

Article

# Ultrafiltration/Granulated Active Carbon-Biofilter: Efficient Removal of a Broad Range of Micropollutants

Christian Baresel \* , Mila Harding and Johan Fang 

IVL Swedish Environmental Research Institute, Box 210 60, 100 31 Stockholm, Sweden; mila.harding@ivl.se (M.H.); johan.fang@ivl.se (J.F.)

\* Correspondence: christian.baresel@ivl.se; Tel.: +46-010-7886606

Published: 18 February 2019



**Abstract:** Pharmaceutical residues, and other organic micropollutants that pass naturally through the human body into sewage, are in many cases unaffected by treatment processes at conventional wastewater treatment plants (WWTPs). Accumulated in the environment, however, they can significantly affect aquatic ecosystems. The present study provides an evaluation of a treatment system for the removal of pharmaceutical residues and other micropollutants. The system is based on a Membrane Bioreactor (MBR), including ultrafiltration (UF), followed by a biofilter using granulated active carbon (GAC) as filter material. It was found that all investigated micropollutants, such as pharmaceutical residues, phenolic compounds, bacteria and microplastic particles, present in wastewater, could be removed by the treatment system to below detection limits or very low concentrations. This shows that the combination of filtration, adsorption and biodegradation provides a broad and efficient removal of micropollutants and effects. The tested treatment configuration appears to be one of the most sustainable solutions that meets today's and future municipal sewage treatment requirements. The treatment system delivers higher resource utilization and security than other advanced treatment systems including solely GAC-filters without biology.

**Keywords:** water quality; Membrane Bioreactor; GAC-biofilter; sewage treatment; micropollutants; pharmaceutical residues; activated carbon

---

## 1. Introduction

Micropollutants (MPs), generally summarizing pharmaceutical residues and other emerging substances, pass through traditional wastewater treatment plants (WWTPs) and end up in the receiving waters and sludge. Various studies reported recipient concentrations with expected effects on aquatic organisms [1–6]. MPs released via WWTPs may also enter the aquatic food web and cause effects in higher organisms such as fish-eating birds or mammals including humans. Therefore, an increasing demand for supplementary treatment at today's WWTPs for the efficient removal of micropollutants has become obvious.

As current WWTPs are usually unable to remove micropollutants, a number of various treatment technologies have been proposed and evaluated through several large projects, such as those in References [7–9] and the Swedish MistraPharma. Technologies tested include, among others, membrane separation (reverse osmosis, nanofiltration, ultrafiltration), advanced oxidation processes (ozonation, UV-light in combinations with hydrogen peroxide and titanium dioxide) and activated carbon (powdered and granular activated carbon). Especially in Germany and Switzerland, advanced treatment technologies have been tested on a large scale [10,11]. Also in Sweden, technologies have been tested [12–17]. In Germany, Austria and Sweden, first full-scale installations have already been accomplished.

Most of available studies on treatment technologies focused on the efficiency of removing pharmaceutical residues. The processes that are most often considered effective are the treatment with ozone or activated carbon. Generally, ozone treatment implies both a direct chemical reaction of the ozone molecule as well as indirect reactions with hydroxyl radicals, breaking specific chemical bonds within the targeted substances. There exist several studies investigating complementary treatment by ozone [11–15,17–28]. Results indicate that while ozone oxidation generally provides a removal effect on many targeted substances, a sufficient removal of some substances may not be achieved even at very high ozone doses. Further, the main disadvantage of ozone treatment is the fact that the process does not completely degrade most substances. These may be transformed into other substances, normally without aromatic structures. Some of these metabolites might be more or less toxic and require thus an extra treatment step after ozonation [19–22,25–28]. These problems can be handled using a more integrated treatment setup as proposed by [14] using an ozonation step between bio-sedimentation and post-denitrification processes. This configuration is realized as Sweden's first full-scale installation of micropollutant removal at municipal WWTPs. Other challenges when using ozonation are an additional high-energy demand and working environment issues at WWTPs.

The use of activated carbon (AC), either as powdered activated carbon (PAC) or granulated activated carbon (GAC), has been investigated in numerous studies [11,16,29–35]. The use of AC is a widespread technology to remove various pollutants from water. Especially in treatment of fresh water for drinking water production, technical systems using either PAC or GAC have been applied for many years. Thus, significant knowledge on setup and operation of such systems is available. The main advantage of using activated carbon is a broad and effective removal of MPs and that no by-products are generated. During regeneration or destruction of activated carbon, the adsorbed pollutants are destroyed. The currently high environmental impact of AC-applications is caused by the immense energy and resource utilization during production and regeneration of activated carbon. This is identified as a drawback of the technology that can only be solved by increasing the AC-capacity or utilization in different ways or using biochar based on organic waste such as sewage sludge [36].

Filter systems based on GAC are common and a potential biological activity inside the filter will affect adsorbed organic compounds and the overall filter performance. Biological activity, however, is, next to suspended solids in the inflow, the main reason for clogging problems representing a key operational challenge for GAC-filter systems. An excellent pre-treatment and particle-free process waters are generally easier to handle and could improve the application potential of GAC-biofilter systems.

Membrane Bioreactor (MBR) systems are currently considered at more and more WWTPs to meet challenges with increased load as well as more stringent effluent quality requirements. Several WWTPs in Sweden, such as the Stockholm Water and Waste Company (Stockholm Vatten och Avfall), Sweden's largest water service organization, are replacing their existing conventional activated sludge process (CAS) with an MBR. After upgrading, the new process will be one of the world's largest MBR facility with a capacity of 1.6 million PE (predicted load year 2040). MBRs combine the biological activated sludge process with membrane separation, which provide distinct advantages over the CAS. Advantages include a significant better effluent (permeate) quality regarding particles, disinfection capabilities due to the membrane pore size, higher volumetric loading due to higher sludge concentrations in the biology, reduced footprint and process flexibility towards influent changes. Even the treatment of micropollutants (MPs) may be more efficient using MBRs compared to traditional treatment systems. This is partly explained by the fact that MP attached to particles can efficiently be removed by filtration, which also includes for example microplastics.

MBRs have been used for a number of decades but first in the last decade, MBRs gained more attention for the treatment of both municipal and industrial wastewater. This is much due to a significant cost reduction of membranes and process development decreasing energy requirements [37–41], which also implies a significant increase in current and planned installations worldwide.

The aim of this research work was to investigate and evaluate the long-term removal efficiency of a number of micropollutants including pharmaceutical residues, microplastics and so forth, by using a GAC-biofilter applied to MBR-effluent. Through actual pilot process setup as designed for a real WWTP, the current work evaluates the performance of the studied system and its potential role in the way forward for micropollutants removal.

While the removal efficiency of activated carbon and ultrafiltration has been evaluated in previous studies as described, no long-term evaluation of the combination of an MBR process and a GAC-biofilter has been done. The current work further is novel as it focusses on the pharmaceutical residue removal by the biological activity in the GAC-biofilter. Previous evaluations of GAC-filtration systems focus on the adsorption capacity of the activated carbon. The combination with an MBR-process is motivated by recent developments in the sewage treatment that will result in a significant increase in MBR-installations worldwide and thus the relevance of the current study.

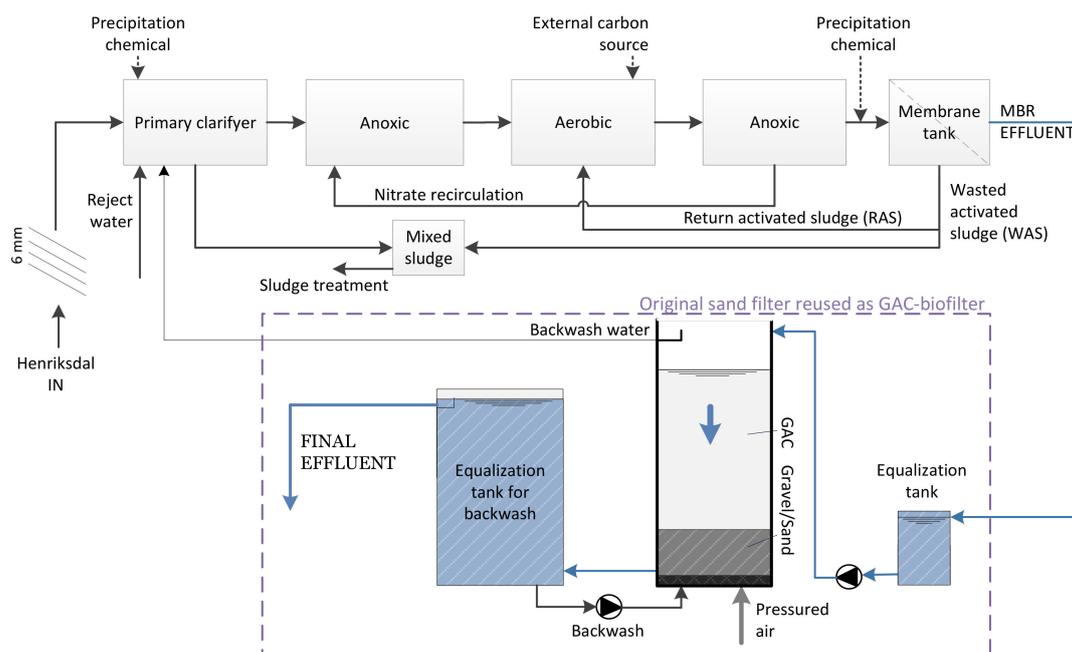
## 2. Materials and Methods

### 2.1. Pilot Characteristics

For the evaluation in long-term tests, an MBR-pilot was applied as the main treatment process. IVL Swedish Environmental Research Institute and the Stockholm Water and Waste Company have together set up, and since September 2013 operated, a pilot-scale treatment line with a capacity corresponding to 0.015% of the total Henriksdal WWTP facility (design year 2040). The pilot is located at the Research and Development (R&D) facility, Hammarby Sjöstadsverk ([www.hammarbysjostadsverk.se](http://www.hammarbysjostadsverk.se)). Wastewater treated by the pilot is taken from the untreated inflow to Stockholm's main WWTP Henriksdal and filtered through a 3 mm strainer (Figure 1). The flow into the pilot is proportional to the flow to the main WWTP and the hydraulic retention time (HRT) in the biological reactor corresponds to 10 hours at average flow. The pilot consists of a primary clarifier, a biological reactor with a total volume of about 29 m<sup>3</sup> including anoxic and aerobic zones, followed by an ultra-filtration (UF). Anoxic and aerobic zones account each for 50% of the process volume. The membrane tank had a total volume of 13 m<sup>3</sup>. Nitrate is recirculated from the beginning of the post-denitrification zone to the beginning of the pre-denitrification zone and sludge is recirculated from the UF to the beginning of the pre-denitrification zone. The ultrafiltration consists of two modules with Flat Sheet membrane type MFM 100 from Alfa Laval (Denmark). The UF units are operated intermittently with relaxation times of 2 minutes after 10 minutes of operation. The nominal pore size is 0.2 microns with a minimum and maximum pore size of 0.17 microns and 0.26 microns, respectively. The total membrane area per module is 79.64 m<sup>2</sup> spread over 44 membrane sheets. A more detailed description of the MBR-pilot configuration and operational characteristics is provided by Baresel et al. (2017) [42].

The nominal pore size of the UF in the MBR-system of 0.2 microns implies that particles of larger size are efficiently removed from the wastewater, including microplastics, bacteria and pathogens. The evaluation of the MBR-process shows that targeted effluent qualities of <0.2 mg TP/L and 6 mg TN/L are achieved under various loads. Previous analyses of pharmaceutical residues in other MBR-effluent showed no increased removal effect of pharmaceuticals by the MBR-process compared to the CAS-process [43–45].

Particle-free MBR treated wastewater was pumped at a constant flow of 1400 L/h to the pilot GAC-filter (Figure 1) with a surface area of 0.3 m<sup>2</sup>. The filter consists of a 10 cm thick sand bed on the bottom and a 1 m layer of commercial granulated carbon (Filtrisorb 400, Chemviron Carbon, density ~ 0.5 kg/L). On the filter bottom, there are a number of nozzles for backwash from an equalization tank equipped with a continuous measurement of the suspended matter content to the top of the GAC filter. The GAC-filter was originally constructed as sand filter and operated as such for many years before it was used as GAC-biofilter in this study.



**Figure 1.** Schematic illustration of the pilot setup including a membrane bioreactor MBR and granulated active carbon (GAC)-biofilter for removal of micropollutants.

With the indicated normal flow and filter volume, a contact time in the filter (HRT or EBCT (Empty Bed Contact Time)) of 13 min was maintained. These operational parameters were based on related pilot trials [46,47] where different residence times in a GAC-filter were tested with water treated in a temporary MBR-pilot.

The water passed through the filter and was collected in an equalization tank for backwash. Backwash consisted of a sequence of pulses of pressured air to terminate eventual pressed layers and backwash with water from the equalization tank. Backwash water was diverted back to the main inflow of the MBR-pilot. The filter was open and the driving force through the column was the difference in level between the water in the column and the level of the outlet. The water level in the GAC-filter was regulated via level gauge controlling the valve opening for outgoing water. The level of control was 40–50 cm above the filter bed.

## 2.2. Sampling and Analysing

The long-term test lasted for almost two years. Automatic samplers continuously collected flow-proportional samples of the untreated wastewater, the MBR-effluent and the final effluent after the GAC-biofilter and stored them cooled. Each week, composite samples were collected and frozen. During start-up and after some weeks of operation, weekly composite samples were sent for analyses. With the analyses at hand, coming weeks for analyses were planned for or previously collected samples were added in order to cover periods with significant changes. Grab samples for bacteria analyses were collected at the final day of a sampling campaign.

Investigated micropollutants include a wide range of relevant pharmaceuticals and other emerging substances, oestrogen effect, bacteria and microplastics (see Table S1 for details about investigated substances). Generally, triplicate analyses were performed on all samples. Only certified laboratories were utilized in the project. Thus, standard analytical methods for all analyses and are not described in detail here. Pharmaceuticals and microplastic particles were analysed at IVL's own certified laboratory using the following methods.

Pharmaceuticals were analysed using aliquots of 100 to 200 mL thawed composite samples that were spiked with 50  $\mu$ L internal standard carbamazepine- $^{13}\text{C}_{15}\text{N}$  (2000 ng/mL) and ibuprofen-D3 (2000 ng/mL). One millilitre of 0.1 wt% ethylenediaminetetraacetate (EDTA- $\text{Na}_2$ ) dissolved in

methanol:water (1:1) was added. Prior to extraction using solid phase extraction (SPE) cartridges (Oasis HLB, 6 mL, Waters), the sample was shaken. Cartridges were conditioned with methanol followed by Milli-Q (MQ) water. Thereafter, the samples were applied to the columns at a flow rate of two drops per second. The substances were eluted from the SPE cartridges using 5 mL methanol followed by 5 mL acetone. The supernatants were transferred to vials for final analysis on a binary liquid chromatography (UFLC) system with auto injection (Shimadzu, Japan). The chromatographic separation was carried out using gradient elution on a C18 reversed phase column (dimensions 50 × 3 mm, 2.5- $\mu$ m particle size, XBridge, Waters, UK) at a temperature of 35 °C and a flow rate of 0.3 mL/ min. The mobile phase consists of 10 mM acetic acid in water.

In addition to pharmaceuticals and phenolic compounds in water, also the contents in the filter material was analysed at the end of the experiment. Pharmaceuticals residues in the carbon were determined after representative samples were taken, dewatered and freeze-dried. The substances were extracted with acetone: acetic acid (20:1). The eluate was then treated as for the water samples.

Even so, replicate analyses have been performed, complex wastewater and filter material matrixes imply challenges during sample preparation and analyses. For example, other organic substances can reduce the recovery during sample preparation and affect the signal during analysis or some substances to be analysed can interact with free ions from the matrix and form chelate complex, which result in reduced recovery and detection. As the test are based on real wastewater including the daily, weekly and seasonal quality variation, analyses uncertainty varies during the 2 years of analyses as also the water matrix varies. Therefore, only average values of replicate analyses are presented in this study.

Microplastic particles were analysed by following method [48] commonly used in screenings in Nordic countries as standards for microplastic analyses are not yet established. The water samples were filtered through filters with a mesh size of 20  $\mu$ m and the material collected on the filters was analysed with a stereo microscope (50 times magnification). All microplastic particles were counted and divided into three groups according to their shape—plastic fragments, plastic flakes and plastic fibres. The term plastic flake was used for very thin particles, whereas thicker particles were called plastic fragments. The term microplastics or plastic particles refer to all three groups. In addition to the microplastics, also non-synthetic fibres of anthropogenic origin were counted. This included textile fibres of for example cotton but not cellulose from toilet paper.

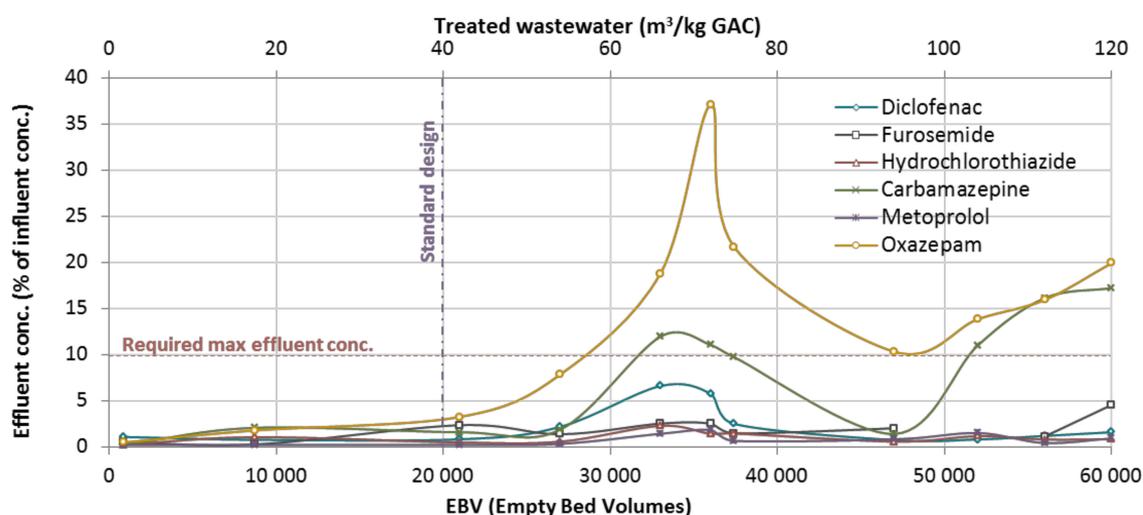
Material suspended before the GAC-filter was measured with an online meter of the Züllig COSMOS 25. The total suspended solids (TSS) was determined by standard method (SS 02 81 12-3) and BOD5 with WTW Oxitop. pH was determined with a hand meter (pH 3110 from WTW) and colour, transmission and absorbance at 254 nm were determined using a spectrophotometer—WTW photoLAB 6600. TOC was determined according to standard method (SS-EN 1484).

### 3. Results and Discussions

Many pharmaceutical substances were already removed in the MBR to levels below the reporting limit. Compared with the full-scale WWTP Henriksdal, the MBR resulted in lower concentrations of for example furosemide, bisoprolol, metoprolol and sertraline. Reasons for the better treatment may be the higher sludge age providing an enhanced biodegradation or certain adsorption to the membrane (sertraline) as also reported by [49].

For the evaluation of the removal efficiency in the GAC-biofilter, only compounds that were always quantifiable before the filter and at least once quantifiable after the filter were considered in the assessment. Figure 2 shows filter effluent concentrations as a percentage of the influent concentration for these compounds. Values below LOQ (limit of quantification) are here set as LOQ/2. The x-axis is graded with the number of Empty Bed Volumes (EBVs) that passed the GAC-biofilter. 60 000 EBV corresponds to 120 m<sup>3</sup> water/kg GAC in the filter, that is 574 days after the start of the experiment when the tests had to be stopped due to reconstruction of the MBR-pilot. The figure also shows the

targeted removal efficiency by the project and common design criteria for GAC-filter where only adsorption of micropollutants is considered.



**Figure 2.** Average reduction of various pharmaceuticals during the whole project period.

Figure 2 shows a good removal of all substances immediately after the operation of the filter was initiated. This is mainly explained by a high adsorption capacity of the fresh GAC as also reported by [16,32]. Up to about 25,000 EBV (about 50 m<sup>3</sup>/kg GAC), the removal was very good for all compounds. Then elevated effluent concentrations for some compounds can be observed. The level of oxazepam and carbamazepine increased to more than 10% of incoming concentrations and the diclofenac concentration exceeded 5% of the incoming concentration. The GAC-biofilter operation, however, was continued to evaluate the long-term removal efficiency of the GAC-biofilter for all substances. As the figure indicates, the removal efficiency improved again without any changes in operating mode. A similar recovery was also noted in earlier trials with a GAC-filter treating the effluent of a WWTP operated as conventional activated sludge process [16]. However, analysed concentrations do not indicate any significant changes in the incoming load to the GAC-biofilter and can thus not explain the temporal increase of concentrations in the GAC-biofilter effluent. In addition, no other test parameters, for example water temperature, changed in a way that could explain observed removal variations in Figure 2. A bio-regeneration inside the GAC-biofilter may be a potential explanation. Bio-regeneration was reviewed before as a more sustainable alternative to conventional regeneration methods but focus has been on bio-regeneration in offline filters [50]. However, it is mentioned that the same process may also take place in GAC-filters with an established biological activity. Although there have been some good research efforts in bio-regeneration, there is still not much known about the factors affecting the regeneration process [50].

After about 50,000 EBV (about 100 m<sup>3</sup>/kg GAC), another increase of effluent concentrations can be observed for oxazepam and carbamazepine. The increase of furosemide is not certain as the level was below LOQ and the high percentage is due to very low concentration levels. At 60,000 EBV (about 120 m<sup>3</sup>/kg GAC), the experiment was terminated due to a required modification of the MBR-pilot. The sampling frequency with weekly composites samples does not provide any information about actual load variations with a higher resolution. It is not self-evident whether the removal in the GAC-biofilter is defined as a certain percentage of incoming concentration, a certain amount per unit of time or down to a certain residual content. Probably it is a combination as also suggest by [51]. Evaluating the actual concentrations in the effluent show that the corresponding curves to Figure 2 have roughly the same shape. However, for Oxazepam the peak appears somewhat later. This is probably due to varying concentrations in the inflow to the filter. Table S2 in the Supplementary Materials shows analysed concentrations of all compounds before and after the GAC-biofilter at the end of the test.

At the end of the experiment, samples of the used GAC were taken from various levels of the filter bed. Higher concentrations of pharmaceutical residues were observed in samples from the top layer of the filter bed despite frequent backwashing during the 2 years of operation. This implies that the frequent backwash did not affect the concentration profile in the filter as also suggested by [16]. A screening analysis of the used GAC indicated very small changes in the size distribution of the carbon particles, which indicates a very morphologically stable carbon. Despite this, a decomposition of carbon particles could be observed in a larger proportion of small particles, which also implies that the number of larger particles was reduced.

After the pilot operation was finalized, a rough mass-balance for the removed pharmaceutical substances by the GAC-biofilter was established. Amounts of substances removed were calculated based on all analyses and the assumption that the concentrations varied linearly between analyses events. For the GAC-biofilter effluent, concentrations below LOQ have been considered as LOQ/2. Analysis of the backwash water showed high levels of suspended biological material, 200-300 mg/L but very low levels of pharmaceutical substances. The recirculation of these substances back to the inflow of the MBR-pilot via backwash water was estimated to be less than 1% of the total load to the GAC-biofilter. The difference between incoming and outgoing mass flows is then determined as the amount removed by the GAC-biofilter. As most of the compounds are considered as stable, they should then be contained in the used GAC. Table 1 shows the amounts of considered pharmaceutical residues found in the GAC. Presented results are corrected for the exchange of the respective substance in the extraction of new spiked carbon. The yield was between 50 and 100 % for the various compounds.

**Table 1.** Total amount of removed pharmaceutical residues in the GAC-biofilter.

	Total Removed mg/kg GAC	Analysed in GAC mg/kg GAC	Adsorbed %
Citalopram	29.2	1.09	3.7
Diclofenac	67.9	0.13	0.2
Furosemide	49.2	0.57	1.2
Hydrochlorothiazide	143.4	3.97	2.8
Ibuprofen	8.1	0.01	0.1
Carbamazepine	41.2	13.1	31.8
Metoprolol	82.5	3.15	3.8
Oxazepam	54.3	7.03	12.9
Propranolol	6.7	0.87	12.0

Despite several uncertainties in the mass balance, it is clear that most of the considered compounds that efficiently have been removed from the wastewater, were not found in the analysed GAC. After initially being adsorbed by the GAC, the compounds may have been broken down biologically by the established biological activity in the filter as also discussed by [50]. Even a metabolization of the substances in the filter may be possible, as applied analytical methods could not measure metabolites of the considered pharmaceuticals. Measured COD/TOC in the effluent of the filter was stable and the change of Spectral Absorption Coefficient (SAC) over the filter remained stable. A microbial screening of the biofilm in the filter material and a related quantification of the removal of substances by either adsorption or biodegradation is difficult [50] and they were not performed in this project. The assessment of the adsorbed contaminants in the GAC as shown in Table 1, supports the assumption of a bio-regeneration in the GAC-biofilter, which extends the lifetime of the system (see also [50]).

In general, the MBR-process provides a high quality, particle-free effluent compared to traditional activated sludge processes. Bacteria, including multiresistant bacteria, of all sizes larger than the membrane pore size were efficiently removed from the wastewater by the MBR-process. However, very low concentrations (<65 cfu/100 mL) of bacteria were still detected in the MBR-effluent. It could, however, not be determined if these bacteria originated from sample contamination or contact of the permeate with the atmosphere. Both aspects are almost impossible to avoid in sewage treatment environments. Total coliforms in the treated MBR-effluent were further reduced with >85% by the

GAC-biofilter. Interestingly, faecal coliform removal was absent during the first weeks of operation while a reduction of more than 90% was achieved after 3 months of operation. This might be explained by the established biology in the filter that outcompetes faecal coliforms.

The studied phenolic compounds triclosan and bisphenol A were reduced to below detection limit. Most of nonylphenol and octylphenol was removed as well. It was difficult to extract several of the phenolic compounds from the carbon. Thus, a mass balances for these compounds over the GAC-biofilter was not possible to perform. High levels of nonylphenol, triclosan and bisphenol A in the backwash water suggested that they were largely bound to the flushed biomass and thus returned to the biological process in the main treatment.

Not a single microplastic particle was detected in the MBR-effluent (removal efficiency 100%), whereas effluent water from the full-scale CAS-process including a final sand filtration contained both plastic fibres and plastic fragments (removal efficiency 90.7 %). Non-synthetic fibres were found in both MBR and CAS effluents.

Compared to complimentary treatment of the final effluent from the main WWTP Henriksdal, that is the same influent water, [16,52], a significant reduction of clogging and backwash frequency was achieved in the GAC-biofilter when treating MBR-effluent. Both aspects have a direct impact on the operational cost of the GAC-biofilter system. The better quality of MBR-effluent compared to traditional CAS-effluent (even with sand filtration [15]) provided better conditions for the GAC-biofilter operation.

The initial adsorption of pharmaceutical substances and thus concentration build-up on the filter material provides good conditions for the establishment of a biology. Compared to treatments system that use the same technology combination but in a different order [51], are more specialized biology may be able to establish as easier degradable organic contaminants have already been removed by the preceding MBR-process. High oxygen concentrations in the effluent from the MBR due to continuous air scouring of the membranes may enhance the biological breakdown of organic micropollutants in the following biofilter.

The evaluation of the pilot operation and related removal of micropollutants indicates that some aspects need further confirming experiments in order to utilize the findings in the most optimal way. Here the recovery of the removal capacity in the biofilter is the most interesting aspect for further investigation as also pointed out by [50].

#### 4. Conclusions

The combination of Membrane Bioreactor (MBR) and biofilter with granulated activated carbon (GAC) as filter material have not received the same attention as resource efficient removal alternative for micropollutants as other technologies. The combination of an enhanced biology and ultrafiltration in the MBR, followed by adsorption and biological degradation in the GAC-biofilter, however, is a powerful treatment alternative. Considering the increasing number of MBR installations in municipal sewage treatment worldwide, the treatment combination has a significant potential to meet requirements for less micropollutant discharge to the environment in a resource-efficient way, especially in large WWTPs. The combination of an MBR system and GAC-biofilter cannot only remove a broader range of micropollutants than ozonation. Further, the system does not impose any risk of the formation of toxic residues and has greater improvement potential regarding environmental sustainability and costs.

The long-term evaluation of the GAC-biofilter subsequent of an MBR-treatment shows that about 90–98 % of the pharmaceutical residues could be removed from the water. The assessment illustrates the importance of long-term tests to determine the actual capacity of a biological active filter. This combination of the different treatment technologies and associated removal processes not only facilitates a more efficient removal of pharmaceutical residues, but it also prolongs the lifetime of the filter material. The performed analyses and mass balances show that only a minor amount of the removed substances was adsorbed to the filter material. The majority of the removed pharmaceutical substances was broken down by the established biology in the filter. The results further indicate that

the biological activity in the GAC-biofilter can provide a bio-regeneration of the GAC by decomposing targeted substances and thereby restoring adsorption capacity of the GAC. This finding may have significant impact on the overall resource efficiency of such treatment systems, both regarding costs and overall environmental impact of the additional treatment.

The investigation further shows the advantage of using GAC as filter material as the high adsorption capacity of GAC ensures a high removal efficiency right from the start-up of the filter even so a microbial community on the GAC surface requires time to establish. The initial adsorption of pharmaceuticals substances and thus concentration build-up on the filter material provides good conditions for the establishment of a specialized biology.

In general, the project results show that the combination of an MBR-process with a GAC-biofilter provides a complementary treatment system able to meet various demands for efficient sewage treatment to low effluent concentrations of organics, nutrients, suspended solids and micropollutants. As requirements on sewage treatments including the removal of micropollutants will continuously become stricter, the investigated treatment system of MBR and GAC-biofilter may be one of the most attractive solution for a resource-efficient removal of a broad range of micropollutants from sewage. Even so, more research on this treatment system is necessary; the current study clearly indicates the potential of the system.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2076-3417/9/4/710/s1>.

**Author Contributions:** The three authors have made equal substantial contributions to the planning, setup and operation of the pilot-test and interpretation of the results.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Brodin, T.; Fick, J.; Jonsson, M.; Klaminder, J. Dilute Concentrations of a Psychiatric Drug Alter Behavior of Fish from Natural Populations. *Science* **2013**, *339*, 814–815. [[CrossRef](#)] [[PubMed](#)]
2. Deblonde, T.; Cossu-Leguille, C.; Hartemann, P. Emerging pollutants in wastewater: A review of the literature. *Int. J. Hyg. Environ. Health* **2011**, *214*, 442–448. [[CrossRef](#)] [[PubMed](#)]
3. Fick, J.; Lindberg, R.H.; Kaj, L.; Brorström-Lundén, E. *Results from the Swedish National Screening Programme 2010, Subreport 3, Pharmaceuticals*; B2014; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2011.
4. Fick, J.; Lindberg, R.H.; Schwesig, D.; Gawlik, B.M. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. *Water Res.* **2013**, *47*, 6475–6487. [[CrossRef](#)]
5. Kim, S.D.; Cho, J.; Kim, I.S.; Vanderford, B.J.; Snyder, S.A. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Res.* **2007**, *41*. [[CrossRef](#)] [[PubMed](#)]
6. Vasquez, M.I.; Lambrianides, A.; Schneider, M.; Kümmerer, K.; Fatta-Kassinos, D. Environmental side effects of pharmaceutical cocktails: What we know and what we should know. *J. Hazard. Mater.* **2014**, *279*, 169–189. [[CrossRef](#)] [[PubMed](#)]
7. Rempharmawater. Ecotoxicological Assessments and Removal Technologies for Pharmaceuticals in Wastewaters. Project Reference: EVK1-CT-2000-00048. 2003. Available online: <http://www.unina.it> (accessed on 22 August 2018).
8. POSEIDON. Assessment of Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse. Project Reference: EVK1-CT-2000-00047. 2004. Available online: <http://www.eu-poseidon.com> (accessed on 22 August 2018).
9. RiSKWa. *Risk Management of Emerging Compounds and Pathogens in the Water Cycle*; Bundesministerium für Bildung und Forschung (BMBF): Bonn, Germany, 2013; Available online: <http://www.bmbf.riskwa.de> (accessed on 22 August 2018).
10. Abegglen, C.; Siegrist, H. *Mikroverunreinigungen aus Kommunalem Abwasser. Verfahren zur Weitergehenden Elimination auf Kläranlagen (Micropollutants from Municipal Wastewater. Method for Further Elimination on Sewage Treatment Plants)*; Umwelt-Wissen Nr. 1214: 210; Bundesamt für Umwelt: Bern, Germany, 2012.

11. Arge Spurenstoffe NRW. Teilprojekt 6. *Elimination von Arzneimitteln und Organischen Spurenstoffen: Entwicklung von Konzeptionen und Innovativen, Kostengünstigen Reinigungsverfahren (Elimination of Pharmaceuticals and Organic Trace Substances: Development of Concepts and Innovative, Cost-Effective Cleaning Methods)*—Abschlussbericht zur Phase 2; Arge Spurenstoffe NRW: Bochum, Germany, 2013.
12. Baresel, C.; Ek, M.; Harding, M.; Bergström, R. *Treatment of Biologically Treated Wastewater with Ozone or Activated Carbon*; B2203; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2014.
13. Baresel, C.; Dahlgren, L.; Nikolic, A.; de Kerchove, A.; Almemark, M.; Ek, M.; Harding, M.; Ottosson, E.; Karlsson, J.; Yang, J. *Reuse of Treated Wastewater for Nonpotable Use (ReUse)*—Final Report; B2219; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2015.
14. Baresel, C.; Malmberg, J.; Ek, M.; Sehlén, R. Removal of pharmaceutical residues using ozonation as intermediate process step at Linköping WWTP, Sweden. *Water Sci. Technol.* **2016**, *73*, 2017–2024. [[CrossRef](#)] [[PubMed](#)]
15. Baresel, C.; Ek, M.; Ejhed, H.; Allard, A.S.; Magnér, J.; Dahlgren, L.; Westling, K.; Wahlberg, C.; Fortkamp, U.; Søhr, S. *Handbook for the Treatment of Micropollutants at Sewage Treatment Plant—Planning and Installing Treatment Techniques for Pharmaceutical Residues and Other Micropollutants*; Final Report SystemLäk Project; B2288; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2017.
16. Ek, M.; Baresel, C.; Magnér, J.; Bergström, R.; Harding, M. Activated carbon for the removal of pharmaceutical residues from treated wastewater. *Water Sci. Technol.* **2014**, *69*, 2372–2380. [[CrossRef](#)] [[PubMed](#)]
17. Wahlberg, C.; Björleinius, B.; Paxéus, N. *Läkemedelsrester i Stockholms Vattenmiljö—Förekomst, Förebyggande Åtgärder och Rening av Avloppsvatten (Pharmaceutical Residues in Stockholm's Aquatic Environment—Prevention, Prevention and Treatment of Sewage)*; Stockholm Vatten AB: Stockholm, Sweden, 2010; ISBN 978-91-633-6642-0.
18. Altmann, J.; Ruhl, A.S.; Zietzschmann, F.; Jekel, M. Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water Res.* **2014**, *55*, 185–193. [[CrossRef](#)]
19. Abegglen, C.; Escher, B.; Hollender, J.; Siegrist, H.; von Gunten, U.; Zimmermann, S.; Häner, A.; Ort, C.; Schärer, M. Ozonung von gereinigtem Abwasser zur Elimination von organischen Spurenstoffen. Grosstechnischer Pilotversuch Regensdorf (Schweiz) (Ozonation of purified wastewater to eliminate organic trace substances. Large-scale pilot test Regensdorf (Switzerland)). *Korrespondenz Abwasser Abfall* **2010**, *57*, 155–160.
20. Gerrity, D.; Snyder, S. Review of Ozone for Water Reuse Applications: Toxicity, Regulations, and Trace Organic Contaminant Oxidation. *Ozone Sci. Eng.* **2011**, *33*, 253–266. [[CrossRef](#)]
21. Magdeburg, A.; Stalter, D.; Oehlmann, J. Whole effluent toxicity assessment at a wastewater treatment plant upgraded with a full-scale post-ozonation using aquatic key species. *Chemosphere* **2012**, *88*. [[CrossRef](#)] [[PubMed](#)]
22. Magdeburg, A.; Stalter, D.; Schlüsener, M.; Ternes, T.; Oehlmann, J. Evaluating the efficiency of advanced wastewater treatment: Target analysis of organic contaminants and (geno-)toxicity assessment tell a different story. *Water Res.* **2014**, *50*, 35–47. [[CrossRef](#)] [[PubMed](#)]
23. Maus, C.; Herbst, H.; Ante, S.; Becker, H.-P.; Glathe, W.; Bärgers, A.; Türk, J. Guidance on the interpretation and design of ozonation plants for micropollutants elimination. *Korrespondenz Abwasser Abfall* **2014**, *61*, 998–1006.
24. Reungoat, J.; Escher, B.I.; Macova, M.; Keller, J. Biofiltration of wastewater treatment plant effluent: Effective removal of pharmaceuticals and personal care products and reduction of toxicity. *Water Res.* **2011**, *45*, 2751–2762. [[CrossRef](#)] [[PubMed](#)]
25. Stalter, D.; Magdeburg, A.; Weil, M.; Knacker, T.; Oehlmann, J. Toxication or detoxication? In vivo toxicity assessment of ozonation as advanced wastewater treatment with the rainbow trout. *Water Res.* **2010**, *44*, 439–448. [[CrossRef](#)] [[PubMed](#)]
26. Stalter, D.; Magdeburg, A.; Oehlmann, J. Comparative toxicity assessment of ozone and activated carbon treated sewage effluents using an in vivo test battery. *Water Res.* **2010**, *44*, 2610–2620. [[CrossRef](#)] [[PubMed](#)]
27. Stalter, D.; Magdeburg, A.; Wagner, M.; Oehlmann, J. Ozonation and activated carbon treatment of sewage effluents: Removal of endocrine activity and cytotoxicity. *Water Res.* **2011**, *45*, 1015–1024. [[CrossRef](#)] [[PubMed](#)]
28. Wert, E.C.; Rosario-Ortiz, F.L.; Drury, D.D.; Snyder, S.A. Formation of oxidation byproducts from ozonation of wastewater. *Water Res.* **2007**, *41*, 1481–1490. [[CrossRef](#)] [[PubMed](#)]

29. Alt, K.; Mauritz, A. Projekt zur Teilstrombehandlung mit Pulveraktivkohle im Klärwerk Mannheim (Project for sidestream treatment with powdered activated carbon in the sewage treatment plant Mannheim). *Korrespondenz Abwasser Abfall* **2010**, *57*, 161.
30. Boehler, M.; Zwickenpflug, B.; Hollender, J.; Ternes, T.; Joss, A.; Siegrist, H. Removal of micropollutants in municipal wastewater treatment plants by powderactivated carbon. *Water Sci. Technol.* **2012**, *66*, 2115. [[CrossRef](#)] [[PubMed](#)]
31. Clausen, K.; Lübken, M.; Pehl, B.; Bendt, T.; Wichern, M. Einsatz reaktiver Aktivkohle von Wasserwerken zur Spurenstoffelimination in kommunalen Kläranlagen am Beispiel Düsseldorf (Use of reactivated activated carbon from water works for the elimination of trace substances in municipal sewage treatment plants using the example of Düsseldorf). *Korrespondenz Abwasser Abfall* **2014**, *61*, 1007–1012.
32. Grover, D.P.; Zhou, J.L.; Frickers, P.E.; Readman, J.W. Improved removal of estrogenic and pharmaceutical compounds in sewage effluent by full scale granular activated carbon: Impact on receiving river water. *J. Hazard. Mater.* **2011**, *185*, 1005–1011. [[CrossRef](#)] [[PubMed](#)]
33. Kovalova, L.; Siegrist, H.; von Gunten, U.; Eugster, J.; Hagenbuch, M.; Wittmer, A.; Moser, R.; McArdell, C.S. Elimination of Micropollutants during Post-Treatment of Hospital Wastewater with Powdered Activated Carbon, Ozone, and UV. *Environ. Sci. Technol.* **2013**, *47*, 7899–7908. [[CrossRef](#)] [[PubMed](#)]
34. Luo, Y.; Guo, W.; Ngo, H.H.; Nghiem, L.D.; Hai, F.I.; Zhang, J.; Liang, S.; Wang, X.C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* **2014**, *473–474*, 619–641. [[CrossRef](#)] [[PubMed](#)]
35. Metzger, S.; Tjoeng, I.O.; Rößler, A.; Schwentner, G.; Rölle, R. Kosten der Pulveraktivkohleanwendung zur Spurenstoffelimination am Beispiel ausgeführter und in Bau befindlicher Anlagen (Cost of powdered activated carbon application for the elimination of trace substances using the example of selected plants under construction.). *Korrespondenz Abwasser Abfall* **2014**, *61*, 1029–1037.
36. Baresel, C.; Ek, M.; Harding, M.; Magnér, J.; Allard, A.S.; Karlsson, J. *Complementary Tests for a Resource Efficient Advanced Sewage Treatment*; Subreport SystemLäk Project; B2287; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2017.
37. Barillon, B.; Ruel, S.M.; Langlais, C.; Lazarova, V. Energy efficiency in membrane bioreactors. *Water Sci Technol.* **2013**, *67*, 2685–2691. [[CrossRef](#)] [[PubMed](#)]
38. Ioannou-Ttofa, L.; Foteinis, S.; Chatzisyneon, E.; Fatta-Kassinos, D. The environmental footprint of a membrane bioreactor treatment process through Life Cycle Analysis. *Sci. Total Environ.* **2016**, *568*, 306–318. [[CrossRef](#)] [[PubMed](#)]
39. Larrea, A.; Rambor, A.; Fabiyi, M. Ten years of industrial and municipal membrane bioreactor (MBR) systems—Lessons from the field. *Water Sci. Technol.* **2014**, *70*, 279–288. [[CrossRef](#)] [[PubMed](#)]
40. Meng, F.; Chae, S.-R.; Shin, H.-S.; Yang, F.; Zhou, Z. Recent Advances in Membrane Bioreactors: Configuration Development, Pollutant Elimination, and Sludge Reduction. *Environ. Eng. Sci.* **2012**, *29*, 139–160. [[CrossRef](#)]
41. Pinnekamp, J. Membrantechnik für die Abwasserreinigung (Membrane Technology for Wastewater Treatment). In *Siedlungswasser- und Siedlungsabfallwirtschaft Nordrhein-Westfalen*; Aktual, A., Ed.; FiW-Verl: Aachen, Germany, 2006.
42. Baresel, C.; Westling, K.; Samuelsson, O.; Andersson, S.; Royen, H.; Andersson, S.; Dahlén, N. Membrane Bioreactor Processes to Meet Today's and Future Municipal Sewage Treatment Requirements? *Int. J. Water Wastewater Treat.* **2017**, *3*. [[CrossRef](#)]
43. Lipp, P.; Kreißel, K.; Meuler, S.; Bischof, F.; Tiehm, A. Influencing parameters for the operation of an MBR with respect to the removal of persistent organic pollutants. *Desalin. Water Treat.* **2009**, *6*, 102–107. [[CrossRef](#)]
44. Radjenović, J.; Petrović, M.; Barceló, D. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. *Water Res.* **2009**, *43*, 831–841. [[CrossRef](#)] [[PubMed](#)]
45. Sipma, J.; Osuna, B.; Collado, N.; Monclús, H.; Ferrero, G.; Comas, J.; Rodriguez-Roda, I. Comparison of removal of pharmaceuticals in MBR and activated sludge systems. *Desalination* **2010**, *250*, 653–659. [[CrossRef](#)]
46. Ek, M.; Bergström, R.; Magnér, J.; Harding, M.; Baresel, C. *Aktivt kol för Avlägsnande av Läkemedelsrester ur Behandlat Avloppsavatten (Activated Carbon for Removal of Pharmaceutical Residues from Treated Wastewater)*; B2089; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2013.

47. Ek, M.; Bergström, R.; Baresel, C. *Avskiljning av Läkemedelsrester Med Granulerat Aktivt kol–Försök vid Himmerfjärdsverket (Removal of Pharmaceutical Residues with Granulated Activated Carbon)*; U4492; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2013.
48. Magnusson, K.; Jörundsdóttir, H.; Norén, F.; Lloyd, H.; Talvitie, J. *Micro litter in Sewage Treatment Systems: A Nordic Perspective on Waste Water Treatment Plants as Pathways for Microscopic Anthropogenic Particles to Marine Systems*; TemaNord, Nordic Council of Ministers: Copenhagen, Denmark, 2016.
49. Park, J.; Yamashita, N.; Park, C.; Shimono, T.; Takeuchi, D.M.; Tanaka, H. Removal characteristics of pharmaceuticals and personal care products: Comparison between membrane bioreactor and various biological treatment processes. *Chemosphere* **2017**, *179*, 347–358. [[CrossRef](#)]
50. El Gamal, M.; Mousa, H.A.; El-Naas, M.H.; Zacharia, R.; Judd, S. Bio-regeneration of activated carbon: A comprehensive review. *Sep. Purif. Technol.* **2018**, *197*, 345–359. [[CrossRef](#)]
51. Sbardella, L.; Comas, J.; Fenu, A.; Rodriguez-Roda, I.; Weemaes, M. Advanced biological activated carbon filter for removing pharmaceutically active compounds from treated wastewater. *Sci. Total Environ.* **2018**, *636*, 519–529. [[CrossRef](#)]
52. Baresel, C.; Cousins, A.P.; Hörsing, M.; Ek, M.; Ejhed, H.; Allard, A.S.; Magnér, J.; Westling, K.; Wahlberg, C.; Fortkamp, U.; et al. *Pharmaceutical Residues and Other Emerging Substances in the Effluent of Sewage Treatment Plants—Review on Concentrations, Quantification, Behaviour, and Removal Options*; B2226; IVL Swedish Environmental Research Institute: Stockholm, Sweden, 2015.



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).