CWPharma 2
CLEAR WATERS FROM PHARMACEUTICALS

Advanced wastewater treatment for API elimination at WWTP Hillerød

Feasibility study

GoA2.2: Applying recommendations for planning of API removal and plant optimization

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Chapter contributions (institution):

- Introduction (HFORS)
- Ambition of the API elimination technology (HFORS, KWB)
- Status of the WWTP (HFORS, KWB)
- A summary of API monitoring campaigns at Hillerød WWTP (HFORS)
- Evaluating different AWT options (HFORS, KWB)
- Preliminary design of AWT technology (KWB, HFORS)
- Costs (KWB, HFORS)
- Overall evaluation (HFORS, KWB)
- On implementing the CWPharma Guideline for advanced API removal (HFORS)
- Appendix: Effluent quality (HFORS, KWB, AU)

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Introduction

This report describes the use of the CWPharma *Guideline for Advanced API Removal*[1] at at a feasibility study at Hillerød WWTP.

There are four modules of implementation described in the CWPharma Guideline for advanced API removal: "**WWTP Fitness check**", "**Feasibility study**", "**Detailed planning**" and "**Optimizing existing systems**" (if possible).

This report is based on the results of the "**Feasibility study**" module, which is recommended to include: "Ambition of the API elimination technology", "Status of the WWTP", "API monitoring campaigns", "State of the art / knowledge of AWT", "Preliminary design of AWT technology", "Costs" and "Overall evaluation".

A review on the state of the art is not included as such, but several treatment options are evaluated, based on the CWPharma Guideline for advanced API removal.

Preliminary design values for GAC-filtration from the Guideline was used for design of the pilot plant which including ozonation + GAC-filtration.

An on-site pilot test, at Hillerød WWTP, which is described in appendix was also part of the CWPharma 2 and result from this test is given in report GoA2.3.

Ambition of the API elimination technology

The ambition at Hillerød WWTP is to deliver clean water that already in the effluent fulfils all the water quality standards for good ecological conditions, bathing water and drinking water.

Conventional "state-of-the-art" WWTPs can only remove APIs that are either easily biodegradable and/or absorbable to activated sludge, whereas other API's can pass the treatment process with no or only minor reductions.

Therefore, reduction of a broad range of APIs can only be achieved by using targeted advanced wastewater treatment (AWT) techniques, such as ozonation or application of powdered and granular activated carbon.

These technologies for API removal are already used at full-scale WWTPs and have proven their practical and economical suitability.

Decreasing the API load of the environment is the overall goal for Hillerød WWTP. The target is to reduce API's to below Predicted No Effect Concentration (PNEC) in the environment using a Best Available Technique (BAT) solution for API removal at Hillerød WWTP.

The Hillerød WWTP effluent is led to a sensible estuary "Roskilde Fjord" through a small stream Pøle Å.

The effluent from the WWTP is not expected to impact drinking water sources and has little or no impact on the bathing waters.

API or micropollutant removal is not yet generally required in Denmark and therefore HFORS is working together with the local authority (Hillerød Kommune) to find target APIs to use for control in the future.

Potential synergies of AWT at Hillerød WWTP is a combination with further reduction of phosphorous and nitrogen.

Status of the Hillerød WWTP

Hillerød WWTP is a mid-size WWTP in Denmark with a relatively high portion of industrial load.

Hillerød WWTP handles wastewater from around 23 000 households and several industries, of which two are large pharmaceutical companies adding substantially to the load of the plant.

The treatment capacity corresponds to 68 000 PE with the possibility to expand to 100 000 PE to make room for a developing city and new industries.

The Hillerød WWTP (HCR Syd) is a mechanical – biological – chemical multistage plant taken into service in 2018. A flow diagram is shown in Figure 1.

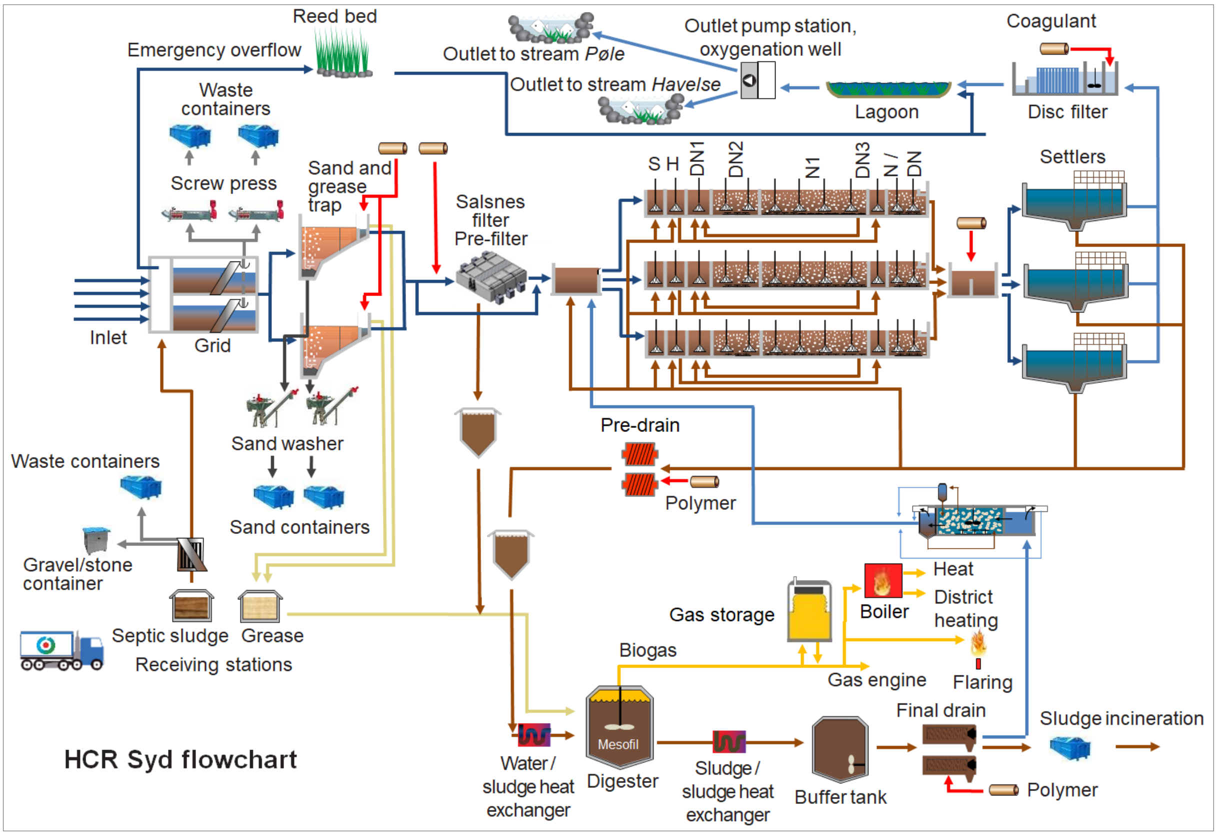

Figure 1. Hillerød WWTP process scheme.

Larger materials are removed in the inlet grid whereas sand and grease are removed in a trap.

Instead of a conventional primary clarifier, 6 Salsnes filters are installed for pre-treatment. Primary sludge from pre-treatment is sent to the anaerobic digester.

The biological treatment is handled in 3 process lines each consisting of a selector tank (S), a hydrolysis tank (H) for bio-P enhancement, 3 step denitrification tanks (DN1/2/3), nitrification tank (N) and one swing zone for both nitrification and denitrification (N/DN).

Internal recirculation from the N-tank to the DN1 tank is possible up to 5 x process flow. It is possible to dose coagulation and precipitation chemicals in the inlet to the secondary clarifiers where sludge is settled, and phosphorus precipitated.

The last step before led to the recipient the wastewater is polished in disc filters to ensure a low content of suspended solids and phosphorus.

Secondary sludge from the clarifiers is dewatered in drum filters and sent to the anaerobic digester to produce gas. Heat produced from the gas is used to heat the process buildings and processes where needed and the rest, about half, is sold to the district heat network.

Sludge from the anaerobic digester is dewatered in screw presses. The N-rich reject water from the dewatering is treated in an Annamox process to reduce the N-load before circulated back to the process tanks.

The WWTP is fully covered and build with a sedum green roof for ecological improvement and biodiversity and to impose less nuisance to surroundings and future neighbours. See Figure 2.

Figure 2. WWTP in Hillerød. The pre-treatment, process tanks and clarifiers with pumps etc. are fully covered inside two buildings built in the landscape with green roofs.

The plant discharges to a local freshwater system, which is classified as environmentally vulnerable, thus strict requirements to the discharge quality are necessary. Table 1 shows the current load, discharge quality and discharge permits at HCR Syd.

Table 1. Average load and discharge January '21 -October '21 (incl.), and discharge permits, HCR Syd, Hillerød, Denmark.

Parameter, (unit)	2021 average load	2021 average discharge	Discharge permit
Q (m^3/day)	15 919	16 195	18 356
SS (mg/l)	277	3.0	5.0
COD (mg/l)	548	24.6	75
Tot-P (mg/l)	8.09	0.134	0.182
Tot-N (mg/l)	42.6	2.34	3.66

API monitoring campaign at Hillerød WWTP

Several groups of micropollutants, such as heavy metals, VOCs, phenols and phthalates, are monitored regularly in the Hillerød WWTP effluent and influent, but there is no regular monitoring of APIs so far.

APIs have been measured in the pilot test. The values are presented in the report GoA2.3 "Testing and developing the CWPharma suggestions for the removal of pharmaceuticals - example Hillerød WWTP". API monitoring results have not been in the preliminary planning, which was based on literature values and an API measurement campaign (5 samples) in 2019.

In figure 3 and 4 is given an overview of the measured API's in the effluent from HCR Syd during the pilot test. Also included are some transformation products (TP). In the figures Benzotriazole (8.05 ± 1.81 µg/l) is excluded as not an API and Iohexol (7.88 ± 3.97 µg/l) is excluded as a non-poisonous x-ray contract medical used in high doses.

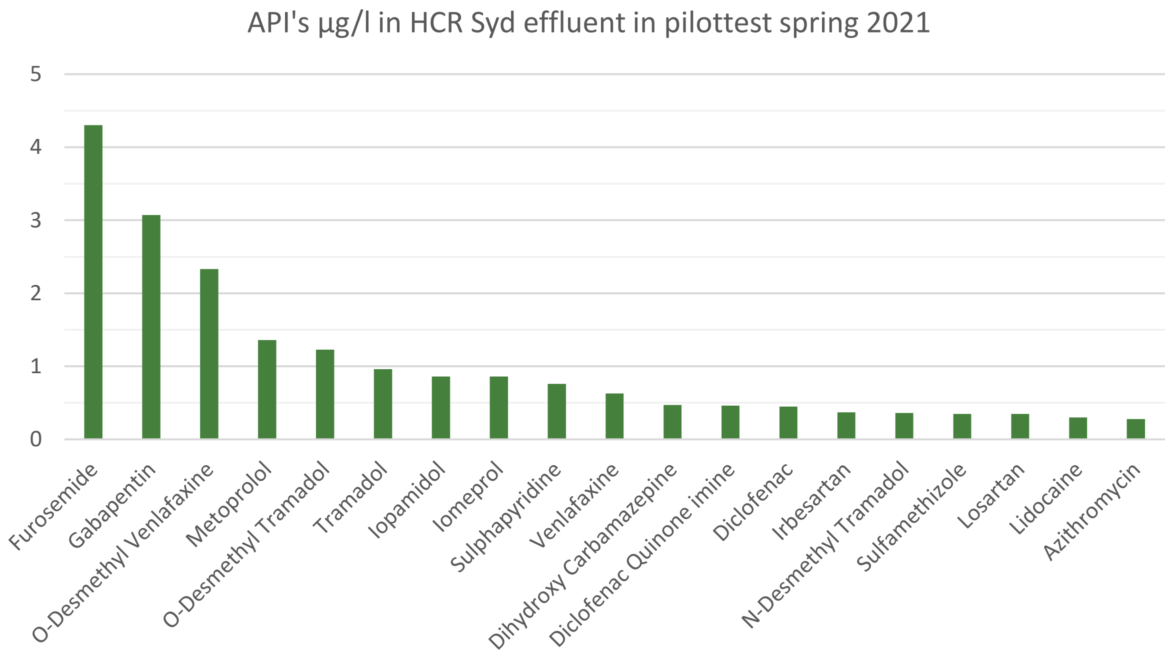

Figure 3. The most common API and TPs measured at HCR Syd in the pilot test in spring 2021.

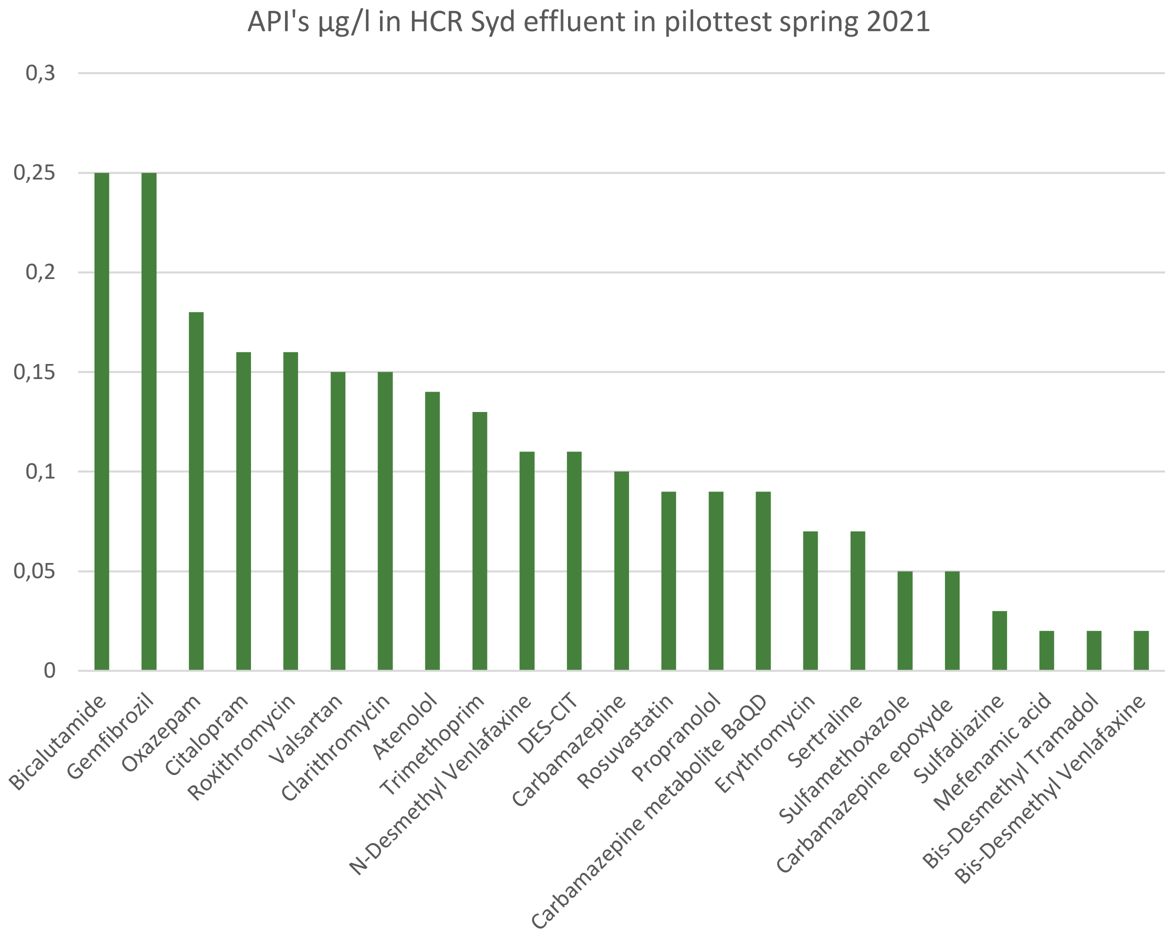

Figure 4. The less common API and TPs measured at HCR Syd in the pilot test in spring 2021.

Worth notice is the fact that the biological treatment at HCR Syd is creating some TP's in measurable concentrations. Thus TP's are not only made by the advanced oxidation processes (AOP) but can also be made biologically just in presence of normal oxygen.

Water quality parameters relevant for AWT (Ozonation)

Relevant parameters for AWT has been measured in table 2.

Table 2. Hillerød WWTP influent load.

Parameter	Measured concentration
DOC (mg/l)	13.8 +/- 3.2
Nitrite (mg/l)	< 0.015
Bromide (mg/l)	0.137 +/- 0.036

The water quality effluent at Hillerød WWTP is well suited for application of AWT technologies based on oxidation.

Evaluating different AWT options

Discuss the choosing of the scenarios

The feasibility of different treatment options with GAC and/or ozonation for Hillerød WWTP were evaluated in co-operation between HFORS and KWB.

The future plans for Hillerød WWTP is to include an effluent polishing consisting of about 10 μ filtration, ozonation, and GAC filtration, which is considered BAT technology in 2021.

Use of PAC as an option at Hillerød WWTP has been excluded in an early stage due to the fact that a cleaning stage for TP is needed after ozonation.

Potential barriers and limitations

There are some potential barriers limiting the feasible options or causing requirements for post treatment for Hillerød WWTP.

The barrier of insufficiently working clarifiers is identified as a clear hazard for the AWT treatment, which can course more frequent flushing of GAC filters. This can be solved by a filtration step with a suitable particle size cut-off and high filtration stability.

The digested and dried sludge from Hillerød WWTP is incinerated. This means that there for the time being is no public concern on the organic micropollutants in WWTP sludge. But that can change in the future.

There is not enough space for a post treatment step at the current facility and a separate new building is needed, which is costly. The post treatment step will most likely have to be built and covered like the rest of the facility.

Unless stated otherwise, all AWT processes are to be placed downstream of the current process and possible effluent polishing for phosphorus removal.

1. GAC filtration

API removal with granular activated carbon (GAC) is based on adsorption on the surface of the filter media. Activated carbon has a very high surface area.

GAC is used as a filter, which can be down flow or for example fluidised upflow.

In time, GAC will be saturated and to prevent a breakthrough of API, it will have to be replaced or reactivated. Reactivating GAC significantly decreases the need for new GAC. GAC filter material should be exchanged or reactivated typically after 20 000 – 30 000 bed volumes of wastewater depending on wastewater quality.

2. Ozonation

API removal by ozonation is based on oxidation. Important water quality parameters are DOC and nitrite (ozone consumption, dimensioning) and bromide (risk of bromate formation).

Compared to activated carbon, ozonation is in general less efficient for API removal, although certain compounds that cannot be removed by adsorption can be degraded with ozonation.

Ozone must be produced on site and the residual ozone in the off-gas must be destroyed using a thermic or a catalytic ozone destructor.

Producing ozone from oxygen has a high-energy consumption, roughly equivalent to energy consumption for aeration of the activated sludge process. Also, oxygen must either be purchased, or it must be produced from air. Producing oxygen from air more than doubles the energy consumption of ozonation on the site.

Ozonation can produce by-products that are even more harmful than the original compounds. Particularly if the wastewater contains bromide, ozonation effluent may have a higher ecotoxicity than ozonation influent. Ozonation requires a post treatment step to eliminate or reduce the ecotoxicological potential of ozonation by-products. The choice of the post treatment option may have a significant impact on the space requirement and operational costs. After ozonation the wastewater has a high oxygen concentration, which may be beneficial or problematic depending on the post treatment.

3. Ozonation and GAC filtration

If ozonation is combined with GAC filtration, the API removal is more efficient as some API are not removed by ozonation alone and some are not adsorbed on activated carbon.

Activated carbon does not remove bromate, but it does remove other ozonation by-products acting as efficient post treatment for ozonation, but not sufficient when high concentrations of bromide are present in the AWT influent.

The footprint of the treatment option is comparable to ozonation with sand or anthracite filtration and the operation costs include both the high-energy consumption of ozonation and the need to reactivate and replace GAC.

An activated carbon filter can also be used as a biologically enhanced activated carbon filter (BAC), particularly after ozonation, which breaks the DOC into more readily biodegradable compounds. The biological activity breaks down organic compounds, which slows down the saturation of the activated carbon. Also, some API may be removed or transformed by the biological activity itself. Thus, a lower GAC exchange rate may be sufficient.

Preliminary design of the AWT technology

The dimensioning is mainly made using an Excel-template developed by KWB. The values used are either "typical"/literature/German values suggested by KWB or based on the earlier preliminary planning. The numbering of process options is equivalent to the numbering used in the previous chapter: Evaluating different AWT options.

Dimensioning flows and parameters

The preliminary design for API removal has been made for the estimated flow of 2031-2041 and current (2021) effluent quality. The hydraulic influent loads for 2021 and the estimated load for 2031-2041 are presented in Table 3 and the effluent quality in table 5.

Table 3. HCR Syd Flow in 2021 and estimated for 2031-2041.

Flow HCR Syd	2021 l/s	2031-2041 l/s
Seldom low	116	120
Median	208	260
Seldom high	278	350
Maximum	350	450

Considerations about the development in flow etc. in the period 2021-2041 has lead to the decision in table 4 that dimension flow will be 350 l/s, at the start 2024-2025 with possibility to add on an other 100 l/s in capacity when needed.

Table 4. Design flow for 2021-2041.

Flow	m³/d	m³/h	l/s
Q_{DIM}	30.240	1.260	350

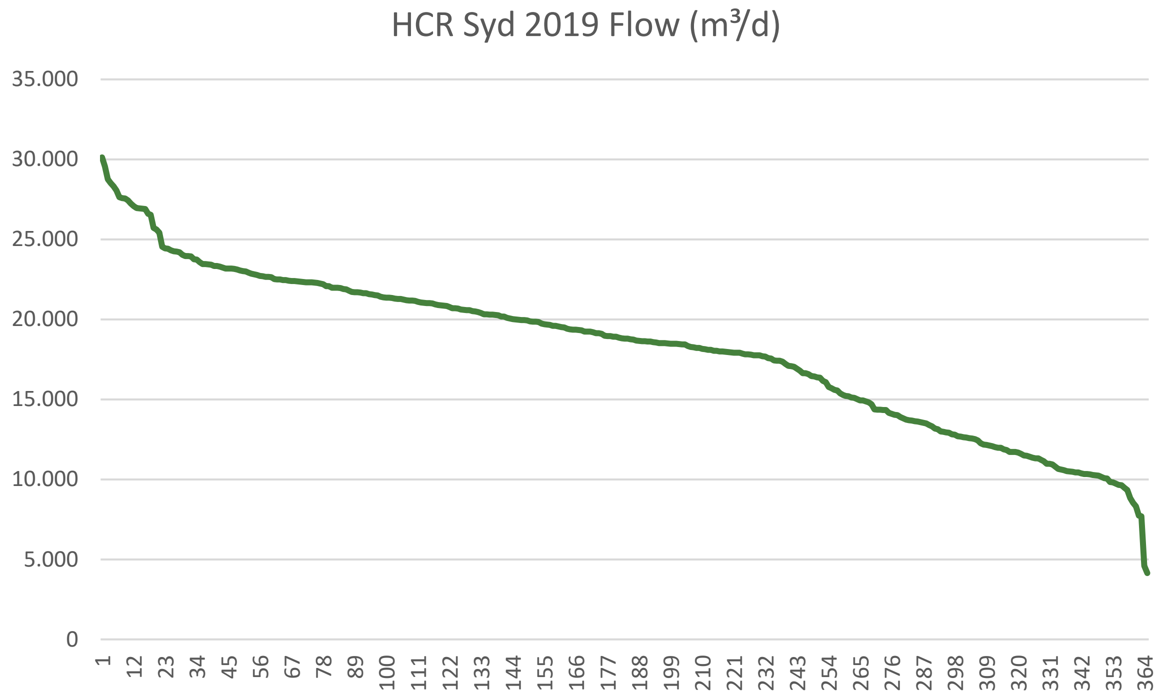

Figure 6. The influent flow duration curve in the rainy year 2019 at HCR Syd.

The wastewater effluent quality in HCR Syd is presented in table 5.

Table 5. Effluent quality parameters, average concentrations in January to October 2021. Asterisk (*) indicates that few data were measured in the pilot test.

Parameter	Unit	Value +/- std. dev.	Demands
COD_{Cr}	mg/l	26 +/- 5	75
BOD5	mg/l	1.9 +/- 1.1	6
DOC*	mg/l	13.8 +/- 3.2	-
SS	mg/l	3.1 +/- 1.3	5
N_{tot}	mg/l	2.19 +/- 0.57	3.66
NO_3-N	mg/l	0.82 +/- 0.65	-
NO_2-N*	mg/l	< 0.015	-
NH_4-N	mg/l	0.17 +/- 0.24	1
P_{tot}	mg/l	0.136 +/- 0.071	0.182
PO_4-P	mg/l	0.046 +/- 0.044	-
Br*	mg/l	0.137 +/- 0.036	-

Ozonation

Ozonation is not sufficient alone for post treatment for Hillerød WWTP as some important pharmaceuticals is not degraded. Ozonation can be used as part of the solution since no significant bromate formation can be expected.

Table 6. Dimensioning of ozonation after the pilot test at 6.000.000 m^3/year.

Parameter	Unit	Value
Ozone dose	mg O_3/mg DOC	0.5
Ozone consumption	mg O_3/L	7
	kg O_3/year	42 000
HRT for ozonation	Min	15-20
Energy consumption for ozone production	kWh/kg O_3	9
	MWh/year	378

Ozone must be produced from oxygen, which may either be purchased or produced from air with a PSA unit.

Table 7. Oxygen for ozonation.

Parameter	Unit	Value
Oxygen required	kg O_2/kg O_3	10
	ton O_2/year	420
	ton O_2/day	1.15

If oxygen is purchased, weekly deliveries of about 8 ton are needed. If oxygen is produced on site, the annual energy consumption for producing oxygen has to be added to that for ozone production.

GAC filtration

The dimensioning is made for the maximum load in 2024 and prepared for predicted load in 2040. This is given for the flow of 1.260 m^3/h and an annual load of 6.000.000 m^3 in table 8.

Table 8. Conservative dimensioning of GAC filtration.

Parameter	Unit	Value
EBCT (min)	Min	20
Hydraulic load (max)	m/h	6
Filter (GAC) depth	m	2,0
Filter area	m^2	270
Filter volume	m^3	540
GAC exchange frequency	BV (bed volumes)	20 000
GAC consumed	m^3/year	300
	Ton/year	150

Figure 7. The WWTP HCR Syd in Hillerød today.

Figure 8. The WWTP HCR Syd in Hillerød in the future.

Costs

The operational costs for different treatment options are based on the carbon, chemical and electricity consumptions presented in Table 9 and 10.

The CAPEX was estimated from prices in the Danish market.

The costs used in calculating the OPEX for process based on typical Danish prices.

Table 9. Unit costs for GAC and operation.

Parameter	Unit	Value
GAC (new)	€/m³	800
GAC (regenerated)	€/m³	500
Electricity	€/kWh	0.10
Personnel	€/person/a	60 000

Table 10. Estimated investment and operational costs for process options.

Cost	Ozone + GAC
Investment (M €)	10
Carbon (€/a)	150 000
Electricity (€/a)	80 000
Other (€/a) *	170 000
Total cost expected	400 000

*) Labour, sludge disposal (incineration)

Overall evaluation

Ozonation appears to be highly feasible for the Hillerød WWTP effluent.

Because Hillerød Community is situated > 5 kilometres from the coast and 3 - 89 meters above sea level so there is no risk of bromide-rich seawater entering the sewage system.

The high-energy requirement of ozonation conflicts with HFORS's goals for reducing energy consumption and achieving energy independence in wastewater treatment.

GAC filtration alone has several benefits such as a broader API removal and low energy consumption compared to ozonation. But some important APIs and micropollutants are not adsorbed on activated carbon.

Ozonation plus GAC filtration can be beneficial as the GAC can reduce transformation products (TPs) and oxidation by-products (OBPs) formed by the ozonation process.

Ozonation reduces the aromaticity, molecular size, and hydrophobicity of the bulk DOC, which in turn reduces the competition with APIs for adsorption sites at the GAC (less GAC required).

The combination of ozonation and GAC filtration can significantly reduce the required GAC exchange frequency. In this combination, ozonation can be operated at a lower dosage, which also reduces the formation of undesired OBPs.

Combining two processes can affect the overall complexity, costs, carbon footprint, and workload for maintenance and needs to be assessed site-specifically.

All process options can be combined with phosphorus removal if needed, but with an impact on the dimensioning.

The investment costs for all post-treatment options are high, partially due to the building needed.

The operational costs of all process options are high and AWT will significantly increase the cost of wastewater treatment.

References

1. Stapf, M.; Miehe, U.; Bester, K.; & Lukas, M. *Guideline for advanced API removal.* CWPharma project report for GoA3.4: Optimization and control of advanced treatment. December 2020.

Appendix

Pilot plant setup in CWPharma 2

The used ozone generator (SI-Figure 1) had a capacity of 60 g/h ozone rented from Enviroprocess, Odder, Denmark.

SI-Figure 1. The ozone generator.

The ozone treatment process takes place at ambient temperature and pressure with a 1800 L volume of which 420 L are used in the experiment and a 7 minutes hydraulic retention time.

Thus, 60 L are treated per minute, corresponding to 3.6 m^3/h. Ozone was transferred into water by using a Roturi® gas mass transfer device also from Enviroprocess. It is based on the generation of a large reaction surface for achieving an instant gas-mass-transfer.

The surface area is created between the water, the equipment's surface and the gas matrix. The ozone dosage in this pilot was determined by controlling gas flow and electrical power settings of the ozone generator.

The ozone reactor treated effluent water from the disc filters (Figure 1).

Ozonation and GAC filtration

Set up of GAC Pilots at HFORS for operation on site

In the pilot plant at the HCR Syd two GAC filters of about 1.8 meter height were installed. One for treatment of water directly from the HCR Syd effluent, and the other as ozonation post treatment. The filters were filled with GAC BRENNSORB 1240 from the company Brenntag.

SI-Figure 2. GAC pilot plant filters with samplings points at WWTP in Hillerød.

Flow through the columns was initially set by a pressure drop over the columns of 0.3 meter. During the test this meant a flow through the columns of starting with 1 800 litres per hour (equalling a flow of 24 bed volumes/day) reduced to 600 litres per hour at the end of the experiment due to accumulated suspended solids. This is corresponding to a contact time (EBCT) of 30 minutes in the start up to 90 minutes in the end of the experiment. No Backwash was tested to remove the sludge layer.