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Master Thesis

TREATMENT OF INDUSTRIAL WASTEWATER OF THE METAL INDUSTRY – REDUCTION OF CARBON AND NITROGEN – A PILOT PLANT STUDY

Submitted by

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Abstract

Sinter processes in the steel industry make up about 50% of dust emissions of integrated steel works. The easily separated fraction of the dust is returned to the sinter feed, the fine dust needs further treatment to reduce the pollutant load.

This thesis concerned itself with the treatment of wastewater on a pilot plant scale. The wastewater consisted of leached MEROS process residue. The objectives were reducing the carbon and nitrogen loads in the leachate to meet effluent standards, as well as reducing the amount of landfill bound material. The treatment methods originated from successful laboratory trial runs which have been scaled up.

To fulfill the objectives and treat the leachate, two Pilot Plants were built in the technical hall of BOKU Muthgasse, Vienna. Pilot Plant 2019 utilized a given industrial wastewater treatment process consisting of filtration, Fenton process, heavy metal precipitation and sedimentation, as well as sand and activated carbon filtration. Pilot Plant 2020 had an air stripping column for ammonium-nitrogen reduction and used an UV treatment device for advanced oxidation processes.

Only 12% of filterable substances remained after preparing a leachate. The objective of reduction of landfill volume was therefore achievable.

Due to treatment of the soluble residue in Pilot Plant 2019 initial COD concentrations were reduced by 77% to a value of 84 mg/l. The TOC was reduced to 22 mg/l, which is a reduction of 97%. The removal of nitrogen was unsuccessful.

Neither nitrogen nor carbon reduction complied with European and international effluent standards in Pilot Plant 2020. Air stripping was used to reduce the ammonium-nitrogen concentrations of the leachate, with an average removal rate of 11% NH_4-N. The methods show a lot of promise in the laboratory and pH and water temperature are easily adjustable parameters to increase efficiency of treatment. Carbon removal using AOP was not successful.

Kurzfassung

Diese Arbeit befasst sich mit der Behandlung des MEROS-Prozessrückstands. Ziel war es, die Kohlenstoff- und Stickstoffbelastung des Rückstands zu verringern, um die Emissionsstandards für Industrieabwässer zu erfüllen. Auch sollte die Menge an deponiegebundenem Material verringert werden. Die Behandlungsmethoden stammten von erfolgreichen Laborversuchen, deren Dimension vergrößert wurde.

Um die Prozessrückstände zu behandeln, wurden im Technikum der BOKU Muthgasse, Wien, zwei Pilotanlagen gebaut. Die Pilotanlage 2019 verwendete eine vorgegebene Abwasserbehandlung, die aus Filtration, Fenton-Verfahren, Schwermetallfällung und Sedimentation sowie Sand- und Aktivkohlefiltration bestand. Die Pilotanlage 2020 verfügte über eine Luftstrippungs-Säule zur Ammonium-Stickstoff-Reduktion und verwendete eine UV-Gerät für Advanced Oxidation Processes.

Der Prozessrückstand hatte durchschnittlich 12% filtrierbare Stoffe, es wurden daher fast 90% des Rückstands gelöst. Das Ziel der Reduktion des Deponievolumens war daher erreichbar.

Die Behandlung des gelösten Rückstands in der Pilotanlage 2019 war teilweise erfolgreich. Die anfänglichen CSB-Konzentrationen wurden um 77% auf 84 mg/l reduziert. Der TOC wurde auf 22 mg/l reduziert, was einer Reduktion von 97% entspricht. Die Entfernung von Stickstoff war nicht möglich.

In der Pilotanlage 2020 waren weder Stickstoff- noch Kohlenstoffreduktion erfolgreich. Luftstrippung wurde verwendet, um die Ammonium-Stickstoff-Konzentrationen des Sickerwassers zu reduzieren. Die durchschnittliche Entfernungsrate betrug 11%. Die Methode war im Labor sehr erfolgreich und die Parameter pH und Wassertemperatur sind an der Anlage leicht anpassbar, um die sie zu betreiben. Die Kohlenstoffentfernung mit AOP war nicht erfolgreich.

List of abbreviations

$AgNO_3$	Silver nitrate
AOP	Advanced Oxidation Processes
BOD	Biological Oxygen Demand
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
H_2O_2	Hydrogen Peroxide
HNO_3	Nitric acid
IC	Ion Chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
JIS	Japanese Industry Standard
$KMnO_4$	Potassium permanganate
MEROS	Maximum Emission Reduction of Sintering
$Na_2C_2O_4$	Sodium oxalate
NH_4-N	Ammonium nitrogen
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_3-N	Nitrate nitrogen
TOC	Total Organic Carbon
TNb	Total Nitrogen bonded

1. Introduction

Sinter processes in the steel industry make up about 50% of dust emissions of integrated steel works. An integrated steel work carries out the complete steel making process, from ore to the finished product. Relevant pollutants are heavy metals, sulfur oxides, nitrogen oxides, hydrogen chloride, hydrogen fluoride, hydrocarbons and carbon monoxide. The off-gas produced in the sinter process is collected and the dust is separated. The easily separated fraction of the dust has a very similar composition to the raw material on the sinter feed and is therefore recycled and returned to the sinter feed (Remus et al., 2013). The fine dust needs further treatment to reduce the pollutant load.

To reduce pollutants in the fine dust fraction of the off-gas the MEROS process can be used. MEROS stands for Maximum Emission Reduction of Sintering. It is an end-of-pipe technique and reduces emissions by adding lime or sodium bicarbonate as additives into the exhaust gas flow and filtering the conditioned off-gas (Primetals Technologies Austria GmbH, 2020). The process residue of the MEROS treatment needs to be disposed of, as it cannot be recycled into the sinter process. Recycling is not possible, due to the high load of heavy metals and alkali chlorides. The residue needs to either be landfilled or treated further. In this thesis the focus lies on the treatment and reduction of the volume of the residue, especially on reducing carbon and nitrogen concentrations. Due to the high alkali chloride and sulfate concentrations, the residue from the sinter process gas cleaning system is very soluble in water. This solubility is used in treating the residue by creating a leachate. Approximately 90% of the residual dust is soluble, a sizeable reduction in landfill bound material is theoretically possible. The ensuing water is not biodegradable, chemical means of treatment are therefore necessary to reduce the chemical load, consisting of heavy metals, sodium, potassium and chloride, in the leachate.

2. Objectives

This thesis investigated the treatment of the dissolved residue, called leachate from the sinter process gas cleaning system MEROS in a semi-technical plant. The methods originated from successful laboratory trials and were adjusted to fit the scaled-up pilot plant. Treatment focused mainly on means of reduction of carbon and nitrogen. The approach could be separated into two phases.

Phase one was the optimization of a given industrial wastewater treatment process. This included laboratory trial runs to optimize the given treatment process on a small scale, as well as testing of MEROS residue to gauge substances contained in the residue and initial concentrations. Further, phase one consisted of up scaling the optimized process, building an appropriate Pilot Plant and performing trial runs with said Pilot Plant.

Phase two was the upscale of a newly developed process on a semi-technical scale. It involved more laboratory testing to determine the efficiency of reduction of carbon and nitrogen, as well as building another Pilot Plant and executing trial runs.

Objectives of the thesis were:

- Successful scale-up of laboratory methods befitting the pilot plant.
- Reduction of carbon and nitrogen concentrations in the leachate.
- Comparison to European and international effluent standards to emit effluent back into the water cycle.
- Reduction of residue volume of MEROS process to decrease amount of landfill bound material.

3. Fundamentals

3.1 Sinter Process

Fine ore and additives such as lime or olivine are the starting materials of the sinter process. Recycled iron-bearing materials from downstream processes and coke breeze, to enable ignition, are added to the mixture. The materials to be sintered are placed on travelling grates, where gas burners ignite the coke breeze in the mixture. Fans draw process-air through the sinter bed in a down-draft process (Remus et al., 2013).

The off-gas is collected in mains with de-dusting devices for emission reduction control. The waste gas flow from a sinter plant is approximately 1500 to 2500 Nm^3/t graded sinter. The off-gas contains heavy metals, alkali chlorides, sulfur oxides, nitrogen oxides, hydrogen chloride, hydrogen fluoride, hydrocarbons, carbon monoxide and polycyclic aromatic hydrocarbons (PAH) (Remus et al., 2013).

The dust is a two-component mixture, with a coarse (100 µm) and a fine (0,1-1 µm) fraction. The heterogeneity of the dust is due to two dust forming processes. Coarse dust is formed at the beginning of the sinter feed and its composition is similar to said material. It is therefore easily separated by electrostatic precipitators (Remus et al., 2013). The electrodes in an electrostatic precipitator create an ionized atmosphere at high voltage, which charges the passing particles. Once charged the particles are pulled towards the collecting plates and separated from the off-gas stream (Narzroff & Alvarez-Cohen, 2001). The fine fraction of the dust, originating from the sinter feed after complete water evaporation took place, cannot be separated by electrostatic precipitation. The dust consists mainly of alkali chlorides and bag filters need to be employed to comply to emission standards (Remus et al., 2013).

3.2 MEROS process

The MEROS process, short for Maximized Emission Reduction of Sintering, is a dry-type off-gas cleaning process, which can be employed after electrostatic precipitation to treat the fine dust fraction. The process removes substances with countercurrent flow injection of additives and gas cleaning can be operated with either hydrated lime or sodium bicarbonate (Primetals Technologies Austria GmbH, 2020).

A desulfurization agent is added to the off-gas stream in countercurrent direction. The gas stream is then led to the conditioning reactor, where gas is cooled and moisturized to 90 to 100ºC by injecting a mist of water and air. This enhances the chemical reaction of binding and removing sulfur dioxide and acidic gas components. The cooled gas is then treated by pulse jet filtration. Dust and pollutants are trapped in high-performance fabrics, building a filter cake. Once the pressure drops due to a built-up filter cake, an air pulse activates, and the filter cake falls off the fabric into a dust collection vessel. To reduce additive costs and enhance gas cleaning efficiency a portion of the dust from pulse jet filtration is recycled into the off-gas stream after the conditioning reactor. The rest of the dust is stored in silos for landfilling or further treatment (Primetals Technologies Austria GmbH, 2020).

3.3 Effluent Standards

Effluent standards are regulatory standards used for wastewater discharge into receiving waters. Each parameter has its own standard set according to available technology in reducing said parameter. Effluent standards are a way to control water pollution and guarantee safe use of water (Ragas et al., 2005). There are national effluent standards, and in some countries, like Japan, see Table 2, local governments set their own standards as well, which are more stringent than the national standards.

Table 1 Effluent Standards in Austria, Japan and Korea

Parameter	Limit		
	Austria[1]	Japan[2]	Korea
COD (O2)	150 mg/l	160 mg/l	20 mg/l
BOD		160 mg/l	10 mg/l
TNb	45 mg/l	120 mg/l	20 mg/l
Suspended Solids	50 mg/l	200 mg/l	10 mg/l
pH	6.5-8.5	5.0-9.0	5.8-8.6
Ammonium	20 mg/l		
Arsenic		0.1 mg/l	0.25 mg/l
Cadmium	0.1 mg/l	0.03 mg/l	0.1 mg/l
Copper	0.5 mg/l	3.0 mg/l	3 mg/l
Dissolved Iron	2.0 mg/l	10 mg/l	10 mg/l
Dissolved Manganese		10 mg/l	10 mg/l
Fluoride	30 mg/l	15 mg/l	15 mg/l
Lead	0.5 mg/l	0.1 mg/l	0.5 mg/l
Mercury	0.005 mg/l	0.005 mg/l	0.005 mg/l
Nitrite	1.00 mg/l		
Phosphorus		16 mg/l	1 mg/l
Selenium		0.1 mg/l	
Sulfite	1.0 mg/l		
Total Chromium	0.5 mg/l	2 mg/l	2 mg/l
Zinc	1.0 mg/l	2 mg/l	5 mg/l

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[1] Verordnung des Bundesministers für Land- und Forstwirtschaft über die Begrenzung von Abwasseremissionen aus der Aufbereitung, Veredelung und Weiterverarbeitung von Eisenerzen sowie aus der Eisen- und Stahlherstellung und -verarbeitung 2019 (AEV Eisen – Metallindustrie). In: BGBl. II Nr. 345/1997 idF BGBl. II Nr. 128/2019

[2] (Ministry of the Envrionment Government of Japan, 2015)

Table 2 Effluent Standards of Local Governments in Japan, daily averages in parenthesis, unit: mg/l (Okada & Peterson, 2000)

Parameters	Kanagawa Prefecture								Shiga Prefecture		National effluent standards
	“A” area				“B” area		Coastal area				
	Lakes with water quality conservation		Other lakes								
	new	existing	new	existing	new	existing	new	existing	new	existing	
Health Items											
Cd & its compounds		ND	ND	0.05					0.01		0.1
CN compounds		0.5		0.5					0.1		1
Organic phosphorus compounds		ND	ND	0.2	0.2		0.2		ND		1
Pd and its compounds		0.05	0.05								0.1
Cr(VI) compounds		0.05	0.05						0.05		0.5
As & its compounds		0.01	0.01						0.05		0.1
F and its compounds		0.8	0.8						0.05		8 river & lake 15 coastal area
Living Environmen Items											
pH							5.8-8.6		6.0-8.5		5.8-8.6 river & lake 5.0-9.0 coastal area
BOD	5(3)	20(15)	15(10)	25(20)	25(20)	60(50)			15-120	20-120	160(120)
COD	5(3)	20(15)	15(10)	25(20)	25(20)	60(50)	25(20)	60(50)	15-120	20-120	160(120)
SS	15(5)	50(35)	35(20)	70(40)	70(40)	90(70)	70(40)	90(70)	60-150	60-150	200(150)
n-Hexane extract (mineral oil)	3	3	3						5		5
n-Hexane extract (animal fat & vegetable oil)	3	3	3	5	5	10	5	10	20		30
Phenols		0.005	0.005	0.05	0.5	0.5	0.5	0.5	1		5
Cu	1	1	1	1	1		1		1		3
Zn	1	1	1	1	1	3	1	3	1		5
Dissolved iron	0.3	0.3	0.3	1	3		3		10		10
Dissolved manganese	0.3	0.3	0.3	1	1	1	1	1	10		10
Cr		0.1	0.1	1					0.1		2
Number of coliform group (/cm³	(1000)								(3000)		(3000)

Effluent standards of these countries were chosen to demonstrate that success of a treatment in terms of meeting the effluent standards, depends on the country. In certain cases success of treatment also depends on the province, which might have stricter standards than the national standards.

3.4 Treatment Options

During extensive literature research a number of treatment options have been found for each parameter in need of treatment. As this thesis focused on reduction of carbon and nitrogen, the treatment options relevant for these parameters are explained in more detail.

3.4.1 Organic Carbon

3.4.1.1 Advanced Oxidation Processes

Advanced Oxidation Processes (AOP) use the formation of radical species to oxidize organic compounds and other substances in water (Gassie & Englehardt, 2017). The high reactivity of HO• drives the oxidation process and complete mineralization can be achieved (Andreozzi et al., 1999). The HO• radicals are non-selective, have a fast reaction rate and are therefore able to treat multiple contaminants at once (Vilhunen & Sillanpää, 2010), at normal temperature and pressure conditions (Tchobanoglous et al., 2002). There are several methods to produce HO• radicals, such as TiO_2/UV, hydrogen peroxide/UV, ozone/UV and Fenton reaction (Gassie & Englehardt, 2017). Studies of Chidambara Raj & Li Quen, 2005 and Cokay Catalkaya & Kargi, 2007 were done with industrial wastewater, with comparable TOC concentrations as the wastewater of this study. The chloride content in these studies is in a single-digit range of mg/l.

3.4.1.1.1 Hydrogen peroxide/UV

Hydrogen peroxide is injected into the water solution and irradiated with UV. During irradiation the peroxide reacts to hydroxyl radicals, as seen in Equation 1 (Gassie & Englehardt, 2017, Andreozzi et al., 1999). The wavelength of the UV device is significant. For hydrogen peroxide/UV treatment a wavelength within a range of 200 to 280 nm is most effective (Andreozzi et al., 1999, Tchobanoglous et al., 2002, Vilhunen & Sillanpää, 2010).

$$H_2O_2 - hv \rightarrow 2HO\bullet \qquad \text{Equation 1}$$

A single dose of hydrogen peroxide is more effective, than several doses spread out over the treatment process. The circulation rate is insignificant (Chidambara Raj & Li Quen, 2005). The treatment is dependent on pH of the water to be treated. Efficiency of photolysis of hydrogen peroxide increases in alkaline conditions and maximum TOC reduction is reached at pH 11 (Chidambara Raj & Li Quen, 2005, Cokay Catalkaya & Kargi, 2007). During oxidation the pH of the treated water decreases. The load of total suspended solids influences treatment, as particles scatter the light. If the amount of suspended solids is high, light is lost (Andreozzi et al., 1999), which increases the already high energy demand of the treatment (Gassie & Englehardt, 2017). TOC removal increases with increasing hydrogen peroxide concentration up to 50 mM/l. At higher concentrations hydrogen peroxide serves as free radical scavenger (Equation 2) and causes a decrease in free radical concentration. The TOC in this study was at 110 mg/l (Cokay Catalkaya & Kargi, 2007) which is comparable to the TOC range where this method was used.

$$HO\bullet + H_2O_2 \rightarrow OOH\bullet + H_2O \qquad \text{Equation 2}$$

Another free radical scavenger is bromide. Hydrogen peroxide based treatments lead to reduction of hypobromous acid and hypobromite to bromide, preventing formation of bromate (von Gunten & Oliveras, 1998).

3.4.1.1.2 Fenton reaction

The Fenton reaction is a reaction of hydrogen peroxide with iron ions to form free radicals (Equation 3) that oxidize organic and inorganic compounds (Pignatello et al., 2006).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \qquad \text{Equation 3}$$

Oxidation efficiency depends on: hydrogen peroxide concentration, Fe^{2+}/H_2O_2 ratio, pH, reaction time, initial concentration of pollutant and temperature (Barbusiński, 2009). Inhibitors of oxidation can be phosphate, sulfate, fluoride, bromide and chloride ions, depending on the concentration. Inhibition occurs due to precipitation of iron, scavenging of HO• and coordination to dissolved Fe(III) forming a less reactive complex.

Chloride and bromide ions inhibit reaction due to scavenging, as they are relatively weak ligands of Fe(III).

$$X = Cl, Br \qquad \text{Equation 4}$$
$$HO\bullet + X^- \leftrightarrow HOX\bullet^- \leftarrow H^+(-H_2O) \rightarrow X\bullet \leftarrow X^- \rightarrow X_2^-$$

In Equation 4 chloride and bromide ions are a limiting factor in the Fenton reaction, especially in water containing high concentrations of halide salts.

Sulfate and fluoride ions can inhibit the Fenton reaction as well. Even though they are poor HO• scavengers and complexes with Fe are soluble, they inhibit the reaction by reducing Fe(III) reactivity through coordination (Pignatello et al., 2006).

3.4.1.2 Adsorption

Activated carbon is used for removal of organic and inorganic compounds by accumulating substances in solution on their surfaces (Tchobanoglous et al., 2002). It has a high adsorption capacity and a high degree of surface reactivity, as well as mechanical strength and resistance to heat and radiation (Huang et al., 2018).

3.4.2 Nitrogen

Figure 1 shows the pH and temperature dependency of ammonium species: At low pH ammonium ions (NH_4^+) are present in the wastewater, at high pH the equilibrium shifts to favor ammonia (NH_3) (Equation 5).

$$NH_4^+ + OH^- \leftrightarrow H_2O + NH_3 \uparrow \qquad \text{Equation 5}$$

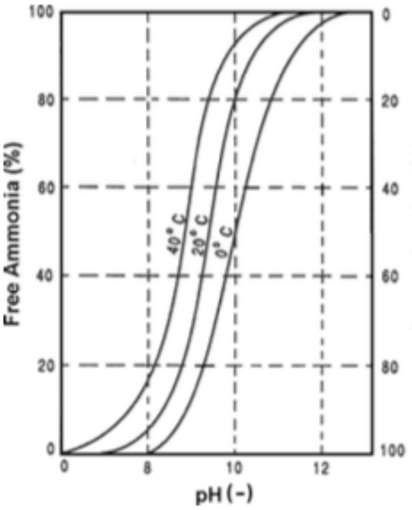


Figure 1 Free ammonia fraction as a function of temperature and pH (Capodaglio et al., 2015)

Depending on the treatment method pH needs to be adjusted to maintain the favorable ammonium species in the wastewater (Tchobanoglous et al., 2002).

3.4.2.1 Air Stripping

To remove ammonium-nitrogen with air stripping, the pH of the water needs to be approximately 11, as ammonia-nitrogen is removed via the gaseous form (Tchobanoglous et al., 2002). In general, the pH of the wastewater is adjusted, sprayed over a column packed with carriers to distribute the water for more air contact and air is introduced. The gaseous ammonia is then transferred out of the wastewater with the introduced air flow (Guštin & Marinšek-Logar, 2011).

The removal efficiency of air stripping depends on the pH, water and air temperature, size of facility and efficiency of air-water contact. With decreasing temperature, the amount of air required increases (Tchobanoglous et al., 2002) and the efficiency decreases (U.S. EPA, 2000). The air stripping method works well in the range of 10 to 100 mg/l NH_4-N, with higher concentrations other methods are suggested (U.S. EPA, 2000).

Different variations of air stripping are possible. The Jet Loop Reactor circulates treatment water and air to provide high specific interfacial areas for high mass and heat transfer without mechanical stirrers (Degermenci et al., 2012). Another variation is steam stripping, were steam with 95ºC is introduced instead of air. This is very efficient and due to the high temperature possible at pH 7. The method is very costly (Tchobanoglous et al., 2002). Closely related to this is vacuum thermal stripping, where a boiling temperature is reached at 65ºC due to the vacuum. This method is also very costly, similar to steam stripping (Ukwuani & Tao, 2016). Instead of conventionally heating the wastewater for air stripping, microwave radiation can be applied. Microwave radiation allows a high chemical reactivity and selectivity by specific thermal and radiation effects due to molecular level heating. Microwave radiation assisted air stripping has a 20-25% higher ammonia removal performance than conventionally heated air stripping (Ata et al., 2017). The downside to this treatment is the high amount of electricity needed for heating and additionally the glass of the treatment column needs to be replaced regularly due to the stress of microwave radiation. The treatment therefore has very high ongoing expenses (Lin et al., 2009).

3.4.2.2 Adsorption

Ion exchange processes are used to adsorb ammonium ions. The pH of the wastewater must be lower than 7 to ensure ammonium is present in ionized form. The ion exchange process is endothermic, therefore if the temperature is increased, the exchange capacity will increase as well (Demir et al., 2002). Adsorption occurs in pores, where negative charges are balanced and exchanged with positive charged cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) (Malekian et al., 2011), the exchange capacity varies depending on the cation presence (Demir et al., 2002).

Zeolithe is a very common adsorbent. It has a high ion-exchange capacity, high specific surface area, is inexpensive (Gupta et al., 2015) and has a great affinity for ammonium ions. In the study of Gupta et al., 2015 the NH_4-N concentration was between 20 and 300 mg/l depending on the trial. Ammonium ions replace Na^+, the ion-exchange capacity therefore increases with decreasing Na^+ concentration (Malekian et al., 2011). Additional to natural zeolithe, there are also synthetic zeolithes with improved adsorption capacity and removal efficiency, as well as a higher specific area and bigger total pore volume than natural zeolithe (Huang et al., 2018). Depending on the zeolithe the adsorption capacity is in a range of 5 to 300 mg/l NH_4-N (Huang et al., 2018).

Volcanic tuff can also be used as adsorbent for ion-exchange with ammonium. The tuff shows high selectivity towards ammonium ions and the presence of other cations (Cd^{2+}, Zn^{2+}, Ca^{2+}) does not diminish the adsorption capacity, which is similar to zeolithe (Marañón et al., 2006).

Two more adsorbents are available for ammonium adsorption: Activated carbon, which has a high adsorption capacity and high degree of surface reactivity and carbon nano tubes, which are superior adsorbents but very expensive (Huang et al., 2018).

3.4.2.3 Precipitation

Ammonium ions are precipitated as struvite, also called MAP (Magnesium Ammonium Phosphate). The product of Equation 6 has low water solubility. The reaction is controlled by pH and temperature and influenced by impurities (Capodaglio et al., 2015).

$$Mg^{2+} + PO_4^{3+} + NH_4^+ + \ 6H_2O \ \rightarrow MgNH_4PO_4 \bullet 6H_2O \ \downarrow \qquad \text{Equation 6}$$

Magnesium chloride, which is expensive, is most commonly used in the reaction (Capodaglio et al., 2015). To reuse MAP, the ammonium ion is eliminated by heating (Equation 7) and the resulting magnesium hydrogen phosphate can be reused to remove ammonia (Equation 8) (Sugiyama et al., 2009). The study of Sugiyama et al., 2009 was done in industrial wastewater with a concentration of 2900 mg/l NH_4-N.

$$MgNH_4PO_4 \ - hv \rightarrow NH_3 + MgHPO_4 \qquad \text{Equation 7}$$

$$MgHPO_4 + NH_3 \ \rightarrow MgNH_4PO_4 \qquad \text{Equation 8}$$

3.4.3 Fluoride

Typical fluoride removal techniques are precipitation and adsorption. Most commonly, lime is used to precipitate fluoride, although the pH reached during treatment is quite high. A more elegant version of precipitation is a limestone reactor. It is made up out of two columns: in the first column lime is dissolved by introduced carbon dioxide (Equation 9), to precipitate fluoride as calcium fluoride (Equation 10).

$$CaCO_3 + H_2O + CO_2 \ \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{Equation 9}$$

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \qquad \text{Equation 10}$$

In column two the calcite is precipitated. The second column is not necessary for fluoride removal (Reardon & Wang, 2000). The concentrations of fluoride and sodium are 10 mg/l and 15 mg/l respectively.

Adsorption methods remove fluoride by surface chemical reaction or ion exchange. These methods need regular column regeneration once adsorption capacity has been reached. The traditional approach in adsorption media is activated alumina, although zeolithe and volcanic ash have also been used (Reardon & Wang, 2000). Activated alumina is efficient in a treatment range of 1 to 9 mg/l and a pH of 7. Above pH 7 adsorption rates are low, as silicates and hydroxyl ions compete with fluoride ions for alumina exchange sites (Ghorai & Pant, 2005).

Another method of fluoride removal is electrocoagulation, the creation of metallic hydroxide flocs in the wastewater by electro-dissolution of soluble anodes (anodized aluminum), which are then precipitated (Khatibikamal et al., 2010). The study was done in industrial wastewater, the fluoride concentration was in the single digit range of mg/l, chloride and sodium concentrations were 220 mg/l and 130 mg/l respectively.

3.4.4 Heavy Metals

Precipitation of heavy metals, such as arsenic, barium, cadmium, copper, mercury, nickel, selenium and zinc, through addition of lime or sodium hydroxide to a pH of minimum solubility is very common in wastewater treatment. The pH of minimum solubility varies for different metals and depending on the constituents in the wastewater (Tchobanoglous et al., 2002), generally a pH of approximately 9,5 is efficient. Additionally, sulfides are used for precipitation, as well as polymers for coagulation and subsequent sedimentation (Charermtanyarak, 1999). Charermtanyarak‘s study used lime followed by polymer to precipitate zinc, cadmium, manganese, the concentrations were 450 mg/l, 150 mg/l and 3150 mg/l respectively.

Zeolithes, especially clinoptilolite can also be used to adsorb heavy metals and are a low-cost option (Tchobanoglous et al., 2002).

3.4.5 Bromide

During oxidation bromide acts as a free radical scavenger and can further accelerate the transformation of undesired compounds. Treatment with hydrogen peroxide reduces hypobromide to bromide and therefore inhibits oxidation to bromate (a carcinogenic substance) (von Gunten & Oliveras, 1998). Treatment methods are reverse osmosis, nanofiltration, electrolysis and adsorption techniques like ion exchange resins (Watson et al., 2012).

4. Material and Methods

The master thesis can be separated into two phases: first the preliminary testing and treatment with Pilot Plant 2019 (PP19) and second, treatment with Pilot Plant 2020 (PP20).

The following chapters give an overview of the schedule and the analysis methods used to determine the success of treatment, as well as outline the two phases in more detail.

4.1 Material

The MEROS process residue was supplied by an Austrian sinter plant. The dust was very fine and was stored in closable plastic barrels, at the Technikum (BOKU Muthgasse).

4.2 Schedule

The schedule is outlined in Table 3.

Table 3 Time schedule

	2019			2020						
	Oct.	Nov.	Dec.	Jan.	Feb.	…	Sept.	Oct.	Nov.	Dec.
Preliminary Tests (Laboratory)	■	■								
Fenton process trials (Laboratory)	■	■								
PP19 planning	■									
PP19 construction	■	■								
PP19 safety inspection		■								
PP19 trial runs			■	■	■					
PP19 sample analysis			■	■	■					
Literature study						■				
PP20 planning							■			
PP20 construction							■			
PP20 Air Stripping trials								■		
PP20 AOP trials									■	■
PP20 sample analysis								■	■	■

4.3 Analytical procedures

Preliminary tests were done at the laboratory to assess the composition of the MEROS dust residue. The amount of filterable substances was evaluated, as well as inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) were employed. The analyses were done by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG).

Several different parameters were analyzed in the samples taken from both Pilot Plants. As the focus was on reducing carbon and nitrogen concentrations the analyses were centered on TOC, DOC and TNb measurements, also done by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG). Further measurements of COD, NO_3-N and NH_4-N were done with a Hach Photometer. H_2O_2 was measured with the Supelco MQuant Peroxide Test and dissolved iron was measured with the Supelco MQuant Iron Test. Lastly COD was also measured according to JIS (Japanese Industry Standard).

4.3.1 Filterable Substances

The amount of filterable substances was measured according to SOP: 5 g of the dust were dissolved in 50 ml of water and stirred for two hours. About 10 ml of the leachate were filtered through a dried and weighted 0.45 µm filter with pressure filtration. Filtration was repeated 6 times with new filters. The filters were then dried and weighted. The difference between the empty filter and the filter after filtration was the weight of the filterable substances. The average in percent was the percentage of filterable substances.

4.3.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

To gain better understanding about the heavy metals in the dust, the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG) analyzed the dust with inductively coupled plasma mass spectrometry (Elan DRC-e ICP-MS). Figure 2 shows a schematic ICP-MS instrument. The plasma is inductively heated gas (Argon) by an electromagnetic coil. The sample is introduced into the plasma which converts the atoms of the elements in the sample to ions. The ions are separated by mass/charge ratio and detected by the mass spectrometer. The detector detects the particles based on charge and the signal intensity is directly proportional to the concentration of the elements in the sample.

Limit of quantification (LOQ) is shown in Table 17 in the Appendix. The analysis method is based on DIN EN ISO 17294-2 (E 29): 2004 and DIN EN ISO 17294-1 (E 36): 2003.

The dust was analyzed for the total concentration and the dissolved concentration of heavy metals with ICP-MS. The sample size was 100 g of the dust per 1000 ml water, mixed for 2 hours, filtered with 0.45 µm and acidified to pH 2.7 with HNO_3 suprapur.

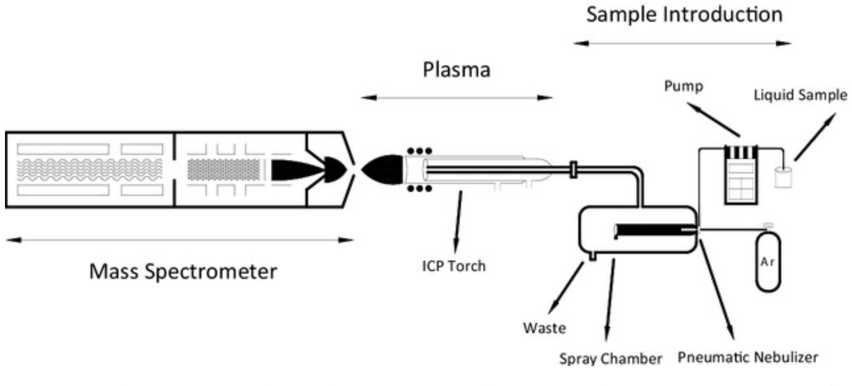


Figure 2 Schematic ICP-MS Instrument (Kashani & Mastaghimi, 2010)

4.3.3 Ion Chromatography (IC)

Ion Chromatography is the separation and quantitative analysis of anions and cations. The analysis was done by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG) with a DIONEX ICS 3000. The ions in the sample are carried through the system by an eluent and the different ions are separated in a column packed with ion exchange resin. The method is based on EN ISO 10304-1 (D20): 2009, , EN ISO 10304-3 (D22): 1997 and

EN ISO 10304-1 (D19): 1995 for anions and EN ISO 14911 (E34): 1999 for cations. Limit of quantification is shown in Table 18 in the Appendix.

4.3.4 TOC, DOC and TNb

The filtered samples (0.45 µm membrane filters) from the pilot plants were analyzed for TOC/DOC and TNb with the instrument SHIMADZU TOC V by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG).

TOC and TNb are analyzed simultaneously. To prepare the sample it must be acidified to a pH below 2 to remove all inorganic carbon, in this case H_2SO_4 96% was used. Pre-acidification with H_2SO_4 96% was necessary to ensure a pH below 2, as the samples had a high pH and puffer capacity. The samples are then sparged with synthetic air. The carbon remaining is organic. The sample is then combusted at high temperature (720ºC) in an oxygen-rich environment. The resulting CO_2, product of the organic carbon combustion, is measured with a NDIR sensor (nondispersive infrared sensor). The bonded nitrogen is converted to NO due to the combustion and further reacts to NO_2. NO_2 emits photons, which are measured with a chemiluminescence detector. The combustion products are transported to the detectors by a carrier gas. First the CO_2 is measured by the NDIR and then the sample is transported further to measure the NO_2 by the chemiluminescence detector, as schematically shown in Figure 3. Evaluation is then done with the saved calibration curves. Results are given as the average of the duplicate determination and diluted samples need to be multiplied by their dilution.

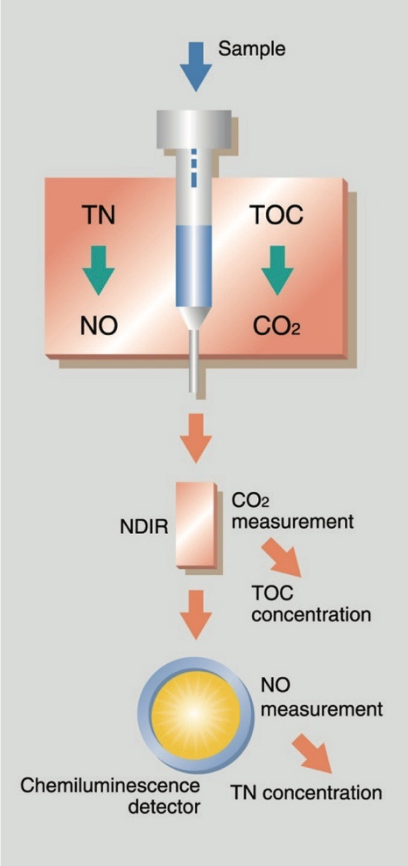


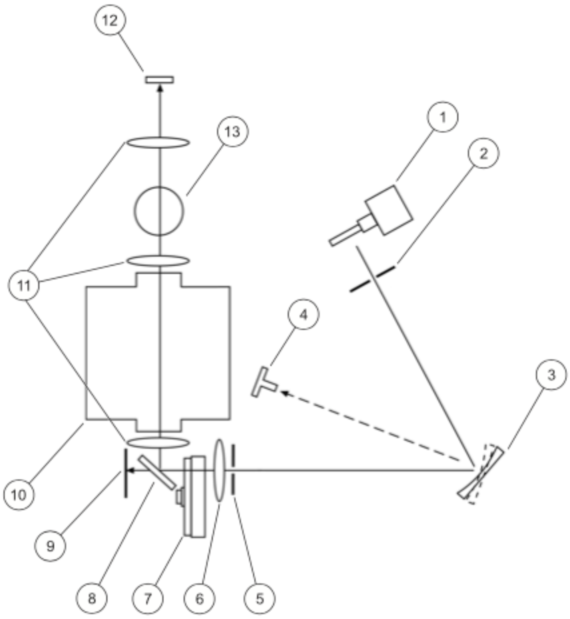
Figure 3 Simultaneous TOC and TNb measurement (Shimadzu, No. SCA-130-503)

DOC samples are filtered with 0.45 µm before combustion, whereas TOC samples are measured as they are. For the samples of the pilot plants filtration with 0.45µm membrane filters took place before analysis. The analysis on the SHIMADZU TOC V was done for TOC but actually measures the DOC value of the samples.

4.3.5 VIS spectrophotometry

The samples were analyzed for COD, NO_3-N and NH_4-N with the Hach DR 3900 and their respective Hach LCK Cuvette tests.

The DR 3900 is a VIS spectrophotometer with a wavelength range of 320 to 1100nm (Hach Company, 2020). The VIS spectrophotometer works according to the principle of light absorbance. Absorbance is the amount of absorbed light at a certain wavelength. It depends on the concentration and path length of light through the cuvette. A light source, in this case a halogen lamp (1), transmits light to the grating (3), which splits the light into different wavelengths which are then transmitted through the sample (13). The transmitted light is measured with a reading element (12), which measures the intensity of the light transmitted and compares it to a reference measurement of the same light source.



1	Halogen lamp	**8**	Splitter mirror
2	Entrance slit	**9**	Reference element
3	Grating	**10**	Cell compartment (2) for rectangular cells
4	Grating angle indicator	**11**	Lens
5	Exit slit	**12**	Reading element
6	Lens	**13**	Cell compartment (1) for round cells
7	Filter wheel		

Figure 4 Beam path of DR 3900 (Hach Company, 2020)

The samples needed to be diluted, as most samples of the pilot plants had intrinsic color which disturbed the measurement and additionally had very high expected substance concentrations, which were outside the measurement range of the LCK cuvettes.

4.3.6 COD

To measure COD, LCK 1014 cuvettes were chosen, as they are applicable for samples containing up to 4000 mg/l chloride. The measuring range is 100 – 2000 mg/l O_2. The analysis according to DIN 38409-H41-H44 works as follows: oxidizable substances react with potassium dichromate using silver sulfate as catalyst, the green coloring of Cr^{3+} is analyzed. Chloride is masked with mercury sulfate (Hach Lange GmbH, 2019).

4.3.6.1 Procedure

The samples were prepared by filtering with a 0.45 µm membrane filter. The samples were then diluted in Erlenmayer flasks. The COD test cuvettes were shaken to bring the sediment into suspension and the sample was pipetted into the cuvette. The cuvette was shaken to mix sample and reagents and then heated. After cooling the cuvette was measured with the DR 3900.

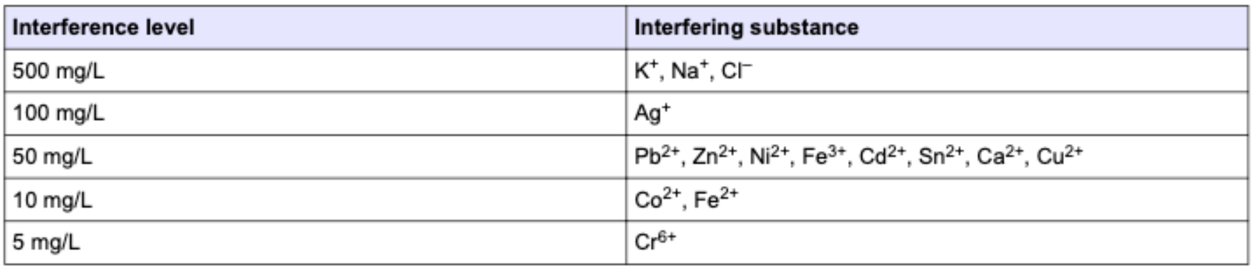
4.3.7 NO_3-N

To measure NO_3-N, LCK 339 Nitrate cuvettes were used. The measuring range is 0.23-13.5 mg/l NO_3-N or 1-60 mg/l NO_3. Nitrate ions react with 2,6-dimethylphenol to form 4-nitro-2,6-dimethylphenol in solutions containing sulfuric and phosphoric acids. The pH of the sample needs to be between 3 and 10 (Hach Lange GmbH, 2019).

4.3.7.1 Procedure

To prepare samples they were filtered with a 0.45 µm membrane filter, as the samples contained a high amount of solid substances. The samples were diluted 1:10, 1:50 and 1:100 to reduce eventual interferences and matrix effects and also to carry out a plausibility check. Then the sample and a reagent were pipetted into the cuvette and inverted to mix. After 15 min the cuvette was measured with the DR 3990.

Table 4 Interference of individual substances against given concentrations (Hach Lange GmbH, 2019)



Interference level	Interfering substance
500 mg/L	K^+, Na^+, Cl^-
100 mg/L	Ag^+
50 mg/L	Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Sn^{2+}, Ca^{2+}, Cu^{2+}
10 mg/L	Co^{2+}, Fe^{2+}
5 mg/L	Cr^{6+}

Dilution of the sample was important, as it was known that the sample contains a high amount of other substances and the cumulative effects and influence of other ions had not been determined. By diluting the sample matrix effects might be lessened or avoided and the concentration of the individual interfering substances was reduced. Dilution was further important, due to the fact that high COD concentrations (>200 mg/l) cause changes in color (Hach Lange GmbH, 2019). Especially potassium, sodium and chloride ions made dilution necessary for the pilot plant samples, as the concentrations of these ions were 3-4 times higher than the interference level given in Table 4.

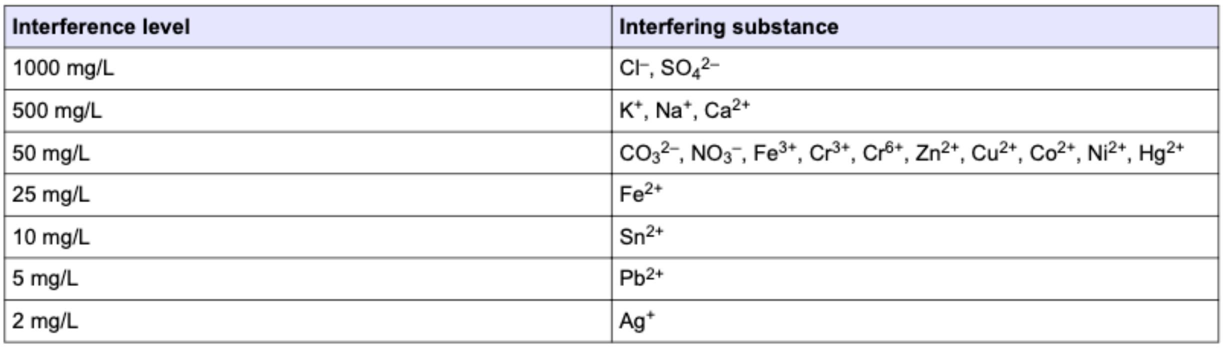
4.3.8 NH_4-N

To measure NH_4-N, LCK 303 Ammonium cuvettes were used. The measuring range is 2 to 47 mg/l NH_4-N or 2.5 to 60.0 mg/l NH_4. The ammonium ions in the sample react at pH 12.6 with hypochlorite ions and salicylate ions to form indophenol blue with sodium nitroprusside as a catalyst (Hach Lange GmbH, 2019). The pH of the sample needs to be between 4 and 9.

4.3.8.1 Procedure

As the sample contained a high amount of other substances, the samples were diluted to reduce eventual interferences and matrix effects and also to carry out a plausibility check. If needed the pH of the samples was adjusted to fit within the needed range. The cuvette was prepared by adding the reagent and then adding the sample. After shaking to mix sample and reagent and a 15 min waiting time the sample was measured with the DR 3900.

Table 5 Interference of individual substances against given concentrations (Hach Lange GmbH, 2019)



Interference level	Interfering substance
1000 mg/L	Cl^-, SO_4^{2-}
500 mg/L	K^+, Na^+, Ca^{2+}
50 mg/L	CO_3^{2-}, NO_3^-, Fe^{3+}, Cr^{3+}, Cr^{6+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}
25 mg/L	Fe^{2+}
10 mg/L	Sn^{2+}
5 mg/L	Pb^{2+}
2 mg/L	Ag^+

The samples of the pilot plants contained nitrate, sodium, potassium and chloride above the interference level. Dilution of the samples was therefore important. It was also known that the sample contained a high amount of other substances and the cumulative effects and influence of other ions had not been determined. By diluting the sample matrix effects might be lessened or avoided and the concentration of the individual interfering substances was reduced.

4.3.9 H_2O_2 test method

The samples were analyzed for H_2O_2 with the Supelco MQuant Peroxide Test. The test strips have a measuring range of 1 – 3 – 10 – 30 – 100 mg/l H_2O_2 with a color scale graduation. The strips were immersed in the sample for 1 second and color could be determined after 5 seconds. The color is an oxidation product where the peroxidase transfers peroxide oxygen to an organic redox indicator. The pH of the sample must be in the range of 2 -12, no pH adjustments were needed for analysis.

4.3.10 Fe-test method

Samples were analyzed for bivalent and trivalent dissolved iron with the Supelco MQuant Iron Test. The iron concentration is measured via color comparison, as the iron ions in the sample react with the testing substance containing a triazine derivative in a thioglycolate-buffered medium to form a red-violet complex. The measuring range is 0.2 - 0.4 – 0.6 - 0.8 – 1.0 – 1.3 – 1.6 – 2.0 – 2.5 mg/l Fe. The pH must be in the range of 1 – 10, and turbid samples need to be filtered.

5 ml of the sample were put into the test tubes, the blank was left as it is, 3 drops of reagent Fe-1 were added to the measurement sample. The sample plus solution were mixed and left for 3 min. Colors were compared with the color card until closest color match between blank and measurement sample was reached.

4.3.11 COD according to JIS

COD according to JIS (Japanese Industry Standard) was measured with a titrimetric approach. This analysis method was used for samples from preliminary laboratory tests and samples of Pilot Plant 2019.

The oxygen demand (mg/l O) is expressed by the amount of oxygen corresponding to the amount of potassium permanganate consumed (Japanese Standards Association, 2016).

4.3.11.1 Reagents

- H_2SO_4 30%
- $AgNO_3$ (200 g/l)
- $Na_2C_2O_4$ (12.5 mmol/l)
- $KMnO_4$ (5 mmol/l)

To prepare the $KMnO_4$ solution 0.8 g of potassium permanganate were dissolved in 1050 ml of water and then gently boiled for one to two hours. The solution needed to stand overnight and was then filtered with a G4 glass filter. The filtrate should be preserved in a colored glass bottle.

4.3.11.2 Procedure

A suitable amount of sample needed to be added to 300 ml Erlenmayer flask. The amount of sample depended on preliminary testing of the amount of COD in the sample. Water was added to make 100 ml. Then 10 ml of sulfuric acid, 10 ml of silver nitrate solution and 10 ml of potassium permanganate solution were added whilst shaking. The flasks were then put in boiling water for 30 min. After the water bath 10 ml of sodium oxalate solution were added and the solution was shaken until the reaction was complete. Potassium permanganate was then titrated into the solution until the solution developed a faint red color. The whole process was also done with 100 ml of water to determine factor b of Equation 11.

4.3.11.3 Calculation

$$COD = (a - b) * f * \frac{1000}{V} * 0.2$$

Equation 11

COD	oxygen demand by potassium permanganate at 100ºC (mg/l O)
a	volume of potassium permanganate required for titration (ml)
b	volume of potassium permanganate required for titration of 100 ml of water (ml)
f	factor of potassium permanganate (gained from standardization procedure outlined in JIS)
V	volume of sample (ml)
0.2	mass of oxygen corresponding to 1 ml of potassium permanganate

4.4 Pilot Plant 2019

Pilot Plant 2019 (PP19) was built in the technical hall of the Institute of Sanitary Engineering and Water Pollution Control (SIG) at Muthgasse, Vienna. PP19 ran batch trials to test the performance of the given industrial wastewater treatment process.

4.4.1 Installation

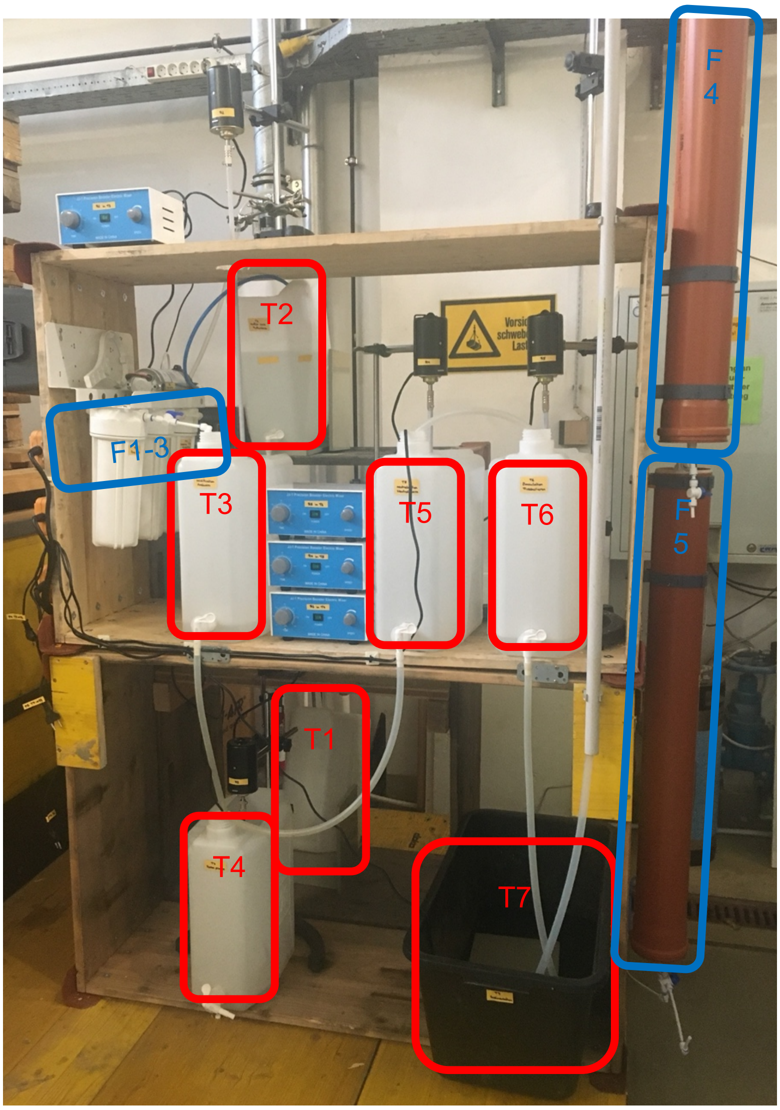


Figure 5 Pilot Plant 2019

The experimental setup is made up of:

- 6 PE tanks of 20 l each (T1-6)
- 1 PE basin of 60 l (T7)
- 3 cartridge filters (TECNOPLASTIC) (F1-3)
- 2 filter columns (F4&5)
- 5 stirrers
- 1 peristaltic pump (1 l/min) (P1)
- 1 membrane pump (2 l/min) (P2)
- 3 aquarium pumps (5 l/min) (P3-5)

For the schematic drawing of PP19 see Appendix, Figure 60.

4.4.1.1 Hose Connections

The hoses connecting the individual tanks were silicone with a diameter of 6mm except for the hose connections from F1-3 and F3 to T3 which were PE with a diameter of ¼ inch due to the hose screw connections used on the filter. The hose screw connections used were PE with a ¼ inch diameter.

4.4.1.2 Filters

F1 was a stainless steel filter with a mesh size of 155 µm wrapped with construction fleece for a slightly tighter mesh of 120 µm.

F2 and F3 used woven filters, size 20 µm (TECNOPLASTIC).

F4 was a sand filter, filled with sand (0.4-0.8 mm) constrained at top and bottom with a construction fleece (120 µm) fixed with a tension ring to prevent washing out, with gravel (5-8 mm) above and below (Figure 6). To fill the filter, 2 kg of gravel and 4.9 kg of sand were used.

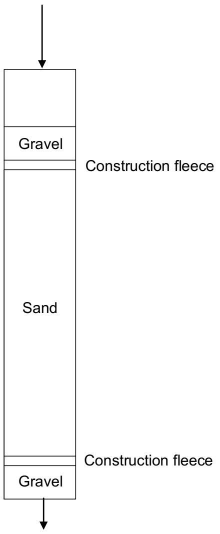


Figure 6 Schematic drawing of sandfilter (F4)

F5 was an activated carbon filter. Donau Chemie activated carbon XC30 provided by the company Donau Chemie was used to set up the filter. The activated carbon filter column was 305 mm high and was filled with 1.2 kg of activated carbon.

Filter columns F4 and F5 both had a diameter of 200 mm.

4.4.2 Procedure

Treatment of the dust was done in batches. First a leachate of 1 kg dust and 9.7 kg tap water was prepared. This dissolved 90% of the dust (T1). Then part of the particles of the leachate were sedimented in the buffer tank (T2) to reduce the particle load. To further clarify the leachate it was pumped through 3 column filters with a membrane pump. The first filter was a coarse 155 µm filter wrapped with construction fleece (F1) to tighten the mesh, the second and third were 20 µm woven filters (F2&3). The leachate was then acidified to pH 2.7 with sulfuric acid (T3), to prepare for the Fenton Process where $FeSO_4$ and H_2O_2 were added to lower the carbon concentration (T4). After the Fenton Process the leachate was alkalified to pH 9 with sodium hydroxide to precipitate heavy metals (T5). Organic sulfide was added to further increase the precipitation of metals and lastly anionic polymer was added to flocculate small particles to decrease sedimentation time (T6). After sedimentation (T7) the leachate was at first filtered through the sand filter (F4) and then through the activated carbon filter (F5). Sulfuric acid was added to attain a pH of 7. Working procedure of Pilot Plant 2019 with description, time, chemicals used and measurements applied follow in Table 6 and Table 8.

Table 6 Equipment and procedure of Pilot Plant 2019

Device	Description	Mixer Nr.	Residence time	Chemicals added	Measurement
T1	Leachate preparation	1	1h	-	-
P1	Pump	-	-	-	-
T2	Buffer tank	-	35min	-	-
P2	Membrane pump	-	-	-	-
F1	Coarse filter 155µm	-	-	-	-
F2	Fine filter 20µm	-	-	-	-
F3	Fine filter 20µm	-	-	-	-
T3	Acidification	2	35min	H_2SO_4	pH
T4	Fenton process	3	2h	$FeSO_4$ H_2O_2	ORP
P3	Pump	-	-	-	-
T5	Alkalinization	4	20min	NaOH	pH
P4	Pump	-	-	-	-
T6	Flocculation	5	20min 20min	Organic Sulfide Anionic Polymer	-
T7	Sedimentation	-	overnight	-	-
P5	Pump	-	-	-	-
F4	Sand filter	-		-	-
F5	Activated carbon filter	-		-	-

T	tank
P	pump
F	filter

4.4.2.1 Leachate Preparation

To treat the dust, it was first dissolved in water to create a treatable leachate. For this 1 kg of dust was added, while stirring continuously, to 9.7 kg of water in T1 (Figure 7) to give a 1:10 solution. To transfer the loose dust, one must wear a disposable coverall, gloves and a full protection breathing mask with a particle filter of FFP3, to avoid any contact with the dust. These safety precautions were taken, as the dust is an irritant and toxic by inhalation.

The value of 9.7 kg water was determined by experiments with a 1:10 solution. For the experiment 10 g of the dust were added to a volumetric flask and filled up with water until it reached the 1 l mark. This was done for ease in weight correction.

Figure 7 Creation of leachate (T1)

4.4.2.2 Filtration

The woven 20 µm filters were replaced very frequently as they clogged easily due to the high amount of fine particles caught (Figure 8). In case of clogging, the pressure in the filter candle got too high, the filter was compressed (Figure 9) and the leachate was pushed out of the filter through the screw connection. To avoid this issue, the filters were replaced after filtration of 20 l of leachate.

Figure 8 used 20 µm woven filter

Figure 9 compressed 20 µm woven filter

4.4.2.3 Acidification

To prepare the leachate for the Fenton Process, the water was acidified with H_2SO_4 30% until it reached pH 2.7. A WTW Microprocessor pH Meter "pH 196" with a pH probe was used to continuously measure the pH. The pH meter was calibrated weekly to ensure correct data, which was done with two buffer solutions, with pH 4 and pH 7.

4.4.2.4 Fenton Process

The Fenton Process was used to lower the carbon concentration of the leachate. It was chosen due to the relative ease in handling the reagents and the avoidance of bromate formation during treatment. Treatment with ozone was not possible due to the risk of bromate formation during treatment.

$FeSO_4$ and H_2O_2 were added to the leachate and stirred for 2 hours. First the total amount of $FeSO_4$ was added and then the calculated H_2O_2. The oxidation reduction potential (ORP) was measured with a WTW Microprocessor pH Meter "pH 196" and an ORP probe. ORP values were monitored during the treatment process and adjusted to a desired value by adding H_2O_2 to the leachate, depending on trial run, for an optimal treatment. The H_2O_2 concentration was tested with a Supelco MQuant Peroxide Test to gauge if there was a surplus of H_2O_2. If no surplus was present, more H_2O_2 was added to adjust the ORP value. The progression of ORP values was documented. At the end of the treatment another H_2O_2 test was done to assess if any H_2O_2 was left after treatment, as leftover H_2O_2 falsified the result of the COD analysis according to JIS (more in chapter 4.5.4).

$FeSO_4$ and H_2O_2 concentrations were calculated for each trial run and adjusted to evaluate the most efficient combination of concentrations.

4.4.2.5 Alkalinization

After the Fenton Process treatment step the pH of the leachate was at approximately 2. To precipitate the heavy metals in the leachate the pH was raised to pH 9 using NaOH. The pH was measured with a WTW Microprocessor pH Meter "pH 196" with a pH probe. NaOH was added until pH 9 was reached and stable for 5 minutes. The amount of NaOH was recorded and included in further substance calculations.

4.4.2.6 Flocculation

For a further increase in metal precipitation organic sulfide 20% (SANCELER ES-20, sodium diethyldithiocarbamate) with a concentration of 0.1 g/l was added to the leachate and stirred for 20 min.

To increase particle size and therefore the speed of sedimentation, the leachate was flocculated with an anionic polymer 0.1% (Himoloc V-330) with a concentration of 2 ml/l. The leachate was then stirred for another 20 min.

4.4.3 Sampling

For PP19 samples were taken at several points in treatment to gauge the effectiveness of the individual treatment steps. 400 ml of sample were taken after the following treatment steps:

1. Acidification
2. Fenton Process
3. Flocculation
4. Sand Filter
5. Activated Carbon Filter

The samples were analyzed for the parameters: DOC, TOC, TNb, COD (JIS), NO_3-N, NH_4-N and H_2O_2. The samples were filtrated with pressure filtration through 0.45 µm. See

Table 7 below for details.

Table 7 Sample description and parameters measured for individual treatment steps

Treatment step	Vessel	Sample description	Parameters
Acidification	T3	AV I	DOC, TOC, TNb, COD (JIS), NO_3-N, NH_4-N
Fenton Process	T4	AV II	DOC, TOC, TNb, H_2O_2
Flocculation	T6	AV III	DOC, TOC, TNb
Sand Filter	F4	AV IV	DOC, TOC, TNb, NO_3-N, NH_4-N
Activated Carbon Filter	F5	AV V	DOC, TOC, TNb, COD (JIS), NO_3-N, NH_4-N, dissolved Fe
Activated Carbon Filter pH 7		AV VI	DOC, TOC, TNb, COD (JIS)

Figure 11 unfiltered samples I to VI of trial run 5

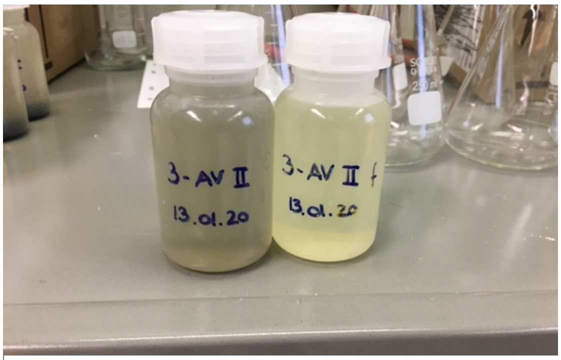


Figure 10 Sample II of trial run 3, left: unfiltered, right: filtered

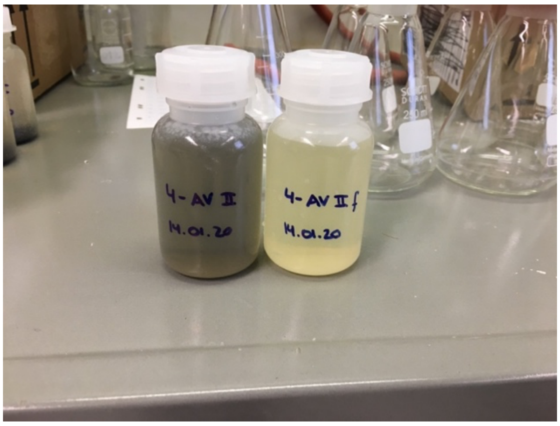


Figure 12 Sample II of trial run 4, left: unfiltered, right: filtered

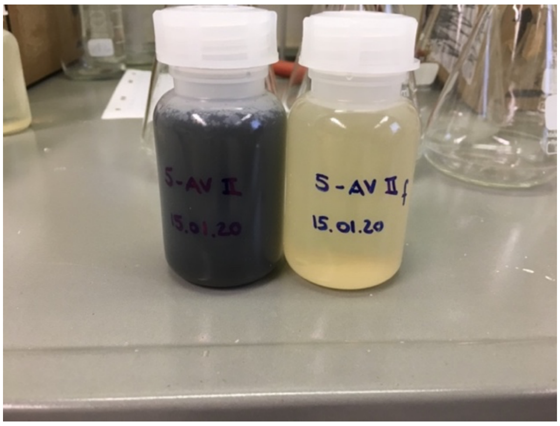


Figure 13 Sample II of trial run 5, left: unfiltered, right: filtered

4.4.4 Trial runs in Pilot Plant 2019

Table 8 gives all substance concentrations and additions used in the individual trial runs. Concentrations in ml were calculated according to the amount of leachate. H_2O_2 33% adjusted gives the amount of initial H_2O_2 added to the leachate plus H_2O_2 added to adjust to the desired ORP value. H_2O_2 tests were done to determine if there is surplus H_2O_2.

Trial run 1 is not further explained as it was discarded due to improper dilution of the dust.

Table 8 Substance concentrations of chemicals used in trial runs

Trial run	**dust [kg]**	**Amount of leachate [l]**	**$FeSO_4$ [mg/l]**	**H_2O_2 [mg/l]**	**H_2SO_4 30% [ml]**	**$FeSO_4$ 20% [ml]**	**H_2O_2 33% initial [ml]**	**H_2O_2 33% adjusted [ml]**	**NaOH 8M [ml]**	**org. sulfide [ml]**	**anionic polymer [ml]**
2	1	10	0.07	1.2	84	3.54	48.86	62.50	102.5	19.54	0.97
3	1	10	1.2	0.7	62	57.97	19.48	23.14	74.5	0.94	18.83
4	1	10	0.3	0.2	68	14.50	42.24	79.24	112.5	0.94	18.88
5	1	10	1.2	0.7	69	58.01	18.42	44.47	119.0	0.95	18.98
6	1	10	1.2	0.7	63	55.58	17.65	30.15	80.0	0.86	17.26
7	1	10	1.2	1.2	68	58.01	31.58	31.58	94.0	0.95	18.91
8	1	10	1.2	1.2	70	58.02	31.58	37.58	83.3	0.94	18.85

4.5 Pilot Plant 2020

Same as PP19, Pilot Plant 2020 (PP20) was built in the technical hall of the Institute of Sanitary Engineering and Water Pollution Control (SIG) at Muthgasse, Vienna. PP20 was a newly designed pilot plant, mostly built of reused parts from PP19. PP20 was designed to be able to operate continuously, due to time constraints, only batch trials were performed, operating only the air stripping column and the AOP setup (UV device, T3&4).

4.5.1 Installation

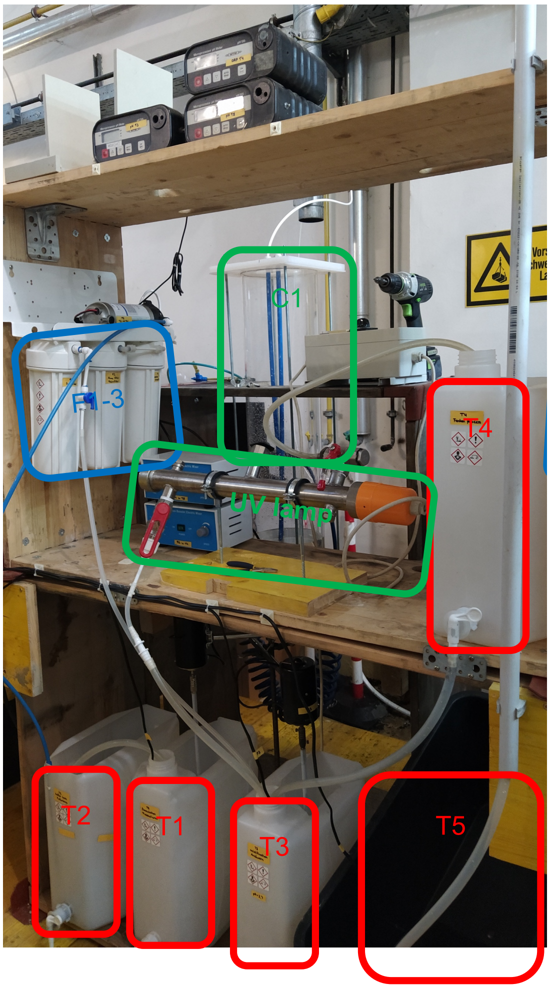


Figure 14 Pilot Plant 2020

The experimental setup was made up of:

- 4 PE tanks of 20 l each (T1-4)
- 1 PE basin of 60 l (T5)
- 3 cartridge filters (F1-3)
- 2 filter columns (F4&5)
- 2 stirrers
- 1 membrane pump (2 l/min) (P2)
- 3 aquarium pumps (5 l/min) (P1,3&5)
- 1 air stripping column (C1)
- 1 glass bottle of 4 l (B1)
- 1 UV lamp 254 nm

For the schematic drawing of PP20 see Appendix, Figure 61.

Hose connections, screws and filters are of the same specification as PP19.

4.5.1.1 Air Stripping Column

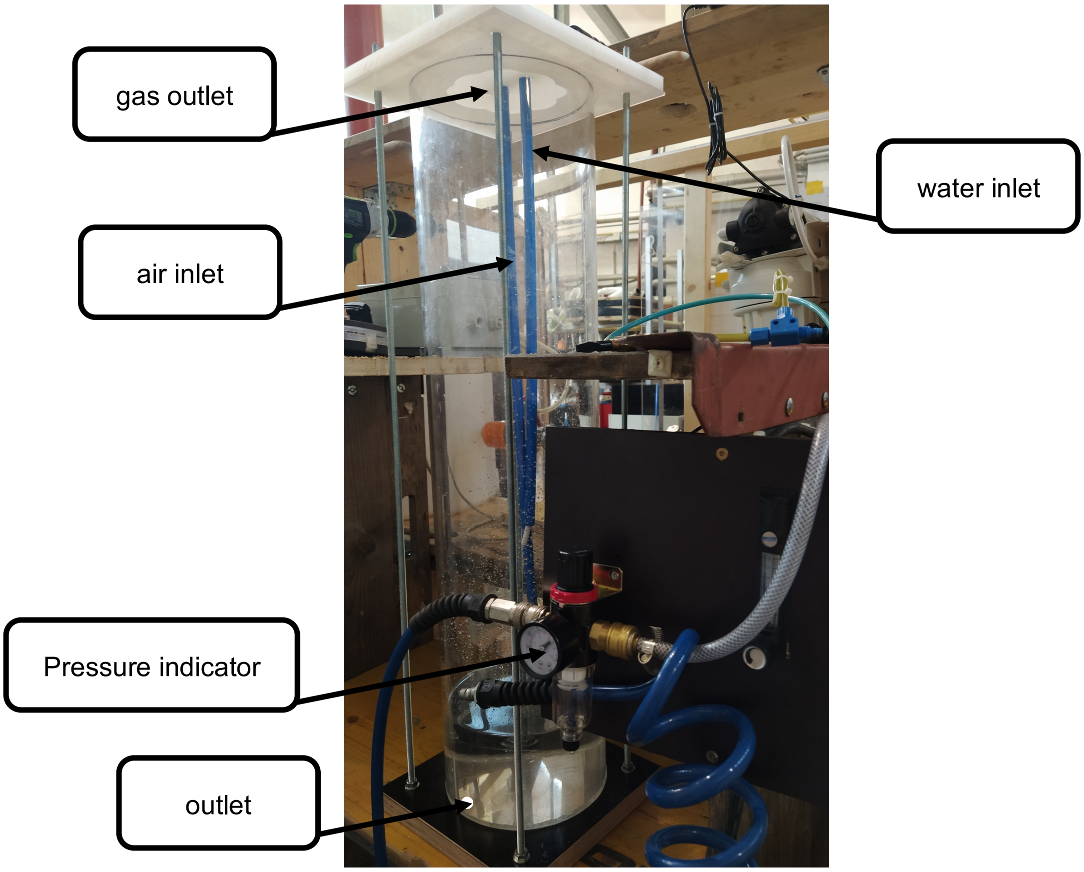


Figure 15 Air Stripping Column (C1)

The air stripping column (Figure 15) consisted of a 900 mm high Plexiglas column with a diameter of 190 mm. It was closed with a PPE plate, with a thickness of 20 mm, that was connected to the wooden plate at the bottom of the column via threaded rods. The lid could be secured via four wing nuts at the top. To ensure gas tightness of the vessel a silicone mat (3 mm) was placed between the top plate and the rim of the column. At the bottom of the column there was an outlet to release the treated leachate into another tank (T1). All screw connections were plastic with a ¼ inch diameter. The top plate had a gas outlet, that lead into a 4 l glass bottle (B1), a water inlet that was supplied by a water main, supplying cold water only, and an air inlet that supplied pressurized air. The pressurized air passed by a pressure indicator where it was regulated. The air stripping column was placed on a scale (not pictured), to weight the substances as they entered the column.

4.5.2 Procedure

Treatment in PP20 was set up to be able to run continuously, although in this thesis only parts of the plant were worked with, in batches, due to time constraints. Therefore, some of the parameters such as flocculation and sedimentation time are unknown and will not be further elaborated in this work. Table 9 shows the intended working procedure for the complete process of PP20.

Nitrogen removal with an air stripping column was investigated, as well as organic carbon removal with AOP, using H_2O_2 or $Na_2S_2O_8$ as oxidation agent in addition to UV irradiation of the sample.

Table 9 Set up of Pilot Plant 2020

Device	Description	Stirrer	Time	Chemicals
C1	Air stripping column	-	2h	NaOH
G1	Gas collection vessel	-	while C1 is in use	H_2SO_4
T1	Flocculation	1	unknown	Anionic polymer
P1	Pump	-	-	-
T2	Sedimentation	-	unknown	-
P2	Membrane pump	-	-	-
F1	Coarse filter 155µm	-	-	-
F2	Fine filter 20µm	-	-	-
F3	Fine filter 20µm	-	-	-
T3	Oxidation	2	1h	H_2O_2 or $Na_2S_2O_8$
P3	Pump	-	-	-
UV	UV device	-	-	-
T4	UV treatment	-	-	-
T5	Sedimentation	-	unknown	-
F4	Sand filter	-	-	-
F5	Activated carbon filter	-	-	-

C	column
F	filter
G	gas collection
P	pump
T	tank

4.5.2.1 Air Stripping Column

An air stripping column was built to reduce the ammonia nitrogen load. As unionized ammonia is mainly present at a higher pH (Equation 12), pH was adjusted to approximately 10.5.

$$NH_4^+ \rightarrow NH_3 + H^+ \qquad \text{Equation 12}$$

The ratio of dust and water for this treatment was 1:4 for all trials. First 3 kg of dust were added to the column. Appropriate safety gear such as gloves, coveralls and a FFP3 mask had to be be worn when handling the dust. Then NaOH in solid form was added to increase the pH. Concentrations were calculated according to puffer capacity trials done in the laboratory (Table 19 in Appendix). Some trials were done using CaO (calculation in Table 10) in addition to NaOH to precipitate F^-, but the practice was dismissed. The column was then closed with wing nuts ensuring it is gas tight.

To catch the stripped ammonia nitrogen a H_2SO_4 solution was used, for calculation see Table 11. The gaseous ammonia nitrogen went through the gas outlet and a silicone hose to a glass bottle (B1) filled with 4 l of the H_2SO_4 solution (170 mmol). Due to the low pH of the solution the ammonia nitrogen converts back to its ionic form and stays in the solution (Equation 13).

$$NH_3 + H^+ \rightarrow NH_4^+ \qquad \text{Equation 13}$$

After adding 3 kg of dust and the calculated amount of NaOH, the lid was attached by closing the wing nuts tightly. The gas collection vessel (Figure 16) was attached to the gas outlet of the column. Once everything was closed airtight, 9 kg of water were added, using a scale. The water had a temperature of approximately 12ºC directly from the cold water outlet. The slower the water was added, the better the dust was solved. Once all the water was added, pressurized air was introduced into the column. All trials were done with a pressure of approximately 3 bar and a flow rate of 15-20 l/min. During aeration, the gaseous ammonia-nitrogen was removed from the leachate and transported through the gas outlet into the sulfuric acid solution, where it was trapped. Depending on the trial the leachate was aerated for either one or two hours.

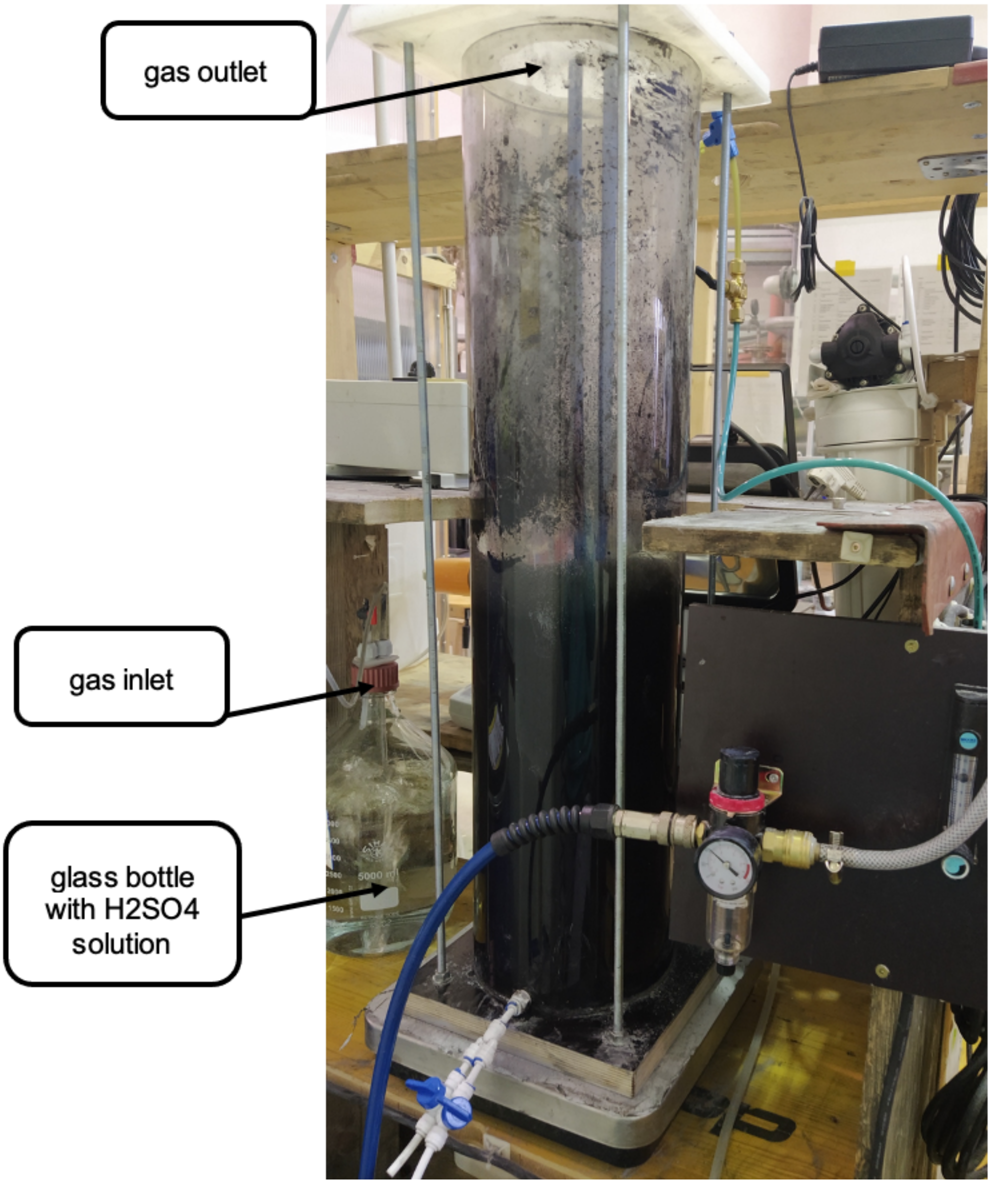


Figure 16 Air Stripping Column (C1) with Gas Collection Vessel (B1)

4.5.2.1.1 Calculation of CaO concentrations

CaO was used to precipitate F^- from the leachate in the air stripping column. The amount of CaO needed was calculated with a ratio of 1:3.

Table 10 Calculation of CaO concentrations

calculation CaO		
$m(F^-)$	310	mg/l
$M(F^-)$	18.99	mg/mmol
$n(F^-)$	16.32	mmol/l
$n(Ca^{+2})$	48.96	mmol
M (CaO)	56.08	mg/mmol
m(CaO)	2745.84	mg/l

$m(F^-)$, the mass of F^- in the dust, in mg/l, is taken from IC measurements of the leachate. $M(F^-)$, the molar mass of F^-, in mg/mmol. According to the chemical equation

$$Ca^{2+} + 2F^- \rightarrow CaF_2 \qquad \text{Equation 14}$$

a molar ratio of 1:2 was needed, but 1:3 was used to ensure precipitation in presence of scavengers.

Amount of CaO needed for treatment (m(CaO)) according to calculation in Table 10 was multiplied by the amount of water used in trial. CaO was added in solid form.

4.5.2.1.2 Calculation of H_2SO_4 solution

To produce the H_2SO_4 solution for the gas collection vessel the maximum amount of strippable NH_4-N (Table 11) according to IC measurements of the leachate was taken. To get the amount of NH_4^+ in the dust it was multiplied by a factor of 1,2878 $\left(\frac{M(NH_4)}{M(N)}\right)$.

Table 11 Calculation of H_2SO_4 solution

calculation H2SO4			
NH_4^+-N	265	mg/l	
NH_4^+	341	mg/l	
M (NH_4^+)	18.04	mg/mmol	
n (NH_4^+)	18.92	mmol	/l
Volume trial leachate	9000	ml	
$n(H_2SO_4)$	170	mmol	/l
$M(H_2SO_4)$	98	mg/mmol	
$m(H_2SO_4)$	16700	mg	/l
$m(H_2SO_4)$	16.7	g	/l
density (H_2SO_4)	1830	g/l	
V (H_2SO_4)	9.13	ml	/l
Volume of H_2O in vessel	4000	ml	
V (H_2SO_4) necessary	36.50	ml	/4000 ml
V (H_2SO_4) + 20%	43.80	ml	/4000 ml

To convert all gaseous NH_3-N back to ionic NH_4-N an equal molar amount of H_2SO_4 was needed according to the chemical equation:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad \text{Equation 15}$$

The amount of H_2SO_4 needed was then calculated with its density and an excess of 20% was used to make sure the solution was able to absorb all input NH_4-N.

4.5.2.2 AOP

To reduce the carbon load of the leachate created in the air stripping process, AOP batch trials were introduced. The AOP methods chosen were H_2O_2/UV and $Na_2S_2O_8$/UV. Decision for these methods was due to simplicity in handling the reagents and the avoidance of bromate formation during treatment.

For the trials, the oxidizing agent was added to the decanted leachate and then exposed to the UV lamp. The UV lamp had a wavelength of 254nm. The leachate used for the trials was taken from the air stripping trial runs. The leachate was decanted after a 24 hour sedimentation period. Depending on the trial the oxidizing agent was either H_2O_2 or $Na_2S_2O_8$ of varying concentrations. Irradiation took place in batches either cycling through the UV treatment device or stationary, specifications in Table 13 and Table 14. For the cycling trials a peristaltic pump (Figure 17) was used to move the leachate.

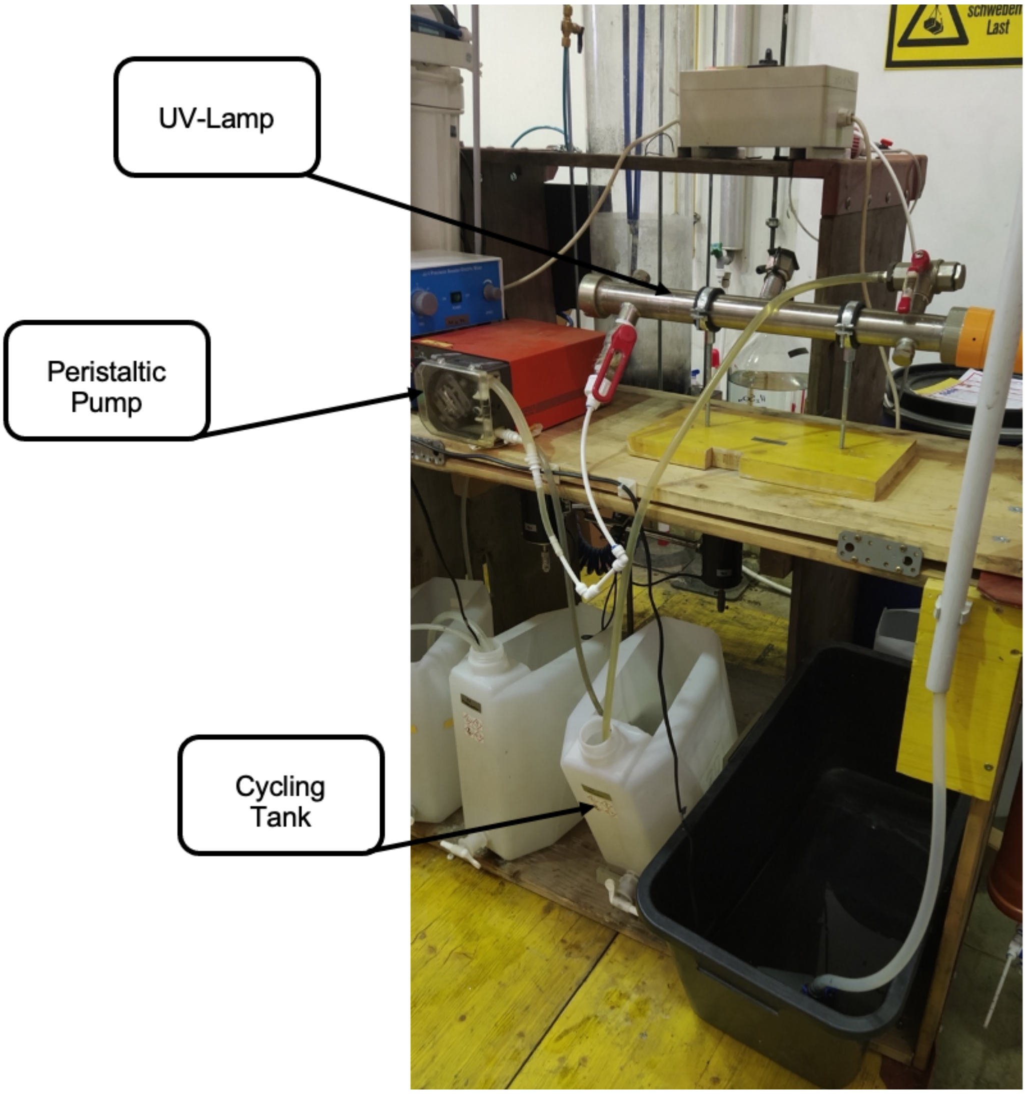


Figure 17 AOP trial set up

4.5.3 Sampling

Samples of 200 ml each were taken after air stripping and after AOP trials.

Samples of the air stripping trials were taken from the decanted leachate as well as from the H_2SO_4 solution. The samples from the decanted leachate were analyzed for TOC and TNb by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG). The samples of both the decanted leachate and the H_2SO_4 solution were analyzed for NH_4-N with the Hach spectrophotometer.

The samples from the AOP trials were taken after completion of each trial and analyzed for TOC and TNb by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG).

As mentioned before, the samples taken from the air stripping column had to be filtered before analysis, as the organic carbon content in the particulate matter was too high for proper analysis. Additional to filtering the samples, they were also diluted 1:3 to be in the measuring range. Samples were filtered with 0.45µm (with pressure filtration system), making the actual analysis a measure for the DOC instead of TOC, using TOC analysis methods.

Figure 18 Stable sediment cone at outlet during decanting

4.5.4 Trial runs

4.5.4.1 Air Stripping

Additional to air stripping to reduce NH_4-N in the leachate, it was thought about reducing F- via precipitation with CaO, but as the residue containing F^- cannot be recycled back into the sinter feed, the concept was abandoned after two trials. Due to this fact it was not possible to use lime to adjust the pH of the leachate. Sodium hydroxide was used instead.

Table 12 Substance amounts used in air stripping trial runs

trial	dust [kg]	water [l]	NH_4-N origin [mg/l]	NH_4^+ [mmol/l] calculated	NH_4-N mmol in trial	H_2SO_4 necessary [ml/l]	Volume [ml]	V (H_2SO_4) + 20% [ml]	V total H_2SO_4 solution [ml]	NaOH [g]	treatment time [min]
Str0014	1	3	265	18.92	56	12.17	4000	14.60	4014	8, 4	60
Str0016	3	9	265	18.92	170	36.51	4000	43.81	4044	24,12	60
Str0017	3	9	265	18.92	170	36.51	4000	43.81	4044	24,12	120
Str0018	3	9	265	18.92	170	36.51	4000	43.81	4044	24,12	120

Volume of H_2SO_4 solution in the gas collection vessel and treatment time as well as amount of NaOH used to adjust pH can be seen in Table 12.

Str0015 was a laboratory trial and is therefore not in the list.

4.5.4.2 UV/H_2O_2

Trials H2O2_UV_01 to H2O2_UV_04 were trials that circulated through the UV treatment device and the Cycling Tank. The peristaltic pump was at 25% (Table 13, column “pump performance”) of its performance speed which was approximately 1 l/min. Circulation time varied, as did the molar ratio of initial TOC:H_2O_2 used in treatment. Trials H2O2_UV_05 to H2O2_UV_07 were batch trials where the leachate was stationary in the UV lamp, time in the lamp depending on the trial was 30 min to 2 hours. All trials were done with the same batch of leachate. Each time initial TOC was measured to account for changes over time.

Table 13 UV/H_2O_2 trial specifications

trial	date	volume [ml]	H_2O_2 33% [ml]	molar ratio TOC:H_2O_2 [mmol]	circulation time [min]	pump performance %
H2O2_UV_01	19.11.20	1000	0.5	1:7	30	25
H2O2_UV_02	19.11.20	1000	0.5	1:7	60	25
H2O2_UV_03	19.11.20	1000	5	1:70	30	25
H2O2_UV_04	19.11.20	1000	5	1:70	60	25
H2O2_UV_05	07.12.20	500	2.5	1:70	30	0
H2O2_UV_06	07.12.20	500	2.5	1:70	60	0
H2O2_UV_07	07.12.20	500	2.5	1:70	120	0

4.5.4.3 UV/$Na_2S_2O_8$

Trials Na2S2O8_UV_01 to Na2S2O8_UV_04 were batch trials where the leachate was stationary in the UV device. The amount of $Na_2S_2O_8$, the molar ration of TOC before treatment with $Na_2S_2O_8$ as oxidizing agent and the circulation time varied according to trial (Table 14).

Table 14 UV/$Na_2S_2O_8$ trial specifications

trial	date	volume [ml]	$Na_2S_2O_8$ [g]	molar ratio TOC:$Na_2S_2O_8$	circulation time [min]	pump performance %
Na2S2O8_UV_01	09.12.20	300	3.9	1:4	30	0
Na2S2O8_UV_02	09.12.20	300	3.9	1:4	60	0
Na2S2O8_UV_03	09.12.20	300	7.8	1:8	30	0
Na2S2O8_UV_04	09.12.20	300	7.8	1:8	60	0

5. Results and Discussion

5.1 Filterable Substances

Two samples were analyzed for filterable substances (Table 15). As the sample was 5 g of dust dissolved in 50 ml of water, the grams of filterable substances were divided by 0.05 to gain [g/l]. The percentage of filterable substances was equal the filterable substances in [g/l]. The average percentage of filterable substances was 12%. Meaning that almost 90% of the dust was dissolved when preparing a leachate for treatment. The high percentage of dissolvable substances confirmed the claim of a high salt concentration in the dust. For treatment and further landfilling a low amount of filterable substances insinuated that a reduction of deposition goods was achievable.

Table 15 Calculation of filterable substances

Nr.	**weight**		**Filterable substances**		
	tray + filter [g]	tray + filter + sample [g]	[g]	[g/l]	[%]
2	48.1870	48.3012	0.1142	-	-
4	47.5955	47.7580	0.1625	-	-
5	52.1714	52.2693	0.0979	-	-
6	48.1477	48.2427	0.095	-	-
8	46.9779	47.0520	0.0741	-	-
9	48.4103	48.4458	0.0355	-	-
		sum	0.5792	**11.584**	**11.58**
10	49.6463	49.8268	0.1805	-	-
11	49.7906	49.8582	0.0676	-	-
12	47.8138	47.8737	0.0599	-	-
13	50.2017	50.3225	0.1208	-	-
14	46.591	46.6987	0.1077	-	-
15	48.8305	48.8655	0.035	-	-
		sum	0.5715	**11.430**	**11.43**

5.2 Total concentration of elements in the dust

Measuring the dust with the ICP-MS method revealed very high concentrations of metals, as can be seen in Figure 19. Although reducing the heavy metal concentration was not the main focus of this thesis, heavy metal reduction was attempted in PP19.

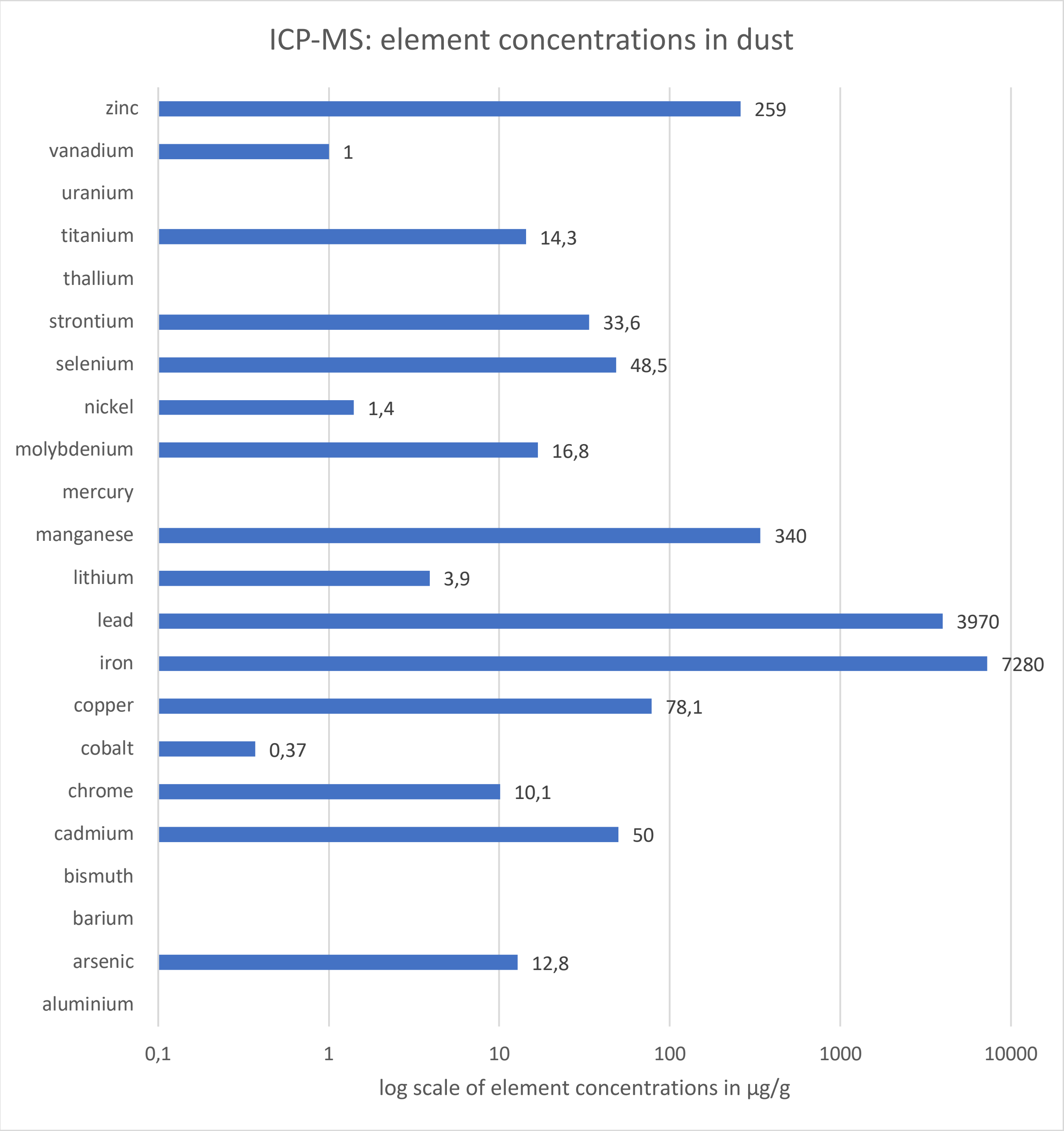


Figure 19 ICP-MS: element concentrations in dust

The analysis of a 1:10 leachate, filtered with 0.45 µm, revealed a high amount of dissolved heavy metals (Figure 20). Due to the high concentrations it was attempted to precipitate heavy metals in the leachate by raising the pH to 9 and further adding organic sulfide for a better result in PP19. The precipitate was then sedimented and the leachate filtered for a successful reduction of heavy metal concentration in the leachate.

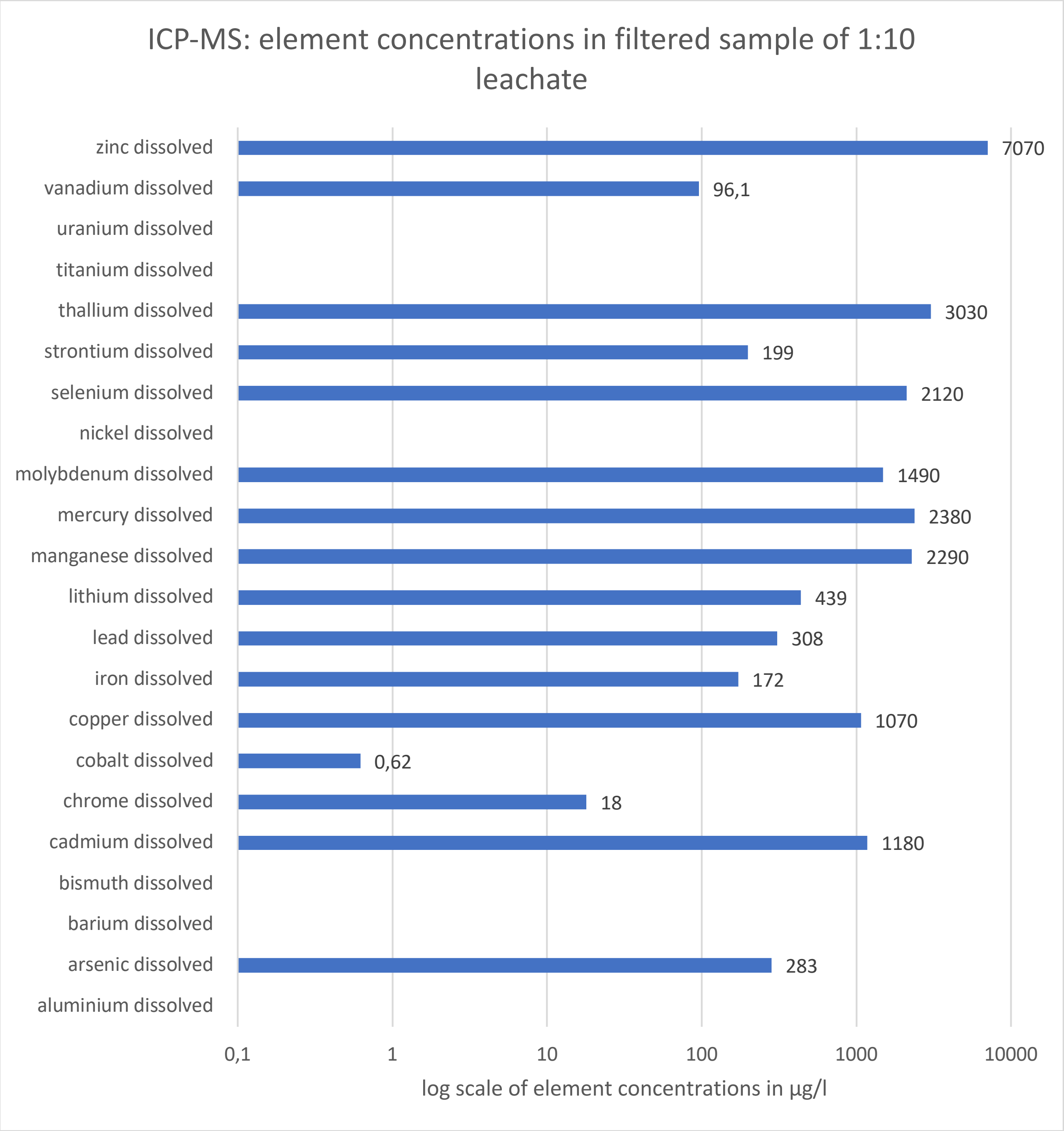


Figure 20 ICP-MS: element concentrations in filtered sample in 1:10 leachate

As the element concentrations of the dust sample were given in µg/g the concentration values from the ICP-MS were multiplied with 100 to get the same unit as the element concentrations of the filtered sample. The filtered sample has a dust concentration of 100 g/l therefore the equation as follows:

$$element\ concentation\ \left[\frac{\mu g}{g}\right] * 100\left[\frac{g}{l}\right] = element\ concentration\ \left[\frac{\mu g}{l}\right] \qquad \text{Equation 16}$$

Equation 16 was applied to compare the total and soluble element concentrations in Figure 21. In Figure 21, element concentrations of the dust sample give the total element concentration and the dissolved and filtered sample gives the soluble fraction of the element concentration.

A quarter of the total element concentration was soluble for the elements arsenic, cadmium and zinc. Only 2% of chrome and cobalt were soluble and 6% of manganese and strontium. Copper had a solubility of 14% and selenium of 40%. 89% of molybdenium was soluble and for lithium and vanadium the total element concentration was soluble.

One can infer that the reduced concentration in the soluble fraction was due to the presence of these metals in particle form, which had been filtered out during sample preparation. Nickel was only present in particulate form. Mercury and thallium were only present in dissolved form, there were no measurable traces in the dust sample.

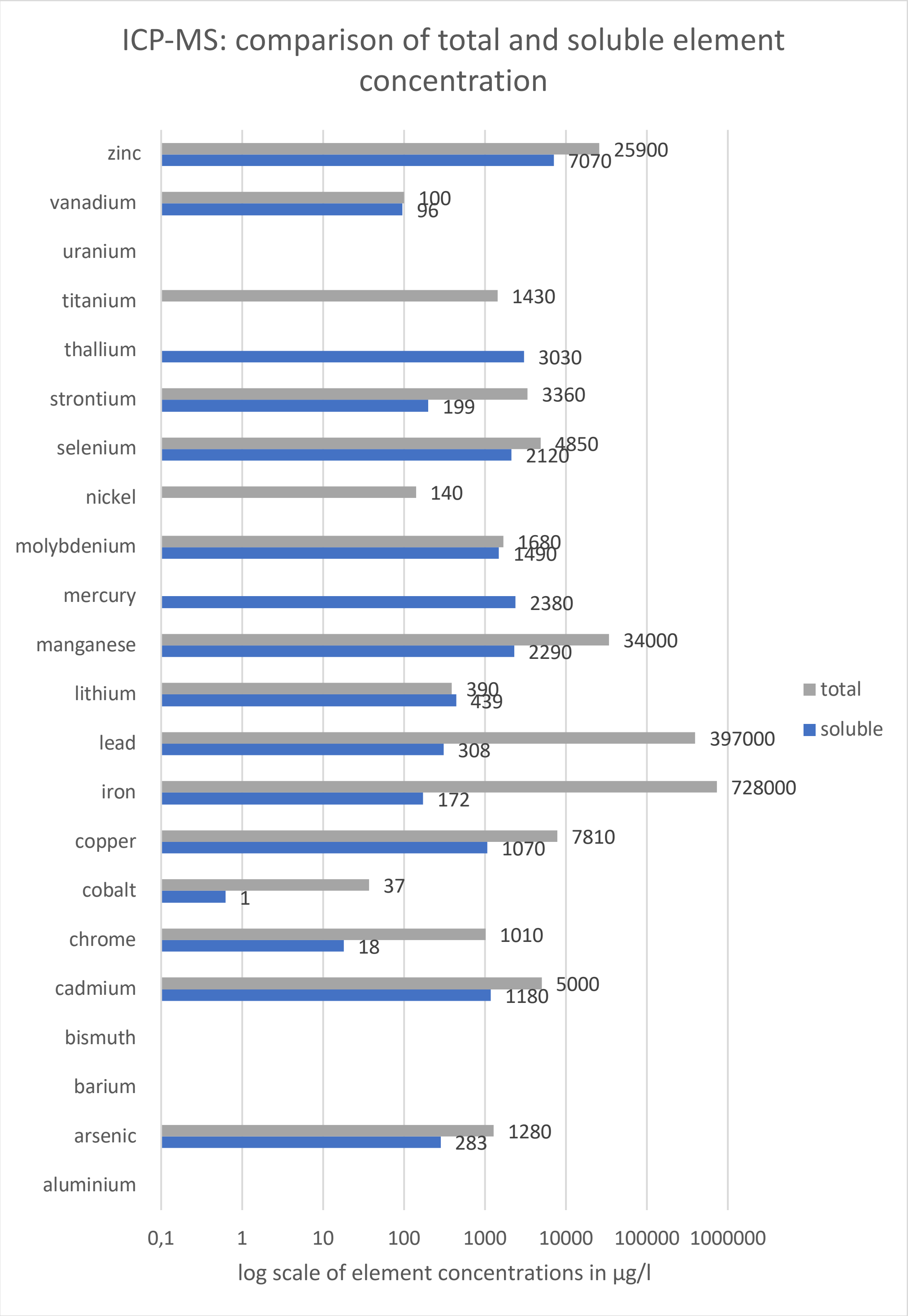


Figure 21 ICP-MS: comparison of total and soluble element concentration

5.3 Ion Chromatography (IC)

Figure 22 illustrates the ion concentrations from a filtered sample (0.45 µm) of the leachate. The ion chromatography yielded high values for sulfate, sodium, potassium and chloride, with 41000 mg/l, 22100 mg/l, 11100 mg/l and 14000 mg/l respectively. Further, concentrations for ammonium-nitrogen, bromide and fluoride were 124 mg/l, 220 mg/l and 90 mg/l respectively.

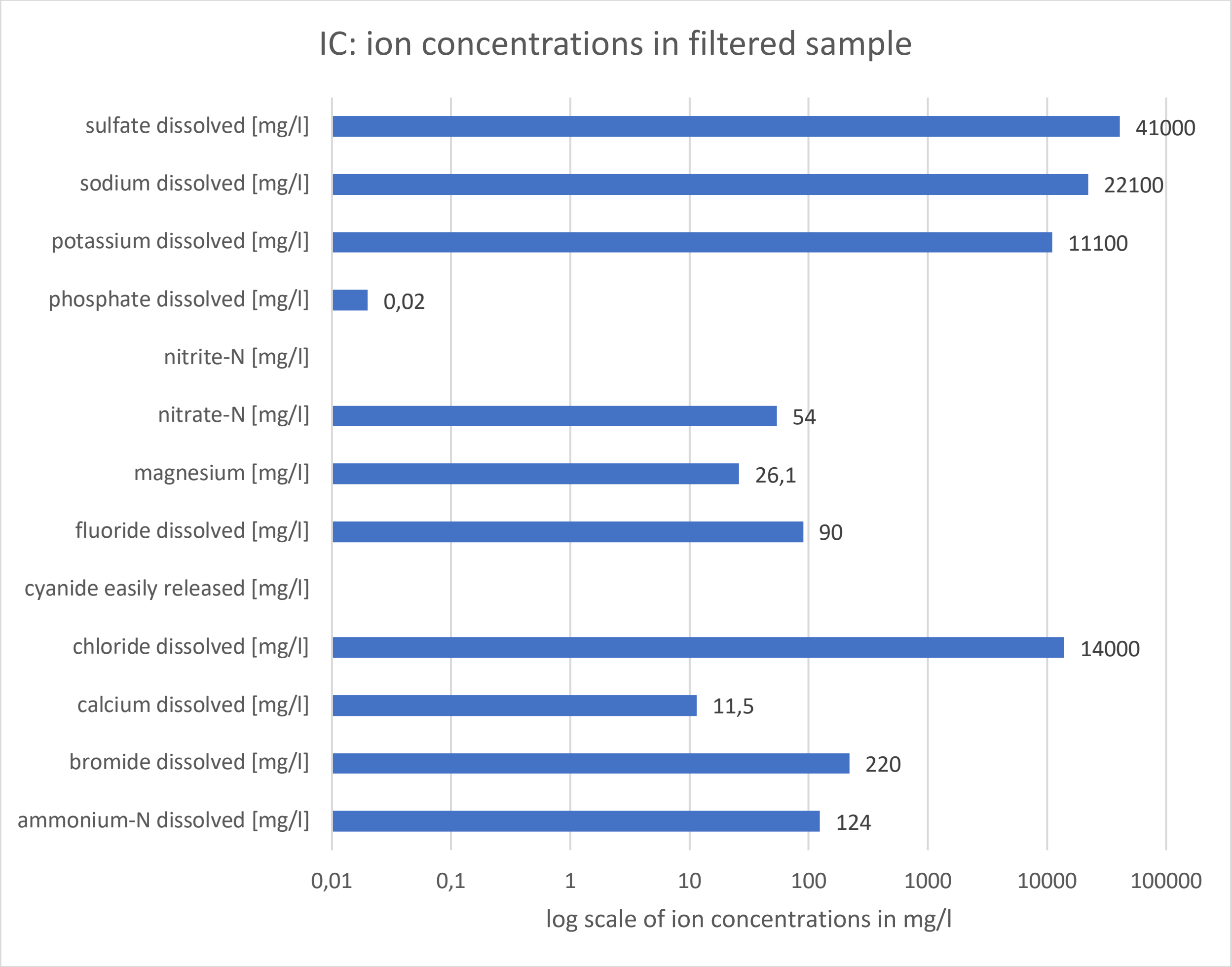


Figure 22 IC: ion concentrations in filtered sample

The Ion Chromatography yielded high values for sulfate, sodium, potassium and chloride and further ammonium-nitrogen, bromide, fluoride and nitrate-nitrogen.

Due to these results, it was decided to reduce ammonium-nitrogen and fluoride via air stripping in PP20.

The elevated bromide and chloride concentrations were suspected to highly interfere with the Fenton Process in PP19. As can be seen in Equation 4, Br and Cl are H• scavengers (Pignatello, et al., 2006).

5.4 Pilot Plant 2019

5.4.1 Initial Concentrations

After filtration with the column filters, F1 to F3 of the Pilot Plant 2019 setup and acidification to pH 2.7 in T3 of the setup, the initial concentrations of DOC, TOC, NH_4-N and TNb were measured. As already described in 4.4.2.1 Leachate Preparation, the leachate was prepared in a 1:10 dilution.

Figure 23 shows the initial DOC concentrations after column filtration (F1-F3) and additional 0.45 µm pressure filtration. Trial runs 2 to 8 are pictured, as well as an additional value of a sample prepared and filtered in the laboratory (trial run 0, blue column). The orange line depicts the average value of the DOC samples at 66 mg/l. The standard deviation is 7.8 mg/l. The dust was therefore assumed to be fairly heterogenous.

In Figure 24 the initial TOC concentrations after column filtration and no additional filtration rose slowly from trial run 2 to 5. Then there is a sharp peak in concentration for 6 and 7, and a drop at 8. Reason for the sharp peak is failure of the column filters, which were unable to filter the vast amount of fine particles from the leachate. As already mentioned in the chapter Methods a regular exchange of the 20 µm filters was necessary for proper operation.

NH_4-N and TNb concentrations were measured after column filtration and additional 0.45 µm pressure filtration.

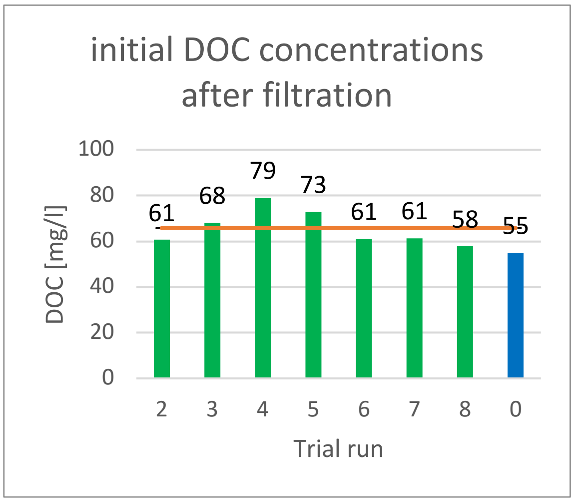


Figure 23 Initial DOC concentrations after filtration

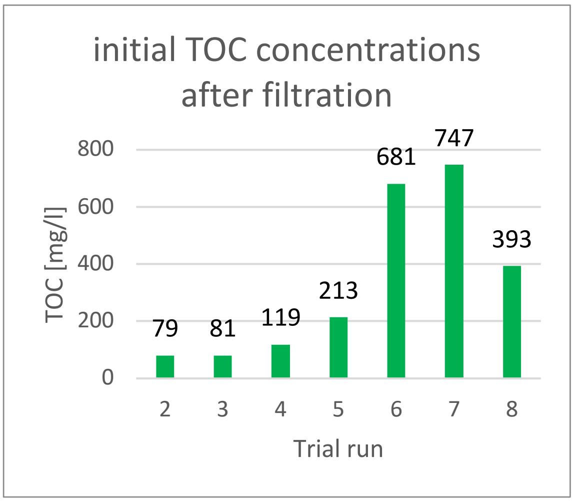


Figure 24 Initial TOC concentrations after filtration

The average NH_4-N concentration is 131 mg/l (see orange line in Figure 25), with a standard deviation of 4.7 mg/l. The samples of PP19 were comparatively homogeneous in the regard of NH_4-N, only the sample prepared in the laboratory had a significantly higher value.

Initial TNb concentrations (Figure 26) had an average value of 251 mg/l and a standard deviation of 15.3 mg/l, inferring that TNb was somewhat heterogeneously distributed in the dust.

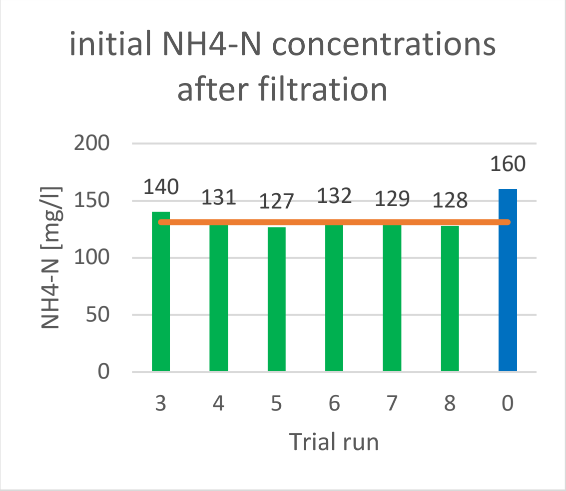


Figure 25 Initial NH4-N concentrations after filtration

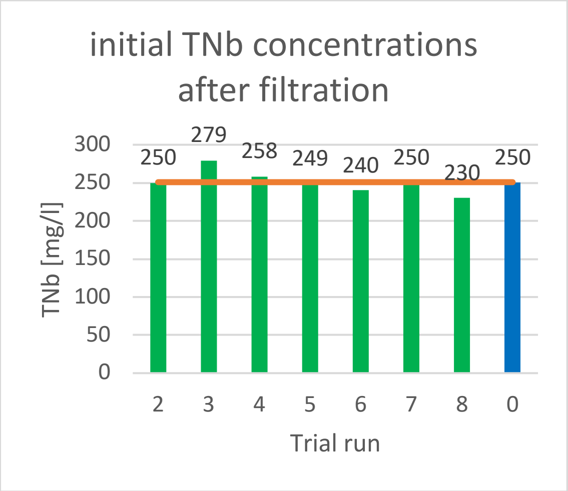


Figure 26 Initial TNb concentrations after filtration

Comparing the initial concentrations of TNb and NH_4-N, it can be concluded that approximately 50% of total nitrogen bonded was NH_4-N.

5.4.2 Trial runs

Table 8 gives the amounts of $FeSO_4$, H_2O_2, NaOH, organic sulfide and anionic polymer used in the individual trial runs. Concentrations in ml were calculated according to the amount of leachate. H_2O_2 33% adjusted gives the amount of initial H_2O_2 added to the leachate plus H_2O_2 added to adjust to the desired ORP value. H_2O_2 tests were done to determine if there is surplus H_2O_2.

Trial run 1 is not further explained as it was discarded due to improper dilution of the dust.

5.4.2.1 Trial run 2

For trial run 2 concentration of $FeSO_4$ was 0.07 mg/l and H_2O_2 was at 1.2 mg/l. Organic sulfide and anionic polymer concentration and time of addition were interchanged in this trial run, flocculation could therefore be influenced. In Figure 27 DOC, TOC and TNb concentrations in mg/l are shown after each treatment step. There was a slight decrease in concentration visible after the sand filter, but most of the decrease in carbon and nitrogen concentration was after the activated carbon filter.

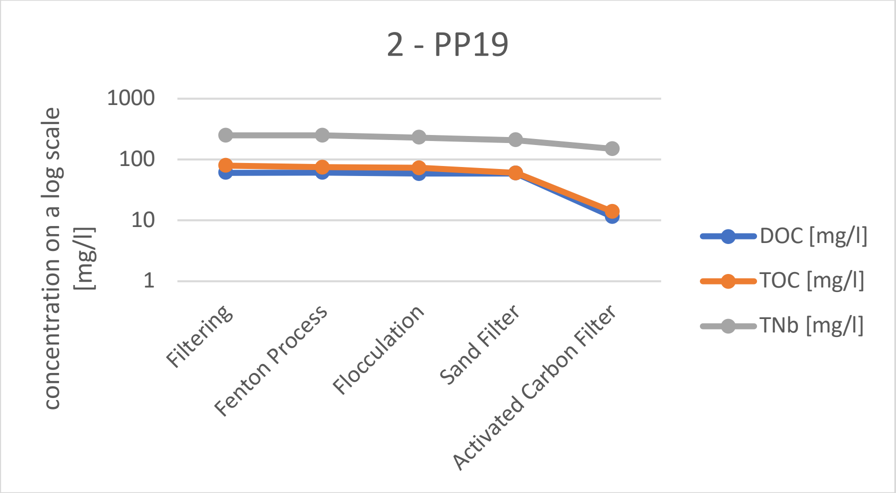


Figure 27 Concentrations for DOC, TOC, TNb - trial run 2

5.4.2.2 Trial run 3

Figure 28 shows the progression of DOC, TOC, TNb, NH_4-N and NO_3-N. DOC and TOC remained stable after the Fenton Process, intended to reduce the carbon concentration and the concentration only decreased after the activated carbon filter. TOC decreased from 80.7 mg/l to 16.2 mg/l and DOC from 68.1 mg/l to 18.9 mg/l. TNb was also reduced in concentration by the activated carbon filter, from 279 mg/l to 138 mg/l, as well as NH_4-N, which was further reduced by acidifying the sample with H_2SO_4 to pH 7, dropping from 140 mg/l to 54.8 mg/l after acidification. Contrary to NH_4-N, NO_3-N and TNb concentrations increased after acidification. TNb concentrations rising from 138 mg/l to 213 mg/l and NO_3-N more than doubling from 4.2 mg/l to 11.5 mg/l. See Figure 29.

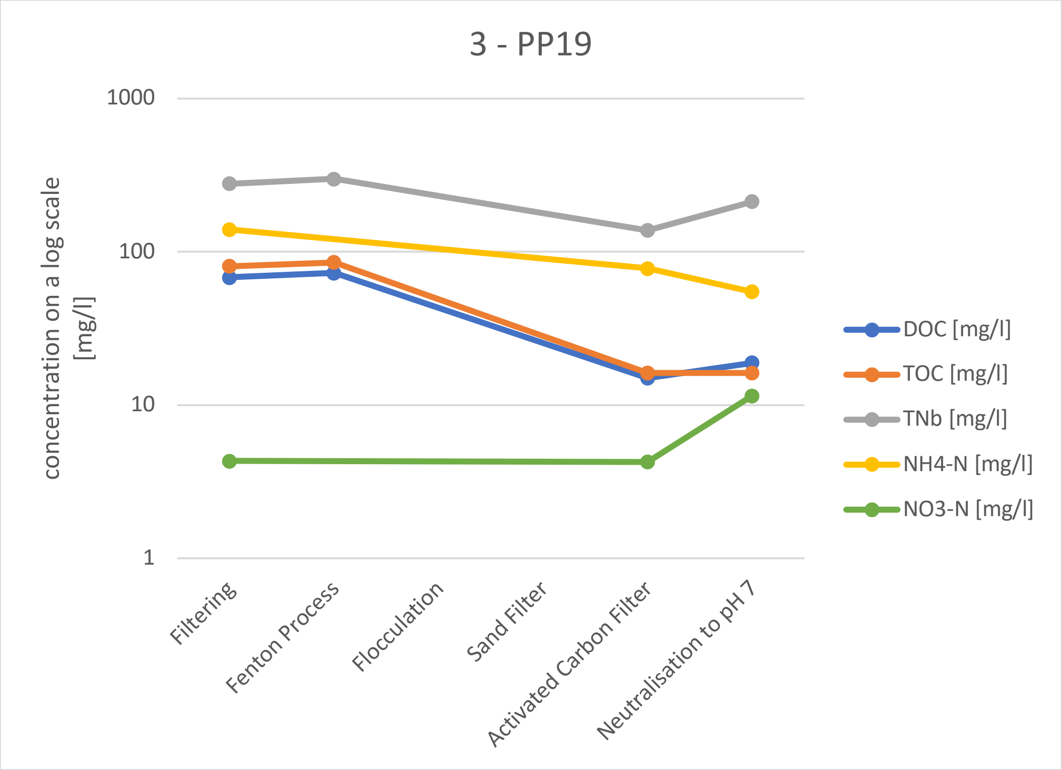


Figure 28 Concentration of DOC, TOC, TNb, NH_4-N, NO_3-N - trial run 3

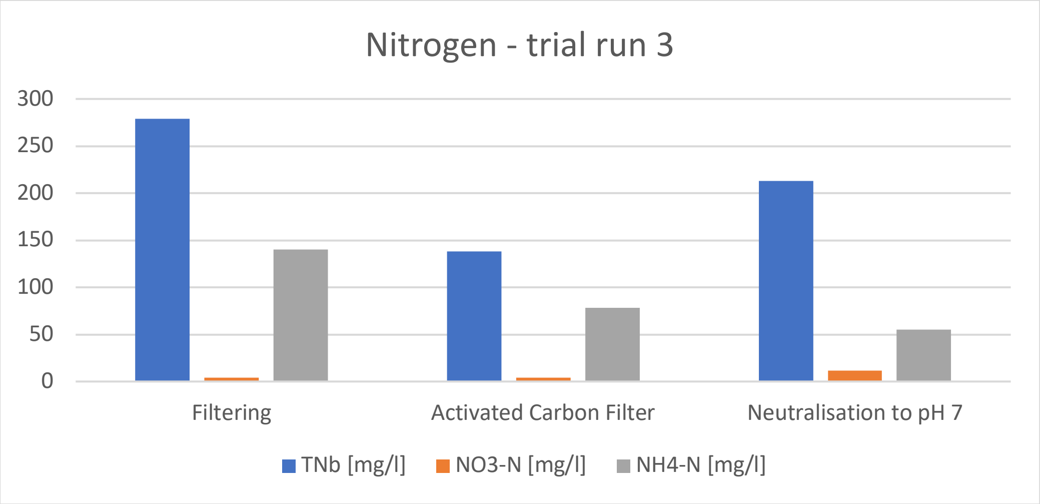


Figure 29 Nitrogen species concentrations - trial run 3

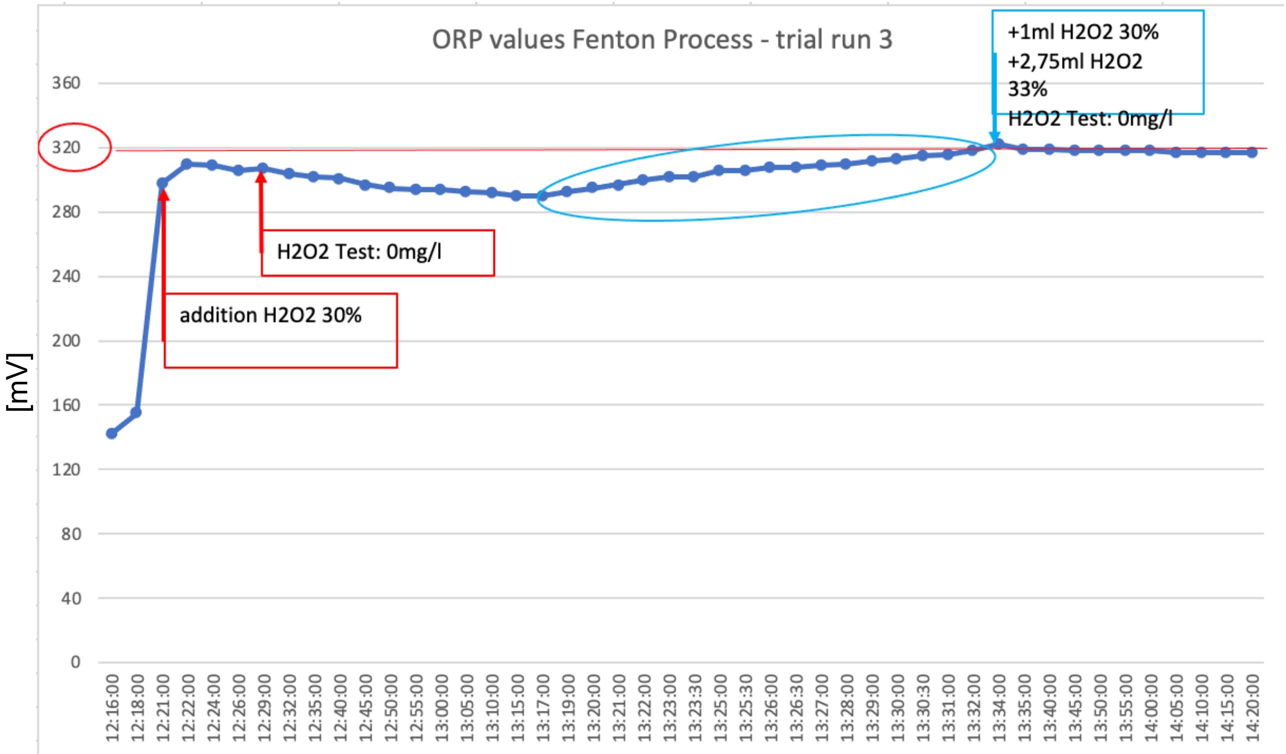


Figure 30 ORP values on a time scale - trial run 3

ORP values for trial run 3 were kept relatively stable underneath the aspired ORP value of 320 mV (red line in Figure 30). No surplus of H_2O_2 was found at the end of the treatment time.

5.4.2.3 Trial run 4

During trial run 4 the concentrations of the nitrogen species as well as TNb remained very stable with no significant reduction. As had been the trend for the previous trial runs, DOC and TOC concentrations only dropped after treatment in the activated carbon filter (Figure 31). TOC concentrations went from 119.1 mg/l to 16.2 mg/l and DOC decreased from 68.1 mg/l to 15 mg/l. The ORP values in Figure 32 show that increasing the ORP from 200 mV to 320 mV took 35 ml of H_2O_2 33%, whereas increasing the value from 320 mV to 390 mV only took adding 2 ml. At this point the H_2O_2 test showed a surplus of H_2O_2 of 3 mg/l. At the end of the treatment time no surplus H_2O_2 was found. The aspired ORP value was 320 mV (red line in Figure 32).

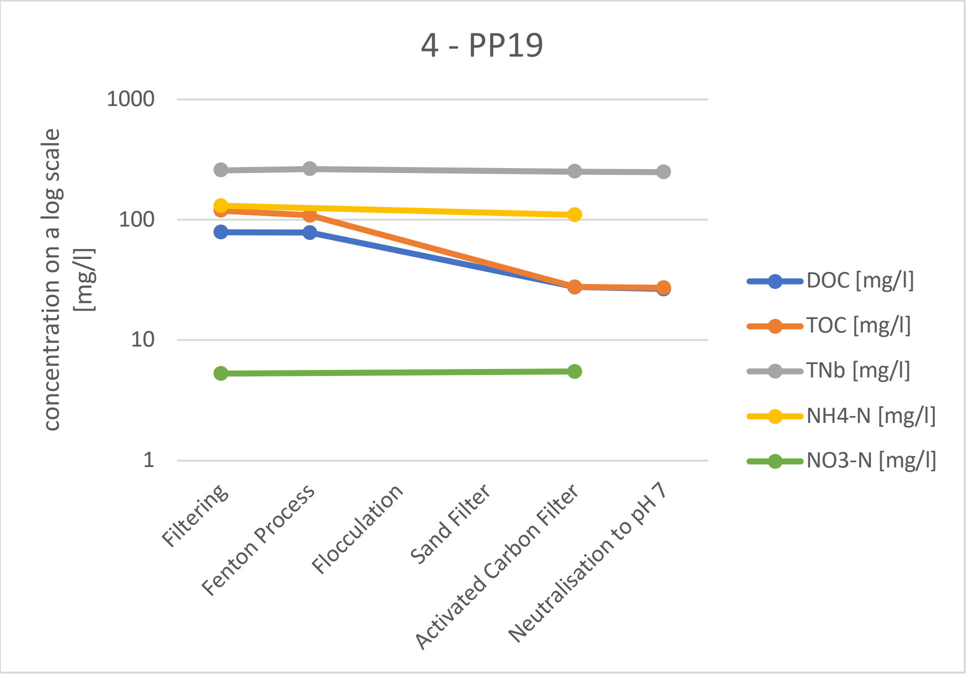


Figure 31 Concentrations of DOC, TOC, TNb, NH_4-N, NO_3-N - trial run 4

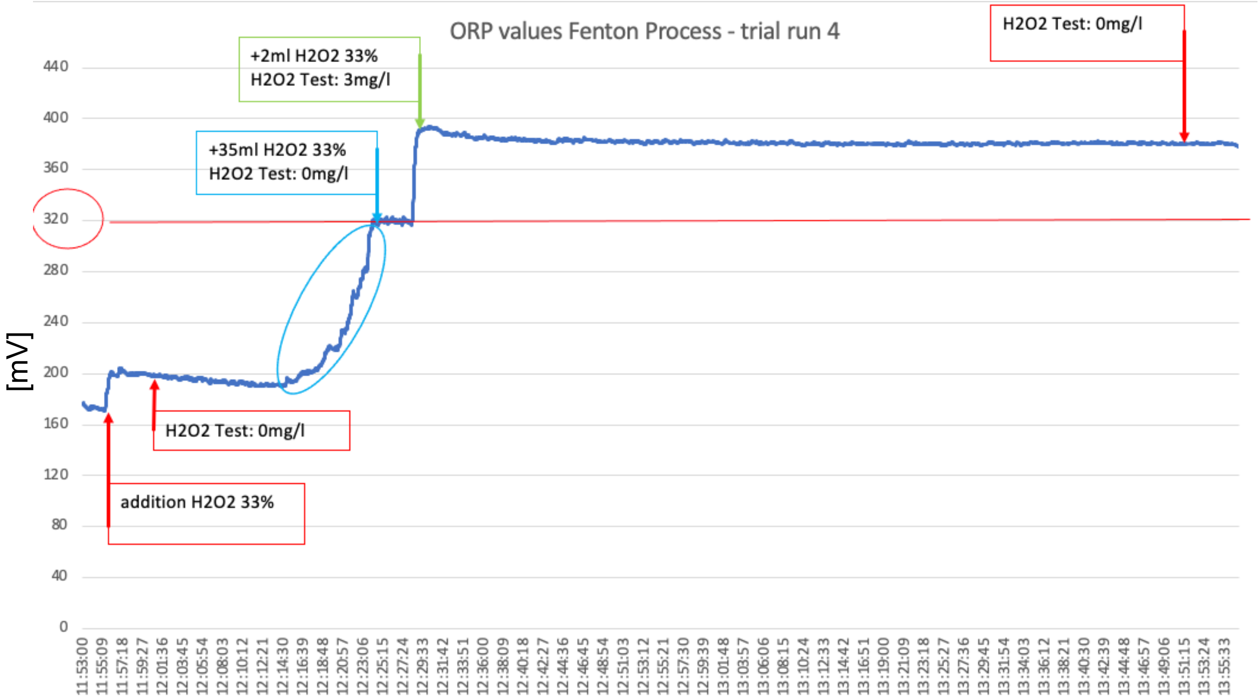


Figure 32 ORP values on a time scale - trial run 4

5.4.2.4 Trial run 5

As in trial run 4, NH_4-N and TNb remained stable during trial run 5 (Figure 33). The concentration of NO_3-N doubled after activated carbon filtration, from 5.32mg/l to 10.8 mg/l. DOC and TOC concentrations dropped after activated carbon filtration according to trend. DOC concentration values decreased from 72.9 mg/l to 24.0 mg/l and TOC values dropped from 213.3 mg/l to 24.3 mg/l. ORP values were raised above 320 mV to achieve a surplus of H_2O_2 at the end of the Fenton Process. Although ORP values remained high at 480 mV no surplus H_2O_2 was achieved (Figure 34).

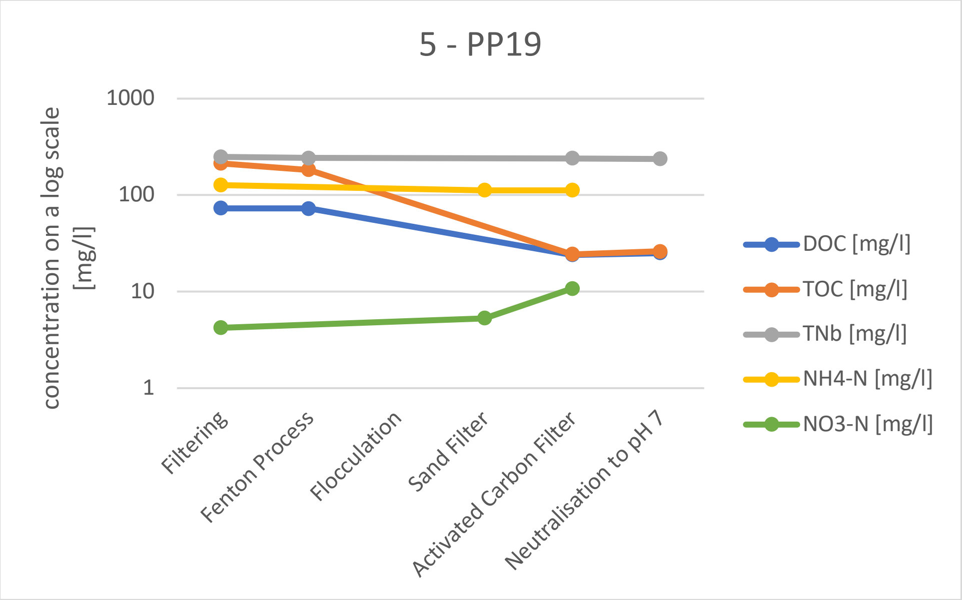


Figure 33 Concentrations of DOC, TOC, TNb, NH_4-N, NO_3-N - trial run 5

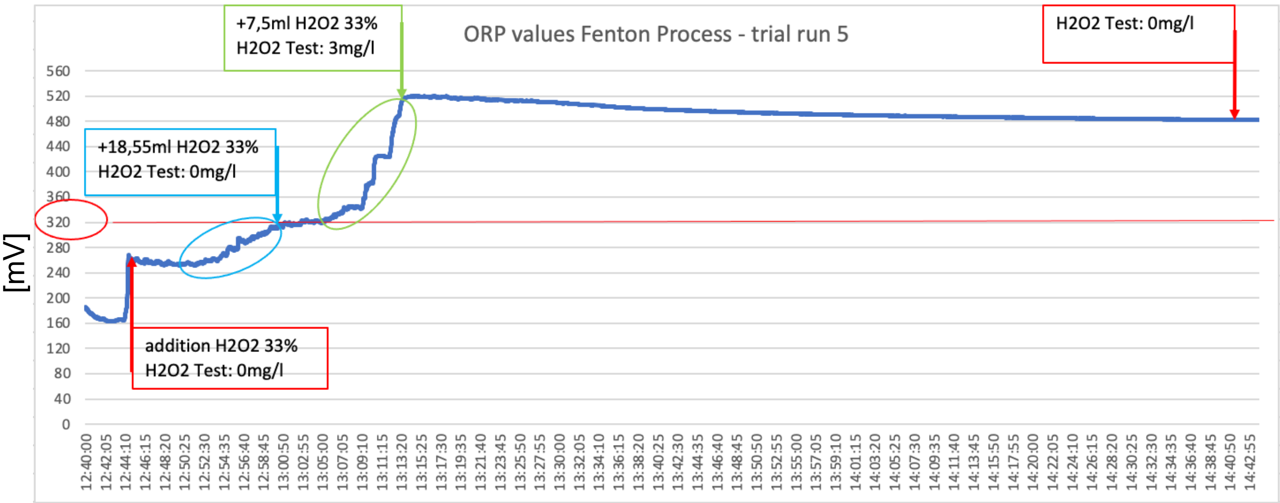


Figure 34 ORP values on a time scale - trial run 5

5.4.2.5 Trial run 6

As in trial runs 4 and 5, the TNb and NH_4-N concentrations did not change throughout the treatment process. NO_3-N on the other hand fluctuated in the range of 4.45 mg/l to 9.95 mg/l. As in the previous trial runs DOC and TOC concentrations dropped after activated carbon filtration, although more samples were taken in this trial run so Figure 35 shows that the TOC concentration was also lowered significantly after sand filtration, by reducing the concentration from 681 mg/l to 74.1 mg/l, activated carbon then further reduced the concentration to 24.1 mg/l. The sand filtration did not influence the DOC concentrations but activated carbon filtration reduced the concentration from 61 mg/l to 25 mg/l. Additionally COD according to JIS was measured. Treatment was able to reduce COD concentrations from 430.1 mg/l O to 70.1 mg/l. ORP values were kept at 320 mV, adding H_2O_2 to adjust. There was no surplus H_2O_2 during any step of the treatment (Figure 36).

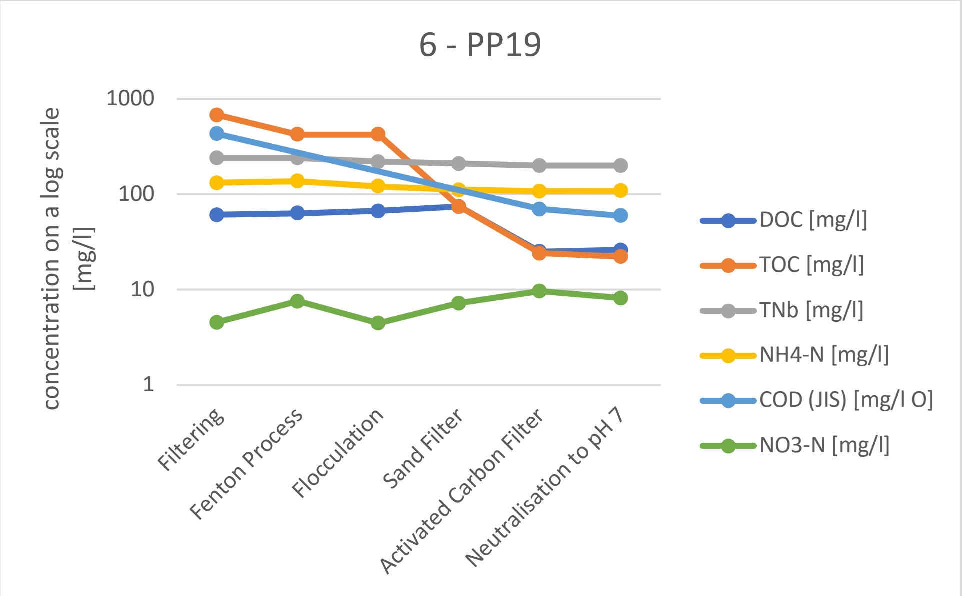


Figure 35 Concentrations of DOC, TOC, TNb, NH_4-N, COD, NO_3-N - trial run 6

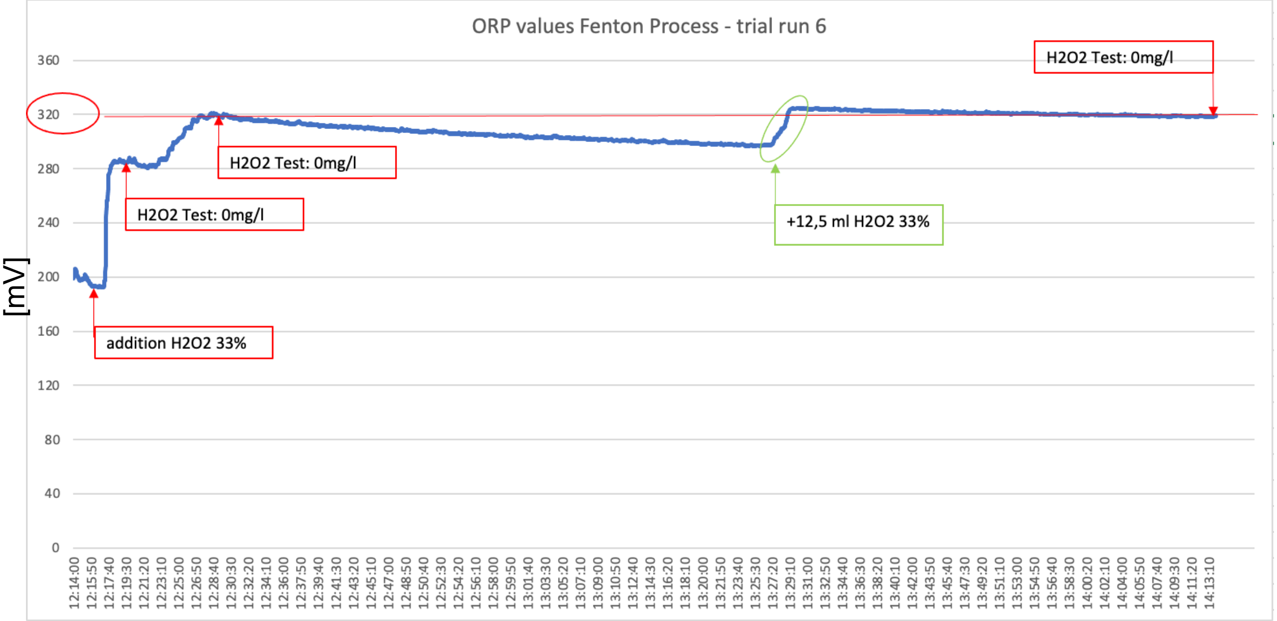


Figure 36 ORP values on a time scale - trial run 6

5.4.2.6 Trial run 7

All parameters reacted similarly to the previous trial run, with TNb and NH_4-N being stable throughout the treatment and NO_3-N fluctuating (Figure 37). As in the previous trial runs DOC dropped after activated carbon filtration, from 61.2 mg/l to 24.0 mg/l. TOC concentration values were reduced in two steps, similar to trial run 6. First sand filtration reduced TOC concentration from 747 mg/l to 71.7 mg/l, then activated carbon filtration reduced TOC further to 24.6 mg/l. No additional H_2O_2 was added to adjust ORP values after dropping under 320 mV. At no point in this treatment a surplus of H_2O_2 was present (Figure 38).

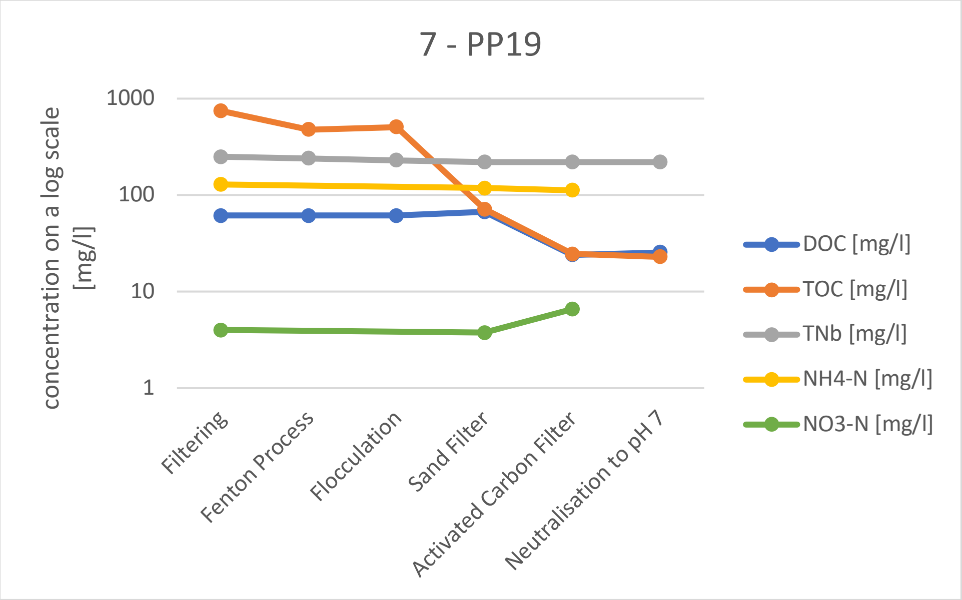


Figure 37 Concentrations of DOC, TOC, TNb, NH_4-N, NO_3-N - trial run 7

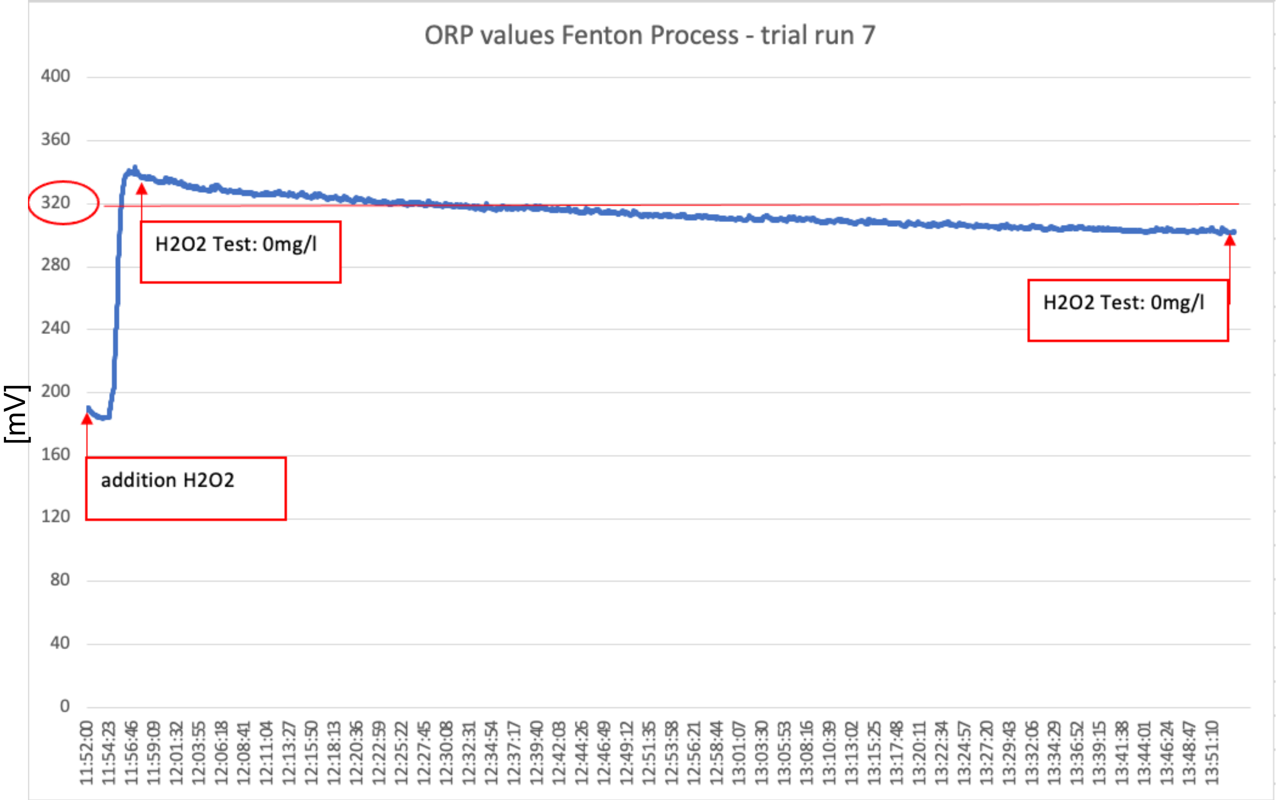


Figure 38 ORP values on a time scale - trial run 7

5.4.2.7 Trial run 8

Trial run 8 was done with the same concentrations of $FeSO_4$ and H_2O_2 than trial run 7. Overall, the trial run behaved similarly to trial run 7. For this trial run an ORP of 340 mV was to be achieved (see red line in Figure 40) to check if this would get a surplus of H_2O_2 at the end of the treatment step. Additional 6 ml of H_2O_2 33% were added relatively late to raise the ORP value, but no surplus of H_2O_2 was detected.

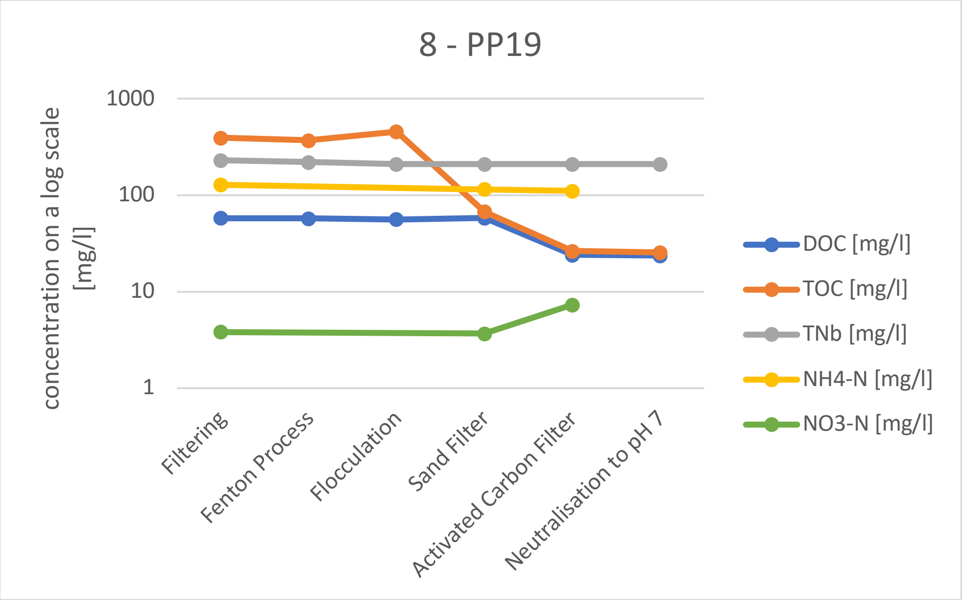


Figure 39 Concentration of DOC, TOC, TNb, NH_4-N, NO_3-N - trial run 8

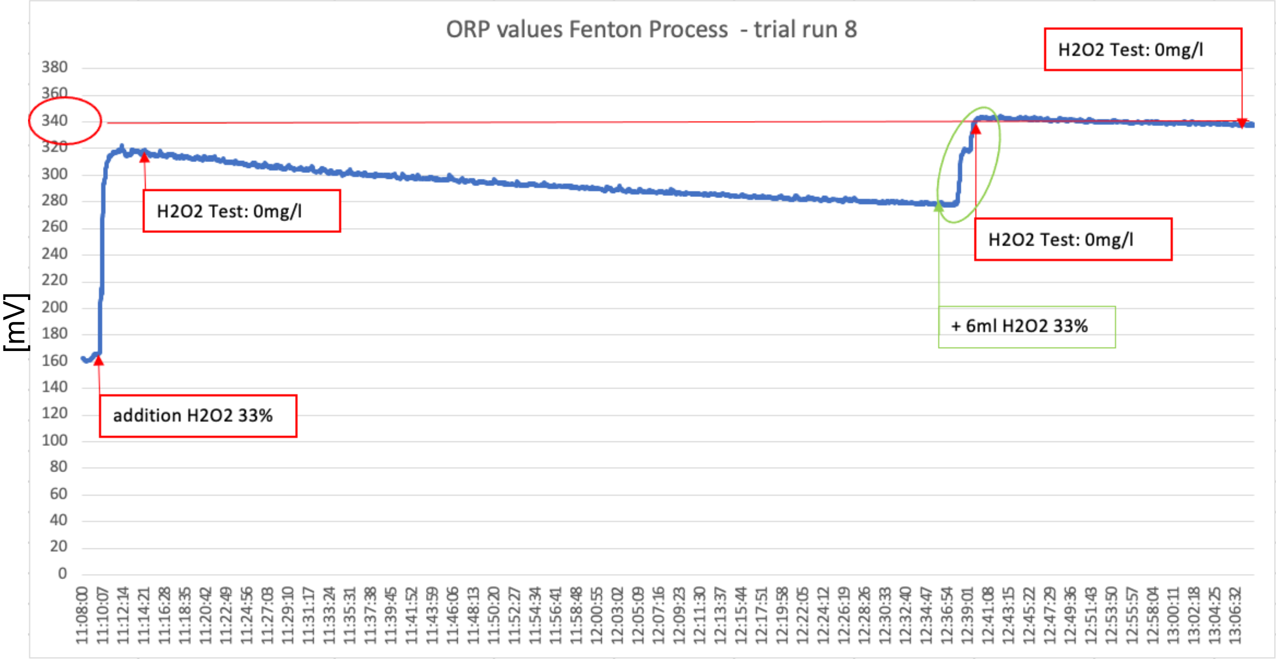


Figure 40 ORP values on a time scale - trial run 8

5.4.2.8 Comparison of trial runs

Goal of adding H_2O_2 to adjust the ORP value during the Fenton Process was finding the optimal ORP value to transform all added $FeSO_4$ using H_2O_2. Achieving a surplus of H_2O_2 during treatment was preferred, although no H_2O_2 was to remain after the Fenton Process, as it interfered with the analysis of COD according to JIS. The samples for this analysis were taken after activated carbon filtration. A comparison of ORP values and the dissolved iron concentration in mg/l is shown in Figure 41.

During trial run 3 an ORP value of 320 mV was reached, and although there was no surplus H_2O_2 during treatment the dissolved iron concentration after treatment was very low with 0.08 mg/l. Trial run 4 reached an ORP value of 390 mV and at its peak had a surplus of 3 mg/l H_2O_2. Just as desired, there was no surplus H_2O_2 at the end of the treatment step. Although a surplus of H_2O_2 was present, the dissolved iron was not completely converted, leaving a concentration of 1.2 mg/l after filtration. Trial run 5 reached a very high ORP value of 480 mV with a surplus of 3 mg/l H_2O_2. No surplus was present at the end of treatment. For this trial run, the dissolved iron concentration was 0.18 mg/l after filtration. For trial run 6 the ORP value was kept stable at 320 mV, adding H_2O_2 when necessary. Even though no surplus H_2O_2 was present during treatment the dissolved iron concentration after filtration was low with 0.1 mg/l. During trial run 7 no additional H_2O_2 was added, therefore the ORP value dropped to 300 mV and there was no surplus of H_2O_2 during treatment. The dissolved iron concentration after filtration was 1.4 mg/l. In trial run 8, additional H_2O_2 was used to raise the ORP value to 340 mV to try reaching a surplus of H_2O_2 during treatment. No surplus of H_2O_2 was measurable and this trial run has the highest dissolved iron concentration with 1.5 mg/l. There was no visible connection between ORP values and dissolved iron concentration after activated carbon filtration. Trial run 3 and 6 both had an ORP of 320 mV and low dissolved iron concentrations after filtration, but considering the other trial runs there was no visible trend.

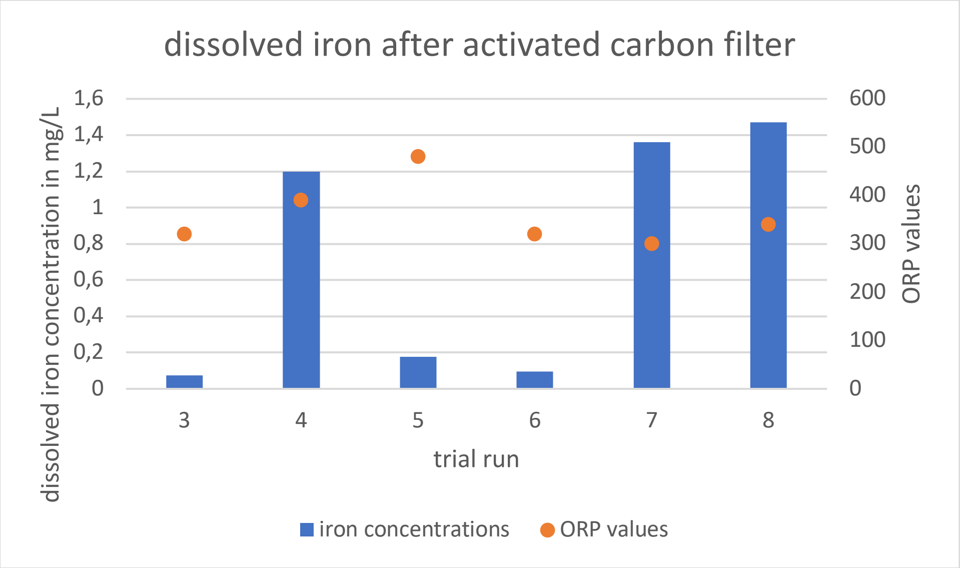


Figure 41 Dissolved iron after activated carbon filtration compared to ORP values

As already mentioned in 3.4.1.1.2, Equation 3 dissolved Fe^{2+} reacts with H_2O_2 to Fe^{3+} (Pignatello, et al., 2006). The solid Fe^{3+} was then removed from the leachate by heavy metal removal and activated carbon filtration. The remaining iron concentration after activated carbon filtration was therefore dissolved Fe^{2+}.

The inability of additional H_2O_2 in the Fenton process to transform all $FeSO_4$ could be due to the high chloride and bromide concentrations in the leachate. As mentioned earlier, chloride and bromide are HO• scavengers (Equation 4), reducing the amount of free radicals intended to transform $FeSO_4$ (Pignatello, et al., 2006). An option to counter this problem would be the removal or reduction of chloride and bromide before the Fenton Process, which is not very feasible.

Other inhibitors of the Fenton Process are fluoride and sulfate ions, which reduce the reactivity of Fe(III) and are also highly concentrated in the leachate (Pignatello, et al., 2006).

Independent of $FeSO_4$ and H_2O_2 concentrations used in treatment, all trial runs followed the same trend concerning TOC. Trial runs 6,7 and 8 show, that TOC dropped after the Fenton Process treatment, if very high concentrations of TOC were present. Trials 2,3,4 and 5 had much lower initial TOC concentrations, the drop after the Fenton Process was not visible in these trial runs. The wide range of initial TOC concentrations was due to a problem with the column filtration system which was before of the first sampling point. The 20 µm filters were not efficient enough in removing the fine particles from the leachate and clogged easily. Another drop in TOC concentration for TOC values above 200 mg/l could be observed after sand filtration, where TOC concentrations of all trial runs were in the same range, no matter the initial TOC concentration. Activated carbon filtering reduced the TOC concentration even more, therefore a 88% reduction in TOC concentration was possible on average. Filtering, whether it was sand filtration or activated carbon filtration proved to be very successful in removing particulate organic carbon from the leachate. The average TOC concentration after activated carbon filtration was 22.4 mg/l. Compared to the average DOC concentration of 21.6 mg/l one could infer that most particulate organic carbon was removed from the leachate.

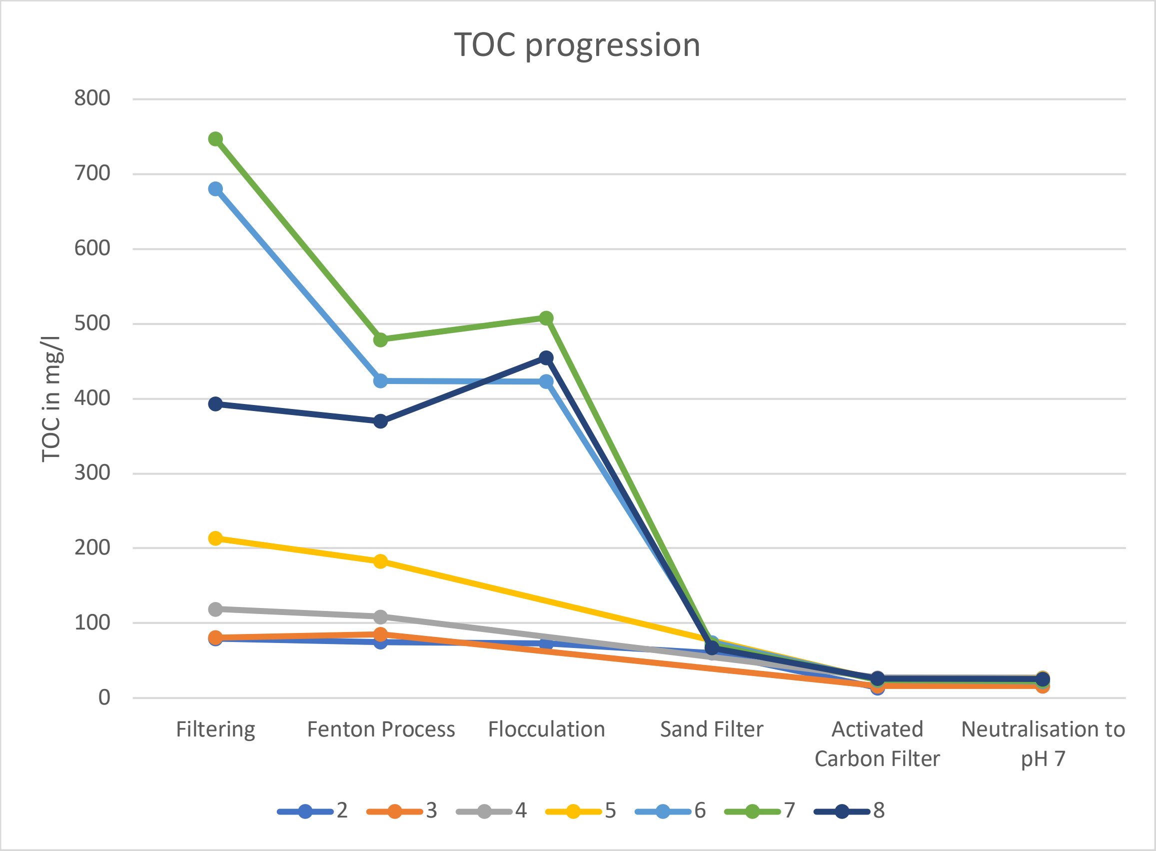


Figure 42 TOC progression during trial runs

Completely unfiltered leachate had a TOC of 2360 mg/l (measured in a laboratory trial run). The used filters therefore managed to remove more than half of the TOC, but for optimal treatment efficiency a smaller pore size than 20 µm is required.

Just as the TOC progression during treatment, all trial runs followed the same trend of concentrations levels dropping after activated carbon filtration for DOC. Concentrations after flocculation and sand filtration were not measured for trial runs 3,4 and 5 but are assumed to follow the same trend as the other trial runs. DOC concentrations remained stable up until after flocculation, meaning that the Fenton Process, which was designed to reduce the carbon concentration in the leachate was not efficient in removing dissolved organic carbon. The DOC concentration then rose after sand filtration, possibly due to deposition of previous trial runs and remobilization. The only efficient treatment step in removing dissolved organic carbon from the leachate was activated carbon filtration, which removed on average 67% of DOC in the leachate, the average concentration of DOC was 21.6 mg/l after activated carbon filtration.

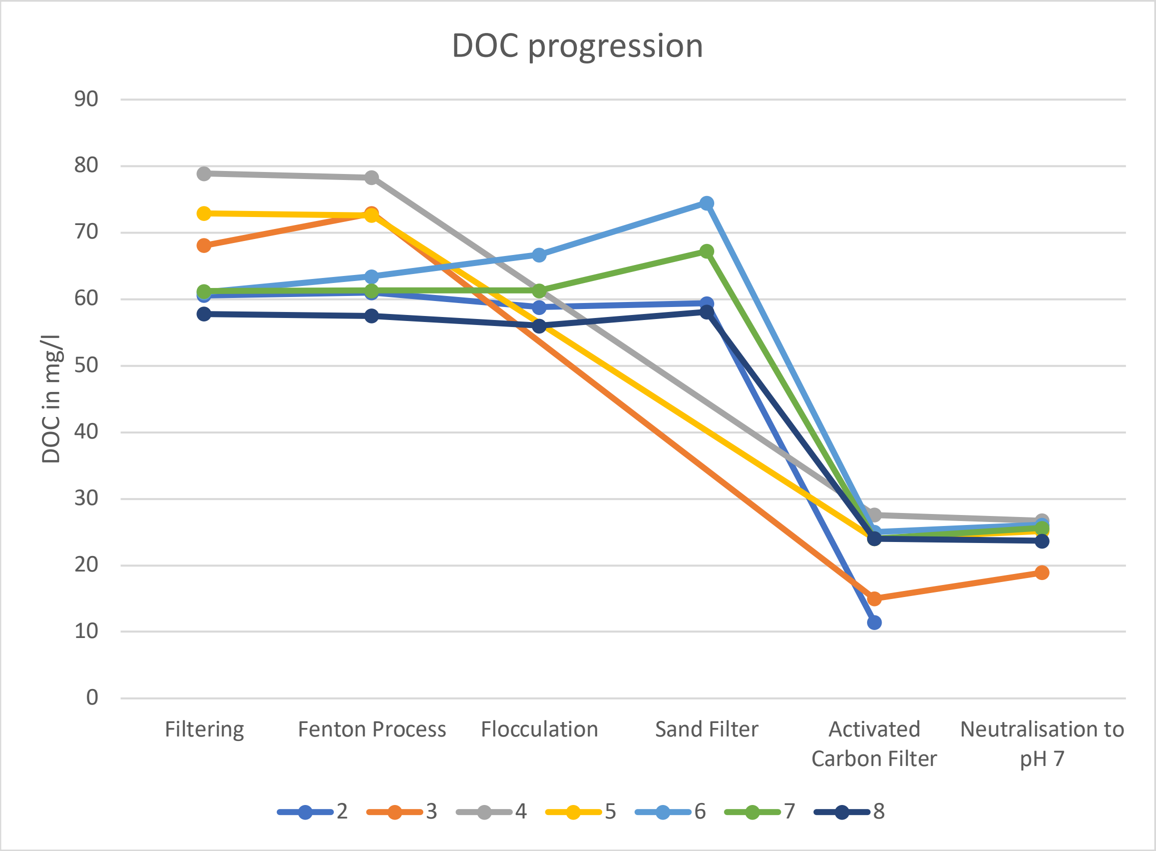


Figure 43 DOC progression during trial runs

The TNb concentrations were stable throughout the treatment process, with no relevant reduction in bonded nitrogen species observable (Figure 44). Trial run 2 and 3 were outliers which were not considered in the analysis. A similar trend was observable with NH_4-N concentrations, with an average reduction rate of only 14%, also not considering trial runs 2 and 3 (Figure 45).

As already mentioned in the Methods section, ammonium ions replace Na^+, the ion-exchange capacity of the activated carbon filter therefore increases with decreasing Na^+ concentration (Malekian et al., 2011). The leachate in this study had a high sodium concentration of over 22000 mg/l, decreasing the effectiveness of activated carbon filtration to remove nitrogen species tremendously.

The treatment in PP19 was overall not successful in reducing the nitrogen concentrations in the leachate and another method of reduction is needed in PP20.

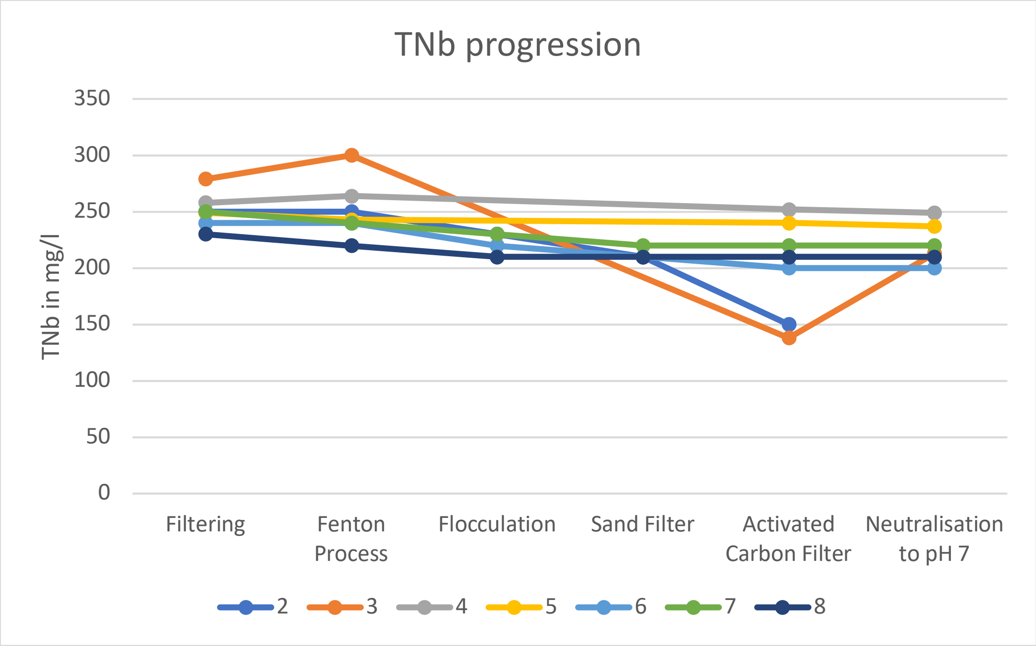


Figure 44 TNb progression during trial runs

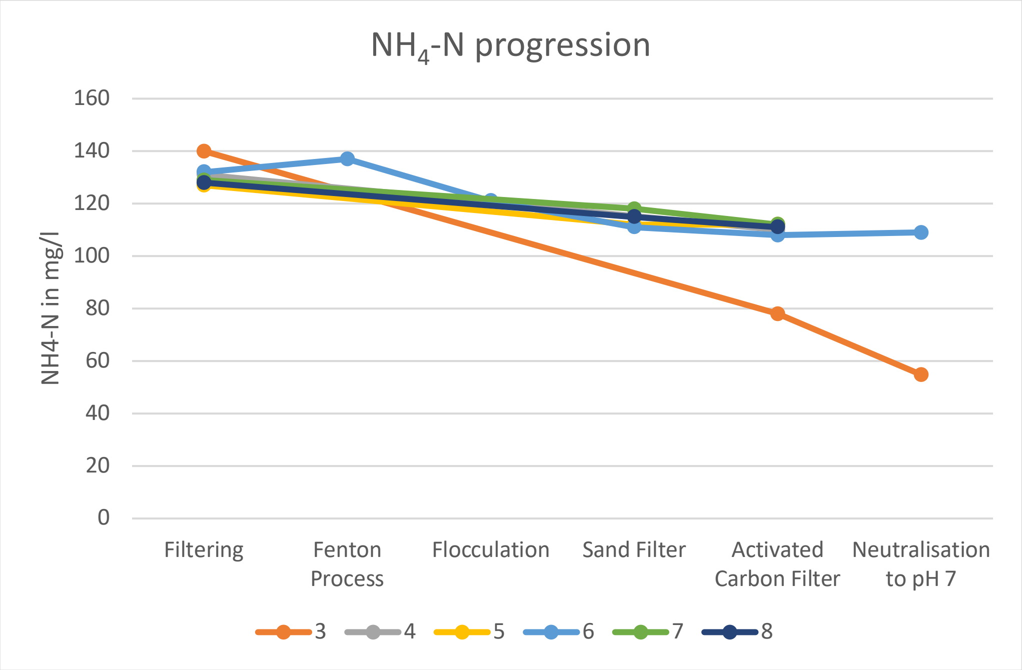


Figure 45 NH_4-N progression during trial runs

In Figure 46 the average and standard deviation of each parameter was calculated from all trial runs. DOC concentration after filtration, which was the start of sampling, was at 66 mg/l. At the end of the treatment process, after activated carbon filtration, the concentration was at 21.6 mg/l on average, yielding a DOC reduction of 67%. This correlated well with the DOC reduction of the individual trial runs. The standard deviation at both sampling points was low, with 8 mg/l and 6 mg/l respectively.

At the beginning of the treatment process the average TOC concentration was 331 mg/l, with a very high standard deviation of 284 mg/l. As already mentioned before, the high deviation was due to a malfunction in the filter system. At the end of the treatment process the TOC concentration was at 22 mg/l with a standard deviation of 5 mg/l. A TOC reduction of 97% on average was achieved.

The TNb concentration at the beginning of the treatment was 251 mg/l with a standard deviation of 15 mg/l. After treatment the TNb concentration was 201 mg/l, with a high standard deviation of 43 mg/l.

NO_3-N concentrations at the beginning of treatment were low at 4.4 mg/l with a minimal standard deviation of 0.5 mg/l. At the end of treatment, the concentration increased by 54% to 6.7 mg/l with a relatively high standard deviation of 2.8 mg/l.

Concerning NH_4-N, at the beginning of the treatment the concentration was at 131 mg/l with a standard deviation of 5 mg/l. After treatment NH_4-N was reduced by 23% to a concentration of 101 mg/l on average, with a standard deviation of 17 mg/l.

The COD (JIS) concentration before treatment was at 358 mg/l O, with a very high standard deviation of 102 mg/l O, due to the very heterogenous dust. After treatment, the COD concentration was at 84 mg/l O and the standard deviation 20 mg/l O. The reduction of COD during treatment was 77%.

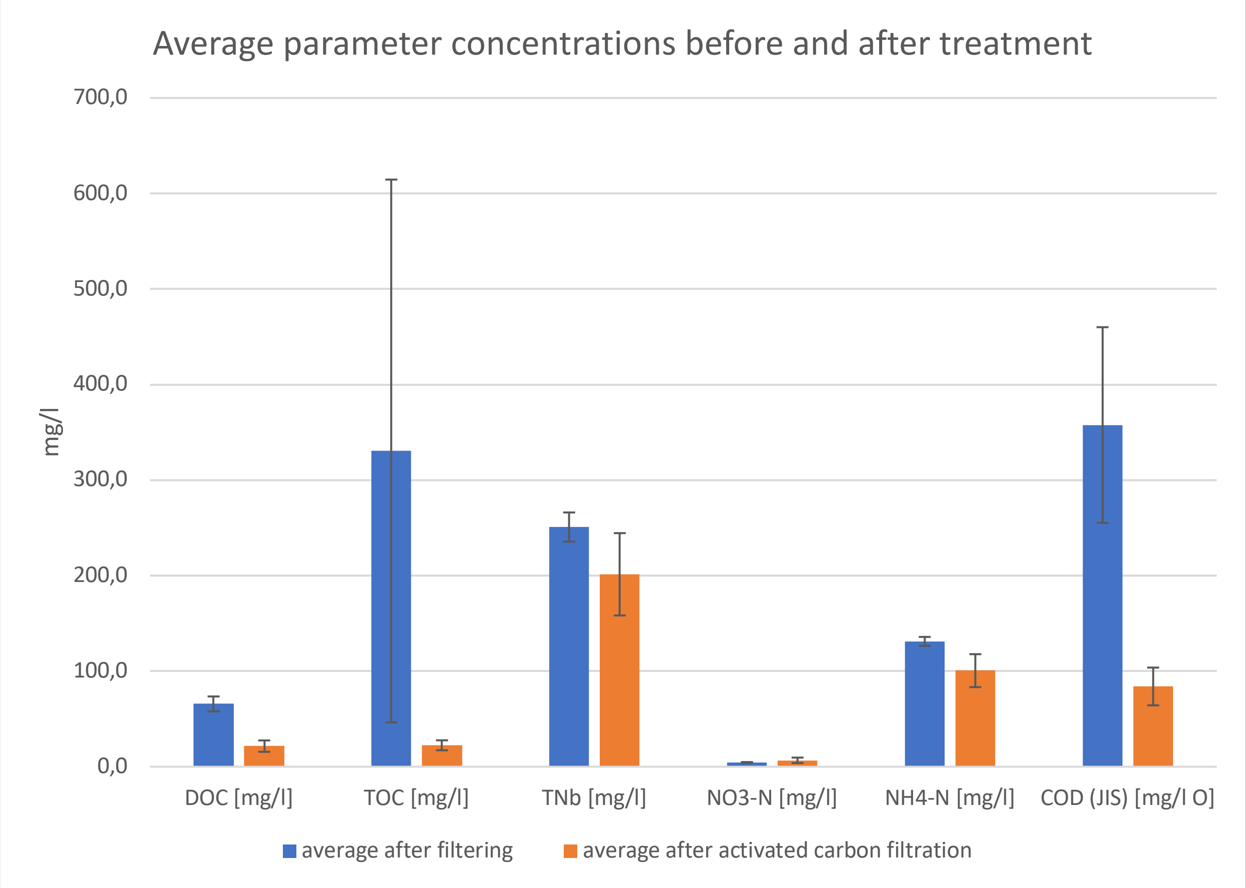


Figure 46 Average parameter concentrations before and after treatment

For parameters DOC, TOC and COD the average percentage of reduction was enough to meet effluent standards of most countries. As already mentioned earlier, the reduction in concentration of all nitrogen species was not successful in this Pilot Plant. A specific treatment method concerning nitrogen is needed for reduction to meet effluent standards.

The average concentration and standard deviation of COD, TNb, NH_4-N and dissolved iron was calculated from the sample values taken after activated carbon filtration. In Figure 47 it can be seen, that the average concentration of COD complied with the effluent standards of Austria and Japan, but not with the effluent standards of Korea, which are considerably lower. The nitrogen parameters, TNb and Ammonium were not able to meet the effluent standards of any country. As already discussed, the given industrial treatment was not suitable in reducing nitrogen species. The concentration of dissolved iron was very low and was the only parameter which met all three countries national effluent standards.

National effluent standards differ considerably from each other, both in terms of concentrations for specific parameters and also in selected parameters. Parameters, and parameter concentrations which might be a problem in one country might not be a problem in another country. Therefore, there is no treatment that fits all.

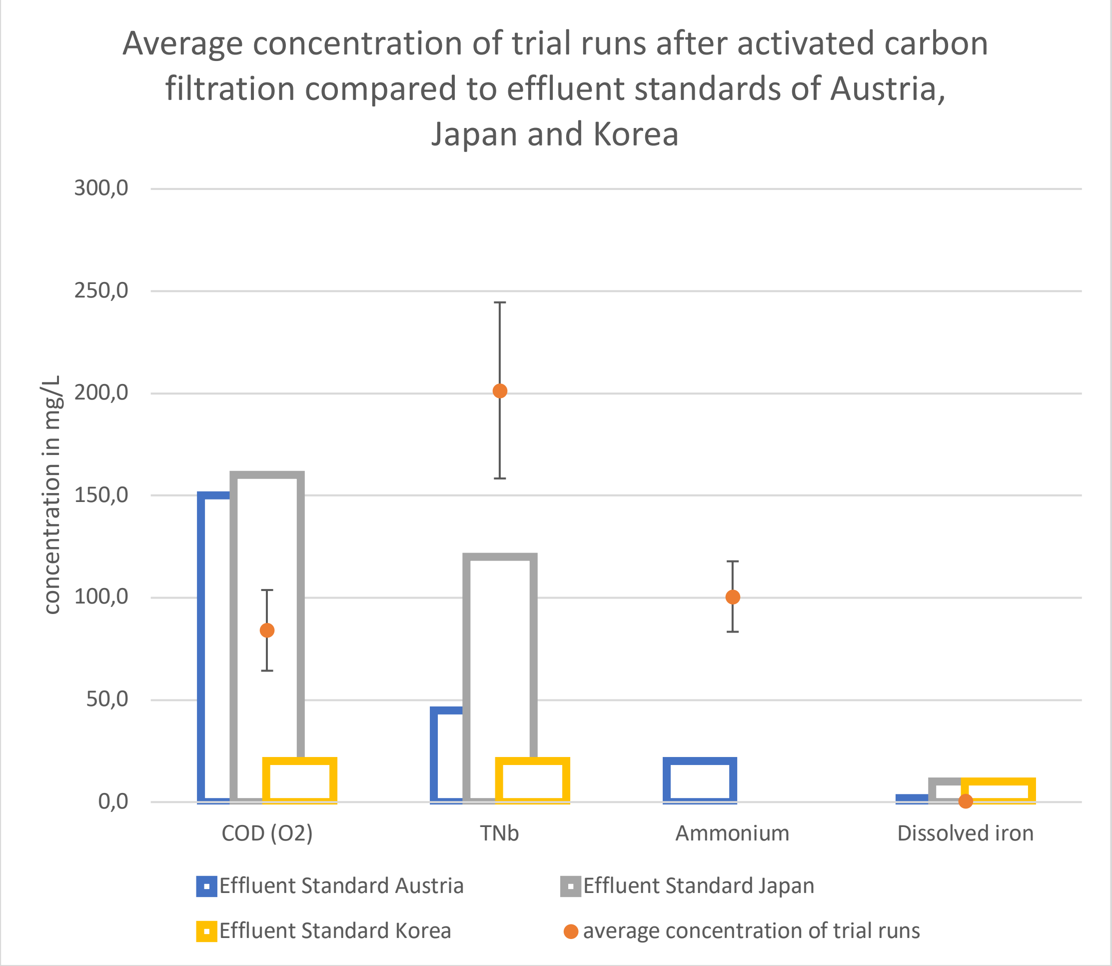


Figure 47 Average concentration of trial runs after filtration compared to effluent standards

5.5 Pilot Plant 2020

5.5.1 Air Stripping

Additional to air stripping to reduce NH_4-N in the leachate, it was thought about reducing F- via precipitation with CaO, but as the residue containing F^- cannot be recycled, the concept was abandoned after two trials. Due to this fact it was not possible to use lime to adjust the pH of the leachate. Sodium hydroxide was used instead.

Volume of H_2SO_4 solution in the gas collection vessel and treatment time can be seen in Table 12.

In Figure 48 the NH_4-N concentration in the H_2SO_4 solution for Str0014 was lower due to the trial only using 1 kg of dust and 3 kg of water compared to three times the amounts in all the other trials, while the volume of H_2SO_4 solution stayed the same. Taking that into account a trend of decreasing treatment efficiency was apparent, as with each stripping less NH_4-N was removed from the leachate and brought into the H_2SO_4 solution.

The same trend can also be observed in Figure 49, where the NH_4-N concentrations of the leachate after stripping were approximately 20 mg/l higher for each stripping than of the previous one. This could be due to the fact, that the solid residue, from Str0016 onwards, was left in the air stripping column after decanting in preparation of running PP20 continuously.

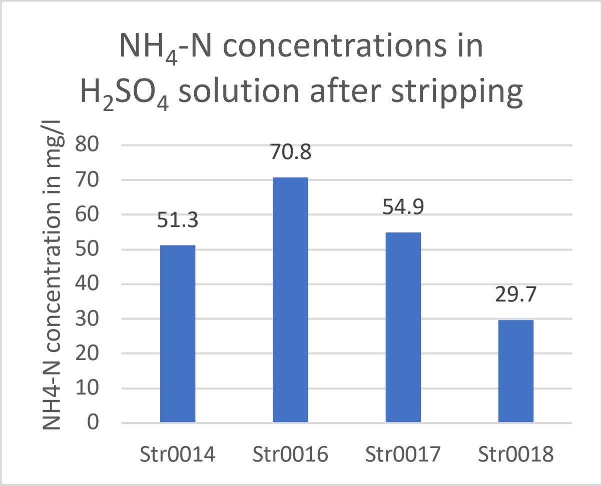


Figure 48 NH_4-N concentrations in H_2SO_4 solution after stripping

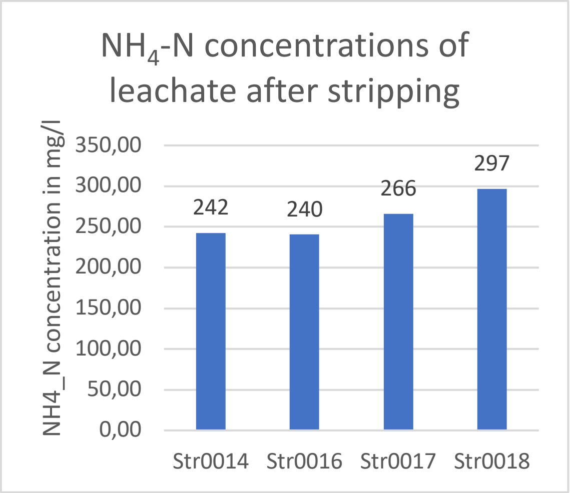


Figure 49 NH_4-N concentrations of leachate after stripping

In Figure 50 the same loss of treatment efficiency after each trial run can be observed. The NH_4-N concentrations are given in mg/trial. NH_4-N (H_2SO_4) after stripping (blue) is the amount of NH_4-N in the 4 l H_2SO_4 solution in the gas collection vessel, NH_4-N total (orange) is the sum of NH_4-N (H_2SO_4) after stripping and NH_4-N in the 9 l of leachate after treatment. NH_4-N transported (grey) is the percentage of NH_4-N transferred from the air stripping column to the gas collection vessel. It is the value that best describes the success of the treatment. As observable in Figure 50 the percentage of NH_4-N transported drops significantly after each trial. The drop in treatment efficiency could be due to sediment of previous trial runs which was left in the stripping column, causing error in the calculation of substance amounts used for the stripping trials.

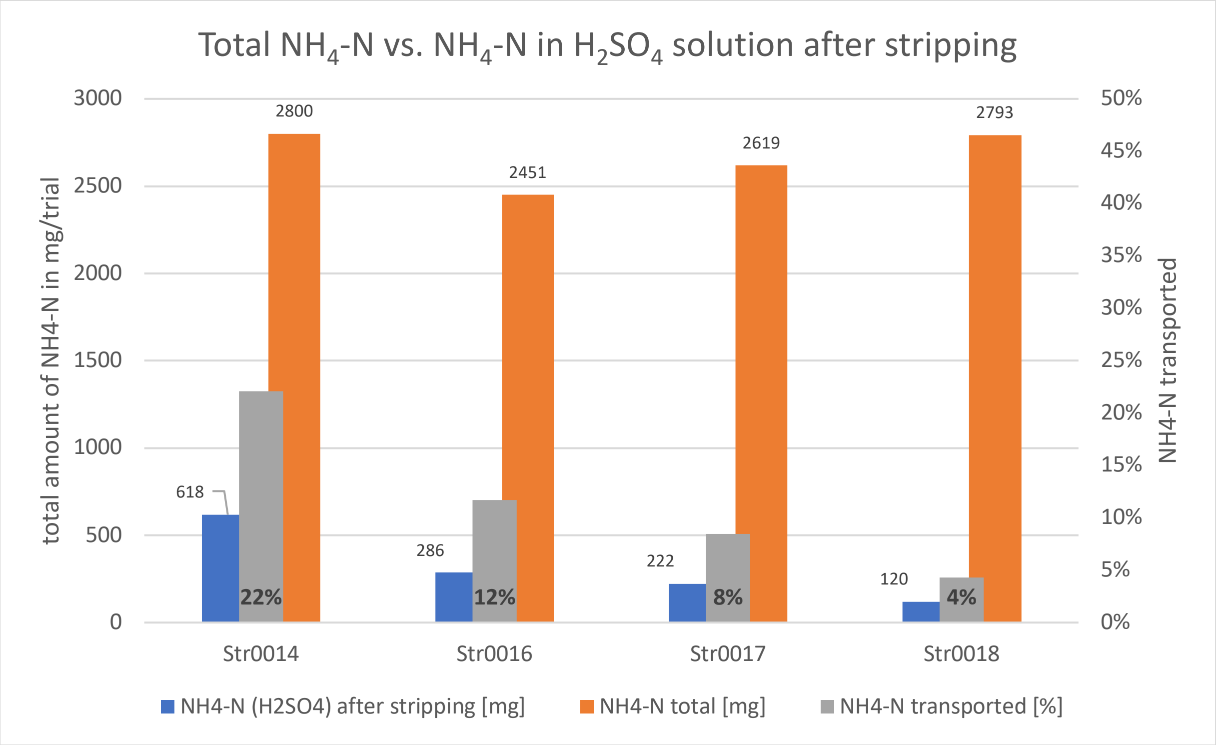


Figure 50 Total NH_4-N vs. NH_4-N in H_2SO_4 solution after stripping

Compared to small scale trials in the laboratory, treatment in the pilot plant was not as efficient. The upscaling from laboratory trials to pilot plant trials needs more adjustments. Various factors differ between the two treatments, such as:

1. Water temperature
2. Amount of air
3. Size of air bubbles
4. Amount of dust treated

The pH of both trials was the same. The water used in the laboratory had a temperature of 60ºC, whereas the water in the pilot plant only had a temperature of 12ºC. Due to technical difficulties, it was impossible to install hot water for PP20. The amount of air input was about 5 l/min, whereas at PP20 it was 15-20 l/min due to the higher amount of leachate to be treated. The size of the air bubbles was the same for the laboratory and PP20, but the column at PP20 was a lot bigger than the apparatus used in the laboratory, therefore the distribution could be different. In laboratory trials the amount of dust treated was significantly less than in the air stripping column in PP20. This might also influence the efficiency. Reducing the NH_4-N load with an air stripping treatment is promising, although further investigations in terms of water temperature need to be done.

Low temperature, as well as an NH_4-N load far over 100 mg/l might be cause for less efficient trial runs in the pilot plant. As stated above, with decreasing temperature, the amount of air required increases (Tchobanoglous et al., 2002) and the efficiency decreases (U.S. EPA, 2000). Further, the air stripping method works well in the range of 10 to 100 mg/l NH_4-N, with higher concentrations other methods are suggested (U.S. EPA, 2000).

The average NH_4-N concentration of leachate after stripping compared to TNb effluent standards of Austria, Japan and Korea in Figure 51 shows, that NH_4-N concentrations were far above each countries effluent standards. Considering that NH_4-N is only one species of nitrogen that is part of TNb, the reduction through the treatment of air stripping needs a lot of optimization work before being able to reduce nitrogen species on an industrial scale. The average concentration of NH_4-N was a factor 6 times bigger than the Austrian effluent standard, for Japan and Korea the factor was 2 and 13 respectively.

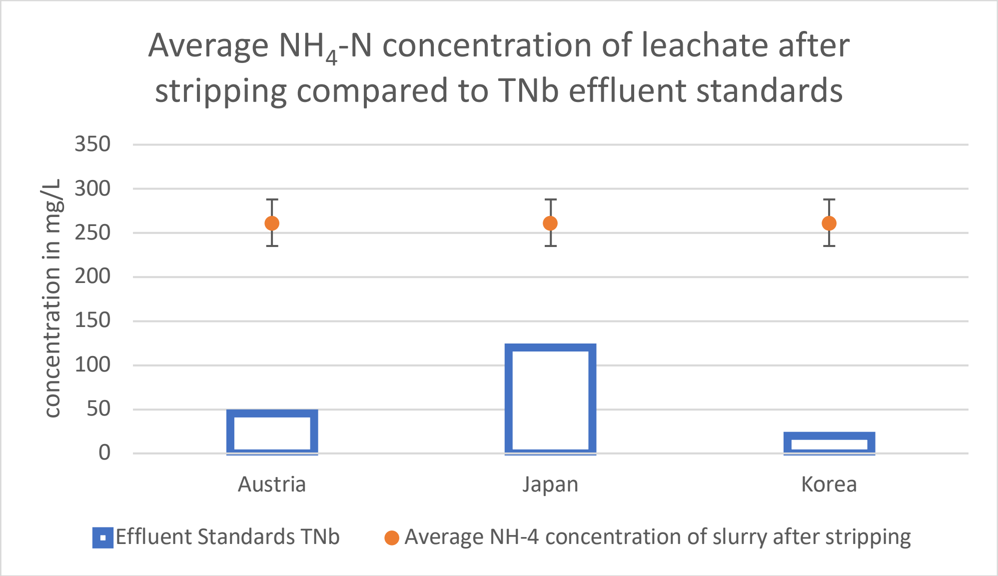


Figure 51 Average NH_4-N concentration of leachate after stripping compared to TNb effluent standards

5.5.1.1 Sedimentation

Sedimentation was a slow process. The leachate takes approximately 24 hours to settle properly. Once settled, samples could be taken and the leachate could be treated further without the need of a complex filtering system. In Figure 52, Figure 54 and Figure 53 the stripping column is shown after 24 hours of sedimentation. The sediment on the bottom forms a sludge (Figure 55). It cannot be removed by draining from the bottom. The leachate drained through the bottom after the sludge formed a drain funnel (Figure 18).

Of course sedimentation was only applicable for batch trials, to filter the leachate in the continuous trials an appropriate filtering system was planned. In a continuous process sediment would be taken out of the stripping column in suspension in the leachate, and then filtered.

Figure 52 Sediment of AV_CaO/Str 0014

Figure 53 Sediment of AV_Str0017

Figure 54 Sediment of AV_Str0018

Figure 55 Sediment left after drainage

5.5.2 AOP

For the Advanced Oxidation Process (AOP) trials two different oxidizing agents, H_2O_2 and $Na_2S_2O_8$, were used. The TOC and TNb analysis of the samples was done in replicate determination (analysis was done twice for each sample). Table 16 shows the results of the concentrations before treatment. The average TOC concentration in the decanted leachate before treatment was 162 mg/l with a standard deviation of 4mg/l. The average concentration of TNb in the decanted leachate before treatment was 383 mg/l with a standard deviation of 20 mg/l.

Table 16 Concentrations of TOC and TNb before treatment

H2O2_UV_Orig	TOC [mg/l]	167
19.11.20	TNb[mg/l]	360
H2O2_UV_Orig	TOC [mg/l]	161
07.12.20	TNb[mg/l]	390
Na2S2O8_UV_Orig	TOC [mg/l]	159
09.12.20	TNb[mg/l]	400

Figure 56 TOC after treatment vs. average TOC before treatment shows TOC concentration [mg/l] on the left y-axis (blue) and TOC Reduction in % on the right y-axis (orange). Further, the average TOC [mg/l] with its standard deviation is given on the right. All 7 trial runs have similar TOC concentrations in the range of 148 to 156 mg/l TOC. The TOC reduction of all trials was below 10%. Considering the standard deviation of the initial TOC concentration the overall reduction using H_2O_2 as an oxidizing agent to reduce the carbon contamination of the wastewater was not successful. Due to the high bromide and chloride concentrations the oxidation process might be disturbed by free radical scavengers, same as in the Fenton Process. A further constraint for H2O2-UV_03 to 07 was the high molar concentration of 70 mmol of H_2O_2, at which H_2O_2 might work as a HO• scavenger itself (Equation 2). The AOP study of Cokay Catalkaya & Kargi, 2007, had a comparable inital TOC range, with a TOC reduction rate of 85%. But compared to the leachate with a chloride concentration of 14000 mg/l, the chloride concentration was in the single digit range of mg/l. This was another indicator, that high chloride concentrations disturb the oxidation process.

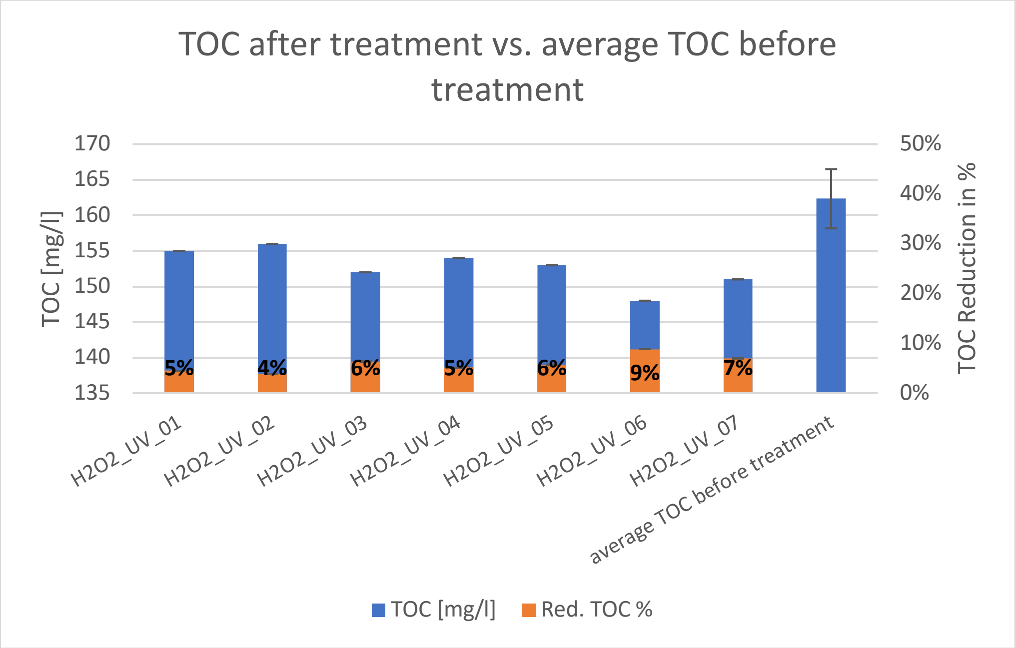


Figure 56 TOC after treatment vs. average TOC before treatment

Figure 57 TNb after treatment vs. average TNb before treatment shows TNb concentrations on the left y-axis and TNb Reduction in % on the right y-axis. The average TNb concentration before treatment with its standard deviation is given on the right side of the figure. The TNb concentrations in mg/l (blue) are shown against the reduction of TNb (orange). The reduction of TNb was slightly above 10% for H2O2_UV_01 to H2O2_UV_04 compared to the average TNb concentration before treatment. Although the reduction was below 10% if compared to the TNb value before treatment measured the day of the trials. Considering the standard deviation, there was no change in TNb concentration for trial runs H2O2_UV_05 to H2O2_UV_07. H_2O_2 as an oxidizing agent was not appropriate in reducing TNb and therefore the nitrogen load of the wastewater to be treated.

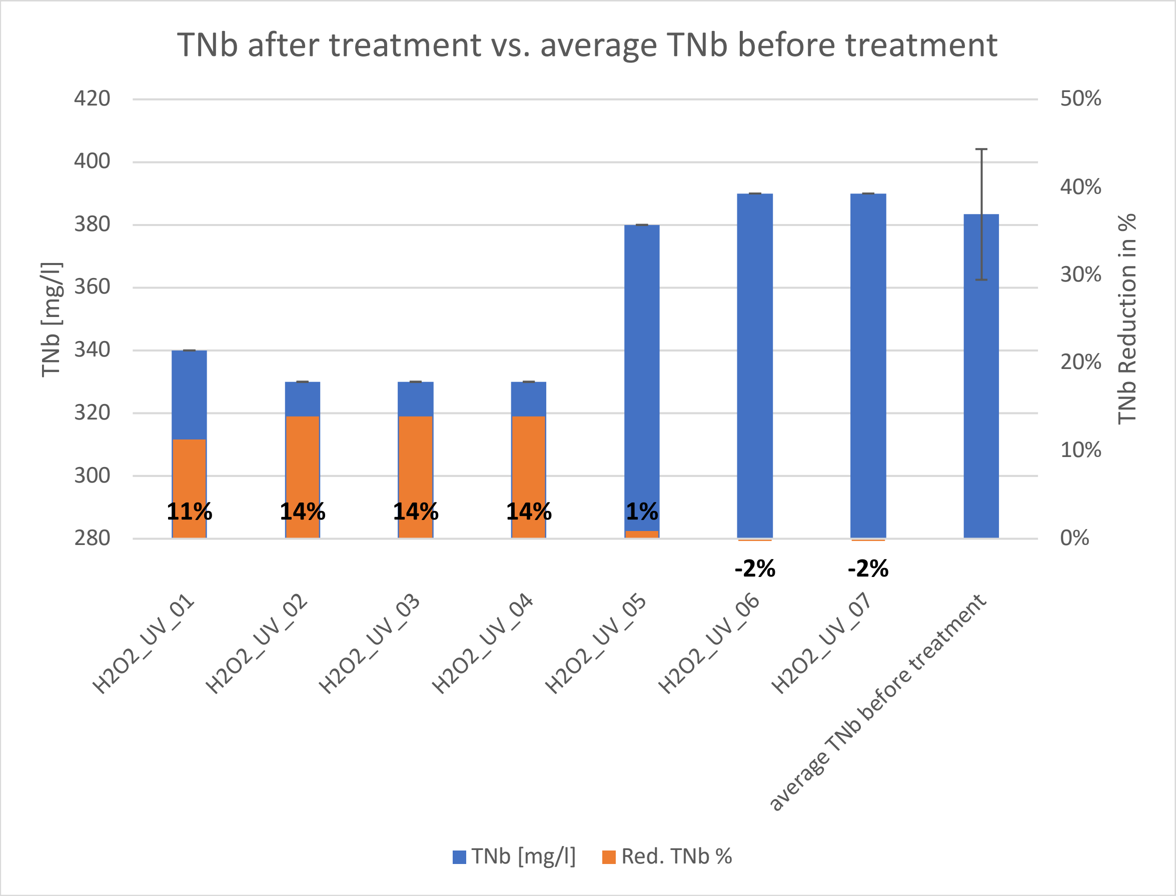


Figure 57 TNb after treatment vs. average TNb before treatment

Figure 58 shows TOC [mg/l] on the left y-axis (blue) and TOC reduction in % on the right y-axis (orange). The average TOC concentration [mg/l] with its standard deviation is given on the right. All trial runs were in the same range of TOC concentration. The TOC reduction of all trials was far below 10%. The initial TOC concentration was measured the day of the treatment. Reduction of carbon content using $Na_2S_2O_8$ as an oxidizing agent was not successful at the applied concentrations.

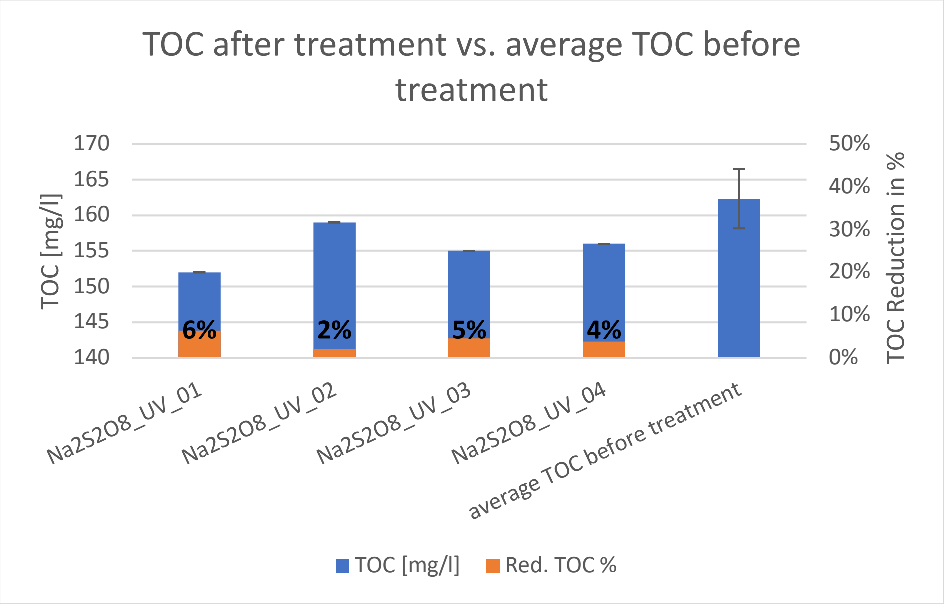


Figure 58 TOC after treatment vs. average TOC before treatment

Figure 59 shows TNb concentrations on the left y-axis and TNb reduction in % on the right y-axis. The average TNb concentration before treatment with its standard deviation is given on the right side of the figure. The TNb concentrations in mg/l (blue) are shown against the reduction of TNb (orange). All TNb concentration values were higher after treatment as before. Taking into account the standard deviation of average TNb before treatment no change in TNb concentration occurred during treatment with UV and the oxidizing agent $Na_2S_2O_8$. The oxidizing agent was therefore not suitable in reducing nitrogen concentrations in the leachate.

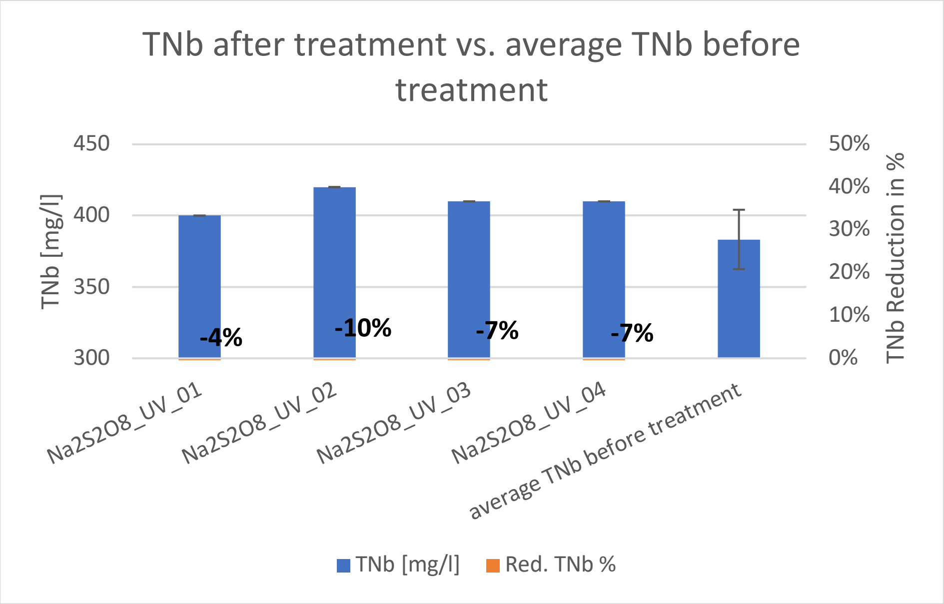


Figure 59 TNb after treatment vs. average TNb before treatment

6. Conclusion

Treatment in both Pilot Plants partly managed to meet the objectives set for this thesis. The reduction of landfill bound material was possible due to the high amount of solvable salts (approx. 90%) in the MEROS process residue, of which most of the filterable substances can be recycled back into the sinter feed.

Reduction of carbon and compliance to European and international effluent standards was possible for COD using treatment in Pilot Plant 2019. A COD reduction of 77% was possible, reaching a COD concentration of 84 mg/l.

Although the Fenton Process did not work as intended presumptively due to interference of chloride and bromide as HO• scavengers and fluoride due to reduction of Fe(III) reactivity, the treatment overall managed to reduce the carbon concentration below effluent standards of some countries. This was mostly due to activated carbon filtration, which needs to be examined as a more central treatment method in the future. It was not possible to reduce the nitrogen concentration below effluent standards with Pilot Plant 2019, which was further investigated in Pilot Plant 2020.

Pilot Plant 2020 did not meet any of the effluent standards. Ammonium-nitrogen reduction was attempted by air stripping. The method was not as efficient in Pilot Plant trial runs, as it was in laboratory trials. Reduction of ammonium-nitrogen was on average 11%, with trials going as low as a 4% reduction.

In laboratory testing the method was successful at a removal rate of above 90%. Parameters in need of further investigation for the Pilot Plant are:

- Option of high temperature operation
- Air distribution
- Possibility of carriers to distribute leachate and give more surface for water-air interaction
- pH adjustments.

AOP processes using UV and H_2O_2 or $Na_2S_2O_8$ respectively were unsuccessful in reducing the carbon concentration. A number of factors might be at fault: similar to the Fenton Process, scavenging of free radicals and lowering of reactivity, but further a scattering of UV light due to fine particles in the leachate.

To tackle the problem of particle interference with treatment, an updated filtration system is needed. Requirements of the filter system are good filtration capacity of very fine particles, smaller 20 µm, more stable filtration and further an option to regenerate the filter, as continuously replacing filters is not very economical.

In terms of reducing the carbon load of the leachate, activated carbon filtration needs to be examined more closely for solutions, as the leachate contains too many interfering substances for an oxidative method.

7. Summary

Sinter processes make up about 50% of dust emissions of integrated steel works, with pollutants like heavy metals, sulfur oxides, nitrogen oxides, hydrogen chloride, hydrogen fluoride, hydrocarbons and carbon monoxide. The MEROS process is used to reduce pollutants in the off-gas. The process is an end-of-pipe technique and reduces emissions by adding additives to the off-gas and conditioning it, before filtration. The MEROS dust residue needs to either be landfilled or treated.

This thesis concerned itself with the treatment of the MEROS process residue. The objectives were reducing the carbon and nitrogen loads in the leachate of the residue to meet effluent standards, as well as reducing the amount of landfill bound material.

To fulfill the objectives and treat the residue, two Pilot Plants were built in the technical hall of BOKU Muthgasse, Vienna. Pilot Plant 2019 utilized a given industrial wastewater treatment consisting of filtration, the Fenton Process, heavy metal precipitation and sedimentation, as well as sand and activated carbon filtration. Pilot Plant 2020 had an air stripping column for NH_4-N reduction and used an UV lamp for AOP.

Success of treatment was measured by analysis of DOC, TOC and TNb, done by the Chemical Laboratory of the Institute of Sanitary Engineering and Water Pollution Control (SIG). Further, the parameters COD, NO_3-N and NH_4-N, as well as hydrogen peroxide and dissolved iron concentrations were measured. Lastly, COD was also measured according to JIS with a titrimetric method.

The residue had an average of 12% filterable substance, therefore almost 90% of the residue dissolved when preparing a leachate. The objective of reduction of landfill volume was therefore achievable.

Treatment of the leachate in Pilot Plant 2019 was partly successful in meeting effluent standards. The COD and dissolved iron effluent standards were met, TNb and ammonium standards could not be reached. Initial COD concentrations were reduced by 77% to a value of 84 mg/l. The TOC was reduced to 22 mg/l, which is a reduction of 97%. Nitrogen removal was not able to meet effluent standards. Even though the treatment overall was successful, the Fenton Process, intended to reduce the organic carbon load in the leachate did not work as expected from the experience in laboratory trials. This might be due to interference of free radical scavengers such as chloride and bromide, which the leachate contains high concentrations of, and further due to fluoride reducing the reactivity of Fe(III). Most of the carbon load was reduced by activated carbon filtration, a treatment method which should be investigated further in the future.

Neither nitrogen nor carbon removal using the air stripping technique and AOP respectively were able to reduce concentrations to effluent standards in Pilot Plant 2020. Air stripping was used to reduce the ammonium-nitrogen concentrations of the leachate. The average removal rate was 11%, with trials as low as 4%. The method has promise, as seen in the laboratory, but several parameters need further investigation to optimize the treatment. Carbon removal using UV and either hydrogen peroxide or $Na_2S_2O_8$ as oxidation agent was not successful. All TOC removal rates were below 10%. This could be due to interference similar to the Fenton Process or due to UV scattering in the treated leachate due to fine particles in suspension.

Timescale of the thesis was October 2019 until December 2020, with a six month break between, due to a semester abroad and COVID-19.

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9. List of figures

10. List of tables

11. Appendix

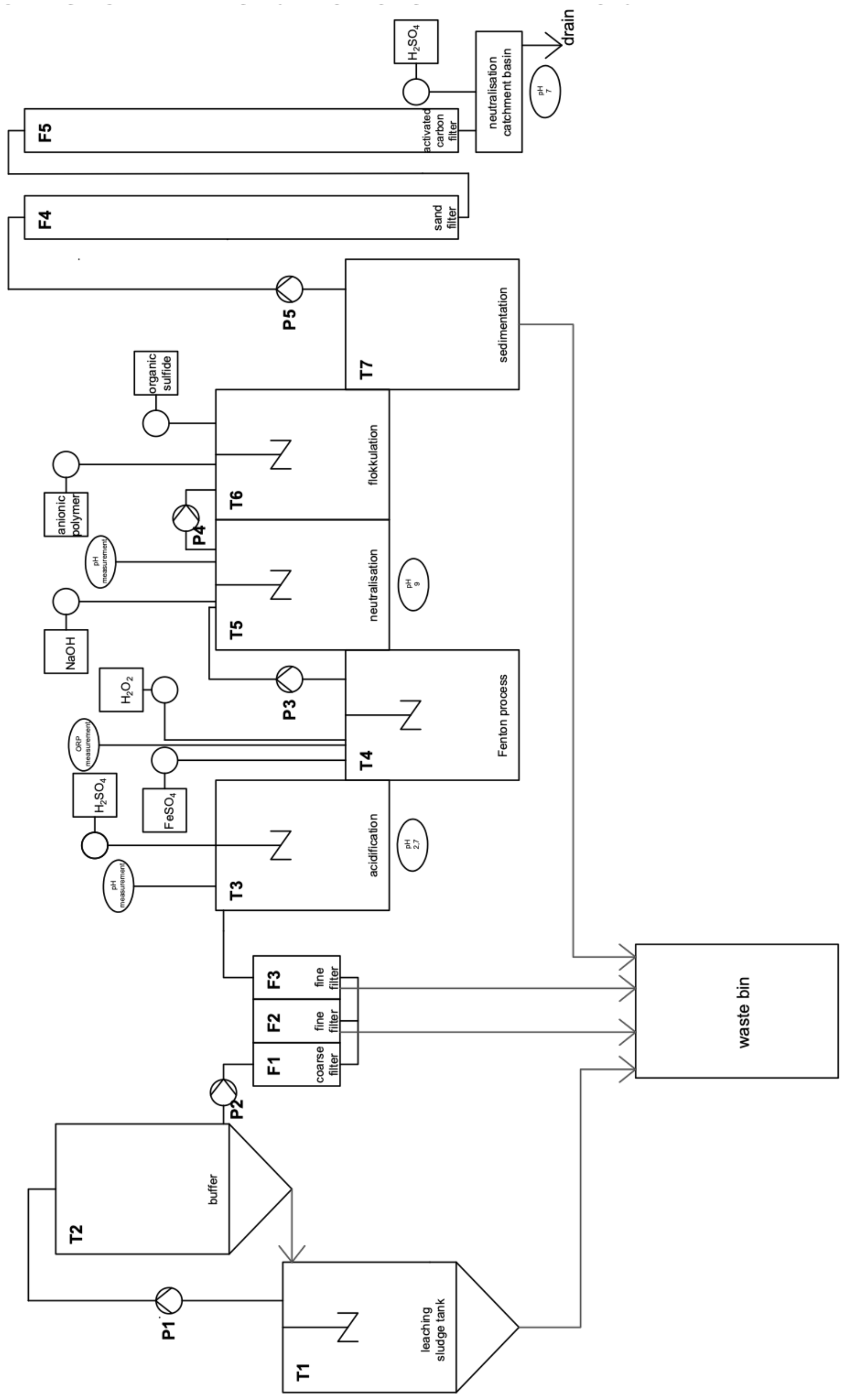

Figure 60 Schematic drawing of Pilot Plant 2019

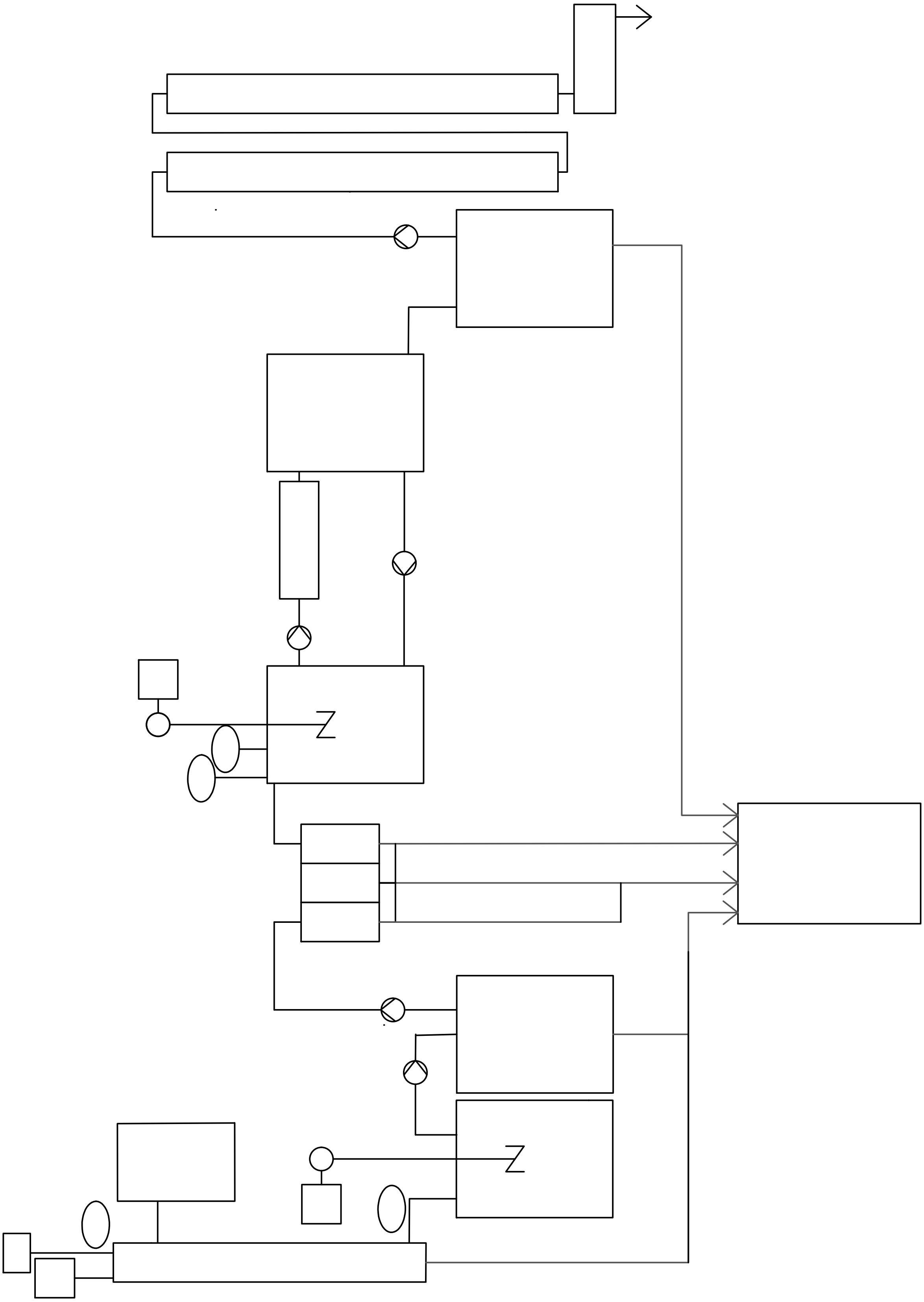

Figure 61 Schematic drawing of Pilot Plant 2020

Table 17 Limit of Quantification for Elan DRC-e ICP-MS

Element	LOQ µg/l solved quant[3]	LOQ µg/l total quant[3]
Ag	0.10 µg/l	0.30 µg/l
Al	5.0 µg/l	12.0 µg/l
As	0.50 µg/l	0.50 µg/l
Au	0.20 µg/l	
B	3.0 µg/l	3.0 µg/l
Ba	0.50 µg/l	1.0 µg/l
Bi	0.50 µg/l	0.50 µg/l
Ca	20 µg/l	
Cd	0.05 µg/l	0.10 µg/l
Co	0.10 µg/l	0.10 µg/l
Cr	0.50 µg/l	2.5 µg/l
Cu	1.0 µg/l	3.0 µg/l
Fe	5.0 µg/l	10.0 µg/l
Hg	0.10 µg/l	0.60 µg/l
K	3.0 µg/l	
Li	0.10 µg/l	0.20 µg/l
Mg	5.0 µg/l	
Mn	0.50 µg/l	0.50 µg/l
Mo	0.50 µg/l	1.5 µg/l
Na	100 µg/l	
Ni	0.50 µg/l	2.0 µg/l
P	0.80 µg/l	0.80 µg/l
Pb	0.50 µg/l	4.0 µg/l
Pd		
Pt	0.10 µg/l	
Rh	0.10 µg/l	
Re	0.10 µg/l	
S	500 µg/l	1200 µg/l
Sb	0.50 µg/l	
Se	0.50 µg/l	2.0 µg/l
Sn	0.50 µg/l	
Sr	0.05 µg/l	0.50 µg/l
Ti	0.50 µg/l	3.0 µg/l
U	0.10 µg/l	0.2 µg/l
V	1.0 µg/l	1.0 µg/l
W	0.05 µg/l	1.0 µg/l
Zn	3.0 µg/l	6.0 µg/l

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[3] (Stach, 2016)

Table 18 Limit of quantification and limit of detection for DIONEX ICS 3000 (IC)

Ion	**LOQ in mg/l**[4]
Chloride	0.1
Nitrate-N	0.1
Sulfate	0.4
Phosphate-P	0.5
Nitrite-N	0.1
Sulfite	0.3
Thiosulfate	0.3
Ammonium-N	0.5
Sodium	0.2
Kalium	0.2
Magnesium	0.2
Calcium	0.2

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[4] (Stach & Ziegenbalg, 2020)

Table 19 Puffer capacity

		Dillution	1:3	1:4	1:6	1:8	1:10
consumption [ml]	mg NaOH (100ml)	NaOH [mg/l]	pH	pH	pH	pH	pH
0	0	0	8.13	8.25	8.706	8.756	8.824
0.1	4	40	8.163	8.301	8.778	8.756	8.946
0.2	8	80	8.194	8.346	8.847	8.99	9.06
0.3	12	120	8.227	8.392	8.92	9.074	9.16
0.4	16	160	8.259	8.437	8.99	9.161	9.26
0.5	20	200	8.292	8.482	9.054	9.242	9.356
0.6	24	240	8.323	8.526	9.119	9.32	9.45
0.7	28	280	8.354	8.57	9.182	9.395	9.543
0.8	32	320	8.385	8.612	9.241	9.468	9.641
0.9	36	360	8.414	8.646	9.3	9.532	9.735
1	40	400	8.443	8.684	9.353	9.6	9.83
1.1	44	440	8.474	8.722	9.41	9.671	9.932
1.2	48	480	8.503	8.756	9.449	9.739	10.017
1.3	52	520	8.53	8.793	9.504	9.811	10.138
1.4	56	560	8.557	8.828	9.561	9.89	10.266
1.5	60	600	8.584	8.862	9.614	9.97	10.405
1.6	64	640	8.61	8.895	9.672	10.055	10.555
1.7	68	680	8.636	8.928	9.729	10.146	10.708
1.8	72	720	8.661	8.96	9.787	10.244	10.849
1.9	76	760	8.687	8.992	9.846	10.351	10.962
2	80	800	8.712	9.023	9.908	10.463	11.058
2.1	84	840	8.736	9.053	9.972	10.588	
2.2	88	880	8.76	9.083	10.04	10.713	
2.3	92	920	8.783	9.112	10.111	10.535	
2.4	96	960	8.805	9.141	10.188	10.656	
2.5	100	1000	8.827	9.196	10.269	10.754	
2.6	104	1040	8.85	9.197	10.35	10.89	
2.7	108	1080	8.872	9.225	10.442	10.983	
2.8	112	1120	8.894	9.252	10.539	11.08	
2.9	116	1160	8.915	9.28	10.57	11.172	
3	120	1200	8.937	9.308	10.67	11.246	
3.1	124	1240	8.957	9.334	10.76	11.318	
3.2	128	1280	8.979	9.361	10.7	11.368	
3.3	132	1320	9	9.388	10.785	11.42	
3.4	136	1360	9.02	9.414	10.88	11.508	
3.5	140	1400	9.04	9.441	10.94	11.508	
3.6	144	1440	9.061	9.467	11	11.55	
3.7	148	1480	9.08	9.494			
3.8	152	1520	9.1	9.521			
3.9	156	1560	9.12	9.548			
4	160	1600	9.138	9.575			
4.1	164	1640	9.158	9.603			
4.2	168	1680	9.177	9.63			

4.3	172	1720	9.196	9.658
4.4	176	1760	9.215	9.685
4.5	180	1800	9.234	9.713
4.6	184	1840	9.254	9.741
4.7	188	1880	9.273	9.769
4.8	192	1920	9.292	9.798
4.9	196	1960	9.311	9.827
5	200	2000	9.329	9.855
5.1	204	2040	9.348	9.887
5.2	208	2080	9.367	9.918
5.3	212	2120	9.385	9.949
5.4	216	2160	9.404	9.982
5.5	220	2200	9.424	10.016
5.6	224	2240	9.443	10.05
5.7	228	2280	9.461	10.084
5.8	232	2320	9.48	10.121
5.9	236	2360	9.5	10.159
6	240	2400	9.519	10.199
6.1	244	2440	9.538	10.238
6.2	248	2480	9.557	10.28
6.3	252	2520	9.576	10.325
6.4	256	2560	9.595	10.371
6.5	260	2600	9.615	10.421
6.6	264	2640	9.634	10.472
6.7	268	2680	9.655	10.5
6.8	272	2720	9.675	10.543
6.9	276	2760	9.694	10.589
7	280	2800	9.715	10.625
7.1	284	2840	9.735	10.665
7.2	288	2880	9.755	10.711
7.3	292	2920	9.776	10.733
7.4	296	2960	9.796	10.752
7.5	300	3000	9.818	10.748
7.6	304	3040	9.839	10.725
7.7	308	3080	9.862	10.76
7.8	312	3120	9.884	10.81
7.9	316	3160	9.906	10.85
8	320	3200	9.93	10.83
8.1	324	3240	9.951	10.826
8.2	328	3280	9.975	10.9
8.3	332	3320	9.999	10.974
8.4			10.024	
8.5			10.049	
8.6			10.075	
8.7			10.102	
8.8			10.129	

8.9	10.157
9	10.186
9.1	10.216
9.2	10.246
9.3	10.278
9.4	10.31
9.5	10.344
9.6	10.378
9.7	10.424
9.8	10.451
9.9	10.49
10	10.525
10.1	10.56
10.2	10.601
10.3	10.62
10.4	10.66
10.5	10.695
10.6	10.74
10.7	10.785
10.8	10.83
10.9	10.871
11	10.914
11.1	10.954
11.2	10.955
11.3	10.99
11.4	11.03

12. Affirmation

I certify, that the master thesis was written by me, not using sources and tools other than quoted and without use of any other illegitimate support.

Furthermore, I confirm that I have not submitted this master thesis either nationally or internationally in any form.

Neusiedl am See, 24.09.21 MAGDALENA HAIDER Magdalena Haider

Place, date *name surname* *signature*