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Decentralised water reuse in Central Europe - Steps towards understanding processes in an anaerobic wastewater treatment plant, including the removal of micropollutants

Master's Thesis

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Abstract

Wastewater from the first decentralised anaerobic-aerobic treatment plant in Switzerland, “IWB”, with micropollutant (MP) elimination step and wastewater reclamation for irrigation, was analysed. Improvements made in the biological treatment, to support the removal of organic pollutants, were monitored. The organic matter was removed up to 81.2% for COD and over 90% for BOD, but showed still too high values for save reuse. Nutrients, such as, NH_4-N, PO_4-P were found to be preserved during the treatment.

During the observation period, the IWB did not achieve the expected treatment performance. It was assumed that the biology was inhibited by some unknown substances in the wastewater. Observations indicated shock loads with detergents and hydraulic short-circuits.

The IWB was screened on two days for estrogenic active substances using the planar-YES bioassay. Estrone (E1) and17β-Estradiol (E2) were found in concentrations of up to 16.3 ng/l for E1 and 17.4 ng/l for E2. The oral contraceptive 17-Ethinylestradiol (EE2) was only measured in the aerobic part of the IWB in the first screening, and in low concentrations. In total six unknown substances were detected, where one of them most likely seemed to be Bisphenol A.

To assess the potential role of biochar and activated biochar for MP elimination in wastewater, a biochar (BC) from cherry stones and three different activated biochars (ABC) from K_2CO_3 impregnated cherry stones, with different impregnation ratios, were produced. The pyrolysis was performed using the Pyreka pyrolysis reactor at 500 °C and a holding time of 10 min. Methylene blue (MB) adsorption experiments were performed with this chars and compared with a regular activated carbon. The BC showed the least adsorption of MB in all experiments. The ABC, activated with an impregnation ratio of 1:1/4, showed the best adsorption among the activated biochars. The best adsorption performance showed the regular AC.

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Glossary

AC	Activated carbon
ABC	Activated biochar
ABR	Anaerobic baffled reactor
AS	Activated sludge
BC	Biochar
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DETEC	Department of the Environment, Transport, Energy and Communications
DWWTP	Decentralised wastewater treatment plant
DWWTS	Decentralised wastewater treatment system
E1	Estrone
E2	Estradiol
E3	Estriol
EAS	Estrogenic active substance
EE2	17α-ethinylestradiol
EEQ	Estradiol equivalent
GAC	Granular activated carbon
HPLC	High-performance liquid chromatography
HPTLC	High-performance thin-layer chromatography
IWB	Integrated use of water and biomass
K_2CO_3	Potassium carbonate
LLE	Liquid-liquid extraction
MB	Methylene blue
MP	Micropollutant

NH_4-N	Ammonium nitrogen
NO_2-N	Nitrite nitrogen
NO_3-N	Nitrate nitrogen
PAC	Powdered activated carbon
PO_4-P	Orthophosphate
SAC 254	Spectral absorption coefficient measured at 254 nm
SSPE	Selective surface polarity effect
TN	Total nitrogen
TP	Total phosphorus
UASB	Up-flow anaerobic sludge bed
WWTP	Wastewater treatment plant

1 Introduction

1.1 Climate change and water reuse

Due to climate change, population growth, and intensive agriculture, clean water as a resource is coming under increasing pressure all around the world. The unusually warm and dry summers in recent years have shown that even countries with large water resources and good infrastructure, like Switzerland, can suffer from water scarcity. Climate reports predict that this trend will continue because of climate change (CH2018, 2018). The need for clean water for irrigation in agriculture or green spaces, parks or trees in urban areas is therefore increasing.

At the same time an enormous amount of wastewater is produced. The average wastewater volume produced per person in Switzerland is between 440 and 650 litres per day. This means a total of almost 1.7 billion m^3 of wastewater per year, which needs to be transported and treated at centralised wastewater treatment plants (WWTPs) (Maurer, et al., 2012). A considerable amount of infrastructure is therefore needed to ensure the smooth operation of the entire wastewater treatment process. This has contributed significantly to the high water quality of Swiss water bodies, the health of the population, and the nation's prosperity.

In terms of population growth, climate change, and increasing challenges in wastewater composition, this centralised approach of wastewater treatment is causing more and more problems. Heavy precipitation, for example, leads to high discharge values of wastewater (stormwater), especially in densely populated areas with combined sewer systems. This causes a severe stress to waterbodies since WWTPs cannot handle the peaks of incoming wastewater, and thus the untreated water is discharged into the water bodies (combined sewer overflow). Furthermore, persistent substances (micropollutants) which were found in the effluent of WWTPs showed negative impacts to the aquatic ecosystem.

Instead of using centralised systems with water discharge into water bodies, decentralised wastewater treatment systems (DWWTSs) could be used to treat a certain amount of this large volume and provide water for irrigation purposes. This system would be of particular interest for urban areas as it would eliminate the need for costly sewer systems. New development projects in urban areas would have the possibility of integrating their own wastewater treatment with recycling in line with local conditions and needs. The implementation of anaerobic DWWTSs could furthermore provide benefits such as nutrient conservation in the treated wastewater and onsite biogas production.

In order to make progress in this area, however, there is still a lack of a legal framework, research options and experience in the field of recycling of purified wastewater.

A first approach towards resource conserving wastewater management in urban areas has been implemented in the settlement project “Stöckacker Süd” in the city of Bern. Authorities and the company Autark Engineering AG have developed a concept and installed an anaerobic-aerobic treatment plant for decentralised wastewater treatment with recycling options. This provides a unique opportunity for research and development towards a new resilient wastewater management system.

1.2 Objectives of this study

In this study the decentralized wastewater pilot treatment plant “IWB Stöckacker Süd” was monitored from August 14, 2018 to November 22, 2018. The aims of the study were:

- To assess the treatment processes at ARA Stöckacker, based on standard wastewater quality parameters
- To compare the performance of ARA Stöckacker with similar anaerobic treatment plants documented in literature
- To discuss the potential reusability of the treated wastewater from ARA Stöckacker, based on these results
- To identify open question for future research, with a special focus on micropollutants and effect-based analysis
- To assess the potential role of biochar and activated biochar in the removal of micropollutants from wastewater

2 Wastewater treatment and water reuse

The safe reuse of treated wastewater is connected with different fields of research and linked with numerous approaches that attempt to turn wastewater into a valuable and reusable resource. This chapter is a summary of the state of knowledge of relevant topics for a possible approach for the decentralised reuse of treated wastewater.

2.1 Wastewater treatment in Switzerland today

2.1.1 Infrastructure and financial aspects

In Switzerland, wastewater is treated by 839 centralised public WWTPs and discharged into rivers and lakes (Abegglen & Siegrist, 2012a). This requires a complex sewer system that transports the wastewater from the individual households to the treatment plants. In the area of public sewer systems, the polluted wastewater must be discharged into the sewer system. There is therefore a legal obligation to connect every household, business, etc. to the sewer system (WPA, 1991). Thereby a connection coverage of 98% was achieved ensuring efficient wastewater treatment and clean water bodies (Maurer, et al., 2012). But exactly this legal obligation makes decentralised treatment and recycling of wastewater impossible.

The total length of the sewer system is meanwhile about 91,000 km (municipal sewer system and house connections, excluding industrial sewer systems). In order to maintain this infrastructure, 2.2 billion CHF would have to be spent annually, but only 1.7 billion CHF are available. This means that the entire infrastructure is subject to an annual depreciation of 500 million CHF. This shortfall will endanger the safe operation of the wastewater infrastructure in the long term (FOEN, 2012).

The centralized wastewater treatment requires that WWTPs are planned for future growth in the catchment area and that sufficient capacity (plant size, land reserves) is planned accordingly, especially in densely populated areas.

2.1.2 Operational aspects and nutrient loss

For the smooth operation of the sewage system, a certain minimum amount of water is required to transport the solids, so that they can reach the WWTP without clogging individual sections (Wu, Hu, & Liu, 2018). This aspect counteracts the objective of saving water and using it more efficiently. In addition, individual sections of the sewer system repeatedly show leaks through which wastewater and undesirable substances enter the groundwater (Fischer & Kiefer, 2014). The purification of wastewater thus remains associated with a very high level of infrastructure, energy and costs.

The biological stage of wastewater treatment generates large quantities of sewage sludge during purification (approx. 50% of the organic load in wastewater becomes sewage sludge). In Switzerland the resulting sewage sludge is mainly used for the production of biogas. After digestion it has to be dewatered and disposed under high demand of energy (Rosenwinkel, et al., 2015). The use of sewage sludge as fertiliser in agriculture is prohibited by Swiss law since 2006 (DETEC, 2003). The nutrients contained in the sludge are thus permanently removed from the nutrient cycle. In the case of phosphorus, for example, the figure is 6,000 tonnes of P per year (Hermann, 2009). Some pollutants, such as residues of pharmaceuticals, pesticides, anti-corrosion agents, etc., still enter the water bodies, despite the treatment in the WWTP, and harm living organisms in rivers and lakes (see chapter 2.4).

2.2 New approaches for water reuse with decentralised anaerobic-aerobic treatment of wastewater

The idea of decentralised wastewater treatment systems (DWWTSs) originates from low- and middle income countries with dry climate and low infrastructure standard. Due to the financial situation in these countries, the transport of wastewater over long distances to centralized treatment systems was infeasible. Furthermore, the scarcity of fresh water forced to the inevitable use of wastewater, mainly for irrigation in agriculture (Capodaglio, et al., 2017). Even if this approach cannot be adopted directly for urban areas, the basic idea remains the same. The idea is that sustainable decentralised sanitation should focus on local treatment and recycling of resources contained in domestic wastewater, and the water itself. Thereby, DWWTSs in urban areas (also industrial countries) offer several advantages compared to the centralised systems, such as:

- Less infrastructure, maintenance and costs since no public sewer system is needed
- No surface runoff (meteoric water) into the reactor and therefore no dilution of the wastewater and less foreign material in the treatment system
- Less heavy metals since DWWTS are not connected to industry and runoff water from traffic
- Several different DWWTSs operate like a “multi pillar system”. In case of toxic substances which may get into the wastewater only on plant (“pillar”) is affected. The DWWTS is therefore a much more resilient system.
- Local reuse of nutrient-rich water for irrigation of parks, green spaces, trees etc.

Several different technological options provide decentralised treatment and nutrient recovery of wastewater (like septic tanks, stabilisation ponds, constructed wetlands etc.). Due to a lack of performance, space requirements, and connectivity, only a few options are suitable for

decentralised wastewater treatment in urban areas. The focus is thereby on anaerobic high-rate reactors with downstream post-treatment (Capodaglio, et al., 2017).

2.2.1 Performance of anaerobic and anaerobic-aerobic DWWTS

The anaerobic treatment achieves biomass decomposition into methane directly in the reactor(s). Thus, different bacteria break down organic compounds (in the absence of oxygen) through basic mechanisms involving a sequence of steps (hydrolysis, acidogenesis, acetogenesis and methanogenesis) (Rosenwinkel, et al., 2015), (Van Lier, et al., 2010), (Anderson, Sallis, & Uyanik, 2003). The anaerobic biology does not have to be aerated and does not produce as much sludge as the aerobic biology in conventional WWTPs (approx. 5% of the organic load, i.e. 10 times less than with conventional aerobic biology) (Rosenwinkel, et al., 2015). As the target is to the keep nutrients inside the water, process steps like aeration for nitrification and precipitation (removal of phosphorous) are not needed. This results in an overall energy and resource benefit compared to conventional systems.

Since anaerobic bacterial kinetics are slower than aerobic kinetics, empirical evidence suggests that these systems are highly depended on reactor design, operating conditions (temperature) and wastewater characteristics (Van Lier, et al., 2010). Also, Capodaglio et al, (2017) reported that in practice anaerobic systems alone achieve only moderate effluent quality, considering the discharge standards in most countries. Various configurations of anaerobic systems are reported in Table 1. In order to fulfil these standards, anaerobic systems usually need an additional treatment step, such as a polishing pond (Stuckey, 2010) or an aerobic post treatment (Table 1, Reactor type: upflow anaerobic sludge bed UASB and activated sludge AS) (Capodaglio, et al., 2017).

Table 1: Performance of anaerobic and anaerobic-aerobic DWWTS. UASB= upflow anaerobic sludge bed, ABR=anaerobic baffled reactor, AS=activated sludge (aerobic post treatment)

Country	V [m^3]	T [°C]	HRT [h]	COD removal [%]	COD effluent [mg/l]	Reactor type	Source
Spain	35	13-15	10-11	54-58	103-143	UASB	(Alvarez, et al., 2006)
Colombia	64	24-26	4-6	65	93	UASB	(van Haandel & Lettinga, 1994)
Brazil	120	23	4.7-9	50-70	95-158	UASB	(van Haandel & Lettinga, 1994)
United Kingdom	30	-	6	50	-	ABR	(Stuckey, 2010)
Brazil	4.2	-	6.8	85-93	50-58	UASB +AS	(von Sperling, Freire, & de Lemos Chernicharo, 2001)

Chan et al, (2009) reported in a review paper that the anaerobic–aerobic combination still shows numerous advantages such as low energy consumption, low chemical consumption, low sludge production, vast potential of resource recovery, less equipment required, and high operational simplicity.

2.2.2 Low temperature treatment

In Europe there is still comparatively little experience with anaerobic-aerobic DWWTSs. It is often argued that anaerobic biological treatment is not suitable in the temperate climate zone. The reason often given is the reduced biological activity of the bacteria at lower wastewater temperatures (< 20 °C) and the resulting lower degradation performance (Van Lier, et al., 2010). A pilot plant with an experimental anaerobic baffled reactor (ABR) in Ellesmere Port (UK), showed in fact a COD reduction of only 50% (see Table 1).

However, Cavicchioli, (2006) reported that psychrophilic methanogens do exist (e.g. *Methanogenium frigidum*). These bacteria can metabolise at temperatures as low as 1 °C (with optima at 15 °C) and it should be possible to develop reactors capable of good to high COD removals at temperatures as low as 10 °C.

Another possibility relates to construction measures which use the temperature of the wastewater more efficiently. The Swiss Federal Office of Energy (SFOE) estimates the average wastewater temperature in the house sewer to 23 °C (van Velsen & Benz, 2013). Considering this value, good planning and installation should keep the wastewater temperature constantly high and allow to operate an anaerobic biology in temperate climate zones.

2.3 Regulations for water reuse at the example of wastewater irrigation

The reuse of treated wastewater for irrigation is an increasingly common practice. Countries suffering from regular water scarcity like the Middle East region, as well as countries in Europe (Portugal, Spain, France and Italy) and parts of USA, practice the reuse of treated wastewater for irrigation regularly (Inbar, 2006). For its sustainable reuse there is a serious need for regulation and monitoring. Several studies reported negative effects of salinity (Norton-Brandao, Scherrenberg, & van Lier, 2013) and heavy metals (Becerra-Castro, et al., 2014) in soil and crops from wastewater irrigation. Malchi et al., (2014) reported a risk for human health caused by micropollutants in roots and leaves of crops irrigated with treated wastewater. High values of nutrients (e.g. ammonium and phosphorous) are also reported to have a negative long term effect on soil quality (Jeong, Kim, & Jang, 2016). So far there is no uniform regulation for the use of wastewater for irrigation. Depending on the country, purpose, and type of irrigation technique, the use is divided into different categories with different quality grades (Becerra-Castro, et al., 2014) (Norton-Brandao, Scherrenberg, & van Lier, 2013).

2.3.1 Exemplary approaches from Israel

Israel is one of the leading countries practising the reuse of treated wastewater. The total amount of wastewater produced in Israel is approximately $5*10^8$ m^3/y including agriculture, industry and others. Approximately $3*10^8$ m^3 of wastewater was reclaimed for irrigation in 2004. Israel's objective is to treat 100% of the country's wastewater to a level enabling unrestricted irrigation without risking soil and water sources and human health (Inbar, 2006). Therefore, since 2010, there is a new regulation that forces all WWTPs to the highest quality level to achieve this goal. This includes advanced treatment technologies, carrying out Nitrogen and Phosphorus reduction, filtration, and disinfection (Inbar, 2006). The elimination of MP (e.g. in the country's largest wastewater reclamation project Shafdan) is achieved by ozonation and currently the subject of research (Zucker, et al., 2015).

2.3.2 BOD/COD-ratio

The ratio between the biochemical oxygen demand (BOD) and the chemical oxygen demand (COD) is used to indicate the biodegradability of wastewater. Values > 0.5 indicate easy biodegradable wastewater, 0.4 – 0.5 average biodegradability and 0.2 – 0.4 slowly biodegradability. Low values are also an indicator for substances that are hard to decompose. The effluent of a WWTP shows in general a BOD/COD ratio between 0.1 and 0.3 (Yi Jing, et al., 2009).

2.3.3 Swiss regulations for wastewater

Although Switzerland does not have a regulation for the reuse of treated wastewater for irrigation, it has a strict regulation for the discharge of wastewater into surface waters (WPA, 1991). Since the Swiss regulation is focused on the elimination of pollutants **and** nutrients, this regulation contradicts the requirements for the reuse of treated wastewater. While the concentrations of pollutants are similar to those of the Israeli regulation, the concentration difference of nutrients (ammonium, total phosphorus) between the two countries shows the urgent need to adapt the regulation for the reuse of wastewater for irrigation purposes (Table 2).

A regulation for the reuse of treated wastewater in urban areas which combines the Israeli and the Swiss regulations, with a focus on nutrient conservation and pollutant elimination, therefore seems to make sense. Thus, a suggestion for a combination of the two regulations was made. A table containing both regulations and the proposed combination is found in the Appendix A (Table 10).

Table 2: Section of the Israeli regulation for unrestricted irrigation (Inbar, 2006) and the Swiss regulation for discharge of treated wastewater. a/b differentiates the discharge values according to population equivalents PE. a=PE<10'000, b=PE≥ 10'000 (WPA, 1991, stand on June 1, 2018)

Parameter [mg/l]	Regulation for unrestricted irrigation in Israel	Regulations for discharge in Switzerland a/b
BOD	10	20/15
TSS	10	20/15
COD	100	60/45
Ammonium	20	2 (at 10 °C)
Total Phosphorus	5	0.8

In addition to pathogenic germs and heavy metals, contamination with micropollutants (MP) poses a risk to the safe reuse of treated wastewater (Becerra-Castro, et al., 2014). These are to be removed as much as possible. The following subchapters therefore deal with the problem of micropollutants, possible measurement methods and their removal from wastewater.

2.4 Micropollutants and treatment methods used in WWTPs

In Switzerland, an estimated 30,000 different synthetic-organic substances are used in various products such as pharmaceuticals, plant and material protection products, body care products and cleaning agents. Since the treatment stages of current WWTPs are often unable to decompose these substances or only decompose them to a limited extent, some of these compounds are discharged into the receiving waters, Even though the concentrations of these substances are usually very low (ng/L or µg/L, hence the term micropollutants (MP)), they can have strongly negative effects on the environment (Abegglen & Siegrist, 2012b).

The Swiss government has recognised the problem and worked with operators of WWTPs and research institutions to develop a concept for eliminating micropollutants. However, since the overhaul of WWTPs requires a greater technical and financial effort, the focus was placed on the largest plants. The concept envisions that WWTPs with more than 80,000 population equivalents (PE) will have a 4th treatment stage for micropollutants (Abegglen, et al., 2016). According to the current state of the art technology, there are two processes for the elimination of micropollutants:

- Adsorption with activated carbon
- Oxidation with highly reactive ozone (ozonation)

Efficient pre-treatment is crucial when using one of these two technologies. A target COD value of 15 mg/l is desired with both technologies. Values above this standard lead to reduced efficiency or result in a higher demand for O_3 or AC (Zwickenpflug, et al., 2010) (Abegglen,

2018). Although both processes are able to eliminate a broad spectrum of micropollutants from wastewater (Abegglen & Siegrist, 2012a), both have advantages and disadvantages. For example, in bromine-containing wastewater (the bromine often originates from waste incineration plants) carcinogenic bromate is formed by treatment with ozone. On the other hand the X-ray contrast agent Iopamidol (most likely present in wastewater from hospitals) is only slightly adsorbed by activated carbon which results in an insufficient elimination. Therefore, the selection of the appropriate elimination process must be checked and evaluated on a project specific basis (Soltermann, et al., 2016).

2.4.1 Test methods for micropollutants determination

In order to test the cleaning effect of processes for eliminating micropollutants, Swiss Federal Department of the Environment, Transport, Energy, and Communications (DETEC) has defined twelve substances (DETEC, 2016). These substances enter the water bodies primarily via the treated wastewater and could therefore be eliminated in a WWTP via a 4th treatment stage. The substances are exclusively pharmaceuticals and anti-corrosion agents (Table 3). To control the cleaning effect, wastewater samples must be periodically analysed on micropollutants (WPA, 1991, stand on June 1, 2018). The sampling points are therefore the inflow of the WWTP (raw wastewater or inflow of the biological stage) and outflow of the WWTP. The cleaning effect must be calculated based on at least six substances.

Table 3: Substances to determine the cleaning effect of an elimination step in WWTP (DETEC, 2016)

	Category 1	Category 2
Substances	Amisulpride	Benzotriazole
	Carbamazepine	Candesartan
	Citalopram	Irbesartan
	Clarithromycin	4-Methylbenzotriazole / 5-Methylbenzotriazole
	Diclofenac	
	Hydrochlorothiazide	
	Metoprolol	
	Venlafaxine	

The ratio of Category 1 substances to Category 2 substances shall be two to one. The required cleaning effect is achieved when the weighted average is at least 80%. In order to determine and quantify these substances in wastewater, samples are analysed through high performance liquid chromatography (HPLC). These analyses are complex and costly. For larger

measurement campaign or operational monitoring on WWTPs the substitute parameter (SAC 254) is used

2.4.2 Spectral absorption coefficient at 254 nanometer (SAC 254)

Numerous organic substances have absorption bands in the ultraviolet light range. The spectral absorption coefficient measured at 254 nm (SAC 254) with an UV-VIS photo spectrometer, can be used as the sum parameter for the detection of dissolved organic water constituents. The SAC 254 is therefore a suitable sum parameter for the detection of MPs in wastewater. It is used for continuous operational monitoring in WWTPs and also used in research to determine the performance of an elimination step (Zeitzschmann, et al., 2014). The use of the SAC 254 method has been tested both in ozonation and in the activated carbon processes of granulated activated carbon (GAC) and powdered activated carbon (PAC) (Schreiber, et al., 2007), (Rössler & Metzger, 2016). In WWTPs the SAC 254 is measured in the inflow- and outflow of the MP elimination stage. In raw wastewater or at the inflow of the biological stage, the measurement of the SAC 254 is not possible due to interference with the background matrix. For processes with activated carbon, the SAC 254 can only be used for processes containing either a downstream contact reactor with sedimentation, a GAC filter, or direct dosing onto the sand filter. Colouring or turbidity of the wastewater, have no influence on the measurements. Turbid samples can be corrected with the spectral attenuation coefficient $\mu(\lambda)_{korr}$ which is measured at 550 nm.

The spectral adsorption coefficient α(λ) is calculated as follows:

$$\alpha(\lambda) = \frac{A(\lambda)}{d} f \qquad \text{F 1}$$

$A(\lambda)$	absorbance of the water sample at wavelength λ, in nanometers (nm),
d	optical path length of the cuvette, in millimeters (mm),
f	the factor to obtain the spectral absorption coefficient in m^{-1},(here f = 1000)

If the water sample is turbid, the corrected spectral attenuation coefficient $\mu(\lambda)_{korr}$ is calculated as follows:

$$\mu(\lambda)_{korr} = \mu(\lambda) - \mu(\lambda_{ref}) = (\alpha(\lambda) + s(\lambda)) - \mu(\lambda_{ref}) = \frac{(A_{254} - A_{550})}{d} f \qquad \text{F 2}$$

μ(λ)	spectral attenuation coefficient at 254 nm
$\mu(\lambda)_{ref}$	spectral attenuation coefficient at 550 nm
s(λ)	spectral scattering coefficient, measured at λ = 254 nm. Standard measure for the attenuation of ultraviolet light by particulate matter during passage through an absorption-free water sample (pure water), standardised to the thickness of the layer

2.4.3 Endocrine disruptors and effect-based analysis: example of the planar-YES bioassay

Micropollutants also include hormone-active substances. If these substances enter the environment via wastewater, they have been proven to be responsible for disturbing the hormonal balance of fish (Jobling, et al., 1998) and are suspected of causing infertility and cancer in humans (Pflieger-Brus, Schuppe, & Schill, 2004), (Prins, 2008). A model for these endocrine disrupting substances is the effect on the estrogen system (Patisaul & Adewale, 2009). A distinction is made between:

- **Natural estrogens** such as female sex hormones like estrone (E1), estradiol (E2), estriol (E3) and esterol (E4).
- **Synthetic estrogens** used for contraception (e.g. 17α ethinylestradiol (EE2))
- **Xenoestrogens**, which are natural and artificial substances that are oestrogen active, but not themselves estrogens (e.g. PCBs, BPAs and phthalates –artificial) and (phyto- and mycoestrogens –natural).

Typical estrogen concentrations in the output of WWTPs are between 1 and 3 ng/l estradiol equivalents (EEQ) (Schoenborn, Kunz, & Koster, 2015). This corresponds to the same biological effect as the concentration of the natural female hormone 17-oestradiol. However, continuous exposure to a concentration of more than 0.4 ng/l estradiol can already lead to the feminization of male fish (Schoenborn, Kunz, & Koster, 2015). The quality criterion for this substance proposed by the EU and the Ecotoxic Centre in Switzerland is 0.4 ng/l (oekotoxzentrum, 2016). So far, endocrine disruptors are not included in the DETEC regulation.

Chemical analysis with HPLC is used to measure endocrine disruptors in wastewater samples. This leads to the same financial expense mentioned in chapter 2.4.1. Therefore, effect-based analysis offers an effective and reliable alternative. The "planar-YES" test method recently developed by ZHAW and other labs, combines high-performance thin-layer chromatography (HPTLC) with a bioassay and offers a new opportunity in effect based analysis (Schoenborn, et al., 2017). The core of this bioassay is a genetically modified yeast strain implanted with a human estrogen receptor. By combining these two methods, the different estrogen-active substances (EAS) contained in the sample can be separated and analysed separately. Thus the estrogen activity of the different components becomes visible.

The planar-Yes allows detection of oestrogenic activity profiles of wastewater samples and track them using the profile patterns. This makes it a more cost-effective method for the detection of endocrine disruptors. The planar-YES has already been successfully used in some WWTPs in the canton of Zurich (Schoenborn, et al., 2017).

2.5 Biochar and activated biochar

In the 4th treatment stage of wastewater treatment, activated carbon (AC) is used as an adsorption medium (Abegglen & Siegrist, 2012a). The raw materials used for AC production are lignite, stone coal or peat. In addition, nut shells or plastics are processed into AC by pyrolysis and subsequent activation (Donau Carbon GmbH, 2016). The activation is achieved by steam or chemical activation agents (at up to 1000 °C). Thereby the pore volume, in favour of the micropores, is increased which increases the BET surface area and therefore the adsorption performance of the char. Furthermore, the higher the pyrolysis temperature, the greater the specific surface area of the char and the better the adsorption capacity (Jindo, et al., 2014). Conventional AC is costly in production and most of the time produced from non-renewable material (Mohan, et al., 2014). In order to close material cycles and support local available resources, AC should no longer be produced from fossil materials.

Alternatives therefore might be biochar (BC) and activated biochar (ABC). Biochar (BC) is an adsorption medium which has been the subject of many studies and which could also be suitable for the elimination of micropollutants. ABC is produced from BC by chemical or physical activation and also showed promising results in several studies (chapter 2.5.2).

2.5.1 Biochar as alternative adsorbent in wastewater treatment

BC is a char that comes exclusively from renewable resources (including waste) and is produced via pyrolysis at temperatures of up to 700 °C. In some studies, BC shows very good adsorption properties due to its multifunctional structure, which are comparable to those of activated carbon (Jindo, et al., 2014) (Chen, Zhou, & Zhu, 2008) (Ahmad, et al., 2013). In addition to the known influence of the size and number of pores on the adsorption capacity of a char, the selective surface polarity effect (SSPE) also seems to have an influence. The SSPE can be attributed to functional groups which originate out of the biomass and are preserved during pyrolysis at comparatively low temperatures (250 °C to 400 °C) (Chen, Zhou, & Zhu, 2008). The functional groups of the original biomass thus have a decisive influence on the adsorption characteristics of the coal. Due to this multifunctional characteristic, BC has the potential to become an efficient adsorption medium.

Another major advantage of BC over conventional AC is that it is less sensitive to dissolved organic carbon (DOC) in wastewater due to its rather coarse-pored structure. Investigations have shown that a high DOC content can have a negative effect on the adsorption of MPs to AC, since free sorbent sites are blocked by organic compounds (background concentration) and thus the removal of the target substances is limited (Zwickenpflug, et al., 2010).

2.5.2 Chemically activated biochar as alternative adsorbent in wastewater treatment

Some studies report the increasing adsorption of BC by activation with a chemical agent such as $ZnCl_2$, K_2CO_3, KOH, H_3PO_4, etc. to ABC (Tay, Ucar, & Karagöz, 2008), (Angin, 2013), (Budi, et al., 2016), (Guo & Lua, 2003). Experiments with K_2CO_3 and KOH activated soybean oil cake pyrolysed at temperatures between 600 and 800 °C showed very good pore characteristics. The chars activated with K_2CO_3 exceeded those activated with KOH by exhibiting a lower ash content and a better pore distribution (Tay, Ucar, & Karagöz, 2008). Guo & Lua, (2003) figured out that the adsorption capacity may not only be determined by its pore characteristics, but also by its surface chemistry via chemisorption. One advantage of the chemical activation is that the pyrolysis temperature can be kept lower, compared to the physical activation with steam. This has the advantage that not only the porosity is increased but also the functional groups are partially preserved (Guo & Lua, 2003). Furthermore, the activation agents avoid the formation of tar and thus prevent the clogging of pores. In addition, the chemical activation agent has to be washed off the char after carbonisation which removes ash that is trapped in pores. Budi, et al., (2016) reported that high chemical concentration or excess reaction time, cause negative effects due to the physical collapse of the carbon structure.

Cherry stones are a material that is well suited for the chemical activation and production of activated biochar. Due to their natural pellet-like shape, granulated biochar fixed-bed filters for MP elimination can be produced from them (Arana & Mazzoco, 2010). Since cherry stones accumulate in large quantities as waste they can be used to improve recycling of natural resources.

2.5.3 Methylene blue adsorption as a method to determine adsorption properties

The adsorption of methylene blue (MB) by active carbon has been described in numerous studies since the procedure was first suggested in 1924. MB is widely used in industry as a dye and has a number of biological uses as well. In aqueous solution it dissociates like electrolytes into MB cation and the chloride ion. The dye-containing cation binds very well to solids (e.g. activated carbon). Therefore MB is used in many studies as a dye for adsorption experiments, whereas the UV absorbance of the aqueous MB solution is measured at its maximum peak before and after the experiment at a wavelength of 665 nm (Pathania, Sharma, & Singh, 2013). Correlating UV absorbance with the amount of AC allows the assessment of its adsorption performance. Thus, the MB adsorption method offers a relatively cheap and effective method to characterise adsorbents for aqueous solutions.

2.6 Conclusion

The increasing challenges in wastewater management and the lack of a legal basis for new wastewater treatment concepts require a paradigm shift. Decentralised wastewater treatment and reuse for irrigation of green spaces, parks and trees could be an option for future wastewater management in urban areas. This would allow nutrients to be returned to the natural cycle and protect water bodies at the same time.

Local water reuse requires a strict quality control of the treated wastewater that goes beyond the usual quality standards. So far, there are only a few quality standards that can be transferred directly to the local water reuse in cities. The following points show a proposal of how a DWWTS with irrigation purpose of treated wastewater in urban areas could be achieved, by combining existing technologies and know-how:

- Decentralised anaerobic-aerobic reactor technology for the decomposition of organic pollutants and the preservation of nutrients in wastewater.
- Elimination of MPs by ozonation or adsorption on AC. Currently only AC is used in WWTPs. Other adsorption media such as BC or chemically activated ABC would be a favourable option. Wastewater should have a COD of 15 mg/l for the efficient use of a MP elimination step.
- Adsorption potential of locally produced adsorbents (BC / ABC) could be estimated by using the methylene blue method.
- The efficiency of the elimination performance of an ozonation or adsorption step in DWWTS could be performed using the DETEC regulation or the SAC 254- method. A bioassay (planar-Yes) could be used to characterize the wastewater for endocrine disruptors.
- Quality standards for irrigation with wastewater come mainly from agricultural use and cannot be directly transferred to the local water reuse in cities. Here, a combination of different approaches seems to make sense. Appendix A contains a table inclosing the Swiss and Israeli wastewater regulations and a combination of the two which complement each other in essential aspects.

As mentioned in chapter 1, the very first Swiss DWWTP with water reuse in urban areas was currently established. Characterisation and technical information about the DWWTP are found in chapter 3. The following tests and analyses were carried out on this DWWTP to investigate the above mentioned points:

- Investigation of the cleaning effect of the anaerobic-aerobic reactor system (degradation COD, BOD)
- Investigation of the nutrient content in wastewater during and after the cleaning process

- Preparation of a BC from cherry stones and activation of the cherry stones to ABC using K_2CO_3 (different impregnation ratios)
- Test of adsorption properties of the produced chars by the methylene blue method
- Production of fixed bed filter elements for adsorption experiments of MP at the pilot plant
- characterize the wastewater for endocrine disruptors using the planar-Yes bioassay

3 Pilot plant “IWB Stöckacker Süd” in the city of Bern

3.1 Introduction

Autark Engineering AG is a company which has specialised in decentralised, reuse-oriented wastewater management for urban environment, using anaerobic biological treatment technology for wastewater purification. Based on successfully implemented projects in India, Papua New Guinea, Nepal and North Korea, Autark Engineering made its first project in Bern, Switzerland for a new housing project in the city. The proprietor, “Immobilien Stadt Bern” (ISB), part of Bern’s city administration, intended to establish an eco-friendly settlement based on the concept of the “2’000 Watt society”, developed in 1998 by the Federal Institute of Technology in Zurich (ETHZ). This concept set new standards in the fields of energy efficient technologies, renewable energy supply, clean mobility systems and sustainable lifestyle concepts. As a part of this endeavours ISB also implemented a pilot project in the field of decentralised wastewater treatment and reuse for one of the three building blocks of the settlement. Its purpose is to enable research and verification of the reuse-oriented urban wastewater management approach as well as to test the technology in a Central European context. The project consists of combined anaerobic-aerobic biological wastewater treatment with subsequent polishing steps for the elimination of micropollutants, which states a new technological approach not been implemented yet in any other settlement project in Switzerland. The project is called integrated use of water and biomass (IWB). This name is therefore adapted in this paper and mainly refers to the wastewater treatment system described in the experimental sector.

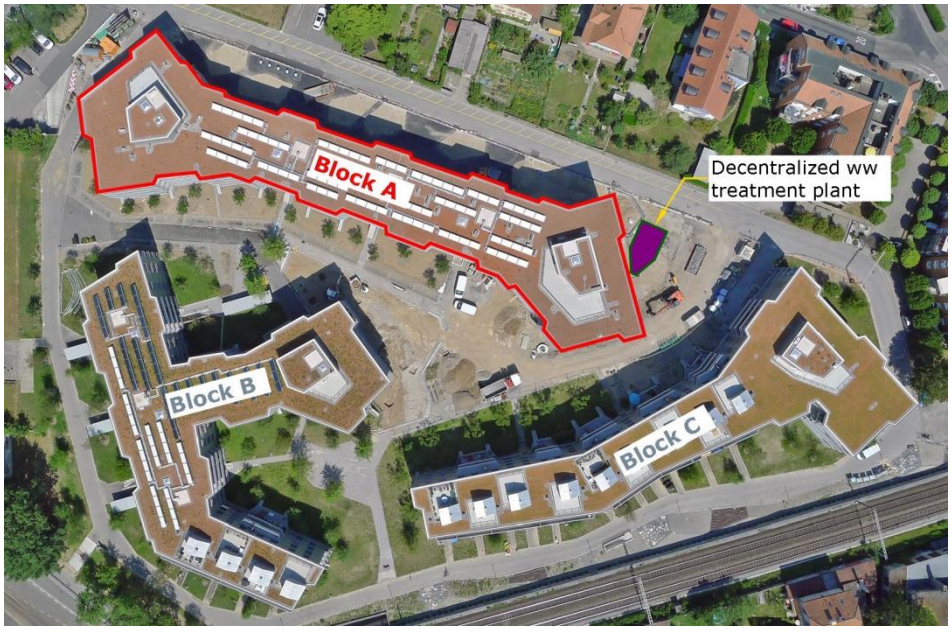


Figure 1: Overview settlement “Stöckacker Süd” in Bern, Switzerland. With building block A and the decentralized wastewater treatment system next to it. Picture. Vistadoc, (2017).

The IWB for block A is situated under a parking space next to the building and has a capacity Q=15 m^3 per day. It is designed to treat the entire wastewater (greywater and blackwater) from 50 apartments with 120 residents and one bistro situated in the building. The size of the apartments and the composition of the residents (singles, pensioners, families with small children, etc.) is highly diverse. The resulting wastewater composition is assumed to be representative for domestic wastewater.

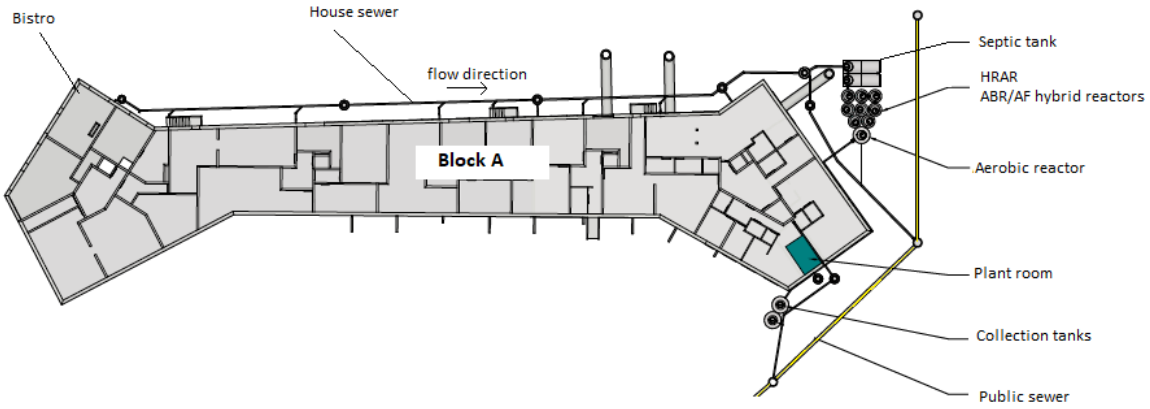


Figure 2: Overview building block A with sewer lines incl. location and connections, main components of the IWB. Picture provided by Autark Engineering AG, (2018), modified

3.2 Technical layout

The following sections describe the setup of IWB as it was at the last sampling of November 22, 2018. The IWB consists of the following modules:

- Two-chamber settler (septic tank)
- High rate anaerobic bioreactor, eight reactor compartments (suspended growth/ fixed-film)
- One aerobic bioreactor (suspended growth)
- Polishing modules: Pressure Sand Filter (PSF), Advanced Oxidation Process (AOP) consisting of Ozonation (O_3) and UV-treatment. Polishing modules, pumps and control unit are located in the plant room in the basement of building block A
- Collection tanks for treated wastewater which is ready for reuse

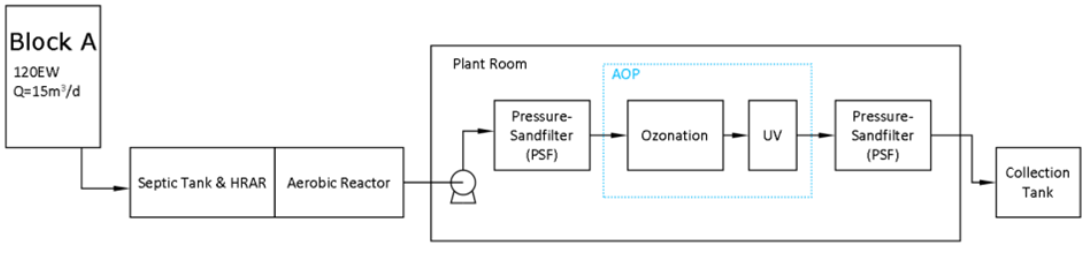


Figure 3: Overview technical layout and main components of IWB. Picture provided by Autark Engineering AG, (2018)

Settler, anaerobic reactors and aerobic reactor were built as underground structure next to building block A. The space above the reactors can be used as car parking with trafficability for up to 400kN (40t).

All reactor chambers are of round shape (Figure 4), as this favours the hydraulics in the tanks, thus minimizing hydraulic and biological dead space. To prevent temperature loss of the incoming wastewater by heat radiation, the entire underground structure is insulated with foam glass gravel. Every reactor compartment is separately accessible through a manhole with two cover slabs. The upper cover slab at ground level allows access to the reactor compartment shaft, the lower cover slab is sealed gastight and allows the access to the actual reactor chamber.

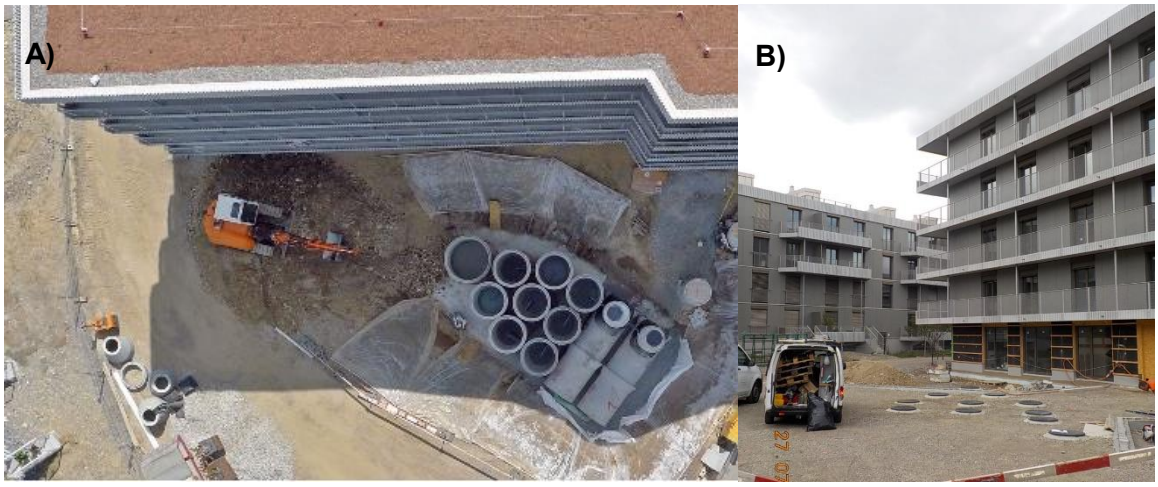


Figure 4: A), Top-view during construction work of the reactor (compartments P1-P11). B), partly finished construction work with installed cover slabs. Picture provided by Autark Engineering AG, (2018)

The combination of anaerobic (basic reduction of organic pollution) and aerobic biological treatment (biological post treatment) was chosen to minimize both energy demand and the requirement of operational control and plant maintenance. The removal of micropollutants and pathogenic organisms is envisaged with an advanced oxygen process (AOP) consisting of ozonation with subsequent UV-treatment (polishing step).

With this technical setup the IWB should be able to decompose the organic compounds (TSS, COD, BOD reduction) and remove micropollutants and pathogenic microbes and viruses. At the same time conserving nutrients like nitrogen and phosphorus makes the effluent water suitable for irrigational purposes.

Biogas produced by the anaerobic treatment process can be tapped through a separate gas pipe, and directed to the top of building block A. By this, the biogas can be used either as an energy source or for further research purposes. During this study the biogas was not used but released into the atmosphere. However, since methane, as a part of biogas, is a greenhouse

gas and its release should be prevented. A technical solution for its reduction before ventilation is envisaged.

The IWB can be bypassed in order to carry out maintenance work or in the event of a fault in the reactors. Then all the wastewater flows through the bypass into the regular sewer system.

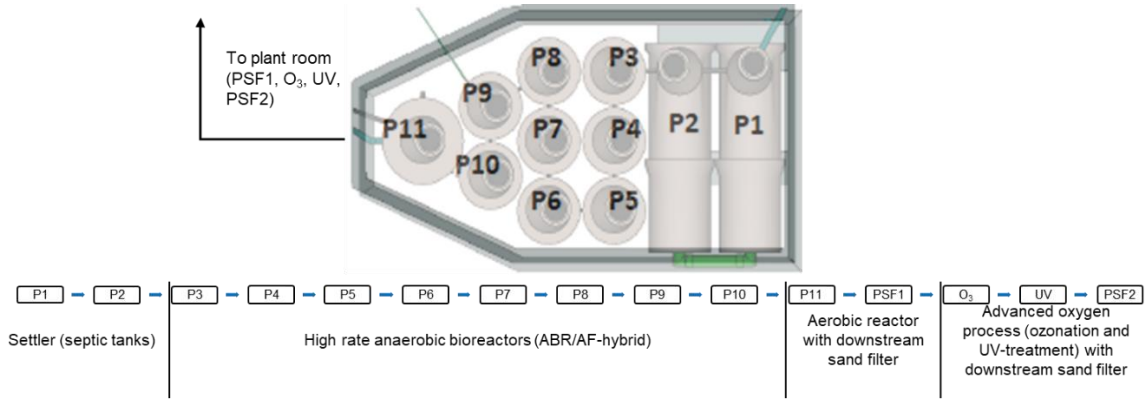


Figure 5: Insight into the arrangement of the reactor compartments and the flow scheme. Picture provided by Autark Engineering AG, (2018), modified.

3.2.1 Anaerobic reactor technology

The anaerobic biological wastewater treatment consists of two different rector technologies:

1. The septic tank is a so called low rate anaerobic reactor. The septic tank has the function to capture and hold back of all settable and floatable solids as well as for its physical and microbiological disintegration and decomposition to such an extent that the effluent consists of just very small particles, widely solved in the water. In the remaining course of the thesis the septic tank is referred to as the settlers P1 and P2 (Figure 5). The two settlers show a hydraulic retention time of 24 h.
2. A hybrid of an anaerobic baffled reactor (ABR) and an anaerobic filter (AF), which are high rate anaerobic reactors (HRAR). The ABR/AF-hybrid has the function to further decompose the organics in the wastewater and achieve a high TSS, COD and BOD reduction. As media for the biofilter, mesh bags filled with reticulated polyurethane-cubes are used. The ABR/AF-hybrid reactor consists of eight compartments P3-P10. Figure 6 shows a simplified scheme of an ABR/AF- hybrid reactor.

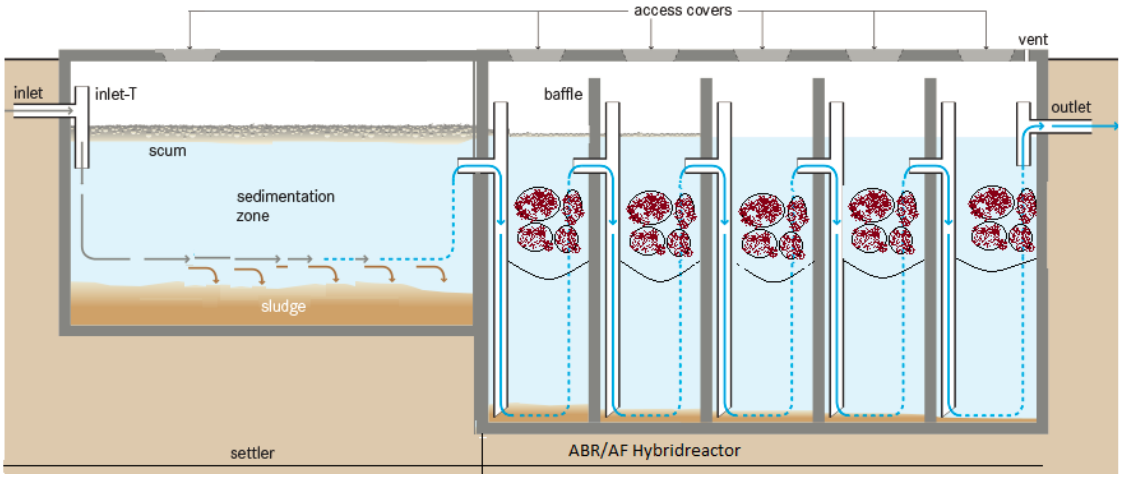


Figure 6: Sketch of the ABR/AF- hybrid reactor incl. mesh bags with filter elements and nets which prevent the sinking of the mesh bags (SSWM, 2018), modified

3.2.2 Aerobic reactor technology

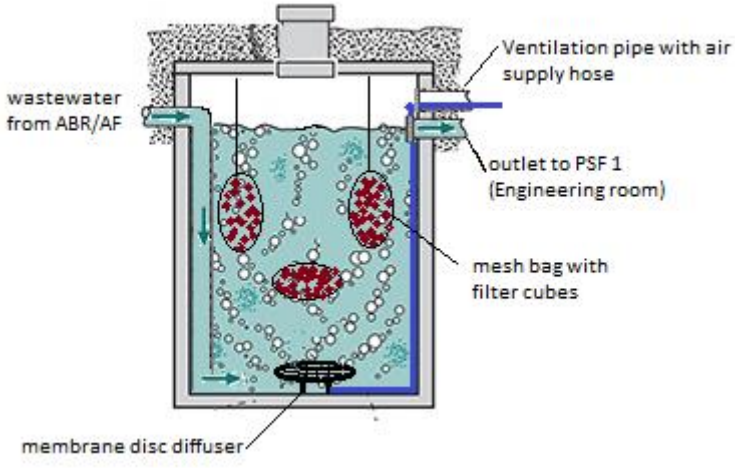


Figure 7: Sketch of the aerobic reactor incl. mesh bags with filter elements and nets which prevent (SSWM, 2018), modified

The aerobic reactor (P11) is designed as suspended growth reactor with extended aeration (Figure 7). It is connected directly after the ABR/AF- hybrid reactor. Fine bubble diffusers, situated at the bottom of the reactor tank, achieve the aeration of the wastewater. Membrane pumps installed in the plant room provide the air for the aeration. Water withdrawal for further treatment after the aerobic treatment is controlled by the signal of a level controller mounted in the tank.

The aerobic post treatment was implemented due to:

1. reduce hydrogen sulfide (H_2S) in the wastewater. H_2S is produced in the anaerobic process, it has a strong smell (rotten eggs), is poisonous in high concentrations for humans and animals and it is highly corrosive. It is therefore recommended to eliminate all H_2S.
2. reduce the BOD in the effluent to a level that it complies with the national discharge standard of BOD<20 mg/l.

3. decompose organic substances which can’t be degraded by the anaerobic biology like anionic surfactants (widely used in detergents and washing powders) and some long chain fatty acids.

3.3 Sand filter

Figure 8: Pressure sand filter (PSF) located in the plant room. Picture: Autark Engineering AG, (2018)

The pressure sand filters (PSF) are located in the plant room. They are filled with activated glass sand, which is negatively charged (zeta potential) to electro-statically attract organics and small particles. It also has permanent metal oxide catalysts, creating a high redox potential, to make the sand self-sterilizing, preventing channelling and biological fouling on the sand-surface. (Figure 5).

3.4 Advanced oxygen process

The advanced oxygen process (AOP) in the IWB combines the advantage of highly reactive ozone and the production of highly reactive hydroxyl radicals (•OH) by splitting the ozone molecules in the wastewater using ultra violet radiation (UV lamp). This allows a very efficient MP elimination of up to 90% (Abegglen & Siegrist, 2012a). In addition, UV radiation is capable to disinfect the wastewater by killing bacteria and viruses. A main benefit of O_3 compared to other chemicals is the very short half-live period of about 20 min (in water at 20 °C) (Lenntech, 2019). Another benefit of this is, that after the O_3 is decomposed no harmful chemicals are left behind from the process.

3.4.1 Ozonation

Ozone has a strong chemical reduction potential, capable to crack and eliminated various molecules. The ozone is produced on site. This is achieved by an oxygen concentrator which takes ambient air and produces an output with 85-99% oxygen purity. The concentrated oxygen gas flows through ozone cells, located in the ozone generator, producing ozone by the method of corona discharge. The ozone is then injected into the water stream.

3.4.2 Ultraviolet radiation (UV-unit)

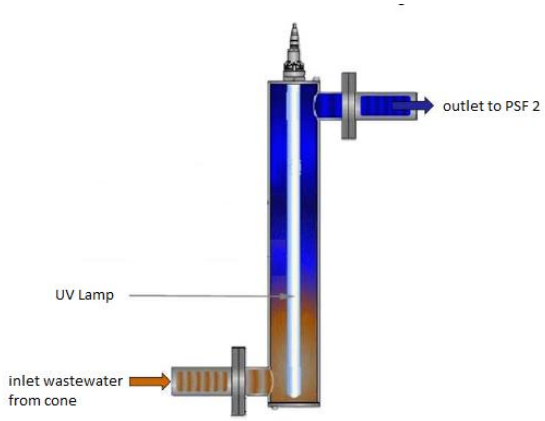


Figure 9: sketch UV-unit (LEVA, 2019), modified

The UV-unit consist of a longitudinal cylinder with an inlet and an outlet. In the centre of the cylinder the UV-lamp is installed. The wastewater flows around the UV-lamp where the high surface area of the lamp is needed for the energy transfer (UV radiation) to the water.

4 Material and methods

4.1 Wastewater analysis

Table 11 in Appendix B shows an overview on which date which parameter was measured. Oxygen and pH were measured onsite with a multi meter HQ 40d (Hach-Lange, Germany). Temperature was measured with an infrared thermometer 62Max+ (Fluke, USA).

4.1.1 Sampling

Wastewater grab samples of the anaerobic reactors P2, P10 and the aerobic reactor P11 were directly collected out of the tanks (Figure 10). The samples PSF, O_3 and AOP were taken from sampling taps in the plant room in the basement of the building (P11 and AOP were only used for analysis with planar-YES). The samples called PSF in the results, taken after pressure sand filter 1, refer to as sampling point for the aerobic section. The samples called AOP in the results, taken after pressure sand filter 2, refer to as sampling point for the complete AOP treatment.

Samples were filtered on site with syringes and 0.45 µm nylon syringe filters (BGB, USA) into 50 ml centrifuge tubes (Corning, USA). Sampling containers were filled up to the top to prevent gas exchange and cooled immediately by putting them in a polystyrene box with cooling elements, until they were put in the freezer (-20 °C) at the laboratory. Samples that were taken between Aug. 14, 2018 and Oct. 24, 2018 were analysed in the laboratory at ZHAW in Wädenswil. Samples that were taken at Nov. 11, 2018 and Nov. 22, 2018 were analysed in the laboratory at the WWTP Werdhölzli in Zürich. All samples were homogenised at 20000 rpm for 1 min with a disperser T25 digital ULTRA TURRAX (IKA, Germany).

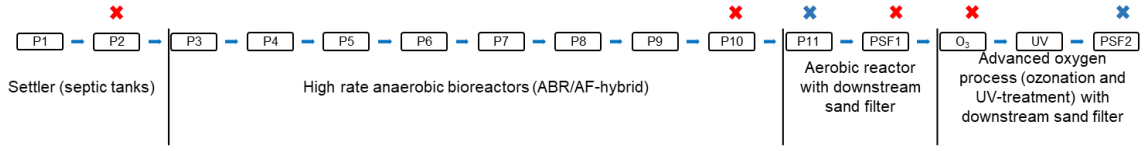


Figure 10: Overview grab samples taken for analysis. Red= samples for regular wastewater parameters and planar-YES, blue= samples taken for planar-Yes only

4.1.2 Hach-Lange vial tests

The wastewater parameters were measured with standard vial tests (Hach-Lange GmbH, Germany). Table 12 in Appendix B shows an overview about which test was used for which parameter. Dilution series were made to determine the correct measuring range.

The thermal decomposition of the samples for analysing the parameters COD, TN and TP were performed with a heating block LT 200 (Hach-Lange GmbH, Germany). The photometric

analysis at the laboratory at ZHAW was performed with a DR 3800 VIS Spectrophotometer (Hach Lange GmbH, Germany) and at the laboratory at WTTP Werdhölzli with a DR 6000 UV-VIS Spectrophotometer (Hach Lange GmbH, Germany).

4.1.3 Biochemical oxygen demand

The biochemical oxygen demand of a 5 day measurement period (BOD_5, here called BOD) was performed according to DIN 38 409 with the OxiTop system (Xylem Analytics Sales GmbH, Germany). Materials and chemicals used are listed in Table 13 (Appendix B). All samples were thawed in a water bath, tempered to 20°C, and then homogenized. Exact 150 ml of each sample was measured with a flask into brown glass WTW bottles. Afterwards the magnets, rubber sleeves and sodium hydroxide pellets were added. The bottles were then closed tight with the WTW measure heads. The sample bottles were then placed in the thermostat cabinet on a stirring platform and incubated at 20 °C for 5 days. All samples were performed in duplicates. Since the program chosen for the analysis was set for 164 ml sample volume, the results were calculated with the following formula:

$$BOD = \frac{MO_2}{R * T_m} * \left(\frac{V_{ges} - V_{fl}}{V_{fl}} + \alpha \frac{T_m}{T_0} \right) * \Delta pO_2 \qquad \text{F 3}$$

MO_2	Molecular weight (32 g mol-1)
R	Gas constant (83,144 l mbar mol-1 K-1)
T_0	Reference temperature (273.15 K)
T_m	measuring temperature
V_{ges}	Bottle volume (nominal volume in ml)
V_{fl}	Sample volume in ml
α	Bunsen absorption coefficient (0.03103)
$\Delta p(O_2)$	Difference of oxygen partial pressure (mbar)

In order to test whether the BOD measures were influenced by the degradation of the ammonium contained in the wastewater (nitrification), a single determination with inhibited samples from Nov. 22, 2018 was carried out. N-Allylthiourea (Fluka, Germany) was used as inhibitor in a concentration of 5 mg/l.

4.2 Planar-YES

The determination of the estrogenic active substances (EAS) in the wastewater was performed as described by Schoenborn, et al., (2017b), with some modifications concerning a) sample extraction and b) the spray-on procedure, (ZHAW, unpublished lab procedure). Some steps and processes of the procedure are confidential and therefore not described here in detail. Tables with materials used are found in the Appendix B

In total two screenings with wastewater samples from P2, P10, P11, PSF1, O3 and AOP were performed. The first screening was performed with samples taken on August 14, 2018. The second screening was performed with samples taken on November 22, 2018. Apart from the applied sample volume on the HPTLC plate, the two screenings were performed exactly the same. All samples were analysed in triplicates (each day on three HPTLC plates).

4.2.1 Sample preparation and extraction

The EAS were extracted from the unfiltered samples (40 ml each) by liquid-liquid extraction (LLE) with Methyl-tert-butylether (MTBE) and stored in dissolved ethanol in a freezer at -20 °C. The samples were thereby concentrated by a factor of 138.1.

4.2.2 Sample application and plate development

HPTLC Silica gel 60 plates 10 x 20 cm (Merck, Germany) were washed with methanol and then activated at 110 °C for 30 min. Afterwards the plates were photographed with the TLC Visualizer (CAMAG, Switzerland) under three different settings to check the plates for damages and impurities. The samples were then applied on separate tracks with the Automatic TLC Sampler ATS-4 (CAMAG, Switzerland) to the HPTLC plates at 10 mm, using a band width of 8 mm. Depending on the type of sample, 5 to 30 µl were applied. The three estrogens E1 (estrone), E2 (17β-estradiol) and EE2 (17α- ethinyl estradiol) were applied in different concentrations and serve as references on tracks 1-3 on all plates. After the application of the samples, the HPTLC plates were photographed again using the TLC Visualizer. The plates were then developed using the Automatic Development Chamber ADC 2 (CAMAG, Switzerland). An acetone-chloroform-petrol-ether-mixture with a ratio of 20:55:25 was used as the mobile phase. The final migration distance on the HPTLC-plate was 75 mm. The plates were then dried in a desiccator and afterwards photographed again with the Visualizer.

4.2.3 Yeast application and incubation

After the development a certain amount of McDonnel yeast suspension (growth, amount and calculation procedure are confidential) was sprayed on the plates using a Derivatizer (CAMAG, Switzerland). After yeast application, the HPTLC plates were put into plastic boxes and incubated with a closed lid for 3 h at 30 °C in an incubation chamber. The plates were then dried with a hair drier. A MUG solution dissolved in lacZ buffer was then sprayed on the dry HPTLC plates using the Derivatizer. Afterwards, the plates were put back into the plastic box and incubated again for 20 min at 37 °C. Finally the plates were dried and then photographed again using the TLC Visualizer.

4.2.4 Evaluation and quantification of the HPTLC plates

Using the image evaluation software VideoScan (CAMAG, Switzerland), the images created from each plate were then evaluated. From the fluorescence intensity of the E2 standards, a calibration line is determined which can be used to determine the estrogenic activity of the band as estrogen equivalent concentration (EEQ). The intensity of the fluorescence of a band corresponds to the area of the corresponding peak in the chromatogram. Using the E2 calibration line, the EEQ can now be calculated from the detected peak of the substance. The substance-specific Rf values (retention factors) of the standards allow to draw some conclusions about the substance composition of unknown samples.

4.3 Production of biochar and activated biochar

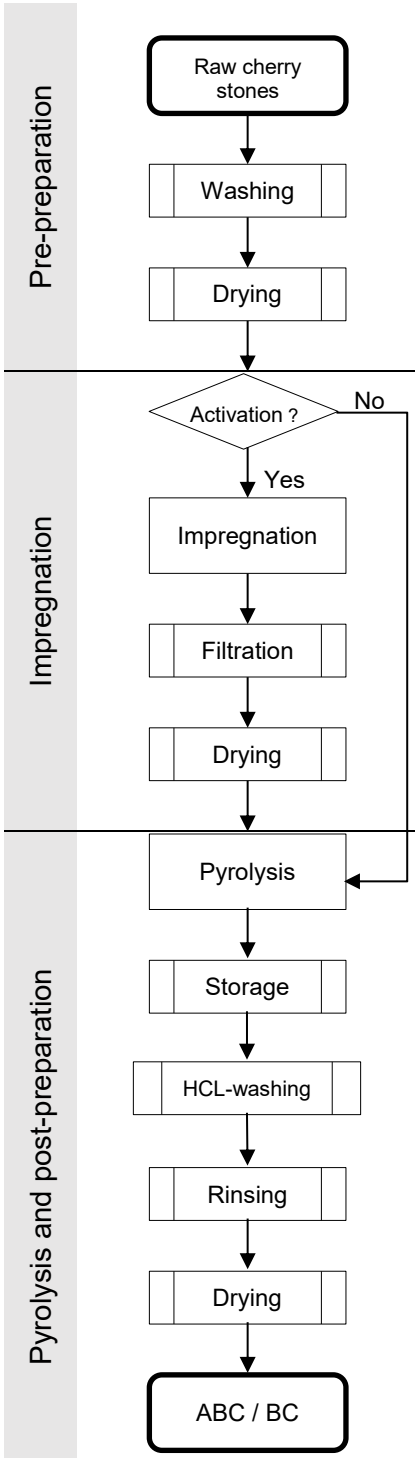
In the current experiments for this thesis, chemical activation of cherry stones was performed using potassium carbonate (K_2CO_3). The activation procedure was similar to those of Tay, Ucar, & Karagöz, (2008) and Angin, (2013) described in their papers.

Figure 11 shows an overview of the production procedure. The process was the same for all chars (except BC which was not activated with K_2CO_3). Only the amount of char produced for the preliminary and main experiments was different. The impregnation ratios by mass of raw cherry stones to K_2CO_3 were chosen 1:1/2, 1:1/4 and 1:1/8 for the small, preliminary experiment and 1:1/4 for the larger main experiments. Additional information is found in Table 16 (Appendix B)

The names of the samples were chosen by the type of char produced at the end of the procedure, the activation ratio and the state of the experiment. “ABC50_PE” for example stands for activated biochar (ABC) with activation ration of 50% (50) and preliminary experiments (PE).

In order to compare the results generated with the produced chars, a standard activated carbon cagesan (Koerner, Switzerland) was used (datasheet, Appendix D). This regular char was called AC in all experiments

The cherry stones for the experiments were purchases from DeinStoff, Switzerland.



To remove dust and dirt the raw cherry stones were washed two times in the double amount of ultrapure water GenPure (IKA, Germany) in Erlenmeyer flasks for one hour with a magnetic stirrer C-MAG HS7 (IKA, Germany). Afterwards the cherry stones were dried in a drying chamber FD 115 (Binder, Germany) at 105 °C for 24 h.

The impregnation for the activation process was carried out in Erlenmeyer flasks. The cherry stones, K_2CO_3 (Sigma-Aldrich, USA) and ultrapure water were added into the flasks and mixed on an orbital Mini Shaker (VWR, USA) at 500 rpm for 24 h at 20 °C to ensure a saturating reaction between K_2CO_3 and the cherry stones. The mixtures were then filtered and the soaked cherry stones were dried at 105 °C for 24 h. The cherry stones used for BC were not impregnated.

The pyrolysis of the cherry stones was performed with a Pyreka pyrolysis reactor (Pyreg GmbH, Germany) at ZHAW in Wädenswil under following conditions:

- Pyrolysis at 500 °C for 10 min
- Nitrogen flow 4 l/min

Leaching of K_2CO_3 and ash was achieved by washing the chars in Erlenmeyer flasks with a magnetic stirrer in the double amount of 1 N hydrochloric acid (HCl) solution for 24 h. Afterwards the chars were rinsed several times with warm distilled water until the pH stabilised. The pH was measured with a portable multi meter HQ40D (Hach-Lange, Germany). Finally the chars were dried at 105 °C for 24 h

Figure 11: Description of the production procedure for the biochar (BC) and the activated biochars (ABCs).

4.4 Characterisation of the chars

4.4.1 Proximate analysis

The proximates volatile solids, ash and fixed carbon were analysed as follows:

All samples were previously ground in a mixer mill MM 400 (Retsch, Germany) at 25 1/s for one minute.

Volatile solids and ash were determined in accordance to ASTM D1762-84 with a L3/C6 muffle furnace (Nabertherm, Germany). About 1.0 g of air dry and milled char was weighted into a porcelain crucible, covered with a lid and put into a drying chamber (105 °C, 2 h). Afterwards the samples were cooled in a desiccator and weighed to get the moisture content. The **moisture content** (%) is the ratio of the mass loss of the air dry sample **A** and the weight of the dried samples after cooling **B**.

$$Moisture[\%] = \left(\frac{A[g] - B[g]}{A[g]}\right) * 100 \qquad \text{F 4}$$

The dried samples were then placed in a furnace at 950 °C for six minutes. For cooling, the samples were placed in a desiccator to cool to room temperature. **Volatile solids content** (%) is the ratio of the mass loss from the dried sample **B** and the weight of the remaining samples after cooling **C.**

$$Volatile\ matter[\%] = \left(\frac{B[g] - C[g]}{B[g]}\right) * 100 \qquad \text{F 5}$$

Afterwards the samples were placed again in the muffle furnace at 750 °C without the lids. The samples were periodically cooled and weighed until weight stability was achieved. The **ash content** (%) is the ratio of the mass of the residues **D** and the initial dry matter **B**.

$$Ash[\%] = \left(\frac{D[g]}{B[g]}\right) * 100 \qquad \text{F 6}$$

The fixed carbon content was calculated according to ASTM 3172-07a:

$$Fixedcarbon[\%] = 100\% - (moisture[\%] + volatile\ matter[\%] + ash[\%]) \qquad \text{F 7}$$

The analysis of each char was carried out in triplicates. In addition to the chars (incl. AC), a sample of raw cherry stones was also analysed.

4.4.2 CHN-Analysis

Carbon (C), hydrogen (H) and nitrogen (N) of raw cherry stones, biochar, activated biochar and active carbon were analysed with a TruSpec Macro Analyser (Leco, Michigan USA) at laboratory in ZHAW Wädenswil. 0.1 g of a dry and ground sample was weighed and put in a tinfoil. All samples were analysed in triplicates. The results are expressed in percent (%) of the weighed dry matter of the sample.

4.5 Methylene blue adsorption experiments

To test the adsorption behaviour of the different chars (BC, ABCs and AC) adsorption experiments with methylene blue (MB) were made. The method for the adsorption experiments was similar to the method Pathania, Sharma, & Singh, (2013) used in their study. One difference was that the pH of the MB solution was not adjusted since the influence of the HCL or NaOH-solution to the adsorption behaviour of the different chars was unclear.

Prior to the adsorption experiments, a dilution series was prepared for calibration. Dilutions with 0.5, 1, 2.5, 5, 7.5, 10 and 15 mg/l of MB solutions for the calibration were prepared with ultrapure water. 100 µl of each MB solution was pipetted into a micro vial plate (in triplicates). Attenuation was measured at 665 nm using an infinite M200 pro UV-VIS spectro-photometer (TECAN, Switzerland). As blank, 10 samples of pure distilled water were used. The resulting calibration curve allowed to calculate the MB concentration in the adsorption experiments.

The adsorption experiments were conducted as batch experiments in a set of test tubes with a total volume of 10 ml containing the adsorbents and 5 ml of MB solution with a concentration of 5 mg/l. All experiments were performed in triplicates. The test tubes were agitated at room temperature in a rotator shaker RS-RR 5 (Phoenix Instruments, Germany) at 60 rpm for 1 hour. After shaking, the tubes were put in a test tube rack for 30 min to let the char settle. 2 ml of each sample (supernatant) were then pipetted into centrifuge tubes and centrifuged with a centrifuge 5430 (Eppendorf, Germany) at 14000 rpm for 10 min. By this it was ensured that no char particles were left in the MB solution. 100 µl of this MB solutions were then pipetted into a micro vial plate to measure the MB concentrations at 665 nm. In total four adsorption experiments were performed. The MB concentration of the test solution used for these experiments was always 5 mg/l, only the amount and type of char varied. All chars were used in pulverised form and therefore previously ground in a mixer mill MM 400 (Retsch, Germany) at 25 1/s for one minute.

- Preliminary adsorption experiment (PAE), 5 mg of each of the four chars (BC_PAE, ABC12.5_PAE, ABC25_PAE, ABC50_PAE
- Main adsorption experiment 1 (MAE1), 5 mg of each of the three chars (BC_MAE, ABC25_MAE, AC)

- Main adsorption experiment 2 (MAE2), 1 mg of each of the three chars (BC_MAE, ABC25_MAE, AC)
- Main adsorption experiment 3 (MAE3), 0.1 mg of each of the three chars (BC_MAE, ABC25_MAE, AC)

Data analysis was performed with the statistics program R. First the data was tested for normal distribution using the Shapiro-Wilk normality test. Afterwards a pairwise comparisons, using t tests with pooled SD and “holm” adjustment method was performed.

5 Results and discussion

5.1 General important findings at the sewage treatment plant

The anaerobic tanks (settler and ABR/AF-hybrid reactor) of the IWB were first filled and inoculated with filtered beef cattle manure-water mixture and then connected to the building on November 24, 2017 (Figure 12). Since microorganisms are growing slow under anaerobic conditions, the build-up of the anaerobic microflora was expected to take three to six months (N. Zimmermann, personal communication). A stepwise listing of findings and maintenance work carried out on the IWB (including adjustments made before the start of this thesis) is found in Table 17 (Appendix C)

At the beginning of June it was noticed, that the floating sludge in settler P1 became very thick and viscous. As a result, the methane gas produced in the settler accumulated under the scum and thereby disrupting the collection and removal of the biogas. The scum layer could also disturb the effluent of the settler and therefore the withdrawal of the wastewater. Therefore the scum had to be removed, for which a pump was used (June 26, 2018).

The pumping of the sludge turned out to be much more difficult as expected due to the thick and viscous consistency. A large amount of wet wipes and other inert material was found in the scum (Appendix E).

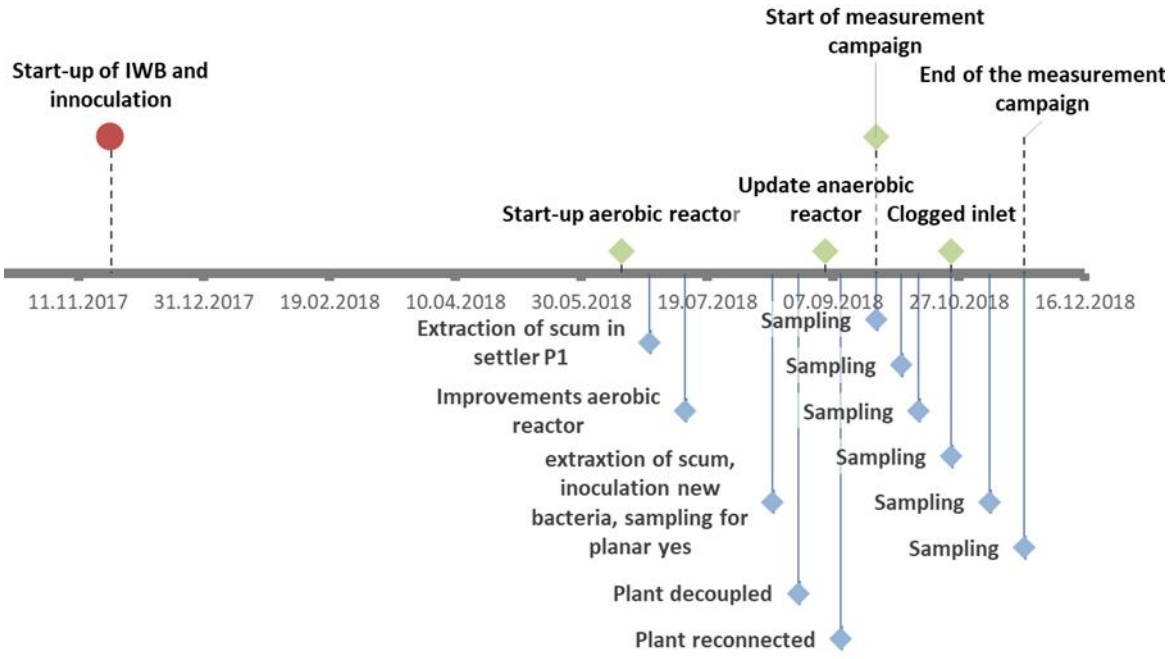


Figure 12: Timeline of the main findings and activities at the IWB since the start-up.

Since the IWB has no mechanical pre-treatment step, larger solids can enter the settler. Although the residents connected to the IWB had been informed in advance, to not dispose

foreign substances in the toilet, a lot of solid items were found. E.g., coffee capsules, candy packaging, condoms, Q-tips and a considerable amount of wet wipes (figures Appendix E).

It turned out that the wet wipes in particular posed a problem for the settler. The wet wipes floated at the boundary layer between wastewater and scum and prevented the degradation of the latter. A large part of the wet wipes also seemed to have bonded with the fat and other biomass and formed the tough scum.

At the beginning of August, Autark Engineering informed the residents again and drew their attention to the problem of unwanted solids with a focus on the wet wipes. Nevertheless, during later checks (Table 17), wet wipes were still found, however in smaller quantities (approx. four wet wipes were found in one litre of scum)

A strong smell of detergents could be detected in nearly all reactor compartments (during sampling on Aug. 14, 2018). In the aerobic reactor strong foam formation was observed, showing high detergent content in the wastewater (Figure 13).

Figure 13: Strong foam formation in the aerobic reactor on Aug. 14, 2018

Two grab samples taken in P2 and at the outlet of PSF1 on Aug. 14, 2018 (pH and COD) revealed, that the IWB had not yet achieved the required performance.

Table 4: Results of pH and COD of random grab samples of the anaerobic compartment (settler P2) and after the aerobic treatments (PSF)

	pH		COD [mg/l]	
	P2	PSF	P2	PSF
Actual value	7.71	8.34	$\bar{x}$ 609	$\bar{x}$ 178
Target value	6.5 – 7.5	6 - 8	-	~30

The results (Table 4) showed a slightly too high pH value for both the anaerobic and the aerobic biology. The COD after biological treatment (including sand filter) did not met the expected values.

Therefore, it was decided to improve the anaerobic biology by inoculation with new specific anaerobic bacteria (settlers) and make additional aeration installation in the aerobic reactor. Thus the IWB was disconnected on Aug 24, 2018, and the improvements were done on Sept. 3. + 4, 2018. After that, the IWB was reconnected on Sept. 10, 2018. Monitoring of the IWB was resumed on Sept. 24, 2018. The following results (chapter 5.2) refer to data collected with grab samples taken between Sept. 24, 2018 and Nov. 22, 2018.

On Oct. 24, 2018 it was found that the inlet into settler P1 had been blocked for an unknown time (max. two weeks, since the last sampling). The blockage was caused by the deposition of grease and solids in the sewer pipe, close to the settler's inlet. During this time the wastewater was automatically bypassed into the sewer system via the overflow. In the period the inlet was clogged, a thin sludge layer formed in settler P2, due to the hydraulic shut down of the system. During water sampling, some parts of the sludge got into the sample vessel. This sample was therefore removed from the dataset. But due to interesting outcomes found during analysis, the Oct. 24, 2018 is discussed separately.

5.2 Assessment of the treatment process

The results of the measurement campaign from Sep.24, 2018 to Nov.22, 2018 are shown in Figure 14 (excepting Oct. 24, 2018, due to the mentioned incident). All values are shown in Table 18 in Appendix C.

5.2.1 Temperature, pH and oxygen

The wastewater temperature was measured sporadically in the settler P2 and after the sand filter PSF in the plant room (Table 5). In general the temperature was found in quite good conditions for the requirements for an anaerobic biology (see chapter 2.2.2). The temperature was found to decrease slightly during the colder season, but showed still values > 20 °C.

Table 5: Temperature in the settler P2 and after pressure sand filter 1 PSF

Date	04.10.2018		11.10.2018		24.10.2018		08.11.2018		22.11.2018	
Location	P2	PSF	P2	PSF	P2	PSF	P2	PSF	P2	PSF
T °C	23.9	24.3	23.4	23.1	23.9	23.0	21.8	23.3	22.3	21.3

The measured values on the last day of the measurement campaign were remarkably good, as the outdoor temperatures in the city of Bern had previously been < 5°C for several days (Bernwetter, 2018) and the temperature in the settler was still above 22°C.

The average pH-value of the anaerobic biology (P10) during the observation period was close to a neutral value (Table 18 and Figure 14). According to literature, this is an optimal value for anaerobic microorganisms and for the efficient degradation of organic compounds by them (Anderson, Sallis, & Uyanik, 2003).The aeration in the post treatment (aerobic reactor, PSF1) led to a pH increase, which also represented an optimal range. This led to the conclusion, that the improvements and the inoculation with the new bacteria stabilised the pH on a good value.

As expected, practically no oxygen was measured in anaerobic biology. In the aerobic reactor (after sand filter) oxygen increased but not to the expected value (Table 6). After ozonation the O_2 was measured most of the time above the LOQ of the measurement device (22 mg/l O_2).

Table 6: Dissolved oxygen measured in the IWB

Date	P2	P10	PSF1	O3	AOP
04.10.2018	0.35	0.35	3.94	>22	>22
11.10.2018	0.09	0.1	5.13	>22	>22
24.10.2018	0.18	0.19	4.24	>22	16.79
08.11.2018	0.21	0.19	3.31	>22	20.48
22.11.2018	0.33	0.21	3.15	21.21	20.07
$\bar{x}$	0.23	0.21	3.95	-	-

5.2.2 Removal of organic matter

The removal of organic matter was assessed using the chemical oxygen demand (COD) and the biochemical oxygen demand (BOD) as sum parameters. The inhibition test showed that nitrification had no effect on the results (see chapter 4.1.3).

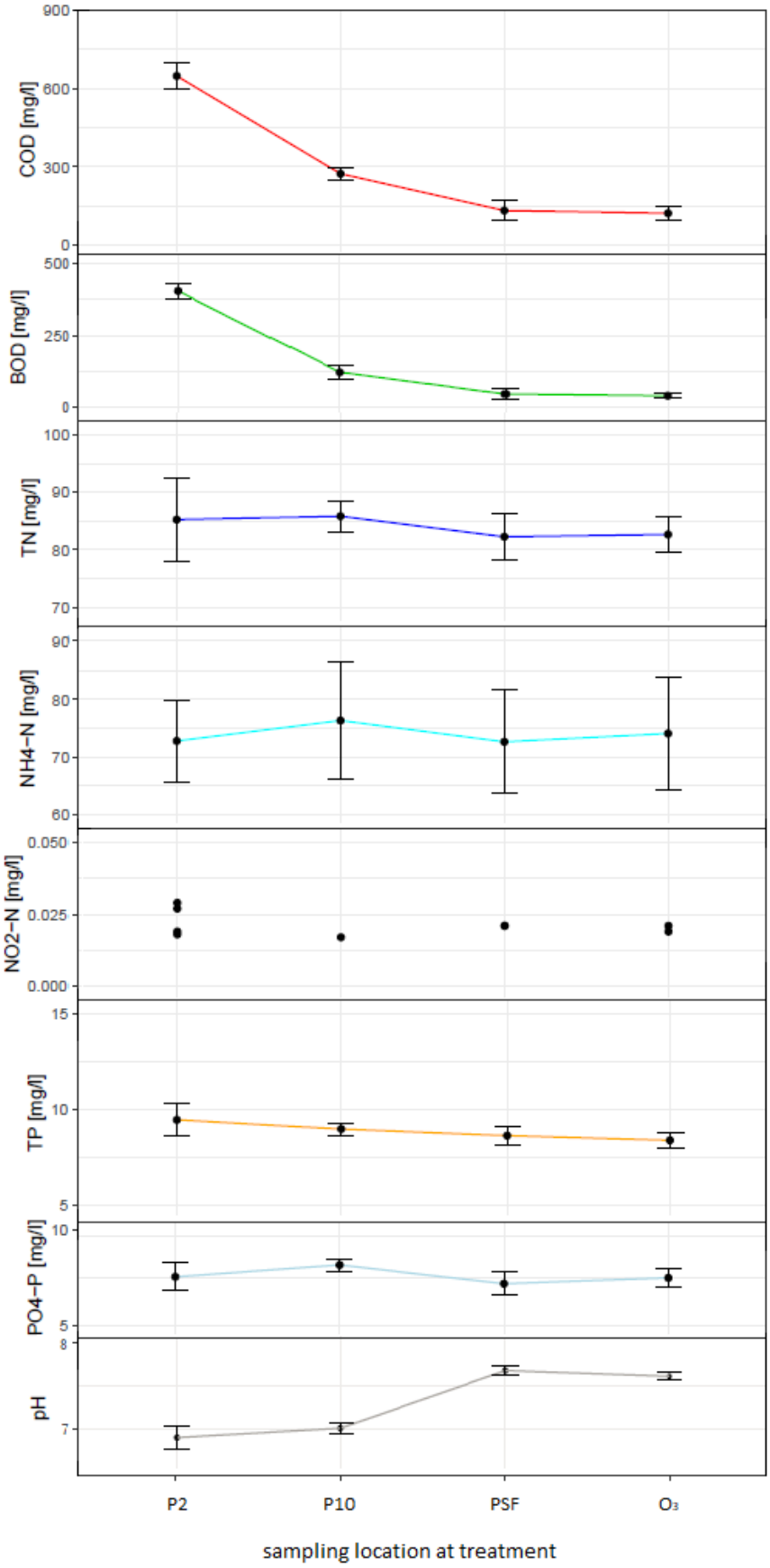


Figure 14: Overview wastewater parameters measured between Sep.24, 2018 to Nov.22, 2018. For further information see Table 18 (Appendix C)

COD

As seen from the overview Figure 14, COD was found to decrease from $\bar{x}$=647.7 mg/l in reactor compartment P2 to $\bar{x}$=121.7 mg/l after ozonation. The decline from P2 to P10 shows the removal in the anaerobic reactor which showed an efficiency of about 57.8%. Considering the entire biological purification process, incl. aerobic biology, a COD reduction of 79.6% was achieved. The complete treatment, including the polishing stage, achieved an average COD reduction of 81.2%.

Figure 15 shows that the COD in the settler P2 fluctuated stronger than in compartment P10 but both showed an overall decrease during the time period the IWB was monitored. COD was reported to increase from Nov. 08 to Nov. 22, 2018 after the aerobic biological treatment (incl. subsequent sand filtration, PSF) and O_3 by about 16%. A possible explanation is described in chapter 5.2.5

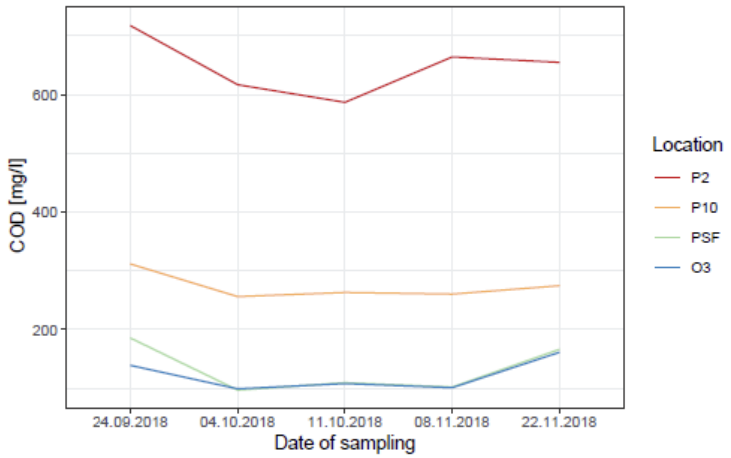


Figure 15: Behaviour of the COD at the four sampling points over the time period the IWB was monitored

BOD

As seen from the overview Figure 14, BOD and COD showed very similar curves. BOD was found to decrease from $\bar{x}$=407.8 mg/l in reactor compartment P2 to $\bar{x}$=38.3 mg/l after ozonation. The anaerobic reactor showed a BOD removal efficiency of about 70.3%. Considering the entire biological purification process (incl. aerobic biology), a BOD reduction of 88.8% was achieved. The complete treatment, including the polishing stage, achieved an average BOD reduction of over 90%.

Figure 16 shows that the BOD showed an overall decrease at all sampling points for the time period the IWB was monitored, except for O_3. Like for COD, an increase for BOD was reported from Nov. 08 to Nov. 22, 2018. Furthermore the BOD after O_3 was measured in higher concentration than after the aerobic treatment (PSF) (samples Oct. 4 and 11, 2018). According

to Takahashi, et al., (1994) and Kubra & Fatih, (2018) this could be explained by the increased biodegradability of organic compounds by ozonation.

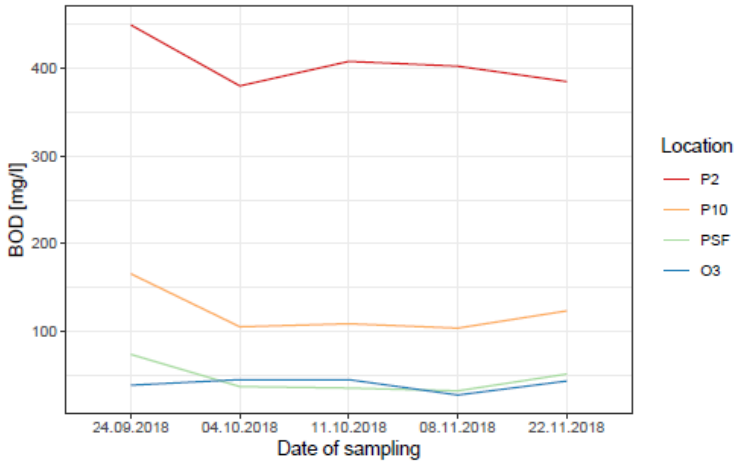


Figure 16: Behaviour of the BOD at the four sampling points over the time period the IWB was monitored

5.2.3 Nitrogen

Apart from total nitrogen TN, ammonium nitrogen NH_4-N and nitrite NO_2-N (only few values) were measured in the wastewater. Nitrate was not measured in any of the wastewater samples. As seen from the overview Figure 14 TN was measured $\bar{x}$=85 mg/l in the anaerobic compartments P2 and P10. Afterwards TN slightly decreased to about $\bar{x}$=82 mg/l but stayed constant during the aerobic post treatment and the ozonation step. NH_4-N influent and effluent concentration over the whole treatment seemed to be quite constant. Figures 14 and 17 show that nitrogen was predominantly present as NH_4-N. Furthermore the temporal course in Figure 17 shows that ammonium has increased during October from approx. 60 mg/l to approx. 80 mg/l. This indicates a better mineralization of the organic N (Fricke, et al., 2006).

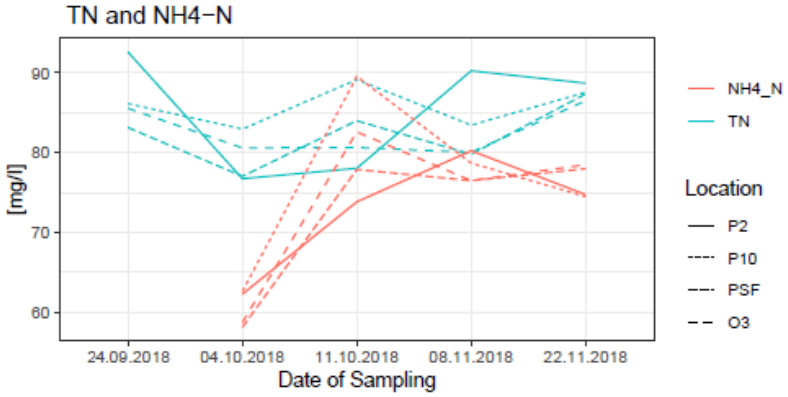


Figure 17: Temporal behaviour of TN and NH_4-N, values ($\bar{x}$ of duplicates) by the date and the location of sampling.

5.2.4 Phosphorous

Phosphorus was measured as total phosphor (TP) and orthophosphate (PO_4-P). TP was found to decrease by 11.3% in average over the treatment process (from $\bar{x}$=9.5 mg/l in P2 to $\bar{x}$=8.4 mg/l after ozonation, Figure 14). TP decrease was most likely to be caused by the growing of biofilms and accumulation of elemental phosphorous in the sludge bed (Keating, et al., 2016). Average PO_4-P increased during the anaerobic treatment from $\bar{x}$=7.56 mg/l in P2 to $\bar{x}$=8.18 mg/l in P10 and afterwards decreased during the aerobic treatment. However, PO_4-P influent and effluent concentration over the whole treatment seemed to be quite constant.

Incident of October 24, 2018

The clogging in the inlet to settler P1 led to a decrease of COD and BOD in reactor compartment P10, as it was never reached during the whole observation period. PSF and O_3 showed higher values for BOD than for COD. This can only be explained by the presence of nitrifies in the wastewater which influenced the oxygen demand during BOD measurement, since this samples were not inhibited with allylthiourea. This could be confirmed by the abrupt rise of the nitrite value found after the aerobic treatment in the sample PSF. This was therefore a very interesting finding, since this nitrite peak did not occur at any of the other days samples were taken. Furthermore, nitrate was still not measured which means, the samples were just taken at a time, nitrifying bacteria (e.g. *Nitrosomonas europaea*) started to develop in the aerobic tank, while nitrate bacteria (e.g. *Nitrobacter winogradskyi*) were still absent. Since it is not possible to say exactly how long the inflow was clogged, no more precise statements can be made about this results.

Table 7: mean values of the incident or October 24, 2018, n=2.
Green=nitrite peak

	P10	PSF	O_3
COD	158.5	75.55	87
BOD	59.65	99.05	92.7
TN	89.5	85.45	83.8
NH_4-N	76.05	71.85	75.6
NO_2-N	0.021	0.4215	0.08
TP	9	7.065	8.33
PO_4-P	9.675	7.19	7.685

5.2.5 Discussion of the treatment process

The wastewater temperature sowed always values > 20 °C and therefore met the minimum requirements mentioned as relevant (Van Lier, et al., 2010). Even when the outside temperatures were found to be below 5 °C the temperature remained stable. Autark Engineering thus disproved the often cited arguments that anaerobic wastewater treatment is not possible in Central Europe, due to the low wastewater temperature. Thus, it showed that through appropriate design and precise construction, the temperature in the wastewater can be kept consistently high. Furthermore, Autark Engineering supported the assumption made by SFOE, who estimated the average wastewater temperature in the house sewer to approx. 23 °C.

The adjustments and the inoculation with the new bacteria showed an improvement of the biological activity in the first settler compartment, visible by rising biogas bubbles at the inlet raiser of P1. Further it could be recognized that the scum newly formed had a better viscosity than before. Additional structural improvements in the aerobic reactor were done at Nov. 22, 2018, which was the final date of the wastewater sampling of this study. Therefore its effect on COD and BOD reduction could not be assessed.

The removal or organic matter showed in general good values compared to literature chapter 2.2.1. The effective numbers of COD and BOD after ozonation are still too high to meet the proposed values for unrestricted irrigation (see Appendix A). The relatively high BOD/COD ratio of the treated effluent after ozonation could therefore be indicative of the poorly biodegradable nature of the COD (Figure 18).

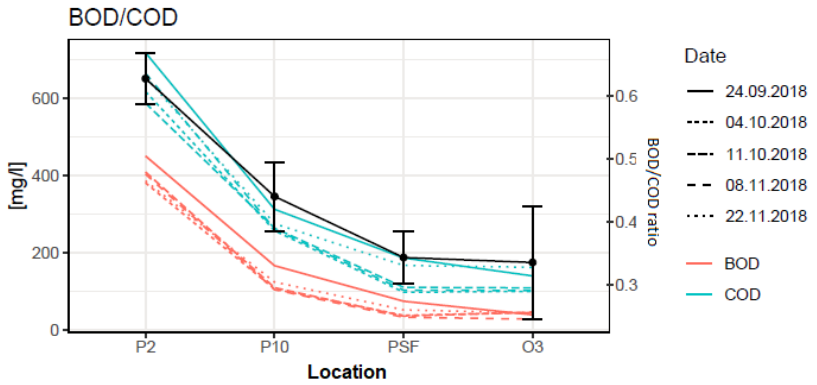


Figure 18: BOD/COD ratio. BOD values= red, COD values=blue, different line types show the date of sampling. Black line with error bars shows the BOD/COD ratio.

Furthermore, the high effluent values of COD $\bar{x}$=121.7 mg/l and BOD $\bar{x}$=38.3 mg/l lead to the assumption that the polishing step (ozonation and UV treatment) could not achieve a measurable elimination of MP, since the O_3 is consumed by the organic matter (Abegglen & Siegrist, 2012a).

Since temperature, pH, and oxygen were found in appropriate values, other factors must have influenced the degradation of the organic matter. A discussion with Autark Engineering led to the assumption that one or the combination of the following aspects could be critical for the IWBs biology:

- **Surfactants:** compared to wastewater in other countries, the wastewater composition in Switzerland seemed to have a much higher amount of cleaning agents (estimation according to experience of Autark Engineering). Several sources in literature confirm, that detergents inhibit the anaerobic biology. Especially surfactants (e.g. linear alkylbenzene sulfonates, LAS), which are found in numerous personal- and household-care products (shampoo, soap, laundry detergents etc.) showed to be able to harm the anaerobic biology at a concentration of already 2 ml/l (Mensah & Forster, 2003).
- **Shock loads of harmful substances:** They are reported to have a negative effect on the biology in WWTPs (Leitao, et al., 2006). At general plant inspections it could be observed that from time to time larger amounts of washing water entered in short time into the settler (laundry machine discharge), which clearly caused a shock of detergents to the biology of the reactor (Figure 19).

Figure 19: Shock load of washing water in settler P1 reported on Aug. 14, 2018. The shock like entry caused the water to flow over the scum and the water level rose rapidly, covering the entire surface in the settler.

- **Toxic substances:** Some detergents are sold as "antibacterial all-purpose cleaners" or “antibacterial toilet cleaners” and contain toxic substances such as KCl, glutaraldehyde etc. This substances are particularly toxic to aquatic organisms.
- **Long chain fatty acids LCFA:** LCFA (e.g. grease from kitchen waste) have been reported to be inhibitory at low concentrations for microorganisms in anaerobic sludge and anaerobic wastewater treatment (Rinzema, et al., 1994). Since the scum in settler P1 showed a sticky composition, which left a greasy layer on the tooling after the checks, it is assumed here, that LCFAs might have an inhibitory effect as well.

- **Hydraulic short-circuit:** Hydraulic short-circuiting between the ABR/AF-reactor chambers (P3-P10) could be observed at a general inspection of the plant at Nov. 21, 2018. During high wastewater inflow the water table in the reactor chambers rose up to the invert level of the ventilation pipes between the chambers, leading to a short-circuiting through the ventilation pipes. By this, it might had happened that a part of the wastewater flowed through the reactors without passing the activated sludge at the bottom of the reactors. It is unknown if this also happened during the sampling period and if so, how much the results were influenced by this short-circuits. Considering the results (chapter 5.2.2), a hydraulic short-circuit might be an explanation for the increase of COB and BOD from Nov. 08 to Nov. 22, 2018. Furthermore the hydraulic short-circuit might explain the inhibition of the whole treatment process, since the entire reactor biology was disturbed.

The composition of the wastewater is significantly influenced by the user behaviour of the residents. If one or several of the above mentioned aspects are met, countermeasures can be taken. This could include a further information campaign for the residents, proposing alternative products that are less harmful to the biology of the IWB.

As seen, most of the relevant nutrients in the wastewater are preserved during the treatment process. According to the suggested irrigation regulation (Appendix A) the nutrient content is in fact higher than recommended. Regarding to this, for irrigation purposes, the wastewater has therefore to be diluted either by fresh water or collected rain water.

There are some important parameters that have not been tested in this study (e.g. potassium, sulphate, heavy metals, chloride etc.). Biogas production and the determination of the bacterial strains in the compartments would provide further information about the condition of the reactor.

Also the presence of pathogenic germs after the treatment should be checked before the water is used for irrigation. In particular, if the water is stored for a longer period, there is a risk of recontamination with pathogens (Environment Protection Authority, 2002), (Al-Gheethi, et al., 2018).

5.3 Screening on estrogenic activity with planar-YES bioassay

The wastewater from IWB was screened on estrogenic activity with the planar-YES on two days, at the beginning and at the end of the measuring campaign of this thesis. Figure 20 shows the results of Aug. 14, 2018, Figure 21 the results of Nov. 22, 2018. Bright blue zones indicate estrogenic activity, while black zones indicate inhibition of the planar-YES bioassay.

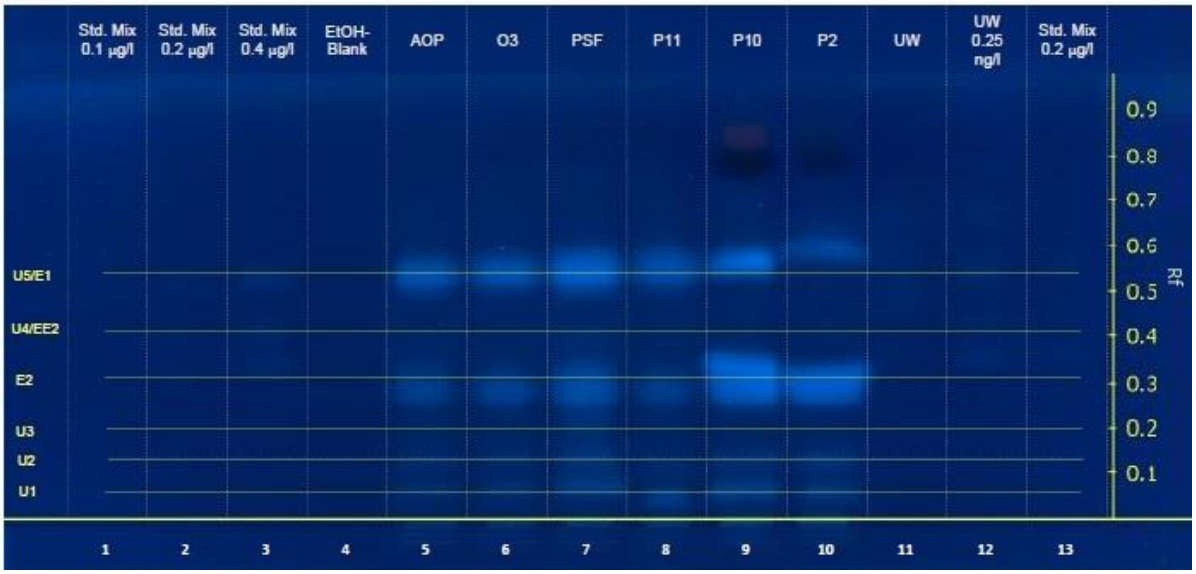


Figure 20: Planar-YES chromatogram of Aug. 14, 2018. Extracted wastewater samples from IWB and controls. Bright blue zones indicate estrogenic activity; black zones indicate inhibition of the planar-YES. UW = ultrapure water (procedural blank); UW 0.25 = ultrapure water spiked with 0.25 ng/l (procedural positive control). Std. = Mix of standard substances E2, EE2 and E1 in different concentrations; EtOH = solvent control of Ethanol; P2, P10, P11, PSF, O3, AOP: sampling points at IWB. Excitation wavelength: 366 nm, Exposure time: 0.549 s

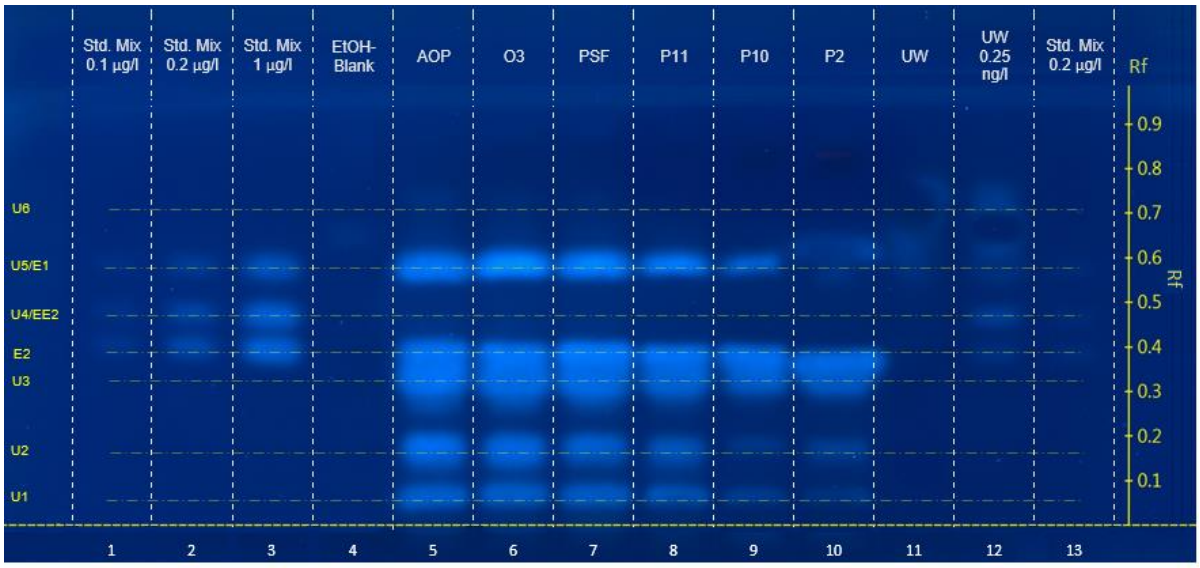


Figure 21: Planar-YES chromatogram Nov. 22, 2018. Extracted wastewater samples from IWB and controls. Bright blue zones indicate estrogenic activity; black zones indicate inhibition of the planar-YES. UW = ultrapure water (procedural blank); UW 0.25 = ultrapure water spiked with 0.25 ng/l (procedural positive control). Std. = Mix of standard substances E2, EE2 and E1 in different concentrations; EtOH = solvent control of Ethanol; P2, P10, P11, PSF, O3, AOP: sampling points at IWB. Excitation wavelength: 366 nm, Exposure time: 0.549 s.

Since the signals of the screening from Aug. 14, 2018 were very close together the application volume of all IWB samples for the screening from Nov. 22, 2018 was reduced by 50%. Thus a

better separation of the signals within the bands was achieved. In addition, the standard mix 0.1 µg/l was replaced by a higher standard mix (1 µg/l). Furthermore, the samples of P2, P10 and P11 (Nov. 22, 2018) were difficult to extract (during LLE) due to strong foam formation in the MTBE. Therefore only 12 ml could be extracted instead of 14 ml. For this samples a concentration factor of 126.1 was achieved instead of 138.1. This was then taken into account in the calculations for those samples.

In general, in a first step, it was controlled whether some of the bright blue zones might be caused by autofluorescence – a feature known from many organic chemicals. Figure 22 shows that this was not the case.

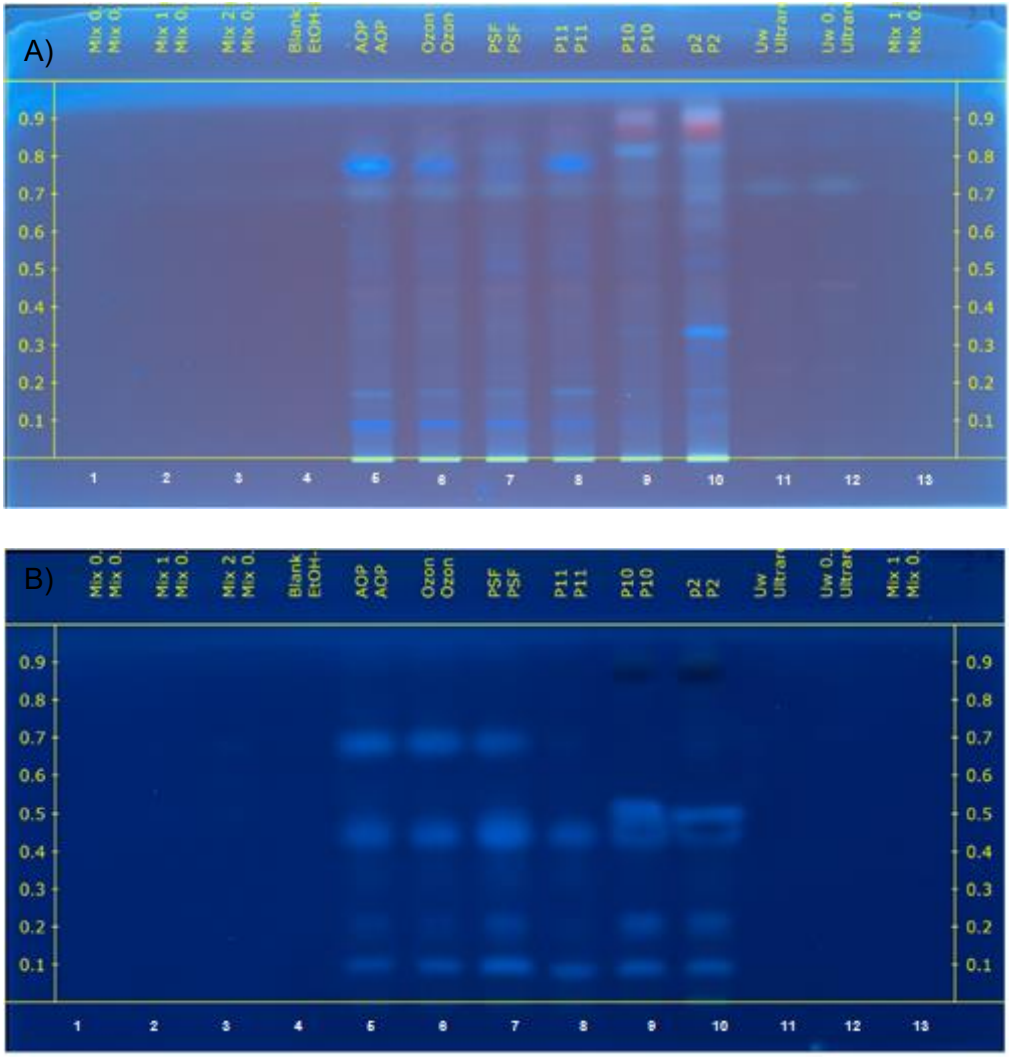


Figure 22: planar-YES chromatograms of plate one (Aug. 14, 2018), showing extracted wastewater samples from IWB and controls. A) after development, B) after planar-YES bioassay. A) shows autofluorescent zone. B) shows zones with estrogenic activity. UW = ultrapure water (procedural blank); UW 0.25 = ultrapure water spiked with 0.25 ng/l (procedural positive control). S = Mix of standard substances E2, EE2 and E1 in different concentrations; EtOH = solvent control of Ethanol; P2, P10, P11, PSF, O3, AOP: sampling points at IWB. Excitation wavelength: 366 nm, Exposure time: 0.549 s (both pictures)

The two black spots towards the end of the solvent front (Figure 22 B), tracks 9+10) correspond to the red zones in Figure 22 A) and indicate a substance that interferes with the bioassay test system.

Furthermore, the signals E1 am E2 from the samples P2 and P10 (tracks 9+10) seem to be diverging (here called “drift”) away from each other, which did not occur in the other samples (tracks 5-8) (see Figure 20 and Figure 21). Although E1 and E2 are over (respectively below for E2) the corresponding Rf values, they were counted as those. The “drift”-effect could indicate a substance that was extracted during the LLE which was inhibiting or toxic to the yeast cells.

All samples taken from IWB (tracks 5-10) show a number of zones with estrogenic activity on both dates. A total of 6-10 unknown activity zones were found on Aug. 14 and Nov. 22, 2018. The delta Rf values of both runs, normalised to E2 (Rf_{E2} = 0) are shown in Figure 23. The estrogen standards E2, EE2 and E1 of both runs had almost exactly the same delta-Rf values. However, the delta-Rf values of the wastewater samples indicate between 6 and 10 unknown zones with estrogenic activity. The dataset of Aug. 14 was too small for statistical analysis, because one of the three plates was unanalysable. The dataset of Nov. 22 provided three data points for each Rf value, which allowed the calculation of a standard deviation.

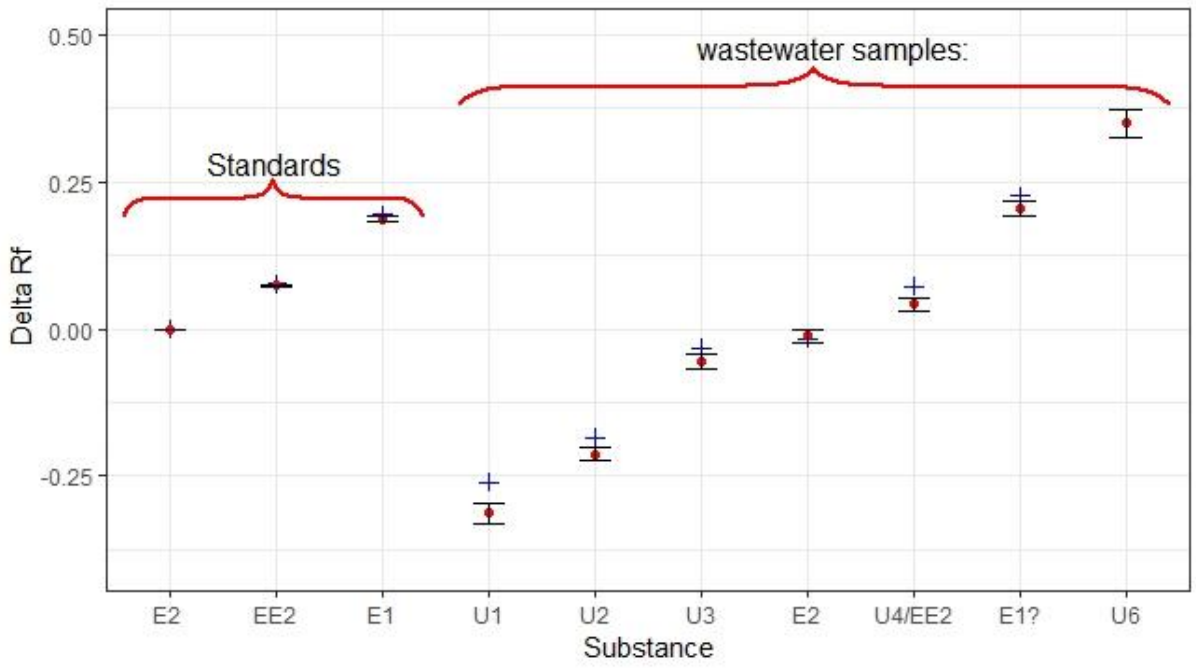


Figure 23: Delta-Rf values of estrogenically active zones on Aug. 14, 2018 (blue cross) and Nov. 22, 2018 (red dot, error bars indicate standard deviation

Table 8 and Table 9 show the delta-Rf values and the calculated EEQ (ng/l) values in the wastewater samples of Aug. 14 and Nov. 22. Four unknown zones were identified on Aug. 14: U1-3 and U5. In the wastewater samples of Nov. 2, five unknown zones were identified (U1-U4, U6). Figure 24 A and B show the cumulative EEQ concentrations (in ng/l) on both sampling dates.

Table 8: Estrogenic activity in IWB on August 14, 2018. Single peak activity and total activity, expressed in nanogram estrogen equivalents EEQ per liter. NC = not calculable

Applied sample	**Delta Rf-value**	**P2**	**P10**	**P11**	**PSF**	**O3**	**AOP**	**% removal**
Applied volume [µl]		10	10	20	30	30	30	
E2	-0.016	10.8	17.4	-	2.1	0.8	0.9	91.7%
EE2	0.077	-	-	0.5	0.6	0.3	0.3	NC
E1	0.194	7.7	16.3	7.7	7.6	4.6	4.5	41.6%
Unknown substance 1a	-0.260	2.9	2.9	1.6	1.2	0.7	0.6	79.3%
Unknown substance 2a	-0.184	3.6	2.4	0.6	1.2	0.6	0.6	83.3%
Unknown substance 3	-0.033	13.2	15.6	3.8	0.8	2.1	1.9	85.6%
Unknown substance 5	0.226	-	-	-	3.22	-	-	NC
Σ estrogenic activity		38.3	54.5	14.1	16.8	9.1	8.8	77%

Table 9: Estrogenic activity in IWB on Nov. 22, 2018. Single peak activity and total activity, expressed in nanogram estrogen equivalents EEQ per liter. NC = not calculable

Applied sample	**Delta Rf-value**	**P2**	**P10**	**P11**	**PSF**	**O3**	**AOP**	**% removal**
Applied volume [µl]		5	5	10	15	15	15	
E2	0	13.6	15.8	7.1	5.2	4.4	3.8	72.0
E1	0.187	6.3	8.5	7.8	4.9	5.9	4.3	31.9
Unknown substance 1b	-0.313	1.8	2.2	2.7	2.0	2.1	2.1	-16.7
Unknown substance 2b	-0.213	4.6	2.8	4.4	3.4	3.7	3.8	17.4
Unknown substance 3	-0.054	8.6	9.9	7.1	4.8	4.6	5.0	41.9%
Unknown substance 4	0.042	-	-	-	0.4	0.5	0.4	NC
Unknown substance 6	0.350	-	-	-	0.6	0.3	0.4	NC
Σ estrogenic activity EEQ [ng/l]		34.9	39.2	29.1	21.3	21.5	19.8	43.3

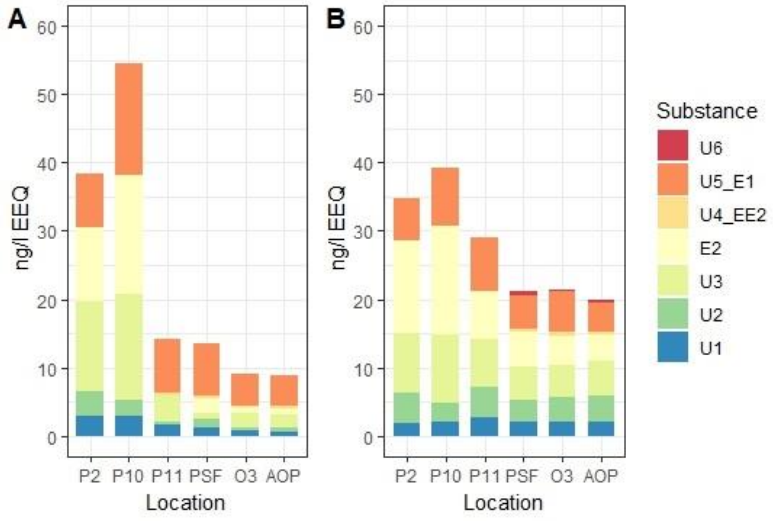


Figure 24: Cumulative estrogenic activity in IWB on a) August 14, 2018, and b) Nov. 22, 2018. U = unknown substance. E2 = 17-beta-estradiol; EE2 = 17-alpha-ethinylestradiol; E1 = estrone

On Aug. 14, the anaerobic part of the samples (P2 and P10) showed a different pattern of estrogenic activity than the aerobic sample P11+PSF and the samples from the polishing stages (O_3, AOP). On Nov. 22, the pattern of estrogenic activity in the anaerobic part was much more similar in the aerobic parts (P11+PSF) (Figure 24).

The **natural estrogen E2** was found in the settler (P2). E2 was degraded in IWB by 91.7% (Aug. 14) and 72% (Nov. 22) between P2 and AOP. The aerobic reactor P11 showed no signal for E2 (Aug. 14) but after the pressure sand filter, the O_3-unit and the AOP-stage, the signal for E2 was detected again. On Nov. 22, E2 was found in all compartments of IWB.

E1-activity was created in the anaerobic treatment process on Aug. 14 (maximum activity 16.3 ng/l EEQ in P10) and removed in the aerobic steps. On Nov. 22, E1 was detected in all samples and remained stable throughout all compartments.

If the **unknowns U1-U3** were really the same substances at both dates, they were removed substantially from the wastewater on Aug. 14. On Nov. 22, their removal took place to a much lesser extent. However, the delta Rf-values (Figure 23) suggest that this might not be the case. According to Schoenborn et al. (2017), the substance U3 may be bisphenol A. The signal of the **unknown U6** appeared in the PSF step and was reduced in the O_3 an AOP steps.

The **oral contraceptive EE2** should be expected in wastewater, but was not detected in the anaerobic reactor compartments. The complete absence of EE2 in domestic wastewater would however be a surprise. In the aerobic reactor and the polishing stage a signal at the Rf-value of EE2 was measured, but in low intensity. It seems highly unlikely that EE2 was formed during the purification process. It is more likely that either an EAS with similar Rf-value was leached from one of the materials in the reactor, or a substance deconjugated under unknown conditions. Therefore, the respective signal is labelled as “U4/EE2?” in Figure 24. A confirmation for this assumption was not found.

The **total Σ EEQ** increased between P2 and P10 on both sampling dates. This accumulation may be explained by the deconjugation of inactive hormones (E1 and E2) into their active form. According to Panter, et al., (1999) the initial transformation of the inactive E2 -conjugates to an estrogenically active product occurs more rapidly than the degradative loss. D'Ascenzo, et al., (2002) reported the deconjugation of estrogens by E.coli bacteria under anaerobic conditions, which meets the assumption stated above. Furthermore E2 showed to be more persistent under anaerobic conditions which may also explain the observed increase from P2 to P10 (Jürgens, et al., 2001).

The decrease in P11 could be explained by biodegradation under aerobic conditions. This might have happened in the following two steps:

- First, E2 was oxidised (degraded) into E1. This has been reported by (Joss, et al., 2004) during aerobic batch experiments of a diluted slurry of activated sludge from a sewage treatment plant.
- Second, E1 mineralised by cleavage of one of its ring structures. Jürgens, et al., (2001), who performed experiments of the biodegradation of hormones in river water and sediments, confirmed both of this steps.

5.3.1 Discussion of estrogenic activity

The HPTLC plates of the two sampling dates showed the same basic pattern with a few unknown substances and the “drifting” hormones E1 and E2, most likely caused through a unknown toxic substance. With a few exceptions, the individual measured values as well as the total concentrations at the two sampling days varied.

Generally the effluent concentrations after AOP (Σ estrogenic activity EEQ [ng/l]) showed higher values on Nov. 22. Since the COD concentration was above the recommended values 15 mg/l, ozonation and UV-treatment were not yet able to eliminate the EAS to the required level.

On both sampling dates, the aerobic treatment (P11) was able to remove the most estrogenic activity. On Aug.14, the aerobic step was much more efficient (74% removal) compared to Nov. 22 (25.9% removal). Since the aerobic reactor was updated with mesh bag-filter-elements (Oct. 24, 2018) and inoculated with a new bacterial culture, one of these changes may have had some negative effects of the decomposition of EAS. On the one hand, this could be the new bacterial culture, which may have degraded the EAS less efficiently. On the other hand, the installation of the filter elements might have disturbed the entire biology and it has not yet regenerated.

The deconjugation of the estrogens under anaerobic conditions, might be an explanation for the increase of E2 found in the anaerobic reactor on both dates. E1 did not increase as much on Nov. 22 as it increased on Aug. 14. Maybe the new inoculated bacteria culture inhibited the deconjugation of E1. The biodegradation of E2 to E1 and the mineralisation of E1 also might be an explanation for their decrease. Although E1 did not decrease as much on Nov. 22 as it decreased on Aug. 14. This could also point to the disturbed, not yet regenerated aerobic biology. In order to confirm these theoretic approaches, more precise analyses would have to be performed by HPLC-MS/MS like D'Ascenzo, et al., (2002) discibed in their study.

The IWB process chain as a whole removed 77% of the total estrogenic activity on Aug.14, but only 43.3% on Nov. 22. Neither ozonation, nor AOP seemed to have a large impact on the removal of EEQ. The cumulative Σ EEQ effluent values of 8.8 ng/l EEQ (Aug. 14) and 19.8 ng/l

EEQ (Nov. 22) are at least 22 times higher than the threshold value of 0.4 ng/l recommended for E2 by the oekotoxzentrum, (2016). The dynamic of sorption, desorption, release, formation and degradation of estrogen active substances in IWB is not understood. The treated wastewater of IWB thus contained a significant amount of estrogen active substances in the outflow and cannot considered to be safe for water reuse.

5.4 Potential role of biochar and activated biochar

Authors note:

Since the wastewater did not meet the stated COD values, the fixed-bed filters with the GAC made from pyrolysed cherry stones could not be used for onsite experiments. Instead, batch adsorption experiments with powdered chars and methylene blue were performed, in the laboratory at ZHAW, as main experiments. The experiments were performed the same way like the preliminary adsorption experiments, but with different amount of chars.

5.4.1 Production of biochar and activated biochar for the preliminary adsorption experiment

The four chars produced for the preliminary adsorption experiment (PAE) showed a strong contamination of foreign material. The foreign material consisted mainly of sand and plant fibres. Also some rice husks could be located. Investigations have shown, that the reactor was used bevor to carbonise a larger amount of horse manure. This material must have got caught in the reactor, so that the screw conveyor in the reactor drive could not transport the material out of the reactor properly. To avoid further problems with foreign materials in the production of chars for the main experiments the reactor was disassembled, cleaned and “flushed” with about 1 kg of wood pellets at 500 °C. The screw conveyor was driven with a very low feed rate to ensure a complete cleaning of the reactor screw conveyor. After this procedure no foreign material could be detected at the end of the pyrolysis process.

Due to the foreign material in the four samples, no exact statement about the weight of the samples before/after the pyrolysis could be made. The results (Table 19 Appendix C) are therefore only approximate values and not representative. It was nevertheless continued with these samples since the effort to produce the chars was very high.

An interesting finding which was not expected was that the char yield increased the higher the impregnation ratio was. This was also reported by Ucar, et al., (2009) and explained with the effect of the chemical activation. Thereby the chemical agent first degrades the cellulosic material and during carbonisation the biomass dehydrates. This results in charring and aromatization of the carbon skeleton and creating the pore structure with less material loss.

The impregnation with K_2CO_3 has led to an obvious visual change (after pyrolysis) of the surface of the chars. The higher the impregnation ratio the stronger was the change of the surface structure of the chars. As seen from Figure 25 some cherry stones from the sample ABC50_PAE showed a coral-like structure, which was quite unstable and could easily be crushed with little effort. Some of the cherry stones looked like they've bursted open and some cherry stones were bigger than before carbonisation. They also had a shimmering metallic, blue and green tint. The cherry stones from sample ABC25_PAE showed a similar structure with shimmering colours but the structure was much more stable compared to ABC50_PAE. The carbonised sample ABC12.5_PAE showed the least change in the surface structure of the three impregnated samples but the shimmering colours were also present like in the other samples. The biochar sample BC_PAE showed no obvious change in surface structure. Also the shimmering colours were absent. The carbonised cherry stones from the BC_PAE sample were very stable, showed no deformation and did not increase in size.

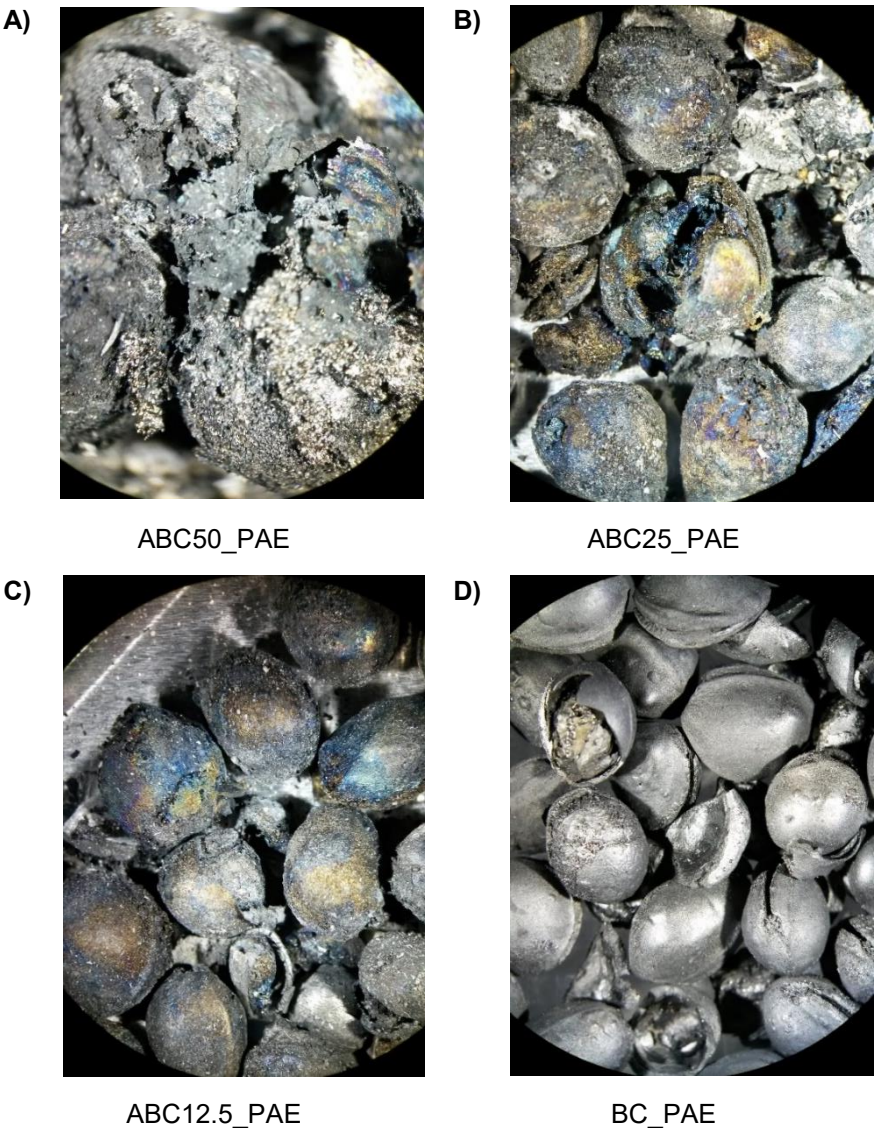


Figure 25: ABC and BC produced for the preliminary adsorption experiment. Pyrolysis temperature 500 °C holding time 10 min. ABC activated with K_2CO_3 A) ABC50, B) ABC_25, C) ABC12.5, D) BC

Proximate analysis

Due to the contamination of the samples with foreign material the proximate analysis was performed after washing the chars with HCl and distilled water. Figure 26 (and Table 20, Appendix C) show the mean values and the standard deviation in percent of the four chars for the PEA and the raw cherry stones. The results show that the moisture content of all samples ranged between 3.5% and 5.7%. Among the four chars the ABC25 showed with about 17.86% the lowest amount of volatiles while the BC showed with 23.59% the highest amount of volatiles. The raw stones showed about 78.21% of volatiles which met the results from other studies (Petrov, et al., 1999). Fixed carbon was measured highest for ABC25 (72.84%) followed by ABC12.5 (75.14%), and ABC50 (72.84%). BC showed the lowest fixed carbon content (69.87%). Ash varied between 1.19% and 1.62% for the four chars while the raw stones showed 1.17% of ash in average.

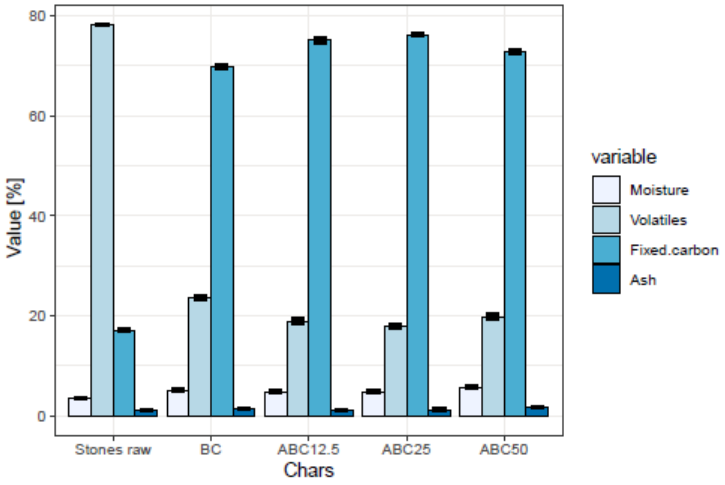


Figure 26: Results proximate analysis of raw cherry stones and chars for the preliminary adsorption experiment. The moisture refers to air dry samples. Moisture, Volatiles, fixed carbon and ash add up to 100%. Error bars show the SD.

CHN Analysis

Total carbon (Ctot) of the raw biomass showed a mean value of 53.30% (Figure 27 and Table 21, Appendix C). This value is similar to those Gonzàles, et al., (2002) reported for their analysis of cherry stones. Ctot of the four chars was measured highest for ABC25 (77.30%) followed by ABC12.5 (75.83%), and ABC50 (75.07%). BC showed the lowest fixed carbon content (52.75%). This contradicts with the results Angin, (2013) reported in her study (activated carbon from sour cherry stones by zinc chloride), where the carbon content increased in correlation with the impregnation ratio. However, it must be mentioned that Angin's impregnation agent was different ($ZnCl_2$). Also the impregnation ratio ranged from 1:1 to 4:1 and was therefore much higher than the one used in this study. A final explanation was not found in literature. Hydrogen decreased with increasing impregnation ratio. This was

consistent with other studies (Angin, 2013). Also the fluctuating nitrogen values were reported by Angin, (2013) and Ucar, et al., (2009).

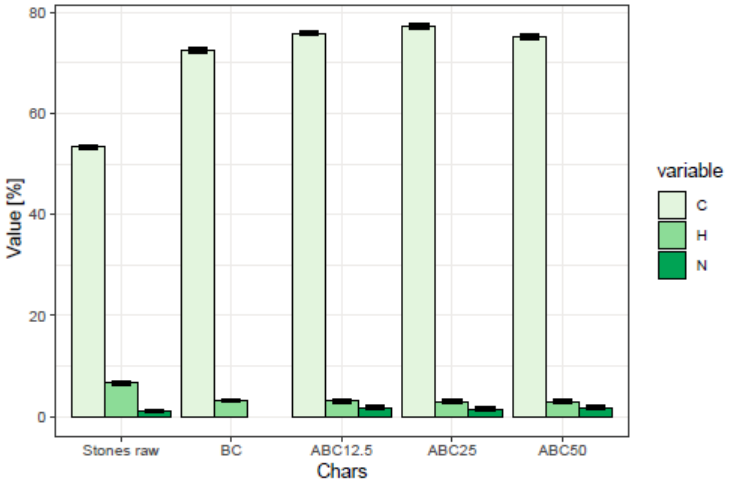


Figure 27: Results CHN analysis of raw cherry stones and chars for the preliminary adsorption experiment. Missing values do to failed analysis only two out of three measurements worked. Error bars show the SD.

5.4.2 Preliminary adsorption experiment

Figure 28 shows the calibration curve performed with the dilution series. The Y-axis shows the absorption values of the UV-VIS device at 665 nm. The x-axis shows the concentration of the dilution series. The r^2 value 0.995 showed a very good fit of the model to the data. The formula $y = 0.015 + 0.064 * x$ was therefore used to calculate the actual concentration of MB after the adsorption of MB to the chars.

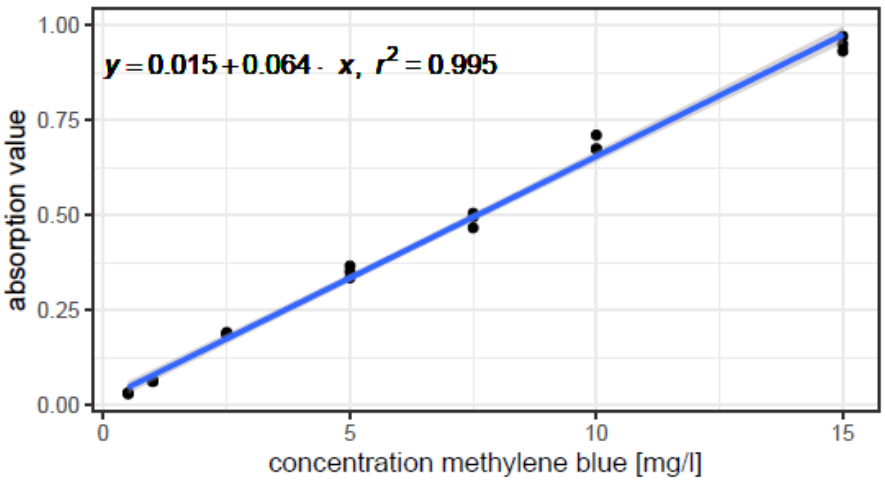


Figure 28: calibration curve of the dilution series for methylene blue adsorption experiments.

Figure 29 (and Table 22, Appendix C) show the concentration of the MB solution after the adsorption experiment with the chars in the test tubes. The biochar BC showed the least adsorption of dye. About 46.5% of the MB was absorbed. The activated biochars ABC12.5 and

ABC50 showed very similar results of about 82% elimination of the dye. The activated biochar ABC25 performed the best and achieved to eliminate over 88% of the dye.

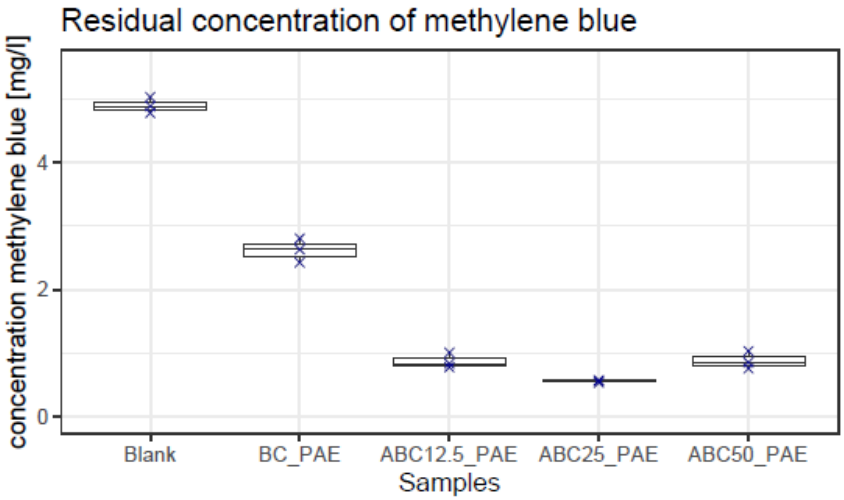


Figure 29: Preliminary adsorption experiment (PAE) with 5 mg of each char and 5 ml of MB solution (c=5 mg/l) in the test tubes. Residual concertation of methylene blue in the solution after the adsorption of MB to the char samples for 1 hour. Blank value referred to as 100 %, n=3.

The activated biochars showed a significant difference to the “regular” biochar (p<a) (Table 23, Appendix C). The p-value of 0.947 of the activated biochars ABC50 and ABC12.5 shows that there is no significant difference. The p-values of 0.038 of the ABC25 showed a significant difference to two other activated biochars.

Conclusion

The activated biochar ABC25 showed the best performance in adsorption of MB. It also showed the highest Ctot and fixed carbon content. Ash content was the second lowest for ABC25 and the examination with the binocular showed a solid structure with moderate changes. Therefore, the same activation procedure for the ABC for the main adsorption experiment with the fixed-bed filters at the IWB was chosen, as for ABC25 in the preliminary adsorption experiments.

5.4.3 Production of biochar and activated biochar for the main adsorption experiment

Although the Pyreka reactor was cleaned properly before each experiment, the biochar and the activated biochar for the main adsorption experiment (MAE) were still contaminated with foreign material. This time the foreign material consisted mostly of carbonised wood pellets. Also small amounts of sand were still found. The chars were therefore sieved (mesh size 1 mm) to get rid of the sand. Wood pellets were removed manually by hand as good as possible. The results in the Table 24 (Appendix C) are therefore only approximate values and not representative.

Proximate analysis

Like the chars from PAE, the proximate analysis was performed after washing the chars with HCl and distilled water. As seen from Figure 30 (and Table 25, Appendix C) the moisture content was measured 4.75% for the BC and 3.09% for the ABC25. AC showed a moisture content of about 9.02% which is more than two times higher than the other chars, but is still close to the value of 8% listed in the data sheet (Appendix D). Among the three chars the AC showed with about 3.96% the lowest amount of volatiles while the BC showed with 21.15% the highest amount of volatiles. Fixed carbon was measured highest for ABC25 (80.37%) followed by AC (78.65%), and BC (73.36%). Ash was measured highest for AC with 8.37%.

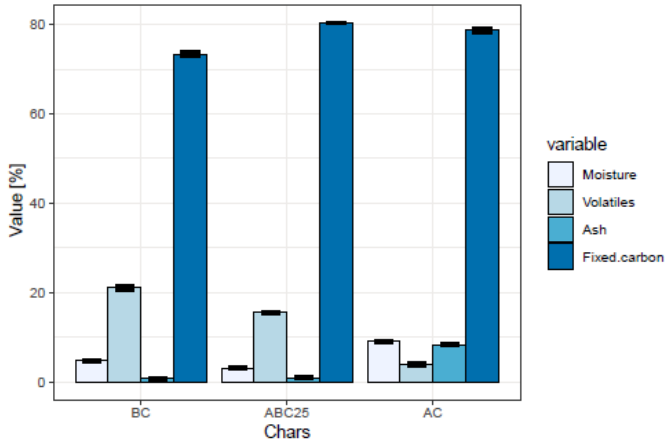


Figure 30: Results proximate analysis of chars for the main adsorption experiment. The moisture refers to air dry samples. Moisture, Volatiles, fixed carbon and ash add up to 100%. Error bars show the SD.

CHN Analysis

As seen from Figure 31 (and Table 26, Appendix C) Ctot of the three chars was measured highest for ABC25 (79.53%) followed by BC (75.83%) and AC (75.00%). The relatively low Ctot value of the AC contradicts to those found in literature Salame & Bandosz, (2001) where active carbon produced from stone coal showed Ctot values of over 90%. No explanation could be found for this. Hydrogen was found highest for BC followed by ABC25 and AC. The same was found for nitrogen.

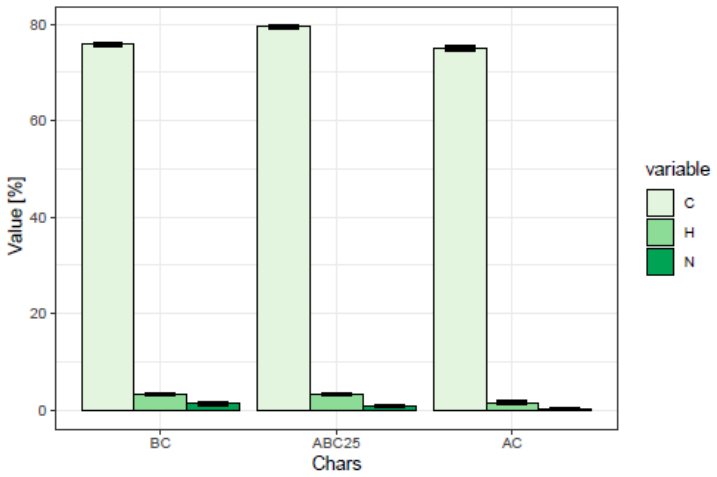


Figure 31: Results CHN analysis of raw cherry stones and chars for the preliminary adsorption experiment. Error bars show the SD.

5.4.4 Main adsorption experiments

Figure 32 shows the removal of the MB dye in the context of the different dosages of char used for the three main adsorption experiments. The complete results are listed in the Appendix C

It can be seen, that the AC showed a nearly complete adsorption of the MB dye for the dosage of 5 mg and 1 mg. The dosage of 0.1 mg was still able to achieve an adsorption of $\bar{x}$=58.6%. The activated biochar ABC25 showed a good removal of MB for a dosage of 5 mg ($\bar{x}$=86%) but only a moderate removal at 1 mg ($\bar{x}$=26.6%) and a low adsorption at a dosage of 0.1 mg ($\bar{x}$=9.2%). The biochar (BC) showed in all experiments the least adsorption of MB dye. At a dosage of 0.1 mg the ABC and BC did not show significant difference in the removal of MB.

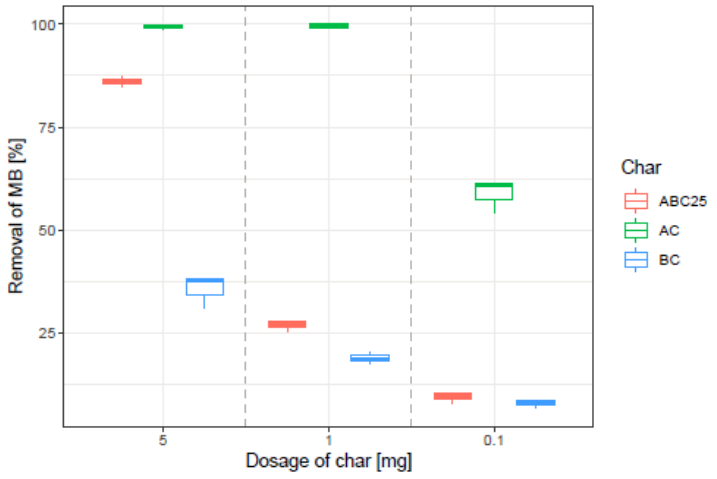


Figure 32: Overview main adsorption experiments 1-3. Removal % of MB from MB-solution c=5 mg/l of the three chars ABC25, BC and AC in the dosages of 5 mg, 1 mg and 0.1 mg, n=3.

5.4.5 Discussion of the potential role of biochar and activated biochar

The chemical activation with K_2CO_3 led to a visible change (colouring, hardness, volume) of the carbonised cherry stones. The higher the impregnation ratio the more intense was this

change. The results of proximate- and CHN- analysis showed that a higher impregnation ratio is not automatically leading to better results. This recognition was confirmed in the preliminary adsorption experiment, where a higher activation ratio showed no significant improvement in the adsorption of methylene blue. There was even a deterioration in adsorption with higher activation ratios. This finding was also reported by Budi, et al., (2016). The main adsorption experiment showed that regular AC showed a much better elimination of MB dye compared to BC and ABC25.

Although the PAE conducted in this study was carried out with different activation rates, temperature and residence time during pyrolysis were the same for all chars. These parameters may not have been optimal for the pyrolysis of cherry stones. Also the duration the cherry stones were soaked in K_2CO_3 was the same for all experiments. More different settings might have yielded more revealing results.

Since the scope of the adsorption experiments was limited to MB only, the potential for the use of ABC and BC as adsorption medium in wastewater remains unanswered.

In order to give a final statement about the use of BC and ABC in waste water treatment, even more extensive tests would have to be carried out.

6 Conclusions and recommendations for future research

Wastewater from the first decentralised anaerobic-aerobic treatment plant in Switzerland, IWB, with MP elimination step and wastewater reclamation for irrigation, was analysed and improvements made in the biological treatment were monitored. The wastewater was analysed for:

- COD and BOD removal
- Nutrient preservation (TN, NH_4-N, NO_2-N, TP and PO_4-P)
- Estrogenic activity using the planar-YES bioassay

Furthermore, a biochar and different K_2CO_3 activated biochars from cherry stones were produced and methylene blue adsorption experiments were made, to assess the potential role of activated biochar for the removal of MPs.

The outstanding planning and construction of the IWB was able to disprove the often mentioned concerns about too low wastewater temperatures and the associated too low activity of anaerobic biology in the temperate climate zone.

The anaerobic biology was found to be inhibited by either harmful or toxic substances in the wastewater and hydraulic short-circuiting of the anaerobic reactor compartments. The aerobic post treatment was therefore not able to lower the COD to the required level for a MP elimination through the polishing step. During the study period, the whole treatment did therefore not achieve the minimum requirements proposed for irrigation. It is recommended here to analyse the wastewater composition in detail (incl. all relevant nutrients and pollutants, such as organic compounds, salts, heavy metals, surfactants, and other detergents) with inductively coupled plasma (ICP) and HPLC. This will further allow to check the suitability of the Hach-Lange vial test for anaerobic wastewater analysis. In addition, it is recommended to measure the biogas production and to determine the bacterial strains in the compartments. This would provide further information about the condition of the reactor.

Nutrients were found to be preserved during the wastewater treatment. According to the suggested wastewater reuse for irrigation (Appendix A) the nutrient concentration is even too high, which is why the treated wastewater even needs to be diluted before its application. Whether the values in the predicted regulation for irrigation in urban areas are meaningful, should be investigated with irrigation studies performed with wastewater form the IWB. Depending on the application of the treated wastewater (green spaces, trees, or other plants) the optimal nutrient content could vary and the regulation could be adapted.

Estrogenic substances (E1 and E2) were found to increase during the anaerobic treatment, most likely caused through deconjugation. The aerobic post treatment showed the most

effective removal of the Σ estrogenic activity. The effluent concentration after the whole treatment showed a still significant amount of estrogen active substances and cannot considered to be safe for water reuse according to (oekotoxzentrum, 2016) This led to the assumption that other micropollutants were also still present in the wastewater, since the elimination step was not yet able to eliminate substances in such a low concentration.

The adsorption experiments performed in this study showed that biochar an activated biochar cannot compete with a regular activated carbon, if they are used in the same concentrations. Since no adsorption experiments have been carried out with wastewater, no direct conclusion can be drawn of the suitability of BC and ABC in wastewater.

In general the wastewater contained a large amount of undesired material and substances, such as wet pipes, detergents etc. The composition of the wastewater of the IWB depends mainly on the user behaviour of the residents. In order to improve the wastewater composition, the user behaviour of the residents must be adapted. The following suggestions are conceivable:

- A letter to the residents explaining the problem of foreign substances in the wastewater (with pictures) and asking them not to dispose solids (except for toilet paper), grease and oil in the toilet or the drain.
- Ask residents to use less and less aggressive detergents and cleaners and at the same time suggest alternatives, which are more suitable for the IWBs biology.
- Regularly inform residents about the condition of the system and point out if anything has improved or deteriorated so that they are made aware of their influence on the system.

Final statement

The IWB offers a unique opportunity to explore and develop alternative wastewater treatment systems, adapted to future needs. It is therefore of great importance to seize this opportunity to make progress in the field of urban water reuse.

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Appendix

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A. Proposal to regulate treated wastewater for irrigation in urban areas

Israel's decades of experience in wastewater management provide plausible values for the use of wastewater for irrigation. Values for nutrients, heavy metals, salts, faecal coliforms, etc. showed to guarantee soil fertility for the long time application of treated wastewater by minimising the risk for human health.

These regulation in combination with the Swiss regulation, which includes the elimination of MP, could well be used for irrigation in urban areas in order to ensure safe management. Although the Swiss regulation requires the elimination of MP only at plant size of 80,000 PE the elimination is considered obligatory here- independent of the population equivalent. Furthermore, lower COD values should be targeted, as MP elimination can only be efficiently achieved at lower values. Here the value from the Swiss Waster Protection Act could be used. A COD of 45-60 mg/l is required for the discharge of wastewater into water bodies. This value is therefore accepted as minimum requirement for the proposed irrigation in urban areas, but a value of 15 mg is recommended, since it was reported as limit for an efficient use of a polishing step.

Table 10: Parameters and values of the Israeli regulation for unrestricted irrigation (Inbar, 2006) and the Swiss regulation for discharge of treated wastewater and a proposal for an irrigation in urban areas. a/b differentiates the discharge values according to population equivalents PE. a=PE<10,000, b=PE≥ 10,000. Values *= refers to discharge regulations for industrial wastewater (WPA, 1991, stand on June 1, 2018)

Parameter	Units	Unrestricted Irrigation (Israel	Regulations for discharge Switzerland a/b	Proposal for irrigation in urban areas
Electric conductivity	dS/m	1.4	-	1.4
BOD	mg/l	10	20/15	10
TSS	mg/l	10	20/15	10
COD	mg/l	100	60/45	45/15
N-NH4	mg/l	20	2	20
Total nitrogen	mg/l	25	-	25
Total phosphorus	mg/l	5	0.8 *	5
Chloride	mg/l	250	-	250
Fluoride	mg/l	2	-	2
Sodium	mg/l	150	-	150

Faecal coliforms	Unit per 100 ml	10	-	10
Dissolved oxygen	mg/l	>0.5	-	>0.5
pH	mg/l	6.5–8.5	6.5-9 *	6.5–8.5
Residual chlorine	mg/l	1	-	1
Anionic detergent	mg/l	2	-	2
specific absorption rate SAR (salts)	(mmol/L)	0.5	5	5
Boron	mg/l	0.4	-	0.4
Arsenic	mg/l	0.1	0.1 *	0.1
Mercury	mg/l	0.002	0.05	0.002
Chromium	mg/l	0.1	2 *	0.1
Nickel	mg/l	0.2	2 *	0.2
Selenium	mg/l	0.02	-	0.02
Lead	mg/l	0.1	0.5 *	0.1
Cadmium	mg/l	0.01	0.1 *	0.01
Zinc	mg/l	2	2 *	2
Iron	mg/l	2	-	2
Copper	mg/l	0.2	0.5 *	0.2
Manganese	mg/l	0.2	-	0.2
Aluminium	mg/l	5	-	5
Molybdenum	mg/l	0.01	-	0.01
Vanadium	mg/l	0.1	-	0.1
Beryllium	mg/l	0.1	-	0.1
Cobalt	mg/l	0.05	0.5 *	0.05
Lithium	mg/l	2.5	-	2.5
Cyanide	mg/l	0.1	0.1 *	0.1
Micropollutants	-	-	Removal efficiency after elimination of min. 80% compared to inlet concentration	Removal efficiency after elimination of min. 80% compared to inlet concentration

B. Supplementary information for material and methods

Table 11. Overview of date and parameter measured at IWB. Green=measured parameter, red= not measured

Parameter/ Date	pH	COD	BOD	NH_4-N	NO_2-N	NO_3-N	TN	TP	PO_4-P	O_2
14.08.2018										
29.08.2018										
05.09.2018										
24.09.2018										
04.10.2018										
11.10.2018										
24.10.2018										
08.11.2018										
22.11.2018										

Table 12: Overview about which Hach-Lange vial test was used for which parameter.

Parameter	Vial test	Notes
COD	LCK1414 LCK114 LCK314	LCK1414 was used to determine the measuring range. The samples were tested with the tests LCK114 and LCK314 depending on the concentration of C.
NH_4-N	LCK302 LCK304	LCK304 was used to determine the measuring range. At the laboratory in Wädenswil LCK302 was used. LCK304 was used at the laboratory in Zürich
NO_2-N	LCK341	LCK341 was use in both laboratories
NO_3-N	LCK339 LCA addista	Plausibility check for nitrate nitrogen was performed with the combined standard and spiking solution LCA addista in the laboratory at Werdhölzli in Zürich. LCK339 was used in both laboratories.
TN	LCK338	LCK338 was used to determine the measuring range and it was used in both laboratories for anaylsis.
PO_4-P	LCK350	LCK350 was used to determine the measuring range and it was used in both laboratories for anaylsis.
TP	LCK350	LCK350 was used to determine the measuring range and it was used in both laboratories for anaylsis.

Table 13: Devices and material used for BOD measurement

Objet	Specification
OxiTop measuring head	WTW
Sample bottle brown glass	WTW PF 600
Rubber sleeves	WTW GK 600 L
Magnetic stirrer	WTW RST 600
Overvlow flask	WTW MK 0164/600, 164 ml
Stirrer platform	WTW IS 12
Sodiumhydroxide Pellets	CAS: 1310-73-2
N-Allylthiourea	CAS: 06064

Table 14: Substances used for planar-Yes bioassay (Schoenborn, et al., 2017b)

Substance	CAS-number
17-α-Ethinylestradiol (EE2)	57-63-6
Estrone (E1)	53-16-7
17 β-Estradiol (E2)	50-28-2
MUG: 4-Methylumbellifreyl ß-D-galactopyranoside	6160-78-7
Acetone	67-64-1
Chloroform	67-66-3
Petroleum fraction	-
Dimethyl sulfoxide	67-68-5
Disodium hydrogen phosphate	10028-24-7
Ethanol, ≥ 99.8 %	64-17-5
Gelrite	71010-52-1
Potassium chloride	7447-40-7
L-Histidin Hydrochlorid Monohydrat	5934-29-2
L-Lysine-monohydrochlorid	657-27-2
Magnesium sulphate heptahydrate	10034-99-8
McDonell Yeast	-
Methanol	67-56-1
Glycerol for molecular biology, ≥99%	56-81-5
Sodium dodecyl sulphate	151-21-3
Sodium phosphate dibasic dihydrate	10028-24-7
Sodium phosphate monobasic monohydrate	10049-21-5
Nitrogen 5.0 (gaseous, compressed)	-
tert-butyl methyl ether (MTBE)	1634-04-4/ T175.1
Ultra-pure water	
Yeast nitrogen base without amino acids	-
α-D-Glucose	50-99-7
Copper(II) sulfate pentahydrate	7758-99-8
HPTLC silica gel 60 Merck 20x10 cm2 and 10x10 cm2	

Table 15: Devices used for planar-Yes bioassay (Schoenborn, et al., 2017b)

Device	Name	Brand	Item number
UV/Vis Spectrometer	Libra S22	Biochem	80-2115-20
Centrifuge	Centrifuge 5810 R	Eppendorf	-
Shaking plate with heater	KS 4000i control	IKA	0003510000
Flowbench	-	-	-
Vortex	VORTEX_GENIE 2	Scientificindustries	SI-0276
Spray cabinet	Derivatizer	CAMAG	22.6232
Dry chamber	-		-
Application device	Automatic TLC Sampler 4 (ATS-4)	CAMAG	22.74
Visualizer	TLC Visualizer	CAMAG	22.978
Automatic development chamber	ADC 2	CAMAG	22.835
Vacuum centrifuge	Vacufuge; Concentrator Plus	Eppendorf	
Spay jet	Desaga ChromaJet DS20	CAMAG	
Test tube holder	Visiprep SPE Vacuum Manifold	Supelco	57030-U

Table 16: Overview of samples and activation ratio with K_2CO_3 made for the preliminary adsorption experiment (PAE) and the main adsorption experiment (MAE).

Experiment type and sample name		Cherry stones [g]	K_2CO_3 added to H_2O [g]	Impregnation ratio	
PAE	ABC50_PAE	25.6	12.6	0.5	1/2
	ABC25_PAE	25.25	6.3	0.25	1/4
	ABC12.5_PAE	25.16	3.1	0.125	1/8
	BC_PAE	25.04	0		-
MAE	ABC25_MAE	900.07	225.0	0.25	1/4
	BC_MAE	776.48	0	-	-

C. Supplementary information for results and discussion

Table 17: listing of findings and maintenance work carried out on the IWB

Date	Maintenance, changes to setup and observations
15.06.2018	Installation of aeration device in aerobic tank for stripping of hydrogen sulfide (H_2S). Capacity of the aeration pump 3 m^3/h at 0.2 bar. Injection via coarse ceramic diffuser DN80mm
26.06.2018	Extraction of excess sludge (scum) in settler P1, pumping volume (sludge and water) 14 m^3
10.07.2018	Extension of the aerobic tank with installation of an additional ventilation plate (fine diffuser, Supratec Oxyflex DN300) and ventilation pumps 2x Osaga MK60 with capacity 2.5 m^3/h at 0.2 bar, each.
03.08.2018	Extension of aerobic tank with installation of an additional aeration plate (fine diffuser Supratec Oxyflex DN300) and aeration pump Thomas LP 150 HN with capacity 9 m^3/h AT 0.2 bar (Osaga pumps out of operation).
14.08.2018	• Pumping off scum from Settler P1, approx. 50 cm layer thickness. • Inoculation of Settler with specific anaerobic bacteria cultures (Bio-Booster 12 tablets). • Ventilation pipe (from reactor to the roof of building A) blocked with water (from condensation), led to odour emissions on the site; water was pumped out. • Samples taken for planar-Yes (P2, P10, P11, PSF, O3, AOP)
24.08.2018	The plant is decoupled because biological activity in the settler is still low (hardly any biogas formation) and the floating sludge layer has built up to 15cm again and is very tough.
03.09.2018 / 04.09.2018	Overhaul work on the high-load reactors: • Bio-filter cubes packed in net bags. • Ventilation pipes between the reactor chambers cleaned. • New inoculation of the plant with a new product of specific anaerobic bacteria cultures (composition of the bacterial mixture is confidential).
10.09.2018	• Plant reconnected • Floating sludge tested in Settler P1, floating sludge still tough but biological activity in Settler clearly developing (good biogas formation).
13.09.2018	Ventilation cap on ventilation pipe (on roof of building A) exchanged with solar fan (solar energy powered device).
19.09.2018	Scum tested in Settler P1. Scum has become more viscous and biological activity in settler is good.
24.09.2018	• Scum tested in Settler P1. Scum builds up but is viscous and good biological activity visible in settler (good biogas production). • Samples taken for analysis in the laboratory (P2, P10, PSF, O3).
04.10.2018	• Scum tested in Settler P1. Scum continues to build up but is viscous and good biological activity visible in Settler (good biogas formation). • Samples taken for analysis in the laboratory (P2, P10, PSF, O3).
11.10.2018	• Ventilation pipe (from reactor to the roof of building A) blocked with water (from condensation)

	• Water samples for laboratory analysis taken from P2, P10, PSF, O3.
23.10.2018	Solar fan for ventilation on the roof had to be removed because it was defective due to corrosive gases produced by the IWB.
24.10.2018	Expansion of aerobic tank: • Installation of hanging filter bags for "fixed-film" Bactria cultures • Improving ventilation pipe with drainage to prevent accumulation of condensation water. • Inlet into Settler P1 blocked. Blockage was repaired, but fat deposits could not been removed completely. • Water samples for laboratory analysis taken from P2, P10, PSF and O3
08.11.2018	Water samples for laboratory analysis taken from P2, P10, PSF and O3
22.11.2018	Expansion of aerobic tank: • Installation of fine diffuser aeration hose DN 400 and additional aeration pump (Alitha AL60 capacity 4.2m3/h at 0.2bar). • Specific bacteria for fat degradation added in the settler P1. • New solar fan on ventilation pipe on roof of building A installed • Water samples for laboratory analysis taken from P2, P10, P11, PSF and O3 (incl. samples for planar-Yes)

Table 18: Wastewater parameter mean values=$\bar{x}$, standard deviation=SD, and number of samples per parameter=n of the IWB in the compartments P2, P10, PSF, O3 over the monitored period 24.9-22.11. 2018

		P2	P10	PSF	O3
COD [mg/l]	$\bar{x}$	647.65	273.05	132.01	121.65
	± SD	49.43	21.78	38.64	25.81
	%	100	42.16	20.38	18.78
	n	10	10	10	10
BOD [mg/l]	$\bar{x}$	407.76	121.14	45.67	38.33
	± SD	27.63	24.99	16.59	9.96
	%	100	29.71	11.20	9.40
	n	9	10	10	8
TN [mg/l]	$\bar{x}$	85.27	85.85	82.27	82.67
	± SD	7.18	2.67	4.01	3.14
	n	10	10	10	10
NH4-N [mg/l]	$\bar{x}$	72.79	76.35	72.64	74.09
	± SD	7.20	10.30	8.98	9.78
	n	8	8	8	8
TP mg/l]	$\bar{x}$	9.47	8.99	8.64	8.40
	± SD	0.87	0.33	0.46	0.43
	n	10	10	10	10

PO4-P [mg/l]	x̄	7.56	8.18	7.20	7.50
	± SD	0.73	0.32	0.62	0.46
	n	10	10	10	10
pH	x̄	6.90	7.01	7.64	7.61
	± SD	0.139	0.057	0.055	0.046
	n	5	5	5	5

Results production chars PAE

Table 19: Results of production of chars for the preliminary adsorption experiment. A cherry stones raw (dry mass [g]), B=cherry stones after impregnation (dry mass [g]), C=char after pyrolysis (contaminated [g]), D=char used to wash with HCL (dry mass [g]), E= final char for PAE (dry mass[g]), F=yield of char in %

Sample	A	B	C	D	E	F
ABC50_PAE	25.2	27.48	11.7	10.06	9.70	38.51
ABC25_PAE	25.25	26.63	8.36	8.05	7.69	30.47
ABC12.5_PAE	25.16	25.84	7.56	7.05	6.69	26.60
BC_PAE	25.04	25.01	5.37	5.02	4.67	18.63

Table 20: Results proximate analysis of raw cherry stones and chars for the preliminary adsorption experiment. The moisture refers to air dry samples. Moisture, Volatiles, fixed carbon and ash add up to 100%. Each sample was analysed in triplicates, n=3.

Sample	Moisture [%]		Volatiles [%]		Fixed carbon [%]		Ash [%]	
	x̄	± SD	x̄	± SD	x̄	± SD	x̄	± SD
Raw Stones	3.53	0.042	78.21	0.085	17.09	0.097	1.17	0.015
BC_PAE	5.13	0.122	23.59	0.500	69.87	0.377	1.41	0.008
ABC12.5_PAE	4.80	0.182	18.87	0.626	75.14	0.607	1.19	0.021
ABC25_PAE	4.76	0.156	17.86	0.333	76.18	0.126	1.20	0.059
ABC50_PAE	5.72	0.284	19.76	0.648	72.84	0.372	1.62	0.048

Table 21: Results CHN analysis of raw cherry stones and chars for the preliminary adsorption experiment, n=3. Missing values do to failed analysis only two out of three measurements worked.

Sample	Ctot [%]		H [%]		N [%]	
	x̄	± SD	x̄	± SD	x̄	± SD
Raw Stones	53.30	0.10	6.69	0.035	1.18	0.021
BC_PAE	72.33	0.404	3.16	0.015	2.33	-
ABC12.5_PAE	75.83	0.321	3.06	0.030	1.79	1.175

ABC25_PAE	77.30	0.458	3.01	0.036	1.53	0.070
ABC50_PAE	75.07	0.306	2.99	0.061	1.83	0.204

Results preliminary adsorption experiment

Table 22: Preliminary adsorption experiment (PAE) with 5 mg of each char and 5 ml of MB solution (c=5 mg/l) in the test tubes. Residual concertation (n=3, $\bar{x}$ in mg/l, and %) of methylene blue in the solution after the adsorption of MB to the char samples for 1 hour. Blank value referred to as 100 %

		Blank	BC_PAE	ABC12.5_PAE	ABC25_PAE	ABC50_PAE
cMB [mg/l]	$\bar{x}$	4.895	2.619	0.875	0.557	0.882
	± SD	0.126	0.189	0.12	0.021	0.139
	%	100	53.5	17.9	11.4	18

Table 23: Results of the pairwise comparisons using t tests with pooled SD and “holm” adjustment method, a=0.05.

	ABC12.5_PAE	ABC25_PAE	ABC50_PAE	BC_PAE
ABC25_PAE	0.038	-	-	-
ABC50_PAE	0.947	0.038	-	-
BC_PAE	$7.9*10^{-08}$	$1.9*10^{-08}$	$7.9*10^{-08}$	-
Blank	$3.8*10^{-11}$	$2.0*10^{-11}$	$3.8*10^{-11}$	$8.3*10^{-09}$

The Shapiro-Wilk normality test of the data showed a p-value of 0.4864 and therefore a normal distribution of the data. The pairwise comparisons using t tests with pooled SD and “holm” adjustment method showed that all chars are significant different to the blank sample ($p<a$).

Results production chars MAE

Table 24: Results of production of chars for the main adsorption experiment. A cherry stones raw (dry mass [g]), B=cherry stones after impregnation (dry mass [g]), C=char after pyrolysis (contaminated [g]), D=char used to wash with HCL (dry mass [g]), E= final char for PAE (dry mass[g]), F=yield of char in %

Sample	A	B	C	D	E	F
ABC25_MAE	900.07	929.76	259.12	243.42	241.54	26.84
BC_MAE	776.48	776.13	198.96	185.95	180.01	23.18

Table 25: Results proximate analysis of the chars for the main adsorption experiment. The moisture refers to air dry samples. Moisture, Volatiles, fixed carbon and ash add up to 100%. Each sample was analysed in triplicates, n=3.

Sample	Moisture [%]		Volatiles [%]		Fixed carbon [%]		Ash [%]	
	$\bar{x}$	± SD	$\bar{x}$	± SD	$\bar{x}$	± SD	$\bar{x}$	± SD
BC_MAE	4.75	0.151	21.15	0.690	73.36	0.826	0.74	0.014
ABC25_MAE	3.09	0.020	15.56	0.037	80.37	0.047	0.98	0.018
AC_MAE	9.02	0.260	3.96	0.624	78.65	0.609	8.37	0.015

Table 26: Results CHN analysis of chars for the main adsorption experiment, n=3.

Sample	Ctot [%]		H [%]		N [%]	
	$\bar{x}$	± SD	$\bar{x}$	± SD	$\bar{x}$	± SD
BC_MAE	75.83	0.058	3.327	0.050	1.36	0.072
ABC25_MAE	79.53	0.153	3.240	0.020	0.77	0.004
AC_MAE	75.00	0.458	1.557	0.032	0.17	0.017

Main adsorption experiments

Table 27: Main adsorption experiment 1 (MAE1) with 5 mg of each char and 5 ml of MB solution (c=5 mg/l) in the test tubes. Residual concertation (n=3, $\bar{x}$ in mg/l, and %) of methylene blue in the solution after the adsorption of MB to the char samples for 1 hour. Blank value referred to as 100 %

		Blank	BC_MAE1	ABC25_MAE1	AC_MAE1
cMB [mg/l]	$\bar{x}$	4.832	3.249	0.707	<LOQ (0.032)
	± SD	0.242	0.209	0.059	<LOQ (0.023)
	%	100	67.2	14.6	<LOQ (0.7)

Table 28: Results statistical analysis MAE 1. Shapiro-Wilk normality test and pairwise comparison with t-test with pooled SD and “holm” adjustment, a=0.05.

Shapiro-Wilk normality test p=0.9963.			
	ABC25_MAE1	AC_MAE1	BC_MAE1
AC_MAE1	0.00097	-	-
BC_MAE1	$1.8*10^{-07}$	$3.7*10^{-08}$	-
Blank	$6.5*10^{-09}$	$2.3*10^{-09}$	$4.6*10^{-06}$

Statistical analysis of MAE 1 showed that all chars are significant different (significance level 0.05) to the blank sample (p<a). Furthermore data model showed that all chars are significant different to each other (all p<a).

Table 29: Main adsorption experiment 2 (MAE2) with 1 mg of each char and 5 ml of MB solution (c=5 mg/l) in the test tubes. Residual concertation (n=3, $\bar{x}$ in mg/l, and %) of methylene blue in the solution after the adsorption of MB to the char samples for 1 hour. Blank value referred to as 100 %

		Blank	BC_MAE2	ABC25_MAE2	AC_MAE2
cMB [mg/l]	$\bar{x}$	5.493	4.097	3.703	<LOQ (0.020)
	± SD	0.098	0.067	0.062	<LOQ (0.014)
	%	100	74.6	67.4	<LOQ (0.4)

Table 30: Results statistical analysis MAE 2. Shapiro-Wilk normality test and pairwise comparison with t-test with pooled SD and “holm” adjustment, a=0.05

Shapiro-Wilk normality test p=0.6739.			
	ABC25_MAE2	AC_MAE2	BC_MAE2
AC_MAE2	$1.1*10^{-11}$	-	-
BC_MAE2	$9.7*10^{-05}$	$6.2*10^{-12}$	-
Blank	$2.6*10^{-09}$	$7.1*10^{-13}$	$1.3*10^{-08}$

The pairwise comparisons, using t tests with pooled SD and “holm” adjustment method, showed that all chars are significantly different to the blank sample without any adsorbent (p<a). Furthermore the data model showed that all chars are significant different to each other (all p<a).

Table 31: Main adsorption experiment 3 (MAE 3) with 0.1 mg of each char and 5 ml of MB solution (c=5 mg/l) in the test tubes. Residual concertation (n=3, $\bar{x}$ in mg/l, and %) of methylene blue in the solution after the adsorption of MB to the char samples for 1 hour. Blank value referred to as 100 %

		Blank	BC_MAE3	ABC25_MAE3	AC_MAE3
cMB	$\bar{x}$	4.801	4.656	4.576	2.086

± SD	0.147	0.041	0.063	0.198
%	100	97.0	95.3	43.4

Table 32: Results statistical analysis MAE 3. Shapiro-Wilk normality test and pairwise comparison with t-test with pooled SD and “holm” adjustment, a=0.05

Shapiro-Wilk normality test p=0.7382			
	ABC25_MAE3	AC_MAE3	BC_MAE3
AC_MAE3	$4.4*10^{-08}$	-	-
BC_MAE3	0.47	$4.2*10^{-08}$	-
Blank	0.19	$3.3*10^{-08}$	0.41

The pairwise comparisons, using t tests with pooled SD and “holm” adjustment method, showed that the BC and ABC25 with p-values of 0.41 and 0.19 were not significantly different to the Blank sample. BC and ABC25 showed also no significant difference between each other (p-value 0.47). The AC showed a significant difference to the two other chars and the blank sample ($p<a$).

D. Data sheet

Koerner
Bio- und Umwelttechnologie

Produktdatenblatt Cegesan® DKO Aktivkohle

Produktbeschreibung

Cegesan® DKO Aktivkohle ist eine extrudierte Aktivkohle mit einem Korndurchmesser von 4 mm, die aus dem Rohstoff Steinkohle durch eine Aktivierung mit Wasserdampf hergestellt wird. Aufgrund ihrer Porenstruktur ist diese Aktivkohle besonders geeignet, organische Verbindungen mit geringen Konzentrationen aus Gasen zu entfernen.

Produktanwendung

Die Aktivkohle Cegesan® DKO ist geeignet zur Aufbereitung und Reinigung von Gasen und Abluft. Bevorzugtes Einsatzgebiet dieser Aktivkohle ist die Adsorption von Siloxanen, die in Deponie- und Klärgasen, teilweise aber auch in Biogasen enthalten sind. Auch kann dieses Produkt zur Entfernung von Gerüchen aus Abluft verwendet werden.

Besonderheiten

Die Aktivkohle Cegesan® DKO bietet folgende Vorteile:

+ Sehr hohes Aufnahmevermögen
+ Geringer Druckverlust
+ Erzielung sehr guter Reinigungswerte
+ Hohe mechanische Härte
+ Gleichmässig hohe und geprüfte Produktqualität

Technische Beschreibung

Rütteldichte	490±30 g/l
Wassergehalt (beim Abpacken)	max. 8 %
BET/Oberfläche (Basiskohle)	850 m^2/g
Abriebhärte	97 %
Zündpunkt	400°C
Korndurchmesser	ca. 4 mm
Aschegehalt	10%
Kornanteil >3.36 mm	min. 98%
Benzolbeladung	
p/ps=0,9 min. 30 %	
p/ps=0,1 min.27 %	
p/ps=relative Sättigungskonzentration, cs bei 20°C = 320 g/m3	

Sicherheitshinweise

Feuchte Aktivkohle adsorbiert Sauerstoff aus der Luft. In geschlossenen und teilweise geschlossenen Räumen oder Behältern kann dies zu einem lebensbedrohlichen Sauerstoffverlust führen. Die Vorschriften zum Betreten geschlossener Räume sowie Sicherheitsdatenblätter sind zu beachten.

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E. Pictures IWB

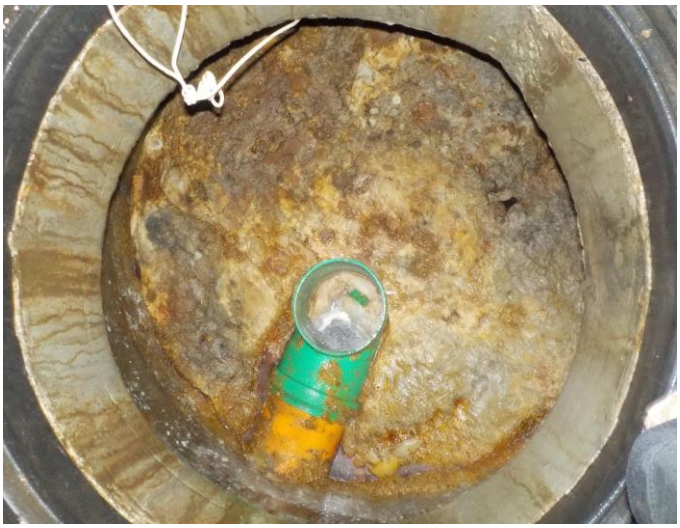

Figure 33: Thick scum layer in settler P1, July 4, 2018

Figure 34: Pumping of scum in settler P1, August 14, 2018

Figure 35: Inside reactor compartment P4 with blue filter cubes

Figure 36: Wet wipes, tampons and other material found in the scum

F.

Plagiatserklärung

Zürcher Hochschule für Angewandte Wissenschaften

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Mit der Abgabe dieser Masterarbeit versichert der/die Studierende, dass er/sie die Arbeit selbständig und ohne fremde Hilfe verfasst hat.

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Bei Verfehlungen aller Art treten Paragraph 39 und Paragraph 40 der Rahmenprüfungsordnung für die Bachelor- und Masterstudiengänge an der Zürcher Hochschule für Angewandte Wissenschaften vom 29. Januar 2008 sowie die Bestimmungen der Disziplinarmassnahmen der Hochschulordnung in Kraft.

Ort, Datum: Unterschrift:

Horgen, 13.02.2019