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Towards application of activated carbon treatment for pharmaceutical removal in municipal wastewater

Victor Kårelid
M.Sc.

KTH Royal Institute of Technology
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KTH Royal Institute of Technology
School of Biotechnology
AlbaNova University Center
106 91 Stockholm
Sweden

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Abstract

Many pharmaceuticals are found in municipal wastewater effluents due to their persistence in the human body as well as in conventional wastewater treatment processes. This discharge to the environment can lead to adverse effects in aquatic species, such as feminization of male fish. During the past decade, these findings have spawned investigations and research into suitable treatment technologies that could severely limit the discharge. Adsorption onto activated carbon has been identified as one of the two main technologies for implementation of (future) full-scale treatment.

Recent research has put a closer focus on adsorption with powdered activated carbon (PAC) than on granular activated carbon (GAC). Studies where both methods are compared in parallel operation are thus still scarce and such evaluation in pilot-scale was therefore a primary objective of this thesis. Furthermore, recirculation of PAC can be used to optimize the treatment regarding the carbon consumption. Such a setup was evaluated as a separate treatment stage to comply with Swedish wastewater convention. Additionally, variation of a set of process parameters was evaluated.

During successive operation at three different wastewater treatment plants an overall pharmaceutical removal of 95% could consistently be achieved with both methods. Furthermore, treatment with GAC was sensitive to a degraded effluent quality, which severely reduced the hydraulic capacity. Both treatment methods showed efficient removal of previously highlighted substances, such as carbamazepine and diclofenac, however in general a lower adsorption capacity was observed for GAC. By varying the input of process parameters, such as the continuously added dose or the contact time, during PAC treatment, a responsive change of the pharmaceutical removal could be achieved. The work in this thesis contributes some valuable field experience towards wider application of these treatment technologies in full-scale.

Keywords: advanced wastewater treatment, granular activated carbon, powdered activated carbon, municipal wastewater treatment, pharmaceutical removal

Sammanfattning

Många läkemedelsrester återfinns i avloppsvattenutlopp på grund av deras beständighet i den mänskliga kroppen samt i konventionell avloppsvattenrening. Detta utsläpp till miljön kan leda till negativa effekter hos vattenlevande arter, såsom feminisering av hanfiskar. Under det senaste decenniet har dessa fynd lett till undersökningar och forskning för att ta fram lämpliga reningstekniker som skulle kunna begränsa dessa utsläpp markant. Adsorption på aktivt kol har identifierats som en av de två främsta teknikerna för (framtida) implementering i fullskala.

Aktuell forskning har lagt större fokus på adsorption med pulveriserat aktivt kol (PAC) än på granulerat aktivt kol (GAC). Studier där båda metoderna jämförts i parallell drift är därför fortfarande sällsynta och en sådan utvärdering i pilotskala var därför ett primärt syfte med denna avhandling. Vid rening med PAC kan kolet återcirkuleras för att optimera behandlingen med avseende på kolförbrukningen. I enlighet med svensk avloppsvatten-sed utvärderades en sådan process i ett separat reningssteg. Dessutom var variationen av en uppsättning av processparametrar utvärderades.

Under drift vid tre på varandra följande avloppsreningsverk uppnåddes genomgående 95% total avskiljning av läkemedelsrester med båda metoderna. Vidare kunde visas att rening med GAC var känslig mot en försämrad utloppskvalitet, vilket ledde till en kraftigt minskad hydraulisk kapacitet. Båda reningsmetoderna gav en effektiv avskiljning av tidigare uppmärksammade substanser såsom karbamazepin och diklofenak. I allmänhet observerades dock en lägre adsorptionskapacitet för GAC. Genom att variera den kontinuerliga dosen eller kontakttiden vid PAC-rening kunde avskiljningen lätt påverkas. Arbetet i denna avhandling bidrar med fälterfarenhet emot en bredare tillämpning av dessa reningstekniker i full skala.

Nyckelord: avancerad avloppsvattenrening, pulveriserat aktivt kol, granulerat aktivt kol, kommunal avloppsvattenrening, läkemedelsrening

List of publications

This thesis is based on the following publications, which are referred to in the text by their roman numerals:

I.

Kårelid, V., Larsson, G., Björlenius, B. (2016) Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. Submitted

II.

Kårelid, V., Larsson, G., Björlenius, B. (2016) Effects of recirculation in a three-tank pilot-scale system for pharmaceutical removal with powdered activated carbon. Submitted

Contribution to papers:

I: VK wrote the manuscript and performed the experiments together with BB.

II: VK wrote the manuscript and was together with BB responsible for the original concept, the planning and execution of the experiments.

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Introduction

Organic micropollutants are ubiquitously found in the effluent wastewater of municipal wastewater treatment plants at concentrations in ng-µg/L range (thus the name), due to various human caused discharge (1–4). While negative effects of many of these substances were frequently identified in the environment, it was only two decades ago since the potential adverse effects due to the presence of pharmaceuticals were discovered (5). This discovery as well as the development of reliable quantification technologies, through which concentrations can be determined down to or below a few ng/L in complex matrices (6–8), accelerated the amount of research performed in this field. To this date, the endocrine disrupting effects of steroid hormones in fish and amphibians are perhaps considered most alarming (9, 10). Adverse effects in various aquatic species have however also been determined to occur at or within a magnitude of environmentally prevalent concentrations of substances belonging to other pharmaceutical classes (11–13). Moreover, from a holistic perspective the discharge of antibiotics is of specific concern in regard to the increasing prevalence of antibiotic resistance (14).

The main entry route for pharmaceuticals into the environment is with effluent wastewater, primarily through excretion following human consumption, but also through careless disposal of unused or expired drugs and with hospital wastewater (15). Another route is discharges from pharmaceutical manufacturing plants, which has been determined globally although more prominently in low-income countries (16). The removal of pharmaceuticals in conventional wastewater treatment can vary considerably depending on substance properties and on the applied treatment technologies (4, 17, 18). For example, the use of biological treatment with nitrogen removal can improve biodegradation of pharmaceuticals, but even then the measured concentrations in the effluent wastewater can reach several µg/L for a variety of substances (19).

The increased knowledge base of the occurrence and effects of pharmaceuticals that are discharged from wastewater treatment has led to the development of additional treatment technologies. An assortment of technologies has been suggested, based on previous success in related applications such as purification of drinking water. The two methods that have been most frequently proposed for full scale application are adsorption with activated carbon and oxidation with ozone, due to their broad removal efficiencies and relatively low cost (20–22). Both technologies have an upside on the other; ozonation is estimated to be the more economically feasible alternative, while activated carbon has the potential for complete removal of substances without formation of potentially toxic by-products (23, 24). Both have

also shown considerably weaker removal than the other method for diverse sets of commonly occurring pharmaceuticals (21, 22). Although both technologies show great promise, in this thesis the practical work was limited to applications of activated carbon adsorption.

Treatment with activated carbon is traditionally presented in two different forms, either as filtration with the granular variety or as continuous dosing in mixed tanks with the powdered variety. While both variants are well suited for pharmaceutical removal, each has a few advantages over the other. For example, operation with granular activated carbon (GAC) simultaneously serves as a particle retention step and the used product can be regenerated (25). On the other hand, the loading capacity of powdered activated carbon (PAC) is believed to be superior due to the smaller grain size (26). Few studies have however compared the two methods under identical conditions in the large scale (27), as well as with regard different effluent qualities. Thus, in this work we set out to compare both methods in parallel operation at different wastewater treatment plants. Furthermore, the influence of a set of process parameters was evaluated for treatment with PAC.

Pharmaceuticals in municipal wastewater

There are today ~6500 approved pharmaceutical drugs world-wide that can treat countless diseases and illnesses (28). The global sales in 2015 amounted to 900 billion USD, and the steady growth which to a significant part takes place in emerging markets (e.g. China, Brazil and India) reveals that this is an industry to be reckoned with in the foreseeable future (29). Although the benefits of the availability of potent medication are obvious from a health perspective, this widespread use has within the last few decades been shown to have the potential to affect the environment.

Effects in aquatic species

The first sign that pharmaceuticals could cause an effect in the environment due to human consumption was in the 1990s when Purdom *et al.* showed that estrogenic effects occurred in rainbow trout, which had been intentionally placed outside of the effluents of wastewater treatment plants (WWTPs) (5). The causing agents were later identified as the natural hormone estradiol and estrone, and the synthetic hormone ethinylestradiol, an active substance in contraceptives (30). In particular, the significant potency of the latter substance has been proven in many studies (31–33), perhaps most notably by the near extinction caused by feminization of male fathead minnow from long-term exposure of ethinylestradiol concentrations of 5-6 ng/L (34). Another group of hormones that have shown high risk are synthetic progestogens, which can also be found in contraceptives. In particular, levonorgestrel was shown to inhibit reproduction in both fish and frogs at low ng/L-range (35, 36). Concern has also been raised regarding mixture effects from simultaneous exposure to multiple substances (9). An additive effect has been confirmed to occur from estrogens with the same mechanism of action (37, 38). Similar observations were also reported for anti-inflammatory drugs and beta-blockers (39, 40).

Regarding other pharmaceutical classes there are several studies pointing to at least moderate adverse effects in exposed species. Environmentally relevant concentrations of the anti-inflammatory drug diclofenac was shown to change gene expression in rainbow trout (11, 41), the anti-depressant oxazepam was shown to cause change of behavioral patterns in wild European perch (12). Moreover, concern has been raised surrounding environmentally persistent drugs, e.g. carbamazepine, which may cause adverse effects in wastewater recipients with poor dilution (42). In general, effect studies have intuitively been focused on species which share drug targets in humans. One example is the beta-

adrenergic receptors common in various fish species. Adverse effects due to exposure of environmental levels of different beta-blockers have however been found to be unlikely (43).

Moreover, the development of antibiotic resistant bacteria is of significant global concern. Although overuse and misuse of antibiotics may be the main routes for this development, some studies report that antibiotics present in wastewater treatment could be an alternate route (44, 45). It was for example indicated that antibiotic resistance genes accumulated during wastewater treatment and subsequently was released to the recipient due to exposure of antibiotics to microorganisms in the biological treatment stage (45).

Apart from the adverse effects of hormones, the most alarming reports of pharmaceuticals in the aquatic ecosystem is perhaps findings of extremely high concentrations in rivers of low income countries, such as India and Pakistan (46–49). In some instances the concentrations were lethal to higher organisms (48, 49). These findings were however not primarily caused by direct human consumption but rather by discharges from pharmaceutical manufacturing plants. Although this type of pollution may be easier to counter since there is specific accountability, it can serve as a friendly reminder to the reader that the work in this thesis is just part of the solution in a global perspective.

Removal in existing wastewater treatment plants

Municipal WWTPs that are subjected to the strictest discharge limits today employ mechanical, chemical and biological treatment for reduction of organic matter (often measured as chemical and biological oxygen demand, COD and BOD), phosphorous and nitrogen compounds, as well as suspended particulate matter (50). Mechanical treatment is located in the beginning and end of the plant, for separation of large solids, and for retention of suspended solids (SS), respectively. Chemical treatment can be employed for precipitation of phosphorous; this forms a chemical sludge, which subsequently is separated in the so-called primary sedimentation step. The treatment continues in the biological treatment step, traditionally performed with the activated sludge process, where ammonium is converted by microorganisms present in the sludge to nitrogen gas. Thus, both primary sedimentation and the activated sludge process generates a solid waste, sludge, which is eventually separated from the liquid phase. Organic compounds in the wastewater, such as pharmaceuticals, can partition in this sludge, i.e. through sorption, although to a varying degree depending on the properties of each compound (51). The octanol-water distribution coefficient, log D, was shown to predict sorption quite well, i.e. a higher log D led to better sorption (52). Log D, takes into consideration both ionizable and non-ionizable compounds and is dependent on the pH of the solution, thus sorption can

change over the course of the treatment stages since optimal pH-ranges differ for the chemical (~5.5-7.5) and biological processes (~7-9) (53, 54). In table 1 the partitioning in sludge through sorption is presented for a few commonly quantified pharmaceuticals as determined by Hörsing *et al.* (55). For these substances, sorption was predominantly insignificant.

Removal of organic matter also occurs in the biological treatment due to the activity of microbial communities in the activated sludge, referred to as biodegradation. For different substances, this naturally varies with their affinity for biodegradation, however in general the process is dependent on the efficiency and diversity of the microorganisms, which in turn is affected by the sludge age (the mean retention time of the sludge), and the pH and temperature of the wastewater. It was suggested that optimal pharmaceutical removal could be achieved with a sludge age of at least 10 days at a temperature of 10°C (19).

During recent years, alternatives to the activated sludge process, primarily membrane bioreactors (MBR), are seeing more use in municipal wastewater treatment. In addition to an increased retention of SS, the process can be operated with comparatively higher biomass concentration and longer sludge independently of the hydraulic retention time, which benefits the microbial activity (56). Several studies have investigated the potential benefit of MBR over the activated sludge process for pharmaceutical removal (19, 57, 58). In general, a slight improvement was observed, in particular for substances that were moderately removed with activated sludge. Installation of MBR was however not recommended for the purpose of only increasing the removal of pharmaceuticals (59).

Occurrence in effluent and surface waters

For the purposes of this thesis, this section primarily covers occurrence of pharmaceuticals following wastewater treatment in industrialized countries. In less developed countries data is not only scarce, but due to low or non-existent sewer connectivity the discharge of pharmaceuticals to the environment is also less predictable and mostly not limited to point-sources, i.e. wastewater effluents.

Detection of pharmaceuticals in municipal wastewater was observed already in the 1980s, but any further action was discouraged since the estimated concentrations in water supplies was considered unlikely to pose a risk to public health (60). Because of the risks that now have been determined in aquatic species, there is also a large knowledge base of the prevalent concentrations in wastewater effluents and surface waters. As discussed in the previous section there are several variables that determine the discharged concentration of a specific pharmaceutical to the aquatic environment. Apart

from sorption and biodegradation in wastewater treatment, the main factors are the amount consumed by the attached population and the dilution from the treatment plant effluent to the recipient water. Effluent points are often strategically located so that the dilution is maximized e.g. by rivers with consistently high flows, to lakes with low retention time, or directly in the sea. A large variation of the dilution can be expected due to the different locations of WWTPs. As a reference, the estimated dilution for the three plants covered in this thesis is between 10 and 100.

Plenty of studies report removals and effluent concentrations in wastewater. Some of them are compiled in table 1 to give a few examples of what has been previously been observed. In some occasions data on surface water concentrations were also recorded. Data for the potent estrogen ethinylestradiol was largely missing, probably because it is often found below the reporting limit. For example, Loos *et al.* stated that the substance could not be detected above their limit of quantification (LOQ), 10 ng/L (4).

A seasonal aspect, and a potential benefit for plants where treatment is performed in the open air is that some pharmaceuticals present in effluent wastewater have proven to go through rapid photolytic degradation when sunlight is accessible. Diclofenac, antibiotic sulfamethoxazole and beta-blocker propranolol showed high affinity for photodegradation, whereas carbamazepine did not (61, 62). Furthermore, temporary high flows, due to e.g. excessive rainfall or thawing of snow and ice, can reduce the removal of pharmaceuticals in conventional wastewater treatment severely, with full recovery after a few days (63).

Regulation and monitoring

The abundant research into the effects and discharge of pharmaceuticals has also been accompanied by investigations regarding eventual regulatory actions. Currently, few concrete regulations have however been implemented in the form of discharge limits. Other regulatory action that is suggested or already is in force includes but are not limited to:

- In Europe, environmental risk assessment is performed on products introduced on the market after 2006. Identified environmental risks do however not currently hinder market approval. (64)

Several amendments to the risk assessment was suggested by Ågerstrand *et al.* In addition to be included as a part of the risk-benefit analysis before market approval, there was a wish for additional assessment topics, such as the impact of mixture toxicity and inclusion of antibiotic resistance genes to the assessment of antibiotics (65).

Table 1: Reported values of the removal in conventional wastewater treatment, effluent concentrations and surface water concentrations in the cited literature

Pharmaceutical	Removal (%)	Effluent concentration (ng/L)	Surface water concentration (ng/L)	Reference
Carbamazepine	7	2100	250	(63)[b]
	8	1630	-[a]	(66)[c]
	14	855	-	(19)[b]
	-	226	25	(3)[c]
	-	740	-	(67)[b]
	<10	-	-	(58)
	-	832	-	(4)[c]
	0	-	-	(55)[d]
Diclofenac	69	810	150	(63)[b]
	17	2510	-	(66)[c]
	0-65	1420	-	(19)[b]
	-	40	3	(3)[c]
	22	-	-	(58)
	27	250	2	(68)[c]
	-	50	-	(4)[c]
	0	-	-	(55)[d]
Ethinylestradiol	-	1.3	<0.3	(3)[c]
	25-99	2	-	(19)[b]
Ibuprofen	90	370	70	(63)[b]
	0-100	22	-	(19)[b]
	-	65	28	(3)[c]
	98	40	2	(68)[c]
	99	-	-	(58)
Metoprolol	83	730	45	(63)[b]
	-	640	-	(67)[b]
	25	-	-	(58)
	0	1500	17	(68)[c]
	0	-	-	(55)[d]
Oxazepam	-	130	-	(67)[b]
	2	290	7	(68)[c]
	-	162	-	(4)[c]
	20-25	-	-	(55)[d]
Sulfamethoxazole	-	136	20	(3)[c]
	74	-	-	(58)
	45	83	5	(68)[c]
	-	142/280	-	(4)[c]
	10	-	-	(55)[d]

[a]Entries given as "-" was either not recorded or unintelligible
[b]Reported median concentration
[c]Reported average concentration
[d]Removal includes only sorption to sewage sludge

- Separate treatment of significant point sources such as hospitals and nursing homes.

Wastewater originating from these facilities may contain significantly higher concentrations of pharmaceuticals than municipal wastewater. Discharge into the environment due to sewage loss in old or combined sewer systems could be mitigated by treatment at the source (69).

- Increased transparency from the pharmaceutical industry through e.g. labeling on pharmaceutical packaging regarding environmental "friendliness" and manufacturing origin (65, 69).

Specific labeling could help the consumer to pick between drugs with a similar mode of action, but pose a divergent environmental risk. Such transparency is scarce, however there are a few pioneering exceptions. For example, since 2005 the Swedish association of the pharmaceutical industry provides environmental risk information for pharmaceutical substances in the medical products list, fass.se (70). The information includes data on persistence in the environment and the potential for accumulation in the tissue of aquatic species, so-called bioaccumulation.

Actual wastewater regulation has, to my best knowledge, currently only been implemented in Switzerland where a large share of the WWTPs are obliged to remove a high-risk selection of organic micropollutants by 80% of the influent concentrations (71). With regard to pharmaceuticals, this selection includes carbamazepine, diclofenac and sulfamethoxazole. Similar regulation could be expected in the near future in the EU. The European commission proposed in 2012 to include estradiol, ethinylestradiol and diclofenac on the so-called Watch list, which consist of pollutants to be monitored for eventual inclusion on the list of prioritized substances (72). Substances on the latter list are accompanied by environmental quality standards, i.e. maximum surface water concentrations. In 2015, the antibiotics erythromycin, clarithromycin and azithromycin were also included on the Watch list (73).

Another concern is the potential release of pharmaceuticals to the environment via digested sewage sludge. In some countries, using this waste as fuel in incineration plants solves this problem. In Sweden ~1% of the generated sewage sludge is incinerated and there is an aim for increased usage of digested sludge as agricultural fertilizer (74). Municipal WWTPs in Sweden can get certified through REVAQ to ensure that their sludge is safe for use in agriculture (75).

Treatment technologies for pharmaceutical removal

The increased awareness regarding adverse effects caused by organic micropollutants in the aquatic environment, along with approaching legislation, has led to investigations and development of treatment technologies, which could significantly reduce the concentrations of these substances. The two main technologies that are considered, oxidation with ozone and adsorption onto activated carbon, were both commonly used in drinking water treatment however primarily for the purposes of disinfection (ozonation) and removal of odor and taste related organics (both) (76–78). In the following sections, these technologies are more thoroughly presented and a few alternatives that have been investigated in the interim are briefly described.

Oxidation with ozone

Ozone is an unstable gas and must thus be produced immediately before use by e.g. electric discharge of oxygen. Due to the reactive nature of ozone, exposure can pose a significant health risk; chronic exposure to high concentrations can lead to lung damage. In the European Union, the daily exposure limit is set to 120 $\mu g/m^3$ (~0.05 ppm) (79). Protective measures to prevent leakage during treatment and sufficient elimination of residual ozone after treatment is therefore required. Ozone has two different mechanisms of action in water matrices; either via direct electrophilic attack by the ozone molecule itself or indirectly by hydroxyl radicals which form during ozone decomposition (80). Ozone easily targets organic compounds with electron donating groups, such as C=C double bonds, amines or activated aromatic structures, which are found in for example carbamazepine, diclofenac and many antibiotics (81–83). Hydroxyl radicals (·OH) target molecules non-specifically, but only increase the overall reaction rate, not the oxidation capacity at dissolved organic matter (DOM) levels observed in effluent wastewater (84). DOM refers to all dissolved organics that are present in a solution, of which pharmaceuticals only contributes a small fraction in wastewater. DOM is quantitatively represented by the concentration of dissolved organic carbon (DOC). The ·OH reaction can be promoted by increasing the ozone dose, raising the pH or by addition of hydrogen peroxide (82, 84). Furthermore, the oxidation of low to moderately removed substances, which are more dependent on the presence of ·OH, is negatively affected by a relatively high DOC, which scavenge ("neutralize") the radicals (82, 83). To some extent a high presence of suspended solids could also lead to a reduced performance.

Ozonation does not lead to complete removal (mineralization) of molecules, but rather degradation into other metabolites. In drinking water treatment, presence of bromide is for example of concern since it is easily oxidized to the carcinogen bromate (81). Oxidation of pharmaceuticals in wastewater seems to lead to an overall loss of toxicity (85, 86), while for some substances an increased toxicity has been observed (87–89). However, it has been indicated that biologically active sand filters could mitigate this increased toxicity (24, 83).

Adsorption with activated carbon

Activated carbon (AC) can be manufactured from a variety of raw materials with high carbon/low ash content, such as coal, lignite or coconut shell. The production process is rather energy consuming and is commonly performed as follows: a slow increase of the temperature to 500°C oxidizes and removes volatile impurities (25). Further increase of the temperature to 1000°C generates steam, which expands the porous structure of the material. During the activation process a distribution of pores with different size are created which extends from the carbon surface into the particles. Pore sizes are categorized into three categories according to the diameter of the pore opening; micropores are <2 nm, mesopores are 2-50 nm and macropores are >50 nm. AC is commercially available in either granular or powdered form, defined accordingly: Granular activated carbon (GAC) has a predominantly larger particle diameter than 0.2 mm, while powdered activated carbon (PAC) has particle diameters smaller than 0.2 mm, although typically in the range of 5-50 μm (90, 91).

Many different factors related to the adsorbent (the AC), the adsorbate (the adsorbed substance) and the water matrix have been shown to influence adsorption. In the latter, i.e. the wastewater, DOM can have a two-fold negative impact; either pore blocking or direct competition for adsorption sites. The first is attributed to large sized DOM which can block the access to micropores and smaller mesopores, suitable for adsorption of organic micropollutants. Pore blocking was shown to be mitigated by ACs that had a wide distribution of pores in the size between 30 and 100 nm (92). Smaller sized DOM directly competes with organic micropollutants for adsorption sites and can thus increase the AC consumption. For example, it was shown during application of PAC that the DOC-normalized dose (mg PAC/mg DOC) was better correlated to the removal efficiency than the volumetric dose (mg PAC/L) (22). The use of DOC-normalized doses have also been reported in ozonation studies (21, 83). DOC is reduced in the wastewater treatment stages, primarily by biodegradation as previously described and it was also shown that dosing PAC to effluent from primary sedimentation led to very inefficient adsorption, attributed to very high DOC (93).

Related to the distribution of pore sizes, a large surface area, which is achieved by a high distribution of micropores and small mesopores, was shown to correlate well with the average removal of organic micropollutants (94). As during sorption to sludge a higher hydrophobicity (log D), was well correlated with better adsorption to AC, which has a predominantly hydrophobic surface (95). In the same study, presence of hydrogen donor/acceptor groups and aromatic rings in the molecular structure of the adsorbate was shown to be beneficial for the adsorption, as compared to the absence. Furthermore, inevitable adsorption of DOM tends to give the carbon surface a negative charge at normal effluent pH (7-8), which promotes electrostatic interactions. Thus positively charged substances generally show better adsorption in such conditions than those with negative charge (21, 96, 97).

Granular activated carbon

Treatment with GAC is normally performed as filtration through one or several fixed bed columns. An important concept for GAC filtration is the mass transfer zone (MTZ), which is where adsorption occurs in the filter bed. The MTZ moves down (or up) the filter bed as the GAC becomes saturated by the adsorbate. If the MTZ extends beyond the filter bed, by applying a high flow or by almost complete saturation, the adsorbate will pass through the filter. Breakthrough occurs at the point when an undesired ratio of effluent to influent concentration (C/C_0) is exceeded. The filter bed has then reached its bed life and is replaced. The accumulative volume that has passed through the filter bed, the throughput, is commonly given in bed volumes (BV) of water that has been treated. Bed lives are typically in the range of several thousand BV. The HRT in a GAC filter bed is often given as the empty bed contact time (EBCT), i.e. with the imaginary assumption that the GAC is completely porous. Some parameters, which were shown to reduce the bed life, are (high) presence of DOM, shorter EBCT i.e. higher flow, and temporarily or consistently high pollutant concentrations. The opposite could be achieved with strategic operation such as parallel operation of several filter columns or so-called lead-lag operation of filters in series (98).

GAC has the advantage over PAC that it can be regenerated for later reuse. This is done in a process very similar to the activation process, i.e. thermal regeneration, during which adsorbates are volatilized and degraded. Thus, the adsorption capacity is completely restored, however, at the cost of a ~10% mass loss (99).

Powdered activated carbon

Treatment with PAC is normally performed in a system composed of one or several contact tanks where the adsorption primarily occurs; they should therefore be properly mixed. Following the contact tank(s) there is a need for a particulate retention step to prevent AC particles from passing through to the effluent. This may be composed of sedimentation and/or physical filtration. Sedimentation may be aided by application of coagulants and/or flocculants. The main operational parameters of PAC treatment are the carbon dose and the HRT of the water in the contact tanks, i.e. the contact time. An increased dose will naturally increase the adsorption capacity and an increased contact time will allow the adsorption to approach equilibrium. It has been shown that adsorption equilibrium is reached after 20-48 hours (22, 26, 27). As this exceeds even the HRT of many WWTPs, efficient use of the adsorption capacity is not feasible if the retention time of the water and the AC is equal. In GAC filtration, equilibrium is naturally reached as long as there exist an MTZ, since the "carbon dose" is preloaded. To mimic this during PAC treatment the carbon retention time needs to be extended. Nicolet and Rott proposed recirculation of PAC as a solution to this problem nearly two decades ago, when they tried to achieve cost-efficient color removal in wastewater, in a separate pilot system (100). When the removal of organic micropollutants during recent years became an emergent topic, this process modification was adapted seemingly by default to achieve an acceptable removal (21, 101). The implication of recirculation in a separate treatment stage (internal recirculation) and the benefit it gives is thus still quite understudied in the large scale (102, 103).

An alternative to internal recirculation has however been more explored, involving recirculation to the biological treatment stage (93, 104, 105). If added slightly after the influent to the biological treatment stage, where DOC is already heavily reduced, it was shown that the superior contact time over a separate treatment led to comparable removal, despite an overall higher DOC (93). This research has solely been conducted in Germany and Switzerland where the digested sludge primarily is incinerated, in contrast to countries like Sweden where the preferred handling of this waste is in conflict with this development (see "Regulation and monitoring"). In a full-scale application with a separate treatment stage, spent PAC would continuously be removed from the system, then be dewatered, dried and finally incinerated to limit transfer of the pollutants into another biome.

Activated carbon variants

A few studies have recently investigated the performance of applications using variants of the conventional activated carbon types which were smaller than the defined particle sizes (106, 107). These

modified ACs gave the benefit of faster adsorption kinetics, thus contact times could be shortened while achieving a comparable removal. The adsorption capacity was however generally not affected since the AC particles maintained their original pore size distributions. It remains to be seen whether this is viable alternative in full-scale applications since the suggested particle sizes currently only can be attained by thorough grinding of commercially available products.

Activated carbon vs. ozonation

A few studies have compared the removal of organic micropollutants with ozonation and PAC in bench and pilot-scale (21, 22). Altmann *et al.* considered both treatments to be well suited for the intended purpose and showed good removal of the critical substances carbamazepine and diclofenac, while ozonation was more suited for the removal of sulfamethoxazole and PAC could remove a few substances including benzotriazole better (22). Margot *et al.* favored PAC with the extension of ultrafiltration (PAC-UF) for particle retention, despite a higher operation cost than ozonation, since PAC-UF led to a higher reduction of toxicity in the effluent (21). Mousel *et al.* compared the energy demand for application of ozonation, GAC and PAC and when combining both energy demands at the WWTPs and the energy demands for production and transportation of raw materials, ozonation was the clear winner followed by PAC (23). For the activated carbon methods it was noted that the energy demand for production and transportation were dominant and that the latter could easily improve in the future if these treatment methods become ubiquitously implemented in wastewater treatment. Implementation of either ozonation or PAC was estimated to raise the nation-wide cost for wastewater treatment in Switzerland by 10-15% (108).

Alternative treatment technologies

Oxidation with chlorine dioxide

Oxidation with chlorine dioxide (ClO_2) for removal of pharmaceuticals was suggested as an alternative to ozonation and removal efficiencies was compared between the methods in a few studies (109–111). For most of the evaluated pharmaceuticals ClO_2 had lower oxidation rate, which is to be expected since it is a weaker oxidant and does not generate ·OH. However, the capacity to remove substances such as diclofenac, ethinylestradiol, sulfamethoxazole and some other antibiotics were similar to that of ozone, while practically no oxidation occurred of carbamazepine and ibuprofen (109–111). Overall, oxidation with ClO_2 show few advantages over ozonation, however, Hey *et al.* suggested it could be an alternative

to ozonation for smaller WWTPs (<2000 person equivalents) depending on future effluent criteria, due to simpler operation and lower estimated operation cost in such a setting (111).

Nanofiltration/reverse osmosis

Filtration with high-pressure membranes, i.e. by nanofiltration and reverse osmosis (NF/RO), has been investigated for the removal of pharmaceuticals in wastewater to some extent. These membranes have pores or cavities that allow the permeation of water, but can retain or reject substances based on a combination of size exclusion, adsorption via hydrophobic interaction and via electrostatic interactions (112). The molecular weight cut-off for the pores is normally in the range of 200-300 g/mol, which theoretically would lead to rejection of many pharmaceutical substances (112). Electrostatic interactions can occur due to the predominantly negative charge of the NF/RO membrane surface when submerged in a water matrix, such as wastewater. It was shown that this could lead to a better rejection of negatively charged than positively charged molecules, due to diffusion through the membrane of the latter (113). Overall, a high removal of pharmaceuticals, comparable to that of AC adsorption (and thus ozonation) is achievable (114). However, the energy demand was estimated to be at least 40% higher than that of these technologies and additional treatment of the rejected wastewater fraction (20-25% of the total flow) is needed to ultimately prohibit any discharge, and would further increase the cost of this technology (69). Thus, substantial optimizations would be required to make NF/RO filtration a competitive alternative to the two main technologies.

Adsorption with zeolites

Zeolites are porous minerals, which like activated carbon, can act as an adsorbent for organic compounds. Unlike AC however, zeolites have more or less uniform pore sizes, which can be selected in the range of the desired molecular diameters. Thus, zeolites can adsorb molecules of a certain size very well. This was shown by de Ridder *et al.*, who in addition could show that organic matter in surface water did not interfere with adsorption by pore blocking, which can be attributed to a more homogenous surface are than that of AC (115). In conclusion, it was recommended that adsorption with zeolites should only be applied as a complement to e.g. AC adsorption due to the very limited affinity range (115).

Conclusion

In table 2, an overview of the technologies described in this chapter is compiled to allow for a rough comparison. An easy conclusion that also have been drawn before (by e.g. Joss *et al.*) is that ozonation and activated carbon adsorption are the most suitable options for stand-alone operation (69). Both technologies have the potential for a high and, perhaps more importantly, broad removal of pharmaceuticals at a relatively low cost. Some of the other technologies, i.e. NF/RO filtration and zeolite adsorption could potentially be considered for combinatorial treatment with the two main alternatives to compliment their shortcomings. In municipal wastewater treatment "affordable" and "simple" are however key attributes when it comes to extension or optimization of the treatment processes, thus this would probably only be applicable in obscure cases.

Table 2: Comparison of the performance of the discussed treatment technologies

Treatment method	Pharmaceutical removal	Cost/energy demand	By-product formation	Disinfectant	References
Ozonation	High/broad	Low to moderate	Yes	Yes	(21–23, 69, 81)
AC adsorption	High/broad	Moderate	No	No	(21–23, 69)
Oxidation with ClO_2	Moderate	Low to moderate	Yes	Yes	(109–111)
NF/RO filtration	High/broad	High	No	No	(69, 114)
Zeolite adsorption	High/specific	Uncertain	No	No	(115)

Present investigation

Aim and strategy

Pharmaceuticals are ubiquitously found in the recipients of municipal WWTPs and are thus commonly occurring in surface water. Although few have been proven to have an immediate, toxic effect on aquatic species the long-term impact of pharmaceuticals in the environment is still uncertain. In agreement with the precautionary principle and in preparation for legislative measures, the development of treatment technologies, which can effectively limit pharmaceutical discharges in recipient waters, is currently ongoing. Oxidation with ozone and adsorption onto activated carbon have proven to target pharmaceuticals widely and at a feasible cost.

The work in this thesis is part of the Swedish environmental research project MistraPharma, which aimed to identify and reduce environmental risks caused by human pharmaceuticals. With regard to the latter part, one objective was to evaluate the removal of high-risk pharmaceuticals by assessing the feasibility of activated carbon adsorption for application in Swedish WWTPs. GAC is not as commonly suggested as PAC internationally, for full-scale removal of organic micropollutants (69, 71), however, in contrast to PAC it can be regenerated for consequent reuse, which allows significant savings of raw materials. In the literature, there is a scarcity of studies which compare the two methods both in parallel operation, and using the same experimental setups for evaluation of treatment of varying effluent qualities, i.e. at different WWTPs. Due to the preferred handling of sewage sludge in Sweden, state-of-the-art treatment with PAC, by applying recirculation, needs to be performed separately from the biological treatment stage. This modification to the process in addition to that PAC, unlike GAC, is dosed continuously leads to a more diverse set of ingoing parameters which may affect the performance.

The aim of this thesis was thus two-fold: first, to determine in parallel operation at WWTPs whether GAC filtration or treatment with PAC is more suitable to achieve high-level removal of a carefully selected set of pharmaceuticals. And secondly, to determine how the performance of treatment with PAC is affected by variations in ingoing parameters.

To cover a variety of municipal wastewater effluents, in agreement with the first part of the aim, three different municipal WWTPs were selected for evaluation of pilot-scale operation. The plants were Käppalaverket (Käppala) in Stockholm, and the two main plants in the neighboring cities Uppsala and Västerås. The main qualifications were that they should vary in regards to attached population size, treatment load and utilization or lack of tertiary treatment methods. Only Käppala applied tertiary treatment in the form of sand filters. Some of the differences between the selected plants are displayed in table 3.

To perform treatment at different locations a mobile pilot-plant was constructed in-house (before this thesis started) at Käppala. Operational equipment and treatment tanks were fit into a 20ft-shipping container, which resulted in the ability to continue treatment at the next plant within 10 days (for a team of 3-4 persons). The GAC and PAC treatment lines are schematically presented in figure 1. GAC treatment was designed with two sequential down-flow filter columns and treatment with PAC was designed with three sequential contact tanks (aerated for mixing), a sedimentation tank and a concluding sand filter column. In the latter system, recirculation of settled PAC sludge could be performed from the bottom of the sedimentation tank to any of the three contact tanks, however only one at a time.

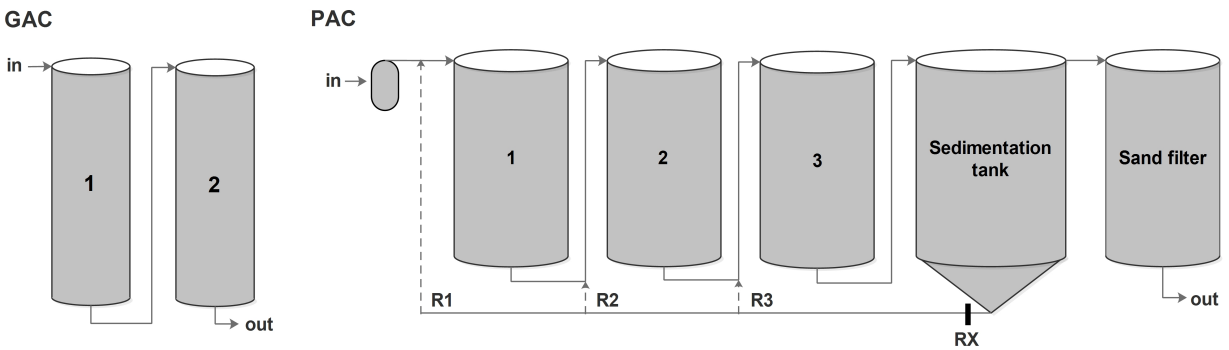

Figure 1: Schematic overview of the GAC and PAC treatment lines. R1, R2 and R3 denotes the different recirculation points in the PAC lines, while RX denotes operation without recirculation. Samples were collected at "in" (collective for all treatment lines) and "out".

To satisfy the overarching aim to target high-risk pharmaceuticals, monitoring of 100 substances, which were prioritized previously within MistraPharma, was performed the three treatment plants. Fick et al. first selected 500 pharmaceuticals based on sales in Sweden and available data on human therapeutic plasma concentrations given in the scientific literature (116). For these substances, surface water concentrations expected to cause a pharmacological effect in fish, i.e. critical environmental concentrations (CEC), were determined. Grabic *et al.* further condensed this list by identifying 100 substances from a diversity of pharmaceutical classes, which also showed a high potential for bioaccumulation in fish. This was approximated by a low ratio between CEC and predicted environmental concentrations (PEC) (8). In this thesis, these 100 pharmaceuticals were monitored, however, only substances that were detected above the LOQ in at least 50% of the effluent samples, were further evaluated (table 4). Pharmaceutical concentrations were determined using a multi-residue method based on solid phase extraction and liquid chromatography tandem mass spectrometry (SPE LC-MS/MS), as described by Lindberg *et al.* (117). Some commonly evaluated substances that did not make it to the selection were the three steroid estrogens, the antibiotics azithromycin, erythromycin and sulfamethoxazole. The hormones showed inconveniently high LOQs with the multi-residue method (30-40 ng/L) and the antibiotics were all detected in an insufficient amount of effluent samples (0-11%).

Table 3: Load and effluent parameters in the WWTPs during (I) and (II)

	Käppala (I)	Uppsala (I)	Västerås (I)	Käppala (II)
Attached population (pe)	425 000	148 000	102 000	440 000
Sludge age (d)	16 ± 1.5	23 ± 0.9	10 ± 1.5	15 ± 1.5
HRT (h)	36 ± 6.2	38 ± 2.9	14 ± 1.0	29 ± 5
Σ pharmaceutical conc. (μg/L)	3.8 ± 2.0	4.9 ± 1.1	6.2 ± 3.0	10.3 ± 4.2
Dilution factor to recipient	100x	15x	11x	100x
Susp. solids in effluent (mg/L)	0.6 ± 0.1	4.6 ± 0.9	3.7 ± 1.7	7.3 ± 4.2
DOC in effluent (mg/L)	9.3 ± 2.0	9.0 ± 3.2	9.4 ± 1.6	12.1 ± 1.1

Pharmaceutical occurrence and variation (I, II)

An essential task in both (I) and (II) was to map concentrations of the selected pharmaceuticals in the wastewater effluents. The removal rates over the conventional wastewater treatment were however not recorded, due to unreliable of influent samples. Using the effluent concentration as a surrogate parameter for the removal, showed no or very weak correlation with parameters which were previously shown to affect the removal, such as sludge age, hydraulic retention time or wastewater temperature (19, 118). In (I), the lowest combined effluent concentration of the evaluated pharmaceuticals was observed in Käppala (table 3). This could be explained by an overall lower consumption of pharmaceuticals (by the attached population) or possibly by biological activity in the tertiary sand filters (83). Operation in (I) was conducted at Käppala during spring/winter, in Uppsala during summer and in Västerås during fall/winter. The comparatively lower variation of pharmaceuticals observed in Uppsala was expected as the seasonally sensitive biological treatment generally gives the most stable performance during the summer months.

In (II), operation was conducted in Käppala, roughly at the same time during the year, the next year. Wastewater was here fed to the pilot treatment lines from the secondary sedimentation effluent rather than the final effluent, thus the permanent sand filters was not in effect. Compared with in (I), effluent concentrations were 3-4 times higher than previously. If influent concentrations were assumed to be roughly the same, biologically active sand filters unlikely contributed fully to this difference. An additional factor could however be that the feed during (II) was taken from the "old" biological treatment trains, as opposed to from the whole plant, where the performance tends to be less stable, especially during colder months. In (II), the sludge age was also 1 day shorter and the wastewater temperature was 0.5°C lower than during same months of operation in (I).

To estimate the value of applying advanced treatment technologies in these specific plants, maximum measured effluent concentrations in (I) were divided by the respective dilution factors and then compared to CECs in table 3. Due to a very high dilution factor in Käppala (x100), only irbesartan was within one magnitude (<10x) of the CEC. The significantly lower dilution factors in Uppsala (x15) and Västerås (x11), as well as generally higher effluent concentrations resulted in that also citalopram was within one magnitude of the CEC at these plants, respectively. Thus, very few (if any) of the evaluated substances are likely to pose a direct threat to the aquatic life in the recipients belonging to these particular plants.

Table 4: Evaluated pharmaceuticals in (I) and (II)

Pharmaceutical class	Substance	CEC[a] (ng/L)	Sales in Sweden, 2014/15[b] (tons)	Charge at pH 7.4[c]
Antibiotics	Clarithromycin	7270	0.07	+1
	Clindamycin	132 000	1.5	+1
	Trimethoprim	3.30x10^6	0.21	+1
Antidepressants	Bupropion (only in I)	116	1.3	+1
	Citalopram	141	1.4	+1
	Mirtazapine	14 000	1.1	0
	Venlafaxine	6110	3.2	+1
Analgesics	Diclofenac	4560	1.9	-1
	Tramadol	4800	4.6	+1
Beta blockers	Atenolol	792 000	2.8	+1
	Bisoprolol	3460	0.32	+1
	Metoprolol	15 400	14	+1
	Sotalol	1.90x10^6	0.49	+1
Other	Carbamazepine	346 000	5.8	0
	Diltiazem (only in I)	27 900	0.66	+1
	Fexofenadine	20 200	0.25	0
	Flecainide	1980	0.38	+1
	Fluconazole	5.00x10^6	0.13	0
	Irbesartan	50	1.5	-1
	Memantine	2230	0.10	+1
	Oxazepam	30 700	0.57	0
	Ranitidine (only in II)	233 000	0.81	+1

[a]Fick *et al*. 2010
[b]Socialstyrelsen.se
[c]Chemicalize.org

Comparison of treatment with GAC and PAC (I)

In (I), treatment with GAC and PAC was evaluated in parallel at the three different WWTPs with the general goal to reach an overall pharmaceutical removal (for the selected substances) of 95% in relation to the effluent wastewater. Throughout the treatment campaign, performance data was generated on a weekly basis. Five GAC products were chosen for evaluation, partly based on a previous trials performed by my supervisor (119), and partly based on carbon properties and recommendations from the manufacturers. PAC products were screened in bench-scale to determine their relative removal efficiency. This performance was then weighted towards the cost and the three best candidates were selected for evaluation in pilot scale. Operation of the PAC treatment lines was performed with recirculation in configuration R1.

Hydraulic performance

Both treatment methods were designed with an incoming flow of ~100 L/h, which in the PAC lines corresponded to 60 min contact time and a total HRT of 3.5 h (incl. sedimentation tank and sand filter). For the GAC lines the corresponding EBCT, i.e. the HRT of the filter column excluding the filter bed, was 20 min. The hydraulic performance was evaluated based on the capability of each systems filter, i.e. the GAC filter bed itself and the PAC sand filter, to accommodate the designed incoming flow.

The hydraulic capacity of the GAC filters proved to be highly affected by the effluent quality. The main reason was likely the difference in suspended solids in the effluent wastewater (figure 2). In Käppala, suspended solids were consistently below 1 mg/L and the designed flow could be used without reaching the capacity, while backwashing was performed every 3-4 days. Likely due to the lack of permanent sand filters in Uppsala and Västerås, the suspended solids in their effluents were on average 5 and 4 mg/L, respectively. Despite installation of temporary shallow sand filters before the pilot plant, which proved to be essential to allow operation of the GAC treatment in Uppsala, the capacity was drastically reduced. Backwashing intervals were reduced to once every to every other day, while the incoming flows were limited to 50-80% of the design value. Change to a GAC product with a larger grain size in Västerås nearly restored the capacity (to ~90%), but also led to a comparatively weaker pharmaceutical removal.

PAC treatment was operated without hydraulic deficiencies. Contact times were 55-73 min, and the main reason for this slight deviation was minor difficulties with controlling the inlet pumps. Backwashing of the sand filter was generally performed at an interval of 7 days; however, even after 14 days without backwashing the capacity of the sand filter was not reached during these conditions.

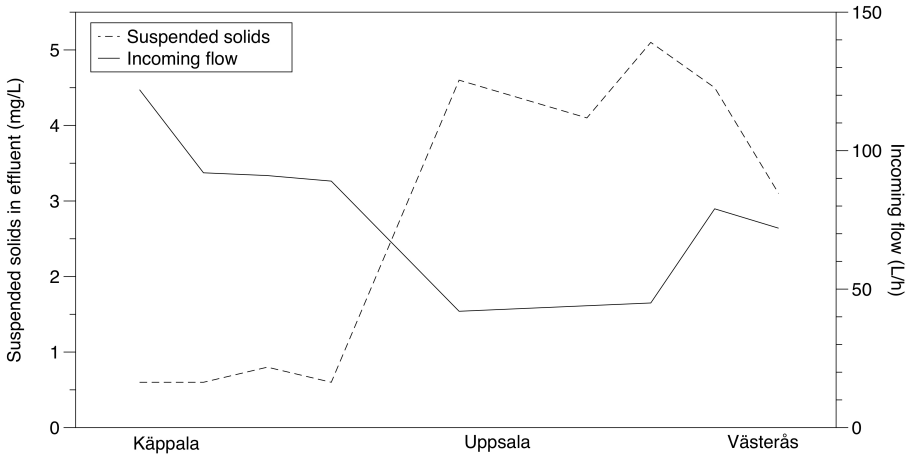

Figure 2: Incoming flow to the GAC treatment lines vs. the suspended solids in the effluent wastewater. The decline of the flow in the beginning Käppala operation was an intended adjustment to meet the design flow (100 L/h).

The hydraulic capacity is relevant for eventual scale-up to full-scale operation. The design criteria in ongoing full-scale trials in Germany and Switzerland regarding upflow velocities are as reported 6-10 m/h GAC filters and 12 m/h for sand filtration after PAC treatment (120). Upflow velocity is determined by the occupied height of the filter column divided by the HRT. In the present experiments, upflow velocities in Käppala for the GAC columns were 5-7 m/h, thus within the range of the full-scale criteria, while the reduced flows in Uppsala and Västerås led to corresponding values of down to 2.5 m/h. Regarding the PAC sand filters, the incoming flows in (I) corresponded to an upflow velocity of 3.5 m/h. In (II), where a shorter contact time was evaluated, the upflow velocity reached 7 m/h without signs exhausting the sand filter capacity, thus up to 12 m/h was potentially possible.

Pharmaceutical removal performance

Operation of the GAC filtration was at all three WWTPs performed in two lines, using a different GAC product in each. GAC A and D were used in Käppala, GAC B was used in Käppala and Uppsala, and GAC C and E were used in Uppsala and Västerås. Comparing the performance of the five different GAC products, it was clear that GAC A and E were weaker overall adsorbents. This is visualized fairly well by the breakthrough curve for carbamazepine (figure 3). Less than 5% breakthrough overall for the

set of pharmaceuticals, i.e. 95% overall removal, was observed for all GACs up to ~2000 BV when the performance deteriorated for GAC A and E. GAC B, C and D were operated up to 6400, 10 000 and 16 000 BV, respectively without reaching 5% breakthrough, which is comparable to the previously cited full-scale trials were GAC was replaced after 7000-15 000 BV (120). Breakthrough of individual substances did however occur. No clear correlation between surface area or particle size could be determined with regards to the different performance of the products. However both GAC A and E (230 mg/g) had a lower methylene blue number than GAC B and C (260 mg/g); no data was available or measured for GAC D. The methylene blue number has traditionally been used to estimate the mesopore volume of adsorbents (121).

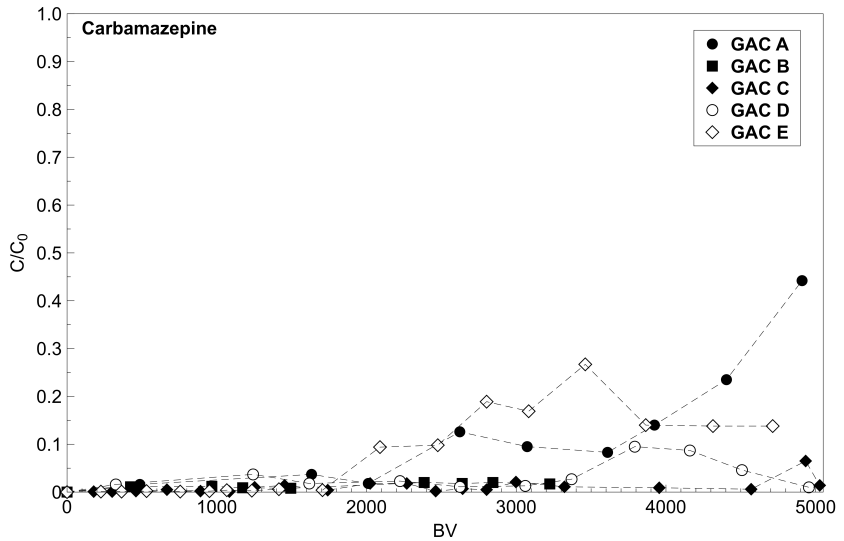

Figure 3: Breakthrough of carbamazepine for all evaluated GAC products. GAC A and D were used in Käppala. GAC B was used in Käppala and Uppsala, and GAC C and E were used in Uppsala and Västerås. Dashed lines were added to improve visual interpretation.

Regarding the three different PAC products, PAC A was used in Käppala and Uppsala, PAC B was used at all three plants and PAC C was used in Uppsala and Västerås. In figure 4, the overall pharmaceutical

removal is plotted against the continuously added, fresh PAC dose, for all the products at the different WWTPs. It is evident that the applied fresh dose was more than sufficient to reach 95% overall removal in both Käppala and Uppsala, while a removal slightly below 95% was achieved in Västerås by applying a considerably reduced dose. Indicative results from the bench-scale screening led to the initially applied dose of ~30 mg/L, which then was stepwise lowered over the course of the treatment campaign. It is thus evident that the PAC, which accumulated in the treatment tanks due to recirculation, contributed a significant increase of the adsorption capacity.

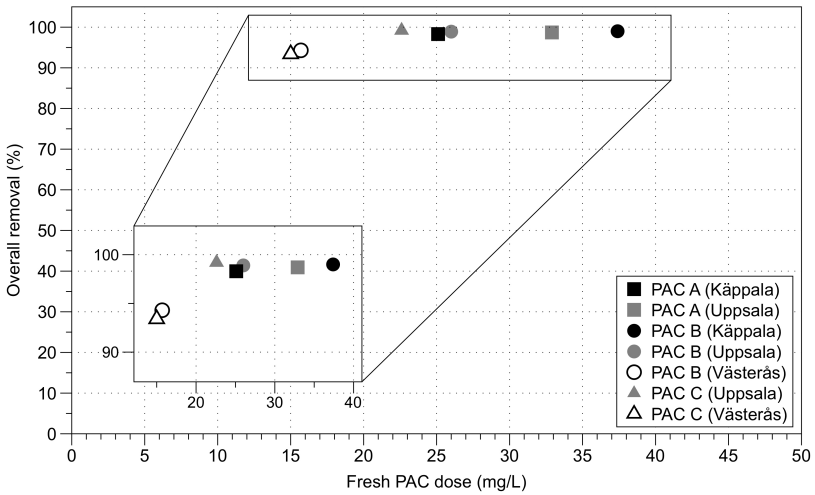

Figure 4: Average overall pharmaceutical removal for each group of experiments using the same PAC product at the different WWTPs.

To better differentiate the performance of PAC A from that of PAC B and C it would have been desirable either use PAC A again in Västerås or to apply a lower dose earlier; during the screening experiments PAC A showed a comparatively weaker performance, while PAC B and C showed practically identical performances, as shown in (I) (data not shown here). In previous pilot-scale studies a fresh dose of 10-20 mg/L have commonly been determined to be sufficient to reach a high removal (>80%) of a broad spectrum of organic micropollutants (21, 26). Regarding the selected set of pharmaceuticals, this could was confirmed by the experiments in Västerås where an average fresh dose

of 15-16 mg/L led to a 93-94% overall removal. The DOC-normalized dose, which usefulness was indicated by Altmann *et al.*, for comparing the performance in effluents of varying quality, was 1.6-1.7 mg/mg DOC for these experiments. An evaluation of all PAC experiments gave however that the fresh dose and the DOC-normalized dose correlated about equally well with the overall removal ($r_{spearman}$ of 0.60 and 0.58, respectively). Perhaps, making this distinction was made difficult due to the very similar DOC at all three WWTPs (table 3), as well as the generally very high removal. Another parameter that was shown to correlate well with the removal, particularly in a system applying recirculation, was the SS concentration of the PAC-sludge (PAC + wastewater + eventual coagulant) in the contact tank(s) (103). SS in the contact tanks was only measured during a little over half of the experiments, but a significant however not as high correlation as the two other parameters was still determined ($r_{spearman} = 0.53$). Thus, it was tentatively confirmed that this could be a useful parameter to follow in order to be able to affect the removal.

Method comparison and individual pharmaceutical removal

The use of recirculation during PAC treatment resulted in accumulation of dosed AC in the treatment tanks. In an attempt to better compare the removal between GAC and PAC on the basis of available carbon, carbon usage rates (CUR), which in (I) was denoted "accumulated dose" for PAC, were determined according to:

- $CUR_{PAC} = \frac{X_{ave}}{V}$
- $CUR_{GAC} = \frac{X_0}{V_{acc}}$

Where, X_{ave} = average amount of PAC in the system during the experiment, V = treated wastewater volume during the experiment, X_0 = amount of GAC preloaded on filter, V_{acc} = accumulative volume of treated wastewater.

CUR-intervals were determined from groups of PAC experiments between which a significant difference of the overall pharmaceutical removal could be determined. They were <30 mg/L, 30-100 mg/L and >100 mg/L. A comparison between the two methods is most apt for the middle interval, since it excludes the weak performing GAC A and E, which never reached below a CUR of 100 mg/L during operation, whereas the lowest interval only contained data points from PAC experiments. Average removal for the evaluated substances at the 30-100 mg/L interval are displayed in figure 5. The removal of some substances was greatly affected by an LOQ which was close to the effluent concentration (names bolded in the figure), thus the removal of these substances were likely both undervalued and

probably more comparable between the two methods than is discernable. Despite this, the removal was in general better for PAC than for GAC. If the four bolded substances are excluded, treatment with PAC achieved on average a ~3% (percentage) higher removal. Including the bolded substances, about half show a very high and comparable removal with the two methods, exceeding or narrowly approaching 95%. Regarding the more poorly removed half, the difference was generally more considerable in favor of PAC. Thus, at least for substances which show a weaker adsorption to AC in general, GAC showed a lower adsorption capacity i.e. required a higher CUR to reach the same removal as PAC.

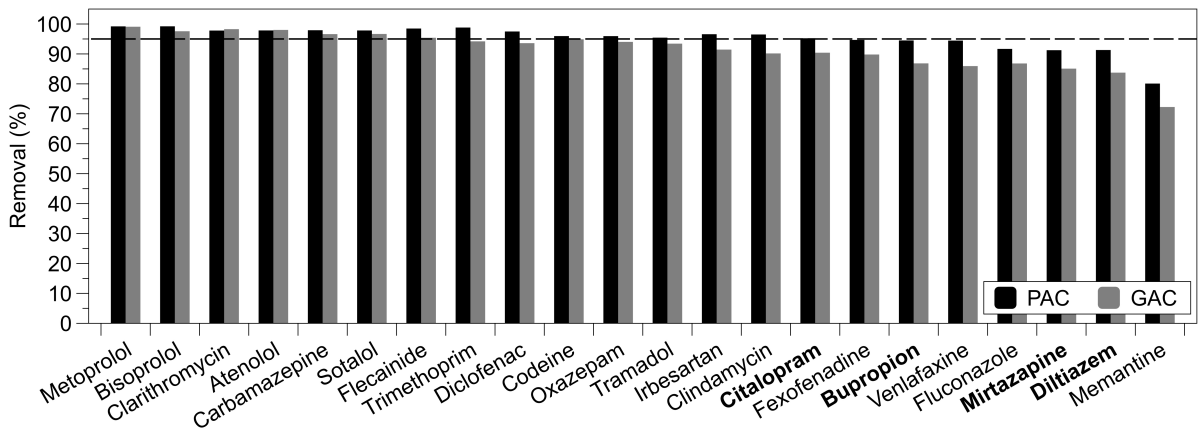

Figure 5: Comparison of the average individual pharmaceutical removal for GAC and PAC at 30-100 mg/L CUR. The removal of the bolded substances may be undervalued due to effluent concentrations being close to the LOQ.

Two physicochemical parameters, which previously were shown to be good predictors for removal, are log D and charge (21, 95). A better removal overall is expected for positively charged substances than negative or neutral substances due to electrostatic interactions with negatively charged DOM on the carbon surface. This was tentatively confirmed by the experiments: If ranked based on removal (and excluding the four bolded substances), the average rank of a positively charged substance was ~8, compared to ~12 for a negatively charged or neutral substance. However, carbamazepine (neutral) and diclofenac (negative) were removed better than average, while venlafaxine and memantine (both

positive) were relatively poorly removed. A good correlation was, in general, not found between removal and log D with the exception that fluconazole which was poorest removed of the neutral and negative substances also had the lowest log D.

Impact of PAC process parameters (II)

As indicated in (I), a fresh PAC dose of 15-20 mg/L could be applied to reach the goal of 95% overall removal of the evaluated pharmaceuticals, while using a contact time of 60 min in configuration R1. In (II), treatment with PAC was evaluated more in-depth with the main focus on varying contact time and recirculation configuration to see how these parameters affected the removal. Most experiments were performed twice to reproduce the result. As previously mentioned (in "Pharmaceutical occurrence…") the treatment lines were fed with wastewater from the secondary sedimentation effluent during this treatment campaign, as in contrast to the final effluent in (I). The effluent quality was reduced accordingly, as displayed in table 3.

Contact time

In figure 6, overall and individual removals are given for three evaluated contact times, 30, 60 and 120 minutes at a fresh PAC dose of ~15 mg/L (1.0-1.4 mg/mg DOC). It is clear that changing the contact time did not have a considerable impact on the overall removal, which reached 95, 97 and 98%, respectively. The adsorption did thus, in general, not appear to be kinetically hindered, even at 30 min. For example, the removal of the commonly evaluated carbamazepine and diclofenac were ~95% or higher at this contact time, while Mailler *et al.* observed 90 and 69% removal of these substances, respectively, using similar fresh dose but a shorter contact time of 10-20 min (97).

Furthermore, the order of performance for the individual pharmaceuticals is largely recognizable from the performance seen in (I) (figure 6), as displayed by fluconazole, memantine and venlafaxine again showing the lowest removals, while many positively charged substances were very well removed. For the few substances that were poorly removed, a 120 min contact time was required to reach 95% removal, with the exception of memantine and venlafaxine. These substances required a drastically increased dose (30 mg/L) for sufficient removal dose as was further evaluated in (II) (data not shown here).

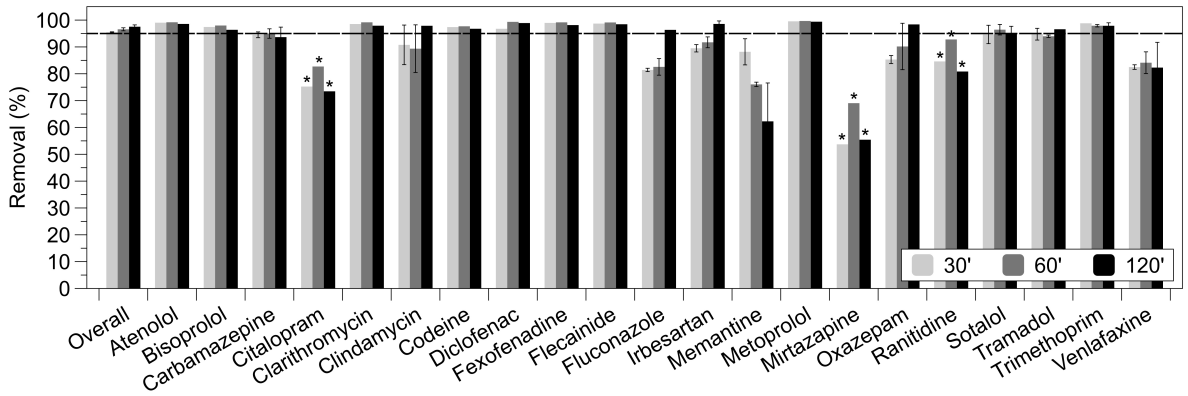

Figure 6: Pharmaceutical removal performance for 30, 60 and 120 min contact time in configuration R1. Bars with an asterisk (*) indicate a removal below 95% *and* below the LOQ. Error bars indicate the standard deviation of duplicate experiments.

Operation without recirculation was also investigated, however only at 60 and 120 min contact time (at ~20 mg/L – 1.7-1.9 mg/mg DOC). While 120 min was sufficient to achieve more than 95% overall removal, 60 min was not as displayed by a 92% overall removal. If the 60 min experiments in configurations R1 and RX are compared it is clear that at least a 25% reduction of the fresh PAC dose resulted in a comparable removal (underestimated due to the higher removal in R1). If compared to literature values, Böhler *et al.* achieved comparable removal with a 50% reduction of the dose when comparing operation with and without recirculation to the biological treatment (104), while Meinel *et al.* achieved a 67% reduction of the dose in an optimized bench-scale setup (102).

Recirculation point

Operation with different recirculation points, i.e. introduction of the recirculation stream to any of the three contact tanks (R1-R3), was evaluated at 30 min contact time. The applied fresh PAC dose was ~15 mg/L (1.0-1.4 mg/mg DOC). In figure 7, it is seen that the performance was very even for all three configurations. Regarding the overall removal, R1 and R2 (95-96%) showed a slightly higher performance than R3 (94%). Comparing operation between configuration R1 and R3 the distribution of SS was heavily skewed towards the last contact tank in R3 (2%/2%/96%), while even in R1 (33%33%34%). It seems that this high accumulation of PAC in R3 did not give an adsorptive advantage,

but rather led to a slight kinetic disadvantage. Further evidence of the weaker performance of R3 is that it was operated at a slightly higher dose (17mg/L - 1.4 mg/mg DOC) than the other two configurations (12-14 mg/L - 1.0-1.2 mg/mg DOC).

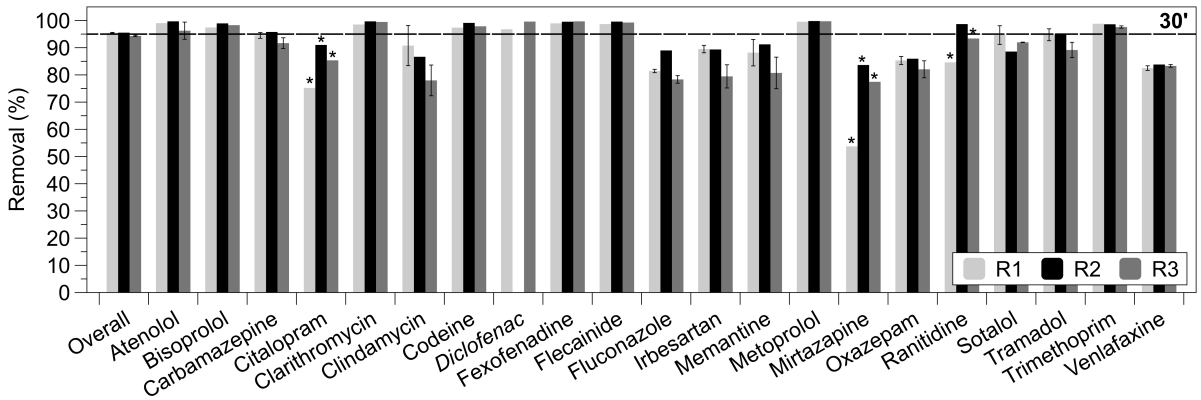

Figure 7: Pharmaceutical removal performance for configurations R1-R3 at 30 min contact time. Bars with an asterisk (*) indicate a removal below 95% *and* below the LOQ. Error bars indicate the standard deviation of duplicate experiments.

Addition of coagulant

All experiments presented in (I) and (II) were operated without the addition of a coagulant, which commonly have been used in related studies when dosing PAC (21, 103). During the same experimental campaign as (II), a few experiments was performed with continuous addition of poly-aluminum chloride (PAX-XL350, Kemira) to the third contact tank at 60 min contact time (configuration R1). Coagulant was added at 4 mg/L Al_2O_3 and the fresh PAC dose was 12 mg/L (1.1 mg/mg DOC). The removal performance was comparable, even slightly higher than the R1-60 min experiment as displayed by an overall removal of 98%. The hydraulic performance was however significantly reduced as overflow nearly occurred in the sand filter column when the next backwash was due after 7 days of operation. Thus the PAC-sludge was less well retained in the treatment tanks and escaped to the sand filter at a seemingly higher rate than during operation without addition of coagulant. Thus, the addition

of coagulant required shorter backwashing intervals, which may be more in line with backwashing routines of e.g. full-scale tertiary sand filters, which normally are backwashed every 24-48 hours (53). No optimization of the mixing was performed, which may have allowed better flocculation and improved the retention of the PAC-sludge.

Concluding remarks

In this thesis the feasibility of activated carbon technologies was evaluated in pilot-scale for the removal of pharmaceuticals in municipal wastewater. We could show that efficient removal of the evaluated pharmaceuticals could be achieved both with adsorption on to PAC and GAC, in the respectively suggested setups.

Extensive sampling of the wastewater effluents during (I) and (II) showed that a much smaller set than the selection which was monitored could be frequently detected. Notably, sulfamethoxazole, which frequently was detected in studies in other countries, was barely detected (LOQ: 5-15 ng/L) at any of the WWTPs.

It was determined that for feasible operation of most of the evaluated GAC products, separation of particulates from the incoming water was essential to reach a hydraulic capacity in accordance with previously suggested full-scale design. Thus, for application of GAC filtration in treatment plants with an inconsistent effluent quality it is crucial to select a product with both good hydraulic, and adsorptive properties when exposed to the particular effluent wastewater.

Regarding treatment with PAC it was shown, in agreement with previous studies, that the fresh dose could be considerably reduced when applying recirculation. Here, it was also shown that a substantial improvement could be expected even if the recirculation occurs much later in the contact zone.

Implementation in full-scale of these and other promising technologies (such as ozonation), will require many considerations that are not necessarily covered by this work, such as automatization of the processes. However, the results in this thesis should contribute to a better understanding of the capabilities of the evaluated technologies.

Abbreviations

AC	Activated carbon
BOD	Biological oxygen demand
BV	Bed volumes
COD	Chemical oxygen demand
CUR	Carbon usage rate
CEC	Critical environmental concentration
ClO_2	Chlorine dioxide
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
GAC	Granular activated carbon
HRT	Hydraulic retention time
LOQ	Limit of quantification
µg/L	Micrograms per liter
NF/RO	Nanofiltration/reverse osmosis
ng/L	Nanograms per liter
PAC	Powdered activated carbon
PEC	Predicted environmental concentration
SS	Suspended solids
WWTP	Wastewater treatment plant

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