smallest pores. This *effective area* with appropriate pore size distribution is more important factor when capacity for some given adsorbate is studied (Montgomery 1985). Pore size distribution controls the capacity for different adsorbates because some pores might be useless if target molecules can't fit in them, and some other target molecules can. Pore sizes can generally be classified on four classes: macropores (>50 nm), mesopores (2-50 nm), micropores (1-2 nm) and minimicropores (<1 nm) (Figure 2) (Parsons and Jefferson 2006).

Chemical structure and surface chemistry of the AC influences also the rate and the capacity of adsorption. Activated carbon is basically set of stacked heterocyclic graphitelike planes of carbon rings (Montgomery 1985; Isoaho and Valve 1986). There are additional elements bonded in these rings, forming functional groups that include carboxylic, carbonyl, phenolic, hydroxyl and peroxide groups (Ishizaki 1974). These groups are the reason for the reactive surface and based on them, activated carbons can have different chemical properties which affect the

adsorption mechanisms. For example activation temperature influences the amount of oxygen on AC and therefore its functional groups (Isoaho and Valve 1986).

Properties of adsorbates have their own crucial influence on their removal by adsorption. Usually, insoluble compounds are adsorbed easier than more soluble ones; this is called Lundelius' rule (Lundelius 1920). Large organic molecules tend to be less soluble than small ones, which advocates the better adsorption, but because of their size, they diffuse more slowly to the adsorbent pores, and they can't penetrate the smallest pores which is why they are described being more poorly adsorbed than smaller molecules (Montgomery 1985; Schreiber *et al.* 2005).

In aqueous solution, non-polar compounds are adsorbed better than polar ones. That is because polar compounds have nitrogen bonds or dipole-dipole interactions with aqueous solution, and breaking these bonds requires lots of energy (Montgomery 1985). Length and number of hydrophobic carbon chains in organic compounds enhance the adsorption, but at the same time very branched molecules are more poorly adsorbed because their spherical shape has smaller area to contact the surface of AC (Isoaho and Valve 1986). What comes to the temperature, adsorption is enhanced when the temperature is decreased because adsorption is exothermic reaction (Isoaho and Valve 1986).

The pH value of the water does not usually affect the adsorption of non-ionized compounds but affects strongly on the adsorption of weak acids and bases because of the acid and base properties of the functional groups on the AC surface, and the preference for the removal of neutral species from aqueous solution (Montgomery 1985; Isoaho and Valve 1986). The best adsorption is achieved when pH level of water equals with dissociation constant of the acid or base (Isoaho and Valve 1986).

There are lots of electrostatic interactions between AC surface and adsorbates. Positive surface charge of AC will attract negative molecules (such as NOM), and negative surface charge will repulse the molecules. However, the number of positively charged adsorption sites on the surface have influence on the amount of adsorbed negative NOM molecules, not the net charge of the AC surface (Bjelopavlic *et al.* 1999). Adsorbed NOM molecules on the surface of AC have also

lateral repulsion on each other which decreases adsorption, and this repulsion increases as the number of adsorbed molecules increases. In addition to that, repulsive interactions between adsorbed NOM molecules and NOM molecules on the solution also occurs (Müller *et al.* 1985; Bjelopavlic *et al.* 1999). The ionic strength of the solution has also an influence on adsorption because salts in water can "screen" electrostatic repulsions and attractions and thus increase or decrease adsorption (Newcombe and Drikas 1997; Newcombe 1999; Bjelopavlic *et al.* 1999).

If there is more than one compound to be adsorbed, these compounds compete for the available adsorption sites on the AC surface (Montgomery 1985; Isoaho and Valve 1986; Pelekani and Snoeyink 1999; de Ridder *et al.* 2011). The ratio of their adsorption depends on their physio-chemical properties again. The compound that is adsorbed more easily will occupy the sites and, in some cases, can result in the displacement of previously adsorbed compounds (Montgomery 1985; Pan *et al.* 2022). Pan *et al.* (2022) proved that presence of NOM can displace previously adsorbed micropollutants. This can be problematic if there are for example toxic compounds which are desorbed back to the solution. Because NOM is usually present in the process of drinking water treatment, its influence on the adsorption of other compounds is one interesting study area. NOM can reduce the removal of other micropollutants either with straight competition with adsorption sites or by blocking the pores because of big molecular size of molecules (Newcombe and Drikas 1997; Pelekani and Snoeyink 1999). Ability to reduce micropollutant adsorption is mostly based on several magnitudes higher concentrations of NOM but also on its surface charge, which is usually negative (Newcombe and Drikas 1997). Negative charge will have electrostatic repulsion on the surface of adsorbent with anionic micropollutants and other NOM molecules which reduces the adsorption of both. The greatest competition is expected to be between compounds of similar structure and molecular size (Pelekani and Snoeyink 1999). NOM varies a lot in molecular size and adsorption capacities of AC for large molecules is expected to be less than for small NOM molecules or other micropollutants, because large molecules can't fit in every pore (Pelekani and Snoeyink 1999; Matilainen *et al.* 2006b). However, adsorption of small NOM molecules is neither significant, but the

greatest efficiency is achieved in the removal of intermediate molar mass molecules (1000–400 Da) (Matilainen *et al.* 2006b). Environmental NOM concentrations are normally several magnitudes higher than other compounds so it is expected that adsorption competition favors NOM to the detriment of the adsorption of these less abundant compounds, and many studies have also shown this kind of results (Newcombe *et al.* 2002; Li *et al.* 2003; Matsui *et al.* 2003; Pan *et al.* 2022).

2.2.2 Adsorption isotherms

Adsorption isotherms are mathematical tools for modelling adsorption kinetics and mechanics. Two very common isotherms are Langmuir isotherm and Freundlich isotherm (Freundlich 1907; Langmuir 1916; Kanô *et al.* 2000; Belhachemi and Addoun 2011). Langmuir isotherm is theoretically derived and it assumes that there is a finite number of identical and equivalent adsorption sites on the surface of activated carbon which is why adsorption is confined to monolayer (Langmuir 1916; Kanô *et al.* 2000). Freundlich isotherm in turn, is experimentally derived and empirical and it predicts for multilayer, heterogeneous adsorption sites (Freundlich 1907; Belhachemi and Addoun 2011). It is usually applied in systems for organic compounds in activated carbon.

Isotherms are used to describe equilibrium relationships between adsorbate and adsorbent. Equilibrium is a phase of adsorption, where adsorption equals desorption after adsorbate and adsorbent has been contacted for sufficient time. Adsorbate concentrations in the solution and surface of the adsorbent are in dynamic balance so adsorbent is reaching the maximum adsorption capacity. Equations of isotherms are used to determine the adsorption mechanism and maximum adsorption capacity for a given compound (Belhachemi and Addoun 2011; Ayawei *et al.* 2017).

Langmuir and Freundlich isotherms are simple, and they may not describe the adsorption completely. It is important to remember that isotherms are just used to model reality at some level. Langmuir and Freundlich isotherms have their limitations which is why plenty of other isotherms exist as well (Ayawei *et al.* 2017). For example, Langmuir isotherm does not take electrostatic forces, like lateral

interactions or steric hindrances, into an account, while they obviously occur in reality. Freundlich isotherm in turn, is useful in middle range of the isotherms, which means it is not functioning well in extreme adsorbate concentrations. There are also more advanced isotherms available to solve some limitations of these isotherms. For example, there are combinations of Langmuir and Freundlich isotherms which take adsorbate concentrations into an account (Ayawei *et al.* 2017). Therefore, some isotherms predict that the adsorption mechanism is the mix of these two isotherms. In reality, the adsorption process cannot be described completely, because it can include wide variety of different mechanisms.

However, the general use of Langmuir and Freundlich isotherms is based on this easiness of the use of two adjustable parameters and fastness of data analysis because possibilities to use graphical data. These two-parameters isotherms can be transformed to linear form, so it is easy to estimate the parameters by for example graphical means. Advanced isotherms can have even five parameters so their use is usually way more complex and for example the graphical analysis becomes impossible.

2.3 Methylene blue

Methylene blue (MB) is a cationic colorant, which has very high water solubility in water and some organic solvents (Figure 3). It has been used as a dye for example in textile industry. It is cheap and easily adsorbed by different adsorbents, which is why it has become a standard method to describe and compare adsorption capacities of adsorbents (Ahmad *et al.* 2007; Hameed *et al.* 2007; Fernandes *et al.* 2007; Belhachemi and Addoun 2011; Chowdhury and Saha 2013; Kumar and Jena 2016). Adsorption of MB has been studied with various different adsorbents, including low cost activated carbons, biochars, natural materials and waste materials (Rafatullah *et al.* 2010). It is easy to monitor the blue color levels with a spectrophotometer by wavelength of 660 nm, where MB has maximum absorbance (Gorman and Shinder 1988; Tschirch *et al.* 2008). Adsorption capacity for MB is one of the first things to be determined when new adsorbent is made, and it is a simple

way to compare different AC products by their adsorption capacities for MB (Rafatullah *et al.* 2010). Physiochemical properties of MB are shown in Table 2.
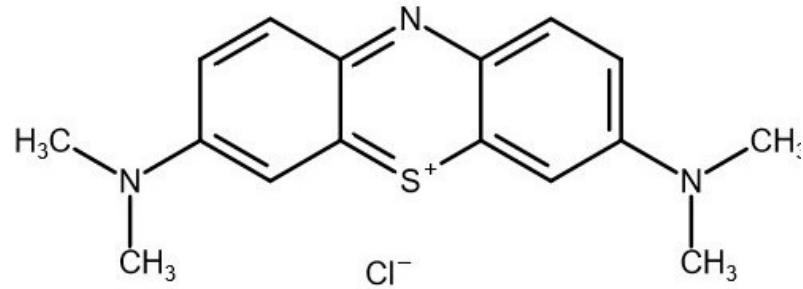

Figure 3. Chemical structure of methylene blue.

Use of methylene blue as a standard compound in adsorption experiments also gives important information for developing wastewater and drinking water treatment plants in the removal of MB. It can end up in environment from industry wastewaters and thus have some adverse effects. For humans, it produces burning sensation in eyes and mouth, and it has many neurotoxic effects like nausea, vomiting and diarrhea (Ghosh and Bhattacharyya 2002; Vutskits *et al.* 2008). Adsorption processes have been found to be superior to other techniques because of its cost, flexibility and simplicity.

2.4 Natural organic matter

Natural organic matter is ubiquitous in waters, soils and sediments. NOM is present in all natural waters and it is from a breakdown of terrestrial plants and metabolic reactions of other living organisms. NOM can be formed in aquatic ecosystems, but it can also end up in water from surrounding environments, via surface runoffs. Humic substances in NOM are amorphous, dark colored and acidic in nature, giving the characteristic features of aquatic ecosystems for example in a boreal forest

zone (Thurman 1985; Frimmel 1998; Fabris *et al.* 2008; Rantakari 2010). In drinking water, NOM causes unpleasant color, taste and odor. It expenses the costs of water treatment and with disinfectants it forms toxic disinfection by-products. By removing the NOM as much as possible, DBP formation and thus cancer risk is decreased (Singer 1999; Iriarte-Velasco *et al.* 2008; Evlampidou *et al.*)

Natural organic matter is a complex mixture of organic compounds. NOM vary widely according to chemical structure and chemical charges (Matilainen *et al.* 2002). It consists of largely aliphatic to highly colored aromatics and it is important to characterize the structures of NOM to get the best results from water treatment (Matilainen *et al.* 2002). One common way for characterizing NOM is to divide it into hydrophilic and hydrophobic fractions. The hydrophilic fractions are composed of aliphatic carbons and nitrogenous compounds such as carboxylic acids, carbohydrates, proteins and sugars (Thurman 1985; Frimmel 1998; Świetlik *et al.* 2004; Fabris *et al.* 2008). Hydrophobic part is rich in aromatic carbon, having phenolic structures and conjugated double bonds (Thurman 1985; Frimmel 1998; Świetlik *et al.* 2004; Fabris *et al.* 2008). Hydrophobic acids form the major fraction in aquatic NOM, constituting more than 50 % of the dissolved organic carbon (DOC) in water (Świetlik *et al.* 2004). These hydrophobic acids may be described as humic substances (HS) containing humic acids (HA), fulvic acids (FA) and humins. In natural waters, NOM is usually negatively charged and in addition to chemical variation, it variates a lot in molecular masses and sizes (Świetlik *et al.* 2004; Ignatev and Tuhkanen 2019). Composition of NOM in water can vary also seasonally and considerably according to the surrounding environment (Fabris *et al.* 2008). Origin of the NOM affects also in local variation; for example, soil originated NOM tends to have more aromatic structure than aquatic NOM, and NOM from peatlands is dominated by low-molecular-weight fulvic acids (Goel *et al.* 1995).

NOM is usually characterized by the measurement of its total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance in a wavelength of 254 nm (UV_{254}), specific UV-absorbance (SUVA), fluorescence, or chemical oxygen demand (COD) (Matilainen *et al.* 2002; Ignatev and Tuhkanen 2019). Additional techniques for

NOM characterization are for example high-performance size-exclusion chromatography (HPSEC) and elemental analysis (Matilainen *et al.* 2002; Wu *et al.* 2007; Ignatev and Tuhkanen 2019). The HPSEC method is based on a fractionating of the NOM molecules by their apparent molecular size and weight (Figure 4). It is good tool for example to follow how the organic matter with different apparent molecular weight are removed in water treatment. Matilainen et. al (2011) gives good a overview of methods used in the analysis of NOM characterization related to drinking water treatment.

Definition of DOC is the organic carbon in water that can be filtered through a 0.45 µm filter. TOC instead, is the sum of particulate and DOC in water. Inorganic carbon, such as carbon dioxide CO_2 or carbonates, is not included in these definitions. In a standard DOC measurement method, inorganic carbon is removed from water by acidification with HCl and purging with N2 gas (Ignatev and Tuhkanen 2019).
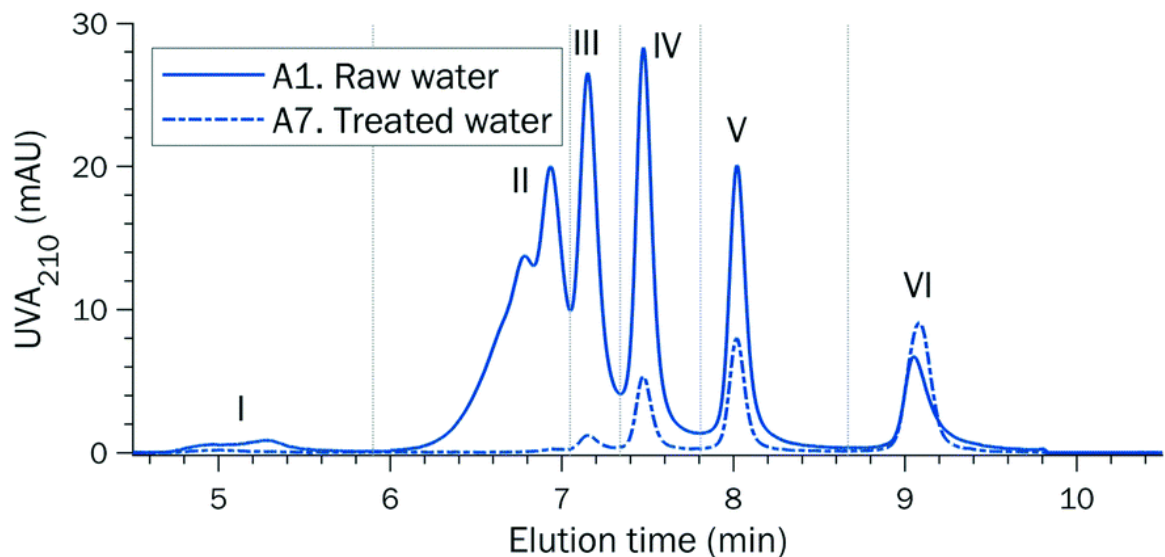

Figure 4. Illustration of different size fractions of NOM in raw water and treated water, separated with HPSEC method and detected with UV detector at 210 nm. Adapted from (Ignatev and Tuhkanen 2019).

The most common and economically feasible processes to remove NOM from drinking water are considered to be coagulation and flocculation, followed by sedimentation and sand filtration (Matilainen *et al.* 2010). After these phases, hydrophobic, high molecular mass matter (about > 4000 Da), peaks I and II (Figure 4), is removed almost completely while hydrophilic, low molecular mass matter (about < 1000 Da), peaks V and VI (Figure 4) is removed the least (Matilainen *et al.* 2006b). GAC filtration won't reduce these size fractions significantly anymore but it is efficient in the removal of intermediate molar mass matter about (1000–4000 Da), illustrated as peaks III and IV (Figure 4) (Matilainen *et al.* 2006b). Area of the peak is telling the concentration and amount of organic matter of specific molecular mass in a water sample. Samples from different phases of water treatment give different peak areas, which tells how either process is removing the organic matter of different molecular mass. Peak is decreasing if the organic matter of that molecular mass is removed.

2.5 Pharmaceuticals

In many parts of the world, sewage treatment capacity, as well as drinking water treatment capacity, is very limited or missing completely, which is great health risk. One emerging problem with drinking water safety is the occurrence of pharmaceuticals in surface waters. Through human metabolism, residues of the pharmaceuticals will end up in wastewater treatment plants (WWTP). Removal of many different pharmaceuticals is incomplete in WWTPs around the world and even in Finland (Andreozzi *et al.* 2003; Vieno *et al.* 2005, 2007b). Abatement of some organic micropollutants is challenging. The reason may be that the engineering technology used in the construction of the WWTPs is insufficient for removing emerging micropollutants. Furthermore, the treatment capacities of the WWTPs have not met the population growth of the cities and increased amount and variety of pharmaceuticals used. Effluent water from WWTPs will transport the pharmaceuticals to the environment and surface waters. Surface waters used in drinking water will be the route of the pharmaceuticals to human body. Drinking water treatment plants are not designed primarily for the removal of

pharmaceuticals, although some of them will be removed, but not everything (Vieno *et al.* 2007a). It is generally agreed that the effects of different pharmaceuticals are unlikely and harmful in environment.

Antibiotics in environment are concerning people around the world. Aquatic environments have been approved to have antibiotics in many countries, no matter if it is developed or developing country (Andreozzi *et al.* 2003; Ngumba *et al.* 2016a, b; Kortesmäki *et al.* 2020; Kairigo *et al.* 2020b). Low levels of antibiotic concentrations in environment won't be enough to kill pathogens, but enough to possibly catalyze the ability of bacteria to develop resistance against antibiotics (Kümmerer 2003; Blair *et al.* 2015; Kairigo *et al.* 2020b). For example in Kenya, concentrations of antibiotics in wastewater treatment plant effluents and surface waters can be high enough to provide medium to high risk of selection for antibiotic resistance (Kairigo *et al.* 2020b). Antibiotic resistance of the bacteria is indeed a major threat to public health as antibiotics are used for the care of bacterial infection, even for deadly ones (Kümmerer 2003). However, usually antibiotics and other pharmaceuticals are detected at extremely low concentrations (nanograms), compared to their medical doses (milligrams). Although drinking water treatment plants are not the most efficient ones for pharmaceutical removal, they can still provide a notable decrease in exposure risk (Vieno *et al.* 2007a). According to Vieno *et al.* (2007a), Finnish drinking water with detected 20 ng/l of ciprofloxacin could be drank 70 years (2 liters per day) to reach the exposure of 1 mg, which is still 1000 times lower than daily medical dose of 1000 mg ciprofloxacin. However, effects of long-time exposure of pharmaceuticals are quite unknown and extra attention is needed for the removal of antibiotics not only in wastewater treatment but also in drinking water treatment.

Purpose of antiretroviral drugs (ARVDs) is mostly to control HIV infection. The use of these pharmaceuticals has tremendously increased since 1983, when HIV was discovered (Ngumba *et al.* 2016b). Today, more than 38 million people lives with HIV/AIDS, most of them in Africa, and about 27.5 million people globally are on HIV therapy (Menéndez-Arias and Delgado 2022). Residuals of these

pharmaceuticals in environment are problem mostly in Africa, like for example in Kenya (Ngumba *et al.* 2016a; Kairigo *et al.* 2020a). Consumption of antiretroviral drugs in Finland is very low. In 2020, consumption of lamivudine was less than 10 kg per year while the consumption of nevirapine was about 15 kg per year (Fimea 2021). For reference, consumption of ibuprofen (pain killer) was more than 120 000 kg. However, Ngumba et al. (2016a) show that antiretroviral drugs can be found also in Finnish surface waters, even though concentrations are rather small, just some nanograms per liter.

3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Water sample

Water samples were taken from Viitaniemi drinking water treatment plant located in Jyväskylä. Samples were taken before activated carbon filtration (Figure 5), so the experiment would correspond the real process in water treatment plant. Because coagulation and sand filtration have been done in previous phases, natural organic matter is mostly present as a dissolved organic carbon DOC, which's molecular size is less than 0.45 µm. Amount of DOC, measured by a fluorescence detector of HPSEC, is considerably lower after coagulation than in raw water (Figure 6). The amount of water taken was 50 l and it was taken in three separate plastic jerry cans. Water was stored in a dark fridge, temperature of 4 °C. The pH level was 7.2 in room temperature. Ultrapure water used in batch experiments and liquid chromatography was generated with Ultra Clear UV plus -system (SG Water, Germany).
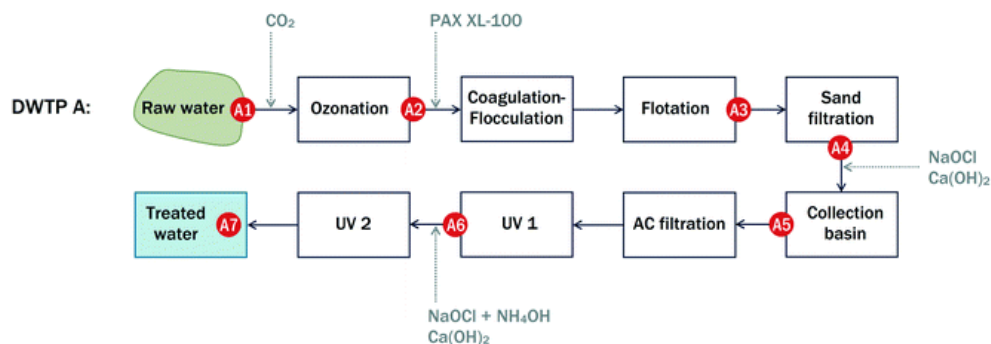
Figure 5. Principal scheme of drinking water treatment plant in Viitaniemi, Jyväskylä. Sampling point for this study was A5. Adapted from Ignatev & Tuhkanen (2019).
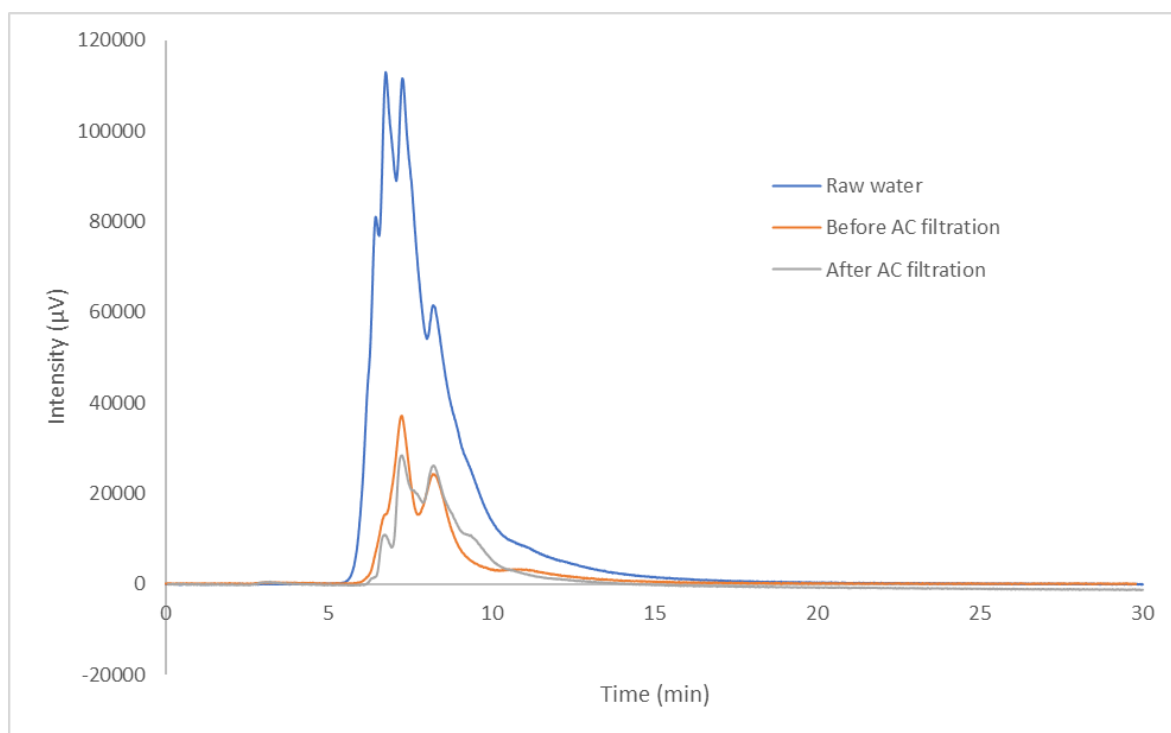
Figure 6. Characterization of DOC in raw water and in water just before and after AC filtration (Figure 5) presented in humic/fulvic-like fluorescence at excitation/emission wavelengths of 330/425 nm. Area of each peak indicates the total amount of DOC.

3.1.2 Activated carbons

There are two different commercial activated carbon products used in Viitaniemi water plant. Products are Silcarbon S835 by Akva Filter Ltd. and Filtrasorb TL830

by Haarla Ltd. Four different activated carbons by Neova Carbons were initially screened and two were selected for further studies. Four activated carbons were made from wood and peat as well as mix of these and a by-product from AC production process. These activated carbons are under research and development (R&D). Two commercial carbons and two R&D products, R&D wood and R&D peat, were studied further in DOC and pharmaceutical adsorption experiments. Commercial ACs were in granular (GAC) form while R&D products were in powdered (PAC) form. That is why commercial ones were crushed with ceramic mortar and pestle for experiments so results between different ACs would be comparable. Physiochemical properties of activated carbons are presented in Table 1. Moisture content has been determined with standard test method ASTM-D2867-09, ash content with ASTM-D2866-94, BET with ASTM-D3663-20 and iodine number with ASTM-D4607-86.
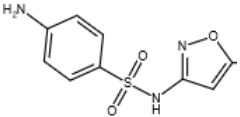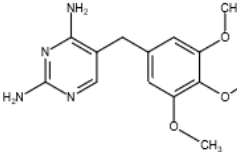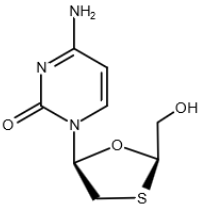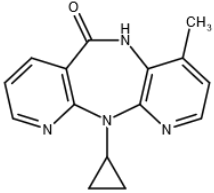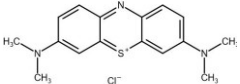
Table 1. Physiochemical properties of used activated carbon.

Adsorbent	Moisture m-%	Ash m-%	BET (m^2/g)	V_{micro} (%)	V_{meso} (%)	V_{macro} (%)	Iodine number (mg/g)
R&D wood	< 1	1.5	793	72	26	1	876
R&D peat	< 1	6.4	733	46	46	9	866
Filtrasorb TL830	< 1	6.6	975	69	25	5	997
Silcarbon S835	5.9	15.5	751	70	21	9	759

3.1.3 Pharmaceuticals

In this study, four different pharmaceuticals were used, two antibiotics and two antiretroviral drugs (ARVDs). Sulfamethoxazole (SMX) and trimethoprim (TMP) represent antibiotics while lamivudine (3TC) and nevirapine (NVP) represent ARVDs (Table 2). Four different pharmaceuticals were chosen by their physiochemical properties so effect of different properties on adsorption could be studied.

Table 2. Physiochemical properties of selected pharmaceuticals and methylene blue. (Pubchem 17.11.2022)

Compound	Chemical structure	CAS no.	Molecular weight (g/mol)	Water solubility (mg/l)	pK$_a$	log K$_{ow}$
SMX		723–46–6	253.28	610	1.6, 5.7	0.89
TMP		738–70–5	290.32	400	7.12	0.91
3TC		134678–17–4	229.26	70000	4.3	-9.54
NVP		129618–40–2	266.30	0.7046	2.8	3.89
MB		61–73–4	319.9	43600	3.14	0.75

The pharmaceutical standards (TMP, SMX, NVP, and 3TC) were purchased from Sigma Aldrich (US) and were of >99% purity. Isotopically labelled internal standards were purchased from Alsachim (France), except [²H₉], which was from Sigma-Aldrich (Steinheim, Germany). HPLC chemicals formic acid was purchased from Fluka (Germany), ammonium hydroxide (25%) from Merck (Belgium), and acetonitrile and methanol from Merck (Germany).

3.2 Methods

Adsorption capacities of activated carbons were investigated with batch experiments, which is a commonly used method in adsorption and adsorption isotherm studies (Iriarte-Velasco *et al.* 2008; Belhachemi and Addoun 2011; Rao *et al.* 2021). Blue color of methylene blue samples from batch experiments were studied with the absorbance detector (Ordior UV mini-1240) while DOC and pharmaceutical samples were processed with liquid chromatography. When the adsorption of DOC was investigated, high-performance size-exclusion chromatography HPSEC was used, but for pharmaceuticals, liquid chromatography-mass spectrometer LC-MS/MS was used.

First, the adsorption of MB was studied. Second, DOC adsorption was studied by batch experiments with VW (Viitaniemi water), which was chemically treated so experiment corresponded the actual water treatment process. Third, experiments of adsorption of selected pharmaceuticals were carried out side by side in MQ water and in VW (Figure 7). DOC concentration in VW was 2.5–3.6 mg/l and pharmaceutical concentrations varied between 2–10 mg/l. Setup allowed the studying of adsorption competition because pharmaceuticals and DOC were in the same matrix.
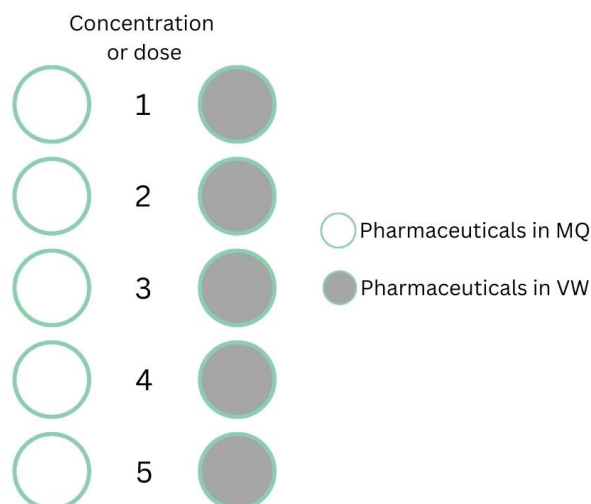
Figure 7. Experimental design of batch experiments with pharmaceuticals. Either the concentration of pharmaceuticals or adsorbent dose were varying while the other was constant. Half of the flasks included ultrapure MQ water and half water with DOC (VW).

3.2.1 Batch experiments

Batch experiments with MB were done just for commercial Silcarbon S835 by Akva Filter and Filtrasorb TL830 by Haarla products, because adsorption capacities of R&D products for MB have already been studied previously (unpublished). In batch experiment, six MB concentrations were used: 1, 2, 4, 6, 8, and 10 mg/l. Solutions were made in 100 ml Erlenmeyer flasks. Amount of activated carbon in each bottle was 0.01 g. Bottles were put in automatic shaker and shaking speed was set at 150 rpm. Samples of 2 ml were taken at varying time intervals (10, 20, 30, 45 and 60 minutes). Absorbance of these samples were measured in room temperature at 660 nm wavelength, where MB has maximum absorbance (Gorman and Shnider 1988; Tschirch *et al.* 2008). Six-point calibration curve from known concentrations of 1, 2, 3, 4, 6 and 8 mg/l were used. Every 2 ml sample was returned to the flask after the UV-absorbance measurement, so the total volume of the solution didn't change. Data was fitted in isotherms and the adsorption capacities were calculated.

Batch experiments with Viitaniemi water including DOC were executed so that the different doses of the adsorbents were tested while the solution volume (250 ml) and DOC concentration was constant. First, R&D wood and R&D peat were tested

with six different doses: 0.025, 0.05, 0.075, 0.1, 0.125, 0.15 g per 250 ml of solution. Second, Filtrasorb TL830 and Silcarbon S835 were tested with five different doses: 0.0125, 0.025, 0.05, 0.075 and 0.1 g per 250 ml of solution. Water (250 ml) was put in Erlenmeyer flasks with weighted powdered (crushed granular) activated carbon. Flasks were put on automatic shaker and shaking speed was set on 150 rpm. To determine the DOC content, 2 ml samples were needed for HPSEC. Samples from shakings with R&D carbons were taken in 0.25, 0.5, 0.75, 1, 1.5, 2, 3.5, 5, and 24 hours, while sampling times with commercial carbons were 0.25, 0.5, 0.75, 1, 1.5, 3, and 24 hours. HPLC samples can't have particles in, so they were filtered. Syringe filters (Phenex, RC Membrane 0.45 µm) were pre-washed with MQ water for possible contaminants. Clean filters were saturated with sample water before 2 ml sample was pushed through the filter to the 2 ml clear vial. For DOC analyzer, about 20 ml sample were taken from each flask after 4.5 hours.

With pharmaceuticals, first batch experiment was done with R&D wood where the adsorbent dose varied while the pharmaceutical concentration was constant. Principal of these batch experiments is same with ones with DOC. Doses of R&D wood product used were 0.01, 0.025, 0.05, 0.07g and 0.1 g to 100 ml solution. Concentration of SMX, TMP, 3TC and NVP was 2 mg/l each. From stock solution (1000 mg/l) of each pharmaceutical, 200 µl were spiked to the 100 ml solution to reach the concentration of 2 mg/l. Sampling times were 10, 20, 30, 45, 60, 90 and 180 mins. Removal of pharmaceuticals from MQ water and VW was studied side by side (Figure 7).

Following batch experiments with pharmaceuticals using rest of the ACs, was done with constant 0.025 g dose of ACs and varying concentration of pharmaceuticals. Sampling times and other details remained the same. Concentration of pharmaceuticals were decided to be in milligrams per liter, which is three orders of magnitude higher than their concentrations in natural waters (Vieno *et al.* 2006, 2007a; Ngumba *et al.* 2016b). Other similar studies of adsorption competition between DOC/NOM and micropollutants have used concentrations of nanograms and micrograms per liter (Yu *et al.* 2008; de Ridder *et al.* 2011; Rodriguez *et al.* 2016),

so this study with the same magnitude concentrations of DOC and pharmaceuticals in one of the few.

3.2.2 HPSEC method

High performance size-exclusion chromatography (HPSEC) with appropriate detectors is useful technique to characterize organic matter in water (Frimmel 1998; Her *et al.* 2003; Matilainen *et al.* 2011; Ignatev and Tuhkanen 2019). Chromatographic methods are based on physical separation, where chemical mixtures can be separated to different components by for example the polarity, size, mass, or the charge of the molecules (Jenkins 2014). In HPSEC, molecules are separated by their molecular weight. In a separation column, small sample molecules retain in small micropores of packing material while large particles pass the column faster. Large molecules will elute first, and the separated size fractions will be seen as peaks in chromatogram. The area of the peaks in chromatogram refers to the amount of DOC in a specific size fraction. The fraction having the lowest retention time (elutes first) refers to the highest molecular weight fraction of DOC while the fraction having the highest retention time refers to the lowest molecular size of the DOC. Total area of peaks in chromatogram refers to the total amount of DOC. Apparent molecular weights are usually presented in Da (1 Da = 1,661 * 10^{-27} kg). Apparent molecular weights of different fractions are estimated with PSS calibration by Ignatev and Tuhkanen (2019) (Figure 8). Estimated apparent molecular weight MW can be calculated with Equation (1):

$$MW = \exp{(64.19x^{-1.11})} \tag{1}$$

where x is elution time.
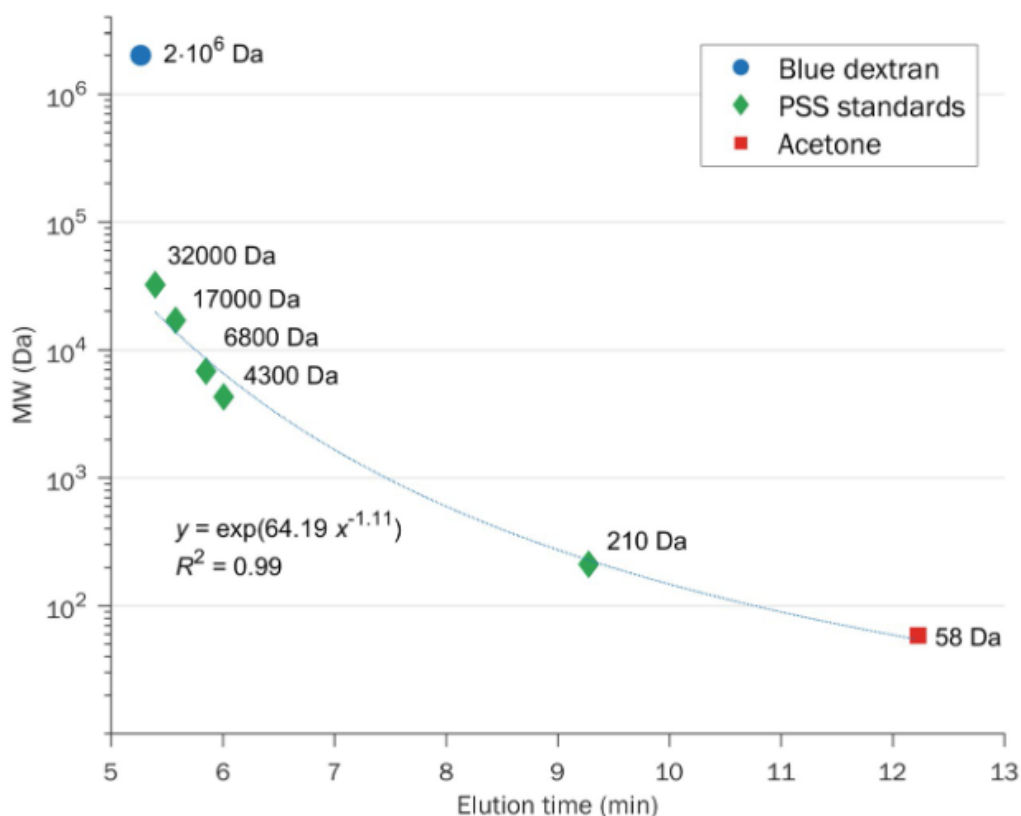
Figure 8. Calibration of the size-exclusion column using acetone, polystyrene sulphonate (PSS) standards, and blue dextran. Adapted from (Ignatev and Tuhkanen 2019).

Size fractions can be detected by various detectors. UV-detector is used to detect for example conjugated double bonds and aromatic structures, which absorbs UV-light at wavelength of 254 nm (Ignatev and Tuhkanen 2019). For further specification of molecules, a fluorescence detector can be used to determine if compounds have for example humic-, fulvic- or protein-like nature (Her *et al.* 2003; Wu *et al.* 2007; Ignatev and Tuhkanen 2019). Specific excitation/emission wavelengths act as a fingerprint of the class of organic compound.

In this study, the chromatography method is adapted from Ignatev & Tuhkanen (2019). To analyze DOC content in samples, Shimadzu LC-30AD instrument was used. The instrument was equipped with online degassing units Shimadzu DGU-20A5R and DGU-20A3R, an autosampler Shimadzu SIL-30AC, a column oven Shimadzu CTO-20AC, a photodiode array (PDA) detector Shimadzu SPD-M20A,

and a fluorescence detector Shimadzu RF-20A XS. Column used was a silica-based Yarra SEC-3000 (300 x 7.6 mm, Phenomenes, USA).

Eluent was 5 mmol/l phosphate buffer with $NaH_2PO_4 \cdot 2H_2O$ = 0.39 g/l and $Na_2HPO_4 \cdot 7H_2O$ = 0.68 g/l at a flow rate of 1 ml/min. Ionic strength of the eluent was 10 mmol/l and pH 6.8. The eluent was pre-filtered through 0.2 µm cellulose acetate membrane filters (Whatman, Germany).

Monitored excitation and emission wavelengths in fluorescence detector were also chosen based on Ignatev & Tuhkanen (2019). Chosen $\lambda_{ex}/\lambda_{em}$ values represents humic/fulvic-like (330/425 nm and 390/500 nm), tyrosine-like (220/310 nm) and tryptophan-like (270/355 nm) fluorescent compounds. Humic/fulvic-like at 390/500 nm can indicate the abundance of highly conjugated aromatic compounds of high molecular weight, whereas fluorescence at 330/425 nm indicate the abundant compounds with lower aromaticity and molecular weight (Fellman *et al.* 2010). Tyrosine-like fluorescence can indicate the abundance of more degraded peptide materials, while tryptophan-like can indicate the abundance of intact proteins and less degraded peptide materials (Fellman *et al.* 2010). Tryptophan-like fluorescence has also potential to measure microbial contamination risk in water (Nowicki *et al.* 2019). PDA-detector (Photo diode array) was set to measure UV-absorbance in range of 200-400 nm.

3.2.3 LC-MS/MS method

Liquid chromatography tandem mass spectrometer (LC-MS/MS) with an electrospray ionization method was used to analyze pharmaceutical levels in samples. Separation was done with reverse phase HPLC, where compounds were separated based on their polarity. Separated compounds continued to mass spectrometry where they were identified and quantified with the ratio of their mass and charge (m/z).

To analyze the pharmaceuticals in samples, Waters Alliance 2795 system (LC, Milford, MA, USA) was used as a liquid chromatography instrument. It was equipped with a tertiary pump, a vacuum degasser, an autosampler and a column

oven. Separation column was reversed phase C18 column (Waters XBridgeTM 3.5 μm, 2.1 x 100 mm with a Vanguard 3.5 μm, 2.1 x 10 mmm guard column).

For mass spectrometry, Quattro Micro triple-quadrupole mass spectrometer was used. Nitrogen was used as the desolvation gas (500 l/h) and as the cone gas (50 l/h) while argon was used as the collision gas at a pressure of 2.8 x 10^{-4} mBar. The desolvation temperature was 200 °C and source temperature was 100 °C. For the ionization of the molecules, electrospray ionization mode (ESI) was used. Multiple reaction monitoring (MRM) was used because of the triple-quadrupole system, and dwell time and interchannel delay was 200 ms. Precursor and product ions, collision energies and cone voltages as well as other parameters of this LC-MS/MS method has been optimized by Ngumba *et al.* (2016b), and Kairigo *et al.* (2020b).

Standard calibrations of pharmaceutical were made with concentrations of 5, 10, 20, 50, 100, 200, 400 μg/l. Seven-point calibration curves were made by plotting the response ratio of the peak area of analyte divided by peak area of internal standard (y-axis) against concentration of the analyte (x-axis). Equations of the curves were used to calculate concentrations of pharmaceuticals in samples taken from batch experiments. The standard calibrations of pharmaceuticals were made separately for treatments with different AC, except treatments with Filtrasorb TL830 and R&D peat, where the same calibration curves were used (Appendix 1).

3.2.4 DOC analysis

DOC content was analyzed with Shimadzu TOC-L with an autosampler ASI-L. Calibration was done with DOC range of 0-30 mg C/l with standard solutions of potassium phthalate prepared by automatic dilution of fresh stock. Sample volume was 20 ml, and they were taken in vials which was calcined in 400 °C for 4 h in air. To remove inorganic carbon like CO_2, samples were acidified with HCl to pH level below 2 and purged with N_2 gas. Injection volume was 100 μl. The result is a mean value of two or three replicate measurements chosen automatically by the instrument. Analysis follows SFS-EN 1484 standard method.

3.2.5 Adsorption isotherms

In order to fit the data for Langmuir and Freundlich isotherms, next parameters are needed from batch experiment results: c_i which is the initial concentration (mg/l) of adsorbate (DOC or pharmaceutical), c_{eq} which is the concentration of adsorbate in equilibrium, x which is the mass (mg) of the adsorbed adsorbate, m which is the mass of activated carbon in solution (g), x/m (mg/g), $c_{eq}/(x/m)$, ln c_{eq}, and ln (x/m). In batch experiments, m or c_i need be varied so there would be enough points to use isotherms. In batch experiments with R&D wood, m was varying and c_i was constant, but with other ACs, m was constant and c_i was varying. Isotherms can be used either way.

To describe the adsorption characteristics, linear forms of Langmuir and Freundlich isotherms are used. Langmuir Equation (2) is given by:

$$\frac{c_{eq}}{x/m} = \frac{1}{ab} + \frac{c_{eq}}{a},$$ (2)

where a is the maximum adsorption capacity (mg/g) and b is the Langmuir isotherm constant showing the binding affinity of the adsorbent. Freundlich Equation (3) is given by:

$$\ln\frac{x}{m} = \ln K + \frac{1}{n}\ln c_{eq},$$ (3)

where K is the Freundlich constant used to measure the adsorption capacity, and $1/n$ is the adsorption intensity.

For Langmuir isotherm, points are plotted in a coordinate system where $c_{eq}/(x/m)$ values are on y-axis and c_{eq} values on x-axis. For Freundlich isotherms, $\ln(x/m)$ values are on y-axis and ln c_{eq} values are on x-axis. These values of factors, derived from measured concentrations of adsorbate from parallel Erlenmeyer flasks, were plotted, and trend line was fitted between the points. Trend line equation will obey the Equation (1) or (2) depending which isotherm is under investigation. The adsorption mechanism is better described by the isotherm which's correlation coefficient R^2 is higher. Separation factor R_L could also be used. It is derived from

equilibrium data as well, and it tells if the adsorption is favorable, in addition of the correlation coefficient (Ayawei *et al.* 2017).

In case of Langmuir isotherm, adsorption capacity *a* is calculated so that *a* = 1/y-axis intercept. In Freundlich isotherm, adsorption capacity K can be obtained straight from the equation of trend line as the anti ln value of y-axis intercept value: K = *e*^ (1/n ln c_{eq}), (1/n ln c_{eq} = y-axis interception).

4 RESULTS AND DISCUSSION

4.1 Adsorption of methylene blue

Adsorption capacities of MB for four different carbons were studied. Figure 9 shows the plots between concentration and time consumed for every studied activated carbon. Sampling times were different for R&D wood and peat and commercial ones, but removal efficiencies can be compared in 30 min sampling time, where every treatment has already reached an equilibrium point (Table 3; Table 4). Unfortunately, studied MB concentrations were different between commercial carbons and R&D carbons, except the concentration of 10 mg/l (Figure 10).
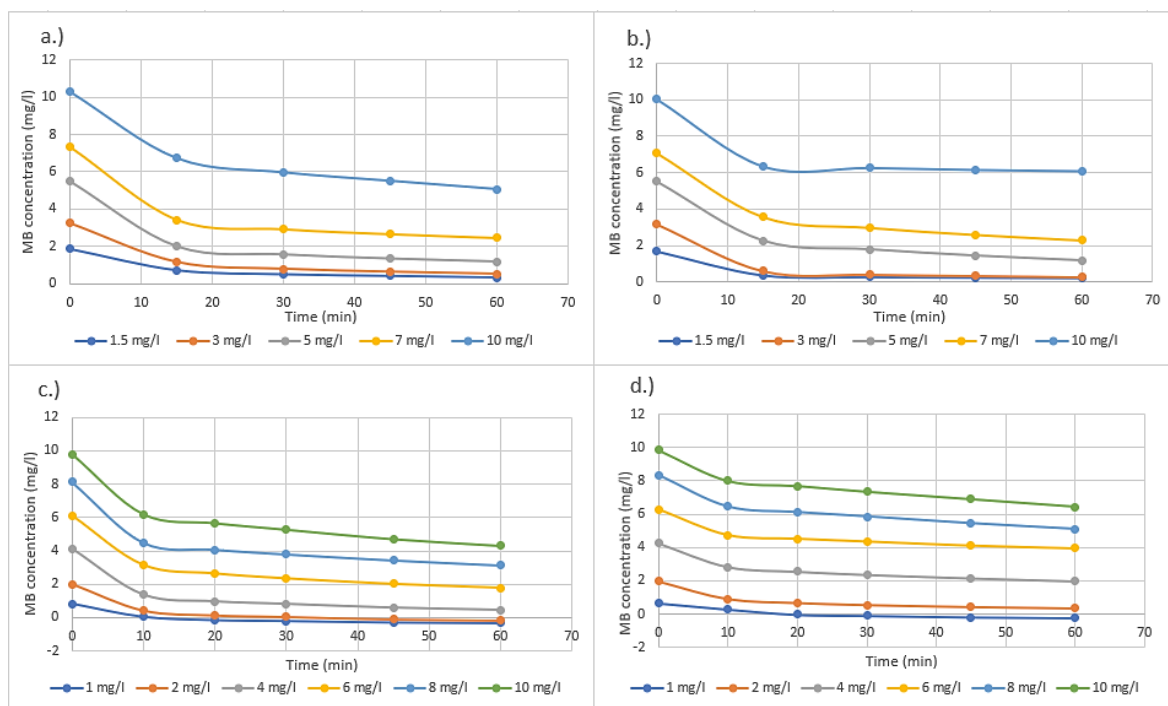
Figure 9. Removal of methylene blue concentration with dose of 0.01 g of a.) R&D peat, b.) R&D wood, c.) Filtrasorb TL830, d.) Silcarbon S835. Color of curves indicates different concentrations of MB.

Table 3. Removal efficiencies with commercial activated carbons (0.1 g/100 ml) in 30 min sampling time for methylene blue in different initial concentrations.

Methylene blue concentration	1 mg/l	2 mg/l	4 mg/l	6 mg/l	8 mg/l	10 mg/l
Filtrasorb TL830	100 %	96.9 %	80.7 %	61.6 %	53.5 %	45.9 %
Silcarbon S835	100 %	71.9 %	44.1 %	30.6 %	29.8 %	25.5 %

Table 4. Removal efficiencies with R&D activated carbons (0.1 g/100 ml) in 30 min sampling time for methylene blue in different initial concentrations.

Methylene blue concentration	1.5 mg/l	3 mg/l	5 mg/l	7 mg/l	10 mg/l
R&D wood	84.7 %	86.8 %	67.5 %	57.8 %	37.7 %
R&D peat	73.2 %	75.6 %	71.6 %	60.1 %	42.0 %
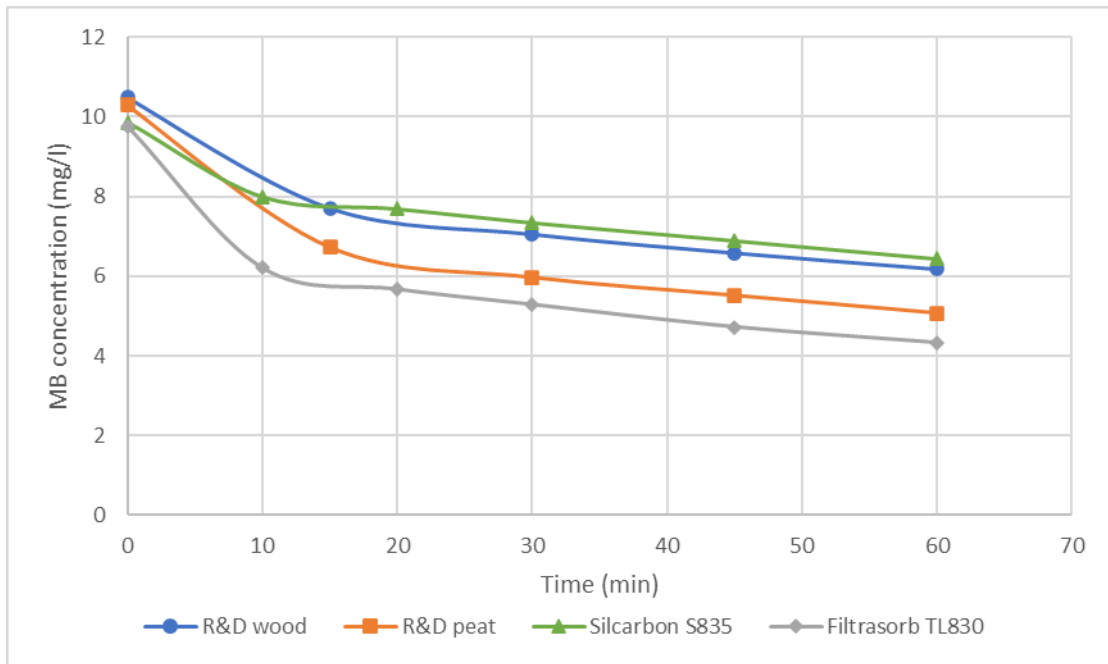
Figure 10. Removal of methylene blue with 0.1 g of each activated carbon, as initial MB concentration was 10 mg/l.

Measurement data (Appendix 2) was fitted to Langmuir (Figure 11) and Freundlich (Figure 12) isotherms. Calculated parameters (Table 5) shows that data fitted better in Langmuir isotherm according to coefficient of determination (R^2). Maximum adsorption capacity of R&D wood reached 107.5 mg/g and R&D peat 87.7 mg/g. The maximum adsorption capacity of Filtrasorb TL830 was about 76 mg/g and capacity of Silcarbon S835 about 16 mg/g. In 10 mg/l MB concentration (Figure 10), Filtrasorb TL830 and R&D peat seemed to be the most effective ones. However, R&D wood was the most efficient one with lower MB concentrations, which leads to the highest adsorption capacity. Even though Freundlich isotherm gave also good correlations, Langmuir isotherm gave systematically higher capacities.
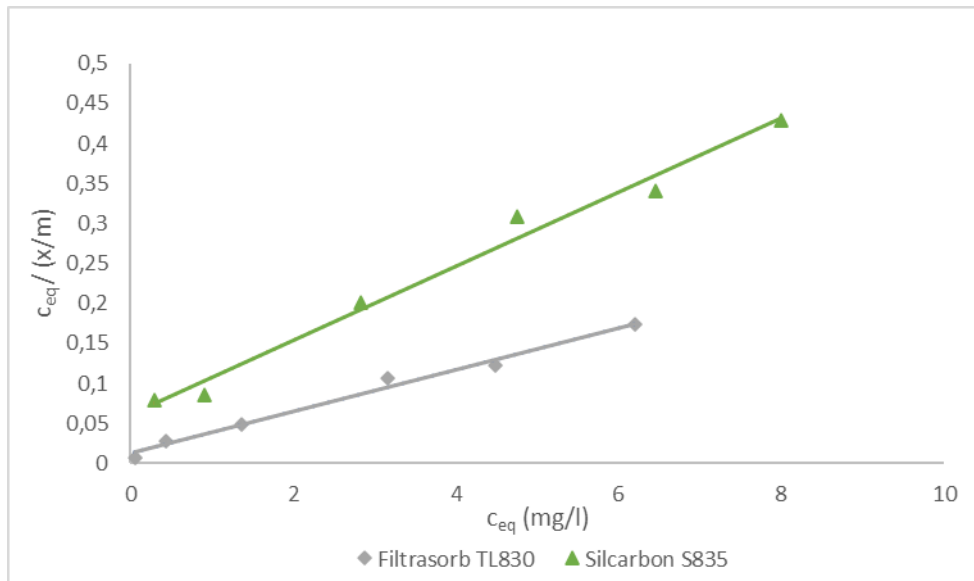
Figure 11. Model fit of Langmuir isotherm of methylene blue adsorption onto two commercial activated carbons
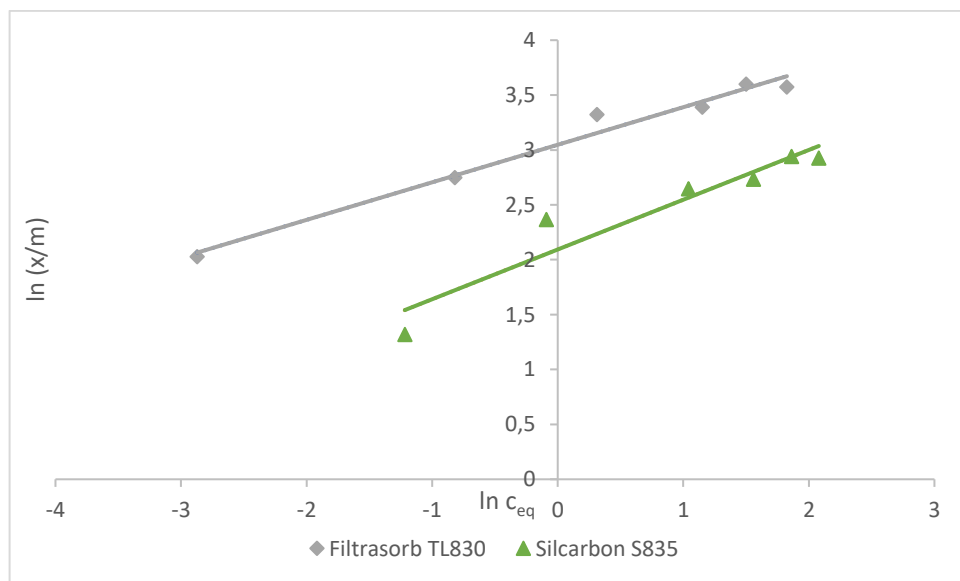
Figure 12. Model fit of Freundlich isotherm of methylene blue adsorption onto two commercial activated carbons

Table 5. Summary parameters for Langmuir and Freundlich isotherms of MB adsorption.

Activated carbons	Langmuir				Freundlich			
	R^2	slope	y-intercept	q_{max} (mg/g)	R^2	slope	y-intercept	K_f (mg/g)
Filtrasorb TL830	0.988	0.026	0.013	75.8	0.977	0.342	3.048	21.1
Silcarbon S835	0.985	0.046	0.062	16.1	0.909	0.453	2.093	8.1
R&D peat	0.990	0.017	0.011	87.7	0.858	0.278	3.586	36.1
R&D wood	0.979	0.015	0.009	107.5	0.981	0.269	3.704	40.6
R&D mix	0.999	0.023	0.012	84.0	0.959	0.203	3.350	28.5
R&D by-product	0.998	0.038	0.053	18.8	0.954	0.278	2.553	12.8

R&D wood had the highest uptake of MB. Compared with R&D peat, R&D wood had higher BET surface area and iodine number, and the most favorable ash content, which may explain the difference (Table 1). However, Filtrasorb TL820 didn't have the highest capacity, even though it had the highest BET surface area and iodine number. These values may not be valid in batch experiments, because commercial carbons were crushed from granular form to powdered form, which could have changed the properties.

Calculated adsorption capacities for MB are not as high as the best capacities found in literature. Adsorption capacities of other wood based ACs are for example 90.9 mg/g for oil palm wood based AC (Ahmad *et al.* 2007), 159.89 mg/g for *Acacia mangium* based AC (Danish *et al.* 2018), and 454.2 mg/g for bamboo based AC (Hameed *et al.* 2007). Peat based activated carbons seems to be rare in literature, but for example Fernandes *et al.* (2007) used dried peat for MB adsorption and got capacity of 324 mg/g.

Rafatullah *et al.* (2010) introduces more than 200 different low-cost adsorbents. About half of them has lower adsorption capacity for MB than R&D peat (87.7 mg/g). Introduced commercial carbons have very high capacities when most of them has capacity more than 200 mg/g, the highest being 980.3 mg/g. Most of the

introduced non-commercial carbons have adsorption capacity between 0-500 mg/g. Capacities of R&D products are much lower than the best commercial ACs, but they are still comparable to most low-cost products and still better than Filtrasorb TL830 and Silcarbon S835, which are still and all approved in Viitaniemi drinking water treatment plant.

4.2 Adsorption of DOC

4.2.1 DOC analysis data

Adsorption of DOC was studied with coagulated water from Viitaniemi drinking water treatment plant, so the largest molecular size fractions were already removed. Major amount of DOC represented so called middle size fraction. First, adsorption of DOC was studied with R&D wood and R&D peat, and initial DOC concentration was 2.5 mg/l. Adsorption with commercial carbons was studied after 56 days with water from the same jerry can, and initial DOC concentration was 2.8 mg/l. DOC concentrations after 4.5 hours for each treatment are presented in Figure 13. These values were used to calculate adsorption capacities of DOC. The most effective removal of DOC was reached with 0.15 g of R&D peat, when removal after 4.5 hours was 86 %. It looks like maximum adsorption is achieved already with dose of 0.05 g/250 ml of R&D wod, R&D peat and Filtrasorb TL830 (Figure 13). Uptake of DOC is not increased anymore with higher doses. Silcarbon S830 instead is needed in higher doses to have good adsorption results.
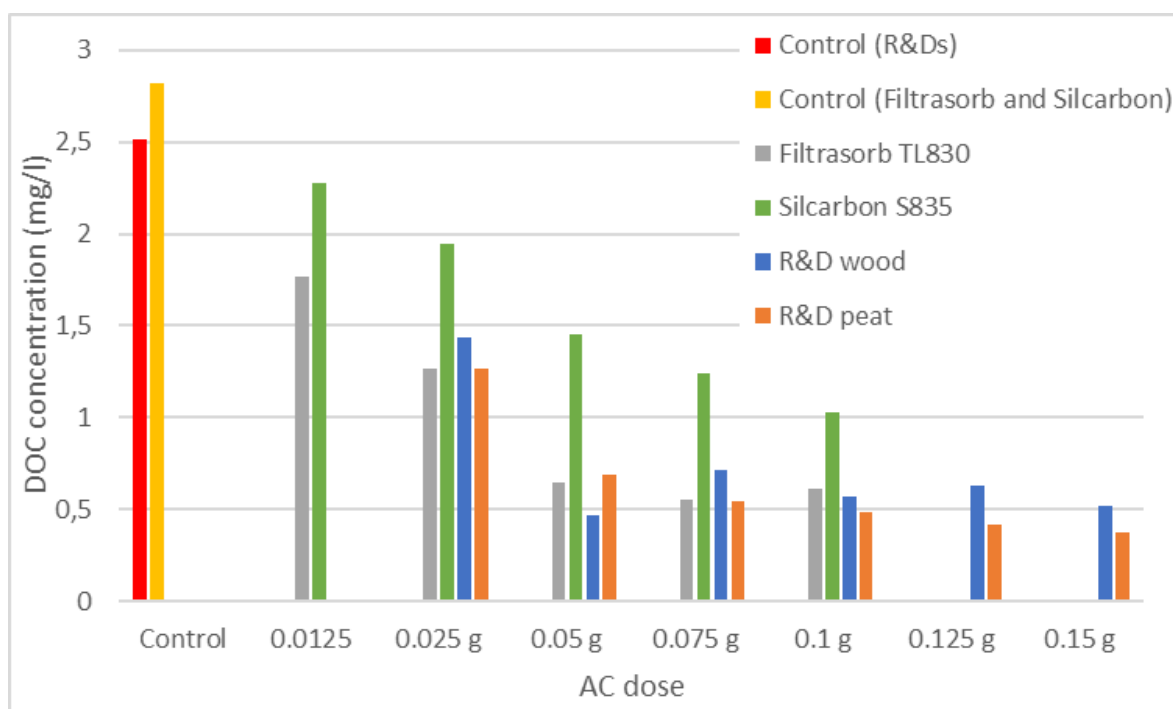
Figure 13. DOC concentrations in equilibrium point (4.5 h) with different doses of each activated carbon (per 250 ml of solution).

Measurement data (Appendix 2) of DOC concentrations was fitted in Langmuir (Figure 14) and Freundlich (Figure 15) isotherms. Calculated parameters (Table 6) shows that data fitted better in Freundlich isotherm according to coefficient of determination (R^2). So adsorption is confined to multilayer. That is understandable since DOC consists of heterogenous humic matter with different molecular sizes and functional groups. Maximum adsorption capacities of DOC were 16.2 mg/g for R&D peat, 12.3 mg/g for Filtrasorb TL830, 7.5 mg/g for R&D wood, and 4.3 mg/g for Silcarbon S835.
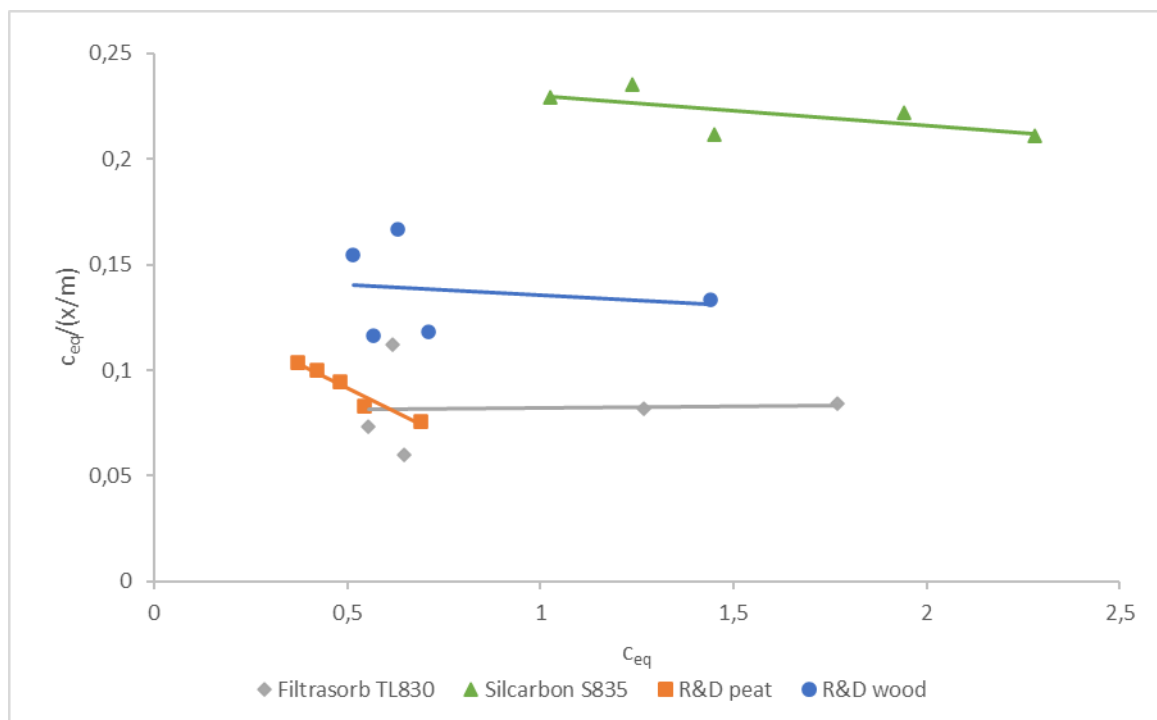
Figure 14. Model fit of Langmuir isotherm of DOC adsorption onto all four studied activated carbons.
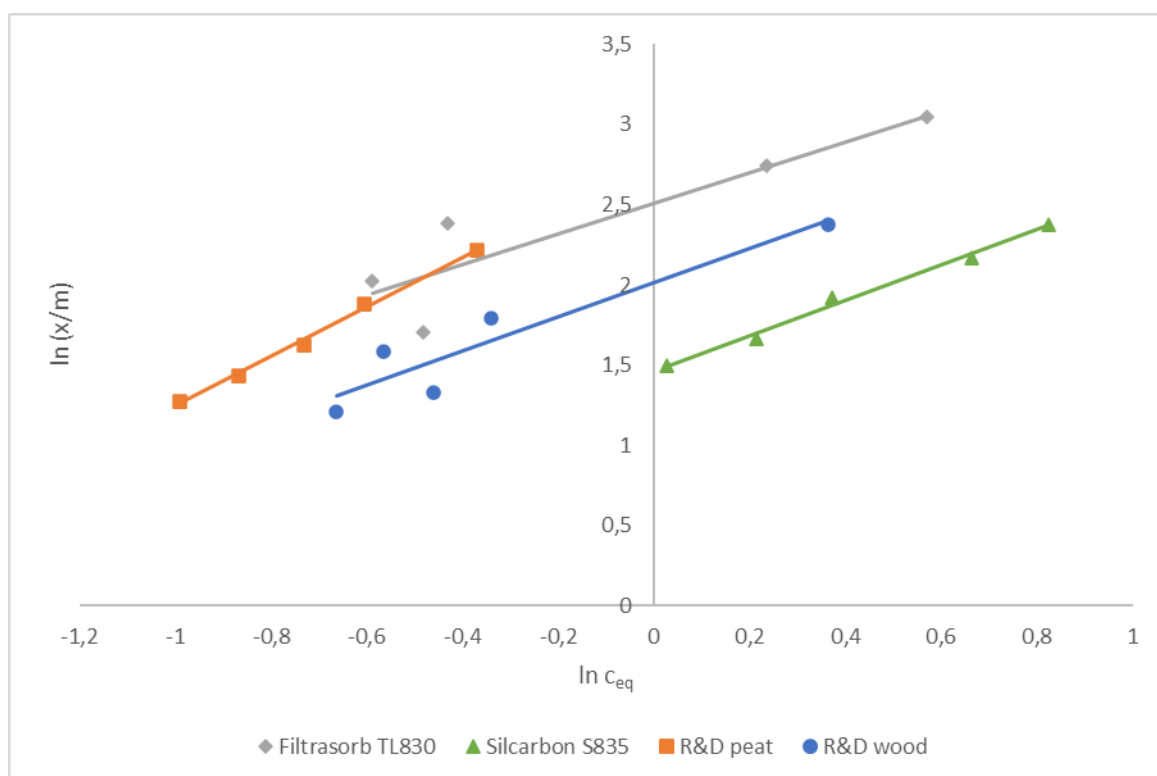
Figure 15. Model fit of Freundlich isotherm of DOC adsorption onto all four studied activated carbons.

Table 6. Summary parameters for Langmuir and Freundlich isotherms of DOC adsorption.

Activated carbons	Langmuir				Freundlich			
	R^2	slope	y-intercept	q_{max} (mg/g)	R^2	slope	y-intercept	K_f (mg/g)
R&D wood	0.028	-0.010	0.145	6.9	0.884	1.065	2.014	7.5
R&D peat	0.953	-0.092	0.138	7.3	0.995	1.538	2.783	16.2
Filtrasorb TL830	0.002	0.001	0.081	12.4	0.823	0.952	2.512	12.3
Silcarbon S835	0.470	-0.014	0.244	4.1	0.991	1.103	1.464	4.3

R&D peat showed the best uptake of DOC. Adsorption capacity of 16.2 mg/g is more than a twice as high as capacity of R&D wood. R&D wood had better performance in MB adsorption, but R&D peat had in turn better DOC adsorption. DOC molecules are relatively large, and because R&D peat has higher relative volume of meso- and macropores than other ACs (Table 1), there are more adsorption sites available and thus the highest adsorption capacity.

Freundlich isotherm gives better correlation coefficients, so adsorption is confined to multilayer. That is understandable since DOC consists of heterogenous humic matter with different molecular sizes and functional groups. This result supports the presumption that adsorption of many organic compounds onto activated carbon fits better to the Freundlich isotherm than to the Langmuir isotherm (Kanô *et al.* 2000).

The AC filtration in Viitaniemi drinking water treatment plant removed hardly no DOC (Ignatev and Tuhkanen 2019). In normal use, DOC concentration was decreased from 2.7 to 2.3 mg/l during AC treatment. AC filtration could have much more potential in DOC removal, because in these batch experiments, DOC was removed up to the level of 0.5 mg/l. However, contact time between adsorbate and adsorbent in treatment plants is usually around 10–20 min (Stuetz and Stephenson 2009), but equilibrium point in these batch experiments came after 4.5 hours. That

could indicate that full scale AC filtration is probably optimized for some other compounds which are adsorbed faster. All in all, the adsorption of DOC looks much slower than for example MB or used pharmaceuticals. Every other equilibrium point was reached within 30 minutes, but DOC required 4.5 hours. DOC has a bigger apparent molecular weight so longer contact time is needed for molecules to go deeper into pores.

4.2.2 Size fractions by HPSEC

Two main peaks were detected in the water used in the experiments by a fluorescence detector in wavelengths of 330/425 nm, 390/500 nm and 270/355 nm. Elution time of these peaks were 7.45 and 8.4 mins (Figure 16). Peaks were combined into two fractions (IV and V, based on fractionating by Ignatev and Tuhkanen 2019) where fraction IV was integrated between 5 and 7.98 min and fraction V between 7.98 and 15 min. Based on the Equation 1, estimated apparent molecular weights are about 1000 Da for fraction IV and about 400 Da for fraction V. In addition, there was a small peak before experiments in tryptophan-like fluorescence at elution time of 3.22 min, which was not investigated further, because it was removed very efficiently in every treatment.

Fraction IV contributed to about 46 %, 53 % and 43 % of the total humic/fulvic-like (330/425 nm), humic/fulvic-like (390/500 nm) and tryptophan-like (270/355 nm) fluorescence, respectively. Fraction V contributed to rest of the fluorescence. Both size fractions exhibited simultaneously all three different fluorescences, which means that humic/fulvic-like compounds and tyrosine-like compounds were eluted at the same time. However, it can't be known if the fluorescence signals come from different fluorophores of one compound or from totally different compounds which eluted at the same time (Ignatev & Tuhkanen 2019). Peak area of 330/425 nm fluorescence was clearly the highest (Figure 16), which indicates abundance of low aromaticity and low molecular weight compounds, which was expected, because compounds with high molecular weights are removed in coagulation. Tryptophan-like fluorescence indicates the abundance of intact proteins. Some highly conjugated aromatic compounds with high molecular weight were also detected in

humic/fulvic like (390/500 nm) fluorescence, although this signal was lower than 330/425 nm and 270/355 nm signals (Figure 16). No proper signal was detected in tyrosine-like (270/310 nm) fluorescence. UV data is not provided since technical problems of UV-detector.
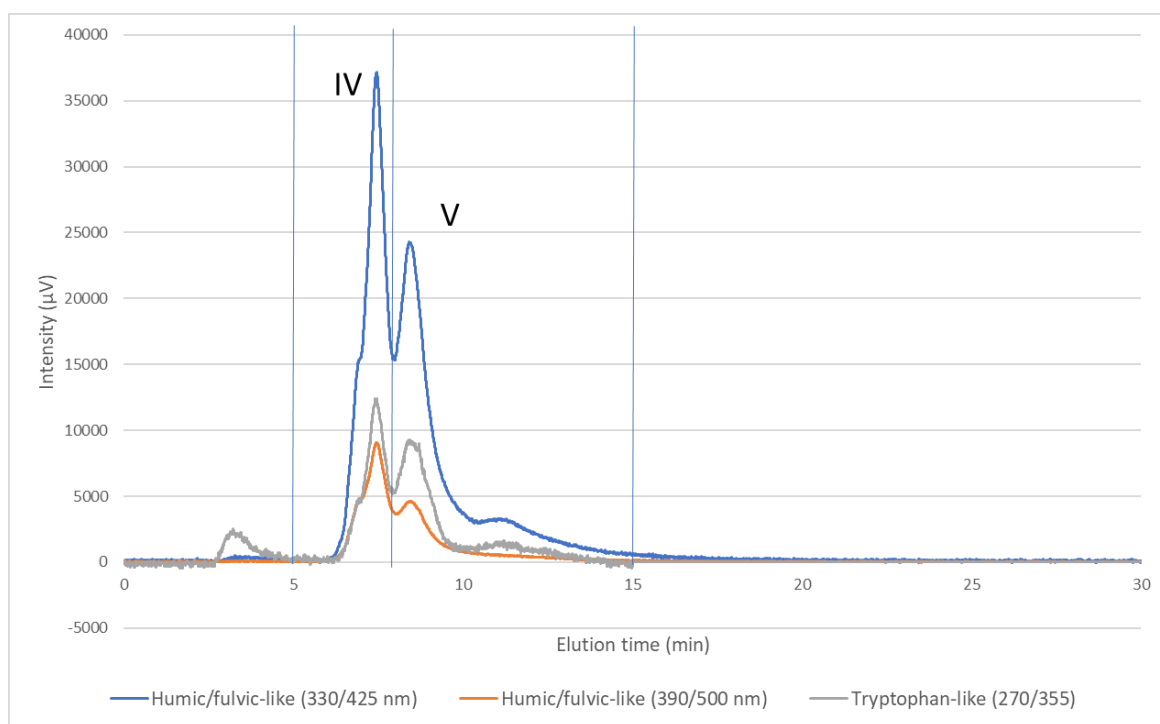
Figure 16. Characterization of DOC by three different fluorescence wavelengths. HPSEC fluorescence chromatograms of chemically treated and sand filtrated water before the batch experiment.

Removal of total humic/fulvic-like (330/425 nm), humic/fulvic-like (390/500 nm) and tryptophan-like (270/355 nm) fluorescences were quite efficient with tested doses of activated carbon. Reduction of total 330/425 nm fluorescence was 62.3–94.5 % with R&D wood and 73.3–96.3 % with R&D peat (Table 7). It is notable that doses varied between 0.025 g and 0.125 g for R&D products while doses for commercial carbons varied between 0.0125 g and 0.1 g. Filtrasorb TL830 reduced 330/425 nm fluorescence 48.4 – 99.1 % and Silcarbon S835 27.2 – 88.7 % (Table 7). Performance of Silcarbon S835 was clearly the worst. For comparison, Ignatev and Tuhkanen (2019) found out that in Viitaniemi drinking water treatment plant, a removal of

330/425 nm fluorescence was 47.9 % (from 53.5 to 27.9 mV min) during AC treatment. Therefore, there could be more potential in removal of this fluorescence in full scale by using these ACs with a longer contact time.

R&D wood reduced 330/425 nm fluorescence, representing low aromatic and low molecular weight compounds, almost completely after 24 hours with all doses except 0.025 g. Almost complete removal after 24 h was achieved also with R&D peat and Filtrasorb TL830 with all doses except 0.025 and 0.05 g. High doses of these adsorbents reduced 330/425 nm fluorescence efficiently, but better comparison of performances can be done with 0.025 g dose (Figure 17).

Table 7. Removal efficiencies of different fluorescences and with different doses of each adsorbent at equilibrium point. Fluorescnece with 330/425 nm represents low aromatic compounds, 390/500 nm represents highly conjugated aromatic compounds and 270/355 nm represents different proteins.

Activated carbon	Dose (g)	Removal efficiency (%) at $\lambda_{ex}/\lambda_{em}$ (nm)		
		330/425	390/500	270/355
R&D wood	0.025	62.3	63.9	62.7
	0.05	96.8	98.7	96.0
	0.075	90.1	92.2	88.8
	0.1	93.8	93.3	92.2
	0.125	94.5	96.4	84.6
R&D peat	0.025	73.3	77.4	72.3
	0.05	89.9	93.0	85.7
	0.075	95.3	96.0	95.9
	0.1	95.8	98.0	95.8
	0.125	96.3	97.6	> 99.9
Filtrasorb TL830	0.0125	48.4	55.6	57.1
	0.025	71.8	78.6	65.7
	0.05	94.1	94.7	88.1
	0.075	98.6	98.6	96.5
	0.1	99.1	98.9	96.4
Silcarbon S835	0.0125	27.2	30.0	20.4
	0.025	47.9	49.2	62.5
	0.05	70.5	70.9	64.4
	0.075	81.7	82.4	81.5
	0.1	88.7	90.3	88.1
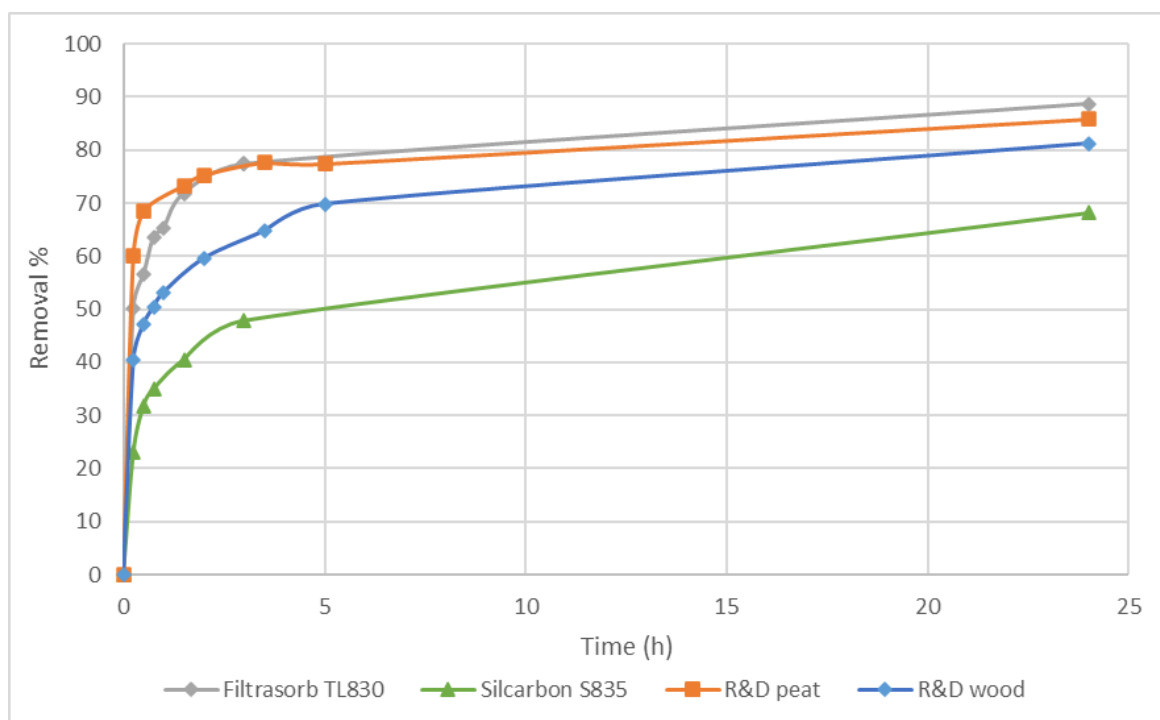
Figure 17. Removal (%) of low aromatic compounds (humic/fulvic-like 330/425 nm fluorescence peak area) with dose of 0.025 g of each activated carbon.

Removal of total humic/fulvic-like fluorescence (390/500 nm), representing highly conjugated aromatic compounds, was 63.9–98.7 % for R&D wood, 77.4–97.6 % for R&D peat, 55.6–98.9 % for Filtrasorb TL830 and 30.0–90.3 % for Silcarbon S835 (Table 7). Performance of Silcarbon S835 was again the worst while Filtrasorb TL830 and R&D peat performed the best. For comparison, Ignatev and Tuhkanen (2019) found out that in Viitaniemi drinking water treatment plant, removal of this fluorescence was 40.0 % (from 10.0 to 6.0 mV min) during AC treatment. This fluorescence (390/500 nm) was reduced very similarly than 330/425 nm fluorescence. Almost complete removal of this fluorescence after 24 hours was achieved with high doses of R&D wood, R&D peat and Filtrasorb TL830. Performances of all adsorbents can be compared with 0.025 g dose (Figure 18).
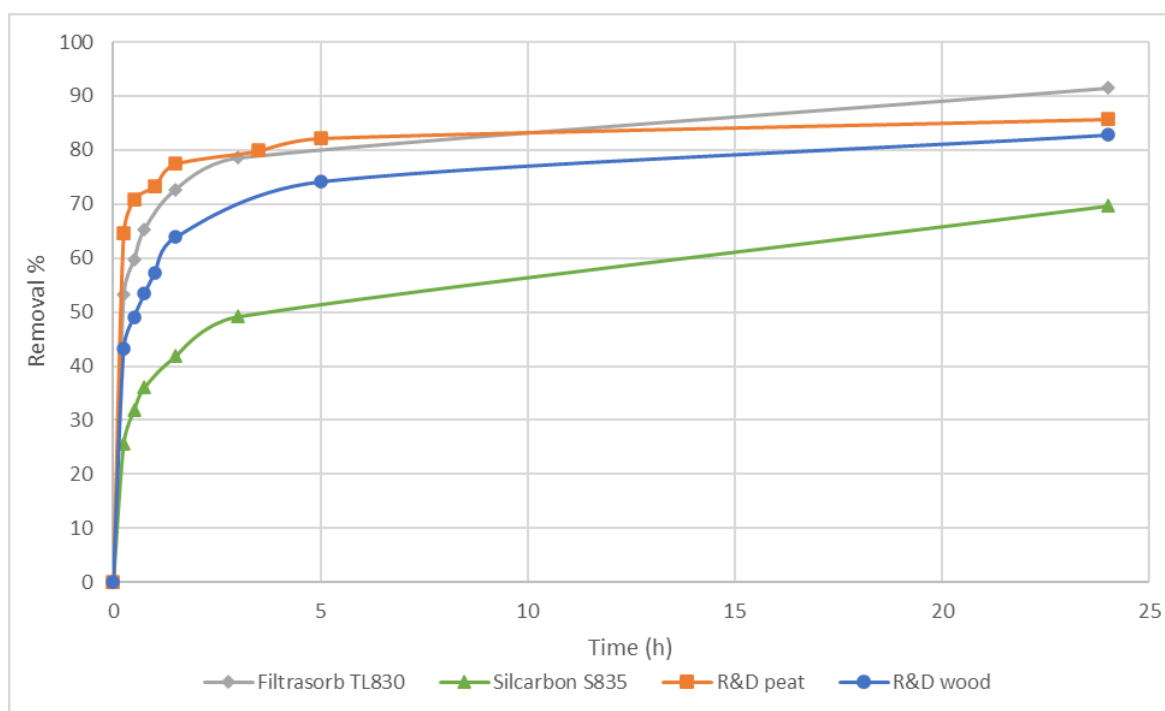
Figure 18. Removal (%) of highly conjugated aromatic compounds (humic/fulvic-like 390/500 nm fluorescence peak area) with dose of 0.025 g of each activated carbon.

Removal of total tryptophan-like fluorescence (270/355 nm), representing the abundance of intact proteins, was 62.7–96.0 % for R&D wood, 72.3–99.9 % for R&D peat, 57.1–96.5 % for Filtrasorb TL830 and 20.4–88.1 % for Silcarbon S835 (Table 7). Silcarbon S835 had similar performance with R&D wood while Filtrasorb TL830 and R&D peat performed the best. Ignatev and Tuhkanen (2019) found out that in Viitaniemi drinking water treatment plant, removal of this fluorescence was 47.6 % (from 20.6 to 10.8 mV min) during AC treatment. With longer contact time, these ACs could have more potential in removal of this fluorescence as well as previous fluorescences (330/425 nm and 390/500 nm).

R&D peat reduced tryptophan-like fluorescence almost completely after 24 hours with all doses except 0.025 g. Complete removal after 24 hours was achieved also with 0.1 g of Filtrasorb TL830. Unlike humic/fulvic-like fluorescences, tryptophan-like fluorescence chromatograms had lots of noise why there might be some

uncertainty in the integration of peaks. Performances of all adsorbents can be compared with 0.025 g dose (Figure 19).
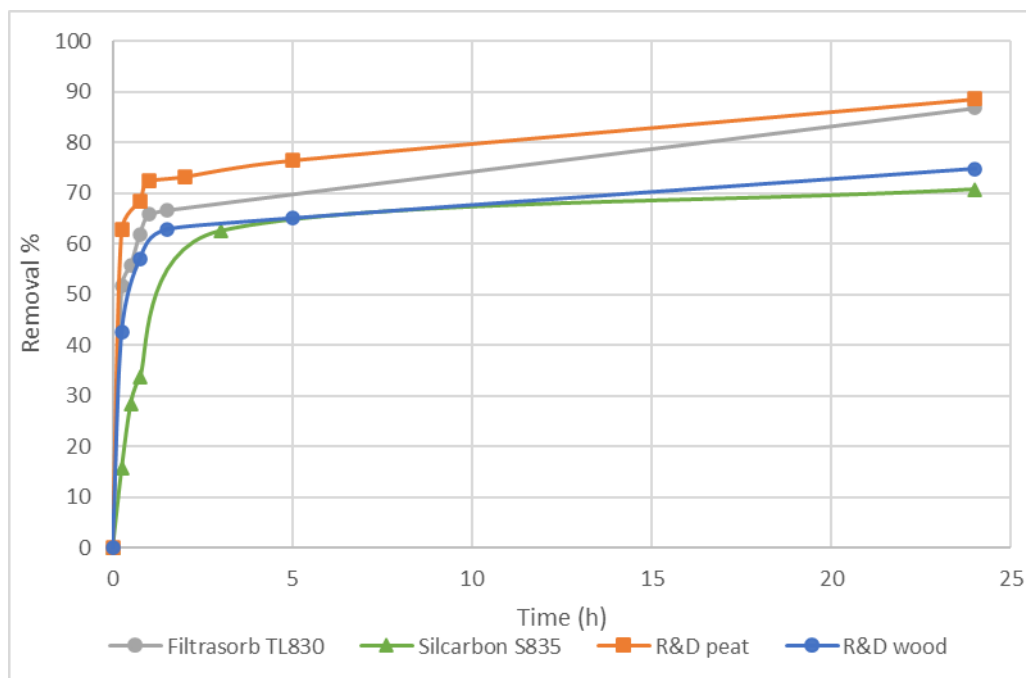
Figure 19. Removal (%) of intact proteins (tryptophan-like 270/355 nm fluorescence peak area) with dose of 0.025 g of each activated carbon.

Silcarbon S835 showed the lowest reduction of every used wavelength of fluorescence. Reason might be its higher moisture and ash contents, which are generally decreasing the adsorption capacity (Table 1). R&D peat and Filtrasorb TL830 are very similar very effective ones in reducing fluorescence signals but also in the removal of measured concentrations of DOC. R&D wood abilities are somewhere between these two extremities. Performances of used activated carbons in reducing of humic/fulvic-like and tryptophan-like fluorescences are in line with calculated adsorption capacities of DOC.

Advanced analysis of removal of each fraction was not done, even though some notes were done. For example, with the dose of 0.025 g/250 ml, the fraction V (400 Da) was removed faster than the fraction IV (1000 Da) during first half an hour. After first half an hour using R&D peat and R&D wood, removal of the fraction V

slowed down, and the fraction IV ended up being most removed fraction. With commercial Filtrasorb TL830 and Silcarbon S835, removal of the fraction V was also faster during first half an hour, but it also ended up being better removed than the fraction IV. In AC filtration of Viitaniemi drinking water treatment plant, fluorescences (330/425, 390/500 and 270/355 nm) of fraction V were removed up to 40 %, while fluorescences of fraction IV were removed just about 10 % (Ignatev and Tuhkanen 2019). Matilainen *et al.* (2006b) found out that intermediate molar mass matter (1000–4000 Da) was removed most efficiently with AC filtration. Fraction IV belongs to this range, and removal of it is in line with results of Matilainen *et al.* (2006b) in case of R&D products. Commercial products in turn removed low molar mass matter (fraction V) better than intermediate molar mass matter, which is line with results of Ignatev and Tuhkanen (2019). Therefore, R&D products and commercial products seem to have different abilities in the removal of these size fractions of DOC. It is also notable, that Matilainen *et al.* (2006b) used UV_{254} data, not fluorescence, for these conclusions. Other doses than 0.025 of AC were not analyzed.

4.3 Adsorption of pharmaceuticals

4.3.1 Batch experiment with R&D wood

Adsorption of sulfamethoxazole (SMX), trimethoprim (TMP), lamivudine (3TC) and nevirapine (NVP), with and without DOC present in water, onto all activated carbons was studied. Concentrations of the pharmaceuticals were calculated based on standard calibration curves (Appendix 1). R&D wood was tested with different AC doses (variable was *m*) and constant initial concentrations (2 mg/l) of pharmaceuticals. The equilibrium point was reached already at the first sampling point which was 10 minutes. Removal efficiencies of pharmaceuticals using R&D wood are shown in Table 8. R&D wood removed TMP completely in every dose after 10 minutes, while the most poorly removed compound was 3TC. It looks like the DOC had no big influence on the adsorption of pharmaceuticals in this experimental setup with R&D wood, except with the dose of 0.025 g. Some notable

difference is seen with the 0.025 g dose of activated carbon, when removal efficiencies are about 10 percentage lower for SMX, 3TC and NVP when DOC was present (Table 8; Appendix 3).

Table 8. Removal efficiencies (%) of pharmaceuticals (2 mg/l) at equilibrium in MQ water and in water from Viitaniemi (VW) using R&D wood. The measured initial concentration of DOC in VW was 2.5 mg/l.

AC dose (g)	SMX MQ	SMX VW	TMP MQ	TMP VW	3TC MQ	3TC VW	NVP MQ	NVP VW
0.01	70.2	69.5	> 99.9	> 99.9	57.2	53.9	70.6	69.6
0.025	92.2	82.0	> 99.9	> 99.9	89.7	74.8	97.8	89.5
0.05	97.2	94.3	> 99.9	> 99.9	98.8	98.4	99.8	99.7
0.075	98.9	98.1	> 99.9	> 99.9	99.5	99.4	99.9	> 99.9
0.1	99.2	99.0	> 99.9	> 99.9	99.7	99.6	> 99.9	> 99.9

4.3.2 Batch experiments with R&D peat, Filtrasorb TL830 and Silcarbon S835

After first batch experiment, following experiments were done with constant AC dose of 0.025 g (R&D peat, Filtrasorb TL830 and Silcarbon S835) and varying initial concentrations of pharmaceuticals. Removal efficiencies of pharmaceuticals from MQ water were at least 60 % even in the highest concentration of pharmaceuticals with every AC (Appendix 3). TMP was removed most efficiently while 3TC was removed most poorly also in this experimental setup. Removal efficiencies of SMX and NVP were similar, and they were between the removals of TMP and 3TC. Although concentrations of DOC and pharmaceuticals were at same level, background DOC indeed affected the adsorption of pharmaceuticals, at least compared with the first batch experiments with R&D wood. Removal of pharmaceuticals, as well as DOC, was expected to decrease in neutral pH (7.2), since most of their pK_a constants were lower than pH, which means they are mostly occurring in anionic form. These anions and also negatively charged DOC molecules cause repulsion between each other and therefore decrease the total adsorption (de Ridder *et al.* 2011). Surface charges of ACs were not known, but it is

possible that surfaces were negatively charged (Bjelopavlic *et al.* 1999), which increases repulsions even more. Furthermore, the adsorption of pharmaceuticals were expected to decrease because a possible pore blocking by large DOC molecules, but also because competition of adsorption sites on the AC surface (Pelekani and Snoeyink 1999) However, it was proved that DOC was able to decrease the adsorption of pharmaceuticals and other micropollutants even without the advantage of several magnitudes higher concentration (,~mg/l vs. ng/l) which is usual in waters entering the real drinking water treatment plants (Vieno *et al.* 2005; Ngumba *et al.* 2016b; Ignatev and Tuhkanen 2019).

Removal of TMP from MQ water was complete, and removal of it was the most efficient among all tested pharmaceuticals, with every AC. Removal didn't decrease in when DOC was present (in VW) with R&D wood at any dose, but some decreasing is seen with other ACs when initial concentration of TMP is high. With R&D peat, removal of TMP from VW was 86.4–97.7 % depending on the concentration and with Filtrasorb TL830 removal was 76.3–97.6 % (Appendix 4). Silcarbon S835 showed the lowest removal of TMP from VW when it went down to 69.7 % with the highest initial concentration. Adsorption capacities for TMP in MQ water could not be calculated, but in VW, adsorption capacities were 192.3 mg/g for R&D peat, 135.1 mg/g for Filtrasorb TL830 and 30.1 mg/g for Silcarbon S835 (Table 9). Adsorption mechanisms of TMP fitted better in Langmuir isotherm (Appendix 5), likewise in many other studies (Bekçi *et al.* 2006; Kim *et al.* 2010; Liu *et al.* 2015). However, differences between fittings of Langmuir and Freundlich isotherms were not clear in every case, so clear conclusions of adsorption mechanisms can't be made. Capacities based on Freundlich isotherms are much lower (Table 9). It is a common problem that more than one isotherm can describe the adsorption mechanism (Cheng *et al.* 2014). All the calculated adsorption capacities are shown in Appendix 6, regardless of correlation coefficient of isotherm.

Table 9. Adsorption capacities (mg/g) for pharmaceuticals in MQ water and Viitaniemi water (VW) for every AC. Capacity is calculated either using Langmuir (L) or Freundlich (F) isotherm. Both results are given if difference in R^2 coefficients between isotherms was less than 0.05. Result with higher R^2 is highlighted by underlining.

Compound	R&D peat	R&D wood	Filtrasorb TL830	Silcarbon S835
SMX (MQ)	<u>29.1 L</u>/14.7 F	107.5 L/<u>17.9 F</u>	102 L	10.8 F
(VW)	11.2 F	98.0 L/<u>9.0 F</u>	<u>18.6 L</u>/12.2 F	4.6 F
TMP (MQ)	-	-	-	-
(VW)	<u>192.3 L</u>/24.7 F	-	135.1 L	<u>30.8 L</u>/18.7 F
3TC (MQ)	23.5 L	200.0 L/<u>10.9 F</u>	<u>29.7 L</u>/13.3 F	4.0 F
(VW)	12.7 F	135.1 L/<u>8.2 F</u>	20.0 L/<u>12.2 F</u>	4.7 F
NVP (MQ)	87.0 L	-	70.9 L	10.8 F
(VW)	53.8 L/<u>17.8 F</u>	12.7 F	<u>47.6 L</u>/18.2 F	11.1 L/<u>9.3 F</u>

TMP being the most easily removed pharmaceutical was unexpected, even though for example NVP had more than 400 times lower water solubility which should favor the adsorption of NVP more than TMP. The reason might be the pK_a constant of 7.12 of TMP and 2.8 of NVP. If the pH value of water is near pK_a constant of the compound, half of the compound molecules is deprotonated and thus negatively charged. If pK_a constant is below pH, the portion of deprotonated molecules is even larger. Because these constants and pH of 7.2, NVP is deprotonated way more than TMP, giving it negative charge. Lots of electric repulsions may occur when most of the NVP is negatively charged. TMP in turn has less deprotonation, which decreases repulsion forces (Berges *et al.* 2021). As well as with aqueous adsorbates, pH will influence on the charge of the adsorbents. However, charges of ACs were not studied. Contradictory information about pH is available: Cheng *et al.* (2014) found maximum uptake (164 mg/g) of TMP onto feather-derived charcoal at pH level 7.5, which is close to the pK_a value of TMP. Kim *et al.* (2010) found out that adsorption capacity of wood-based PAC (257.9 mg/g) and GAC (352.3 mg/g) for TMP in

distilled water was increasing when pH was decreased from 10 to 4. On the contrary, Berges *et al.* (2021) suggest basic environment for the adsorption of TMP (135 mg/g) in distilled water with an antibiotic cocktail with vegetal powdered AC. Furthermore, usually negatively charged DOC makes the electrostatic interactions even more complicated as well as the adsorption competition between molecules.

DOC didn't affect the adsorption of SMX notably by using R&D wood (Table 8), except with the AC dose of 0.025 g, when removal efficiency decreased 10.2 %. Filtrasorb TL830 removed SMX more than R&D peat, but background DOC affected more in Filtrasorb TL830 than R&D peat, when removal efficiencies decreased about 20 % and 5 %, respectively (Figure 20; Appendix 4). Figure 20 also shows how removal efficiency is decreasing when initial concentration of adsorbate is increasing. Silcarbon S835 had the lowest removal on SMX, and background DOC decreased removal efficiencies about 30 % at maximum (Appendix 4). Data was fitted in Langmuir and Freundlich isotherms, which both gave good correlation coefficients (R^2) in some cases (Appendix 5). Therefore, two adsorption capacities are given when R^2 values are similar (Table 9). These correlation coefficients were very high so there is no problem with the fitting, but decision can't be made whether the Langmuir or Freundlich isotherm describe the adsorption mechanisms best. Calculated adsorption capacities of ACs for SMX in MQ water and in VW are presented in Table 9. The best performance in the removal of SMX was given by Filtrasorb TL830 with the adsorption capacity of 102 mg/g, followed by R&D peat and R&D wood.

Figure 20. Removal efficiencies of SMX in equilibrium point in different initial concentrations, using Filtrasorb TL830 and R&D peat (0.025 g/100 ml). Measured initial DOC concentration in VW was 3.6 mg/l.

A clear decrease in adsorption capacities for SMX is seen when DOC is present in solution. For example, by using Filtrasorb TL830 adsorption capacity for SMX decreased from 102 mg/g to 18.6 mg/g which is more than 80 % decrease. According to the changes in adsorption capacities, DOC really has an influence on adsorption of SMX, although it is not clear whether the capacity should be calculated by using Langmuir or Freundlich isotherm.

Adsorption capacities of SMX were quite low compared with literature, although they are not totally out of the range. Tonucci *et al.* (2015) studied the adsorption of SMX from water with four different adsorbents. The best AC was made from a pinus tree, and it had an adsorption capacity of 131 mg/g while worst adsorbent was commercial carbon nanotube, and it had an adsorption capacity of 29 mg/g calculated with Langmuir isotherm. Similar problems with correlations of isotherms were detected in this study as well when Freundlich isotherm gave very good correlations also. However, Tonucci *et al.* (2015) tested just SMX without any competition between different compounds, which can explain slightly higher

capacities. Silva *et al.* (2019) used paper mill sludge-based activated carbons which had adsorption capacities of 194 and 118 mg/g for SMX in ultrapure water with a cocktail of three antibiotics. In wastewater, capacities of same ACs for SMX were 47 and 123 mg/g. Capacities were calculated using Langmuir isotherm. Jaria *et al.* (2019) used also two paper mill sludge-based carbons and obtained adsorption capacities of 44 and 98 mg/g for SMX in ultrapure water with cocktail of three antibiotics. They decided to study capacities calculated by Langmuir isotherm, although in some cases data were fitted better in Freundlich isotherm. Overall, data fittings in both Langmuir and Freundlich isotherms gave good results in literature as well as in this study, but Langmuir isotherm is considered more accurate one in literature as it gives better fitting in most cases.

Like with R&D wood, removal efficiencies of NVP were similar with the removal of SMX in MQ water, and dependent on the AC used, whether the NVP or SMX was removed better. R&D peat removed NVP better while Filtrasorb TL830 removed SMX better. However, decreasing trends in removal efficiencies in the equilibrium point with different initial concentrations of NVP were almost identical with R&D peat and Filtrasorb TL830 (Figure 21). Background DOC decreased removal efficiencies 5 % at maximum. Decreasing trend also proves that initial concentration of the adsorbent is an important factor in the adsorption process; removal percentages were higher with low initial concentrations. Detailed concentrations and removal efficiencies are presented in Appendix 4, and removal graphs in Appendix 3.

Calculated adsorption capacities for NVP in MQ tells that removal was efficient as the capacity of R&D peat reaches up to 87 mg/g and with Filtrasorb TL830 capacity was 70.9 mg/g, both calculated by Langmuir isotherm (Table 9). Adsorption capacity of R&D wood could not be calculated for NVP in MQ because removal was very high with the highest AC doses and isotherms were biased. When it comes to Silcarbon S835, the lowest removal of NVP was given with a small decrease in the adsorption capacity due the adsorption competition with DOC.
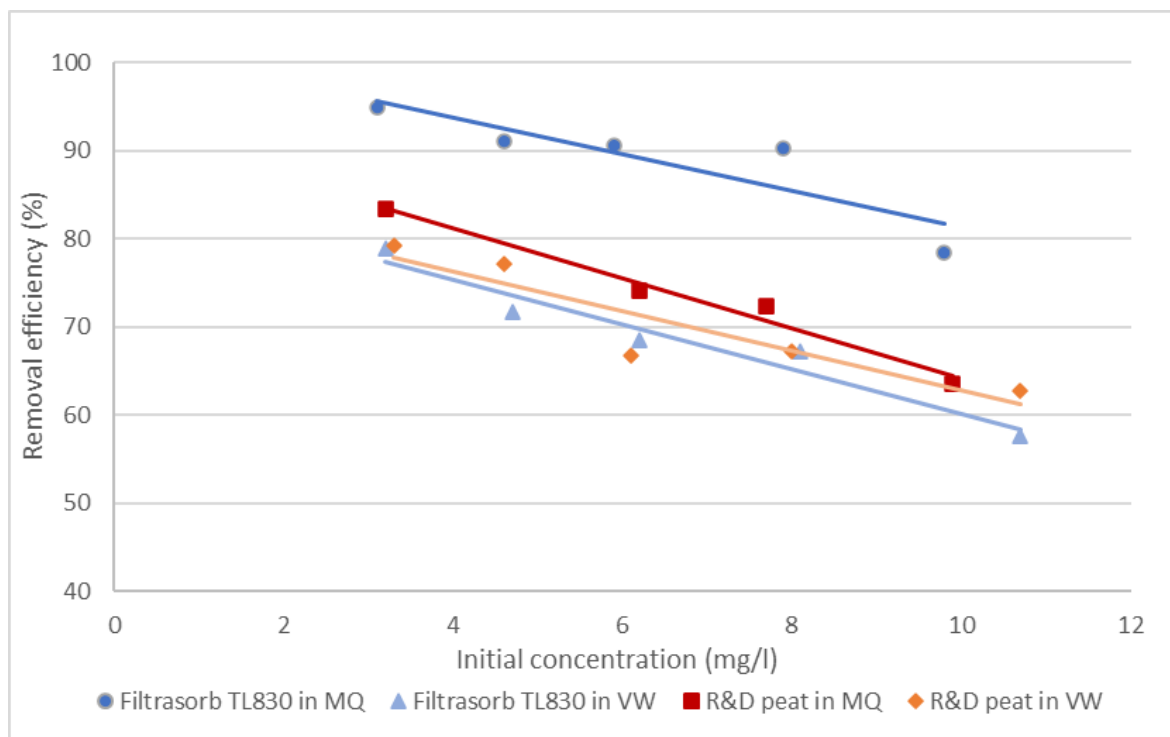
Figure 21. Removal efficiencies of NVP in equilibrium point in different initial concentrations using Filtrasorb TL830 and R&D peat (0.025 g/100 ml). Measured initial DOC concentration in VW was 3.6 mg/l.

Calculated adsorption capacities are in accordance with the capacities in literature. Ndilimeke Akawa *et al.* (2021) used polyvinylpyrrolidone activated carbon alginate to remove two ARDVs from wastewater. Adsorption capacity for NVP calculated using Langmuir isotherm was 44.4 mg/g. It is notable, that adsorption competition in wastewater is high and might decrease the adsorption of some compounds. Adeola *et al.* (2021) did not use activated carbon as an adsorbent, but graphene wool with the adsorption capacity of 48.31 mg/g for NVP calculated using Freundlich isotherm in water containing electrolytes and two ARVDs. Kahilu *et al.* (2022) tested different hydrochars for removing NVP and 3TC. The best capacity for NVP in MQ water was 53.8 mg/g given by hydrochar made from a coal-sewage blend.

Generally, 3TC was removed most poorly from MQ water. Removal efficiencies were lower for 3TC than for other pharmaceuticals with R&D wood and the same trend was visible with other ACs (Table 8; Appendix 4). With Filtrasorb TL830 and

R&D peat, removal efficiencies were just above 80 % at the best when they are clearly above it with other pharmaceuticals. However, 3TC looks the most unaffected one for adsorption competition with DOC at least with Filtrasorb TL830 and R&D peat. There was basically no difference in adsorption between VW and MQ water (Figure 22). Silcarbon S835 removed 3TC from MQ water just 52 % at maximum, which is the lowest reading among all pharmaceuticals and adsorbents (Appendix 4). Interesting part is the fact that with Silcarbon S835, the adsorption of 3TC increased in some flasks containing VW, which was unexpected (Appendix 4). One possible explanation could be the adsorption onto the DOC molecules. Organic matter could adsorb other compounds onto itself, although this phenomenon was not seen with other compounds than 3TC.
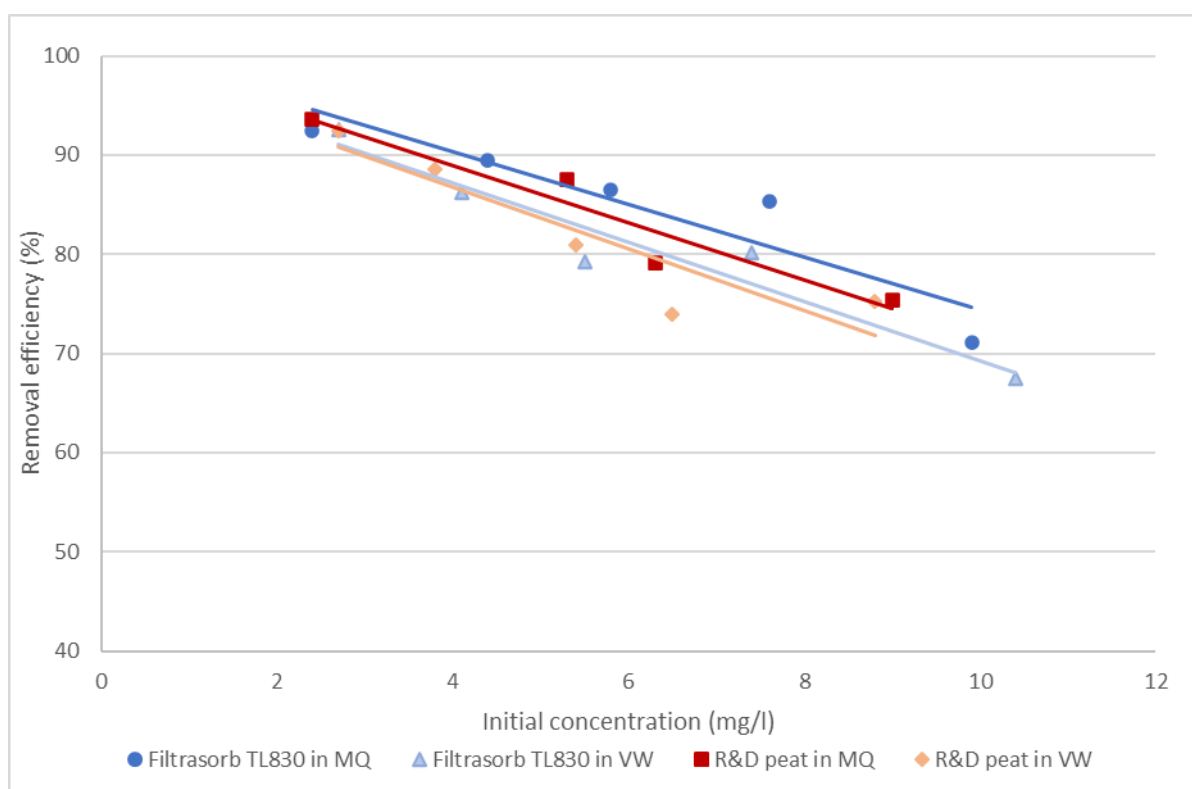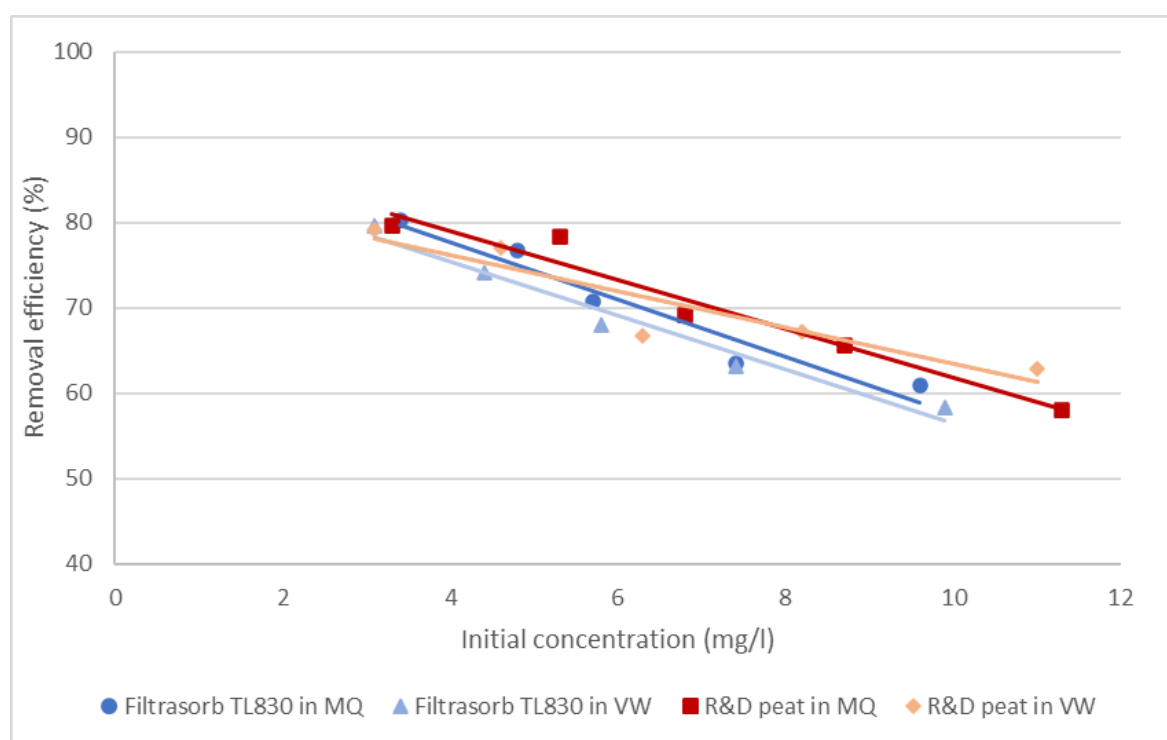

Figure 22. Removal efficiencies of 3TC in equilibrium point in different initial concentrations using Filtrasorb TL830 and R&D peat (0.025 g/100 ml). Measured DOC concentration in VW was 3.6 mg/l.

Calculated adsorption capacities also show that using Silcarbon S835, adsorption capacity for 3TC increased from 4.0 to 4.7 mg/g when background DOC was present (Table 9). It is not known whether this difference is statistically significant or not. Adsorption capacities of other carbons for 3TC are lower than for other pharmaceuticals, which confirms that 3TC was removed the most poorly (Table 9). The best explanation for poor removal is its high water solubility (Table 2), because these molecules are strongly bonded with water molecules and thus require lots of energy to be adsorbed. 3TC is about 100 000 times more water soluble than NVP, so other explanations are not needed at this point. One interesting notice is adsorption capacities of R&D wood. Even though Freundlich isotherm gave higher correlation (Appendix 5), Langmuir isotherm had quite good correlation also and it gave the capacity of 200 mg/g for 3TC in MQ water, which is the largest reading among all ACs and pharmaceuticals. Based on removal graphs (Appendix 3), it looks like 3TC really is better adsorbed than for example SMX which can explain higher capacity of R&D wood for 3TC, if Langmuir isotherm is the one followed. However, most points in Langmuir isotherm are focused on small area (Appendix 5), because high AC doses removed adsorbents very efficiently. Removals of lower AC doses have big impact on slope of the trend line, which is used to calculate adsorption capacity.

There is very limited amount of adsorption studies with 3TC, so proper comparison of the results can't be made. Kahilu *et al.* (2022) used hydrochars to adsorb NVP and 3TC. Adsorption capacities of three hydrocars for 3TC were 41, 42 and 42.8 mg/g, which are higher than capacities of ACs in this study. The best hydrochar was made from a coal-sewage blend. Adsorption capacities for 3TC were also constantly smaller than for NVP, which was also seen in this study.

4.4 Comparison of DOC and pharmaceutical adsorptions

When adsorption capacities of pharmaceuticals and DOC are compared, it is possible to find some causalities in adsorption competition. The highest adsorption capacity of DOC was 16.1 mg/g, which is tens of times lower than capacity for TMP, for example. Specific chemical properties of DOC are unknown so only measured

and comparable property is apparent molecular weight. For pharmaceuticals, molecular weight varied between 229.26 – 290.32 g/mol, while two size fractions of the DOC present molecular weights of 400 and 1000 Da, a unit that equals g/mol. Molecules of 400 Da (chromatogram peak V) competes mostly for the same adsorption sites than pharmaceuticals because of almost similar molecular weight. Competition between these molecules is probably based on chemical properties. However, DOC molecules of 1000 Da is about 4 times larger than pharmaceutical molecules, which can cause a difference in adsorption rates. There can be lots of pores where these large DOC molecules can't fit, causing a lower adsorption capacity of AC compared to small pharmaceutical molecules, which can penetrate into smaller and deeper pores. A good example about the influence of pore size is that the highest capacity of 16.1 mg/g for DOC was obtained with R&D peat, which differs from other ACs by its relatively higher volume of macropores (Table 1). Pore volumes of other ACs were dominated by micropores. In addition to the straight competition of adsorption sites, present DOC molecules can decrease the adsorption of pharmaceuticals by blocking the pores. There could be more adsorption sites for pharmaceuticals to occupy, but DOC molecules could have blocked the pore, so some adsorption sites are "wasted", leading to a decreased adsorption capacity for pharmaceutical. Similarly, pore blocking affects also to the adsorption of 400 Da DOC molecules.

4.5 Isotherm discussion

Like stated earlier, it is difficult to decide whether to follow Langmuir or Freundlich isotherm in case of pharmaceuticals. The same problem is common in literature, and in many cases, for example in Jaria *et al.* (2019), Langmuir isotherm is chosen over Freundlich, even though Freundlich isotherm had better correlation in some cases. Choosing only one isotherm allows a better comparison between adsorption capacity values. Comparison of adsorption capacities in this study can be seen in Appendix 6, where all the adsorption capacities are shown, regardless of correlation coefficient of isotherm.

Similar correlation coefficients of Langmuir and Freundlich isotherms wouldn't matter so much if the adsorption capacities were similar. Now we can see that there were big differences in these values (Table 9). Freundlich isotherm predicts multilayer adsorption so higher adsorption capacity could be expected, but it turned out to be opposite situation where Freundlich isotherm gave smaller capacity values. Belhachemi and Addoun (2011) had similar situation, and they concluded that according to this kind of evidence, Freundlich isotherm is not a measure of the total adsorption capacity, but useful for a comparative measure of the adsorption in practice. Freundlich isotherm also works better with large molecules while Langmuir isotherm works with small molecules (Kanô *et al.* 2000). In case of pharmaceuticals, Langmuir could be expected to have better fitting than Freundlich, and in case of for example DOC, Freundlich could be expected to have better fitting, which was also proved in this study (Table 6).

Adsorption process is complex and neither of these isotherms can't describe it in a wide range of adsorbate concentrations (Adamson and Gast 1997; Kanô *et al.* 2000). It is said that Freundlich equation is only useful in the middle range of the isotherm, which means that it doesn't work in extreme adsorbate concentrations (Adamson and Gast 1997; Kanô *et al.* 2000), which maybe have happened in batch experiments in this study. Based on this evidence, following Langmuir isotherm could be justified for calculating adsorption capacity. For easier choice between isotherms, separation factor R_L, of Langmuir isotherm could have been used. An equation of separation factor is derived from equilibrium data as well, and it tells if the adsorption is favorable (Ayawei *et al.* 2017). Knowledge of favorability of adsorption process could make difference between isotherms if it turns out that one mechanism described by some isotherm is clearly less favorable than other, even though correlation coefficients were good, but however, the separation factor was not used in this study.

Although isotherms gave good correlations, in some cases isotherm fittings, at least Langmuir, may be a little rigged because of the high concentration of adsorbent or adsorbate. R&D wood doses were quite high, so plotting points Langmuir isotherm were focused in small area, so points that are further from this concentration of

points have more weight in slope of the trend line and thus y-axis interception, which is used to calculate adsorption capacity (Appendix 5).

With other ACs, concentrations of the adsorbates were varying, and the smallest concentrations turned out to be too small in some cases, because the removal from these low concentrations were complete (Appendix 3; Appendix 4), which led to the same kind of concentration of plotting points in Langmuir isotherm where some points have more weight than others (Appendix 5). This happened especially with TMP but also with SMX and NVP when Filtrasorb TL830 was used. Furthermore, Langmuir and Freundlich isotherms are simple isotherms, and they have limitations in use, which arises discussion about their abilities to describe the adsorption process in reality. For example, Freundlich isotherm is operative only within certain concentration limits, which were maybe exceeded in this study. Adsorption mechanism can also be different in low adsorbent concentrations and different in high adsorbent concentrations (Ayawei *et al.* 2017). That is why mechanism is probably a mix of different mechanisms and does not follow only one isotherm. That is one reason why there can be a lot of uncertainty in adsorption capacities, because they are calculated by two simply isotherms.

4.6 Further needs

It is important to use isotherms to describe the adsorption mechanisms, but for finding out the adsorption capacity of adsorbent, fixed-bed column experiments may be a more reliable method. Fixed-bed column experiments are larger scale experiments, where water is constantly flowing through an adsorbent bed in a column. Column tests can give more realistic results because more realistic contact time and non-ideal mass-transfer. Exhausting of adsorbent is easier to study than in batch experiments and thus easier to calculate adsorption capacity.

All in all, results with R&D activated carbons are good and comparison between commercial carbons show that there is lots of potential for water treatment processes. According to these batch experiments, R&D ACs are promising for further development for use in treatment plants. However, at this point, it is still

unknown how would these ACs perform in a larger scale in granular form. There can be notable differences in for example surface areas between ACs in granular form. Many other factors also come out in the fixed-bed filtrations, like a hardness of AC, a speed of adsorption and long-term durability of AC during regeneration. Although adsorption abilities were high, it would not be cost-effective, if AC granules are crushed because of a low hardness due to very big pore volume. Or if adsorption capacity is high, but it requires longer residence time in water treatment plant than it is realistically possible to have. Next step in development of R&D ACs is to move into the fixed-bed column experiments. New variables are available since it is possible to optimize AC dose, adsorbate concentration, column size or flow rate, for example. The fixed-bed column tests don't still correspond real AC filtration, but they should give more relevant and practical information, like about exhausting of the AC bed.

4 CONCLUSIONS

Batch experiments allowed the studying of adsorption kinetics and adsorption competition between dissolved organic carbon (DOC) and chemically different pharmaceuticals, SMX, TMP, NVP and 3TC, onto activated carbon. Methylene blue (MB) was used as a reference compound since adsorption experiments with MB are considered as a standard method to study and compare different activated carbons. Langmuir (monolayer adsorption) and Freundlich (multilayer adsorption) isotherms were used to describe adsorption mechanisms and to calculate adsorption capacities for MB, DOC and pharmaceuticals in ultrapure MQ water and in Viitaniemi water (VW) which contained DOC.

Adsorption capacities of R&D peat, R&D wood, Filtrasorb TL830 and Silcarbon S835 for MB were 87.7, 107.5, 75.8 and 16.2 mg/g, respectively, given by Langmuir isotherm. Langmuir isotherm gave slightly higher correlation coefficients (R^2) than Freundlich, although correlations by Freundlich isotherm were not bad. Therefore,

adsorption of MB is confined to monolayer. Capacities are not near the best ones in literature but are in the middle range of low-cost adsorbents.

Difference in isotherm fittings was also found in adsorption of DOC. Freundlich isotherm gave clearly higher R^2 values so adsorption is confined to multilayer. Adsorption capacities of R&D peat, R&D wood, Filtrasorb TL830 and Silcarbon S835 for DOC were 16.2, 7.5, 12.3 and 4.3 mg/g, respectively, given by Freundlich isotherm. Adsorption capacities for DOC were considerably lower than for MB and pharmaceuticals. Explanation can be the molecular size of DOC molecules or pore size distribution of the ACs. Two size fractions of DOC in VW were found by HPSEC method, representing the apparent molecular weights of 400 and 1000 Da. Weights are about 2 and 4 times larger than the molecular weights of pharmaceuticals. Molecules of 400 Da were removed faster during first half an hour. Then removal of this size fraction slowed down. With R&D products, the molecular size fraction of 1000 Da ended up being slightly better removed after 24 hours while with commercial products, the size fraction of 400 Da ended up being better removed. It looks like R&D products and commercial products had some different abilities in DOC removal.

In case of pharmaceuticals, it was unclear whether the mechanism follows Langmuir or Freundlich isotherm, because of similar correlation coefficients. Even so, Langmuir isotherm gave higher adsorption capacities than Freundlich, which was problematic. TMP was removed completely from MQ water so capacity could not be accurately estimated. If capacities given by Langmuir are considered like literature proposes, the adsorption capacities of R&D peat, R&D wood and Filtrasorb TL830 for SMX in MQ water were 29.1, 107.5 and 102 mg/g, respectively. For 3TC, the adsorption capacities were 23.5, 200.0, 29.7 mg/g respectively. For NVP, adsorption capacities of R&D peat and Filtrasorb TL830 were 87.0 and 70.9 mg/g, respectively. Adsorption capacity of R&D wood for NVP could not be determined. Silcarbon S835 had considerably lower adsorption capacities for pharmaceuticals than other ACs and Freundlich isotherm appeared to give better correlation coefficients than Langmuir isotherm by using this AC. Adsorption

capacity of R&D wood for 3TC is the highest reading among all numbers, which differs a lot from other ACs so it arises suspicions if it is an out layer.

Experiments in this study showed that adsorption competition between pharmaceuticals and DOC occurs, even though concentrations were in same magnitude, which is not typical for environmental concentrations. DOC molecules can occupy adsorption sites without the advantage of several magnitudes higher concentrations than pharmaceuticals. Removal of pharmaceuticals was lower from VW containing DOC than from ultrapure MQ water in many cases. Capacities of ACs decreased 82 % for SMX at the best, 59 % for 3TC at the best and 80 % for NVP at the best.

The most influencing factor in adsorption seemed to be pKa value of the compound and thus the pH value of the water. TMP was removed most efficiently probably because of its similar pKa constant with pH value (7.2) of water, so it is less ionized than the rest of the compounds, and thus not affected as much by repulsion forces. Other pharmaceuticals were more negatively charged in that pH as well as DOC molecules and probably AC surface too, so repulsion forces surely occurred. NVP was the least water soluble compound, and it had lower pKa value than TMP, and was removed at similar levels than SMX. The most poorly removed compound was 3TC probably because of the clearly the highest water solubility.

Some explanatory factors could be found also from AC properties, like the ash and moisture content of Silcarbon S835, which had the worst performance among all ACs. Pore size distribution can explain for example the great removal of DOC by R&D peat. It had relatively the largest volume of macropores while other ACs had more micropores. There could be more adsorption sites for large DOC molecules to occupy, because of bigger pores. Two ACs under research and development; R&D peat and R&D wood had similar or better performance than commercial Filtrasorb TL830 and Silcarbon S835. Further tests by fixed-bed column test with possibly different pharmaceuticals are executed in future to estimate the abilities of ACs in larger scale filtration.

Based on these results, R&D peat and R&D wood can perform equally or better than commercial carbons. Although adsorption capacities with different kind of ACs in literature may be higher, these results support the use of these carbons in drinking water treatment because of the better performance than used commercial ACs which are already approved in local drinking water treatment plant.

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APPENDIX 1

Calibration graphs of each pharmaceutical in treatments with different ACs.

AC treatment	
R&D wood	
R&D peat and Filtrasorb TL830	
Silcarbon S835	
	SMX TMP 3TC NVP
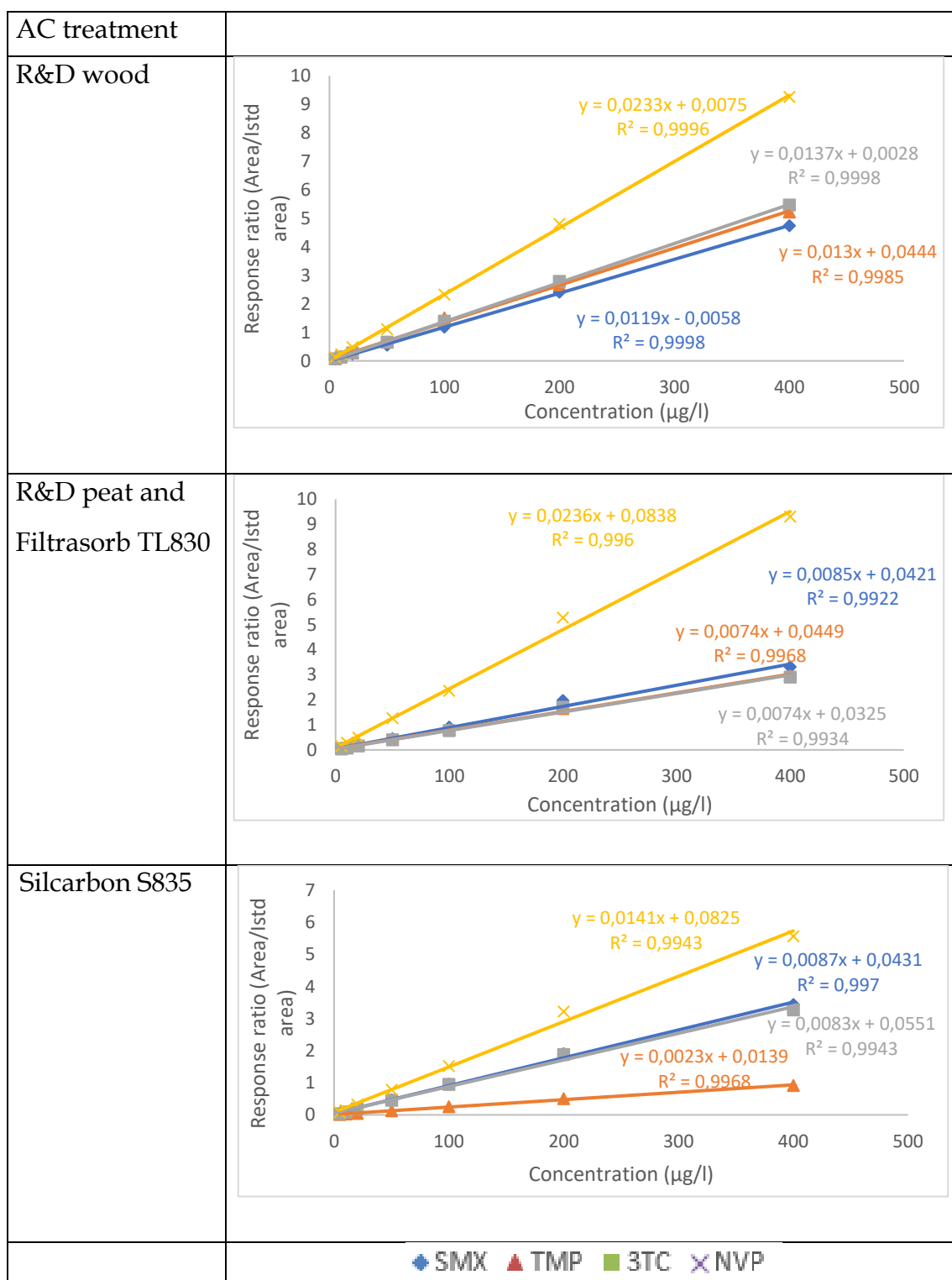
APPENDIX 2

Parameter tables from batch experiments of methylene blue (MB) and dissolved organic carbon (DOC) from Viitaniemi water (VW), where c_i is initial concentration of adsorbate, c_{eq} is equilibrium concentration of adsorbate, x is mass of adsorbate removed from solution, and m is mass of AC.

Parameters for isotherms describing MB adsorption, using Filtrasorb TL830

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	$c_{eq}/(x/m)$	$\ln(c_{eq})$	$\ln(x/m)$
0.82	0.06	0.06	0.01	7.59	0.01	-2.87	2.03
2.00	0.44	0.16	0.01	15.60	0.03	-0.82	2.75
4.14	1.37	0.28	0.01	27.78	0.05	0.31	3.32
6.13	3.16	0.30	0.01	29.64	0.1	1.15	3.39
8.15	4.49	0.37	0.01	36.61	0.12	1.50	3.60
9.77	6.20	0.36	0.01	35.67	0.17	1.82	3.57

Parameters for isotherms describing MB adsorption, using Silcarbon S835

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	$c_{eq}/(x/m)$	$\ln(c_{eq})$	$\ln(x/m)$
0.67	0.30	0.04	0.01	3.74	0.08	-1.22	1.32
1.98	0.91	0.11	0.01	10.66	0.09	-0.09	2.37
4.24	2.83	0.14	0.01	14.09	0.20	1.04	2.65
6.29	4.75	0.15	0.01	15.39	0.31	1.56	2.73
8.34	6.45	0.19	0.01	18.93	0.34	1.86	2.94
9.86	8.00	0.19	0.01	18.67	0.43	2.08	2.93

Parameters for isotherms describing DOC adsorption from VW, using R&D wood

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	$c_{eq}/(x/m)$	$\ln(c_{eq})$	$\ln(x/m)$
2.52	1.44	0.27	0.025	10.78	0.13	0.36	2.38
2.52	0.47	0.51	0.05	10.25	0.05	-0.76	2.33
2.52	0.71	0.45	0.075	6.02	0.12	-0.34	1.80
2.52	0.57	0.49	0.1	4.87	0.12	-0.57	1.58
2.52	0.63	0.47	0.125	3.78	0.17	-0.46	1.33
2.52	0.52	0.50	0.15	3.34	0.15	-0.66	1.21

Parameters for isotherms describing DOC adsorption from VW, using R&D peat

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	c_{eq} /(x/m)	$\ln(c_{eq})$	$\ln(x/m)$
2.52	1.27	0.31	0.025	12.51	0.10	0.24	2.53
2.52	0.69	0.46	0.05	9.13	0.08	-0.37	2.21
2.52	0.55	0.49	0.075	6.58	0.08	-0.60	1.88
2.52	0.48	0.51	0.1	5.09	0.09	-0.73	1.63
2.52	0.42	0.52	0.125	4.20	0.10	-0.87	1.43
2.52	0.37	0.54	0.15	3.58	0.10	-0.99	1.27

Parameters for isotherms describing DOC adsorption from VW, using Filtrasorb TL830

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	c_{eq}/(x/m)	$\ln(c_{eq})$	$\ln(x/m)$
2.82	1.78	0.26	0.0125	21.00	0.08	0.57	3.04
2.82	1.27	0.39	0.025	15.52	0.08	0.24	2.74
2.82	0.65	0.54	0.05	10.85	0.06	-0.43	2.38
2.82	0.55	0.57	0.075	7.54	0.07	-0.59	2.02
2.82	0.62	0.55	0.1	5.50	0.11	-0.48	1.71

Parameters for isotherms describing DOC adsorption from VW, using Silcarbon S835

c_i (mg/l)	c_{eq} (mg/l)	x (mg)	m (g)	x/m (mg/g)	c_{eq}/(x/m)	$\ln(c_{eq})$	$\ln(x/m)$
2.82	2.28	0.14	0.0125	10.80	0.21	0.82	2.38
2.82	1.94	0.22	0.025	8.76	0.22	0.66	2.17
2.82	1.45	0.34	0.05	6.85	0.21	0.37	1.92
2.82	1.24	0.40	0.075	5.27	0.24	0.21	1.66
2.82	1.03	0.45	0.1	4.48	0.23	0.03	1.50

APPENDIX 3

Removal graphs of pharmaceuticals with each activated carbon.

In batch experiments with R&D wood, initial concentrations of pharmaceuticals were 2 mg/l each. Different colors indicate doses of R&D wood per 100 ml solution. Doses (m) of activated carbons were 0.01, 0.025, 0.05, 0.075, 0.1 g.

For R&D peat, Filtrasorb TL830 and Silcarbon S835, dose was 0.025 g and initial concentration of pharmaceuticals varied. Codes C1, C2, C3, C4 and C5 are parallel treatments, where initial concentration of pharmaceutical is increasing in this order. Initial concentration (time = 0) may vary slightly between pharmaceuticals and AC treatments although they have same code.

Removal of pharmaceuticals from MQ water and VW, using R&D wood

	MQ	VW
SMX		
TMP		

Legend: 0.01 g, 0.025 g, 0.05 g, 0.075 g, 0.1 g

Removal of pharmaceuticals from MQ water and VW, using R&D wood

Removal of pharmaceuticals from MQ water and VW, using R&D peat

	MQ	VW
SMX		
TMP		

Legend: C1, C2, C3, C4, C5
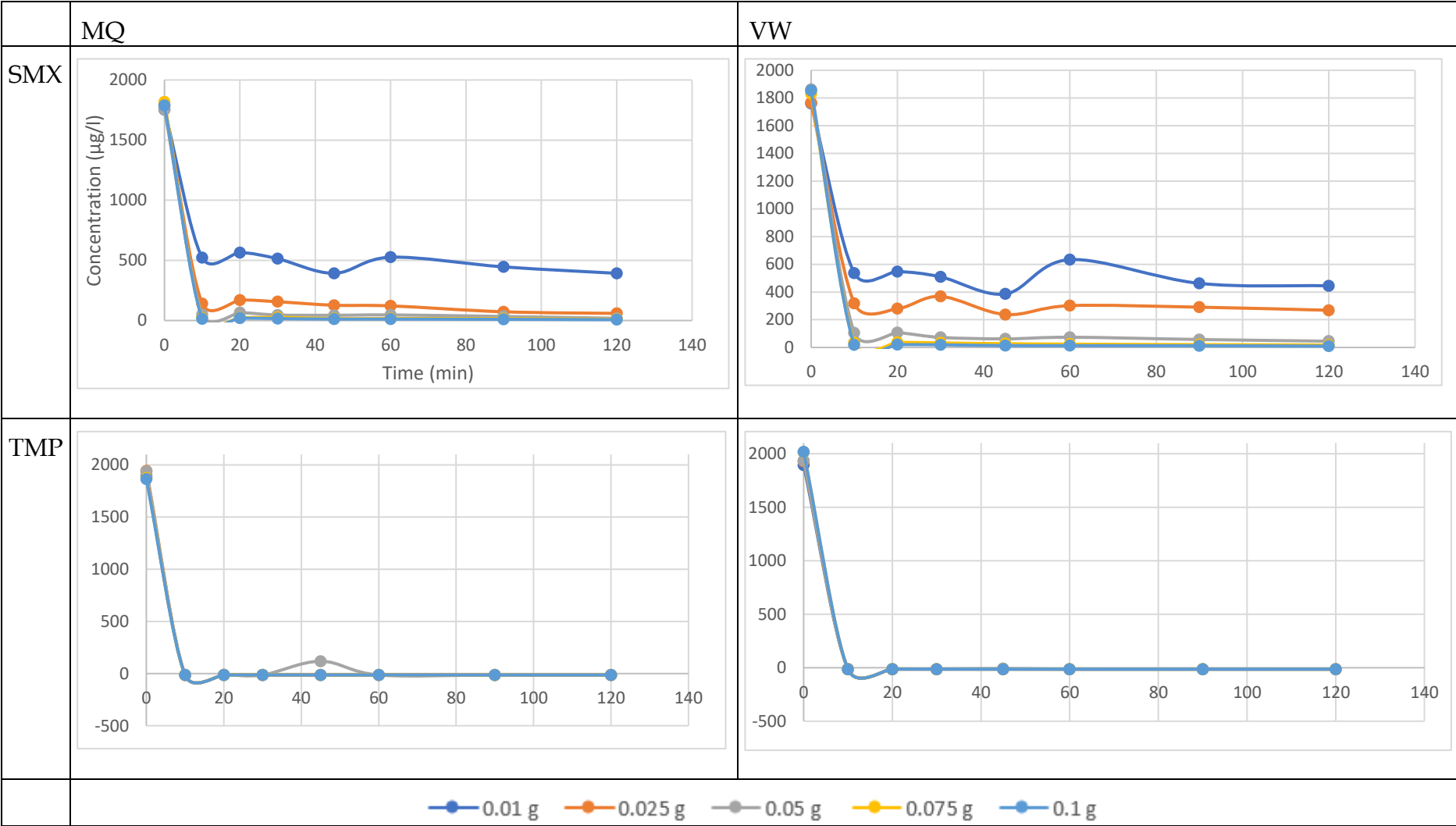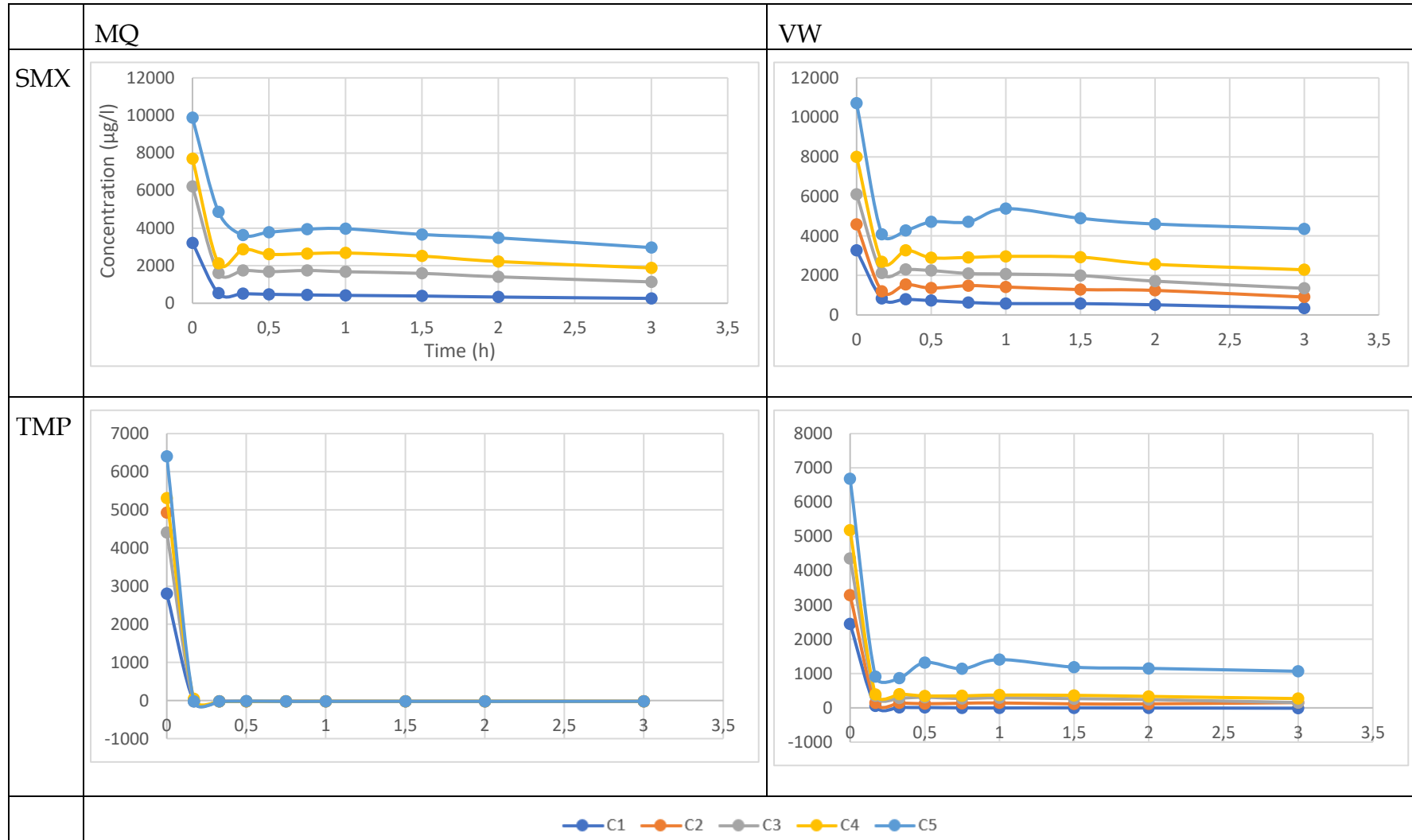
Removal of pharmaceuticals from MQ water and VW, using R&D peat

Removal of pharmaceuticals from MQ water and VW, using Filtrasorb TL830
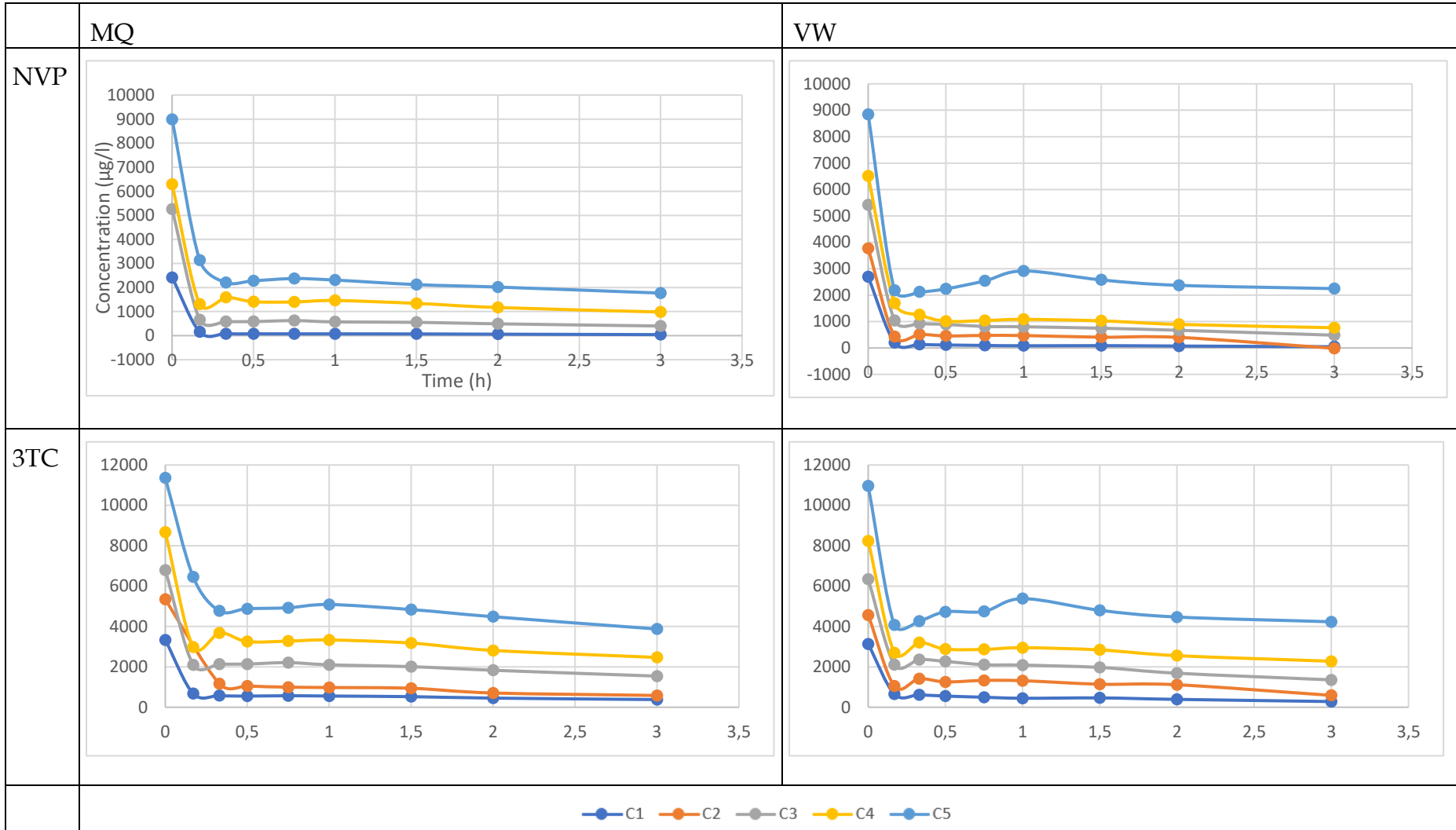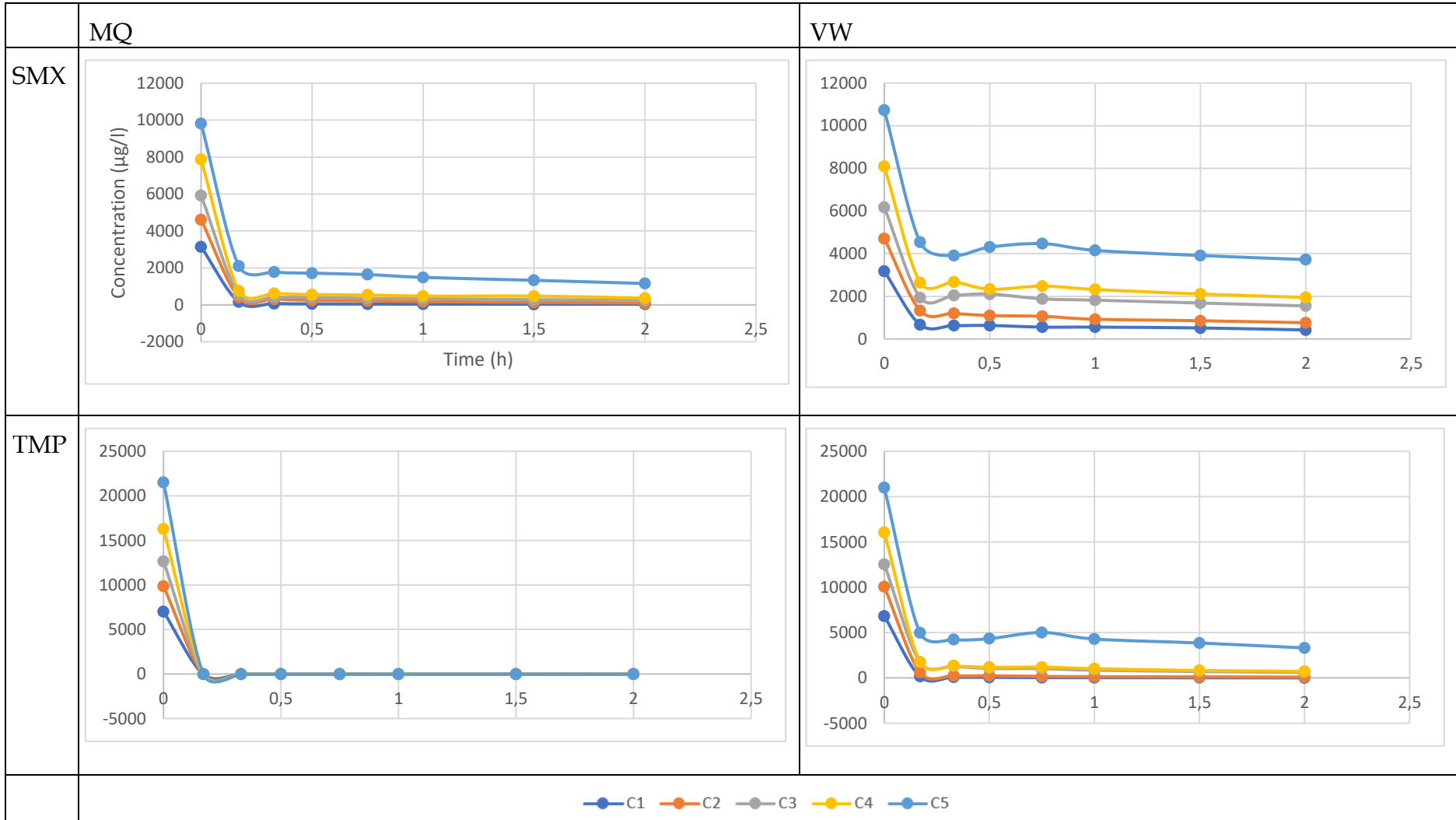
Removal of pharmaceuticals from MQ water and VW, using Filtrasorb TL830

Removal of pharmaceuticals from MQ water and VW, using Silcarbon S835
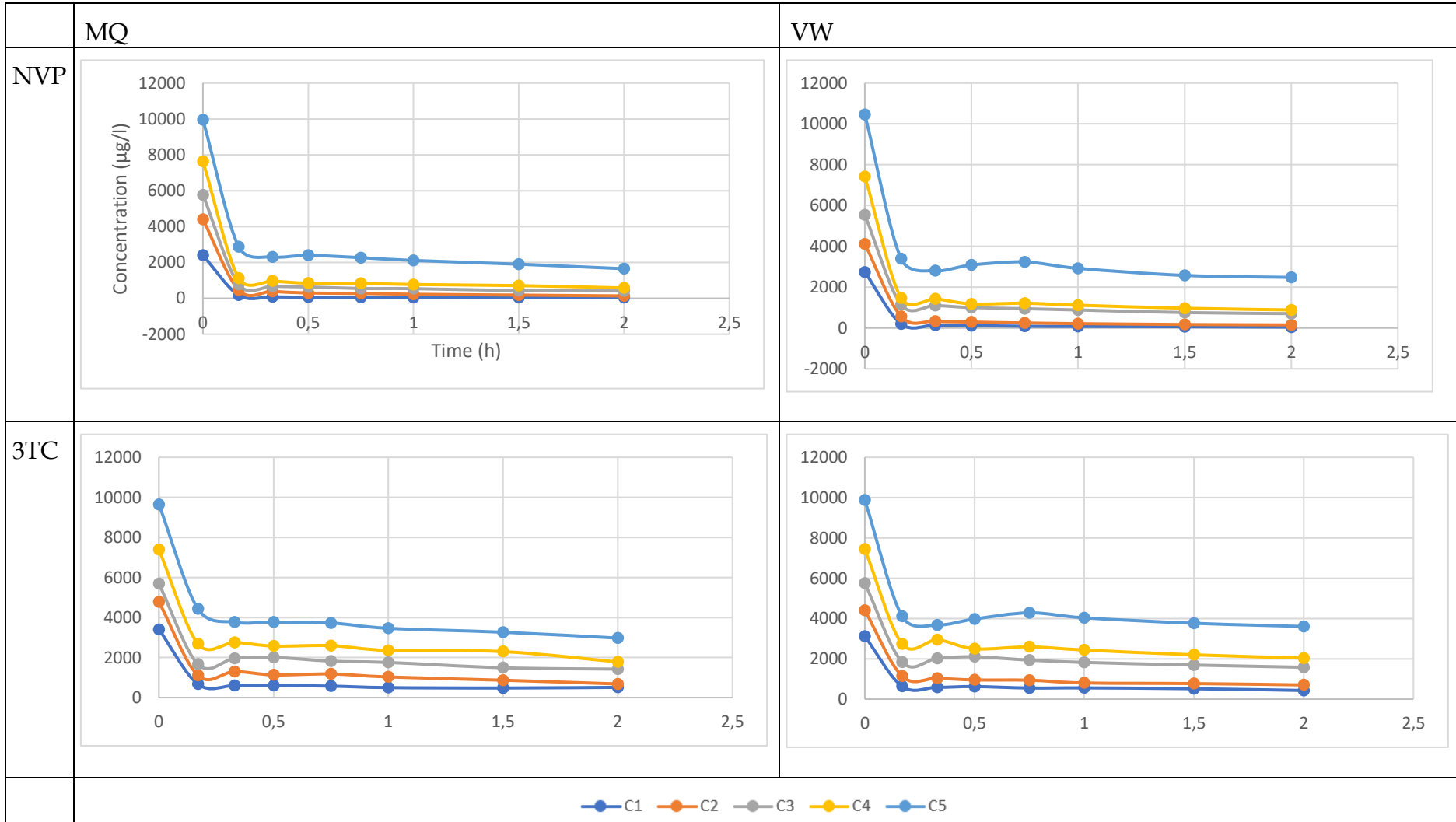
Removal of pharmaceuticals from MQ water and VW, using Silcarbon S835
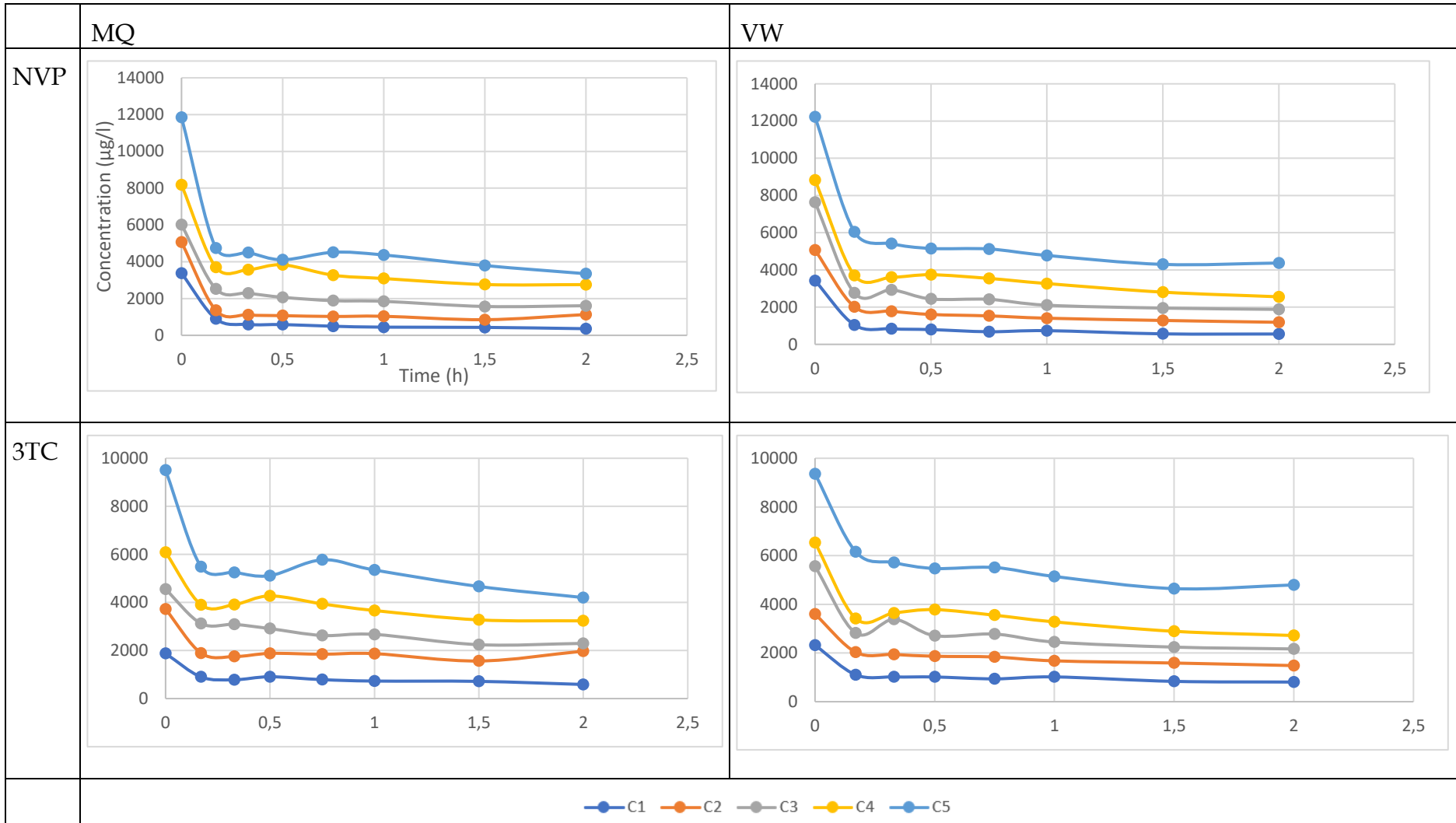
APPENDIX 4

Removal of pharmaceuticals in MQ water and in water from Viitaniemi (VW) at equilibrium point, using R&D peat (0.025 g/100 ml). The measured concentration of DOC in VW was 3.6 mg/l.

Compound	Matrix	c_i (mg/l)	c_e (mg/l)	Removal (%)
SMX	MQ	3.2	0.5	83.4
		6.2	1.6	74.2
		7.7	2.1	72.4
		9.9	4.9	63.3
	VW	3.3	0.8	79.2
		4.6	1.2	77.1
		6.1	2.1	66.8
		8.0	2.7	67.2
		10.7	3.6	62.8
TMP	MQ	2.8	< 0.1	> 99.9
		4.9	< 0.1	> 99.9
		4.4	< 0.1	> 99.9
		5.3	< 0.1	> 99.9
		6.4	< 0.1	> 99.9
	VW	2.4	0.1	97.5
		3.3	0.2	95.4
		4.4	0.4	91.9
		5.2	0.4	92.5
		6.7	0.9	86.4
3TC	MQ	3.3	0.7	79.6
		5.3	1.2	78.3
		6.8	2.1	69.1
		8.7	3.0	65.6
		11.3	4.8	58.0
	VW	3.1	0.7	79.2
		4.6	1.0	77.1
		6.3	2.1	66.8
		8.2	2.7	67.2
		11.0	4.1	62.8
NVP	MQ	2.4	0.2	93.6
		5.3	0.7	87.5
		6.3	1.3	79.2
		9.0	2.2	75.4
	VW	2.7	0.2	92.5
		3.8	0.4	88.5
		5.4	1.0	80.9
		6.5	1.7	74.0
		8.8	2.2	75.3

Removal of pharmaceuticals in MQ water and in water from Viitaniemi (VW) at equilibrium point, using Filtrasorb TL830 (0.025 g/100 ml). The measured concentration of DOC in VW was 3.6 mg/l.

Compound	Matrix	c_i (mg/l)	c_e (mg/l)	Removal (%)
SMX	MQ	3.1	0.2	95.0
		4.6	0.4	91.1
		5.9	0.6	90.6
		7.9	0.8	90.3
		9.8	2.1	78.5
	VW	3.2	0.7	79.0
		4.7	1.3	71.7
		6.2	1.9	68.5
		8.1	2.6	67.3
		10.7	4.5	57.7
TMP	MQ	6.9	< 0.1	> 99.9
		9.8	< 0.1	> 99.9
		12.6	< 0.1	> 99.9
		16.3	< 0.1	> 99.9
		21.5	< 0.1	> 99.9
	VW	6.8	0.2	97.6
		10.1	0.6	93.9
		12.5	1.7	86.3
		16.0	1.8	89.0
		21.0	5.0	76.3
3TC	MQ	3.4	0.7	80.3
		4.8	1.1	76.8
		5.7	1.7	70.7
		7.4	2.7	63.5
		9.6	3.8	60.9
	VW	3.1	0.6	79.7
		4.4	1.1	74.2
		5.8	1.8	68.0
		7.4	2.7	63.2
		9.9	4.1	58.4
NVP	MQ	2.4	0.2	92.5
		4.4	0.5	89.5
		5.8	0.8	86.5
		7.6	1.1	85.3
		9.9	2.9	71.1
	VW	2.7	0.2	92.6
		4.1	0.6	86.2
		5.5	1.1	79.3
		7.4	1.5	80.2
		10.4	3.4	67.5
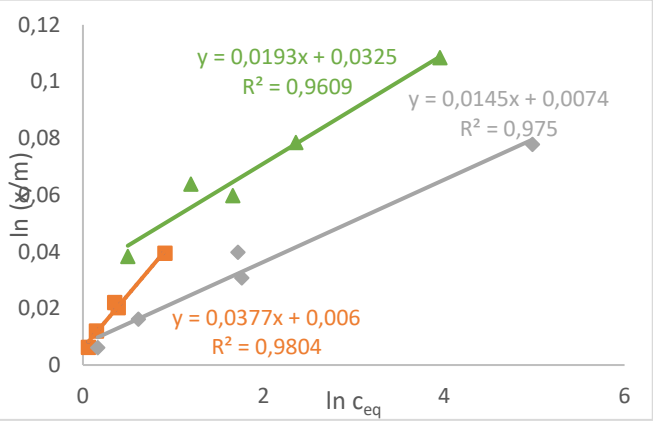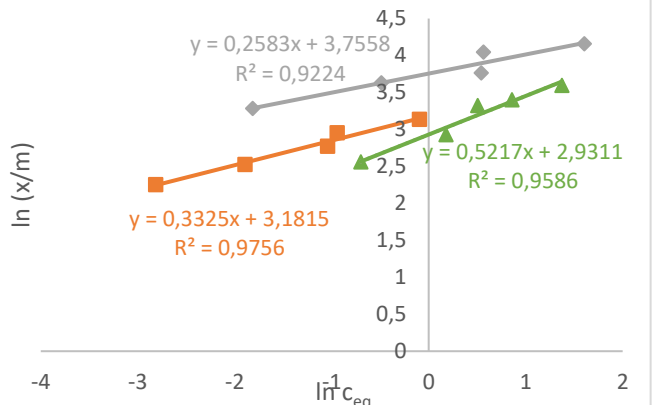
Removal of pharmaceuticals in MQ water and in water from Viitaniemi (VW) at equilibrium point, using Silcarbon S835 (0.025 g/100 ml). The measured concentration of DOC in VW was 3.0 mg/l.
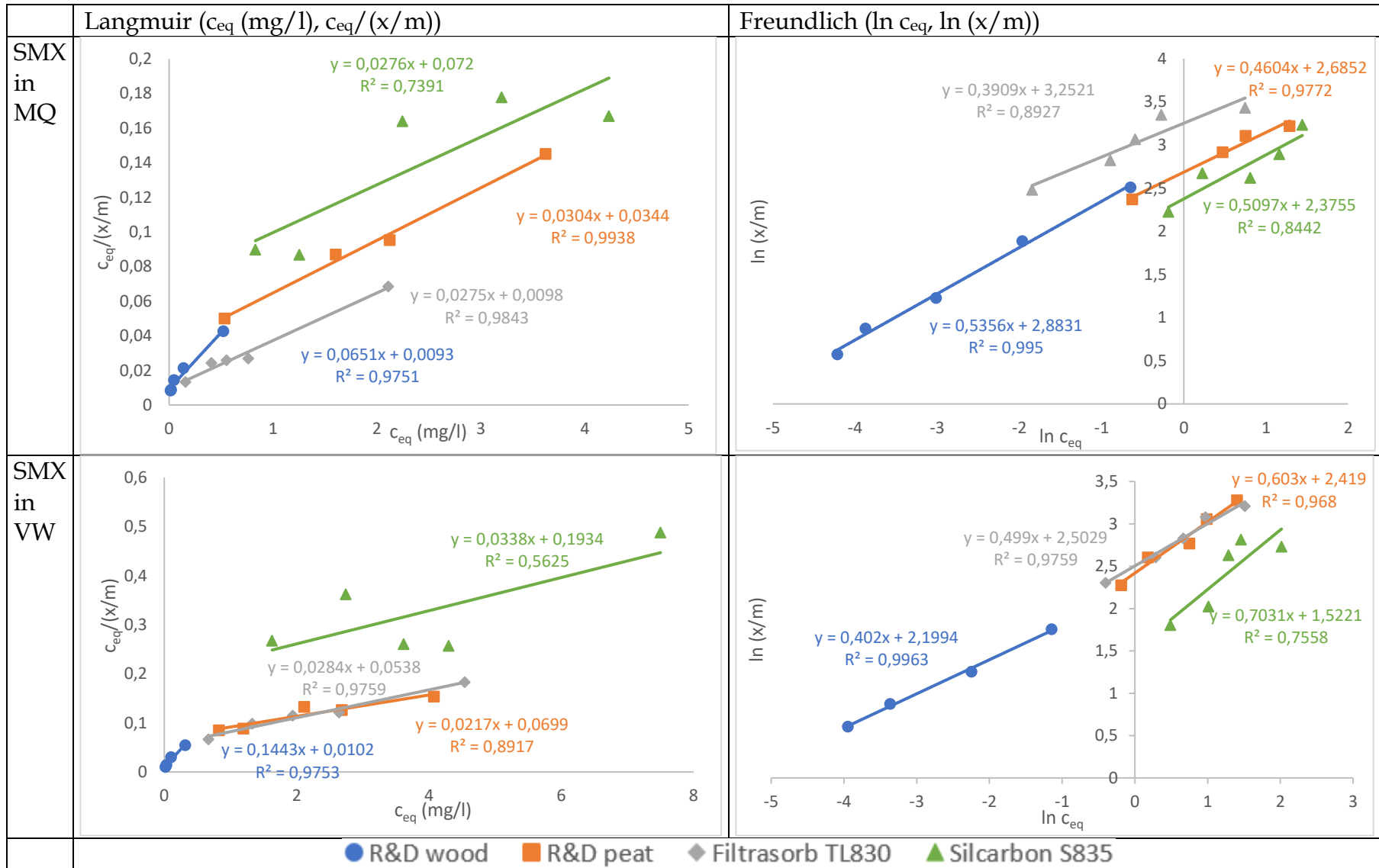
Compound	Matrix	c_i (mg/l)	c_e (mg/l)	Removal (%)
SMX	MQ	3.2	0.8	73.6
		4.9	1.3	74.3
		5.7	2.2	60.4
		7.7	3.2	58.5
		10.6	4.2	60.0
	VW	3.2	1.6	48.3
		4.6	2.7	40.8
		7.1	3.6	49.0
		8.5	4.3	49.3
		11.3	6.8	39.8
TMP	MQ	3.9	< 0.1	> 99.9
		6.3	< 0.1	> 99.9
		7.6	< 0.1	> 99.9
		9.6	< 0.1	> 99.9
		14.2	< 0.1	> 99.9
	VW	3.7	0.5	86.7
		5.9	1.2	79.7
		8.6	1.7	80.7
		9.9	2.4	76.1
		13.1	4.0	69.7
3TC	MQ	1.9	0.9	52.0
		3.7	1.9	49.1
		4.5	3.1	31.3
		6.1	3.9	35.9
		9.5	5.5	42.3
	VW	2.3	1.1	52.4
		3.6	2.0	43.5
		5.6	2.8	49.3
		6.5	3.4	47.7
		9.4	5.7	38.9
NVP	MQ	3.4	0.9	73.5
		5.1	1.4	73.1
		6.0	2.5	58.0
		8.2	3.7	54.7
		11.8	4.7	59.9
	VW	3.4	1.0	69.6
		5.1	2.0	60.2
		7.6	2.8	63.8
		8.8	3.7	58.0
		12.2	5.4	55.8

APPENDIX 5

Model fits of measurement data from batch experiments with pharmaceuticals in Langmuir and Freundlich isotherms. Isotherm fittings are shown separately for each pharmaceutical in MQ and VW. Correlation coefficients (R^2) are shown in graphs. Isotherm with higher R^2 is considered to describe adsorption mechanism better.

	Langmuir (c_{eq} (mg/l), $c_{eq}/(x/m)$)	Freundlich ($\ln c_{eq}$, $\ln (x/m)$)
SMX in MQ		
SMX in VW		

Legend: ● R&D wood ■ R&D peat ◆ Filtrasorb TL830 ▲ Silcarbon S835

SMX in MQ — Langmuir:
$y = 0.0276x + 0.072$, $R^2 = 0.7391$
$y = 0.0304x + 0.0344$, $R^2 = 0.9938$
$y = 0.0275x + 0.0098$, $R^2 = 0.9843$
$y = 0.0651x + 0.0093$, $R^2 = 0.9751$

SMX in MQ — Freundlich:
$y = 0.4604x + 2.6852$, $R^2 = 0.9772$
$y = 0.3909x + 3.2521$, $R^2 = 0.8927$
$y = 0.5097x + 2.3755$, $R^2 = 0.8442$
$y = 0.5356x + 2.8831$, $R^2 = 0.995$

SMX in VW — Langmuir:
$y = 0.0338x + 0.1934$, $R^2 = 0.5625$
$y = 0.0284x + 0.0538$, $R^2 = 0.9759$
$y = 0.0217x + 0.0699$, $R^2 = 0.8917$
$y = 0.1443x + 0.0102$, $R^2 = 0.9753$

SMX in VW — Freundlich:
$y = 0.603x + 2.419$, $R^2 = 0.968$
$y = 0.499x + 2.5029$, $R^2 = 0.9759$
$y = 0.7031x + 1.5221$, $R^2 = 0.7558$
$y = 0.402x + 2.1994$, $R^2 = 0.9963$

	Freundlich (ln c_{eq}, ln (x/m))
TMP in MQ	
TMP in VW	

	Langmuir (c_{eq} (mg/l), $c_{eq}/(x/m)$)	Freundlich (ln c_{eq}, ln (x/m))
3TC in MQ		
3TC in VW		

Langmuir (3TC in MQ):
- y = 0,0346x + 0,2593, R² = 0,215
- y = 0,0405x + 0,0337, R² = 0,9989
- y = 0,0944x + 0,005, R² = 0,9837
- y = 0,0295x + 0,0426, R² = 0,9876

Freundlich (3TC in MQ):
- y = 0,4413x + 2,6228, R² = 0,9434
- y = 0,3301x + 2,5871, R² = 0,957
- y = 0,336x + 2,4245, R² = 0,9853
- y = 0,647x + 1,3942, R² = 0,7483

Langmuir (3TC in VW):
- y = 0,0461x + 0,1695, R² = 0,7712
- y = 0,0326x + 0,0501, R² = 0,9787
- y = 0,1195x + 0,0074, R² = 0,8829
- y = 0,0246x + 0,0546, R² = 0,9146

Freundlich (3TC in VW):
- y = 0,5293x + 2,5448, R² = 0,9694
- y = 0,4434x + 2,4981, R² = 0,9982
- y = 0,2809x + 2,1088, R² = 0,9243
- y = 0,6359x + 1,5549, R² = 0,8392

Legend: ● R&D wood   ■ R&D peat   ◆ Filtrasorb TL830   ▲ Silcarbon S835

Langmuir (c_{eq} (mg/l), $c_{eq}/(x/m)$))	Freundlich (ln c_{eq}, ln (x/m))
NVP in MQ	

NVP in MQ — Langmuir:
y = 0,0264x + 0,0774, R² = 0,6299
y = 0,0393x + 0,0115, R² = 0,9986
y = 0,0301x + 0,0141, R² = 0,9931
y = 0,078x + 0,0009, R² = 0,9971

NVP in MQ — Freundlich:
y = 0,3175x + 2,8842, R² = 0,918
y = 0,4319x + 3,043, R² = 0,9182
y = 0,2366x + 2,6628, R² = 0,976
y = 0,4936x + 2,3773, R² = 0,7859

NVP in VW — Langmuir:
y = 0,0251x + 0,0901, R² = 0,9043
y = 0,0298x + 0,021, R² = 0,9704
y = 0,034x + 0,0186, R² = 0,9116
y = 0,0848x + 0,0028, R² = 0,9102

NVP in VW — Freundlich:
y = 0,378x + 2,9011, R² = 0,9629
y = 0,3682x + 2,8797, R² = 0,9501
y = 0,2419x + 2,5404, R² = 0,9731
y = 0,5797x + 2,227, R² = 0,9271

Legend: ● R&D wood   ■ R&D peat   ◆ Filtrasorb TL830   ▲ Silcarbon S835

APPENDIX 6

Adsorption capacities (mg/g) for pharmaceuticals in MQ water and VW for every AC, calculated by Langmuir and Freundlich isotherms.

Compound	R&D peat		R&D wood		Filtrasorb TL830		Silcarbon S835	
	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich
SMX (MQ)	29.1	14.7	107.5	17.9	102.0	25.8	13.9	10.8
(VW)	14.3	11.2	98.0	9.0	18.6	12.2	5.2	4.6
TMP (MQ)	-	-	-	-	-	-	-	-
(VW)	192.3	24.7	-	-	135.1	42.8	30.8	18.7
3TC (MQ)	23.5	13.8	200.0	10.9	29.7	13.3	-	4.0
(VW)	18.3	12.7	135.1	8.2	20.0	12.2	5.9	4.7
NVP (MQ)	87.0	17.9	-	14.3	70.9	21.0	12.9	10.8
(VW)	53.8	17.8	357.1	12.7	47.6	18.2	11.1	9.3