H_2S laden wastewater end-of-pipe treatment

MSc Thesis

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Jes Vollertsen

Abstract:

The thesis examines the H_2S removal by oxidizing total sulfide from wastewater with end-of-pipe technology. The oxidation of the total sulfide was conducted using aeration and Sulfide Oxidizing Bacteria (SOB). Both methods were tested in a laboratory-scale and a pilot-scale setup with 1 L and 110 L wastewater capacity respectively. The pilot-scale test results showed rapid oxidation with an average total removal of 85 % under 30 minutes. Therefore, the results show that the application of SOB biofilm did not oxidize the total sulfide quicker than the aeration, which indicates, that biofilm oxidation did not happen in the reactors due to the inconsistent H_2S dosing. Measuring the H_2S in the water and air phase showed a gradually decreasing trend, thus oxidation happens in both the water and air phase. The treatment time can be further shortened by applying a trained SOB biofilm with a constant dose of H_2S-rich wastewater.

Contents

Preface

The thesis is a result of a semi-long project (45 ECTS) of Réka Ignácz from 2022 September until 2023 June within the Department of the Built Environment at Aalborg University.
The chapters, sections, and subsections are numbered and the appendices are alphabetically named. All equations, tables, and figures are numbered in the thesis. The caption of the figures is shown below the figures, while the caption of the tables is shown above. References can be found in parentheses as numbers in the order they occur in the thesis.

I would like to thank my supervisors Asbjørn Haaning Nielsen and Jes Vollertsen for their supervision, great advice, and support during the project. I also would like to thank Jytte Dencker and Henrik Koch for their technical assistance and advocacy.

Réka Ignácz
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Chapter 1

Introduction

The sewer networks are designed to keep the wastewater flow secure and inaccessible to the public for health reasons. Due to its way of construction, an anaerobic medium develops on the pipe wall that contributes to the formation of hydrogen-sulfide (H_2S).

Sulfate reduction bacteria (SRB) are producing H_2S and sulfate (SO_4^{2-}) in an anaerobic environment. The H_2S emits from the water phase to the air phase, where a thin moisture layer on the wall of the sewer pipes absorbs the H_2S gas. Corrosion occurs by the oxidation of H_2S to Sulfuric acid (H_2SO_4) [1, 2].

$$H_2S + 2O_2 \longrightarrow H_2SO_4 \tag{1.1}$$

The presence of H_2S, also known as "sewer gas" or "swamp gas" [3] in wastewater also causes serious odor problems. H_2S is a colorless gas with a strong rotten egg odor. It causes skin and eye irritation in small concentrations, but a permanent injury can happen above 100 ppm. In case of exposure over 700 ppm, H_2S causes immediate death [4].

Due to its toxicity and corrosive nature, many methods had been developed to remove H_2S through the decades. The most common method is adding chemicals into the water to eliminate the H_2S. The most frequently used chemicals are iron salts, hydrogen-peroxide (H_2O_2), chlorine, and potassium-permanganate are studied as efficient options [5, 6]. A fairly new method, Downstream Nitrite Dosage is gaining space, to control H_2S and Methane (CH_4) concentrations in sewers [7]. Chlorine dioxide (ClO_2) is usually applied, at or close to the outlet. The chemical reaction with H_2S is very rapid, but in higher dosages, the ClO_2 can remove the biofilm layer in the system [8].
The common problem with these technologies is that the concentration of H_2S in wastewater is a hardly predictable number. The concentration of H_2S depends on pH, temperature, and retention time. Therefore, the amount of these chemicals needed can be only assumed. To keep the concentrations under the regulations, overdosing can happen.

Adding harsh chemicals into the wastewater raises sustainability and working safety concerns.
By keeping the concentrations low, several thousand liters of chemicals are used annually at problematic locations, putting cities and industries under huge economic pressure. To solve the problem of concrete corrosion and odor pollution more sustainably, biological/biochemical technology could be the solution.
In the following chapters, the biological reactor uses an aerobic biofilm layer and aeration is introduced to provide a sustainable and cost-effective alternative.

Chapter 2

Literature rewiev

H_2S is a colorless, flammable gas with a strong rotten egg odor with a density of 1.36 kg/m^3 which makes it heavier than air [9]. The anhydrous H_2S is less corrosive to carbon steel or aluminum, compared to hydrous H_2S [10]. H_2S gas is highly toxic by inhalation and the sense of smell can become fatigued quickly [11]. Besides inhalation, H_2S can be absorbed through the skin and the digestive tract lining. Since H_2S is quickly oxidized to sulfate by our immune system and the sulfate is excreted by the kidneys, it is not considered as a cumulative toxin [12].

Sewer networks are essential parts of our life since the Middle Ages as one of the key infrastructure aspects, providing closed, underground wastewater transportation [13]. The estimated average age of most of the Danish sewer network we know this day is 35 years [14]. Although the system was constantly expanded and modernized, problems like corrosion and malodor in the network arise. To maintain the good condition of the sewer system, and avoid health issues or accidents, the control of components, like H_2S or NH_3 is essential.
By the design of the sewer, two main types are specified, gravity sewers and depressed sewers. The gravity sewers are designed to have a minimum 5-10% headspace of the full depth and it requires sufficient ventilation. In depressed sewers, pressure is used to fill up the full depth of the pipes with wastewater regardless of the size of the flow.

1 H_2S formation

The sulfur cycle takes place both in the water phase and the sewer atmosphere [13]. The dissolved sulfur components due to sulfate reduction under strictly anaerobic conditions, by the bacteria Desulfovibro and Desulfotomaculum, convert to H_2S and Bisulfide (HS^-) [15]. The sulfate reduction happens in the SRB biofilm layer in the water phase. Oxida-

tion can happen in the water if aerobic conditions occur and S^0 or SO_4^{2-} can be formed. Furthermore, H_2S gas is emitted into the sewer atmosphere, where it reacts with oxygen and forms H_2SO_4, causing corrosion problems.

The following equation shows the redox reaction of sulfate, where sulfate is the electron acceptor and CH_2O is the organic matter.

$$SO_4^2 - +2CH_2O + 2H^+ \longleftarrow 2H_2O + 2CO_2 + H_2S \tag{2.1}$$

The whole sulfur cycle in the sewer system is shown in the following figure.

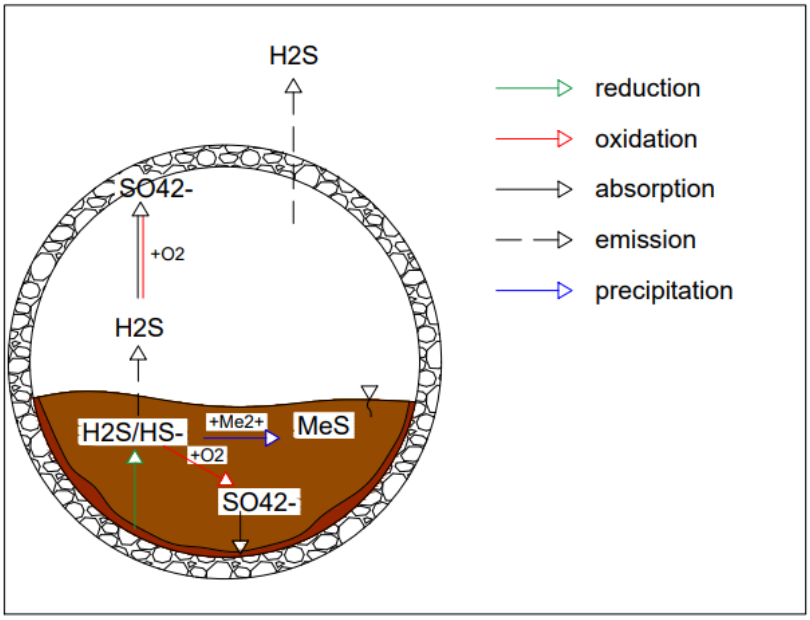


Fig. 2.1: Sulfur cycle in the sewer system. Figure was made after [16].

1.1 Temperature

The sulfate reduction rate in the wastewater is dependent on the temperature. According to Wang et al. [17] the activity of SRB gradually increased up to 30 °C. The activity at 30 °C is double compared to 15 °C and over 30 °C it is stabilized, The average temperature range of the wastewater in a year is around 5-12°C [18]. The sulfate-reducing species can adapt to relatively high and low temperature conditions. The minor difference in wastewater temperature between summer and winter time resulted in a quite constant sulfide production [13].

1.2 pH

pH is a key parameter when talking about chemical reactions or biochemical processes. It can control the availability of nutrients, and biochemical cycles, and affects the stability of substances. The optimum pH range for the SRB is between pH 6-9. After a study by Wang et al. [17], the optimal pH value for SRB with the higher sulfide production was pH=7. From lower values, the SRB activity constantly increased up to pH=7, and above 7 a decreasing trend described the activity.

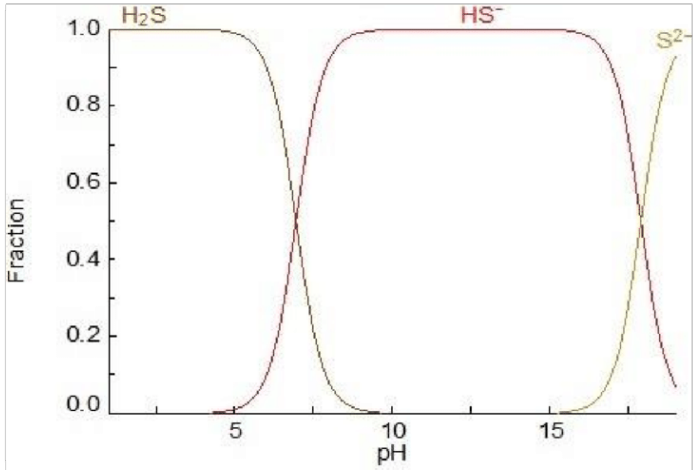


Fig. 2.2: pH dependence of aqueous sulfide species. Source: [19]

Figure 2.2 shows the different sulfide fractions in the function of pH. Regarding H_2S, only the unionized form can be emitted into the air phase. It is seen, that at pH=7, approximately 50 % of sulfide occurs as H_2S, but at pH=8, it dropped to 10 %.

2 Risks of H_2S in sewers

2.1 Concrete and metal corrosion

As mentioned earlier in this chapter, the H_2S diffuses into the air phase, where due to the oxidation H_2SO_4 forms. Concrete corrosion is one of the most significant problems for many decades in sewerage works [20, 21, 22], depending on sulfide concentration, pH, moisture, temperature, sewer line length, and porosity [2, 23]. Around the sewage level, the corrosion rate is typically the highest, due to the presence of water and nutrients providing suitable conditions for the oxidizing bacteria [24]. In the US, many of

the sewer mains over a million kilometers were installed after World War II, that now damaged and need to be replaced due to corrosion [25].
Metal corrosion caused by H_2SO_4 appears as dark rust and porous bumps on metallic surfaces. The rust is formed by the H_2SO_4 reacting with heavy metals, turning it into metal sulfide.

$$H_2SO_4 + Me \longleftarrow MeSO_4 + H_2 \tag{2.2}$$

The most exposed parts of the sewer system to metal corrosion are the pumping stations and electronic appliances.

2.2 Health and odor problems

The sewer system is built and constructed for the purpose of collecting and transporting wastewater from urban areas, thus the sewer atmosphere and the related problems usually do not take priority over the technical aspects of transportation [13]. Besides H_2S, NH_3 and organic compounds, like amines and aldehydes are also malodorous substances. According to a couple of studies, H_2S was chosen as a universal indicator for odor level [26, 27].

Table 2.1: H_2S concentrations and effects on human health. Source:[12]

Concentration [ppm]	Effect on human health
0.1	Minimal perceptible odor
5	Easily detectable, moderate odor
10	Eye irritation begins
27	Strong, unpleasant odor
100	Coughing, eye irritation, loss of smell after 2-5 minutes
200-700	Marked conjunctivitis, respiratory tract irritation after 1 hour
500-700	Loss of consciousness, death possible in 30-60 minutes
700-1000	Rapid unconsciousness and death

Above 50 ppm exposure, H_2S loses its specific rotten egg odor which makes it extremely dangerous. Therefore, where it can occur in such high concentrations, like in manholes, it has to be measured with sensors and workers must be equipped with proper protective gear.

3 Costs

Previous studies investigated the repair costs caused by concrete corrosion. According to R. Sydney [28], only 10 % of the sewer pipes in Los Angeles County would have cost

approximately 400 million euros. In Germany, to restore all the damaged parts of the sewer lines, the repair cost was estimated at around 100 billion euros each year [29].

In 2010, San Diego had a population of over 2.2 million people, generating around 180 million gallons of wastewater each day. The total use of iron salts in 2007 was approximately 32.5 tons per day. Implementing the PRI-SC (Peroxide Regenerated Iron - Sulfide Control) technology, the required amount of iron salts dropped to 19.3 tons per day, still considered an excessive and expensive use of chemicals. The price of iron salt increased from 2004 to 2010 by 100 %. 2010 iron salts were over 650 USD per ton [30]. Using the PRI-SC technology, the treatment cost of H_2S in San Diego reached 4.5 million USD annually.

Chapter 3

Methodology

In this chapter, the implementation of the laboratory-scale and pilot-scale reactors will be described alongside the laboratory measurements and pilot tests. Two types of sulfide oxidations were tested in both setups. Chemical oxidation, which uses aeration-provided oxygen and naturally occurring biomass in the wastewater. The second oxidation method was Sulfur Oxidizing Bacteria (SOB) oxidation, which included SOB biofilm oxidation and aeration-provided oxidation.

1 H_2S removal with Sulfur Oxidizing Bacteria

There are two types of SOB based on metabolism, phototropic and chemotrophic. Due to the lack of light, only chemotrophs occur in the closed treatment reactor. These chemotroph bacteria play an important role in the sulfur cycle while using reduced sulfur species as electron donors. Chemotroph SOB has a very high tolerance to a wide range of pH and temperature changes [31]. The presence of SOB gets rid of the unwanted sulfur species such as thiosulfate, polysulfate, elemental sulfur, sulfide, and sulfite [32]. SOB microorganisms can be acidophilic, neutrophilic, and alkaliphilic based on their affinity of pH and psychrophiles, mesophiles, and thermophiles based on their temperature affinity [33]. Due to their tolerance to extreme environments, SOB can be used in domestic wastewater and industrial wastewater. Chemical and SOB sulfide oxidation have the same end products and intermediates affecting stoichiometry. The following reactions occur while sulfide oxidation [13]:

$$2HS^- + O_2 \longleftarrow 2S^0 + 2OH^- \tag{3.1}$$

$$2HS^- + 2O_2 \longleftarrow S_2O_3^{2-} + H_2O \tag{3.2}$$

$$2HS^- + 3O_2 \longleftarrow 2SO_3^{2-} + 2H^+ \tag{3.3}$$

$$2HS^- + 4O_2 \longleftarrow 2SO_4^{2-} + 2H^+ \tag{3.4}$$

According to Equation 3.1 - 3.4, the end product of the oxidation is highly dependent on the molar oxygen/sulfide (O/S) ratio. If the O/S ratio is lower than 0.6, mainly $S_2O_3^{2-}$ is produced as a major product. When the O/S ratio is around 0.7, the most typical product is S^0, while if the O/S ratio is above 1, there is a significant SO_4^{2-} production [34, 35, 36].

The method has many great advantages over strong oxidizing chemicals, such as low operational costs, no needed catalysts, high pH and temperature resistance, and safe byproducts and final products formed.

2 Laboratory-scale reactor and analysis

A 1 L laboratory-scale reactor was built to investigate the chemical and SOB sulfide removal in detail and specify features for the pilot system. The laboratory experiments were conducted in batches, where the total sulfide removal was measured in 1 L wastewater.

2.1 Reactor description

The reactor was built using a 1 L reaction vessel and a bubbler for air recirculation by applying a membrane and peristaltic pump. To design and build the reactor, the most important factors like a completely closed system to avoid volatile H_2S escape and recirculated headspace air providing nonlimited oxygen had to be taken into consideration. The final version of the reactor is shown in Figure 3.1 with a peristaltic pump connection and the submerged biofilm carrier.

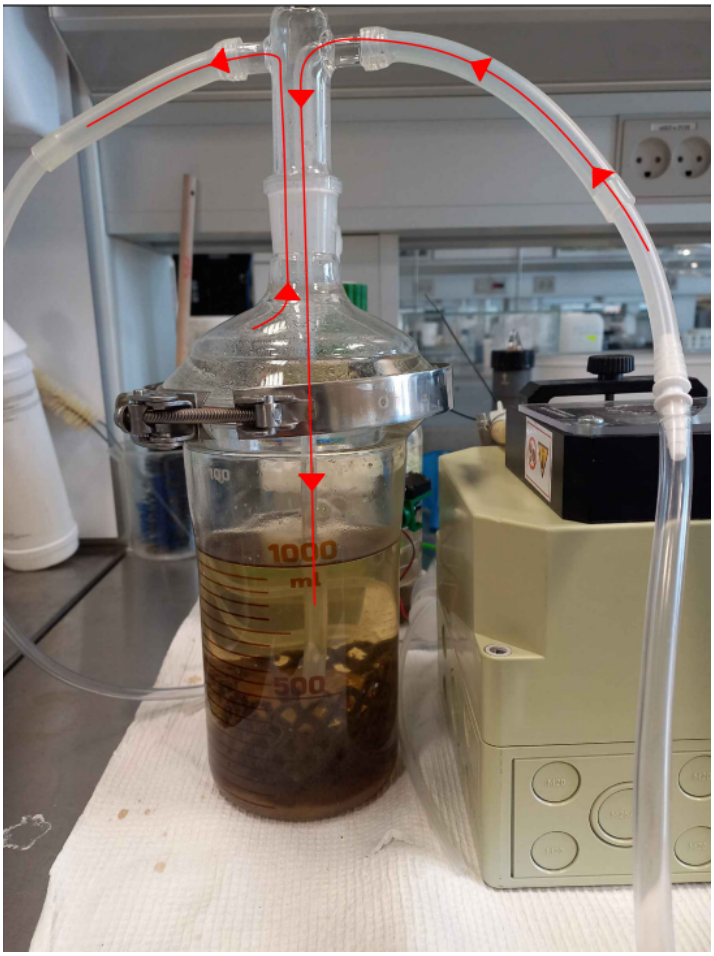


Fig. 3.1: Laboratory-scale treatment reactor.

Aeration

Constant aeration provided an oxygen-rich environment for the aerobic bacteria and contributed to quicker sulfide removal. Just only by aerating the wastewater with an open output, the H_2S would be stripped out. In this case, the compound would not be decomposed, but only moved to a different phase, causing further odor problems. The headspace air was recirculated and bubbled back to the water to ensure the H_2S gas is not leaving the system.

The lid of the reactor was constructed with the pipe driven into the vessel approximately 3 centimeters under the water surface. The tank was filled up with 1 L of fresh wastewater. To make sure the whole water column is saturated with O_2 and to take advantage of the mixing effect of the bubbling, the pipe had to be extended by 6 centimeters.

Two types of pumps were used for different purposes during the tests, a membrane pump and a peristaltic pump. A membrane pump was used to provide a constant aerobic environment in the tank between measurements. A couple of measurements were conducted with the membrane pump as well, but due to its low air flow rate, more than an hour was needed to raise the Dissolved Oxygen (DO) level of the fresh wastewater up to 30%. The peristaltic pump was connected to an adjustable power supply for better control of the airflow rate. Although, in constant use, the hose of the pump can be ruptured by the moving mechanical parts and cause leaking and a decrease in flow rate.

Carriers

During the experiments, two types of carriers were used.

1, Polyethylene (PE) balls were tested as carriers with a 0.3-0.5 mm diameter. Due to the polyethylene density being less than the water density, the balls are floating on the surface.

A couple of problems arose with the PE carriers. It was assumed, that the particles are going to sink due to the density increase caused by biofilm formation. The biofilm layer was very uneven because not all the particles were in touch with the water and the PE carriers filled up 1/5 of the reactor volume, which indicates, that only just the very first layer of carriers were in touch with the water, the rest of it was dry. The uneven biofilm coverage makes the H_2S removal calculation unfeasible. In contrast to what was awaited, the humid headspace air was not sufficient enough for biofilm growth. To ensure the whole surface area of the carrier is covered, a fully submergible version had to be taken into consideration with a known surface area.

2, In the knowledge of the disadvantages of the PE carriers, a new, mesh carrier was used, from EXPO-NET, BIO-BLOK 80 HDG type. The surface area of the mesh carrier is 80 m^2/m^3 with the shape of net-like cylinders. The structure makes it easy to monitor the biofilm growth on the surface and the untreated surface of the carrier is ideal for microorganisms' growth. In order to keep the carrier fully submerged, a metal weight was tied to the cylinder, see Figure 3.2.

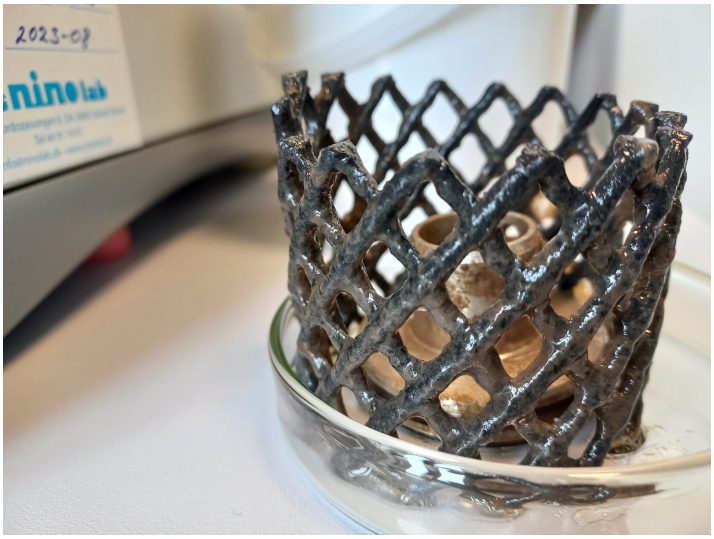


Fig. 3.2: Aerrobic biofilm layer on the laboratory-scale mesh carrier.

Sensors

To monitor what processes are taking place in the reactor a WTW MultiLine 3630 IDS type pH and DO sensor was used. Due to the closed construction of the reactor, the sensors could not be placed into the wastewater for constant measurement. Both the pH and the DO logger have a longer delay time and need approximately a minute to show the actual pH or DO level, which makes it unfeasible to use between two sulfide sampling, thus both were measured before and after the sulfide removal experiments.

2.2 Total sulfide analysis

The used wastewater in the reaction tank was collected from Frejlev Monitoring Station and the total sulfide level was set up using a stock solution. Total sulfide measurements were conducted using Cline spectrophotometric analytical method [37], which is further described in Appendix A. Before each test, the tank was filled up with freshly collected wastewater, and a stock solution made 2 weeks or so earlier was used during the tests.

3 Pilot-scale reactor and analysis

3.1 Location of the reactor

The pilot-scale reactor was placed at The Frejlev Sewer Research and Monitoring Station. Frejlev has approximately 3000 inhabitants and an average wastewater flow of 4-5 L/s. The peak dry-weather water flow was estimated at 10 L/s [38]. The monitoring station has a divided 300 mm diameter dry-weather pipe and a 1000 mm wet-weather pipe. From the dry-weather pipe, an automatized valve transports wastewater into a settling tank, and from the settling tank, a water pump transports the water into a 1000 L reservoir. When the water reached a certain level in the reservoir, a submerged pump pushes through the water in a 400 m long pressure main. The pressure main provides the anaerobic environment for H_2S production. The retention time in the pressure main depends on the water flow in the dry-weather pipe. The force main is connected directly to the pilot-scale reactor with a 63 mm diameter pipe. When the submerged pump is transporting the fresh wastewater into the pressure main, it pushes the H_2S-rich wastewater into the reactor.

3.2 Design of the reactor tank

For the reactor, a 220 L barrel was used with a sealed lid to avoid any odor problems in the monitoring station. The wastewater inlet was connected from the bottom of the tank with a 63 mm hose to the 400 m long spire hose system. The outlet was connected from around the middle of the tank with the same hose size into the drains. The water volume this way can be changed by operating the pump, which lifts up the water through the hose from the inlet, and with the constantly rising water level, the excess flows out.
Taking into account all the benefits and drawbacks of the laboratory scale reactor, the final version was designed based on the same idea with some necessary adjustments to make a working system with the least interruption.
The aeration system was built by using a 0.5 cm diameter 125.6 cm long metal pipe with drilled holes every 2 cm. Therefore, the pipe was arced into a 40 cm diameter circle to fit in the bottom of the barrel. In the case of a completely closed system, with only the recirculation of the current headspace air through the inlet and outlet stub, the oxygen would run out in a couple of days or hours due to oxidation and biofilm metabolism. In order to have a constant supply of oxygen without any human intervention, a 5 cm aeration hole was drilled on the lid to provide fresh air and enough oxygen. In case of a high H_2S emission through the aeration hole, a cylinder was put on top of it. The cylinder has an adequate size for an odor logger to measure the H_2S emission or if there are higher concentrations, a piece of steel wool can be put in a cylinder to absorb the escaping H_2S gas.

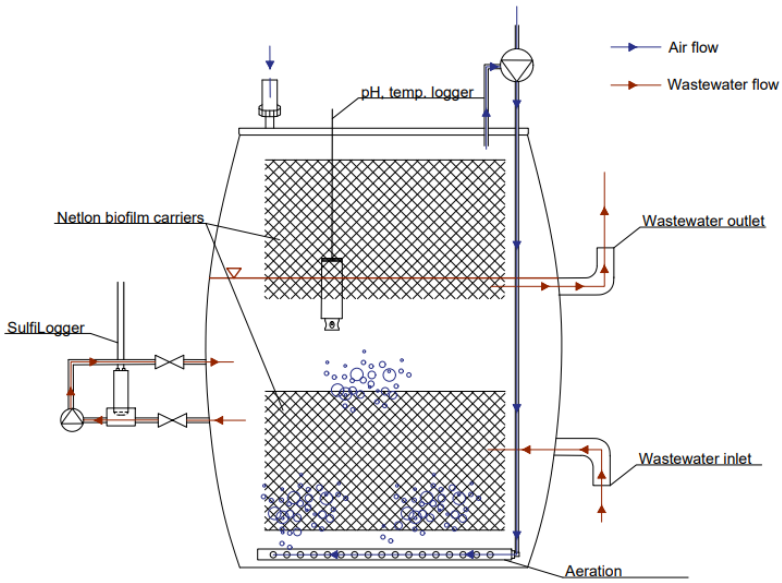


Fig. 3.3: Pilot scale reactor drawing.

The same mesh carriers were used, then in the laboratory-scale reactor. Oxygen Uptake Rate (OUR) had to be taken into account for the bacterial removal to ensure, the headspace air and aeration can provide enough oxygen to keep a constant aerobic condition.
Two cylinder-shaped carriers were placed in the tank, a fully submerged one on the bottom and one above the water level. The top carrier during the biofilm growing, training, and between measurements was placed in the water. Both carriers had a diameter of 43 cm and a height of 27 cm. Due to the water level in the tank, the top carrier was only half submerged during the growing period, which means the biofilm coverage was only 13.5 cm in height. Since the H_2S is a volatile compound, to avoid stripping out of the system without treatment, besides the air recirculation, the half-submerged carrier was used to accelerate the removal. The carrier has to be completely submerged between the experiments to prevent the biofilm from drying out. The top carriers allow the system to remove the H_2S from the headspace.

For constant and reliable H_2S concentration monitoring, a SulfiLogger S1/X1-1020 H_2S sensor with a measurement range of 0-5 mg/L was used. The sensor is very robust and applicable in wastewater, air, or gas flow as well, furthermore, it can withstand temperature and pressure, and also humidity between 0 and 100 %. The logger is con-

nected to a PowerCom Box, which provides power to the sensor either using disposable batteries or directly connected to the 24V DC power. The box has a second purpose, it transmits the H_2S data to an online cloud platform via cellular connectivity [39]. The sensor has dimensions of 240 mm in length and 48.3 mm in diameter. With the heavy aeration and a very humid headspace, the sensor was placed in a flow cell outside of the tank to protect the cables. If the sensor would be hung from the bottom, another outlet would have been needed for the cables, risking the H_2S gas escaping from the tank.
The flow cell was placed between two taps and the water flow was provided by a peristaltic pump every hour for 5 minutes. The flow cell makes the sensor easier to access and maintain.

For the headspace measurements, the Thermo Fisher Odalog L2 type H_2S logger was used with a measurement range between 0 ppm and 1000 ppm. The logger provides a reliable and long-term measurement with a built-in data-collecting option.
A pH and temperature sensor was placed into the system since the pH affects the concentration and presence of the different sulfate species. For this purpose, a HOBO pH and Temperature Data Logger was chosen. The logger is able to read and store pH and temperature data in the long term and uses Bluetooth to connect and communicate with mobile devices. The logger is robust and completely submergible with a PVC house which attributes make it feasible to use in a very humid and corrosive environment.

Fig. 3.4: Final pilot scale setup.

After the carrier was covered with the 0.3 mm thick biofilm layer, the bacteria had to be "trained" to be able to remove sulfide from the wastewater. The carrier was placed into a barrel with H_2S-rich wastewater to accelerate the process, where the conditions are adequate for both the biofilm growth and training process.

3.3 Total sulfide analysis

The pilot scale setup provided a constant H_2S formation and was added into the reaction tank in batches. The measurements were conducted by filling up the tank with fresh wastewater. As mentioned previously, pumping fresh wastewater from the bottom of the tank slowly changes the water volume.
In the knowledge of the pump flow, the required time to change the water volume in the tank was calculated by the following. Firstly, the flow was measured by filling up a 1 L beaker while measuring the time. The pump filled up the 1 L volume in 5 seconds. The maximum water level in the reactor is at the outlet height of the 220 L reactor, and based on the timed gravimetric method, the time was calculated as follows:

$$V/t = Q \tag{3.5}$$

$$V_b/V = t_{refill} \tag{3.6}$$

Where,

V	Volume	[L]
t	Time	[s]
Q	Water flow	[L/s]
V_b	Barrel water volume	[L]
t_{refill}	Water change time	[s]

Based on the calculation, the average wastewater flow of the pump was 0.2 L/s, which changes the water volume in the barrel in approximately 9 minutes.

After the barrel was filled up, the pH logger, the peristaltic pump, and the aeration were started while constantly measuring the H_2S concentration. The raw field measurement data is found in Appendix C. The H_2S concentration, pH, and DO were measured every minute.

4 Laboratory-scale Oxygen Uptake Rate and biofilm surface calculation

4.1 Oxygen Uptake Rate calculation

The used stoichiometric coefficient values for chemical and biological sulfide oxidation were 0.82 mgO_2/mgS and 0.5 mgO_2/mgS respectively, after Nielsen et al. [40, 41]. Based on the coefficients, in the case of every 1 mg S/L treated sulfide concentration, the amount of oxygen needed during the experiment was calculated with the following equation.

$$OUR_c = c_{S^{2-}} \cdot R_{C(S^{2-})} \tag{3.7}$$

$$OUR_b = c_{S^{2-}} \cdot R_{B(S^{2-})} \tag{3.8}$$

Where,

OUR_c	Oxygen uptake rate for chemical oxidation	$[mgO_2/L]$
$c_{S^{2-}}$	Sulfide concentration	$[mgS/L]$
$R_{C(S^{2-})}$	Surface area of carrier	$[[mgO_2/mgS]$
$R_{B(S^{2-})}$	SOB biomass covered surface	$[[mgO_2/mgS]$
OUR_b	Oxygen uptake rate for biological oxidation	$[mgO_2/L]$

The OUR for the chemical and SOB oxidation is 0.82 mgO_2/L/mgS and 0.5 mgO_2/L/mgS respectively, which is required for a nonlimited DO environment.

If the wastewater has a close to zero DO value, the headspace should provide all the necessary oxygen for SOB oxidation. To ensure the headspace contains enough amount oxygen, the following equation was used.

$$m_{O^2} = (\rho_a ir \cdot V_h) \cdot 0.21 \tag{3.9}$$

Table 3.1: Input parameters used to calculate biological oxygen demand

Abbr.	Parameter	Value	Unit
ρ_air	Density of air	1.204	kg/m^3
V_h	Volume of headspace	0.0005	m^3

The freshly ventilated headspace air contains 0.126 g of oxygen, which is adequate for the chemical removal of 153 mg S/L and the SOB removal of 252 mg S/L total sulfide without changing the air in the reactor.

4.2 Biofilm coverage

Before determining the total biofilm-covered surface of the carrier, an average biofilm thickness of the SOB biofilm layer was chosen with a value of 0.3 mm based on literature [42, 43]. As seen in Figure 3.2 the biofilm appears to be a very thin, less than 0.5 mm thick almost transparent layer on the carrier surface.
The dimensions of the mesh carrier used for the biofilm can be found in the following table.

Table 3.2: Laboratory-scale biofilm carrier dimensions.

	Size	Unit
Diameter of outer circle	0.0675	m
Height	0.05	m
Surface area	80	m^2/m^3

Based on Equation 3.10, the total surface of the SOB biofilm is 0.01432 m^2.

$$A_{biomass} = \pi \cdot r^2 \cdot h \cdot S \tag{3.10}$$

Where,

r	Radius of carrier	[m]
h	Height of carrier	[m]
S	Surface area of carrier	$[m^2/m^3]$
$A_{biomass}$	SOB biomass covered surface	$[m^3]$

4.3 Pilot-scale biofilm coverage

Based on Equation 3.10, the submerged and the headspace biofilm-covered carrier surface was calculated. The used parameters can be found in Table 3.3.

Table 3.3: Pilot-scale biofilm carrier dimensions.

	Size	**Unit**
Submerged carrier height	0.27	m
Headspace carrier height	0.13	m
Carrier surface area	80	m^2/m^3
Carrier diameter	0.43	m

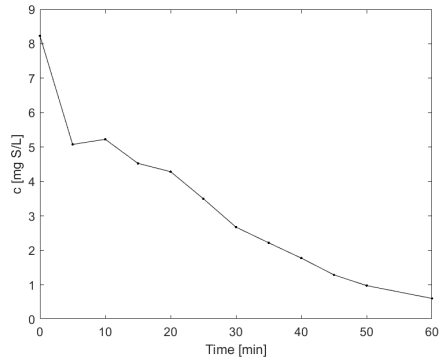
The total used biofilm surface in the pilot-scale reactor tank is 4.64 m^2 with 3.14 m^2 submerged and 1.51 m^2 headspace biofilm surface. Divided the biofilm total surface with the treated wastewater volume, the biofilm surface can be calculated for each liter of treated water. Dividing the submerged biofilm surface with the 110 L, the SOB for each liter of wastewater is 0.029 m^2. Half of the 220 L tank is filled up with wastewater during treatment and 110 L of the tank is used as a headspace volume to provide nonlimiting oxygen for oxidation and to fit the headspace carrier. The total headspace biofilm surface for each liter of air is 0.014 m^2.

Chapter 4

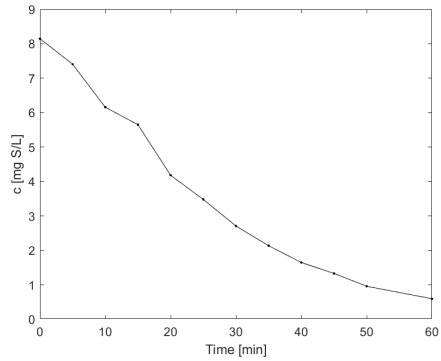
Results and discussion

1 Chemical sulfide removal

The laboratory-scale total sulfide removal was measured based on the Clein method, described in Appendix A. In order to have a better understanding of SOB removal, chemical sulfide removal experiments using aeration had to be conducted.
The used wastewater for the laboratory experiments was collected from Frejlev Monitoring Station. To reach the desired total sulfide concentration, the wastewater was spiked with Na_2S stock solution.
Under 1 mg S/L, odor problems won't arise, therefore an approximately 5-8 mg S/L concentration was targeted trying to simulate a likely occurring H_2S concentration in sewers.



(a)



(b)

Fig. 4.1: Total sulfide concentrations during chemical sulfide oxidation.

As it is shown in Figures 4.1a and 4.1b, the first 3 values (0, 5, and 10 min) show a noticeable difference between the two measurements. The first data point represents the initial concentration immediately after adding the stock solution. The difference between the first two measurement points in the first figure is derived from uneven mixing. When the stock solution is added, it is crucial to take out samples as fast as possible to avoid further oxidation of the samples due to air contact. In Figure 4.1a, the results show a linear decreasing trend in concentration with approximately 50 min treatment time to reach a total sulfide concentration under 1 mg/L.

1.1 SOB sulfide removal

As described in Chapter 3, the experiment was conducted in a 1 L reaction tank with a total biofilm surface of 0.01432 m^2 aerobic bacteria. Fresh wastewater was added be-

fore each experiment to provide nutrients for the bacteria during the removal and stock solution was used to set up the total sulfide concentration.

The measurements with biofilm were conducted from March to May. During this period, stock solution was added manually to the system, to maintain the ability of sulfide removal. Although the results were very inconsistent almost in every case, the removal stopped after a certain time, see Appendix B..

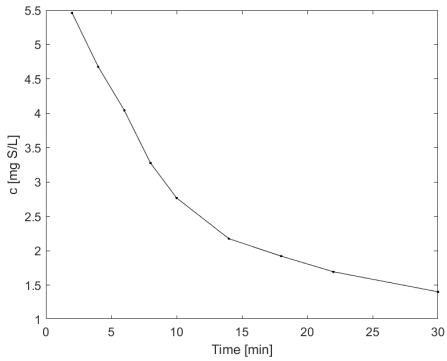


Fig. 4.2: Results from laboratory-scale H_2S removal with biofilm.

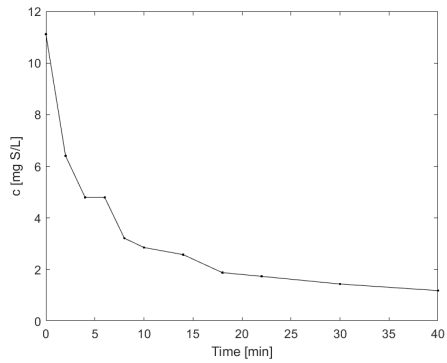


Fig. 4.3: Results from laboratory-scale H_2S removal with biofilm.

As it is seen in Figure 4.2 and 4.3, compared to the results from chemical oxidation, the total sulfide concentration decreased from 5-6 mg S/L to 2 mg S/L in 15-20 minutes. In comparison, chemical sulfide removal took 30 minutes to go down from 5 mg S/L

to 2 mg S/L. Despite that the removal was slightly quicker, a clear conclusion on SOB oxidation cannot be drawn since the experiment could not be repeated. The more intense decreasing trend in sulfide concentrations could be the reason for a heavier aeration caused by a more powerful air pump.

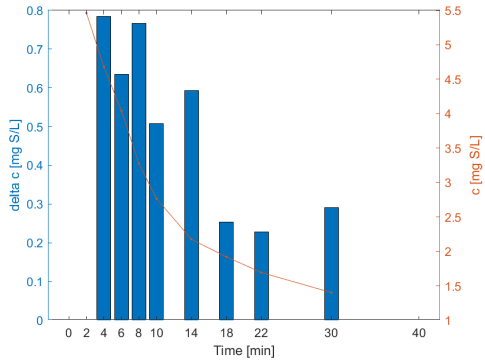


Fig. 4.4: Results from laboratory-scale H_2S removal with biofilm and the concentration change at every sampling point.

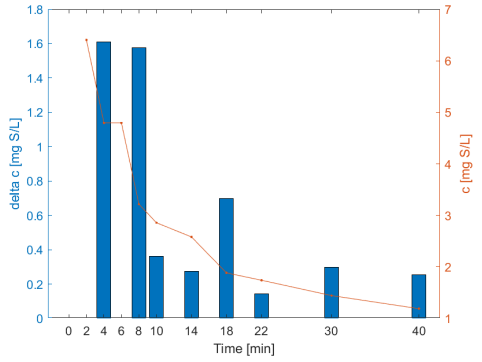
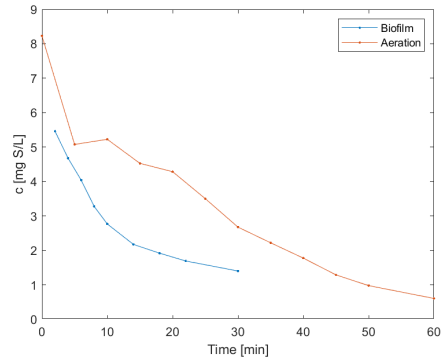
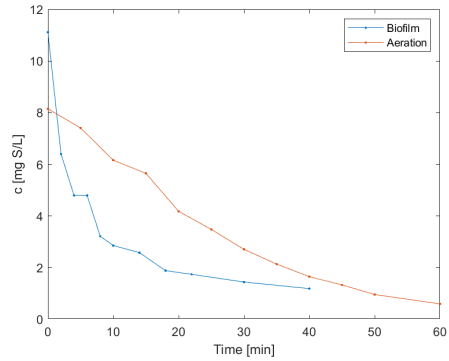


Fig. 4.5: Results from laboratory-scale H_2S removal with biofilm and the concentration change at every sampling point.

For a better visual comparison, Figure 4.1a was plotted with Figure B.3 and Figure 4.1b together with Figure B.4.



(a)



(b)

Fig. 4.6: Comparison of the two plotted chemical and biological oxidation results.

In these two cases, the compared chemical and SOB removal starting concentrations were close to the same value. In Figure 4.6a, the end concentration was reached after 30 minutes, while with only aeration, the same concentration was only reached after 45 minutes. On the other hand, in Figure 4.6b, the end concentration of the SOB removal was reached at the same time as the chemical removal. The SOB treatment shows a rapid removal in the first half of the treatment period, but in the total removal under the given time, there is no significant difference. There is a possibility, that the reason for the quick removal with SOB is better aeration and the greater airflow of the peristaltic pump and not the result of the biofilm. The difference between the two chemical removal rates is derived from the uneven mixing. From some test results, the first measurement point had to be taken out due to the unrealistically high measured total sulfide level. With a higher starting point under the same treatment time, the actual removal rate

would be higher, closer to the 0.13 value.

The chemical oxidation results can be compared with a previous study by Nielsen et. al [44]. The experiment in active wastewater was conducted in total for 4 hours. The initial sulfide concentration was 10 mg S/L and with chemical oxidation the 100 % removal was achieved after approximately 4 hours. In the first hour of the treatment, the concentration decreased by 70 %. The laboratory-scale chemical oxidation results showed an approximate 90 % removal in under 1 hour. The starting concentration was lower than the literature experiments, and the removal is more rapid in the first hour which can cause the 20 % difference in removal in the first hour.

Table 4.1: Laboratory-scale total sulfide concentrations at the start and end points with the total treatment time for biological and chemical oxidations.

Chemical oxidation				
Date	**Start [mg S/L]**	**End [mg S/L]**	**Time [min]**	**Total removal [%]**
11.16.	5.08	0.61	60	88
11.17.	8.15	0.60	60	93
Biological oxidation				
03.29.	5.46	1.40	30	74
03.29.	6.40	1.1	40	81

1.2 Changed factors

Many laboratory scale experiments were conducted using the same setup principle, adjusting different factors, such as DO or organic matter, as well as minor adjustments on the setup, like stirring, biofilm coverage, or airflow and volume by changing pump types. The results from the experiments with a brief explanation can be found in the appendix.

Firstly, the experiment was conducted with different total sulfide concentrations varied between 6-1.5 mg S/L. The measurement time was different in each case, considering the absorbance values during the experiment. As is seen in Appendix B, the curve flattened out mostly at approximately 10-20 minutes, but in some cases, the decreasing trend stopped almost immediately. Apparently, the concentration does not affect the total sulfide concentrations from stopping, it occurred at different times and at different concentrations. However, the problem took place every time a measurement was conducted.

Air flow rate

Different air flow intensities were used to investigate, whether the DO level has an effect on the removal. Naturally, the wastewater from Frejlev had a DO level between 0-10 %. During the experiments, the aeration started immediately after the wastewater was poured into the tank and stock solution was added. Constant DO measurements could not be conducted due to the construction of the setup. The reactor tank has to be closed in order to keep the volatile H_2S in the system and the lid had only one opening which was used for the aeration, therefore the DO level was measured before and after the treatment. The measurements showed a significant increase in DO, up to 40 % during the treatment.

Magnetic stirrer operation and organic matter oxidation

To investigate further the reason for the stopping removal rate and the lack of chemical oxidations, organic matter removal, and a more intense stirring effect were looked into. A magnetic stirrer was added to the setup, to provide better water movement, a homogeneous total sulfide and DO concentration, and to increase the oxygen and H_2S gas absorption.
In the wastewater, the organic matter is oxidized in a heterotrophic transformation, if heterotrophic biomass is present. To ensure that the DO is used by the SOB, the wastewater in the tank was aerated for a couple of hours and for over a day before the conducted experiments, see Appendix B. The water was left in the tank with constant aeration for one day before the experiment was conducted, based on the experiments of Nielsen et. al [40], where the DO concentration was used by the oxidation of heterotrophic biomass in the first 18-24 hours. After a day, the starting DO level was 45 % with an oxygen-rich headspace before the treatment, but the total sulfide level flattened out after the first 2 minutes and stayed approximately at the same level until the end of the experiment.

Biofilm training

After the biofilm was taken out from the pilot-scale tank after 2 weeks of training, the stock solution was added to the laboratory-scale system daily, besides the regular experiments. Based on the results, it was supposed, that the 2 weeks of training for the biofilm was not enough time, it was put back into the pilot-scale tank for 1 more week. After that 1 more week, the carrier was placed back into the lab scale tank and more experiments were conducted on the same day. For the results, see Appendix B.
The removal of the total sulfide concentrations did not show any improvement, the level stagnated in both higher and lower concentrations as well.

The stagnating trend occurred regardless of DO level, pH, stock solution concentration, treatment time, or any change in the setup, for example, the addition of a magnetic stirrer or a cleaned, sediment-free tank.

Chapter 5

Pilot-scale measurements

1 Dissolved Oxygen and pH change

As it is described in Chapter 2, the H_2S level in the water highly depends on the pH. The starting and ending pH values of the pilot tests. The average pH of the raw wastewater inlet was 7.63, which increased gradually during treatments.

Table 5.1: Start and end pH and temperature values during pilot tests.

	Start pH [-]	**End pH** [-]	**Start temp.** [C]	**End temp.** [C]
03.23.	7.65	7.65	8.24	8.42
03.31.	7.81	7.79	11.71	9.53
03.31.	7.77	7.79	7.67	7.44
04.26.	7.37	7.84	11.42	11.3
05.03.	7.58	7.95	12.41	12.22
05.09.	7.95	7.89	13.35	13.16
05.10.	7.83	8.01	14.34	13.98
Average	7.71	7.85	11.31	10.86

Stripping the CO_2 out of the wastewater by aeration can increase the pH range up to 8-9 [45, 46]. Around pH=7, the main form of inorganic carbon in the water is HCO_3^-. The pH increase caused by HCO_3^- is described by the following equation.

$$HCO_3^- = CO_2(g) + OH^- \tag{5.1}$$

CO_2 removal has different mechanisms in high and low pH. In the low pH range,

with the decreasing concentration of CO_2, with the dissociation of HCO_3^- new CO_2 is released into the gas phase.

$$HCO_3^- + H^+ \longleftarrow CO_2(g) + H_2O \tag{5.2}$$

In case of high pH, CO_2 is formed by the reaction of HCO_3^- with water.

$$HCO_3^- + H_2O \longleftarrow H_2CO_3 + OH^- H_2CO_3 \longleftarrow CO_2(g) + H_2O \tag{5.3}$$

As is seen in Figure 5.1, the pH changes regarding the DO content, which indicates, that the stripping affects the pH level. With heavy aeration, the CO_2 is removed and replaced by oxygen while increasing the pH at the same time. By raising the pH level with aeration the presence of H_2S can be lowered. At pH=8, only 10 % of the sulfate species appears as H_2S and at pH=9 there is no H_2S in the water.

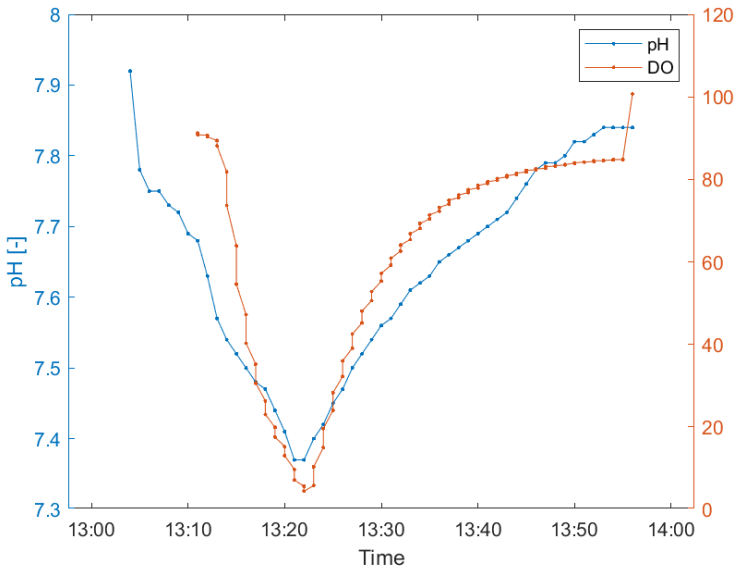


Fig. 5.1: pH and DO correlation

The H_2S concentration in the wastewater depends on the total sulfur and pH. The measured pH of the water was between 7.5 and 8.0. According to Figure 2.2 at this pH level only 20-30 % of the sulfide actually occurs as H_2S. As seen in the figures later, the removal already starts during the tank refilling.

The aeration is turned off during the refilling time to ensure the H_2S is not stripped out before the SOB treatment. The DO level during the tank refilling constantly decreased; after the complete water change, the DO was below 10%. After the water pump was stopped and the aeration was turned on, the DO level started to increase and by the end of the treatment reached the level of 70%. By placing an odor logger into the reaerating cylinder the H_2S emission was measured during refilling and the treatment. In the refilling period with the air, pump turned off, there was a 0.5-10 ppm H_2S emission, depending on the total sulfide concentration of the water, but as soon as the air recirculation was turned on the H_2S concentration in the cylinder was 0 ppm.
The DO and pH change during the pumping and treatment time followed the same pattern. Since the pH and DO levels seem to be synchronized, the possible answer to the pH rise could be related to the aeration driven CO_2 stripping.
According to many investigations of the stochiometry of sulfide oxidation by SOB, the main product is sulfate with the intermediate of elemental sulfur [47, 32, 48]. In a pilot-scale reactor, the total sulfide removal can not be measured based on only the DO consumption because of the heterotrophic oxidation of organic matter. Therefore, it is crucial to provide enough oxygen due to the overall oxidation that happens in the system.

2 Total sulfide measurements

The total sulfide concentrations based on the SulfiLogger H_2S data and the pH were calculated using tailor-made software. The removal rate was calculated by dividing the concentration change by the total measurement time if a constant oxidation intensity is assumed. The values are found in the following table.

Table 5.2: Pilot-scale total sulfide concentrations at the start and end points with the total treatment time for biological and chemical oxidations.

Biological oxidation				
Date	**Start [mg S/L]**	**End [mg S/L]**	**Time [min]**	**Total removal [%]**
03.31.	6.5	0.5	25	92
03.31.	4.2	0.9	26	79
04.26.	15.5	5.5	39	65
05.09.	13.5	0.7	25	95
Chemical oxidation				
05.03.	7.5	0.7	29	91
05.10.	5.75	0.88	25	85

Most of the experiments were conducted for the same 25-29 minutes period of time.

The starting total sulfide concentrations vary because of the different retention times of the wastewater in the anaerobic pipe system. Except for one measurement, the final concentrations were kept under 1 mg S/l. To have a better understanding of the laboratory results and the processes in the reactor tank, both chemical and SOB oxidation of sulfide were tested. During the experiments, the H_2S concentration in the water phase, the pH, and the DO were measured. In some cases due to technical difficulties, the pH logger lost the Bluetooth connection during measurements and the total sulfide concentration could not always be calculated. These results can be found in the Appendix C.

2.1 SOB sulfide treatment

The total sulfide concentration changes are shown in the following figures. The end of the refilling period which was the starting point of the treatment is shown on the graphs.

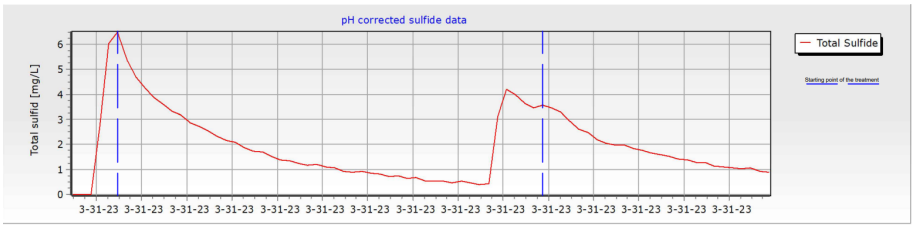


Fig. 5.2: Total sulfide concentration during pilot-scale biological treatment (03.31.)

As seen in Figure 5.2, the total sulfide concentrations by the end of the treatment were under 1 mg S/L. In some occasions, the sulfide removal started already during the refilling, as seen in the second treatment batch, the total sulfide concentration started to decrease in the last five minutes before the aeration was started. The reason could be either that the biological treatment has started or the sulfide began to oxidize while slowly flowing in the already treated DO-rich wastewater. Another possible reason is that during the pumping, the volatile H_2S started to evaporate into the air phase. The measure, an OdaLog was placed into the tank.

To better understand the removal rate, the concentration was raised up to 15 mg S/L with the addition of stock solution. the result is shown in Figure 5.3.

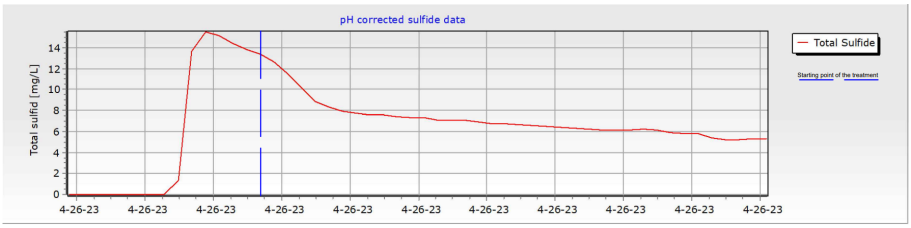


Fig. 5.3: Total sulfide concentration during pilot-scale biological treatment + added stock solution (04.26.)

A couple of minutes after the pump was turned on the aeration was started, there was a breakpoint in the removal after the 5th minute of the treatment, where the average removal was 0.088 mg S/L/min, compared to the rate before the breakpoint, where every minute the concentration decreased with approximately 0.8 mg S/L/min. After 39 minutes, only 66 % of the total sulfide was removed from the water. The same pattern can be seen in the laboratory results.

2.2 Chemical sulfide treatment

The biofilm carriers were taken out of the tank to compare the biological and chemical removal results to better understand how much do the biofilm contributes to the total sulfide treatment. The experiments were conducted for approximately the same time as the biological removals. The results are shown in Figures 5.4 and 5.5.

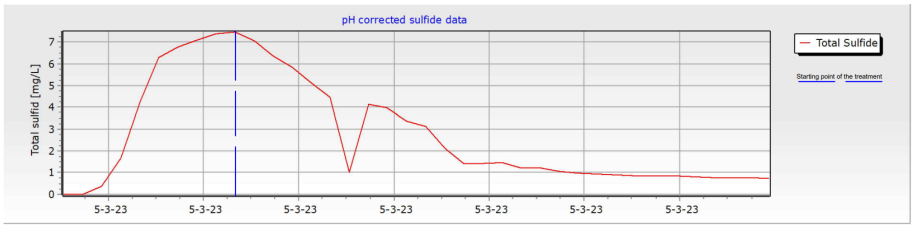


Fig. 5.4: Total sulfide concentration during pilot-scale chemical treatment (05.03.)

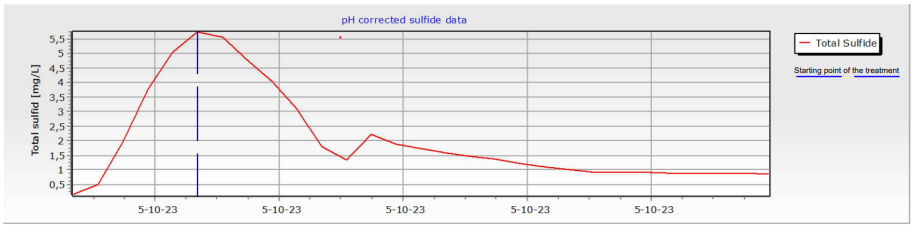


Fig. 5.5: Total sulfide concentration during pilot-scale chemical treatment (05.10.)

The treatment time was 29 minutes and 25 minutes respectively. The total sulfide concentrations went under 1 mg S/L during the treatment, showing the same decreasing trend as the SOB removal. The difference is so neglectable between the chemical and SOB removal, that the results had to be reconsidered. In both chemical removal graphs, there is a sharp drop immediately after an increase in the concentration, possibly caused by the stop of the peristaltic pump and the water flow in the H_2S measuring flow cell, and therefore, the dropped value does not reflect the actual concentration of the sulfide at that one measuring point. The written program for the pump was operating automatically for 5 minutes and it had to be turned on every 5 minutes for a constant measurement. The pump possibly stopped for 1 minute before it was started again, which caused the radical change in the results.

Further conclusions on the SOB removal can not be made, due to the same results with chemical oxidation. Table 5.2 summarized the removal of the total sulfide in both chemical and SOB treatment. From the removal time and efficiency, it is clear that there is no significant difference between the chemical oxidation and the biofilm treatment.

3 H_2S concentration in the headspace

The headspace H_2S concentration was monitored for both chemical and biological removal. The H_2S concentration in the first minute of the treatment, at the end of the treatment, and the total removal is shown in the following table.

Table 5.3: Headspace H_2S concentration change and removal

Date	Start concentration [ppm]	End concentration [ppm]	Removal [%]	Treatment type
05.09.	419	19	95	Chem
05.10.	404	236	42	SOB

During the SOB treatment, one biofilm carrier was in the headspace to observe the performance of the biofilm activity in the air. Although the SOB removal did not show a significant difference from the chemical removal in the water phase, the air phase had a 200 ppm difference by the end of the treatment. The results of the chemical and SOB treatment are shown in the figures below, respectively. The end of the refilling period and the start of the treatment is shown in Figures 5.6 and 5.7.

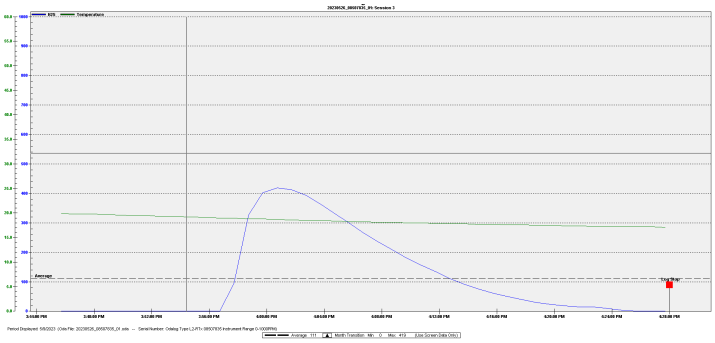


Fig. 5.6: Headspace H_2S concentration change during biological treatment (05.09.).

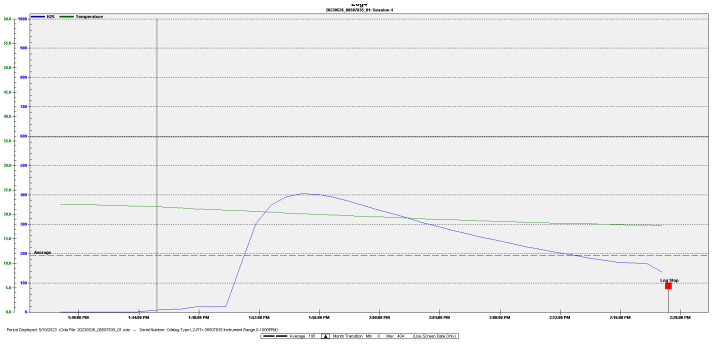


Fig. 5.7: Headspace H_2S concentration change during chemical treatment (05.10.).

Both experiments were conducted for 25 minutes and the starting point concentration was nearly the same. With the carrier in the headspace, the removal rate was 95 % and the aeration only removed 42 % of the total gas-phase H_2S and in both cases, the end total sulfide concentration in the water was under 1 mg S/L. The H_2S air-water equilibrium is pH and temperature dependent, but the pH could not be the reason of the significant difference, as the pH did not change drastically between and during the measurements, see Table 5.1.

Chapter 6

Summary

1 Conclusion

1.1 Laboratory experiments

The biological removal laboratory results consequently showed a short decreasing trend in the total sulfide concentrations and flattened out with time. This change in the removal, based on the results, regardless happened of the concentrations, retention time or DO level. Although, even if the SOB removal fails, due to the constant air recirculation and the higher DO level of the wastewater should be adequate for the chemical removal. The pH level does not affect the sulfide removal, only determines the H_2S and other sulfide species ratio in the water. According to Van den Bosch et al. [35], the O/S molar ratio affects the biofilm activity derived from the different end products at different O/S ratios. If the O/S ratio is under 1 for an extended period of time there is no SO_4^{2-} production which can inhibit the growth of some SOB. The affected SOB species by the O/S inhibition, like the Thioalkalivibrio versutus prefer an approximately pH=10 environment for optimal biofilm growth. The measured 7-8 pH range and 8-13 °C field environment provide optimum conditions for the growth of Thiobacillus which is less likely affected by the O/S ratio.

Change in the DO level, aeration, or organic matter did not improve the removal of total sulfide. Although different factors were taken into consideration during the tests, a further conclusion on the effects could not be drawn due to the stagnating trend. With the broken total sulfide removal a significant problem arose, which indicates the lack of chemical oxidation. The results showed, that the problem is derived from a different reason that prevented the test results with changed factors to help understand the significance SOB limiting factors. The total removal could not be calculated from

the other laboratory tests, because the results show neither the SOBl nor the chemical removal efficiency.

Inhibitory factors

Other inhibitory factors were looked into. Based on the literature, the inhibitory factors of organic and inorganic wastewater components are negligible. The laboratory results show that all the biofilm experiments follow the same pattern. The dissolved oxygen in the raw wastewater ranges between 0-10%, and according to several conducted studies [33, 49] and considering that the SOB oxidation occurs in the sewer system, very low concentration of DO is enough for the SOB. As mentioned in Chapter 3, the final product depends on the O/S ratio. As it is seen from the measurement results, the DO was nonlimited during constant air recirculation.

1.2 Pilot-scale tests

Comparing the test results with and without the biofilm carriers, it is seen, that the removal rate is the same in a given period of time. On average, 87 % of the total sulfide was removed without the biofilm, and 84 % with the biofilm. The difference is so negligible, it is undeniable that the biofilm does not oxidize any sulfide. Based on the laboratory tests no minor changes in the setup to facilitate better aeration or stirring, nor the change in DO or nutrients would improve the removal. Since both the laboratory-scale and the pilot-scale SOB treatment experiments failed, the biofilm had to be taken into consideration as the only common factor in the two setups. Excluding inhibitory factors, the possible explanation, is that the biofilm was not trained for sulfide removal. According to the SulfiLogger live data, only 1-4 batches of H_2S-rich wastewater were pumped into the tank daily. The number of batches is highly dependent on the weather conditions. On average the dry-weather pipe has a flow of 4-5 L/s wastewater under dry weather conditions. The water is pumped through the pressure main pipe system, letting H_2S-rich wastewater in the reactor if the reservoir is filled up. With the current setup, the wastewater batches could not have been more frequent due to technical limitations. The wastewater needs a couple of hours of retention time in the anaerobic pipe system for H_2S production.

The results lead to the conclusion that the biological removal failed, the chemical oxidation of total sulfide still happened in the tank in contrast with the laboratory tests. In one case, the wastewater was spiked with the stock solution to investigate the removal in higher concentrations as well. The sulfide removal stopped after approximately in the 7th minute as shown in Figure 5.3 following the same trend as the laboratory results. The only common factor, in this case, is the stock solution which could be the

reason for the stopping sulfide removal. Both the laboratory and pilot tests showed a short reduction period of the sulfide concentration regardless of the setup scale or the concentration. Although the sulfide could be measured in the laboratory, it was not in an available form for the chemical or SOB oxidation processes. A possible reason could be, that the stock solution or the $Na_2S \cdot {}_9H_2O$ crystals used for the stock solution during the storage formed a compound that can not be oxidized.

Based on the pilot-scale tests, the total sulfide can be removed from the wastewater in under a maximum of 30 minutes regardless of the concentration. Comparing the chemical and SOB treatments, it is clear that the pilot-scale system was operated suboptimal. The headspace H_2S measurements showed that there is a significant H_2S removal as well. The treatment time can be shortened with a better-trained SOB biofilm.

1.3 Full-scale system

Based on the laboratory-scale and pilot-scale removal results, the approximate total removal time is around 30 minutes for lower, 6 mg S/L and higher, 14 mg S/L as well. Considering a retention time and a peak dry-weather flow from Frejlev, a full-scale system can be designed for constant total sulfide removal. Knowing the oxygen consumption and the space that the carrier requires, a more space-efficient reactor can be conducted with 1/3 as a headspace of the total reactor volume. Calculating with 10 L/s peak dry-weather flow at Frejlev Using the same reactor principle, the upscaling for a full-scale setup was calculated using the following equations. The pilot-scale tests resulted in an average 85 % removal rate under a maximum of 30 minutes for a total sulfide range of 4.2-15.5 mg S/L. Using the calculated biofilm surface for each liter of wastewater, the peak dry-weather flow, and the average retention time of the water, the dimensions of a full-scale system can be determined.

Table 6.1: Input parameters for full-scale treatment reactor calculation.

Retention time (t_{ret}) [**min**]	**Biofilm surface** (A_{biof}) [m^2]	**Peak dry-weather flow** (Q_p) [m^3/min]
30	0.00013	0.6

$$V_{full} = Q_p * t_{ret} \tag{6.1}$$

$$A_{b,full} = V_{full} * A_{biof} \tag{6.2}$$

Based on Equation 6.1, the needed volume for a maximum 30-minute peak dry-weather flow batch is 18 m^2. Using 1/3 of the total volume of the tank as headspace

for aeration, the total calculated full-scale reactor tank volume is 27 m^3, which can be implemented as a 3m x 3m x 3m dimensions square.

The needed oxygen demand for nonlimiting conditions had to be calculated using the oxygen uptake rate of organic matter oxidation and the stochiometric coefficient for SOB sulfide oxidation. The OUR value for organic matter oxidation was used based on [47], where the OUR measurements were calculated using Frejlev wastewater. Taking into consideration the results of the three OUR measurements, the maximum occurred OUR value in the first 1 hour was chosen. The used input parameters for the oxygen demand calculations are shown in Table 6.2.

Table 6.2: Input parameters for full-scale oxygen demand calculation.

Max. OUR of OM [g $O_2/m^2/h$]	**Biol. Oxid. Coeff.** [mgO_2/mgS]	Rho_{air} [kg/m_3]	V_head [m_3]
10	0.17	1.204	9

$$OUR = OUR_{OM} * V_{water}/2 \tag{6.3}$$

$$R_{S^{2-}full} = c[S^{2-}] * V_{water} * R_{S^{2-}} \tag{6.4}$$

$$m_{O^2} = \rho_{air} * V_{head} * 0.21 \tag{6.5}$$

According to the equations above, the amount of oxygen in 9 m^2 headspace air is 2.276 kg O_2. The maximum needed oxygen was 10 g for 1 m^3 wastewater in 1 hour. The OUR for organic matter oxidation is 90 g O_2 in 18 m^3 wastewater for 30 minutes retention time. In order to remove a maximum occurred 15 mg S/L total sulfide concentration biologically from 18 m^3 wastewater, using the stochiometric coefficient, 45.9 g O_2 is needed.

Using the same biofilm surface and wastewater ratio, the needed carrier diameters can be calculated with an easy upscaling step. The used mesh carrier has a surface area of 80 m^2/m^3. If the pilot scale system had 0.0285 m^2 biofilm for each liter of wastewater, 18 m^3 wastewater requires 513 m^2 biofilm surface. Using the surface area of the netlon carrier, it was calculated, that 6.4 m^3 submerged netlon carrier is needed to provide the biofilm surface, which can be implemented with a 1.85m x 1.85m x 1.85m dimensions square piece. Calculating the headspace carrier size with the same principle, a total 123.3 m^2 biofilm surface area was determined. Using the same length and width dimensions as the submerged carrier, the needed dimensions are 1.85m x 1.85m x 0.44m.

2 Further perspectives

With major changes in the pilot-scale setup, the SOB removal could be measured and compared with the chemical sulfide removal. Using a smaller, 10 L tank with the same, mesh carriers for the biofilm could provide a better solution. The tank material should be made out of highly resistant Polyethylene (PE) or Polyvinylchloride (PVC). Due to the smaller size of the tank, the SulfiLogger can be fitted in the same flow cell for better mobility and space-saving purposes in the oxidation area. For the airflow, a pump with 2-5 L/min would provide an adequate amount of air recirculation and water movement. A membrane pump would be preferred to ensure a steady airflow in a long-term run in a highly corrosive environment. For constant recirculation in the flow cell, a more durable water pump should be used with a flow rate of 2-3 L/min. To avoid unnecessary H_2S emission from the tank, iron wool can be placed in the aerating cylinder.

The training stage of the biofilm can be monitored by measuring the H_2S concentration for 2-3 minutes after the barrel was refilled and for 2-3 minutes before the tank is filled up with a new batch of H_2S-rich wastewater. With a constant measurement of the H_2S, the removal rate can be monitored and adjustments can be made in the frequency of water volume change. The water flow was often obstructed by the clogged valve that opens the water flow from the dry-weather pipe into the settling tank. A more frequent back-aeration would be sufficient to avoid clogging or a shut-off valve installed right before the settling tank. During purging, the air goes in the direction of less resistance, which is often in the direction of the settling tank making the cleaning effect of the purging insufficient in the valve.

Appendix A

Total sulfide analysis in aqueous samples

The method is using the principle of the sulfide precipitation as ZnS in zinc-acetate. The sulfide reacts with Fe(III) and N, N-dimethyl-p-phenylenediamine, and methylene blue is formed as a result. The absorbance of the methylene blue can be measured at 665 nm using a photometer [50].
Used chemicals:

- Zinc-acetate (10 %) [ZnAc]
- Diamine reagent
- Sodium sulfide nonahydrate [$Na_2S \cdot 9\,H_2O$]

The sodium-sulfide (Na_2S) stock solution was freshly prepared every 1-2 weeks by mixing approximately 0.1 g $Na_2S \cdot 9\,H_2O$ into 100 ml ZnAc 1 %. A previously prepared Diamine reagent was used for the experiments.

Procedure

- Samples between the range of 0.5 ml and 9 ml were taken using a syringe to avoid air contact.
- The wastewater samples were fixed into 1 ml 10 % ZnAc by the needle into a test tube. The samples than were diluted with distilled water to a total volume of 10 ml.
- 0.8 ml Diamine reagent was added to the sample using a pipette. After the sample was mixed thoroughly, a minimum of 30 minutes and a maximum 2-hour waiting time was needed for the complete methylene blue formation.

- The samples were measured in a 1 cm cuvette at 665 nm using a photometer. The total sulfide was calculated from the absorbance and dilution.

The total sulfide concentration was calculated using the following equation.

$$c[mgS/L] = (B * A - C) * D \tag{A.1}$$

Where,

A	Absorbance
B	Constant calculated from standard curve
C	Constant calculated from standard curve
D	Dilution

Appendix B

Laboratory results

1 Chemical H_2S removal with oxygen

Table B.1: Laboratory-scale H_2S removal from wastewater using aeration.

Time [min]	Abs 1 (665 nm)	Abs 2 (665 nm)	C1 [mg S/L]	C2 [mg S/L]	Sample size [ml]	Dilution
0	0.402	0.398	8.23	8.15	0.5	20
5	0.253	0.363	5.08	7.41	0.5	20
10	0.26	0.304	5.23	6.16	0.5	20
15	0.227	0.28	4.53	5.65	0.5	20
20	0.418	0.408	4.29	4.18	1	10
25	0.344	0.342	3.50	3.48	1	10
30	0.266	0.269	2.68	2.71	1	10
35	0.223	0.215	2.22	2.14	1	10
40	0.181	0.169	1.78	1.65	1	10
45	0.135	0.139	1.29	1.33	1	10
50	0.475	0.466	0.98	0.96	5	2
60	0.299	0.295	0.61	0.60	5	2

The plots of the chemical experiments can be found in Chapter 4.

2 Analysis with biofilm, unlimited DO

Table B.2: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mgS/L]	Sample size [ml]	Dilution
0	0.7	7.27	1	10
2	0.368	3.76	1	10
4	0.327	3.32	1	10
6	0.578	2.99	2	5
8	0.582	3.012	2	5
10	0.541	2.80	2	5
12	0.521	2.69	2	5
14	0.53	2.74	2	5
16	0.498	2.571	2	5
20	0.442	2.27	2	5
24	0.432	2.22	2	5
28	0.418	2.14	2	5
32	0.398	2.037	2	5

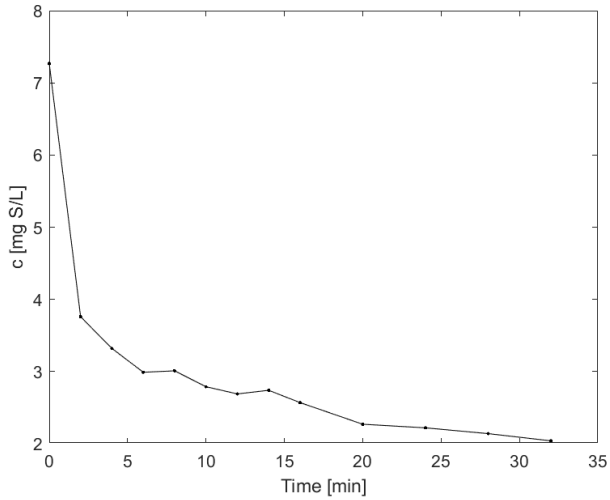


Fig. B.1: Laboratory-scale H_2S removal result.

Table B.3: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	1.016	10.62	1	10
2	0.557	5.76	1	10
4	0.416	4.27	1	10
6	0.699	7.26	1	10
10	0.321	3.26	1	10
14	0.228	2.27	1	10
18	0.374	1.91	2	5
22	0.345	1.76	2	5
26	0.372	1.90	2	5
30	0.353	1.80	2	5
34	0.356	1.82	2	5
40	0.317	1.61	2	5

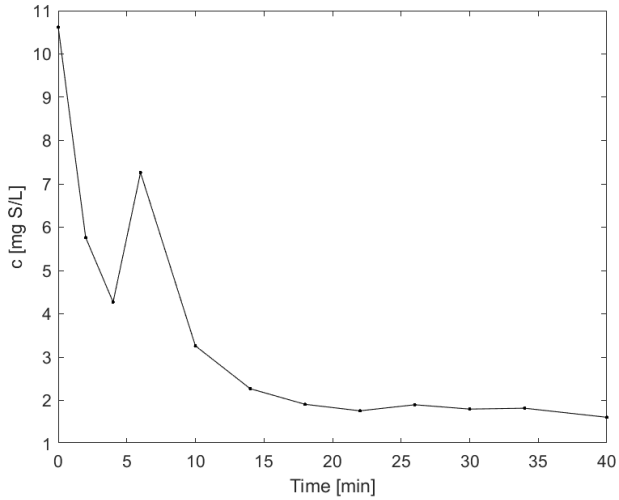


Fig. B.2: Laboratory-scale H_2S removal result.

Table B.4: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
2	0.529	5.46	1	10
4	0.455	4.68	1	10
6	0.395	4.04	1	10
8	0.632	3.28	2	5
10	0.536	2.77	2	5
14	0.424	2.18	2	5
18	0.376	1.92	2	5
22	0.333	1.69	2	5
30	0.278	1.40	2	5

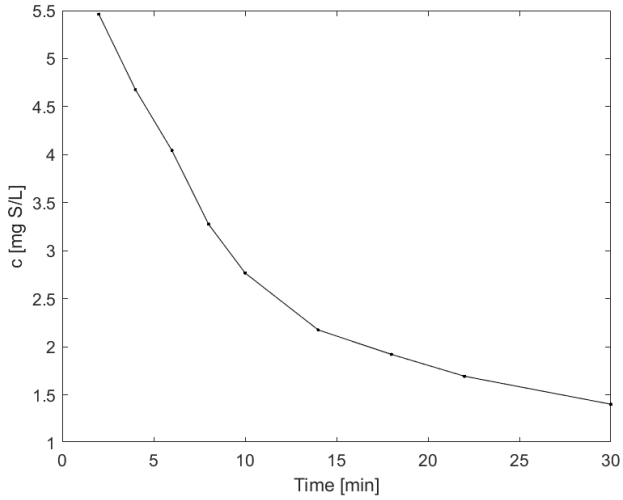


Fig. B.3: Laboratory-scale H_2S removal result.

Table B.5: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	1.063	11.12	1	10
2	0.618	6.40	1	10
4	0.466	4.80	1	10
6	0.466	4.80	1	10
8	0.317	3.22	1	10
10	0.283	2.86	1	10
14	0.257	2.58	1	10
18	0.369	1.88	2	5
22	0.342	1.74	2	5
30	0.422	1.44	3	3.33
40	0.35	1.19	3	3.33

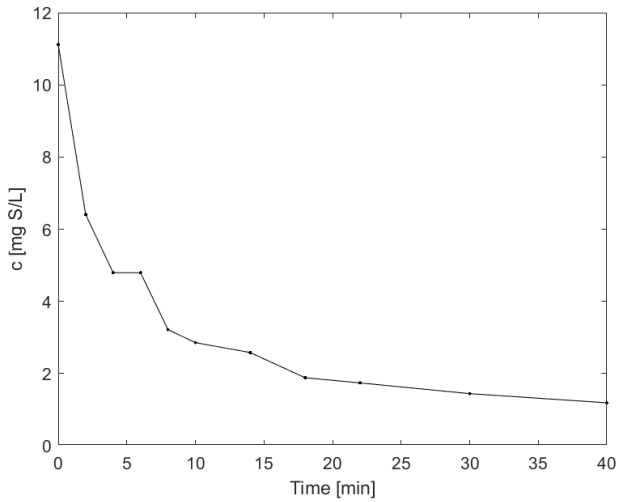


Fig. B.4: Laboratory-scale H_2S removal result.

Table B.6: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.521	10.75	0.5	20
2	0.642	6.66	1	10
4	0.586	6.07	1	10
6	0.523	5.40	1	10
10	0.474	4.88	1	10
14	0.408	4.18	1	10
18	0.37	3.78	1	10
25	0.33	3.35	1	10

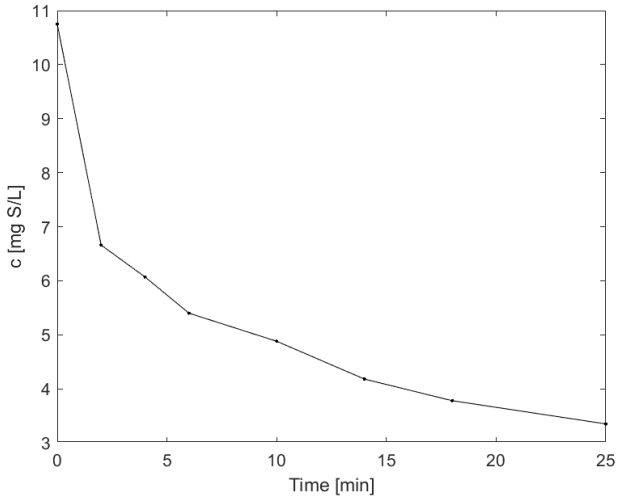


Fig. B.5: Laboratory-scale H_2S removal result.

Table B.7: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.49	5.05	1	10
2	0.462	4.75	1	10
4	0.448	4.60	1	10
6	0.399	4.09	1	10
8	0.354	3.61	1	10
10	0.398	4.07	1	10
15	0.28	2.83	1	10
18	0.461	2.37	2	5
22	0.556	2.87	2	5
26	0.469	2.41	2	5
30	0.461	2.37	2	5

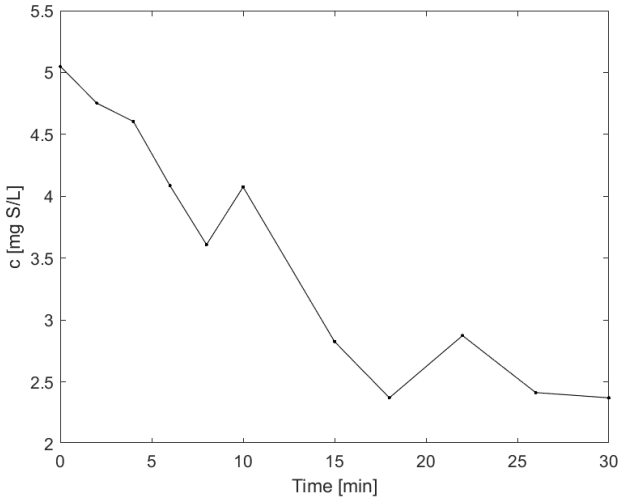


Fig. B.6: Laboratory-scale H_2S removal result.

Table B.8: Results from laboratory-scale H_2S removal with biofilm.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.26	5.23	20	0.5
2	0.545	5.63	10	1
4	0.329	3.34	10	1
7	0.606	3.14	5	2
10	0.688	3.57	5	2
14	0.527	2.72	5	2
18	0.495	2.55	5	2
25	0.753	3.92	5	2

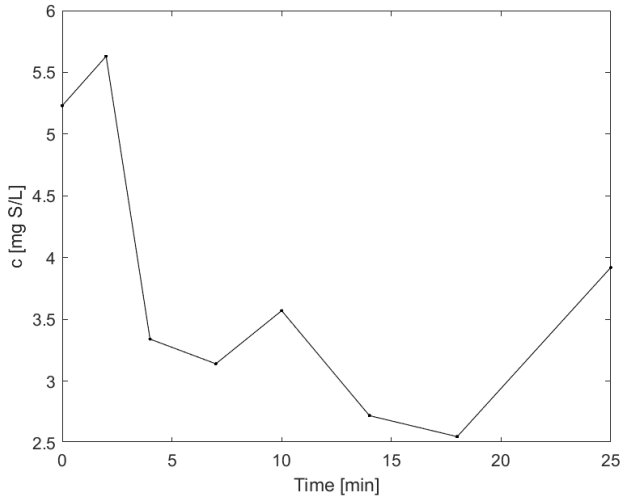


Fig. B.7: Laboratory-scale H_2S removal result.

3 Analysis with biofilm, unlimited DO after training the biofilm with 1 more week

Table B.9: Results from laboratory-scale H_2S removal with biofilm after more training time.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.504	5.20	1	10
2	0.134	1.28	1	10
4	0.344	1.17	3	3.33
6	0.539	1.11	5	2
8	0.787	1.02	8	1.25

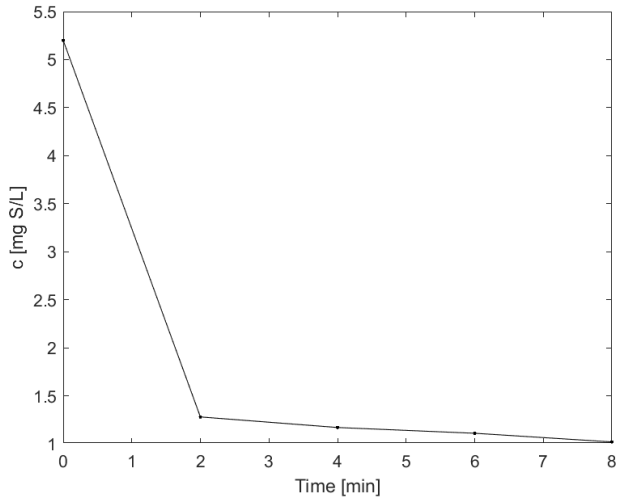


Fig. B.8: Laboratory-scale H_2S removal result with biofilm after more training time.

Table B.10: Results from laboratory-scale H_2S removal with biofilm after more training time.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.182	1.79	1	10
2	0.31	1.57	2	5
4	0.567	1.47	4	2.5
6	0.657	1.36	5	2
8	0.934	1.22	8	1.25
10	0.927	1.21	8	1.25
15	0.866	1.13	8	1.25

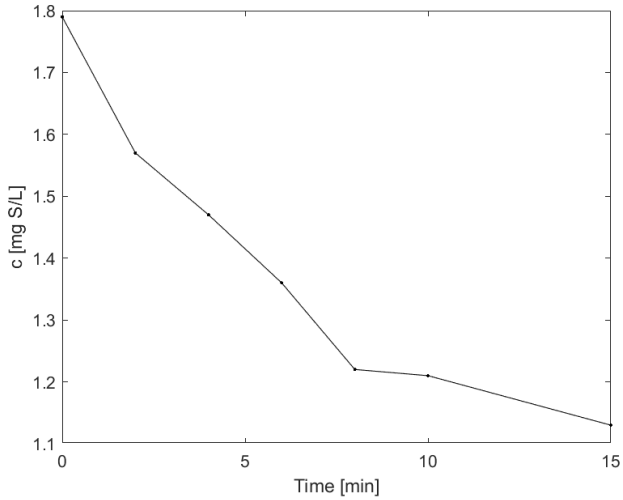


Fig. B.9: Laboratory-scale H_2S removal result with biofilm after more training time.

4 Analysis with biofilm, pre-aerated water before treatment, nonlimited DO

Table B.11: Results from laboratory-scale H_2S removal with biofilm in pre-aerated wastewater.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.26	5.23	20	0.5
2	0.545	5.63	10	1
4	0.329	3.34	10	1
7	0.606	3.14	5	2
10	0.688	3.57	5	2
14	0.527	2.72	5	2
18	0.495	2.55	5	2
25	0.753	3.92	5	2

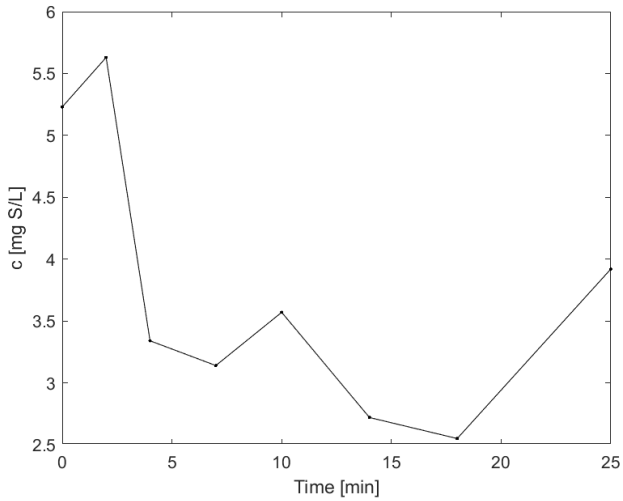


Fig. B.10: Laboratory-scale H_2S removal results with biofilm in pre-aerated wastewater.

Table B.12: Results from laboratory-scale H_2S removal with biofilm in pre-aerated wastewater.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.165	1.61	10	1
3	0.278	1.40	5	2
6	0.264	1.33	5	2
9	0.361	1.23	3.33	3
12	0.311	1.16	3.67	3
15	0.311	1.05	3.33	3
20	0.509	1.05	2	5
25	0.518	1.07	2	5
30	0.512	1.06	2	5

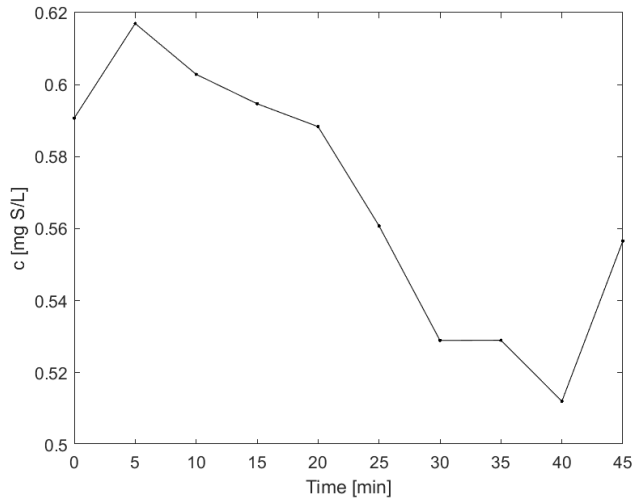


Fig. B.11: Laboratory-scale H_2S removal results with biofilm in pre-aerated wastewater.

5 Analysis with biofilm, pre-aerated water before treatment, nonlimited DO, fully oxidized organic matter content

Table B.13: Results from laboratory-scale H_2S removal with biofilm in pre-aerated wastewater and oxidized organic matter.

Time [min]	Abs	c [mg S/L]	Sample size [ml]	Dilution
0	0.604	6.26	1	10
3	0.277	2.80	1	10
6	0.311	3.15	1	10
9	0.257	2.58	1	10
12	0.349	3.56	1	10
15	0.289	2.92	1	10
20	0.24	2.40	1	10
25	0.276	2.78	1	10

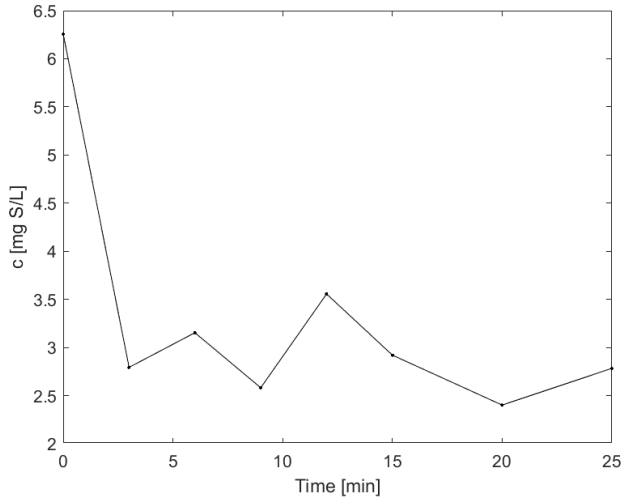


Fig. B.12: Laboratory-scale H_2S removal results with biofilm in pre-aerated wastewater and with fully oxidized organic matter content.

Appendix C

Raw field data

1 2023.03.23.

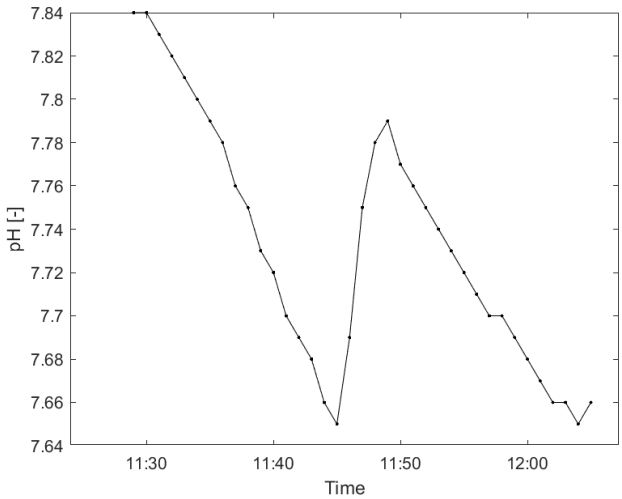


Fig. C.1: Pilot-scale total sulfide treatment pH change. (2023.03.23.)

The H_2S data could not be downloaded, due to an air bubble in the flow cell that caused a very inconsistent and fluctuating rend which did not represent the actual H_2S concentration.

2 2023.03.31.

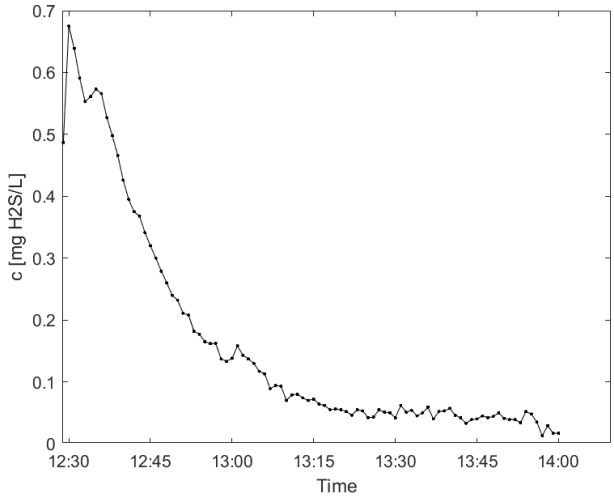


Fig. C.2: Pilot-scale total sulfide treatment H_2S change. (2023.03.31.)

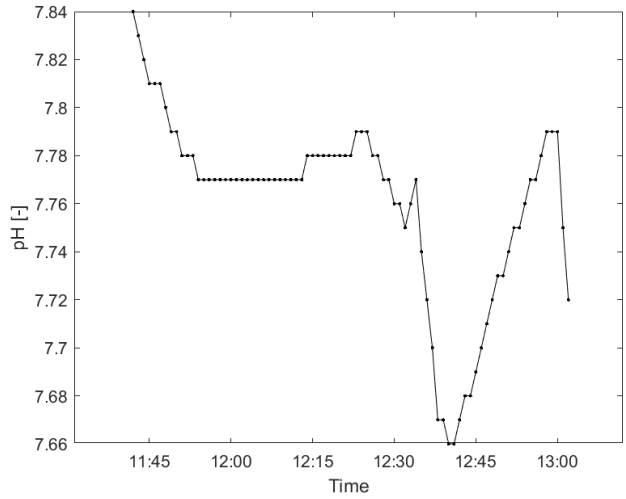


Fig. C.3: Pilot-scale total sulfide treatment pH change. (2023.03.31.)

3 2023.04.20.

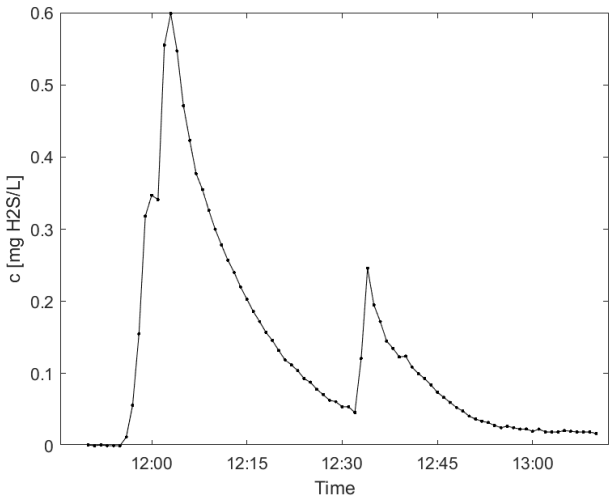


Fig. C.4: Pilot-scale total sulfide treatment H_2S change. (2023.04.20.)

The pH logger lost connection during the test due to a low battery. The results therefore could no be downloaded.

4 2023.04.21.

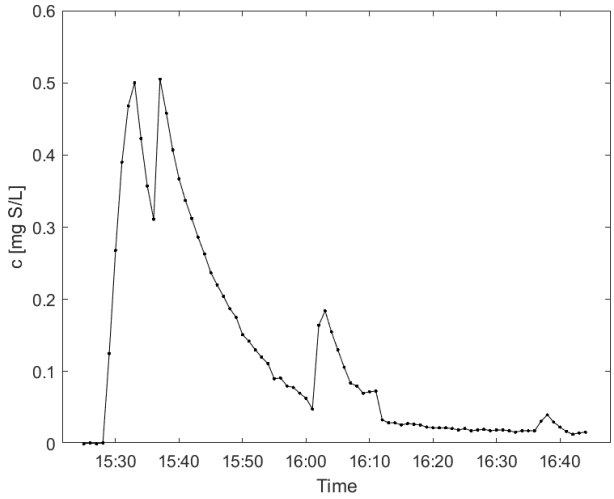


Fig. C.5: Pilot-scale total sulfide treatment H_2S change. (2023.04.21.)

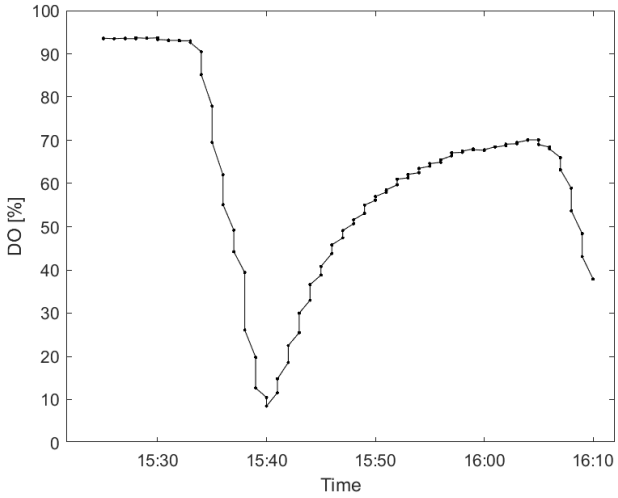


Fig. C.6: Pilot-scale total sulfide treatment DO change. (2023.04.21.)

5 2023.04.26.

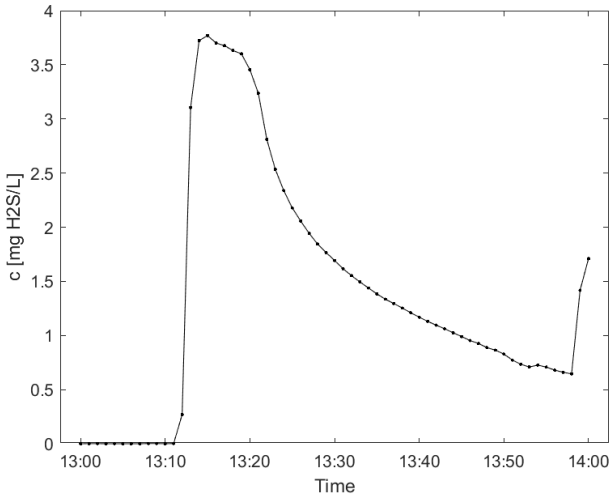


Fig. C.7: Pilot-scale total sulfide treatment H_2S change. (2023.04.26.)

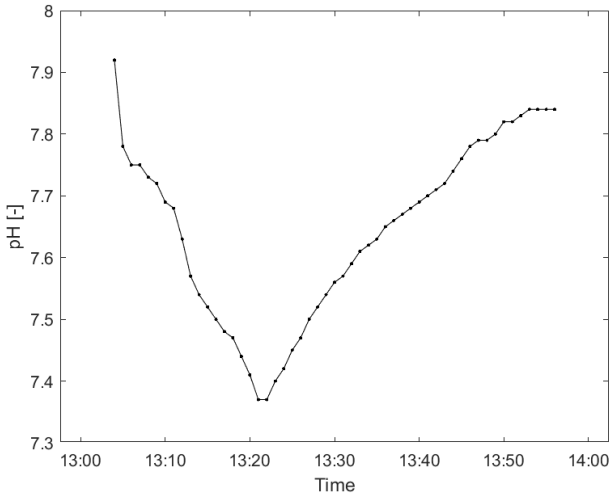


Fig. C.8: Pilot-scale total sulfide treatment pH change. (2023.04.26.)

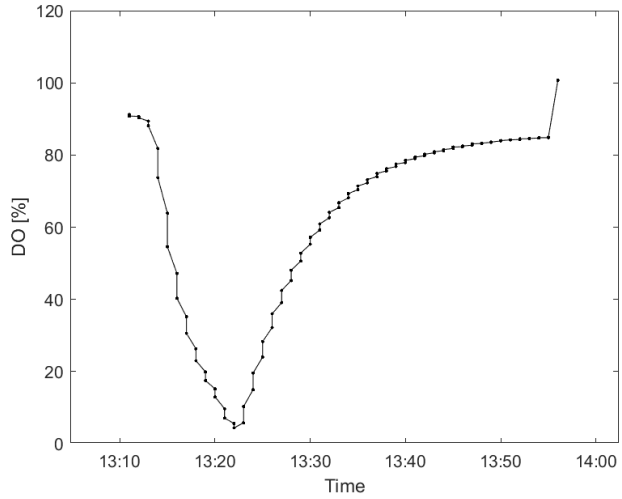


Fig. C.9: Pilot-scale total sulfide treatment DO change. (2023.04.26.)

6 2023.05.03.

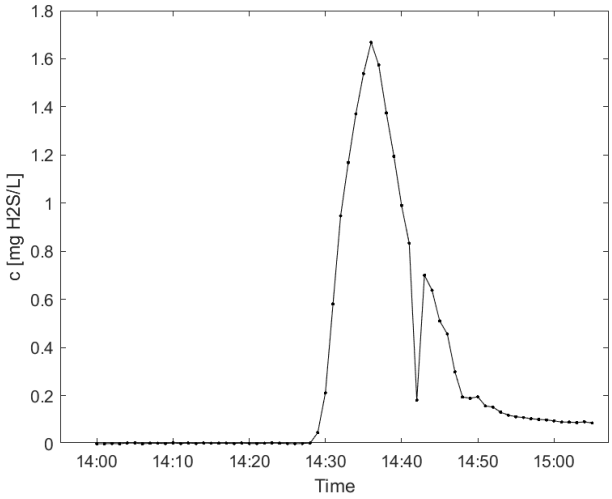


Fig. C.10: Pilot-scale total sulfide treatment H_2S change. (2023.05.03.)

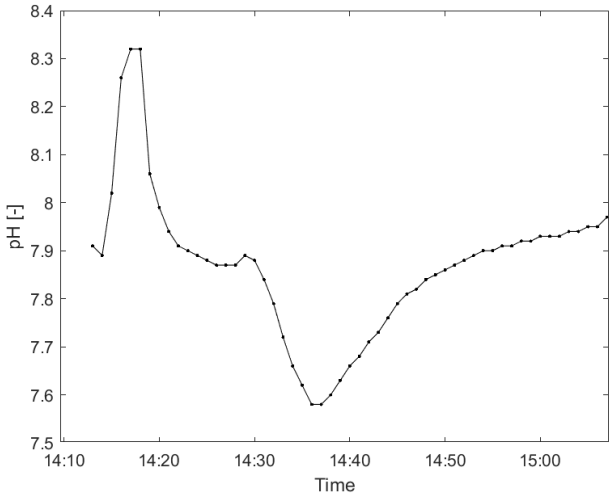


Fig. C.11: Pilot-scale total sulfide treatment pH change. (2023.05.03.)

7 2023.05.09.

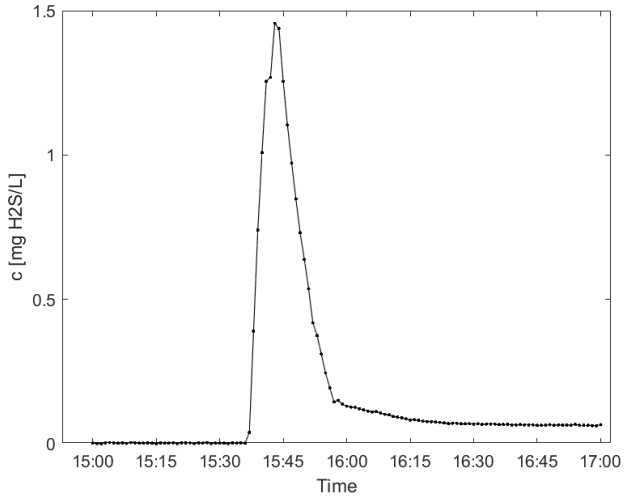


Fig. C.12: Pilot-scale total sulfide treatment H_2S change. (2023.05.09.)

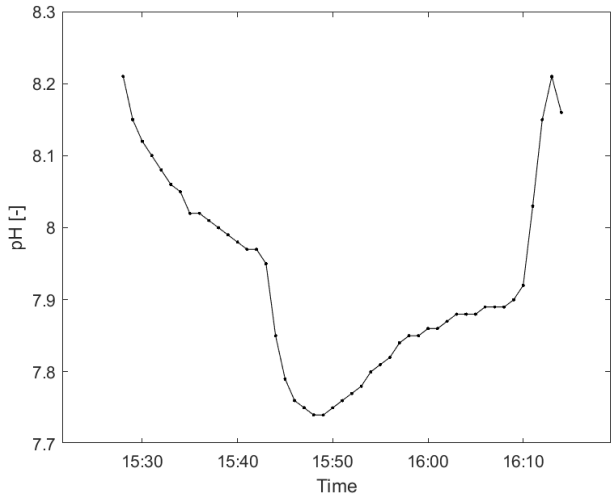


Fig. C.13: Pilot-scale total sulfide treatment pH change. (2023.05.09.)

8 2023.05.10.

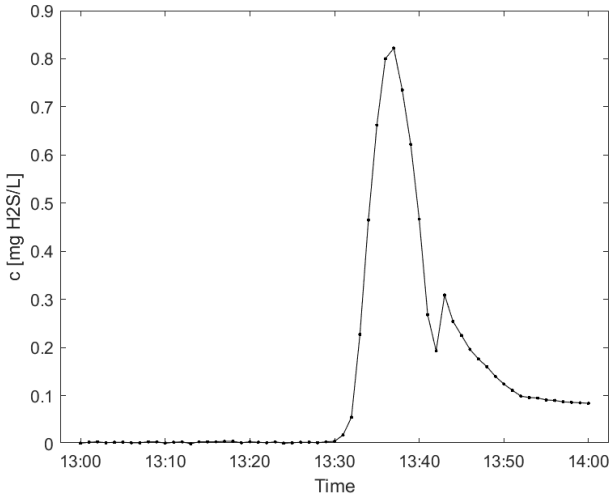


Fig. C.14: Pilot-scale total sulfide treatment H_2S change. (2023.05.10.)

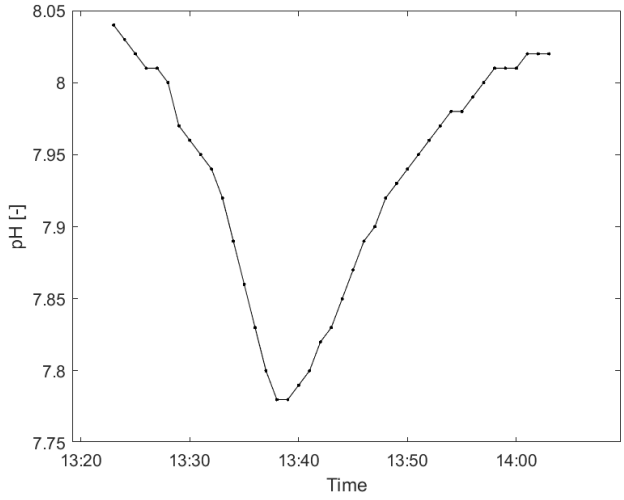


Fig. C.15: Pilot-scale total sulfide treatment pH change. (2023.05.10.)

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