

Summary

Wastewater treatment plant in Kretinga city is a conventional WWTP, where activated sludge is used for wastewater treatment with enhanced N and P removal. The size of WWTP in Kretinga is designed for 32000 PE. Average daily flow – 5160 m³/day. Treated wastewater from Kretinga WWTP is discharged to a small river “Tenžė” situated about 250 m away from the treatment plant. The whole city is close to the Baltic sea so eventually micropollutants from Kretinga WWTP reaches the seawaters. According to previous investigations, pharmaceutical concentrations coming to Kretinga WWTP are one of the biggest in the region since there is a big Hospital in the region therefore, in order to reduce the impact on Baltic sea, JSC “Kretinga Water” decided to implement a pilot unit for GAC filtration and test it' efficiency.

The whole idea behind such pilot plant is to investigate if it is possible to retrofit existing conventional wastewater treatment plants with similar GAC units in order to reduce the concentration of pharmaceuticals, which are discharged to Baltic Sea every year. This is extremely important since latest studies have shown that existing WWTP process with conventional activated sludge design is not efficient enough – which causes negative impact on environment.

The construction of the GAC pilot plant was started in the 1'st quarter of 2020 and finished in the 2'nd quarter. When pilot unit was started – samples of water before and after treatment were taken and frozen for analysis in laboratory. These samples were sent in two batches for testing in laboratory. During the whole project period, experiences have been shared between pilot plants in Sweden and Denmark.

The pilot unit treats about 22 m³/h of wastewater which corresponds to 15 % of the average daily influent to Kretinga WWTP. During the test period, up to 60000 m³ or 9500 Bed volumes of wastewater was treated in the pilot unit. Wastewater was analysed for 34 micropollutants by Kristianstad University. The treatment efficiency of up to 99 % was observed during the whole period testing period.

Filter removal efficiency started dropping at about 7000 of treated bed volumes for almost all analysed substances. Analysis at 9500 bed volumes did not show complete breakdown of filter removal efficiency therefore further sampling should be made to analyse removal efficiency dynamics in more detail.

The GAC filter in Kretinga WWTP is a big scale pre-test and development case for future full-scale solution which could also be implemented in other WWTP's in Lithuania. The investment costs into this pilot unit reaches about 120 000 Eur (including equipment, project documentation and consulting). This pilot plant study shows that it's possible to remove pharmaceuticals from conventional WWTP's with a rather simple solution which could be retrofitted in most existing plants, but economical side of the project needs to be considered. Further investigation will be ongoing in Kretinga WWTP to analyse filtration dynamics and operational costs in long term.

Foreword

This report is part of the project LESS IS MORE - Energy-efficient technologies for removal of pharmaceuticals and other contaminants of emerging concern. The project was financed by the Interreg South Baltic Programme 2014-2020 through the European Regional Development Fund.

Partners in the project were: Lund University, Department of Chemical Engineering; Sweden Water Research AB, Kristianstad University, Slagelse Utility, Slagelse Municipality, JSC "Kretinga Water" and Gdansk Water Fund.

The project started 1st of January 2018 and completion date was 30th of June 2021.

The specific project objective was to demonstrate, test and validate - new technological solutions for removing pharmaceuticals and other CECs as well as antibiotic-resistant bacteria that are suitable for small and middle sized WWTPs, and to disseminate information on new technologies to the end-users.

This paper is reporting the treatment technology/efficiency for the Lithuanian pilot plant which is one out of three national reports within Deliverable 4.1. This deliverable also includes one consolidated summary report.

JSC "Kretinga water" was the project partner from Lithuania being responsible for the construction and operation of the Lithuanian plant. Kretinga water used a large scale GAC (Granulated Activated Carbon) pilot unit to measure the effectiveness of pharmaceutical removal from wastewater.

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1 KRETINGA WASTEWATER TREATMENT PLANT

Kretinga wastewater treatment plant is owned and operated by JSC “Kretinga water” which is essentially a utility company responsible for water, wastewater, and stormwater handling in Kretinga region. The company owns and operates 43 WTP’s, 12 WWTP’s, 52 pumping stations and more than 200 km of wastewater piping networks. Kretinga WWTP treats wastewater from Kretinga city, which has a population of 16 600 inhabitants. Kretinga city is located close to the Baltic sea and is shown in the picture below.



Figure 1-1: Location of Kretinga city

The size of WWTP in Kretinga is designed for 32000 PE. Average daily design flow – 5160 m³/day and about 158 m³/h. This WWTP runs on conventional activated sludge process with nitrogen and phosphorus removal. Wastewater is firstly treated in mechanical treatment part where sand, screenings and grease is separated. Then wastewater is treated inside an activated sludge bioreactor. After the treatment, wastewater is directed to secondary clarifiers, where sludge is separated from treated wastewater. All the treated wastewater is then directed to Tenžė river which is only 250 m away from WWTP site.



Figure 1-2: Location of Kretinga WWTP

2 CHEMICAL ANALYSIS OF PHARMACEUTICALS

Pharmaceuticals constitute a large group of substances and there are several hundred approved active substances (APIs) on the market. To be able to analyse and identify drugs in environmental samples, several different techniques and methods have been developed at different laboratories. Over the years the list has grown, and methods have been added. It is not uncommon for a method to involve analysis of up to 100 substances. The consequence of these so-called multi-methods is, on one hand more results that describe the presence of drugs in the environment, on the other hand the many substances to be analysed lead to increased complexity, which in turn can cause greater measurement uncertainty and lower method sensitivity. The comparability between different analyses can also be made more difficult if the same substances are not measured in the different methods.

Within this project several micropollutants were selected to be analysed. The chosen substances were selected based on the answers given to the following questions:

- What are the typical concentrations of pharmaceuticals emerging from a sewage treatment plant?
- Which pharmaceuticals should be monitored in the present project?

The discussions emerged in a list of 35 compounds, which was the starting point for the analysis task. During the project the list was somewhat modified.

2.1 Analytical method

To be able to analyse pharmaceutical residues and other organic micropollutants (OMPs) in water samples, which often occur in low to very low concentrations, special sample preparation and analysis techniques are required. During sample preparation, the OMPs are separated and concentrated. Furthermore, background-disrupting substances, such as humic acid, are separated from the sample. Two common sample preparation techniques in environmental analysis are LLE (Liquid Liquid Extraction) and SPE (Solid Phase Extraction). In organic trace analysis of polar to semipolar micropollutants, it has almost become standard to use SPE. When SPE is used, the micro-contaminants are transferred to an adsorbent consisting of a polymer enclosed in a sample cartridge. After extraction, the samples are eluted with a suitable organic solvent(s). The samples are then evaporated and transferred to special sample vials pending final analysis. Analysis of the samples is done by chromatography in combination with mass spectrometry, called HPLC-MS/MS or GC-MS/MS, depending on whether the chromatography takes place with a liquid column (HPLC) or a gas column (GC). Within Less is more only HPLC-MS/MS was used. In the literature, the analytical chain is often shortened to SPE-HPLC-MS/MS.

2.2 Sample preparation

At MoLab, Kristianstad University specific techniques for sample preparation have been invented, and unique analysis methods have been developed for optimized analysis of polar to semipolar micropollutants (Svahn, 2016). The special sample processing technology that has been developed and used in the analysis in LESS IS MORE enables analysis of the entire water sample, without filtration through a 0.45 µm filter that is otherwise usually the case (Svahn & Björklund, 2019). A detail in the developed

technology; a sand filter which is placed in the SPE column, and which is then kept throughout the analysis chain. The EU's watch list states that "In order to ensure comparable results from different Member States, all substances must be monitored in whole water samples.". The method, which includes analysis of most of the constituent micro-pollutants in the study, and which is based on the technology above, was published in its entirety in the work High Flow-Rate Sample Loading in Large Volume Whole Water Organic Trace Analysis Using Positive Pressure and Finely Ground Sand as a SPE-Column In-Line (Svahn & Björklund, 2019).

2.3 Final analysis UPLC MS / MS

As previously mentioned, so-called multi-methods developed for the final analysis in HPLC-MS / MS risk being subject to a number of analytical compromises because they have to handle a large number of substances with large chemical differences. A large part of the compromise ends up in the chromatography part (HPLC) when only one method and column is used, almost exclusively performed using an acidic buffer. To reduce the element of compromise, MoLab's UPLC-MS / MS method is instead based on three individual chromatographic methods, each of which has its own column linked to; an acidic-, a basic- and a neutral method. During method development, each compound is evaluated for chromatographic conditions and mass spectrometric optimization. The strategy makes better use of the full potential of a UPLC-ESI-MS / MS system, and is thus better adapted to cover assorted chemical differences, which minimizes the number of compromises and contributes to more robust and more flexible methods with higher analytical sensitivity.

Each sample is injected three times (1 + 1 + 10 μ l) and the total analysis time is 6.5 + 6.5 + 8 = 21 min, including washing of the system and equilibration of the column between individual injections. The method for the UPLC MS / MS part is published in the work "Increased electrospray ionization intensities and expanded chromatographic possibilities for emerging contaminants using mobile phases of different pH" (Svahn & Björklund, 2016). The methods are validated according to the standard method, 1694, published in 2007 by the US Environmental Protection Agency (US EPA), Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC / MS / MS (EPA , 2007).

3 PILOT PLANT

The pilot GAC filter plant was designed and built to treat approximately 15 % of total incoming wastewater, which amounts to 22 m³/h. During the test period, up to 60000 m³ or 9500 Bed volumes of wastewater was treated in the pilot unit. Wastewater was analysed for 34 micropollutants by Kristianstad University. The treatment efficiency of up to 99 % was observed during the whole period testing period.

An existing tertiary treatment building was used for pilot unit installation.

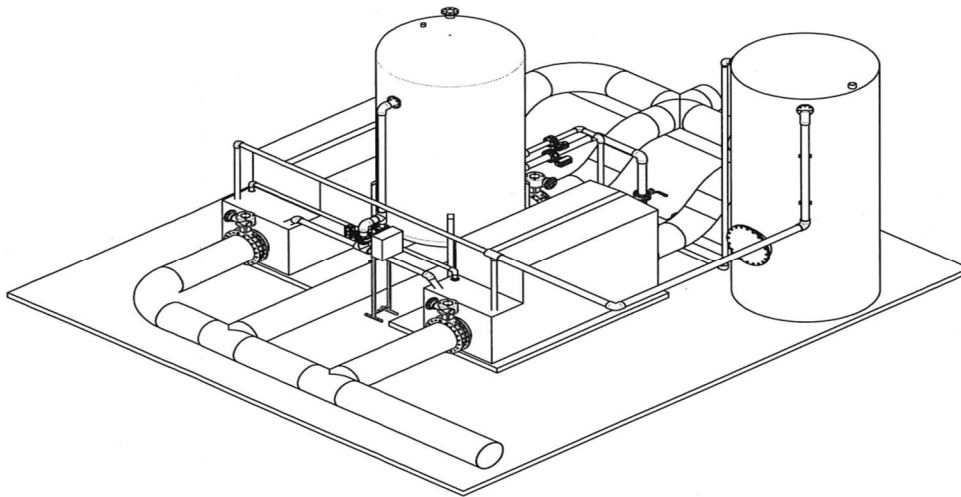


Figure 3-1: GAC filter placement design

The layout of the whole pilot unit installation is shown in the picture below:

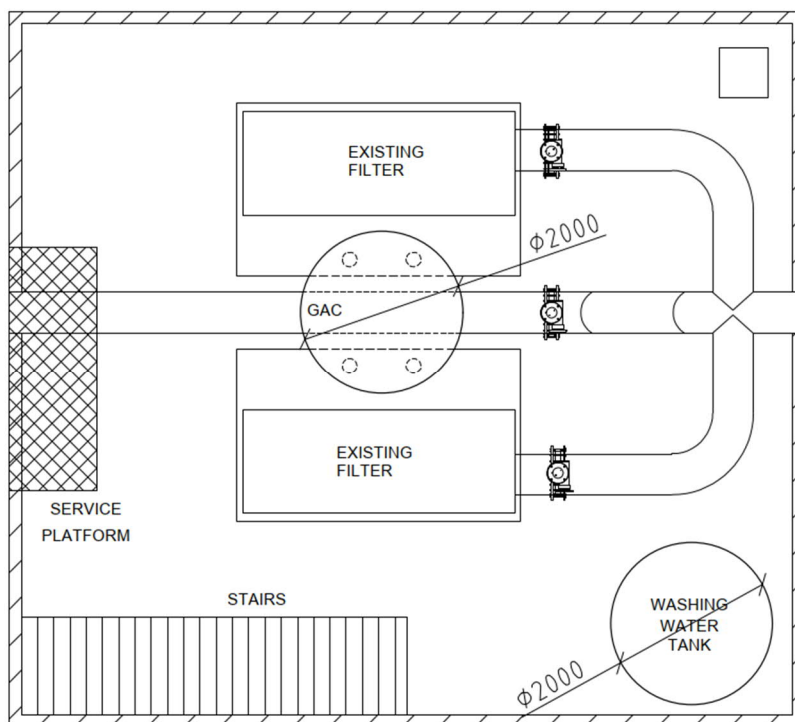


Figure 3-2: Layout plan for GAC filter in Kretinga WWTP

In order to fit new equipment in existing building, an in-depth analysis was performed to find the most suitable placement. Since there wasn't much space left in the room, it was decided to lift the filter on beams and to install it above existing piping system as shown in the section below.

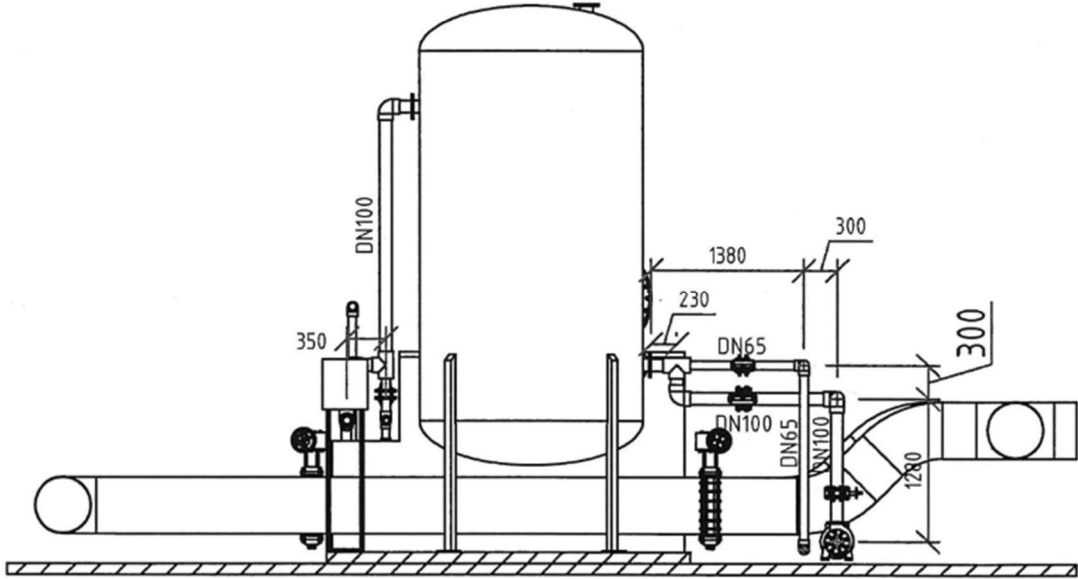


Figure 3-3: Section view for GAC filter in Kretinga WWTP

As a result of detail design, there was no need to construct additional buildings for the GAC filter, or to put the unit outside, which would mean that additional insulation and heating is required to be safe from freezing. Because of an optimised placement of pilot unit, no additional heating was needed.



Figure 3-4: GAC filter photo in Kretinga WWTP

3.1 Short process description

The whole concept of GAC filter is to take biologically treated wastewater from existing WWTP and polish it inside a filter, where pharmaceuticals are adsorbed on granulated activated carbon particles. It is important to note, that not only pharmaceuticals/micropollutants are adsorbed on GAC particles, but also suspended solids (SS). This means that a filter can be clogged with SS, reducing the hydraulic parameters of the filter and also capacity for micropollutant adsorption.

For this reason, additional treatment step after secondary clarifiers should be introduced to reduce SS concentration prior GAC filters. In Kretinga WWTP, an existing tertiary treatment system was already in place, so there was no need to install equipment for additional SS reduction.

Also, a backwash system is necessary in order to guarantee continuous GAC filter operation. When the pressure drop in the filter is too big – backwash procedure is needed. Best results are achieved when washing with a mixed system where water and air is introduced to the vessel tank.

The pilot plant in Kretinga WWTP is dimensioned to treat 22 m³/h or 528 m³/d. The flow scheme of pilot plant is shown in the picture below.

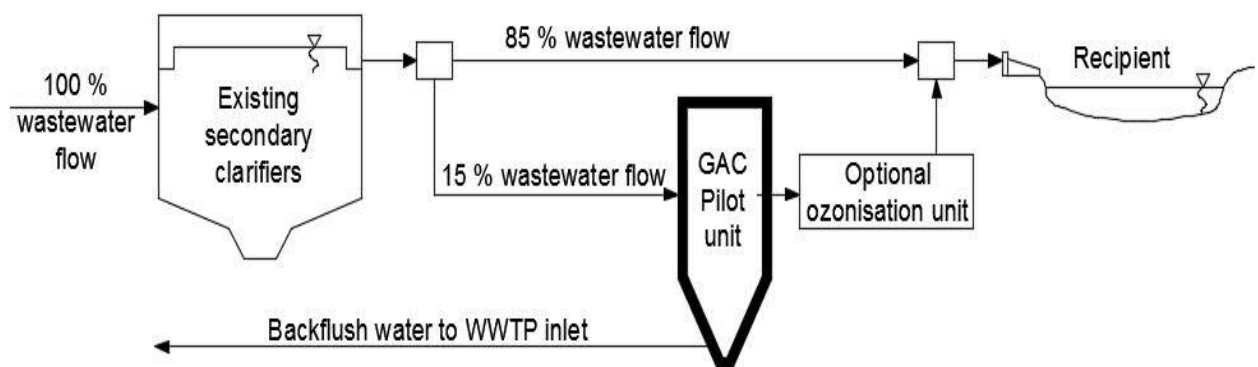


Figure 3-5: Flow scheme for pilot unit in Kretinga WWTP

Wastewater from secondary clarifiers is routed to GAC filter. Treated water is then routed to the recipient river together with remaining 85 % of treated wastewater from secondary clarifiers. Backflush water from filter washing is pumped to the inlet of Kretinga WWTP. In the future, an ozonisation unit is considered after the GAC filter to increase treated water quality further. The main design parameters for pilot unit are described in the table below:

Table 3-1: Pilot unit design parameters

Design parameter	Value	Unit
Design Flow	22.0	m ³ /h
Filtration velocity	7.0	m ³ /m ² h
Empty Bed Volume	6.28	m ³
Empty Bed Contact Time	17	min
Cross sectional area	3.14	m ²
Bed height	2.0	m
Filter Vessel height	4.1	m
Filter Vessel diameter	2.0	m

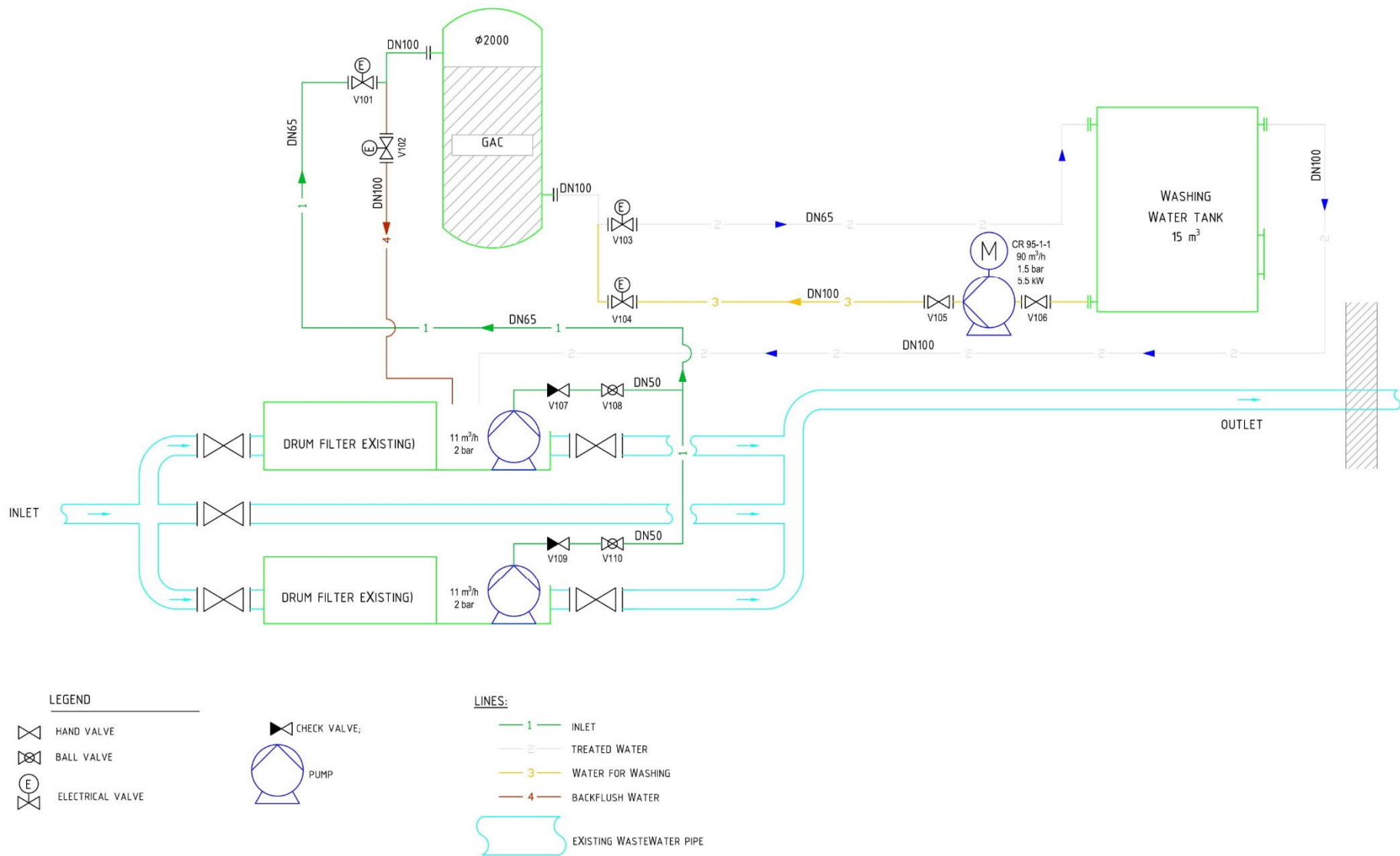


Figure 3-6: Pilot unit flow scheme in Kretinga WWTP

3.2 Wastewater parameters

During the whole testing period no additional testing was made for conventional wastewater parameters in the effluent such as COD, total nitrogen, total phosphorus, or suspended solids. Since only 15 % of the incoming wastewater was treated in the pilot unit – impact on overall wastewater quality regarding mentioned parameters is minimal and therefore was not observed separately.

The main focus of testing was to analyse micropollutants which were selected and coordinated between all project partners:

1. Acetamiprid
2. Atenolol
3. Carbamazepine
4. Fluconazole
5. Clarithromycin
6. Diclofenac
7. Erythromycin
8. Imidacloprid
9. Losartan
10. Naproxen
11. Methotrexate
12. Metoprolol
13. Oxazepam
14. Sertraline
15. Thiamethoxam
16. Trimethoprim
17. Azithromycin
18. Citalopram
19. Ciprofloxacin
20. Ketokonazole
21. Paracetamol
22. Propranolol
23. Sulfamethoxazole
24. Tramadol
25. Venlafaxine
26. Zolpidem
27. Estrone
28. Perfluorooctanoic Acid
29. Perfluorooctanesulfonic acid
30. Ibuprofen
31. Furosemide

4 PHARMACEUTICALS AND INDUSTRIAL CHEMICALS

The analysis for pharmaceuticals in Kretinga WWTP were carried in batches during the test period from April 2020 to February 2021. Wastewater samples were taken in points:

- I. River upstream from Kretinga WWTP;
- II. River downstream from Kretinga WWTP;
- III. Inlet to Kretinga WWTP;
- IV. Outlet from Kretinga WWTP;
- V. Outlet from Pilot unit.

The sampling frequency varied during the test period and the analysis was performed in two separate batches. First batch of samples was collected from April 2020 to September 2020, frozen and then placed in a freezer. It was then sent to Kristianstad University, where wastewater samples were analysed in laboratory.

The second batch of samples was collected from October 2020 to February 2021. Then it was sent again to Kristianstad University for laboratory analysis.

The laboratory analysis results were then statistically analysed. All the measurements where micropollutants were not detected or below LOQ were given a value of zero to make statistical analysis possible. All sampling values are in ng/l.

Sample test results are shown in the table below:

Table 4-1: Chemical analysis

Measuring point/ Micropollutants	WWTP Inlet		WWTP Outlet		Effluent from pilot unit	
	Average	Max	Average	Max	Average	Max
Acetamidiprid	1.3	5.4	1.3	2.3	0.0	0.0
Atenolol	291.3	716.0	13.3	31.5	0.0	0.0
Carbamazepine	354.5	1083.1	319.6	605.8	11.0	92.5
Fluconazole	539.6	2464.0	73.1	102.1	3.4	26.3
Clarithromycin	572.5	1660.5	206.0	627.3	17.2	135.5
Diclofenac	4812.5	11722.6	3894.3	4687.5	152.3	1092.3
Erythromycin	0.0	0.0	0.0	0.0	0.0	0.0
Imidacloprid	39.4	163.5	24.6	30.5	0.8	6.5
Losartan	219.1	298.6	63.5	107.3	1.1	9.9
Naproxen	2719.0	4012.8	103.4	503.2	11.1	110.9
Methotrexate	8.4	40.7	0.0	0.0	0.0	0.0
Metoprolol	1266.7	2013.8	769.9	926.4	24.1	172.7
Oxazepam	79.0	133.6	73.8	92.7	2.7	20.7
Sertraline	9.9	15.2	4.9	6.8	0.3	2.2
Thiamethoxam	2.8	7.7	5.7	14.4	0.1	1.2
Trimethoprim	167.7	305.4	29.7	78.4	2.4	21.2
Azithromycin	725.1	1582.5	125.5	467.1	3.2	21.4

Measuring point/ Micropollutants	WWTP Inlet		WWTP Outlet		Effluent from pilot unit	
	Average	Max	Average	Max	Average	Max
Citalopram	86.0	129.3	51.1	83.4	2.3	17.1
Ciprofloxacin	716.6	1566.0	62.1	133.5	7.3	59.5
Ketokonazole	383.5	848.3	7.4	13.8	0.0	0.0
Paracetamol	24020.8	37745.0	0.0	0.0	0.0	0.0
Propranolol	35.4	55.0	14.9	18.3	0.0	0.0
Sulfamethoxazole	811.7	1676.6	97.1	147.6	4.0	31.7
Tramadol	339.6	655.4	332.3	484.4	11.3	80.2
Venlafaxine	38.3	69.8	47.1	78.7	1.7	13.7
Zolpidem	3.9	7.0	1.3	2.3	0.0	0.0
Estrone	49.4	77.6	3.4	7.6	0.2	1.4
Perfluorooctanoic Acid	0.7	5.2	0.0	0.0	0.9	10.5
Perfluorooctanesulfonic acid	0.0	0.0	0.0	0.0	0.0	0.0
Ibuprofen	3479.8	4795.2	0.0	0.0	9.8	137.4
Furosemide	1036.6	2513.2	129.5	172.0	4.5	31.9

According to the table 6-1 we can clearly see that in all of the cases effluent from GAC pilot unit is much better quality than effluent from conventional WWTP. Micropollutant removal efficiency in conventional WWTP is shown below.

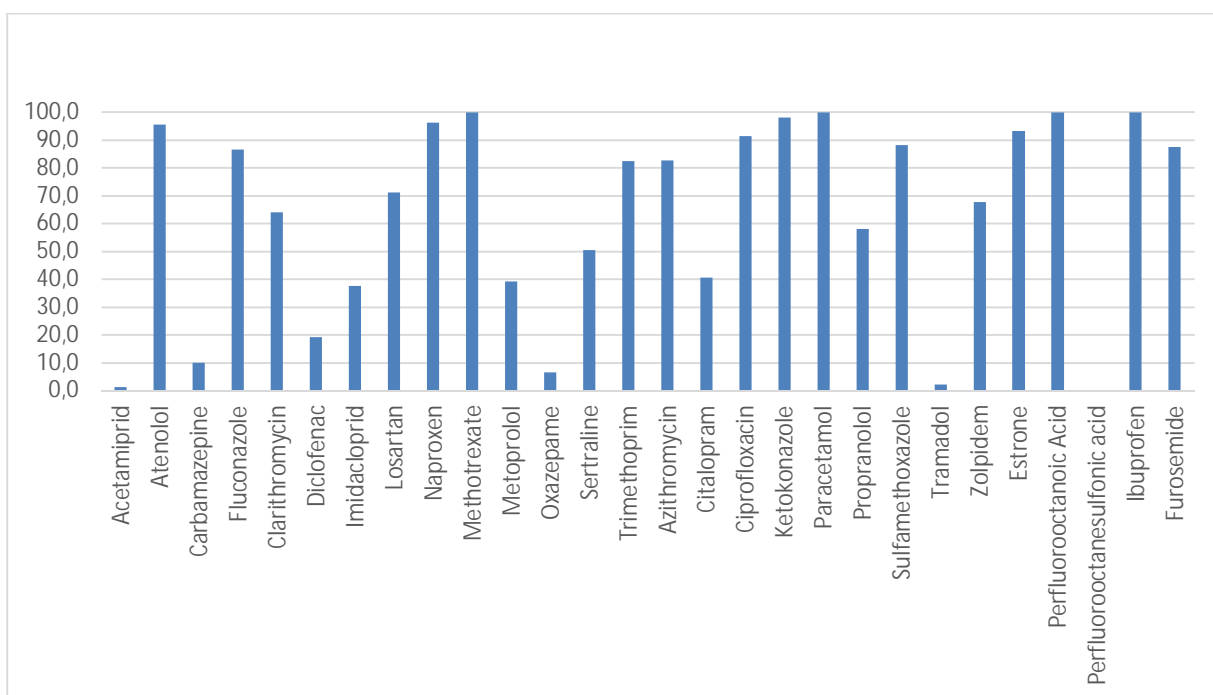


Figure 4-1: Micropollutant removal efficiency in Kretinga WWTP using conventional treatment process

As we can see from figure 6-1, even in conventional treatment plants with activated sludge process, some part of pharmaceuticals is removed from the wastewater. Atenolol, naproxen, methotrexate, ketoconazole, paracetamol, perfluorooctanoic acid and ibuprofen removal efficiency reaches 100 % or close to 100 % according to laboratory analysis.

Removal efficiency of Pharmaceuticals using GAC filter is calculated according to difference between Kretinga WWTP outlet concentrations and GAC filter outlet concentrations. This is done because inlet water to GAC filter is basically treated wastewater from conventional WWTP process. Removal efficiency results are shown in the figure below. For some cases, where conventional WWTP removal efficiency reached 100 %, GAC filter efficiency was not measured, because inlet concentrations of that specific contaminant was equal to 0 ng/l.

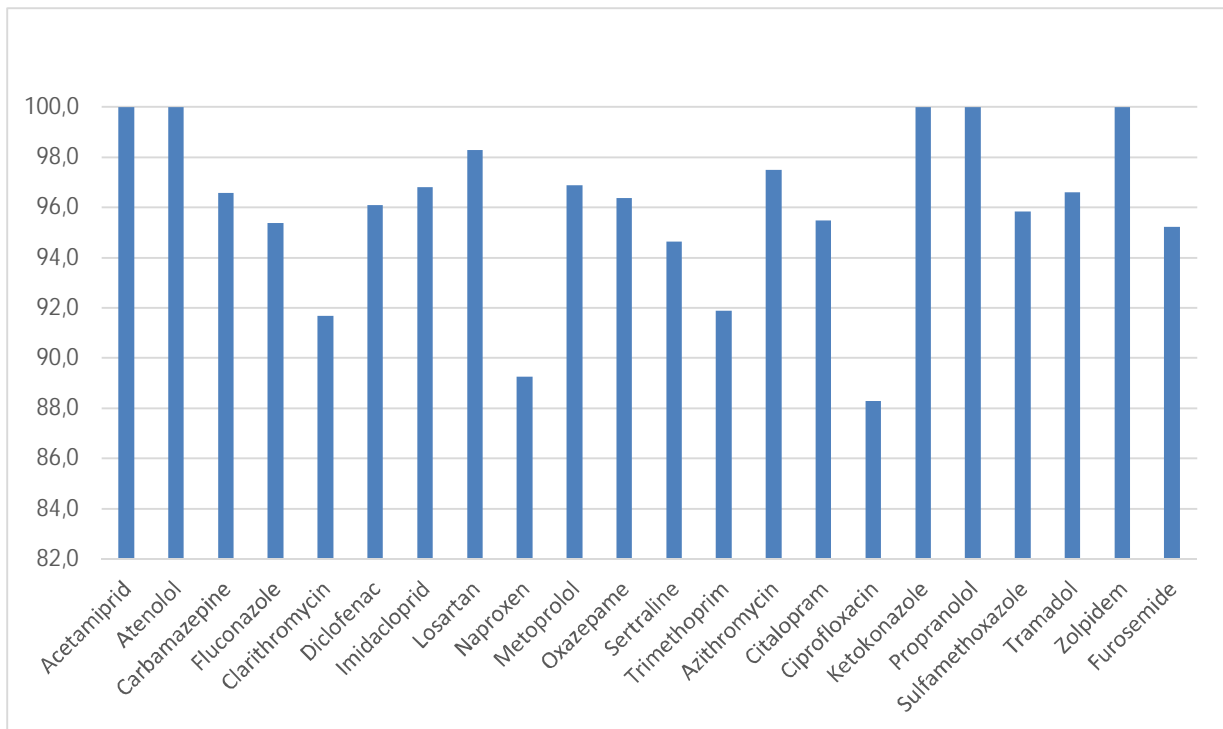


Figure 4-2: Micropollutant removal efficiency in Kretinga WWTP using GAC filter

As seen in the figure 6-2, GAC filter efficiency varies for specific pollutants, but in all cases removal efficiency is above 88 %. GAC filter also helps greatly with micropollutants, where conventional treatment plant had basically 0% removal efficiency.

For example, Acetamidiprid removal efficiency in conventional activated sludge process was barely 1 %, while using GAC filter – 100 % removal efficiency was reached. Almost the same effect is observed with carbamazepine, oxazepam and Tramadol.

4.1 Pilot plant breakthrough

In order to find the breakthrough point in the GAC filter, relation between filtered bed volumes of wastewater and removal efficiency for critical substances was calculated. Some of the substances, as observed in figure 6-1, are already removed in conventional WWTP, therefore they are removed from further analysis.

Table 4-2: GAC filter in Kretinga WWTP removal efficiency

BED VOLUME	657	1478	2627	3054	3842	3941	4368	5353	6010	7007	7533	8518	9500
Atenolol	100	100	100	100	100	100	100	100	100	100	100	100	100
Carbamazepine	100	100	100	100	100	100	100	100	100	100	100	82	69
Fluconazole	100	100	100	100	100	100	100	100	100	100	100	80	54
Clarithromycin	100	100	100	100	100	100	100	100	99	100	98	82	77
Diclofenac	100	100	100	100	100	100	100	100	100	100	100	79	61
Imidacloprid	100	100	100	100	100	100	100	100	100	91	100	81	77
Losartan	100	100	100	100	100	100	100	100	100	98	95	82	78
Naproxen	100	100	100	100	100	100	100	100	100	100	97	78	80
Metoprolol	100	100	100	100	100	100	100	100	100	100	100	81	74
Oxazepam	100	100	100	100	100	100	100	100	100	100	99	83	65
Sertraline	100	100	100	100	100	100	100	100	100	100	100	59	56
Thiamethoxam	100	100	100	100	100	100	100	100	100	100	100	80	62
Trimethoprim	100	100	100	100	100	100	100	100	100	100	100	82	70
Azithromycin	100	100	100	100	100	100	100	100	100	100	99	87	80
Citalopram	100	100	100	100	100	100	100	100	100	100	98	83	76
Ciprofloxacin	100	100	100	100	100	100	100	100	100	100	63	25	83
Ketokonazole	100	100	100	100	100	100	100	100	100	100	100	100	100
Propranolol	100	100	100	100	100	100	100	100	100	100	100	100	100
Sulfamethoxazole	100	100	100	100	100	100	100	100	100	100	97	77	52
Tramadol	100	100	100	100	100	100	100	100	100	100	100	83	65
Venlafaxine	100	100	100	100	100	100	100	100	100	100	100	0	68
Estrone	100	100	100	100	100	100	100	100	99	99	98	82	-
Furosemide	100	100	100	100	100	100	100	100	100	100	100	82	72

The relation between treated wastewater amount and contaminant removal efficiency (table 6-2) shows that filter breakthrough in Kretinga WWTP starts at about 7000-7500 bed volumes of treated wastewater. After that, removal efficiency is reducing at a more rapid speed. It's important to note that for some contaminants, removal efficiency still reaches 100 % even at 9500 bed volumes (f.e. atenolol, ketoconazole, propranolol).

At 9500 bed volumes estrone removal efficiency in GAC filter was not calculated, because the effluent value for it was smaller at the WWTP effluent sample. This was probably caused by bad sampling timing. Further sampling should be done in order to find out removal efficiency dynamics when treated wastewater amount is above 9500 bed volumes. Venlafaxine and ciprofloxacin had very low removal efficiency values at 8500 bed volumes, but it got back up at 9500 bed volumes. This was probably caused by a bad sample data.

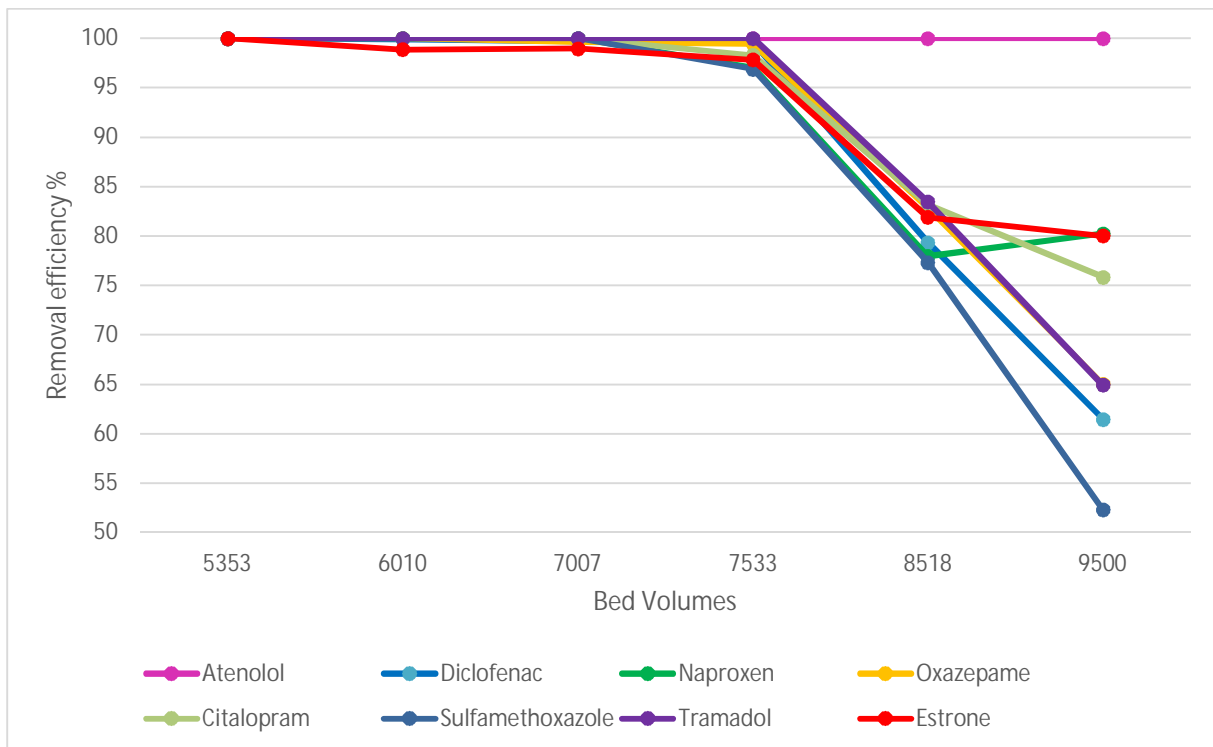


Figure 4-3: Pilot plant breakthrough analysis

As observed in figure 6-3, at around 7000 there was a filter breakthrough in removal efficiency for almost all contaminants. Further dynamics of removal efficiency should be investigated to find the exact point where GAC filter stops functioning properly and needs regeneration of activated carbon.