



REPORT

GUIDELINES FOR THE SELECTION OF TERTIARY WASTEWATER TREATMENT TECHNOLOGY

Erki Lember and Argo Kuusik
Tallinn University of Technology, 2020



Table of Contents

1. Main outcomes	3
2. Introduction	4
3. Post-treatment.....	6
4. Mass balance of hazardous substances in the wastewater treatment plants examined ...	8
5. Overview of the tests and analyses carried out	10
5.1. <i>Description of the pilot plant</i>	<i>13</i>
5.2. <i>Selecting the right post-treatment technology</i>	<i>15</i>
5.3. <i>Phosphorous and heavy metals removal</i>	<i>16</i>
5.4. <i>Phosphorus removal.....</i>	<i>19</i>
5.5. <i>Heavy metals removal.....</i>	<i>20</i>
6. Comparison of granular filter and disc filter	23
7. Conclusions	25
8. Contacts of the project team.....	26
9. References	27

1. Main outcomes

The purpose of this study was to analyse the various post-treatment technologies for the removal of phosphorus and heavy metals in the wastewater treatment plant. A total of 14 different technological solutions were studied, including both chemical and physical treatment technologies. The impact of the studied technological solutions on the removal of organic loading (COD, BOD) and nitrogen removal was further assessed. The study also analysed investment and operating costs related to the various post-treatment technologies.

The main conclusions of the study were the following:

- There is no universal treatment technology that would remove all phosphorus and the heavy metals relevant to us. Therefore, laboratory tests should be carried out prior to planning of each new equipment to assess the efficiency of the proposed equipment in removing the pollutant of concern. However, in many countries, for example, the problematic heavy metal Zn was best removed by increasing the pH level to 10, and Cu as another substance of concern was best removed with greensand and AFM, with the disc filter proving equally efficient.
- The pH manipulation, which reduces solubility of heavy metals and allows them to be filtered out, proved to be the most efficient of the solutions studied. However, it should be borne in mind that, with the backwash of filters, much of the pollutant loading is returned to the treatment process, thus increasing the concentration of heavy metals e.g. in waste activated sludge. Therefore, post-treatment filters always require a solution to problems related to backwash water.
- In case only phosphorus removal is required, the tests showed that phosphorus was most efficiently removed when coagulation and flotation processes were applied prior to filtration.
- In comparison of the granular filter and the disc filter, the filter filled with medium is certainly more flexible because we can use different filter media like sand, activated carbon, etc., whereas the disc filter is easier to operate. However, in terms of the size of investment, it should be borne in mind that the granular filter needs more space and the equipment is also more expensive overall. Therefore, if the problems are caused by suspended solids and phosphorus, then a disc filter is sufficient to remedy the problem, but if it is to remove the heavy metals and in the future, for example, pharmaceutical residues, i.e. to add the ozonation and the activated carbon medium to the filter, a granular filter should be considered.

2. Introduction

The wastewater treatment process generally consists of three stages: mechanical treatment, biological treatment and chemical treatment. During mechanical treatment, foreign matter, sand and, in the case of larger wastewater treatment plants, raw sludge from the primary clarifiers is removed in order to reduce the load fed to the biological treatment. The most important part is the biological treatment, where organic matter (BOD₇, COD), nitrogen and phosphorus are removed through the metabolism of micro-organisms. (Davis 2010) As a result of these processes, excess sludge is produced which can be used as a fertilizer, planting soil, etc. after being treated. Since micro-organisms are highly sensitive to various environmental conditions such as pH, temperature, and also potentially inhibitory compounds originating from industry, like heavy metals, it is important that such wastewater is biologically easy to treat. In addition, hazardous compounds affect the properties of sewage sludge, which is why it is often not possible to reuse it in a circular economy. (Gray 2004; Haiba 2017)

The wastewater treatment plants receiving also industrial effluent often face problems with meeting certain effluent limits. There are mostly two types of problems. Those where the wastewater treatment plant is often overloaded and nutrient ratio appears unsuitable, due to either a high load of pollutants or a short-term high load. Or those where the industry discharges various hazardous compounds to the wastewater treatment plant that inhibit biological treatment or make it impossible to reuse the sewage sludge. (Çeçen, Semerci, and Geyik 2010; Dhokpande 2013; Luo et al. 2006)

For example, the food industrial effluent typically contains high concentrations of various nutrients, such as phosphorus, nitrogen and organic matter (BOD₇, COD). The problem for the wastewater operators lie not so much in the high concentrations, but in the nutrient ratio, which should be 100:5:1 (BOD-N-P). If one of these parameters is extremely high then it is almost impossible to perform an effective biological treatment. Also, effluent received from that type of industry often has a pH unsuitable for the biological treatment. (Gray 2004; Badejo et al. 2017; Henze et al. 2011)

The sources of heavy metals include both various products and use thereof, as well as many industrial plants. Potential sources may include cosmetics industry/cosmetic products, products covered with protective anti-corrosion coating (e.g. zinc roofs), plastic industry, wood industry, electronics industry. Similarly, the wastewater treatment plants receive a significant load of heavy metals with stormwater that has been exposed to, for example, worn vehicle brake pads, copper/zinc roofs, crash barriers, etc. Heavy metals posing the greatest risk to the biological wastewater treatment can be

ranked as follows: Cd, Cr, As, Hg, Pb, Cu and Zn. And since the heavy metals do not decompose, the wastewater treatment plants only have two options - the heavy metals are either bound to sludge and get removed with the excess sludge, or they pass through the wastewater treatment plant and are discharged to receiving waters. (Chipasa 2003; Ramrakhiani et al. 2016; González-Acevedo et al. 2018; Charters, Cochrane, and O’Sullivan 2016; Bernard, Jimoh, and Odigure 2013)

Table 1. Source of different heavy metals. (Lember 2018; González-Acevedo et al. 2018; Kobielska et al. 2018; Sani, Gaya, and Abubakar 2016; Tahri et al. 2017)

Heavy metal	Anthropogenic sources
Zn	Anti-corrosion agents, roofs, road barriers, PVC stabilizer, skin creams, welding, rubber industry, medicinal products, paints
Ni	Anti-corrosion agents, roofs, road barriers, PVC stabilizer, skin creams, welding, rubber industry, medicinal products, paints
Pb	Plastic, various alloys, Pb batteries
Cu	Roofs, water pipes, kitchen appliances, alloys, cosmetic products, medicinal products
Cr	Wood industry, cooling water piping protection, plating, textile and leather industry, colour pigments
Cd	Plastic stabilizers, Ni-Cd batteries, coal burning

Consequently, it is important that the industrial effluents have constant pollution load, pH, and temperature in order to ensure effective biological treatment. Also, the wastewater should not contain various hazardous compounds which may inhibit biological treatment or are bound to sewage sludge, making it difficult to reuse. A certain proportion of hazardous compounds pass through the wastewater treatment plants that lack adequate technological solutions to remove these compounds, and are discharged to receiving waters.

Therefore, this study compiled within the BEST – Better Efficiency for Industrial Sewage Treatment project will examine various combined post-treatment technologies in order to reduce the phosphorus load reaching the Baltic Sea and to remove heavy metals during the same treatment stage before discharging the effluent to receiving waters. The study will assess the cost effectiveness of technological solutions. In addition, the mass balance of heavy metals in various wastewater treatment plants is analyzed and the possibilities for re-using the sewage sludge in a circular economy are assessed. In other words, how much of the heavy metals are bound to sewage sludge,

will this make it more difficult to re-use the sludge, and what kind of pre-treatment should be implemented by the industries in order to avoid exceeding the established limits.

This study has been co-funded by the European Union Regional Development Fund Interreg Baltic Sea Region Programme.

3. Post-treatment

Post-treatment is a treatment process that follows the conventional treatment, i.e. usually the secondary clarifiers. The need for post-treatment arises when the technology that has been used so far is no longer able to process the wastewater to meet the required standards, so an additional treatment stage is added. This may also be due to the following reasons:

- Increasing loads from the expanded wastewater collection area,
- Increasing industrial effluents,
- Need to increase the removal of nutrients to limit the eutrophication of sensitive waters,
- The emergence of new substances of concern, such as pharmaceutical residues.

The main post-treatment technologies include:

- Sand filter,
- Disc filter,
- Ozonation,
- Adsorption with activated carbon,
- Disinfection.

Chemical precipitation, also called coagulation, is a process where mainly colloidal particles are bound to larger particles that can be filtered out by physical methods. Coagulation is also the chemical removal of phosphorus, where dissolved phosphate is precipitated, for example, as insoluble iron salt. In heavy metals removal, the compounds dissolved during coagulation are rendered insoluble, thereby allowing for filtering out. (Weimar 2014; Bischof 1998)

The combination of coagulation and flotation allows for more effective removal of colloidal particles and phosphorus. All in all, compounds produced by coagulation are bound to even larger particles, thereby improving their removal, for example, in lamella clarifier, sand filter and disc filter. (Bischof 1998)

Adsorption usually refers to the removal of various organic pollutants by the forces of Van der Waals, where pollutants accumulate on the surface of an adsorbent. In the main, activated carbon is used as an adsorbent, which successfully removes various hazardous compounds such as heavy metals and pharmaceutical residues. (Karnib et al. 2014; Kobielska et al. 2018; Barakat 2011)

Filtration is defined as the process of separating insoluble particles from a liquid, by causing the liquid to pass through a filter. Depending on the filtering medium, the filters are divided into two groups: thin-layer filters (fabric, fine mesh) and granular filters, using, for example, quartz sand, anthracite and activated carbon as a filtering medium.

Disc filters are thin-layer filters that act as a flow-through system. The technology consists of several discs vertically located in a tank. The technique used can be either inside-out or outside-in.

In filters using the inside-out technique, the water enters through a pipe or conduit in the center of the discs. Water is fed into the lower parts of the disc filter and through the filtering medium by gravity. The water level increases between the inflow and outflow due to the suspended solids that accumulate in the filter. Once the water has reached the maximum permitted level, the particles collected on the filtering medium are removed during backwash. (Metcalf & Eddy et al. n.d.; Qasim and Zhu 2018)

Filters using the outside-in technique work the other way round - the water flows by gravity through the filtering medium to the collector in the center of the discs and from there, the water is then conveyed out of the disc filter system. The backwash is generally carried out using vacuum. The vacuum equipment is on both sides of the discs, designed to reverse the direction of the flow of water. The filtrate is retracted through filters, carrying along particles collected on the filtering medium. The vacuum equipment cannot remove all the particles collected on the filter, and after some time, this will lead to efficiency loss of the filter. This is recognizable when the vacuum at the backwash needs to be increased and the interval between the backwash cycles becomes shorter. In this case, a high-pressure jet wash mentioned above shall be applied. (Metcalf & Eddy et al. n.d.; Qasim and Zhu 2018; Davis 2010)

The pore size of the filtering medium is generally between 5 and 40 μm . The backwash is estimated to take 2-5% of the flow-through. Disc filters have a low ecological footprint (50-70% smaller compared to flotation or sand filters), they come in a wide product range and have relatively low maintenance and energy costs, which is why they are also been widely used. Also, discs are washed automatically without interrupting the treatment process. (Qasim and Zhu 2018)

Sand filtration technology is one of the earlier water treatment technologies. Either a single-layer

filter or a multi-layer filter is used. The most common filtering media are mainly quartz sand and gravel. In addition, anthracite, activated carbon, various calcareous materials, greensand and other materials have been widely used. The thickness of the filter layer is generally ca 1 m. In two-layer filters, the most typical combination would be 700 mm of anthracite and 300 mm of sand. The sand filters are effective in removing suspended solids. The backwash is estimated to take ca 5% of the filtered water. It is also a fairly reliable system that does not require much maintenance. (Metcalf & Eddy et al. n.d.; Nowak, Österreich, and Dresden 2011)

4. Mass balance of hazardous substances in the wastewater treatment plants examined

To map the issue of hazardous compounds, a mass balance of hazardous compounds was drawn up on the basis of data gained from 4 wastewater treatment plants in Estonia, 1 plant in Latvia and 1 plant in Poland. These results can be used to estimate how much of the heavy metals are bound to the sludge on average, adversely affecting the possibility of re-using it. The proportion of heavy metals depends on their solubility, the lower the solubility of the metal, the more it accumulates in the sludge. Cr, Ni and As accumulate the least and their removal often poses a problem for many wastewater treatment plants. Therefore, one of the objectives of this project is to examine whether various post-treatment methods allow further reducing of the load of heavy metals currently reaching the effluent.

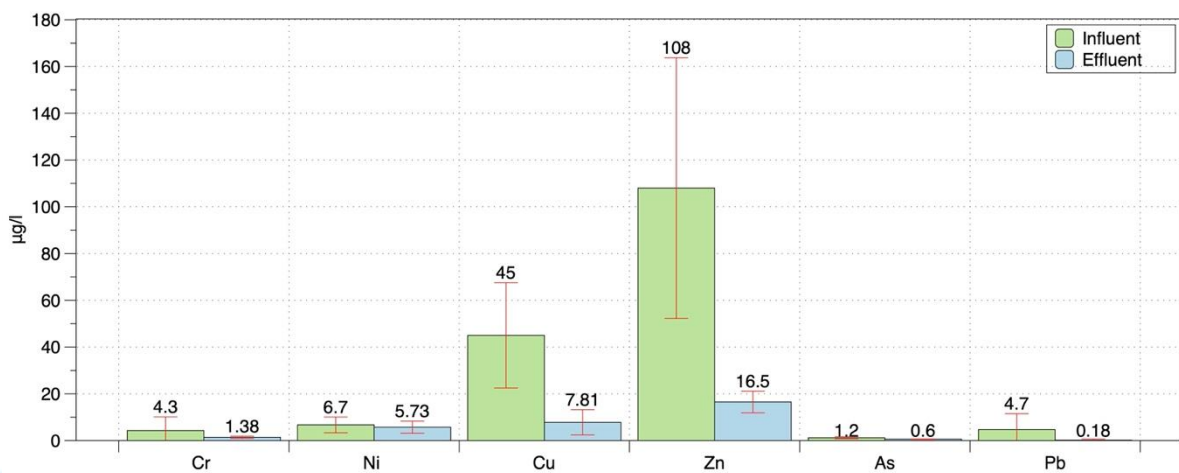


Figure 1. Concentrations of heavy metals in influent and effluent of the Estonian wastewater

treatment plant analyzed in 2011-2016 (n=118). The difference between the results indicates the proportion of heavy metals accumulated in the sludge. (Lember 2018)

Figure 2 shows the balance of heavy metals in the wastewater treatment plants examined, where the influent is 100%. The proportions of heavy metals that have accumulated in the sludge and reached the effluent have been indicated separately.

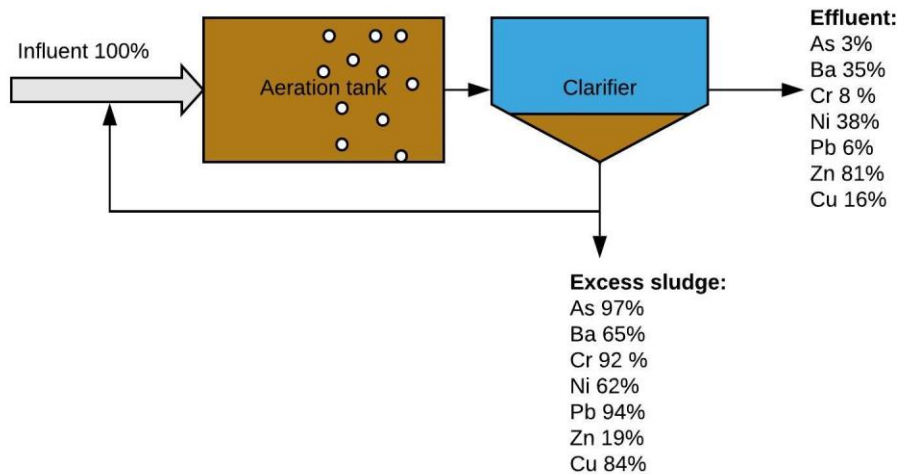


Figure 2. Mass balance of heavy metals in the wastewater treatment plants examined.

Contrary to the results found in an earlier study, it can be seen that mainly As, Cr, Pb and Cu accumulated in the sludge. It can be assumed that these compounds were present in the influent of the wastewater treatment plants examined mainly as insoluble compounds. Higher concentrations of Ba, Ni and Zn reached the effluent. The concentration of some heavy metals in the sewage sludge indicates that there is no use of the post-treatment in removing them. It is therefore necessary to identify the source of the formation of these compounds and to work on towards keeping these pollutants from being released into the sewers in order to ensure the potential for the re-use of sewage sludge. It can be concluded from the results that the greatest risk to the quality parameters of sewage sludge is the presence of As, Cr, Pb and Cu and therefore, under certain circumstances, re-use of the sludge may be impossible and the sludge must be incinerated instead. Since the permitted limits for heavy metals for the re-use of sewage sludge vary from country to country, so these limits have not been separately listed here.

5. Overview of the tests and analyses carried out

As part of the project, a pilot plant was designed to allow various treatment processes such as filtration, coagulation, flocculation, pH manipulation, and adsorption with activated carbon to be examined. The pilot plant was operated in parallel, if possible, with the existing post-treatment equipment, i.e. the disc-filters in this project.

Granular filtration is already being used widely today in the tertiary wastewater treatment, mainly to reduce the load of suspended solids and thus, the proportion of particulate phosphorus. Sand, anthracite, mixed media, activated carbon, etc. are used as filter media. The removed pollutants accumulate on the filter surface and consequently the filter's filtration rate drops (resulting in a headloss) and the filter backwash must be periodically carried out. Depending on the characteristics of the removed pollutants, the backwash water must be further treated (in the case of hazardous compounds) or, in the case of nutrients, the water is usually fed back to the beginning of the treatment process, thereby increasing the load of the influent. (Qasim and Zhu 2018)

Table 2. Various design rules for granular filters and parameters used in the project.

Method	Filtration rate (design rules), m/h	Effective size (design rules), mm	Filtration rate (used in project), m/h	Effective size (used in project), mm
Sand	5-15	0.4-0.8	4	0.4-0.8
Anthracite	5-15	0.8-2	4	2-3
Sand + anthracite	5-24	0.4-0.8:1-2	4	2-3
Green sand (AFM)	-	-	4	0.4-2
Gravel	-	-	4	2-3
Activated carbon ¹	6-15	1-3	4	0.6-2.36
Zeolite ²	5-15	0.3-32	4	0.4-1

¹ For the initial sizing of activated coal filters, the Empty Bed Contact Time method is often applied, which means dividing the height of the activated carbon layer (empty bed volume) by the flow rate. In the project examined, it was 7 min. Some design rules recommend 4-66 min, but this depends directly on the wastewater to be treated.

² Natural ion exchanger mainly used for ammonia removal, but there are also some studies about heavy metals removal.

The use of disc filters has become increasingly popular in order to reduce the load of phosphorus reaching the environment. Technologically, disc filters fall into three types: disc filters, drum filters and diamond filters (honeycomb filters). This project examines the diamond filters, which were already operating on a full scale. Table 2 shows the basic operating parameters suggested by the design rules, as well as the parameters of the equipment analyzed in the study, which depend mainly on whether an inside-out or outside-in filtration is used. (Qasim and Zhu 2018; Davis 2010)

Table 3. Basic operating parameters for disc filters.

	Outside-in filter	Inside-out filter	Estonia A	Estonia C
Filtration rate, m/h	5-12	5-20	12	12
Pore size, μm	5-10	10-40	10	10
Backwash req., % per filtered water	2-5	2-4	1-3	2-4

Pilot tests were carried out in 3 wastewater treatment plants in Estonia and in 1 wastewater treatment plant in Latvia. In addition, the wastewater composition from these countries and from the wastewater treatment plants in Poland was examined in order to assess the proportion of industrial effluents and its impact on the operation of the respective treatment plants. The results helped generating the mass balances of hazardous compounds and phosphorus and assessing the value of the produced sewage sludge in a circular economy.

For the confidentiality of the wastewater treatment plants examined, the plants are only characterized using the necessary parameters, such as the pollution load (PE), a description of the proportion of industrial effluents and other important comments.

Table 4. Description of the wastewater treatment plants examined.

	PE load	Description of industrial effluents	Comments
Estonia A	215 000	Food industries; metal industries; pharmaceutical industries; wood production. Ca 5% of the influent was industrial.	Activated sludge system (plug and flow), with biological and chemical P removal, anaerobic sludge stabilization and post-treatment with disc filters.
Estonia B	63 700	Manufacture for melamine-faced chipboards; company for thermal processing of oil shale producing shale oil, phenols and lower calorific value gas; dairy industry; fertilizers industry. Ca 34% of the influent was industrial.	Activated sludge system (plug and flow), with chemical P removal.
Estonia C	19 000	Industrial harbour: liquid bulk terminals, container terminals, fertilizer terminals, grain terminals; food manufactures, shipbuilding industries, pharmaceutical industries. Ca 24% of the influent was industrial.	Activated sludge system (sequencing batch reactor), chemical P removal and post-treatment with disc filters.
Latvia D	15 000	Food industries;	Activated sludge system (plug and flow), without chemical P removal.
Poland E ³	160 000	Chemistry industries, mechanical engineering companies, mining companies.	Activated sludge system, chemical P removal.

All of the wastewater treatment plants examined were using the activated sludge system, which is the most common method of biological treatment. During the activated sludge process, excess sludge is produced containing the necessary elements for plants, such as phosphorus and nitrogen, but the sludge may also contain hazardous compounds depending on the composition of the influent received at the wastewater treatment plant.

³ In case of Poland only a theoretical analyze was done, too find out, whether the tested technologies are usable in other locations too or not. The data was also used for the mass balance, but in overall the influent effluent results were very similar to Estonian and Latvian data.

5.1. Description of the pilot plant

A water treatment test rig was built to examine various post-treatment methods. The test rig is a working model of water treatment technology and consists of four main elements:

- aeration system,
- coagulation-flocculation system,
- clarifier,
- filtration system.

During the tests, input data and indicative operational parameters were tested for the selection of post-treatment technologies and the sizing of tanks.

The rig allows to:

- A. experiment with coagulant doses and dosing points. To remove the sludge, the test rig has a lamella clarifier which does not preclude the use of flocculation in the reconstructed treatment plant;
- B. experiment with various filtering media such as anthracite, sand, gravel, activated carbon, etc.;
- C. experiment with oxidising chemicals in the case of raw water and stabilising chemicals in the case of treated water;
- D. dose base or acid to manipulate the pH of the water and thereby reduce the solubility of certain pollutants;
- E. test the technological input parameters found in previous batch tests, including:
 - coagulant and flocculant marks (types) and doses;
 - coagulation parameters;
 - amount of sludge and its (physical) properties;
 - properties of treated water;
 - filtration and filter wash parameters.

Basic parameters of the rig:

- Sand filter's filtration rate 4-10 m/h, was operated at 4 m/h;
- Retention time in contact chamber 20 min.



Figure 3. The test rig for tertiary wastewater treatment, built for and used in the project.

Table 5. The removal of pollutants with various technological solutions.

Technology	A	B	C	D	E	F	G	H	I	K	K	L	M	N
Problem														
As	-	-	-	-	-	-	-	-	-	-	-	-	+	+
Ba	-	+	-	+	-	+	-	+	+	+	+	-	-	-
Cr	+	-	+	-	+	+	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	-	-	-	+	-	-	-	-	-	-	-	-	-	+
Zn	-	-	-	+	-	-	+	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	+	-	-	+	-	-	-	+
BOD ₇	+	+	-	+	-	-	+	+	+	+	-	-	-	+
COD	+	+	-	-	-	-	+	+	-	+	-	+	-	-
PO ₄ -P	-	+	+	+	-	+	-	-	-	-	+	+	+	-
P _{tot}	+	+	+	+	-	+	-	+	-	-	+	+	+	-
SS	+	+	-	+	+	+	+	+	+	+	+	+	+	+
N _{tot}	-	-	-	-	-	-	-	-	-	-	-	-	-	-

A – sand filter and anthracite, B – coagulation using ferric, C – manipulating pH to 8.5, D – manipulating pH to 10, E – adsorption with GAC, F – coagulation and flocculation, G – green sand AFM, H – green sand AFM with potassium permanganate dosing, I – green sand AFM with reduced potassium permanganate dose, J – green sand AFM with coagulation and flocculation, K – green sand AFM and aluminium coagulant and flocculation, L – green sand and pH manipulation to 11, M – zeolite ion exchange, N – disc filtration.

5.3. Phosphorous and heavy metals removal

The reduction of the load of nutrients such as nitrogen and phosphorus in the Baltic Sea has been one of the region's priorities for the last decade. Although agriculture is the main source of that load, a significant amount of nutrients is discharged into the marine environment also by the wastewater treatment plants. The efforts are made to increasingly reduce that amount. The first measure is always to reduce the load of phosphorus from households and industries, as phosphorus is a key ingredient in many cleaning agents and high loads of phosphorus often come from the food industry. If this is not sufficient, chemical and/or biological treatment for phosphorus removal must be carried out in the wastewater treatment plants. However, the application of these technological solutions is often no longer sufficient, since further post-treatment is required to achieve the phosphorus limit of 0.5 mgP/l, in order to reduce the amount of particular phosphorus, i.e. to remove

the suspended solids prior to the discharge of the effluent to receiving waters. The fact how much of the phosphorus can be removed by this method depends on the composition of the wastewater, as phosphorus can be divided into three: particulate phosphorus, dissolved reactive phosphorus and dissolved non-reactive phosphorus. Particulate phosphorus can be removed with filtration, dissolved reactive phosphorus by coagulation, where dissolved phosphorus is rendered into insoluble, so that it can be filtered, and for the removal of dissolved non-reactive phosphorus there is no technology available.

Heavy metals are defined as metals with a density greater than 5 g/cm^3 , and these are toxic to living organisms already at low concentrations. Although certain heavy metals are the necessary trace elements for the metabolism of organisms in dissolved form, they are usually toxic at higher concentrations. The hazard of heavy metals lies in their persistence in the environment because heavy metals do not degrade. (Gulyás et al. 2015; Ong et al. 2010) The dissolved heavy metals are considered particularly hazardous because they are more mobile in the environment and accumulate more easily in living organisms. The pollution from insoluble heavy metals is more likely to endanger the direct surroundings. In the wastewater treatment plant, insoluble metals are mostly bound to excess sludge and insoluble heavy metals reach the environment. (Gulyás et al. 2015; Luo et al. 2006)

Various technological solutions are known for removing heavy metals and have been extensively studied. However, due to the new effluent standards established for the wastewater treatment plants, it is difficult for many operators to comply with these requirements, so they avoid cooperation with the companies causing heavy metal loads. In Estonia, for example, more stringent requirements for heavy metals are established for treated effluent than for drinking water, wherein the effluent limit for copper is $15 \text{ } \mu\text{g/l}$, whereas the drinking water limit is set at 2 mg/l .

As the processes for removing heavy metals examined so far have not analyzed the stable achievement of such low concentrations, 14 different processes will be examined in this project to determine whether the achievement of these limits is technologically feasible. Further, it is assessed whether the processes analyzed ensure also a stable phosphorus removal at the same time, as the operators often lack sufficient space to build several stages of post-treatment. Therefore, the most efficient way is to carry it out within one treatment stage.

Processes examined in the project and their description (technical specifications, to be complemented by principles):

- A. Sand filter + anthracite: physical filter removes all insoluble particles, including hazardous compounds contained in suspended solids;

- B. Coagulation: coagulation using ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), where by adding the coagulant, smaller colloidal particles start to aggregate, forming larger flocks that are then filtered out. In addition, the dissolved phosphate will precipitate;
- C. pH 8.5: from the scientific literature on pH, it is known that the solubility of most of the heavy metals is reduced at a higher pH, meaning that we can increase the filtration of heavy metals;
- D. pH 10: reduction of solubility of heavy metals through pH elevation;
- E. GAC: use of granular activated carbon for the adsorption of heavy metals;
- F. Flocculation: As with coagulation, flocculants are used, which even more effectively aggregate colloidal particles, forming larger flocs, meaning that overall, both organic load and phosphorus, and presumably also the proportion of insoluble fractions of heavy metals are reduced. An anionic flocculant was used in the test;
- G. Green sand AFM for better adsorption;
- H. Green sand AFM with potassium permanganate dosing to oxidize soluble heavy metals to insoluble metals;
- I. Green sand AFM with 1/2 reduced potassium permanganate dosing to oxidize soluble heavy metals to insoluble metals;
- J. Green sand AFM with coagulation and flocculation;
- K. Green sand AFM and aluminium coagulant ($\text{Al}_2(\text{SO}_4)_3$) with combined flocculation process;
- L. Green sand AFM and manipulated pH to 11 to reduce the solubility of heavy metals;
- M. Zeolite ion exchanger to reduce nitrogen and heavy metals in combination with particular phosphorous removal;
- N. Disc filter: disc filters are used by a large number of wastewater treatment plants mainly for the suspended solids removal, thereby reducing the load of phosphorus. Whereas, on the other hand, the reduction of heavy metals load has been little studied. The reduction of heavy metals load has been little studied.

5.4. Phosphorus removal

Figure 5 shows the treatment efficiency when using various technological solutions. Although the main objective was to assess the reduction in phosphorus load, other important wastewater parameters such as BOD, COD, suspended solids and N_{tot} were also examined. Especially in the industrial effluents, the BOD/COD ratio is often low, less than 0.3, indicating that the effluent contains organic matter that is poorly biodegradable or that the effluent is toxic to microorganisms. Therefore, in certain cases, a reducing of the COD load is also important.

The study showed that the best phosphorus removal efficiency was achieved by the combination of physical filtration and coagulation and flotation, where the dissolved phosphate was coagulated into insoluble phosphorus before the filtration. As a result of this process, phosphorus load decreased by 64% on average. The most efficient was the process with aluminum-based coagulant. The disc filter reduced phosphorus load by an average of 13%, that is by the insoluble fraction.

All the treatment processes removed a significant portion of the COD, but the best removal was achieved using the sand filter, green sand AFM and zeolite, where the average removal efficiency was 43%. The results are somewhat surprising, since coagulation and flotation may have also been expected to improve the removal of colloidal COD in water. The disc filter removed an average of 18% of COD.

With regard to suspended solids, good removal efficiency was observed for all treatment processes, sometimes achieving the result below the limit of detection, i.e. 100% removal. The most effective processes were coagulation, green sand AFM and green sand AFM and coagulation with $\text{Fe}_2(\text{SO}_4)_3$, where removal efficiency was 92%.

As nitrogen is mostly dissolved in effluent, the nitrogen removal remained modest. The expected removal efficiency was given by zeolite, which is mainly intended for $\text{NH}_4\text{-N}$ adsorption.

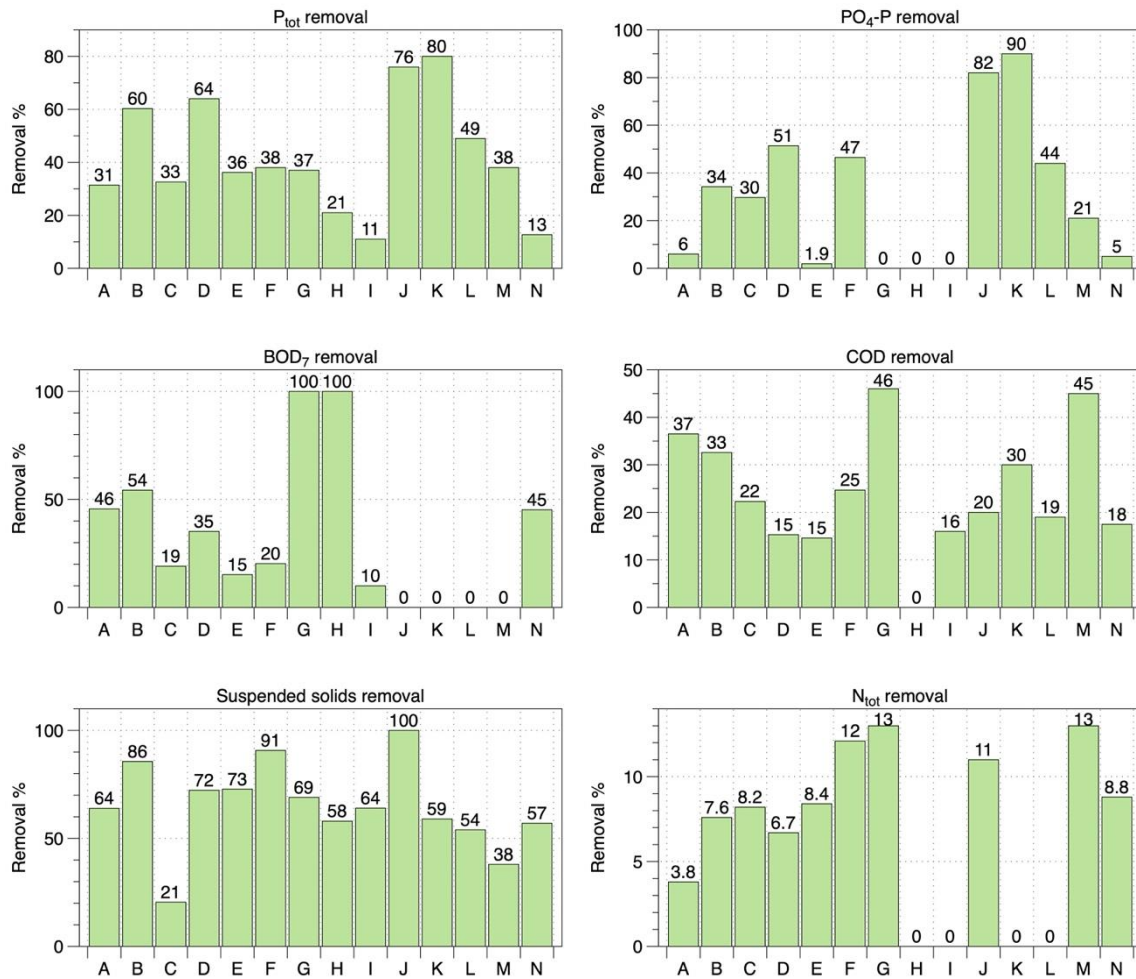


Figure 5. Phosphorus removal and removal efficiency of other pollutants with various post-treatment methods. A – sand filter and anthracite, B – coagulation with ferric, C – manipulating pH to 8.5, D – manipulating pH to 10, E – adsorption with GAC, F – coagulation and flocculation, G – green sand AFM, H – green sand AFM with potassium permanganate dosing, I – green sand AFM with reduced potassium permanganate dose, J – green sand AFM with coagulation and flocculation, K – green sand AFM and aluminium coagulant and flocculation, L – green sand and pH manipulation to 11, M – zeolite ion exchange, N – disc filtration.

5.5. Heavy metals removal

At such low concentrations, the removal of heavy metals proved a challenge. The load is often increased, mainly from filtering media or water treatment chemicals used. Ba and Cr were relatively

well removed. As for Ba, the most efficient was raising the pH to 10, which presumably reduced its solubility, and coagulation using $\text{Fe}_2(\text{SO}_4)_3$ and green sand coagulation processes, where Ba levels decreased by 47% on average. For Cr, good removal efficiency was achieved by flocculation, green sand and potassium permanganate oxidation and raising the pH to 11. The average removal efficiency with these processes was 87%.

Removing Cu, causing concern to many wastewater treatment plant operators, was the most difficult, and good removal efficiency was achieved only by using the disc filter and green sand AFM. The disc filter removed an average of 88% of Cu, indicating that it mainly occurs in wastewater as an insoluble compound. However, it is important to keep in mind that the backwash water from the disc filters is re-routed into the treatment process, so it will accumulate in the wastewater treatment plant and will only be removed with the excess sludge. Rather, the concentration of Cu even increased as a result of all the processes examined. Many wastewater treatment plants also have problems with the Zn load, which can come from the wood industry and various electronics companies. In addition, a significant Zn load reaches wastewater through the stormwater. The best Zn removal was achieved by raising the pH to 10. But also the disc filter removed a small fraction of insoluble Zn by 20%.

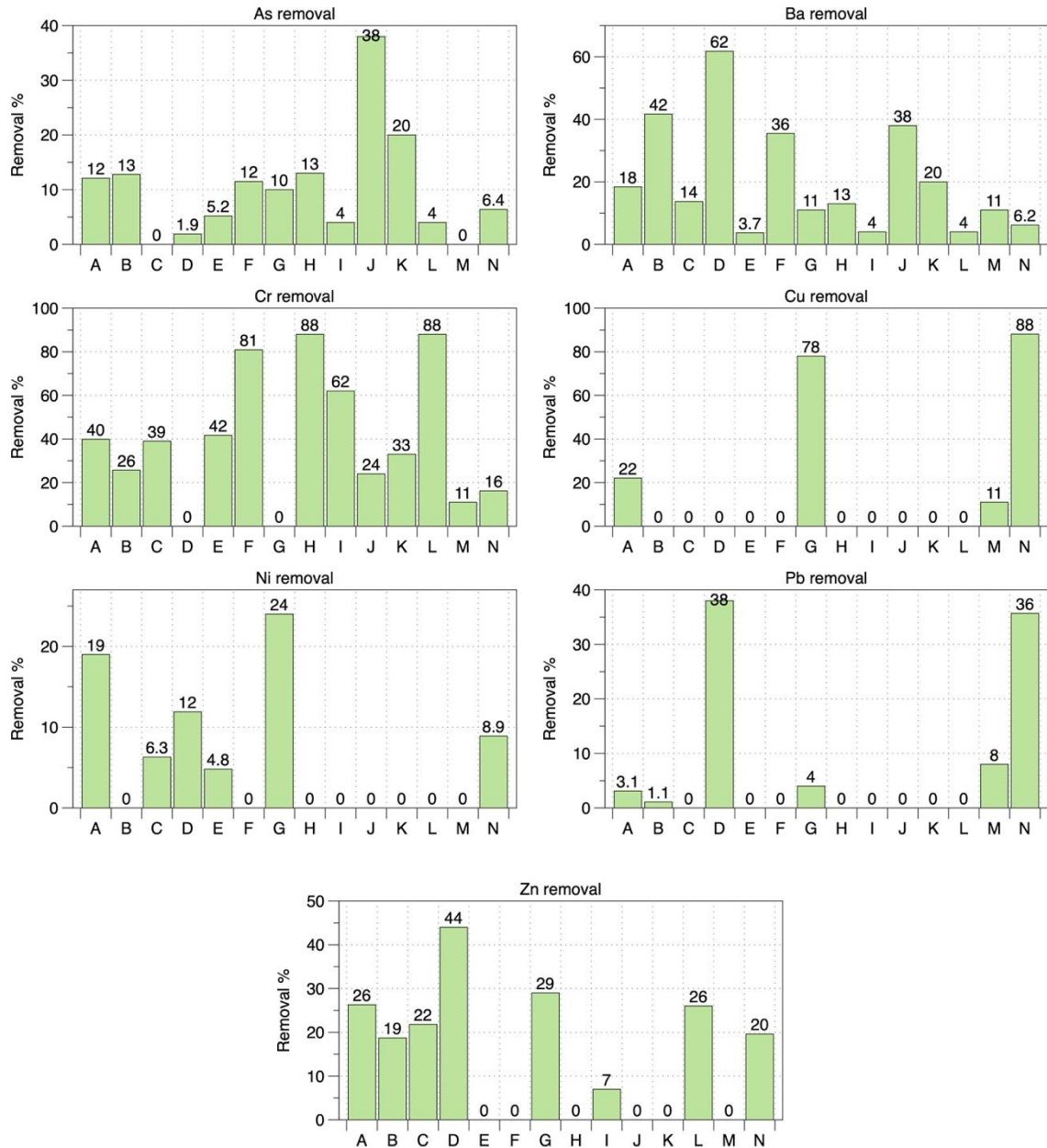


Figure 6. Heavy metals removal efficiency with various post-treatment methods. A – sand filter and anthracite, B – coagulation with ferric, C – manipulating pH to 8,5, D – manipulating pH to 10, E – adsorption with GAC, F – coagulation and flocculation, G – green sand AFM, H – green sand AFM with potassium permanganate dosing, I – green sand AFM with reduced potassium permanganate dose, J – green sand AFM with coagulation and flocculation, K – green sand AFM and aluminium coagulant

and flocculation, L – green sand and pH manipulation to 11, M – zeolite ion exchange, N – disc filtration.

6. Comparison of granular filter and disc filter

The project examined 14 different technological solutions to remove both phosphorus and various hazardous compounds. This chapter compares two post-treatment technologies, treatment with granular filter and treatment with disc filter. Although, to date, the wastewater treatment plant operators have preferred disc filters, which ensure effective removal of suspended solids and thus phosphorus removal, then due to the emergence of new problems, the operators have started to look at granular filters, which allow multiple problems to be solved at the same time due to the modified filter medium. Topical issue is, for example, pre-ozonation to break down the poorly adsorbed pharmaceutical residues into smaller particles and thereby improve their removal by using activated carbon.

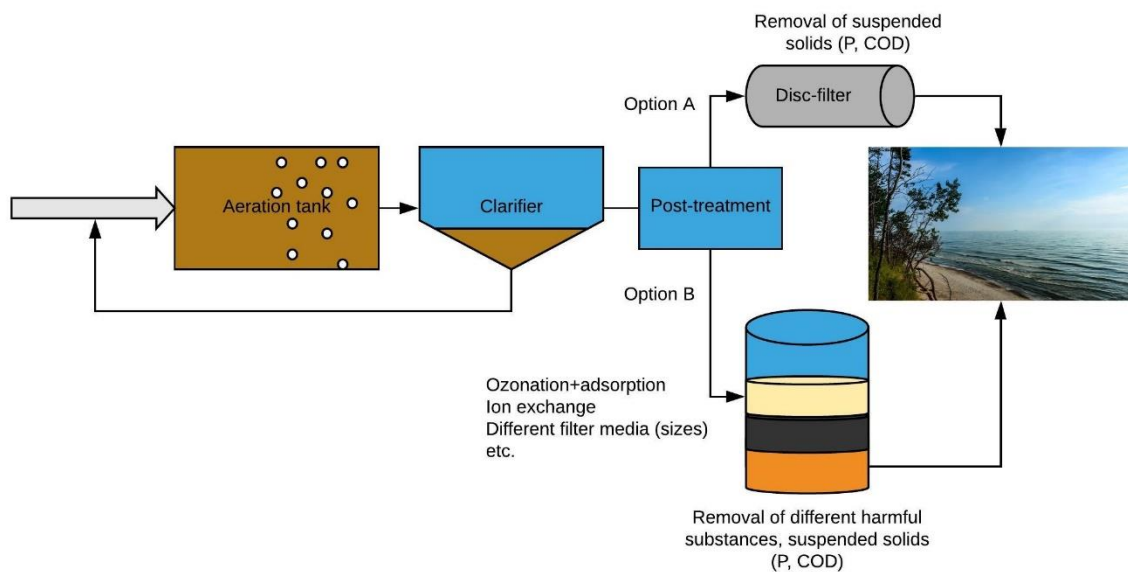


Figure 7. Two options for tertiary wastewater treatment.

Figure 7 illustrates two options for the selection of post-treatment technology. While the disc filter is suitable for the removal of suspended solids and thus phosphorus removal, the granular filter allows multiple treatment processes to be carried out in one treatment stage, such as physical

filtration, adsorption, ion exchange and pre-ozonation in combination with adsorption with activated carbon, which is receiving increasing attention. The disc filter in combination with ozonation is dangerous because it gives degradation products that may ultimately be more hazardous than the original pollutant. Therefore, adsorption is required after ozonation.

Table 6 compares the operation and design of the granular filter and disc filter examined in the project.

Table 6. Comparison of granular filter and disc filter used for post-treatment.

	Granular filter	Disc filter
Efficient removal of (>30%) ⁴	Ba, Cr, Pb, Zn, Cu, BOD ₇ , COD, PO ₄ -P, P _{tot} , SS.	As, Pb, Cu, BOD ₇ , SS
Needed footprint per 1,000 m ³ /d, m ²	20-30 m ²	10-15 m ²
Backwash water consumption (% of filtrated water)	4-6% (depends on suspended solids concentration)	3-5% (depends on suspended solids concentration)
Chemical consumption, gFe/m ³	2.4 gFe/m ³	-
Chemical consumption, gAl/m ³	0.2 g Al/m ³	-
pH manipulation with NaOH 50% ⁵	to 8.5 130 ml/m ³ to 10 230 ml/m ³	
Comments	Possibility: to add ozonation; to change the filtering medium, adding e.g. adsorption etc; to manipulate the pH; to add coagulation;	Possibility: to add coagulation;

Table 6 shows that the granular filter is able to remove more various pollutants because its filtering medium is interchangeable. However, the results of the test showed that the granular filter needed more backwash water for its operation than the disc filter – ca 4-6% of the filtered effluent. The backwash depends directly on the load, if the secondary clarifiers are operating properly, then it may

⁴ Using various operating modes like pH manipulation, coagulation etc.

⁵ Depends on buffering capacity (alkalinity) of wastewater.

be also half smaller. In addition, granular filter does not need chemical wash such as disc filters to reduce biofouling and scaling. In conclusion, this filter is more flexible because it allows various processes to be carried out on the same equipment, from the removal of suspended solids and phosphorus to the reduction of heavy metals and, for example in combination with ozonation, also reduction of pharmaceutical residues.

As shown in the table, the pH manipulation has relatively high chemical consumption, with the average consumption of 50% NaOH to raise pH to 8.5 and 10 being 130 ml/m³ and 230 ml/m³, respectively. Also, after pH 10, the wastewater should be neutralized again. As for heavy metals, the removal efficiency increased due to the increase in pH mainly for Ba, Pb and Zn.

For disc filters, the need for back wash water was ca 3-5% of the filtered water. Although disc filters are easy to install and size, their use is limited, as the filtration mainly removes the suspended solids and some of the insoluble phosphorus. Disc filters can be combined for chemical phosphorus removal (with coagulation), which increases removal efficiency, but increases the need for backwash water, etc. Heavy metals are only partially removed, mostly the insoluble ones, and those bound to suspended solids. However, the backwash water is re-routed to the treatment process, so these hazardous compounds slowly start to accumulate in the sewage sludge.

In the Baltic Sea countries, using granular and disc filters generally require closed weatherproof buildings, with an average space requirement of 10-15 m² per 1,000 m³/d of wastewater. This includes a reserve for the control panels of the equipment and for service paths.

7. Conclusions

This study analyzed the loads of heavy metals to various wastewater treatment plants and produced mass balances to assess how much of these compounds are bound to the sewage sludge and how much, on average, are discharged with the effluent to receiving waters. A large proportion of As, Cr and Pb were bound to the sludge in the wastewater treatment plants examined, and the largest proportion of Ba, Zn and Ni reached the receiving waters. The amount of heavy metals bound to the sludge depends, in most cases, on the solubility of a specific metal. The lower the solubility, the more is bound to the sludge, the higher the solubility, the more of these pollutants end up in receiving waters. For most of the heavy metals, the solubility decreases when pH is increased and the acid medium makes them more mobile in the environment.

Additionally, granular filter operation was examined at 14 different modes using various filtering media, performing chemical coagulation and pH manipulation to reduce the solubility of heavy

metals. The results showed that the highest phosphorus removal efficiency was achieved with coagulation and flocculation, where the insoluble compounds formed were removed with sand filter. In this process, the phosphorus load decreased by 64% on average. An average of 13% of phosphorus removal was achieved with disc filters, as no prior chemical phosphorus removal was applied with this technology.

For heavy metals removal, Ba and Cr were relatively well removed, with 62% of Ba and 88% of Cr removed, respectively, using various technological solutions. The most effective in Ba removal was the pH increase to 10 and in Cr removal pH increase to 11, respectively, and oxidation with potassium permanganate.

A comparison of two different post-treatment technologies found that both the disc filter and the granular filter require almost the same amount of backwash water, approximately 3-6% of the filtered water. The need for backwash water directly depends on the level of suspended solids in water to be filtered. It was also found that the required space for both technologies was approximately 10-15 m² for treating 1,000 m³/d of wastewater. However, the biggest difference lies in the flexibility of the technologies, the interchangeable filter allows the use of various filtering media such as activated carbon, various grain size of the sand fraction, etc., which increases the number of removable pollutants. For example, ozonation is used to remove pharmaceutical residues, and after this stage, adsorption with activated coal should be followed in order to reduce the content of degradation products of pharmaceutical residues entering the environment. This can be done in combination with a sand filter. If only the suspended solids and phosphorus are the problem, it is also worth considering a disc filter that is delivered as a ready-to-use solution and, in most cases, is already set up and will certainly work more reliably due to its simplicity than a sand filter with a slightly more complex design.

8. Contacts of the project team

- Project manager: Professor Karin Pachel, e-mail: Karin.Pachel@taltech.ee;
- Researcher: Argo Kuusik, e-mail: Argo.Kuusik@taltech.ee;
- Researcher: Erki Lember, e-mail: E.Lember@taltech.ee
- Project coordinator: Maret Merisaar, e-mail: Maret.Merisaar@taltech.ee

9. References

- Badejo, Adedayo A., David O. Omole, Julius M. Ndambuki, and Williams K. Kupolati. 2017. "Municipal Wastewater Treatment Using Sequential Activated Sludge Reactor and Vegetated Submerged Bed Constructed Wetland Planted with *Vetiveria Zizanioides*." *Ecological Engineering* 99: 525–29. <https://doi.org/10.1016/j.ecoleng.2016.11.012>.
- Barakat, M. a. 2011. "New Trends in Removing Heavy Metals from Industrial Wastewater." *Arabian Journal of Chemistry* 4 (4): 361–77. <https://doi.org/10.1016/j.arabjc.2010.07.019>.
- Bernard, E, a Jimoh, and J O Odigure. 2013. "Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell." *Research Journal of Chemical Sciences* 3 (8): 3–9.
- Bischof, Wolfgang. 1998. *Abwassertechnik: Mit Zahlreichen Beispielen*. Teubner.
- Çeçen, Ferhan, Neslihan Semerci, and Ayşe Gül Geyik. 2010. "Inhibition of Respiration and Distribution of Cd, Pb, Hg, Ag and Cr Species in a Nitrifying Sludge." *Journal of Hazardous Materials* 178 (1–3): 619–27. <https://doi.org/10.1016/j.jhazmat.2010.01.130>.
- Charters, Frances J., Thomas A. Cochrane, and Aisling D. O'Sullivan. 2016. "Untreated Runoff Quality from Roof and Road Surfaces in a Low Intensity Rainfall Climate." *Science of the Total Environment* 550: 265–72. <https://doi.org/10.1016/j.scitotenv.2016.01.093>.
- Chipasa, Kangala. 2003. "Accumulation and Fate of Selected Heavy Metals in a Biological Wastewater Treatment System." *Waste Management* 23 (2): 135–43. [https://doi.org/10.1016/S0956-053X\(02\)00065-X](https://doi.org/10.1016/S0956-053X(02)00065-X).
- Davis, M.L. 2010. *Water and Wastewater Engineering. Design Principles and Practice*.
- Dhokpande, Sonali R. 2013. "Biological Methods for Heavy Metal Removal- A Review." *International Journal of Engineering Science and Innovative Technology (IJESIT)* 2 (5): 304–9.
- González-Acevedo, Z. I., M. A. García-Zarate, E. A. Núñez-Zarco, and B. I. Anda-Martín. 2018. "Heavy Metal Sources and Anthropogenic Enrichment in the Environment around the Cerro Prieto Geothermal Field, Mexico." *Geothermics* 72 (May 2017): 170–81. <https://doi.org/10.1016/j.geothermics.2017.11.004>.
- Gray, N F. 2004. *Biology of Wastewater Treatment. Series on Environmental Science and Management*. Dublin: Imperial College Press. <http://www.cabdirect.org/abstracts/19901360656.html>.
- Gulyás, Gábor, Viktória Pitás, Bence Fazekas, and Árpád Kárpáti. 2015. "Heavy Metal Balance in a Communal Wastewater Treatment Plant." *Hungarian Journal of Industry and Chemistry* 43 (1): 1–6. <https://doi.org/10.1515/hjic-2015-0001>.

- Haiba, Egge. 2017. "Optimization of Sewage Sludge Composting : Problems and Solutions." Tallinn: TTÜ kirjastus.
- Henze, Morgens, C.M Mark Loosdrecht, A. George Ekama, and Damir Brdjanovic. 2011. *Biological Wastewater Treatment*. London: IWA Publishing.
- Karnib, Mona, Ahmad Kabbani, Hanafy Holail, and Zakia Olama. 2014. "Heavy Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite." *Energy Procedia* 50: 113–20. <https://doi.org/10.1016/j.egypro.2014.06.014>.
- Kobielska, Paulina A., Ashlee J. Howarth, Omar K. Farha, and Sanjit Nayak. 2018. "Metal–Organic Frameworks for Heavy Metal Removal from Water." *Coordination Chemistry Reviews* 358: 92–107. <https://doi.org/10.1016/j.ccr.2017.12.010>.
- Lember, Erki. 2018. *Harmful Substances in Wastewater, Possible Technical Solutions for Their Removal*. Tallinn: TUT.
- Luo, Sheng Lian, Lin Yuan, Li Yuan Chai, Xiao Bo Min, Yun Yan Wang, Yan Fang, and Pu Wang. 2006. "Biosorption Behaviors of Cu²⁺, Zn²⁺, Cd²⁺ and Mixture by Waste Activated Sludge." *Transactions of Nonferrous Metals Society of China (English Edition)* 16 (6): 1431–35. [https://doi.org/10.1016/S1003-6326\(07\)60033-8](https://doi.org/10.1016/S1003-6326(07)60033-8).
- Metcalf & Eddy, George Tchobanoglous, H. David Stensel, Ryujiro Tsuchihashi, Franklin L. (Franklin Louis) Burton, Mohammad Abu-Orf, Gregory Bowden, and William Pfrang. n.d. *Wastewater Engineering : Treatment and Resource Recovery*. Accessed December 11, 2019. <https://www.rahvaraamat.ee/p/wastewater-engineering-treatment-and-resource-recovery/963452/et?isbn=9780073401188#>.
- Nowak, Otto, Graz Österreich, and Bönisch Dresden. 2011. "Abwässer Aus Der Photovoltaikindustrie Und Ihr Einfluss Auf Die Kommunale Abwasserreinigung" 2011 (10): 935–41. <https://doi.org/10.3242/kae2011.10.002>.
- Ong, Soon An, Eiichi Toorisaka, Makoto Hirata, and Tadashi Hano. 2010. "Adsorption and Toxicity of Heavy Metals on Activated Sludge." *ScienceAsia* 36 (3): 204–9. <https://doi.org/10.2306/scienceasia1513-1874.2010.36.204>.
- Qasim, Syed R., and Guang Zhu. 2018. *Wastewater Treatment and Reuse, Theory and Design Examples, Volume 1: Post-Treatment, Reuse and Disposal*.
- Ramrakhiani, Lata, Sourja Ghosh, Subhendu Sarkar, and Swachchha Majumdar. 2016. "Heavy Metal Biosorption in Multi Component System on Dried Activated Sludge: Investigation of Adsorption Mechanism by Surface Characterization." *Materials Today: Proceedings* 3 (10): 3538–52. <https://doi.org/10.1016/j.matpr.2016.10.036>.

- Sani, Ali, Maryam Bello Gaya, and Fatima Aliyu Abubakar. 2016. "Determination of Some Heavy Metals in Selected Cosmetic Products Sold in Kano Metropolis, Nigeria." *Toxicology Reports* 3: 866–69. <https://doi.org/10.1016/j.toxrep.2016.11.001>.
- Tahri, M., M. Larif, B. Bachiri, S. Kitanou, B. Rajib, K. Benazouz, M. Khimani, M. Taky, M. Elamrani, and A. Elmidaoui. 2017. "Characterization of Heavy Metals and Toxic Elements in Raw Sewage and Their Impact on the Secondary Treatment of the Marrakech Wastewater Treatment Plant." *Journal of Materials and Environmental Science* 8 (7): 2311–21.
- Weimar, Bauhaus-Universität. 2014. *Abwasserbehandlung Gewässerbelastung, Bemessungsgrundlagen, Mechanische Verfahren Und Biologische Verfahren, Reststoffe Aus Der Abwasserbehandlung, Kleinkläranlagen*. VDG Weimar.