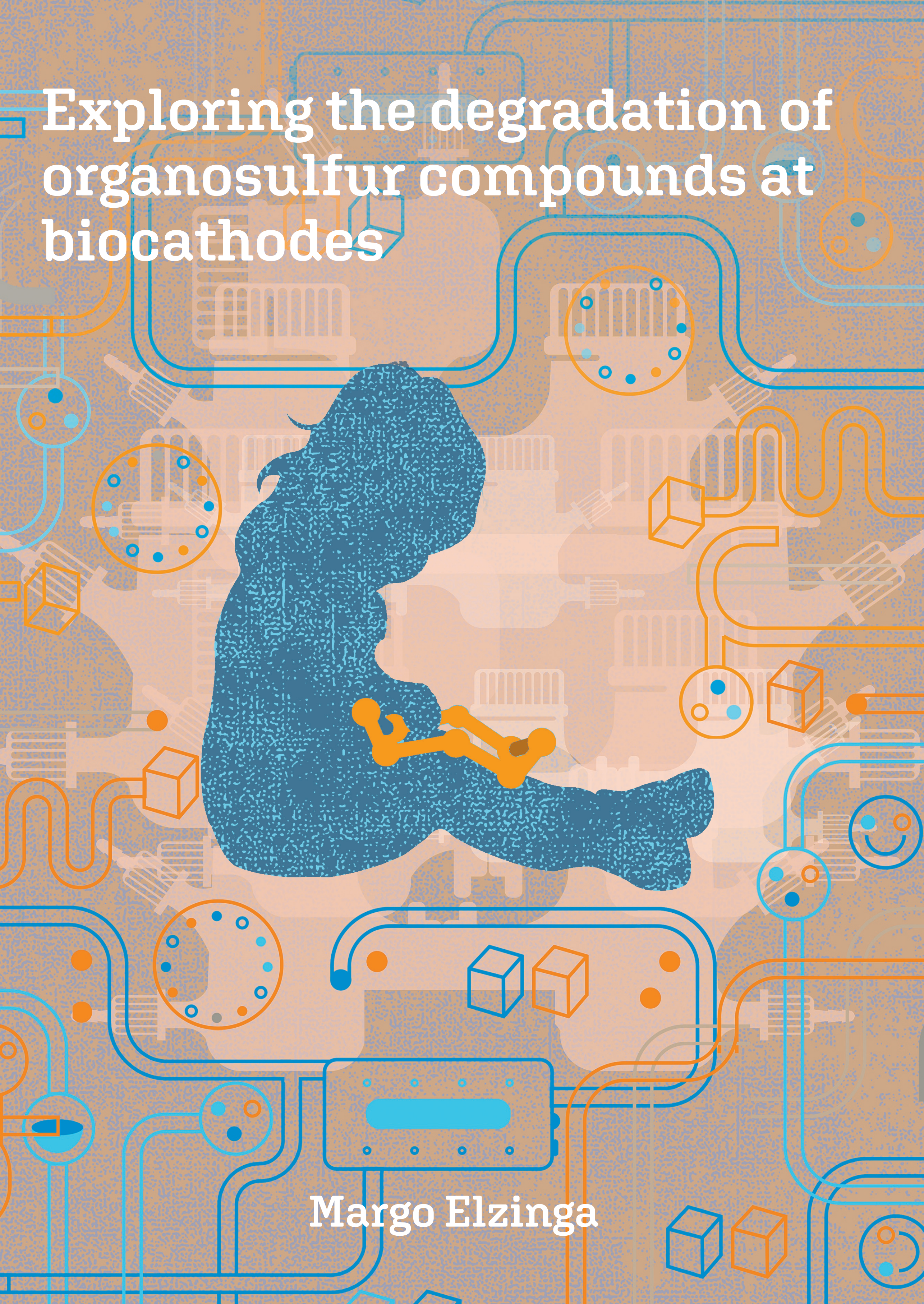
Exploring the degradation of organosulfur compounds at biocathodes



Margo Elzinga

Propositions

1. Oxygen is harmful in thiol converting experiments.

   (this thesis)

2. The impact of thiol formation is overlooked in techno-economic analyses and sustainability life cycle assessments concerning renewable fuels.

   (this thesis)

3. Sulfur becomes a scarce commodity without new recovery technologies.
4. Refraining from providing an opinion creates more wisdom.
5. Technological solutions inherently form new technological challenges.
6. The exploitation of individuals sustains our modern lifestyle.
7. Common sense is strongly bound to culture, community history, and upbringing.

Propositions belonging to the thesis, entitled

Exploring the degradation of organosulfur compounds at biocathodes

Margo Elzinga
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Exploring the degradation of organosulfur compounds at biocathodes

Margo Elzinga

Thesis

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To my mother

Foar Mem

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Chapter 1

General introduction

1.1 Importance of sulfur in our daily lives

Sulfur is an essential element required to sustain human life or, more precisely, any life on earth [1]. Humans depend on the intake of organic sulfur, whereas many microorganisms and plants can utilize inorganic sulfur to synthesize amino acids and proteins [1]. Sulfur is also used in various (industrial) processes to improve the quality of our daily lives. For example, sulfur is required as a nutrient for healthy crop growth in the agricultural sector and is also used in pesticides [1]. In addition, phosphorus and other minerals that can be used as fertilizer in the agricultural industry are extracted with sulfuric acid from raw ores [1,2]. The chemical industry is the largest consumer of sulfur and utilizes over 245 million tons of sulfur per year [2,3]. In addition to its use for mineral extraction, sulfur is used to produce rayon in soaps as surfactants or in dyes where the sulfonic acid groups increase the color fastness of the fabric [1,4]. Sulfur is also added during the vulcanization of rubber and synthetic rubbers, making them more rigid and increasing their resistance to temperature shifts [1,5]. In medicine, sulfonamides and penicillin are used as antibiotic drugs. Furthermore, sulfur dioxide can be added as a food-conserving agent in, for example, wine [1,6].

1.2 Importance of hydrogen sulfide and thiol treating technologies

Sulfur is a versatile compound and can occur with an oxidation state ranging from -2 to +6. Its versatility is one of the reasons why this compound has become so important in nature and industrial processes. However, some forms of sulfur can cause severe damage to living organisms. For example, the combustion of sulfur-containing petroleum products results in the formation of sulfur dioxide. The emission of sulfur dioxide into the atmosphere contributes to acid rain formation, dry acid deposition, corrosion of metal structures and monuments, smog formation, and affects human health [7,8]. The global sulfur dioxide emissions peaked between 1975 and 1985 and were 7.5 times higher compared to the beginning of the 20th century [9,10]. The increased levels of sulfur dioxide in the atmosphere were visible in leaf damage and loss of crops. Therefore, governments and industries started to actively implement legislation and technologies to reduce anthropogenic emissions of sulfur dioxide into the atmosphere [11,12].

The major fraction of anthropogenic sulfur dioxide emissions originates from the combustion of fossil fuels containing sulfur, e.g., hydrogen sulfide or thiols [9,13]. Over the past 50 years, various hydrogen sulfide removal and sulfur recovery technologies were successfully developed and implemented, resulting in decreased sulfur dioxide emissions [14]. The recovered sulfur from these processes nowadays forms the major sulfur source for industrial processes [3]. However, despite many efforts, no suitable technology has yet been developed for treating thiols. Strategies for chemical and biological thiol removal were explored but are often not economically viable, and flaring of the thiol fraction still occurs, resulting in the formation of sulfur dioxide. In addition to lacking a suitable technology for thiol removal, the presence of thiols in both chemical and biological hydrogen sulfide treating technologies interferes with sulfur removal and recovery technologies [15–18].

With the focus on a carbon neutral (net zero) future, the use of fossil fuels is bound to decrease. New technologies to produce renewable fuels and chemical building blocks are rapidly developing. Even though climate goals and models dictate that the use of fossil fuels should decrease, and government pledges are made worldwide, the reality remains that fossil fuels are still used in vast amounts [19,20]. Over the past decade, natural gas and oil extraction was mainly focused on the less so-called "sour" natural gas pockets and oil wells. These wells contain a relatively small fraction of thiols and hydrogen sulfide compared to the remaining potential extraction sites. The remaining sites will become increasingly "sour" and more complex to treat adequately.

Furthermore, the production of renewable fuels and renewable chemical building blocks will lead to new thiol-containing waste streams. In addition, other industrial processes also encounter the presence of thiols. Thiols are formed during the production of paper [21,22]. Small quantities of thiols are also found in waste(water) treatment plants and landfills. The biogas recovered in these processes contains a variable fraction of thiols. Thiol treatment is required for all these industrial processes, but suitable technologies are often lacking.

1.3 (Bio)chemical properties of thiols and their disulfides

1.3.1 Chemical properties and reactivity

Thiols are structural analogs of alcohols and phenols where the functional hydroxyl group is replaced by a sulfhydryl group. They can be described with the general formula RSH, in which the R group consists of an organic alkyl or aromatic group, and SH represents the sulfhydryl or thiol group. Volatile, lightweight alkylic thiols, including methanethiol (MT), ethanethiol (ET), and propanethiol (PT) (Figure 1), are the most abundant thiols in nature and fossil fuels [23]. Table 1 presents some properties of these thiols and their closely related volatile organosulfur compounds (VOSCs). These related volatile organosulfur compounds do not contain the characteristic thiol group but are easily formed from thiols and vice versa. Thiols can cause severe olfactory hindrance at low concentrations. Their foul odor, described as rotten eggs, decayed cabbage, skunk, etc., sets these compounds apart from most other compounds. Furthermore, these compounds are readily notable, with levels of distinct odor awareness as low as 0.7 ppb [24].

Figure 1 *Molecular structure of methanethiol, ethanethiol, and propanethiol*

Table 1 *Properties of thiols and their related volatile organosulfur compounds.*

Organosulfur compound	**Chemical structure**	**Odor description** [25,26]	**Odor threshold ppb** [24,25,27]	**Boiling point °C** [28–32]	**Solubility in water^a g/L** [28–32]	**Vapor pressure^a kPa** [28–32]	**pKa** [28–33]
Hydrogen sulfide	H2S	Rotten eggs	50	-60.7	4.13	1880^b	7.04; 11.96
Methanethiol	CH_3SH	Rotten cabbage	1.6	5.9	23 .3	202^c	10.30
Ethanethiol	CH_3CH_2SH	Garlic, leek skunk	0.8	35.1	15.6	58.9^c	10.39
Propanethiol	CH_3CH_2-CH_2SH	Unpleasantly pungent	0.7	67.8	1.9	20.7	10.44
Dimethyl sulfide	CH_3SCH_3	Decayed cabbage, unpleasant sweet	1	37.3	22.0	53.2	-
Dimethyl disulfide	CH_3SSCH_3	Onion, garlic	0.1-3.6	109.7	2.5	3.8	-
Diethyl disulfide	CH_3CH_2S-SCH_2CH_3	Cabbage, onion	0.02	154.1	0.3	0.57	-

^{a} *25 °C;* ^{b}*Vapor pressure at 20 °C ;*^{c}*Vapor pressure at 26.1 °C.*

Thiols and alcohols have a similar structural appearance. However, the larger size of the sulfur atom and its lower electronegativity compared to oxygen has a distinct impact on the volatility and reactivity of thiols compared to alcohols. The bonding energy between the S-H bond (366 kJ/mol) is weaker than that of the O-H bond (440 kJ/mol), resulting in less hydrogen bridging, making thiols more volatile and less water-soluble than their corresponding alcohols [1]. Thiols are weak acids with pKa around 10 and are present as their conjugate base (RS^-) under alkaline conditions (Eq. 1). Their acidity enables their removal from gas streams using alkaline solutions in gas absorbers. Depending on the consecutive treatment processes, the pH values to absorb thiols into alkaline solutions can vary between 8-14 [34–36].

$$RSH \leftrightharpoons RS^- + H^+ \qquad \text{Eq. 1}$$

The reactivity of thiols increases with increasing alkalinity [37]. Thiols can readily react to their corresponding disulfides or form asymmetrical disulfides when various thiols are present [1]. The formation of disulfides is an oxidation reaction that releases electrons. In these oxidation reactions, oxygen, hydrogen peroxide, sulfur, and metals may serve as electron acceptors (Eq. 2-4) [1,37]. When metals are used as electron acceptor, this leads to the corrosion of metal structures. This corrosion forms a significant challenge in industrial processes. In addition to alkaline conditions, UV light also stimulates the reactivity of thiols and increases their oxidation rates [37]. The reactivity of thiols decreases with the carbon chain length due to steric hindrance [38].

$2\ RSH + 0.5\ O_2 \rightarrow RSSR + H_2O$ Eq. 2
$2\ RSH + H_2O_2 \rightarrow RSSR + H_2O$ Eq. 3
$2\ RSH + 2\ Fe^{3+} \rightarrow RSSR + 2\ Fe^{2+} + 2H^{+}$ Eq. 4

The S-S bond in disulfide molecules is often the weak link, as the bond energy is lower than, for example, the C-H, C-C and C-S bonds. Thiol disulfide interactions can break the original S-S bond, forming a new thiol and a new disulfide (Eq. 5) [39]. When thiols and elemental sulfur are present together, a series of complex reactions can occur. Thiols can break the S-S bonds in elemental sulfur, resulting in the formation of polysulfides and diorgano polysulfides (Eq. 6-7) [40]. Diorgano pentasulfide is the initial main reaction product which immediately undergoes consecutive reactions to form a wide array of diorgano polysulfides (Eq 8). Additionally, diorganosulfides can be formed in a reaction between thiols and alkenes (Eq 9.) [37].

$RS^{-} + R'SSR' \leftrightharpoons R'S^{-} + R'SSR$ Eq. 5
$RSH + S_8 \rightarrow RS_9^{-} + H^{+}$ Eq. 6
$RSH + RS_9^{-} \rightarrow RS_nR + S_x^{2-} + H^{+}$ Eq. 7
$2\ RS_9R \leftrightharpoons RS_{n-1}R + RS_{n+1}R$ Eq. 8
$RSH + CH{=}CHR' \rightarrow RSCH_2CH_2R'$ Eq. 9

1.3.2 Toxicity of thiols

The reversible formation of disulfides and thiol-disulfide interactions are important in living organisms. These interactions play a major role in linking amino acid chains and the folding of proteins. However, unbound thiols are highly reactive and can break disulfide and alkene double bonds in disruptive places, causing severe damage to molecular structures and leading to the deactivation of proteins [39,41]. Thiols can also inhibit the functioning of enzymes by steric hindrance and hydrophobic interactions [42]. For example, thiols interact (reversibly) with the cytochrome C oxidase protein and block the electron flow in the respiratory system. These interactions with the respiratory center can result in death by respiratory failure similar to hydrogen sulfide [1,37].

The first clinical signs of exposure include irritation in the mucous membranes, headaches, dizziness, nausea, and vomiting. Exposure of humans to 50 ppm ethanethiol immediately resulted in a drop in respiration frequency [30]. After termination of exposure, breathing frequency returned to pre-exposure limits. Therefore, an exposed person should immediately be transferred to a contaminant-free area as primary treatment. Thiols also suppress the central nerve system [43]. Clinical studies showed that olfactory fatigue and adaptation occurred upon exposure to only 50 ppm ethanethiol [30]. Therefore, personal protection equipment is essential for workers as they do not perceive their presence at higher concentrations or during longer exposure periods. The maximum exposure concentration during an 8-hour working day (TLV-TWA) has been set at 0.5 ppm for thiols (See Table 2). Long-lasting adverse health effects can occur after 8 hours of exposure at concentrations of 7.3 ppm for methanethiol and 37 ppm for ethanethiol. Furthermore, exposure to concentrations of 22 ppm methanethiol and 110 ppm for ethanethiol can be life-threatening.

Table 2 *Toxicity and exposure guidelines for thiols and related organosulfur compounds*

Compound	**TLV-TWA[a] ppm/8h [50–52]**	**AEGL 2[b] Disabling ppm/8h [24,30,53]**	**AEGL 3[c] Lethal ppm/8h [30]**	**LD 50[d] inhalation rats ppm/4h [30,54,55]**
Hydrogen sulfide	1	17	31	444
Methanethiol	0.5	7.3	22	675
Ethanethiol	0.5	37	110	4420
Propanethiol	0.5[e]	n.a[f]	n.a[f]	7200
Dimethylsulfide	10	n.a[f]	n.a[f]	40250
Dimethyldisulfide	0.5	n.a[f]	n.a[f]	1310

[a] *Threshold limit value -Time Weighted Average;* [b] *Acute exposure guideline level, disabling concentration to humans after 8 hours of exposure;* [c] *Acute exposure guideline level, life-threatening concentration to humans after 8 hours of exposure;* [d] *Lethal dose to 50% of the animals exposed after 4 hours;* [e] *NIOSH ceiling exposure limit 15 min;* [f] *Not available.*

Thiols are not only toxic to human beings. There are various reports of their inhibitory effect on microbial communities. Though methanethiol can form a substrate for certain microbial species performing methanogenesis, in many other cases, they inhibit microbial growth [44–49]. For instance, the methanogenic activity of granular anaerobic sludge was reduced by 50% at methanethiol concentrations between 7 and 10 mM, ethanethiol concentrations between 6 and 14 mM, and propanethiol concentrations between 7 and 14 mM [48]. Thiols can be detoxified by methylation. For example, the microbial formation of dimethyl sulfide (DMS) from methanethiol is commonly encountered in nature [44–46]. The formation of dimethyl **di**sulfide (DMDS) from methanethiol might form another detoxification mechanism. However, dimethyl disulfide is also toxic to microorganisms, and an inhibitory effect on methanogenesis was shown for concentrations as low as 0.26 mM [49]. Furthermore, the presence of thiols also inhibits the biological oxidation of hydrogen sulfide to elemental sulfur in biodesulfurization processes (See section 1.4.3) [18,47].

1.3.3 Natural cycling of VOSCs

Methanethiol and dimethyl sulfide (DMS) make up the majority of natural VOSC emissions, and their natural cycle is widely studied.

Figure **2** provides a simplified overview of the natural flux of methanethiol, dimethyl sulfide, and dimethyl disulfide. Although these compounds can be formed in geochemical processes, such as volcanic eruptions, their natural flux mainly originates from saline ocean waters, salt marshes, swamps, and soils [4,56]. In oceans and saline waters, organosulfur compounds are primarily formed from osmolytes, dimethylsulfoniopropionate (DMSP), which are present in marine algae. In freshwater systems, they are primarily produced through the methylation of hydrogen sulfide [57]. In swamps and soils, they are mainly formed through the decay of organic matter and proteins under aerobic and anaerobic conditions [4,57].

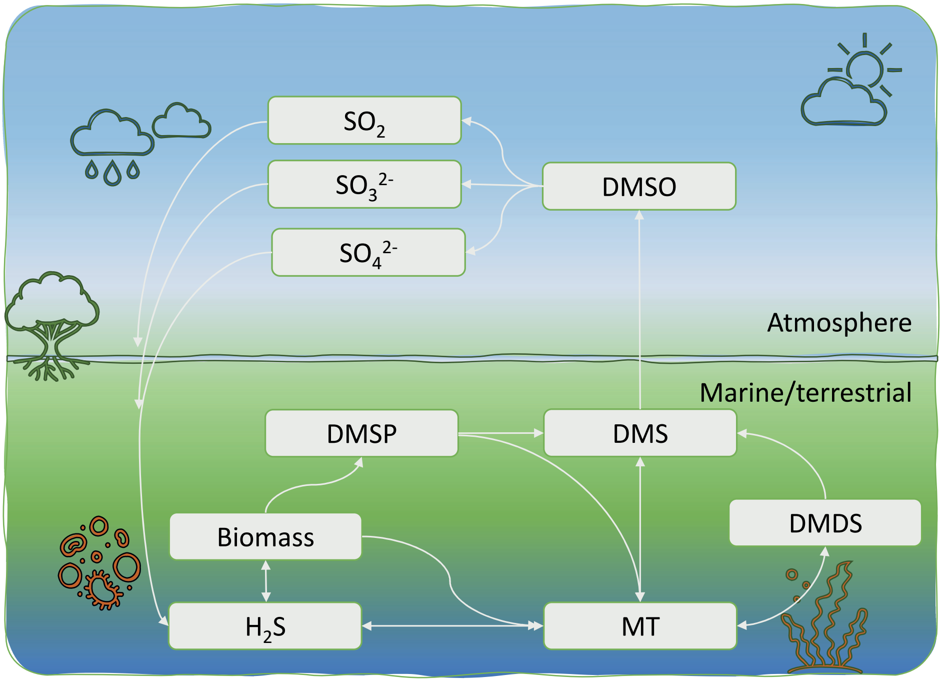

Figure 2 *Simplified scheme of the natural cycling of methanethiol, dimethyldisulfide, and dimethylsulfide adapted from [44]*

The formation of dimethyl sulfide from methanethiol through its methylation is an important step in the degradation process. Natural emissions of DMS into the atmosphere are counteracted by photooxidation processes, which convert DMS to dimethyl sulfoxide (DMSO) and ultimately to sulfur dioxide, sulfate, and thiosulfate. These compounds are deposited in water and soil, where they can be used by plants and microorganisms for growth. The decomposition of DMS in the atmosphere by photo-oxidation forms one pathway for the degradation of these compounds. However, aerobic and anaerobic microbial processes convert over 90% of the formed DMS in aquatic environments before it reaches the atmosphere. These microbial processes include the reduction of DMS towards methanethiol and hydrogen sulfide and the oxidation of methanethiol towards dimethyl disulfide. Therefore, microbial processes play an important role in the global flux of organosulfur compounds.

In contrast to methanethiol, little information is available on the natural formation and degradation of ethanethiol and propanethiol. Ethanethiol can be formed from the degradation of proteins and a reaction between ethionine and methanethiol, but its natural degradation pathways are not well described.

Thiols are also formed in crude oil and natural gas. During these geochemical processes, reduced sulfides and elemental sulfur react with organic matter and form various complex organic sulfur compounds, including thiols. However, they remain trapped in the subsurface and do not significantly contribute to the natural cycling of volatile organosulfur compounds without human interference [58]. However, when these compounds are extracted and released into the atmosphere, they can be toxic to the surrounding environment, contribute to severe olfactory discomfort and disturb the natural sulfur cycle. The average lifetime of methanethiol in the atmosphere is estimated at 9 hours [59]. Methanethiol reacts in the atmosphere with OH and NO_3 radicals. The formed products are not well defined yet. Lee and Brimblecomble (2016) proposed similar degradation products as observed for DMS [4,59].

1.4 Thiol removal: a challenge

1.4.1 Chemical removal and recovery strategies

There are numerous technologies available for the removal of thiols. Applied technologies include, amongst others, absorption to caustic or amine solutions, irreversible adsorption to activated carbon or metal oxides, advanced oxidation processes, and combustion. Each of these technologies has its own drawbacks: (1) the absorption in amine and caustic solutions requires further treatment to regenerate the sorption capacity and recover the sulfur, (2) irreversible adsorption to solid materials generates large amounts of toxic waste, and (3) advanced oxidation has high operational costs. Lastly, partial combustion of thiols in a Claus reaction chamber yields elemental sulfur but is only applicable under high sulfide loading rates [60]. The combustion of thiols in a flare can be applied under low sulfide loading rates (i.e., within the limits of environmental permits) and result in the formation of sulfur dioxide which is released into the atmosphere. Some dominant established thiol treating technologies are shortly introduced below. A more detailed overview of the advantages and disadvantages of these and other thiol removal and conversion technologies is provided in **Chapter 3.**

The Claus process is most effective at high sulfide loading rates (feeds containing at least 3 ton-S/day as hydrogen sulfide) [60]. Acidic compounds such as hydrogen sulfide, thiols, and carbon dioxide are extracted from the product stream in amine solutions. The amines can be regenerated at high temperatures by steam injection, which generates a concentrated acid gas stream that is fed to the Claus unit [61]. In the Claus process, thiols are co-combusted with hydrogen sulfide forming elemental sulfur. When the ratio of thiols to hydrogen sulfide is too high, the catalysts in the hydrogen sulfide combustion process cannot operate effectively, and the sulfur recovery is reduced. In such cases, thiols are typically removed and flared or oxidized to their corresponding disulfides in a separate process.

At medium thiol loading rates (200-500 kg S/day), thiol extraction followed by thiol oxidation to disulfides is the commercial standard. Amongst commonly applied processes are the Merox, Merichem, Thiolex, Mericat, and the Sulfrex process. In these multi-step processes, hydrogen sulfide is extracted from the gas phase via absorption in a dilute alkaline (2% NaOH) or amine solution. The second step entails the extraction of thiols in a strongly alkaline (20% NaOH) or amine solution, followed by their oxidation towards disulfides in the presence of a catalyst [61,62]. Low sulfide concentrations are required for the effective removal of thiols as it competes with absorption in the alkaline or amine solutions used in this process. The formed disulfides can then be separated from the aqueous phase and require further treatment, for example, a hydro-treating unit in which sulfide is formed under high pressure and temperatures. These processes require stable thiol loading rates, as the regeneration with oxygen should be carefully dosed. Insufficient oxygen does not fully regenerate the catalyst and lowers the efficiency of the system, while an overdose of oxygen might result in disulfide formation during the thiol extraction. The investment and operational costs of these processes are high due to the post-treatment of the disulfide fraction and the limited lifetime of the catalysts [63].

At low thiol loading rates <200 kg/d, thiols are typically flared or adsorbed to metal oxides or absorbed in alkaline solutions forming so-called spent caustics. The regeneration of these materials is often not cost-effective. Instead, large waste streams are produced.

1.4.2 Biological removal strategies for thiols

Biological processes may form an economically interesting alternative to chemical processes as they do not require expensive catalysts and can operate at ambient temperatures and pressures. The mild operating conditions and omission of heating, pressurizing, and cooling creates fewer risks for operators and lower operational costs compared to chemical technologies. Many studies evaluate the aerobic, anoxic, and anaerobic degradation of methanethiol, dimethyl sulfide, and dimethyl disulfide [64]. However, the application of biological conversions for removing thiols in industrial waste streams is limited due to the low degradation rates.

Biofilters and bio-trickling filters are used in the pulp and paper industry to treat thiols. Various carrier materials like compost, peat, wood chips, lava rock, or ceramics are used in these filters to support microbial growth. In biofilters, gas is recirculated over the filter bed, while in a bio-trickling filter, water is continuously recycled. Electron acceptors like oxygen and nitrate are added to the system to oxidize thiols to sulfate and elemental sulfur. Degradation rates up to 59.9 mM methanethiol/d and 12.5 mM ethanethiol/d were reached using oxygen as an electron acceptor in lab-scale experiments [65–67]. However, the final products in this process, namely sulfate, thiosulfate, and elemental sulfur, cannot easily be recovered. Additionally, the formation of elemental sulfur and biomass growth can limit the performance of the system due to clogging.

Alternatively, anaerobic processes can be applied for thiol degradation. For example, anaerobic degradation of methanethiol in UASB reactors results in the formation of hydrogen sulfide and methane [48,68]. As thiols are typically present in sulfide-rich waste gasses, the formed sulfide from thiol reduction can then be treated in a sulfur recovery unit. Several studies report the successful biological reduction of methanethiol to methane, carbon dioxide, and hydrogen sulfide by methylotrophic methanogens in bio(trickling)filters and UASB reactors [49,68–71]. The obtained degradation rates for methanethiol are up to 50 mM/d [71]. However, these degradation rates are insufficient for industrial applications as they require large reactor volumes. Furthermore, the degradation of ethanethiol and propanethiol under anaerobic conditions has so far been unsuccessful [48,72,73].

Studies on the anaerobic degradation of ethanethiol and propanethiol are limited. The degradation in anoxic sediments yielded trace amounts of ethane and propane with a conversion efficiency of less than one percent. It was suggested that growth on these substrates could not occur, and the observed conversion was solely a result of a co-metabolism [72,73].

1.4.3 Interference of thiols with biodesulfurization technologies

Most hydrocarbon-rich streams contain a combination of hydrogen sulfide and thiols. At small to medium loading rates of <70 tons of sulfur/day, biological desulfurization processes can be more cost-effective in removing hydrogen sulfide than non-biological processes [74]. Without thiols, this process is highly efficient and can reach up to 97% sulfur selectivity [75]. However, when thiols are introduced, they inhibit the microbial oxidation of hydrogen sulfide to elemental sulfur [47,76]. This inhibitory effect is already shown at methanethiol concentrations above 1 µM and a hydrogen sulfide to methanethiol ratio of 200 [77]. The sulfide concentration in the bioreactor can accumulate until toxic levels are reached, and the entire system can collapse [17,47]. However, biodesulfurization processes can withstand low concentrations of thiols, and it was shown that methanethiol-resistant sulfide oxidizing bacteria could be selected in biodesulfurization processes [18]. A high sulfur selectivity could be maintained by gradually increasing the methanethiol loading rate up to 2 mM/d while operating with a fixed hydrogen sulfide loading rate of 58.15 mM-S/d [18].

Thiols not only inhibit the microbial activity, but they also introduce various chemical reactions, attacking the formed elemental sulfur and influencing sulfur crystal formation [23]. Furthermore, the presence of thiols interferes with the traditional control strategy of the biodesulfurization process. This control strategy involves measuring the oxygen reduction potential (ORP) and is used to regulate the oxygen supply to the aerobic reactor. However, thiols interfere with this ORP measurement, leading to changes in the oxygen supply affecting the sulfur selectivity and product formation [78].

1.5 Bioelectrochemistry as a new thiol treatment method

1.5.1 Principle of bioelectrochemical systems

The reduction of thiols in anaerobic degradation processes, such as UASB reactors, has only been reported for methanethiol. Methanethiol was successfully reduced by the methylotrophic pathway [49,68,69]. However, degradation rates remain low, and ethanethiol and propanethiol cannot be degraded in such systems [68]. Therefore, stimulating the biological anaerobic degradation of these thiols is essential to obtain a cost-effective treatment method. The stimulated reduction of thiols towards sulfide and methane in bioelectrochemical systems (BES) could be an alternative strategy to eliminate thiols. The produced sulfide can be treated in conventional treatment facilities to recover sulfur.

A bioelectrochemical system consists of two electrodes that can be separated by an ion exchange membrane (Figure 3). In such systems, the oxidation and reduction reactions are separated at the anode and cathode, respectively. In the anode compartment, oxidation reactions, releasing electrons, take place while at the cathode, these electrons are used to drive reduction reactions that consume electrons. At least one of the electrodes contains microorganisms that catalyze the oxidation or reduction reactions. The electrons flow via an external power supply from the anode to the cathode. Protons or other cations transfer through the cation exchange membrane to maintain electroneutrality. The field of bioelectrochemical technologies is rapidly developing, and a wide range of applications is being studied. The field can be divided roughly into two main directions. The first focuses on energy or hydrogen generation from waste streams in microbial fuel and electrolysis cells and the second on synthesizing chemicals in, so-called, microbial electrosynthesis. In microbial electrolysis cells and microbial electrosynthesis cells, otherwise, non-spontaneous reduction reactions are favored due to the applied potential and the microbial catalysts [79–82].

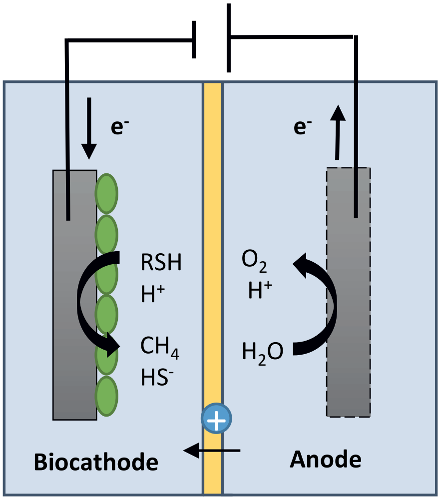

Figure 3 *Schematic overview of a bioelectrochemical system for thiol reduction. With water oxidation as an electron-donating reaction at the anode and thiol reduction as an electron-accepting reaction at the biocathode.*

An advantage of BES is that they can operate under ambient pressure and temperatures. The use of microorganisms omits the need for expensive catalysts. In these systems, microorganisms can exchange electrons with the electrode. The development of an active biofilm on the electrode can increase degradation rates. Therefore, porous materials like graphite felt are often used in application studies as they contain a large surface area to which the microorganisms can attach. The advantage of carbon-based conductive materials like graphite felt or activated carbon is their low costs compared to metal catalysts. The biocatalyst (microorganism) can grow, develop, and renew itself with the input of nutrients, creating a prospect for low costs and effective removal.

In this thesis, the degradation of thiols at biocathodes was studied. A biocathode can be either current or potential controlled to drive reactions. Under current control, the flow of electrons is set, and thus a fixed rate of electrons is supplied for reduction reactions. The potential established under the current controlled conditions depends on the available reactants and reactions occurring at the biocathode. When the current is too high, undesired side reactions, like the formation of hydrogen, may occur, yielding a lower energy efficiency. Alternatively, in case of potential control, the cathode can be poised at a potential versus a reference electrode. When this potential is more negative than the half reaction's thermodynamic equilibrium, this creates a driving force for the reduction reaction. The difference between the thermodynamic equilibrium and the established or applied potential at the electrode is referred to as the overpotential. Setting the electrode potential close to the thermodynamic equilibrium yields a small overpotential and will result in a higher coulombic efficiency. However, it may also result in low currents, slow biofilm development, and low reaction rates.

1.5.2 Degradation of pollutants in bioelectrochemical systems

The use of electrochemical techniques, without biology, for oil spill remediation, has been studied for over 20 years. These systems use cathodes to hydrogenate organosulfur compounds from petroleum products. Hydrogen sulfide is the desired product in this process. However, the downsides of these electrochemical techniques are the deposition of contaminants on the electrode, which deactivates the catalyst, and the high-energy requirements. Potentials below the hydrogen evolution potential are required to reduce organics like thiophenol on a platinum-based catalyst. In such systems, the formation of hydrogen competes with the reduction of sulfur compounds and lowers the desulfurization efficiencies [83].

The degradation of toxic organics in bioelectrochemical systems is an emerging field that gained more interest over recent years [84]. The use of bioanodes to treat recalcitrant chemicals in wastewater, groundwater, and contaminated soils has been studied. These bioanodes can oxidize toxic compounds like benzene, toluene and xylene (BTX) and phenols to carbon dioxide and water [84]. Toxic compounds like perchlorate, azo dyes, and metals can be reduced at biocathodes. While using bioelectrochemical systems for bioremediation is demonstrated on a lab scale, its full-scale application is not yet (commonly) applied [84].

1.5.3 Degradation of thiols in bioelectrochemical systems

The degradation of thiols at bioanodes has several potential restrictions. The partial oxidation of thiols at the anode would result in the formation of elemental sulfur, pacifying the electrode. This passivation has been observed in anodic wastewater treatment processes [85,86]. In contrast, the reduction of thiols to hydrogen sulfide at biocathodes forms an interesting possibility. Theoretically, 2 electrons are required to reduce methanethiol towards methane and hydrogen sulfide. These 2 electrons can originate from different sources, e.g., microbial metabolism, interspecies electron transfer between mixed cultures, or can be derived from a cathode. The reduction reactions for methanethiol, ethanethiol, and propanethiol towards methane and sulfide are provided in **eq. 10-12**. Alternatively, ethane and propane may also be formed at biocathodes. The formed hydrogen sulfide can be detoxified in commercially available (bio) desulfurization technologies that recover elemental sulfur.

$$CH_4S + H^+ + 2e^- \rightarrow CH_4 + HS^- \qquad \text{Eq. 10}$$

$$C_2H_6S + 3H^+ + 4e^- \rightarrow 2CH_4 + HS^- \qquad \text{Eq. 11}$$

$$C_3H_8S + 5H^+ + 6e^- \rightarrow 3CH_4 + HS^- \qquad \text{Eq. 12}$$

1.5.4 Thermodynamic framework for thiol reduction in BES

The half-reactions for thiols reduction towards sulfide and methane are provided in eq. 10-12. However, whether these reactions will occur at the biocathode is currently unknown as these depend on several variables. These include the availability of a metabolic pathway inside the microorganisms to perform the desired reaction, the thermodynamic feasibility of the desired reaction and competing reactions, and energy losses in the system due to internal resistance in the bioelectrochemical system.

A reaction is considered thermodynamically feasible when the Gibbs free energy of formation of the reactants is higher than the Gibbs free energy of formation of the products (See eq. 14). In these cases, energy is released from the combined oxidation and reduction reactions, and the reaction can proceed spontaneously. The tabulated Gibbs free energy of formation is defined at a temperature of 25 °C and a concentration of 1 M. To account for changes in temperature, the standard Gibbs free energy of the reaction can be calculated using equation 15. The actual concentrations in the system can be accounted for using 16.

$$aA + bB = cC + dD \qquad \text{Eq. 13}$$

$$\Delta G_r^0 = \sum \Delta G_{f\,product} - \sum \Delta G_{f\,reactant} \qquad \text{Eq. 14}$$

$$\Delta G_{r(T_1)}^0 = \Delta G_{r(T_0)}^0 \left(\frac{T_1}{T_0}\right) + \Delta H_{r(T_0)}^0 \left(\frac{T_0 - T_1}{T_0}\right) \qquad \text{Eq. 15}$$

$$\Delta G_r = \Delta G_r^0 + \mathrm{RT}\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) \qquad \text{Eq. 16}$$

An electron donor is required to facilitate the reduction of thiols. Water is readily available and can be used as a potential electron donor in biological degradation processes or at the anode coupled to a bio-catalyzed reaction at the biocathode. When considering water as the electron donor, the complete reduction of these thiols towards methane and hydrogen sulfide is thermodynamically unfeasible, as shown in Table 3. Therefore, this reaction will not occur spontaneously under standard conditions.

Table 3 *Gibbs free energy of thiol reduction towards methane and hydrogen sulfide with water as the electron donor under standard and actual conditions.*

Overall reaction	**ΔG_r°**	**ΔG_r**
$CH_4S + 0.5\ H_2O \rightarrow CH_4 + HS^- + 0.25\ O_2$	87.59	71.17
$C_2H_6S + 1.5\ H_2O \rightarrow 2\ CH_4 + HS^- + 0.75\ O_2$	271.82	235.70
$C_3H_8S + 2.5\ H_2O \rightarrow 3\ CH_4 + HS^- + 1.25\ O_2$	448.98	393.16

ΔG_r was calculated at a temperature of 25 °C, at pH 8.5, a thiol and sulfide concentration of 1 mM, and a partial pressure of 0.05% for oxygen and methane.

In bioelectrochemical systems, the oxidation and reduction reactions are separated from each other. Microorganisms can utilize the electrode as terminal electron acceptor or electron donor to sustain their energy metabolism. The electrode potential represents the equilibrium energy level between the oxidized and reduced species in the system. An electron contains more energy at a lower (more negative) potential. The electrode potentials can be altered externally, thereby favoring the reaction. The electrode potential is normally expressed against a stable reference electrode.

The theoretical electrode potential for a system in equilibrium can be calculated with equation 17. Much like the Gibbs free energy, this calculation can also be adjusted from standard to actual conditions (eq. 18). In these calculations, all reactions are noted as reduction reactions. The equilibrium cathode potential for thiol reduction and water oxidizing anode potential under standard and nonstandard conditions are presented in Table 4.

$$E^\circ = -\frac{\Delta G_r^\circ}{nF} \qquad \text{Eq. 17}$$

$$E = E^\circ - \frac{RT}{nF} \ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) \qquad \text{Eq. 18}$$

Table 4 *Electrode potentials for thiol reduction towards methane and hydrogen sulfide and water oxidation under standard and nonstandard conditions.*

	Half reaction	**E° vs Ag/AgCl**	**E vs. Ag/AgCl**
Cathode	$CH_4S + H^+ + 2e^- \rightarrow CH_4 + HS^-$	-0.049	-0.301
	$C_2H_6S + 3H^+ + 4e^- \rightarrow 2\ CH_4 + HS^-$	0.008	-0.370
	$C_3H_8S + 5H^+ + 6e^- \rightarrow 3\ CH_4 + HS^-$	0.039	-0.380
Anode	$2H^+ + 0.5\ O_2 \rightarrow H_2O$	1.019	0.516

E vs. Ag/AgCl was calculated at a temperature of 25°C, at pH 8.5, a thiol and sulfide concentration of 1mM, and a partial pressure of 0.05% for oxygen and methane.

The combined potential of the anode and cathode yields the overall cell potential and is calculated according to equation 19. When the cell potential is negative, the energy content of the electrons at the anode is higher than at the cathode, and additional energy needs to be supplied to drive the reaction. For a system, in equilibrium, an open cell potential of -0.82, -0.89, and -0. 90 V is expected for the reduction of methanethiol, ethanethiol, and propanethiol, respectively. Therefore, additional energy needs to be applied to perform these reduction reactions when combined with water oxidation at the anode.

$$E_{cell} = E_{cathode} - E_{anode} \qquad \text{Eq. 19}$$

Current does not flow when the applied potential equals the equilibrium potential. When a different potential or current is applied, this creates a driving force for oxidation and reduction reactions. Whether these reactions will occur, and electrons will flow between the anode and the cathode, depends on the kinetics at the electrode. These reaction kinetics are influenced by internal resistances, such as interfacial transfer limitations, the activation energy of the species involved, changes in local concentrations, and the established biofilm[87–89]. The extra energy that is required to drive these reactions is referred to as overpotential.

1.6 Scope and outline of this thesis

The removal of thiols with the currently available techniques is a challenge. Using bioelectrochemical systems to drive thiol reduction towards sulfide forms a new potential opportunity to treat these compounds.

The main research question of this thesis was:

Can bioelectrochemical systems become a clean and circular solution for thiol removal and sulfur recovery?

To answer this question, it is important to understand where the future challenges for thiol removal are expected as well as the removal rates and mechanisms of organosulfur compounds in BES systems.

Chapter 2 describes the challenges and opportunities that arise from the transition from fossil fuels to renewable fuels. To understand whether BES holds a place as a future technological solution, it is important to obtain insight into the current and future thiol-containing (waste) streams and the available solutions. Various treatment technologies to treat thiols have been developed over the years, and these are further discussed in **Chapter 3**. This chapter describes these technologies in more detail and discusses their advantages and drawbacks for the current and future markets. In this chapter, it becomes clear that there is a demand for new and adequate technologies that can treat organosulfur compounds so that the sulfur can be recovered.

A proof of concept using bioelectrochemical systems for the conversion of organosulfur compounds to hydrogen sulfide is provided in **Chapter 4**. To further study and understand the removal of organosulfur compounds, it is important to detect and identify these organosulfur compounds and their degradation products. The challenging aspect in the detection of these compounds is their high volatility and their reactivity. A new method was developed in **Chapter 5** to aid the identification and quantification of the substrate and products formed inside the bioelectrochemical system. With this method, the degradation of ethanethiol in a continuous bioelectrochemical system could be closely monitored. The long-term operation of a bioelectrochemical system provides more insight into the process stability and potential applicability. Furthermore, degradation rates, as well as long-term process stability, can be monitored in such a system. The continuous degradation of ethanethiol is described in **Chapter 6**. Additional batch experiments with graphite felt were combined with a model to distinguish between biotic and abiotic processes and gain insight in the degradation kinetics.

Finally, **Chapter 7** combines the gained knowledge in a general discussion and provides an outlook on the scientific challenges and applicability of bioelectrochemical systems for organosulfur compound removal.

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Chapter 2

Nutrient recovery and pollutant removal during renewable fuel production: opportunities and challenges

Abstract

Stimulated by the desire to achieve a Net Zero energy economy, the demand for renewable fuels is growing rapidly. The production of toxic waste streams that accompanies the transition from fossil fuels to renewable fuels is often overlooked. These waste streams include, among others, thiols, ammonia, benzene, toluene and xylene (BTX). When suitable treatment technologies are available, these compounds can be converted to valuable nutrients. In this opinion article, we provide an overview of expected waste streams and their characteristics. We indicate future challenges for associated waste streams, such as the lag in developing resource recovery technologies. Furthermore, we discuss unexploited opportunities to recover valuable nutrients from these waste streams.

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2.1 Renewable fuels are required to achieve a Net Zero energy economy

In 1856, Foote discovered that elevated concentrations of carbon dioxide in the atmosphere would lead to an increase in global temperature [1]. Since then, more than 2400 Gt of carbon dioxide, originating from the combustion of natural gas, crude oil and coal, have been emitted into the atmosphere [2,3]. Even though the use of fossil fuels has accelerated socio-economic development and improved human quality of life, threats of global warming associated with the combustion of these fuels are now globally recognized [4]. These threats include, among others, rising sea levels, increasing frequency of droughts and storms, loss of biodiversity in ecosystems, endangerment of global food security and destabilization of local communities [5–7]. To limit global warming, societies are working towards a Net Zero energy economy in which greenhouse gas emissions are minimized and compensated [8–10]. Goals to reduce greenhouse gas emissions have been established across nations and have already resulted in, for example, stabilizing carbon dioxide emissions in Europe and the Americas [3,10]. To achieve Net Zero, utilization of the earth reserves of fossil fuels should be minimized and supplemented by carbon capture projects, such as reforestation [3,11–13]. Additionally, reduction in carbon emissions can be facilitated through technological solutions, for example, carbon capture storage and utilization or replacing fossil fuels with alternative renewable sources for chemicals and energy, including fuels produced from biomass (biofuels) and other renewable fuels such as hydrogen from electrolysis.

To ensure that global warming is kept below 1.5°C, renewable energy should account for 38% of the global energy consumption by 2030 [11]. As of 2019, the global share of renewable energy accounted for 17%. The increased deployment of solar and wind energy are essential to achieve these goals. Despite being crucial for the energy transition, these technologies have several limitations such as seasonal availability, energy storage and differences between household energy consumption. Firstly, production can be hampered because solar and wind power can vary throughout the seasons. In addition to seasonal variation, they can also vary throughout the day, causing electricity to be produced intermittently and therefore requiring robust storage and distribution technologies. Lastly, while being great harvesting methods for electricity, most energy consumption utilizes nonelectrical forms of power. In 2020, the consumption of electrical energy accounted for less than 18% of the total energy consumed in Europe [14]. Even though many more industries can be transitioned to electricity-based operations and focus on electrification, there will still be a demand for energy-dense molecule-based fuels [14].

Among the sectors that are heavily dependent on fossil fuels are transportation and aviation industry. In these industries, alternative energy carriers are already implemented to a certain extent including battery technology for electrical energy, liquified hydrogen and alcohols [14–16]. Electrical energy, utilizing battery technology, is suitable for personal mobility due to the short distances traveled and limited freight requirements. However, battery technology struggles to meet the demands for long-distance transportation (boats and unelectrified trains), nonroad machinery (construction and agriculture), and the aviation industry in the foreseeable future since the energy density in battery technology must increase tenfold to accommodate these uses [14,17]. The use of liquified hydrogen will likely not fully accommodate the requirements for long-distance heavy freight transportation either, due to its lower energy density compared to fossil fuels. Therefore, it is expected that alternative, renewable, energy-dense energy carriers will remain crucial. Potential energy carriers include, among others, methane, syngas, alcohol and biodiesel.

The global biofuel supply has been gradually increasing over the past 30 years (Figure 1) and should quadruplicate by 2030 according to the Net Zero scenario of the international energy agency (IEA) [18–20]. In this scenario, 64% of the renewable energy demand for the transport sector should originate from biofuels [18]. However, one major challenge to produce these renewable carbon-based energy carriers is the formation of various waste streams containing ammonia, volatile organosulfur compounds (VOSCs) and volatile organic compounds (VOCs) such as benzene, toluene and xylene (BTX).

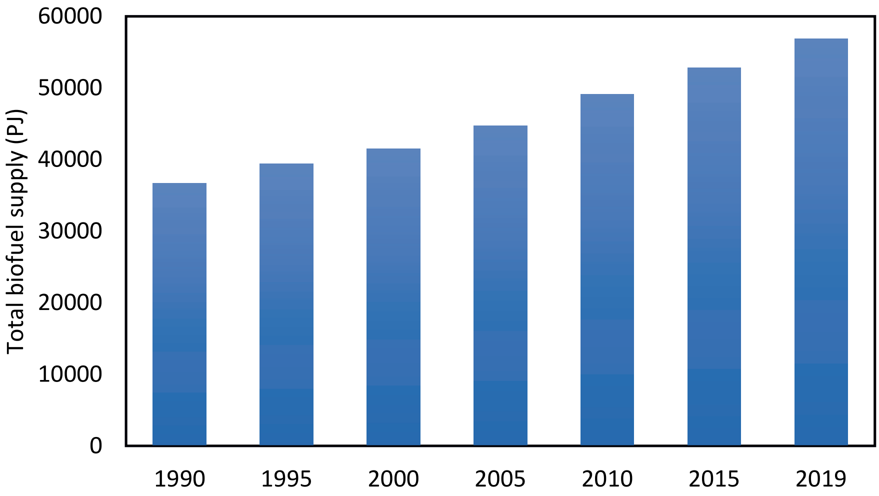

Figure 1 *World biofuel supply between 1990 and 2019. Source: IEA (2022) World Energy Statistics and Balances [20].*

2.2 Waste streams generated in renewable fuel production processes

Energy-dense renewable (bio)fuels are produced from, for example, biobased materials, such as non-food crops, plant residues, algae, pyrolyzed (bio)plastic, or other organic waste streams [21,22]. In renewable fuel refineries, these organic substrates are converted into energy-dense molecules, including methane, ethane, alcohols, diesel, kerosine and naphtha [23,24]. Production of these renewable fuels requires advanced technological processes [25]. Examples of growing technologies to produce renewable fuels are gasification of organic carbon (syngas) and Hydro-processed Esters and Fatty Acids (HEFA). Syngas, a mixture of hydrogen, carbon monoxide, and carbon dioxide, is thermochemically produced via gasification of organic carbon and serves as an intermediate for other fuels such as methanol, ethanol and diesel fuel that can be produced with the Fischer-Tropsch process[26–28]. The HEFA process produces, for example, biodiesel and sustainable aviation fuel (SAF) via catalytic hydrogenation of fatty organic substrates (i.e., treatment with hydrogen and a catalyst) [29]. In each of the mentioned processes, undesired byproducts including ammonia, VOSCs and BTX are formed. These byproducts need to be removed from the product stream because, for example, the concentration of sulfur in gas engine fuels should be below 35.5 ppm [24]. A simplified process scheme of renewable (bio)fuel production processes and the formed byproducts is presented in Figure 2.

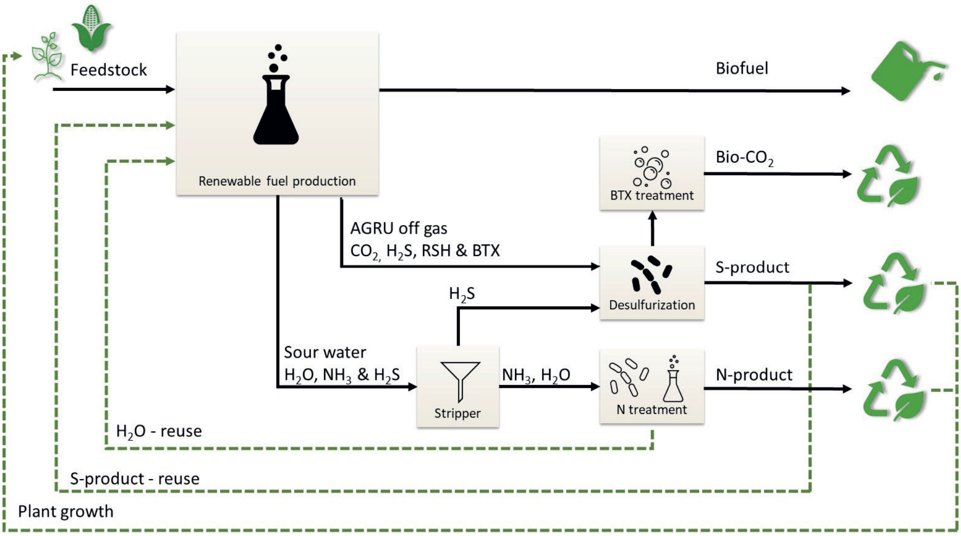

Figure 2 *Simplified process scheme of renewable (bio)fuel production processes and the by-products formed. Organic feedstock is converted to renewable (bio)fuel. In this process, sour water, containing ammonia (NH3) and hydrogen sulfide (H2S), and acid gas, containing carbon dioxide, sulfide, thiols (RSH), and aromatic hydrocarbons, such as benzene, toluene and xylene (BTX) are produced. Acid gas is obtained in the acid gas removal unit (AGRU).*

Various technologies can be used to separate the by-products from renewable fuel production, resulting in multiple liquid and gaseous waste streams. Ammonia and hydrogen sulfide can be absorbed into a caustic solution and separated from the gas stream. VOSCs and BTX are present in the gas phase together with carbon dioxide and hydrogen sulfide. High levels of ammonia, VOSCs, and BTX can also be found in traditional fossil fuel refinery processes. They are typically destructed in the Claus process, classically used to desulfurize gaseous waste streams. However, the Claus process is not suitable as a sulfur recovery unit (SRU) due to the decentralized nature of renewable fuel production and specific quantities of hydrogen sulfide produced. Therefore, different technologies need to be implemented to recover sulfur. These alternative technologies typically do not destroy contaminants such as ammonia (NH_3), VOSCs and VOCs, and the presence of such contaminants can even disrupt the efficiency of alternative desulfurization processes. Thus, there is a need to develop technologies that can prevent emission of contaminants while also recovering them in the form of a valuable resource. This circular process will further reduce the carbon footprint of the production of renewable fuels.

Examples of hydrogen sulfide, VOSCs, ammonia and BTX formed during the production of different renewable fuel products are presented in Table 1. The values provided are indicative and are strongly influenced by the feedstock [30,31], process conditions and the catalyst used. The latter influences the amount of VOSCs produced and its performance is dependent on metal-sulfur bonds [32–34]. To maintain catalytic activity, a continuous supply of hydrogen sulfide is required in the process [30,33]. As a result, hydrolyzed sulfur (e.g. hydrogen sulfide) leaves the process. As the catalyst ages, its selectivity and activity decrease, inevitably leading to a shift in the equilibrium in the hydrotreater. As a result, incomplete hydrolysis of sulfur compounds leads to the formation of VOSCs [32,33,35,36].

***Table 1** Examples of various renewable fuels and their waste stream composition.*

	H_2 %	CH_4 %	CO_2 %	CO %	H_2S ppm$_v$	VOSCs[a] ppm$_v$	BTX[b] ppm$_v$	NH_3 %	Refe
Biogas agriculture		53-57	39-43		2-1000	0.1-10	0.43	3-7ppm$_v$	[37,38]
Biogas Landfill[c]		48	47		5.8	4.8	2.25		[38]
Syngas	25-42	0-12	1-32	5-57	0.06-15300	0.15-600	20-8000	0-2	[39–43]
AGRU off gas[d]	<1	<1	40-95	<1	0.5-50	0-100	0-500	<0.01	[41]
SWS off gas[e]	<1	<1	<1	<1	30-70%		0-100	20-50	[41]
Alcohol from syngas					1.2[f]	4-18[f]	20-200[f]	<0.15[g]	[32,35,36]

[a] Including C1 to C4 thiols; [b] Benzene, toluene and xylene; [c] Landfill containing municipal waste, animal bedding and food waste; [d] AGRU: Acid Gas Removal Unit; [e] SWS: Sour Water Stripper off gas; [f] In liquid product; [g] NH4 in aqueous Fischer Tropsch product with 40 PPMV NH3 in the syngas feed.

2.3 The need for renewable fuel waste stream treatment and resource recovery

2.3.1 Ammonia

Nitrogen is an essential nutrient and forms a large fraction of organic material. Carbon:nitrogen ratios in crops can be up to 0.15 and are highly dependent on plant variety and nutrient availability [44]. When producing renewable fuels from crops and biobased waste, the available nitrogen is converted to ammonia, which is the most reduced form of nitrogen. Although ammonia is a readily available substrate and is used in many fertilizers [45,46], it also can cause issues when released into the environment. Ammonia is a corrosive, irritating gas that can lead to serious lung burns when inhaled. In addition, ammonia in the atmosphere reduces the air quality and depletes the ozone in the stratosphere [47]. On land, ammonia depositions result in the acidification and eutrophication of soils which eventually result in the loss of biodiversity [48]. Furthermore, ammonia is highly soluble in water. The disposal of large quantities of ammonia in water bodies this results in algal blooms, eutrophication, and oxygen depletion leading to fish mortality and overall loss of ecosystems [47]. Therefore, ammonia should be removed from waste streams before they are released into the environment. In addition to harming the environment, the presence of ammonia in, for example, the Fischer-Tropsch process is unwanted because it poisons catalysts that are used to upgrade syngas to longer hydrocarbon fuels [49]. While ammonia can be converted to nitrogen gas in conventional treatment technologies, a more circular process can be achieved if ammonia is recovered directly. Recovered ammonia can be used as a resource for agriculture, chemical industries or as energy carrier [50].

The recovery of ammonia from low-concentrated waste streams, for example in wastewater treatment plants, is limited. Here, ammonia is removed rather than recovered. In wastewater treatment plants, oxygen is typically used to oxidize ammonia to inert nitrogen gas [51]. This process requires a high energy input, and nitrogen fertilizers are simultaneously produced from atmospheric nitrogen gas via the energy intensive Haber-Bosch process [52]. Utilizing the ammonia rich waste stream (20-50%) directly from a renewable fuel production plant would result in tremendous energy savings and may be economically attractive for these types of waste streams. Various technologies are under development for ammonia recovery, including electrochemical treatment, stripping, zeolites, production of struvite, among others. [53]. However, implementation of these technologies remains limited [53,54]. The applicability of these technologies for this type of waste streams should be further evaluated so that ammonia can become a valuable by product rather than a costly waste stream in the renewable fuel production process.

2.3.2 Organosulfur compounds

One major underexposed challenge, arising from renewable fuel production is the formation and or presence of VOSCs. These compounds, also called thiols, are hazardous and toxic at low concentrations because they inhibit the respiratory system and are highly corrosive [55]. Apart from their toxicity, these highly volatile compounds have a foul odor and combined with their very low odor thresholds, can cause severe hindrance at low concentrations [56]. Upon combustion of (bio) fuels, VOSCs form sulfur dioxide, which contributes to the formation of acid rain and dry acid deposition [57]. Therefore, it is important that these VOSCs are removed from both product and waste streams.

Currently, fossil fuel extraction and refining are major sources of anthropogenic VOSCs [58]. Treatment technologies for VOSCs at extraction and refinery sites are optimized for processing streams from the oil and gas markets. These streams have stable process specific compositions, high volumetric flow rates and contain vast amounts of hydrogen sulfide and VOSCs. In contrast, the streams produced in renewable fuel-production facilities have more decentralized characteristics with a fluctuating VOSCs content. The available technologies for the large-scale oil and gas industries may not be suitable to treat the VOSCs containing waste streams from the renewable fuel production process because of the fluctuating VOSC content and lower loading rates. Typically, low loads of VOSCs (200 kg S/>d) are removed by sorption processes which produce large amounts of toxic waste and have limited options for sulfur recovery. Additionally, the composition of the waste streams are different and conventional technologies are not able to achieve sufficient removal in renewable fuel production plants and meet the desired product specifications in the final fuel product. Currently, no technology is available to accommodate the removal and conversion of VOSCs in view of the Net Zero goals.

Besides removal and conversion of VOSCs, sulfur recovery will become increasingly important in the Net Zero energy economy[59]. The current sulfur market is dominated by sulfur production from fossil fuels. For example, 93% of the total elemental sulfur produced in the USA in 2019 came from fossil fuels [60]. The majority of the elemental sulfur produced worldwide is used for the production of sulfuric acid to extract phosphate ores [61].The obtained phosphate and elemental sulfur are both essential in agricultural activities. Therefore, to secure food production in the future, recovery of elemental sulfur and phosphate will be crucial in a Net Zero energy economy.

2.3.3 BTX

BTX are present in natural gas and crude oil, additional BTX are formed during the refinery process. In renewable fuel production processes, the high temperature conversion of biomass also results in the formation of BTX [62,63]. In the chemical industry, these compounds are often used as solvents in, for example, paint, thinners, cosmetics, and pharmaceuticals [64]. Even though they are frequently used in the chemical industry, they are toxic compounds that act as carcinogens or neurotoxins in humans and are harmful to aquatic life [64,65]. Although, these compounds are biodegradable, they are persistent in the environment [65,66]. Therefore, stringent emission limits are implemented in many countries and the presence of these compounds is strictly monitored in drinking water with limits as low as 0.5 ppb[67,68]. To prevent environmental damage caused by these undesired by products, emissions should be avoided, and BTX should be captured and detoxified in an efficient manner.

There are various technologies to treat BTX compounds, including filtration and adsorption to activated carbon and zeolites, combustion, condensation, or various forms of bioremediation [64,69]. Chemical treatment methods require high capital investment along with high operational and maintenance costs while achieving limited removal efficiencies [64,70]. Waste streams containing BTX from traditional fossil fuel plants are typically combusted in the Claus process [71]. However, this requires the additional input of fuels. In-situ bioremediation of polluted environments, in which BTX compounds are converted to carbon dioxide, methane and water, is preferred over ex-situ treatment due to the lower costs and higher efficiencies [69]. Additionally, bioremediation produces useful by products such as methane and carbon dioxide. Methane produced during the bioremediation process can be used as an energy carrier, whereas the obtained carbon dioxide can be utilized in carbon capture or power to gas applications producing more renewable fuel. However, these remediation technologies are relatively slow anaerobic processes focused on low concentration sites e.g. contaminated aquifers with concentrations ranging from 2 µg/L to 25 mg/L [65,72]. In comparison, in renewable fuel production processes gaseous waste BTX can be concentrated up to 500 ppm_v [41]. Therefore, increased removal rates are desired to treat renewable fuel waste streams. Aerobic biodegradation requires vast amounts of oxygen, [73] but could be further explored for the remediation of the highly concentrated waste streams obtained in renewable fuel production.

2.4 Concluding remarks

The production of biobased chemicals and energy-dense energy carriers, such as biodiesel and ethanol will be an important step in the transition toward a Net Zero energy economy. However, production of these renewable fuels will be accompanied by the production of hazardous and potentially toxic waste streams, such as VOSCs, BTX and ammonia if left untreated. These waste streams contain valuable molecules and can be utilized in a biobased Net Zero energy economy, with the aim of closing not only carbon, but nutrient (nitrogen and sulfur) cycles. To achieve this valorization of waste streams by nutrient recovery and reuse, new technologies need to be developed and implemented.

Production technologies for renewable fuels are under constant development. Waste production depends on the biomass source and production technology. The renewable fuel market is expanding and developing rapidly, and the final contribution of each process based on size, technology and feed stock composition is hard to predict. Increased production efficiencies may result in lower VOSCs formation from the catalyst and less losses of valuable organic compounds in the form of BTX. The composition of the produced waste streams may also change once the renewable fuel production process is improved. However, sulfur and nitrogen are present in most organic feed stocks and need to be removed from the product to avoid the formation of nitric oxide, nitrogen dioxide and sulfur dioxide formation upon combustion.

If the waste streams produced during renewable fuel production are left untreated, valuable resources will go to waste. More importantly, when attempting to solve the global carbon emission crisis, we should avoid the creation of the next environmental problem of pollution and waste production. Environmental and economic impacts of different pollutant removal and resource recovery technology need to be considered. Therefore, an integral approach, acknowledging all aspects of the renewable fuel production process in the transition from fossil to renewable fuel, is of utmost importance.

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Chapter 3

Current and future anthropogenic organosulfur emissions and available treatment technologies

Abstract

Currently, the major sources of anthropogenic volatile organosulfur compounds (VOSCs) originate from fossil fuel extraction and refinery sites. With the transition towards a carbon-neutral energy market, the prospects for VOSC production, removal and sulfur recovery will change. Upcoming technologies to produce and store renewable energy carriers will result in new decentralized VOSC production sites, such as the renewable fuel industry and gas storage in former gas wells. The shift to decentralized VOSC production is accompanied by new challenges to remove and convert organosulfur compounds to reusable forms of sulfur. Meanwhile, current challenges in the abatement of organosulfur compound emissions are yet to be resolved. In addition, the shift towards carbon-neutral energy sources will disrupt the conventional global sulfur market. The recovery of elemental sulfur from fossil fuel refineries will decline. In the near future, the sulfur demand will become higher than its supply and sulfur will become a scarce resource. Thus, sulfur recovery from VOSCs produced in a carbon-neutral energy market will gain more attention. This paper explores the different sources of VOSCs in the current and future energy market, the available treatment and recovery technologies, and their compatibility with anticipated VOSCs containing streams. We show that current VOSC treating technologies are optimized for the conventional oil and gas market and are not suitable as a treatment technology due to either the composition or quantities in these new waste streams. Thus, a technological gap is arising, which should be resolved by innovations focusing on maturing conventional technology for the new waste streams or developing new tailor-made technologies.

3.1 Introduction

Volatile organosulfur compounds (VOSCs) are a product of the (incomplete) degradation of organic substrates under anaerobic conditions and occur in, for example, the deep sea, swamps, and soils. Lightweight VOSCs, including methanethiol, ethanethiol, and propanethiol, are hazardous compounds, with a high toxicity and nauseating smell at ppb level [1]. Therefore their emission into the environment should be minimized. The global natural flux of methanethiol was estimated at 6473 Gg-S/year ($6.47 \cdot 10^9$ kg-S/year) in 2016 [2]. However, anthropogenic activities substantially contribute to the worldwide flux of VOSC emissions, with estimated methanethiol emissions accounting for an additional 2119 Gg-S/year. Major contributors are the pulp and paper industry (1680 Gg-S/year), rayon and cellulose production (51.4 Gg-S/year), manure (330 Gg-S/year), and wastewater (51 Gg-S/year) [2]. When economies and thus industries continue to grow, anthropogenic emissions may further increase. Enhanced pollution control is therefore required to maintain, or preferably reduce, emissions of VOSCs. The annual VOSC emission estimates that are reported here do not include the production of organosulfur from fossil fuel extraction sites and refineries, even though VOSCs can be present at high concentrations in this industry.

For example, natural gas, enclosed in gas pockets below the surface of the earth, can contain up to 70% of sulfur compounds [3]. Upon extraction of this gas, VOSCs are released. The gas requires treatment because of the present VOSCs, their toxicity, and their potential to form sulfur dioxide upon combustion. This process can lead to the formation of acid rain and dry acid deposition and damages the environment [4]. Currently, the world economy heavily depends on fossil fuels. They, for example, provided over 82% of the global energy demand and 93% of the global sulfur supply in 2019 [5,6]. To address global warming, the Paris Agreement was signed in 2015, aiming to reduce the global emission of greenhouse gasses [7]. Since then, the implementation of new strategies and incentives to decrease fossil fuel dependency has intensified [8,9].

These incentives have contributed to the increased production of renewable energy. For example, between 2000 and 2019, there was almost a 60% increase in renewable energy generation [10]. Despite this growth, the share of renewable energy in the total global energy demand only increased by 1.3%. This can be attributed to the increasing global energy demand [10]. Stated policy scenario studies (considering the adopted policies and measures) of the International Energy Agency show that fossil fuels will not be phased out before 2050. In fact, the use of coal will likely decrease by almost one-third compared to 2020, while crude oil consumption remains stable, and natural gas will likely increase with nearly 50% over the same period [11]. Biofuel is considered a low-carbon fuel, and its production will likely increase as well. Biofuel accounted for 9.4 % of the world's energy supply in 2019, and its production is predicted to increase from 3.7 EJ to 4.6 EJ by 2024 ($1.02 \cdot 10^{12}$ - $1.28 \cdot 10^{12}$ kWh) [10,12]. The production of renewable fuels, including biofuels, is accompanied by the production of waste streams containing VOSCs [13]. The declined demand for fossil fuel in the long run and the increased production of renewable fuel will result in changes in the VOSC removal technology requirements. The characteristics of these new waste streams, originating from renewable fuel production processes, and the compatibility of existing VOSC treating technologies optimized for the conventional oil and gas market are unknown. Furthermore, recovering valuable nutrients such as sulfur will become increasingly important in future markets. In this paper, we identify the current technological challenges for removing VOSCs in existing streams and the anticipated challenges and requirements for future VOSC-containing streams originating from renewable fuel production. We provide an overview of the currently available technologies and evaluate their suitability for the current and future industries with respect to the process principle, technological application, circularity, and scale.

3.2 Importance of sulfur recovery

Since the turn of the century, the primary source of elemental sulfur has been a byproduct of the fossil fuel industry, mainly from petroleum refineries and natural gas processing plants. Up to 93% of the total elemental sulfur production in the USA in 2019 originated from fossil fuels [6]. The top five countries producing elemental sulfur are China, the United States, Russia, Saudi Arabia, and the United Arab Emirates. Together, these countries account for over 50% of worldwide sulfur production [6]. In the past, elemental sulfur was obtained from different sources (Figure 1). A large fraction of sulfur was mined by the Frasch process, a method to extract sulfur from underground sulfur deposits [14]. Frasch mining became less popular due to new SO_2 emission legislation since it requires desulfurizing fossil fuels, like crude oil and natural gas, before their use. Since sulfur is a byproduct of this industry, Frasch mining became unprofitable [14].

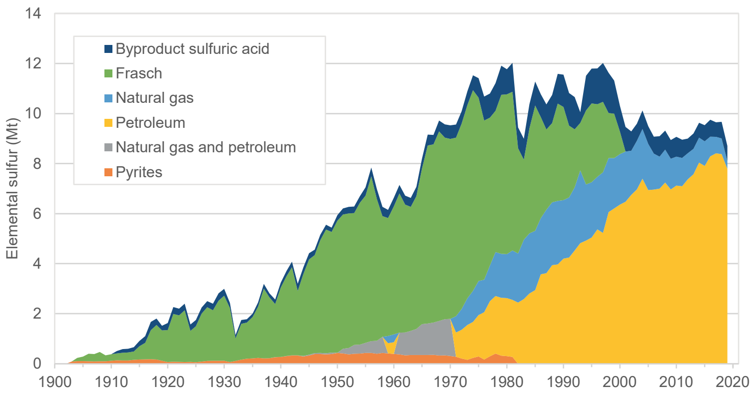
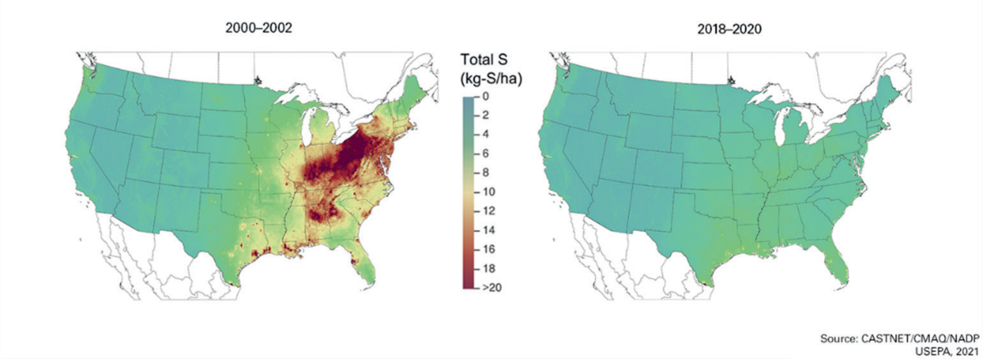


Figure 1 *U.S. sulfur production by source 1900-2019 (adapted with permission from U.S. Geological Survey) [15].*

Elemental sulfur has many uses. The production of sulfuric acid dominates the worldwide consumption of elemental sulfur [16]. Sulfuric acid is mainly used for the extraction of phosphate from ores for fertilizer production. However, it is also used in many other industrial processes, such as metal mining or the production of soaps, surfactants, and fabrics [17]. In a carbon-neutral energy market, substantially less elemental sulfur will be available from fossil fuel sources [14]. The sulfur demand is expected to rise with the growing world population and intensified industrial processes [14]. Furthermore, due to the implementation of effective sulfur recovery technologies since the 1980s, sulfur deposition of sulfur dioxide has significantly lowered (Figure 2). Subsequently, less sulfur is available for crop growth in the soil. Together with intensified agriculture worldwide, a sulfur shortage is now reported for agricultural crops in several regions of the world, such as India, Poland, and the Netherlands [18–21]. Figure 2 clearly demonstrates the difference in sulfur deposition between 2000-2002 and 2018-2020 in the United States.



Source: CASTNET/CMAQ/NADP
USEPA, 2021

Figure 2 *Three-year average total sulfur deposition in U.S. in 2000-2002 and 2018-2020 [22]. Worldwide sulfur shortage in agriculture occurs because of this decreased sulfur deposition and intensified agricultural land use.*

Plants are strongly dependent on sulfur. A sulfur shortage is problematic for plant growth as this element is one of the six macronutrients, next to phosphorus (P), nitrogen (N), potassium (K), magnesium (Mg), and calcium (Ca) [23–25]. Sulfur plays a vital role in crop growth and development. Sulfur is, for example, essential to form proteins, vitamins, chloroplasts, ATP, and co-factors [23–25]. The sulfur requirements strongly vary for different crops. Lettuce, for instance, requires 10-12 kg S per hectare per annum, potato 15-20 kg S per hectare per annum, and cabbage as high as 110 kg S per hectare per annum [26].

In a carbon-neutral energy market, substantially less elemental sulfur will be produced as a byproduct from fossil fuels as mining will decline [14]. Therefore, if alternative sources of elemental sulfur are not explored, an alarming fertilizer shortage will be twofold: as sulfuric acid to mine phosphatic fertilizers and as sulfur fertilizer. Hence, alternative sources of elemental sulfur are essential to ensure the future supply in a biobased economy. Thus, the recovery of sulfur will become increasingly important.

3.3 Current sources of anthropogenic VOSCs

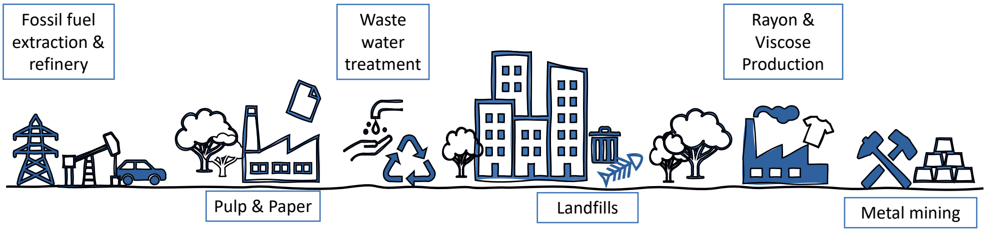


Figure 3 *Examples of current anthropogenic VOSCs sources including fossil fuel extraction and refinery, Landfills, wastewater treatment, pulp and paper production, rayon and viscose production, and the mining industry.*

Figure 3 provides a graphical overview of the industrial sources currently producing VOSCs. Examples of VOSC concentrations encountered at industrial processes are provided in Table 1. The production process and anticipated developments in these VOSC-emitting industries are described in the following sections.

***Table 1** Reported values of sulfur compounds present in current industrial processes that contain VOSCs.*

Source	**H_2S ppm$_V$-S**	**VOSCs[a] ppm$_v$-S**	**References**
Sour natural gas (SNG)	1300-15000	17-177	[28,29]
SNG condensate	90	290	[27]
Flare gas/amine acid gas		0-20000	[28]
Sewer	4	6[b]	[29]
Pulp and paper industry		100	[30]
Wastewater treatment		47[b]	[31]
Landfill off gas	0-5143	0-7.2	[32–35]
Rayon/viscose	0.1-23.7	0.4-5.5[c]	[36]
Metal mining industry	30-40	0-400	[28]

[a] Thiols (C_1-C_4); [b] value in ppb measured in the aqueous phase; [c] value in ppb, measured in the surrounding atmosphere of a rayon production facility.

3.3.1 Fossil fuel extraction and refinery

VOSCs are naturally present in natural gas and crude oil. Additional VOSCs are produced during the refinery process of crude oil. Adsorption and concentration with, e.g., amine treatment is typically applied to capture and concentrate VOSCs in gas streams. Below, we describe the current status and the foreseen changes in the production of these VOSC containing streams.

3.3.1.1 Natural gas

Scenario studies show large variations in the predicted global natural gas demand by 2050, ranging from 36 EJ to 190 EJ per year [37]. This demand is highly influenced by the scenario in play. For example, in the stated policy scenario of the IEA, the natural gas demand increases. In contrast, in the intergovernmental panel on climate change (IPCC) IP1 scenario (low energy use and a global temperature rise <1.5°C), the natural gas demand reduces by three-quarters compared to the demand in 2020 [37]. In each scenario, natural gas is considered an important transition fuel to reach climate goals and limit global warming to 1.5 or 2 degrees. Therefore, natural gas extraction will likely continue in the foreseeable future.

Currently, the "less sour" gas reservoirs, i.e., with lower sulfur content, are being exploited as they require less post-treatment of the gas. Once depleted, more "sour reservoirs" will be used to mine natural gas. These raw gas streams contain more acidic compounds, such as carbon dioxide, hydrogen sulfide, and VOSCs, and treatment costs will increase. The sulfur content in natural gas reservoirs can be up to 70%, while currently exploited reservoirs contain a sulfur content of around 0-5% [3,38]. Most of the present sulfur in natural gas is hydrogen sulfide, followed by methanethiol, ethanethiol, and propanethiol [39]. Concentrations of VOSCs vary significantly at different sites. Nevertheless, more acidic wells with a higher sulfur content will likely be opened for natural gas extraction in the near future.

3.3.1.2 Crude oil refineries

The use of crude oil remains similar until 2040 in stated policy scenarios, while a drastic reduction >50% of crude oil utilization is required in most scenarios to limit global warming [37]. The sulfur content in crude oil typically ranges from 0.1 to 6.0% wt. and consists, amongst others, of inorganic hydrogen sulfide, polysulfides, elemental sulfur, sulfate, sulfones, sulfoxides, VOSCs, and thiophenes [40–43]. The fraction of thiols in crude oils strongly varies and is oil field-specific; for example, almost no thiols are found in some west Siberian fields, while thiols form the main sulfur compound in the Markovo field in east Siberia [44]. At crude oil extraction sites, associated gas is trapped in the wellhead and in the oil itself. This associated gas is released at atmospheric pressure and contains volatile hydrocarbons like methane, ethane, and VOSCs. This gas can be sold as natural gas or used at site for power generation[45,46].

The levels of VOSCs in crude oil are generally low. However, they can cause severe corrosion, produce odor nuisance, and affect the product quality [40]. Processing of crude oil creates additional VOSCs. Various cracking strategies, including hydro cracking, thermal cracking, delayed chocking, and fluid catalytic cracking (FCC) are used to increase the yield of lighter hydrocarbon fractions (e.g., naphtha, diesel or kerosine) of crude oil and decrease the sulfur content in the aqueous products. The fraction and composition of thiols formed during the cracking process depend largely on the applied process and the amount and type of sulfur compounds present in the crude oil [40].

The removal of sulfur from crude oil is an important purification step and occurs partially during the distillation process. The distillation products with the highest boiling points contain a higher sulfur content [40]. The largest fraction of unbranched thiols can be found in the gaseous hydrocarbon fraction and requires adequate treatment.

3.3.1.3 Flare gas and amine acid gas

Amines are used in most natural gas and crude oil refineries to separate carbon dioxide and sulfur compounds from hydrocarbon gas streams [47]. During the amine regeneration process, carbon dioxide, thiols, and hydrogen sulfide are released, forming a concentrated acid gas stream. A Claus unit can process this stream. However, the Claus process is efficient when the hydrogen sulfide content is above 30%. Furthermore, the quantity of sulfur influences the cost-effectiveness of the process. Additional technologies, such as an amine unit, can be installed to create a more favorable feed for the Claus unit [47–49]. However, this requires a higher OPEX and CAPEX. In these cases, alternative technologies can be more favorable. When no suitable technology is available flaring may occur. This flaring requires the addition of valuable methane gas and increases carbon dioxide emissions. Furthermore, during the combustion of sulfur compounds, sulfur dioxide is formed, which contributes to acid rain and dry acid deposition [4].

3.3.2 Pulp and Paper industry

The pulp and paper industry is marked as the sixth largest polluting industry and discharges large amounts of untreated waste [50,51]. In fact, excluding fossil fuel production and refineries, nearly 80% of the annual anthropogenic methanethiol and ethanethiol emissions originate from the pulp and paper industry (1680 gG S) [2]. Even in an increasingly digitalized world, paper production continues to increase due to the growing world population and increasing living standards in developing countries [52].

To produce new paper, raw wood chips are cooked in a sodium hydroxide and sodium sulfide solution to break the lignin, hemicellulose, and cellulose bonds and produce a wood pulp. An important side reaction occurring during this cooking process is the production of VOSCs, which can be up to 2 to 3 % of the sulfur in the cooking liquor [53,54]. While paper can be recycled, adding fresh fibers is required to maintain structural integrity. Therefore, the production of new and recycled paper will contribute to the formation of new VOSCs [55].

3.3.3 Wastewater treatment plants

About 56% of the globally produced household wastewater was treated in 2020 [56]. Discharging untreated water into the environment poses various risks, e.g., disease outbreaks, eutrophication of natural water bodies resulting in biodiversity loss, and the risk of introducing toxic chemicals into the environment [57]. Therefore, clean water and sanitation are indicated as one of the sustainable development goals by the United Nations, and efforts are made to increase the fraction of treated wastewater [58].

VOSCs and hydrogen sulfide can be produced during the collection and treatment of wastewater. The anaerobic conditions in sewer systems and the presence of organic matter can yield these products. Furthermore, wastewater treatment plants treating substantial amounts of organic matter, either obtained from industry or households, often contain an anaerobic conversion step in which organic matter is converted to valuable biogas, and VOSCs can be produced as undesired byproduct [32,57].

3.3.4 Landfills

Landfills contain various waste materials, e.g., food waste, glass, metals, paper, and plastics [59]. Because of the anaerobic degradation of organic matter, landfill off-gas is formed, primarily composed of methane and carbon dioxide. The sulfur present in the organic matter is converted into predominantly hydrogen sulfide and VOSCs. The levels of VOSCs in the off-gas strongly dependents on the waste stored in the landfills [32–35,60]. The global population continues to grow, which leads to an increase in waste generation and landfills. Implementing waste separation and reuse systems may reduce waste sent to landfills [59]. Over the past decades, there has been an increasing interest in recovering methane in landfill off-gas, which can be utilized for energy generation [61–63]. However, adequate implementation of these systems and remediation of existing landfills in the near future seems unlikely while suitable treatment of the landfill off-gas remains necessary to limit greenhouse gas and VOSC emissions.

3.3.5 Rajon and viscose production

Rajon or viscose forms an important resource in the textile industry. The fibers are produced from cellulose obtained from plant material, e.g., wood or bamboo [64]. Like the pulp and paper industry, this cellulose-rich material is treated chemically to break down the fibers. The cellulose-rich pulp is treated with sodium hydroxide, carbon disulfide, and sulfuric acid [64,65]. During these chemical processing steps, VOSCs are formed and released during the fiber spinning process [36]. When no treatment technology is implemented, 100 to 300 kg of sulfur is lost into the atmosphere per ton of viscose produced [53,66].

3.3.6 Metal mining

In the mining industry, sulfuric acid is used to leach valuable metals from the metal ores [67,68]. During this process, sulfuric acid reacts with the organic matter present in the raw material, and VOSCs are formed. The waste streams from this industry can contain high hydrogen sulfide and VOSC concentrations. The financial and environmental benefits of metal recycling are nowadays considered, and metal reuse is widely implemented [28]. However, a circular metal economy is still a long way to go, and fresh metal ores will continuously be extracted, producing new VOSCs.

3.4 New sources of VOSCs in a carbon-neutral economy

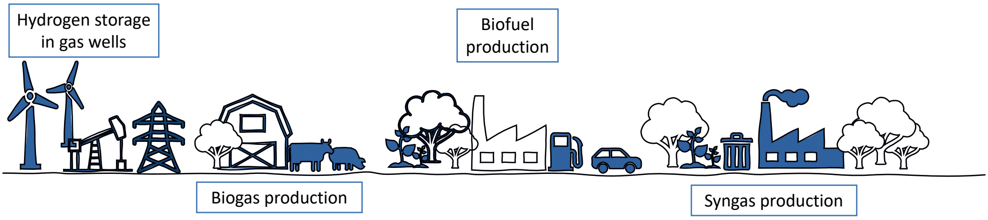


Figure 4 *New sources of VOSCs in a carbon-neutral economy, including hydrogen storage in gas wells, biogas, biofuel, and syngas production.*

Society is transitioning from fossil fuels to renewable energy sources [8,9]. Therefore, VOSC emissions originating from fossil fuels are expected to decline. Within a low carbon economy, however, new sources of VOSCs will arise (See Figure 4). The presence or formation of VOSCs is expected in renewable energy carriers, including hydrogen, biogas, syngas, and alcohol and biodiesel. Examples of VOSC containing product and waste streams that will expand in the future are presented in Table 2 and are discussed in the sections below.

Table 2 *Examples arising thiol-containing product and waste streams and their composition [13].*

Source	H_2S ppm$_V$-S	VOSCs^a ppm$_v$	references
Biogas agriculture	7-6570	0.1-10	[32]
Biogas industrial, food, and municipal waste	2-3174	0-7	[32]
Syngas	0.06-15300	0.15-600^c	[62,63]
Alcohol from syngas	1.2 ppm$_w$	4-63 ppm$_w$	[69–71]

^{a} Thiols (C_1-C_4); ^{b} including thiols, carbonyl sulfide, and carbon disulfide; ^{c} thiols unspecified.

3.4.1 Storage and distribution of hydrogen gas

Solar and wind energy have grown substantially in the past decades, and their contribution to the global energy market is expected to increase [11,72,73]. These renewable power sources have a variable power generation for which long-term storage solutions are required to ensure stable energy availability [73,74]. Smart grid and battery solutions partially mitigate variable energy generation but cannot counteract inter-sessional changes in energy supply [75]. Hydrogen is marked as one of the most promising solutions for long-term energy storage [74,76,77] and can be produced by electrolysis of water with an energy conversion efficiency between 60 and 80% [75,78,79]

Hydrogen has many potential uses. For example, the produced hydrogen can be utilized in the transportation sector and is indicated as a promising carbon-neutral fuel for sustainable aviation [80,81]. Furthermore, hydrogen plays an important role in producing “green” steel and fertilizers[82–85]. In addition, hydrogen can be a chemical building block for biobased compounds like methane and more complex organic compounds like alcohols, carboxylic acids, etc. [76]. Another scenario for hydrogen utilization as an energy carrier is the injection into the natural/biogas grid. Hydrogen additions up to 20% can be added while utilizing the existing infrastructure [75,86]. Reforming the natural gas grid to a hydrogen gas grid is considered a long-term carbon low-energy solution but requires severe investments in the existing infrastructure [87,88].

The storage of hydrogen in underground reservoirs, such as former oil and gas wells, has been proposed as a solution to deal with inter-sessional production variations [89,90]. Recent studies suggest that hydrogen storage can be combined with the storage of carbon dioxide, creating conditions in which bio-methanation can occur. Whether this can substantially contribute to biomethane production needs further evaluation [91–93]. However, individual storage of hydrogen or methane storage will also inevitably lead to contamination of these gasses with VOSCs still present in these former wells. The level of VOSCs will highly depend on the concentrations of VOSCs still present in the former wells and the residence time of hydrogen gas inside the well. Other contaminants that can be found upon extraction of hydrogen gas from these fields include methane, carbon dioxide, carbonyl sulfide, carbon disulfide, and aromatic hydrocarbons. Depending on the future application of the hydrogen, these carbon compounds may also need to be removed, e.g., hydrogen fuel engines require a purity of 99.97% according to the ISO standard [94]. Small quantities of hydrogen sulfide negatively affect fuel cell performance [95].

3.4.2 Biogas production

Methane is proposed as an important energy transition fuel. The substitution of natural gas for biomethane will reduce the emission of nonrenewable carbon dioxide [37]. This biomethane is already produced from various organic waste streams, i.e., manure, municipal waste, municipal wastewater, food waste, and agricultural waste [32]. The composition of the obtained biogas is strongly influenced by the oxidation state of the organic material fed to the digester [32,96]. The substrate composition and sulfur content largely influence the hydrogen sulfide and thiol concentrations in the biogas [32,35,96]. Biogas obtained from raw manure generally has a higher sulfur content in the form of hydrogen disulfide and thiols than co-digestors that convert various types of food or municipal wastes, possibly together with manure [32]. Model studies, based on stated policies, demonstrate that the production of biogas will double between 2020 and 2030 [97].

Alternative routes for methane production include (bio)methanation of syngas [98] and power-to-gas technologies [99,100]. The high pressure applied in the methanation of syngas and some power to methane processes may result in the formation of thiols when sulfur compounds are present in the gas streams or on the catalyst. Bio-methanation of syngas or carbon dioxide can occur at ambient temperatures [98,101] and likely yields fewer VOSCs compared to the chemical process that operates at high temperatures and pressures. Biogas must be upgraded to biomethane before it can be supplied to the natural gas grids. European standards dictate a methane concentration above 95% before injection into the natural gas grid [102]. Furthermore, within the European Union, sulfur needs to be removed from biomethane to hydrogen sulfide concentration below 5 mg/m^3 and a thiol concentration below 5-10 mg/m^3 [102].

3.4.3 Syngas production

Synthetic gas, syngas, consists mainly of hydrogen and carbon monoxide. Historically, syngas is produced by gasifying fossil fuels like coal or methane to produce ammonia using the Haber Bosch process [103]. The produced ammonia is sold as fertilizer or a resource for the chemical industry. However, over the past decades, syngas has gained attention as a potential alternative energy carrier and chemical building block and is nowadays also used to produce renewable fuels. Syngas can be produced from a broad range of organic materials and is regarded as carbon neutral when it is produced from short rotation crops (i.e., <3 years) or wood obtained from sustainable forestry [76,103]. Municipal and industrial waste streams can also be suitable for syngas production [103]. Due to the increased demand for renewable fuels, syngas production from renewable biomass and organic waste will likely increase. The energy density per kg of syngas is half as much as natural gas [104,105]. Therefore, syngas is often upgraded to a more energy-dense fuel like methanol, biodiesel, kerosene, or naphtha with the Fischer-Tropsch process [103]. Alternatively, syngas can be upgraded to biomethane by anaerobic fermentation processes [106].

During the gasification of organic matter (syngas production) under high pressure and temperatures, byproducts, including organosulfur compounds, are formed. The production of these organosulfur compounds is influenced by the type of feedstock [107]. Sulfur concentrations in syngas may be up to 2% [107,108]. However, these levels should be below 35.5 ppm to produce gas engine fuel. Concentrations below 71 ppb are required for the Fisher Tropsch process or methanol synthesis [103]. The desulfurization of syngas produced from coal gasification is traditionally performed with the Claus process [103]. However, the transition from coal gasification to biomass gasification faces challenges. Organosulfur flows in traditional coal and methane gasification installations are constant and high. In contrast, the variation in organosulfur production rates and flows on the municipal waste scale level might render the Claus process not applicable.

3.4.4 Biofuel production

Biofuel refineries produce methane, ethane, alcohols, diesel, kerosene, naphtha, and other hydrocarbon-based molecules from organic matter [109]. The production of these biofuels has increased over the past decades [10,110,111]. First-generation biofuels, originating from, e.g., vegetable oils, compete directly with the food industry and raise political, ethical, and environmental concerns [76]. Second-generation biofuels are produced from waste streams or non-food crops, including woody materials, plant residues, algae, seaweed, and organic wastes. The use of these sources of renewable fuel production has a more sustainable image [76].

There are several methods to produce biofuels. For example, hydrotreated vegetable oil (HVO) can produce biodiesel and kerosene [112,113]. This process requires a catalyst and operates under high temperatures and pressures. Sulfide catalysts are commonly used in this process. However, sulfur leaching from these catalysts causes deactivation of the catalyst, and hydrogen sulfide or other sulfur compounds are added to maintain catalytic activity. Meanwhile, sulfur leaching from the catalysts and the reactions between added sulfide and organic matter produce VOSCs [114].

Alternatively, the gasification of organic matter to syngas can be followed by the Fischer Tropsch process to form the desired liquid hydrocarbons. The Fischer Tropsch process uses elevated temperatures (200-300 degrees Celsius) and pressures (10 to 40 bar) in the presence of metal catalysts [115]. The metal catalysts for biodiesel production are generally iron or cobalt based and yield a hydrocarbon product in the range of 10 to 20 carbon atoms. These catalysts are sensitive to sulfur poising, and VOSCs are formed as undesired byproduct. Therefore, it is important to remove the sulfur in the feed gas beforehand.

To produce alcohols from syngas, alkali promoted molybdenum disulfide (MoS_2) catalysts are used. These catalysts have a high selectivity for short chain alcohols (C1-C5) [71]. During the Fischer Tropsch process, sulfide is lost from the catalyst, and additional hydrogen sulfide is added to maintain catalytic activity and promote hydrocarbon chain growth. Meanwhile, excess sulfur in the feed gas limits the selectivity towards alcohols [70,71]. The sulfur compounds, originating from the catalyst, feed gas, or added substrate, yield undesired VOSCs as byproduct [69]. Levels as high as 67 ppm-S were found in the condensate of a Fischer Tropsch product stream when no sulfur compounds were present in the feed gas. The formed products included methanethiol (13.8 ppm-S), ethanethiol (10.6 ppm-S), and other sulfur products as dimethyl sulfide (21.3 ppm-S) and ethyl methyl sulfide (12.2 ppm-S) [71].

3.5 Applicability of available removal and recovery strategies

Various thiol treatment strategies have been developed over the past decades in industrial applications. Each of these technologies are optimized for a specific niche market. Table 3 provides an overview of established technologies. The application of most processes is either based on the removal or conversion of thiols. Some technologies can be operated as stand-alone technology, achieving both removal and conversion. Each technology is associated with its own environmental impact, varying sulfur recovery efficiencies, specific (de)toxification levels, use of scarce materials, and production of varying levels of (toxic) waste streams. The major established technologies will be discussed in the following sections with regard to four main criteria: 1 process principle, 2 technological application, 3 circularity, and 4 scale.

3.5.1 Process principle and product formation

This section describxes the different removal and conversion technologies for thiol treatment. Commonly applied processes for removing thiols from product streams include combustion, adsorption, oxidation, and separation techniques. The different principles result in various sulfur products and waste streams. For example, the combustion of thiols in a Claus unit yields predominantly elemental sulfur that can be reused, whereas combustion in a flare results in the formation of sulfur dioxide [4].

Adsorption and absorption processes can be applied to remove thiols from the product stream. Liquid scavengers can be added to a gas pipeline to remove traces of VOSCs and form a solid VOSC-scavenger complex that can be removed from the liquid phase. However, these scavengers are non-regenerative and form relatively large toxic waste[122]. Alternatively, solid materials, including iron oxide scavengers and activated carbon, can also adsorb VOSCs. These solid materials can be impregnated with caustic solutions to increase the removal of sulfur compounds from the feed streams [140]. Iron sponge scavengers can be regenerated by air, forming a highly concentrated off-gas that is often combusted. However, this reaction is highly exothermic and can result in self-ignition of the scavenger bed. The filter bed should be impregnated with a caustic solution, and the temperature should remain below 43 °C [141]. Due to the associated risks, regeneration is rarely applied, and these scavengers, therefore, produce large amounts of toxic solid wastes [122]. Thermal regeneration of activated carbon occurs at high temperatures (<400 °C) and results in a concentrated thiol gas stream [120,121]. The regenerability of these activated carbon beds is limited, and they are replaced frequently.

Table 3: *Overview of applied technologies for the removal, conversion, and recovery of thiols.*

	Process principle				Technological application								Circularity				Scale				References
	Combustion	Absorption/Adsorption	Oxidation/reduction	Separation	Bulk removal of thiols	Deep removal of thiols	Bulk conversion thiols	Deep conversion of thiols	None-specific for thiols	Binding RSH to detoxify	liquid treatment	gas treatment	Sulfur recovered for reuse	Limited/zero toxic waste	no waste production	No consumption scarce resources	Minor (<1 kg/d)	Small (1- 200 kg-VOSC-S/ day)	Medium (200 - 500 k-VOSC-S /	large (> 500 kg VOSC-S / day)	
Chemical processes																					
Claus	x				x		x		x			x	x	x		x				x	[116,117]
Flare	x							x	x			x						x	x	x	[4]
Caustic Washing		x			x	x			x									x			[44,118,119]
Activated carbon		x			x	x			x	x				x				x			[120–122]
Thiolex			x			x	x				x								x		[122,123]
MEROX/Merichem /Sulfex / Mericat			x			x	x				x								x		[122,123]
Demerus NG			x			x	x				x								x		[124,125]
Wet air oxidation			x				x		x		x			x					x		[126,127]
Advanced oxidation H_2O_2			x				x		x		x			x			x	x			[128–130]
Deep well injection														x	x	x			x		[131]
Dew pointing				x					x									x	x	x	[122]
Amine treatment		x			x	x			x										x	x	[47,132]
Zeolites/ mole sieves		x			x				x	x								x	x		[122,133]
Scavengers		x				x			x	x							x	x			[120–122]
Biological processes																					
Biofiltration			x		x	x		x	x		x	x		x		x	x				[134–137]
Biotrickling filter			x		x	x		x	x		x	x		x		x	x				[138,139]

Caustic solutions can be applied as liquid absorbents due to the slight acidity of VOSCs [44]. These solutions can absorb thiols from gas and oily phases. This process produces a highly alkaline concentrated thiol solution with concentrations up to 10 wt.% [44,118,119]. The spent caustics are considered waste products. Typically, they are injected into the deep subsurface, where they cannot migrate to potable water aquifers. However, there are concerns about the long-term chemical and biological processes that may occur as well as the risk of leakage from the wells to the surrounding environment [131,142]. Using this principle renders thiols untreated, but it prevents the emission of thiols into the atmosphere.

The oxidation of thiols to their disulfides forms an alternative strategy to treat spent caustics. The hydrophobic disulfides form an oily layer on top of the aqueous phase and can then be separated for further treatment. Chemical catalysts combined with the introduction of oxygen or strong oxidants like peroxides are used for the oxidation process [123,126,143]. When other co-pollutants like hydrogen sulfide are present, sulfate and thiosulfate are formed as a byproduct. The Thiolex and Mericat technologies use a fiber film contactor to adsorb the thiols from the gas phase into the liquid phase. These fiber film contactors consist of cylinders that are packed with metal fibers that function as catalysts aiding the oxidation of thiols to disulfides [123].

Advanced oxidation processes, like the Fenton process [130], only proceed rapidly in the liquid phase. However, these oxidation processes are often incomplete and yield mainly thiosulfate when oxidizing hydrogen sulfide. Oxidation of VOSCs with ozone yields, amongst others, sulfonic acids, sulfones, and sulfonic anhydrides [128–130]. Wet air oxidation requires high temperatures and pressures (more than 320 °C and at pressures between 10 and 210 bar) yielding elemental sulfur as the final product and has high investment and operational costs [126,127].

Amines, molecular sieves, e.g., synthetic zeolites or AlO4 SeO4 can selectively separate thiols from product streams [122,133]. These techniques contain chemicals that can specifically target thiols or other sulfur compounds. The spent material can be regenerated in a second stage, which produces a concentrated stream of thiols that requires further treatment. An alternative strategy to separate thiols from the gas stream is dew pointing. In this process, the temperature of the gas is lowered, which results in the condensation of VOSCs. This concentrated VOSCs containing liquid stream requires further treatment. Dew pointing is nonselective for thiols and other products, e.g., benzene and toluene are also present in the condensate.

There are various applications of microbial VOSC removal. Thiol containing gas streams can be fed to a biofilter containing microorganisms. In these filters thiols are oxidized to sulfate or elemental sulfur by the microbial community using oxygen from the air. Various organic and inorganic carrier materials can be used to support the microbial community. This technique is often applied in the pulp and paper industry that does not contain large amounts of explosive hydrocarbons in the off-gas. Alternative configurations of microbial VOSC treatment plants use 2 step processes. In the first step, thiols are absorbed into a liquid solution, followed by treatment in a bioreactor. These bioreactors can be either aerobic or anaerobic yielding formaldehyde, hydrogen peroxide, sulfide, and sulfuric acid under aerobic conditions [66,134,144] and hydrogen sulfide and methane under anaerobic conditions [134–137]. The anaerobic degradation of thiols with a longer carbon chain than methanethiol not feasible [138,139,145]. These biofilters are sensitive to changes in pH, loading rate, temperature, and pressure variations and thus require stable conditions to operate efficiently.

3.5.2 Technological application

The removal and conversion of VOSCs are often separated into two or multiple processing steps. The bulk removal (>80%) of VOSCs can be achieved with various separation techniques. The deep removal of VOSCs typically occurs via absorption and adsorption processes using, e.g., solid and liquid scavengers and solvents. Here, thiols form a strong bond between the thiol and the sorption material. The processing costs of these technologies highly depend on the regenerability of ad- and absorbents. None-regenerable solid bed scavengers require frequent replacement. Furthermore, the consumed bed contributes to relatively large amounts of solid waste per removed kg of VOSC. Liquid extraction and separation techniques, e.g., caustic solutions, amines, and solid extraction and separation techniques e.g., mole sieves can be regenerated and are cost-effective on small to medium scale.

Bulk gas desulfurization, removing up to 80% of the present thiols, can be performed with a combination of ad- and absorption technologies, amines and mole sieves, and the Claus process. In these technology trains, unwanted components are separated from the product stream into a so-called "acid gas" and subsequently directed to the Claus process. About 60-70% of hydrogen sulfide is converted to elemental sulfur in one Claus thermal processing step. Typically, three steps Claus is applied in the industry to achieve >96% sulfur recovery (up to 99%, including tail gas treatment). In this thermodynamic conversion, VOSCs are co-combusted. The Claus tail gas contains combustible components such as hydrogen, hydrogen sulfide, VOSCs, and carbon monoxide, which is typically treated with a downstream tail gas treatment unit, i.e., absorption and re-fed to the Claus thermal processing step [116,117].

An alternative method to treat process acid gas is to inject the gas in wells, i.e., deep well injection. Compressors compress the gas into liquids and are subsequently injected deep underground. The downside of this technique is that no conversion or detoxification is accomplished.

Thermal destruction of VOSCs is not attractive when VOSCs are present in the liquid phase. Advanced oxidation technologies using, e.g., ozone or peroxide, are generally expensive. These advanced oxidation techniques are typically applied for low concentrations of thiols only, e.g., for removing the odor of drinking water [146].

Another critical aspect to consider in the thiol removal and conversion processes is the selectivity for thiols. The Claus process was initially designed for hydrogen sulfide and can, to a limited extent, also deal with thiols. As hydrogen sulfide is another pollutant that needs to be removed from most product streams, the co-removal of thiols may be beneficial. However, e.g., the liquid oxidation process is less effective when high concentrations of hydrogen sulfide are present in the feed gas. Hydrogen sulfide binds more strongly to the catalyst and limits the removal efficiency of thiols. The sorption capacity of activated carbon and other scavengers may be limited when high sulfide concentrations and other co-pollutants, such as BTEX (benzene, toluene, ethylene, and xylene), adsorb to the materials. Caustic solutions also adsorb other acid gasses like hydrogen sulfide and carbon dioxide, limiting the capacity for thiol removal.

3.5.3 Circularity

Among all the listed technologies in Table 3, only the Claus process produces a reusable sulfur stream. The Claus process does not require expensive catalysts and produces mainly carbon dioxide as a byproduct. All other treatment technologies produce solid bound sulfur that yields a toxic waste stream, sulfate, disulfides, or sulfur dioxide, which requires further treatment. Using scarce resources, such as catalysts, make-up water, sodium hydroxide for caustic solutions and scavenger materials, requires a constant flow of precious materials while producing large amounts of toxic waste. Regeneration of scavengers and caustic solutions can improve the circularity of these technologies. However, there is still a long way to go to achieve a fully circular process in which thiols are removed and recovered as elemental sulfur.

3.5.4 Scale

Small-scale processes that treat less than 200 kg of sulfur originating from VOSCs per day include adsorption and separation techniques. These processes are expensive per ton of sulfur removed compared to the medium and large-scale sulfur removal and recovery techniques. Iron based scavengers have relatively low costs and are commonly applied for small-scale treatment. In theory, iron sponges can be regenerated with oxygen. However, this is rarely performed due to the risk of spontaneous combustion when FeS is exposed to air [122]. These techniques become economically unviable at higher loading rates due to the need for vast amounts of adsorption material and solid waste production.

Oxidation techniques are typically applied for the mid-range loading rates treating between 200 kg and 500 kg of sulfur per day. The oxidized thiols require further treatment, which makes the processing schemes complex and unviable in small operations. Alternatively, molecular sieves can be applied to treat mid-range loading rates. These materials can be regenerated by passing hot air over the spent material, yielding a concentrated stream of VOSCs [122]. At higher treatment volumes (>500 kg S/day), amine treatment combined with combustion to form elemental sulfur in the Claus process is the most cost-effective. This application does require a total sulfur load of 3-ton S/d originating from hydrogen sulfide and thiols to be cost-effective [147]. Flaring can be applied for all sulfur loading rates but is undesired due to the associated sulfur dioxide emissions and the required methane supply to ensure complete oxidation of VOSCs.

3.6 Extended technological requirements of VOSCS removal technologies

The presence of VOSCs in different industries and the looming sulfur scarcity will require a new treatment approach compared to traditional treatment processes. Multiple aspects concerning waste stream production and characteristics should be considered to evaluate a technologies' suitability for future industries. Firstly, in renewable fuels, VOSCs are mainly present in the hydrocarbon-rich product stream, whereas in wastewater treatment, rayon, and paper industries, VOSCs are found in the off-gas. Direct oxidation inside an energy dense hydrocarbon stream may cause severe safety risks and lowers the overall product yields due to oxidation of the hydrocarbons, while this may form a suitable option for the treatment of waste gasses. Secondly, renewable fuel production sites yield decentralized small VOSCs streams compared to full-scale fossil fuel extraction and refinery sites. Thirdly, VOSCs can be found in either the liquid or gas phase requiring alternative treatment approaches. Fourthly, due to the declining sulfur mining in oil and gas fields, the sulfur price will increase, and sulfur recovery will become more important. New technologies should focus on removing, converting, and recovering VOSCs to form sulfur that can be reused as a chemical resource or as fertilizer. Fifthly, sulfur emission legislation has become more stringent over the past decades. It is predicted that increasingly stringent legislation will be implemented to limit environmental damage and odor hindrance caused by these processes. Furthermore, countries that do not yet have these stringent legislations but are in rapid socio-economic development may soon incorporate new legislative standards for the treatment of VOSCs. Thus, new technological approaches are required to deal with VOSC emissions in the upcoming carbon-neutral energy market.

3.7 Outlook

As discussed previously, a carbon-neutral energy market needs to be facilitated with appropriate VOSCs treatment technologies. The demand for large-scale technologies treating high sulfur loads will decrease with the diminished extraction of fossil fuels and natural gas. The decentralized nature of new energy sources inherently results in the production of small and variable VOSCs streams. Numerous technologies can be applied to separate VOSCs from the product streams and obtain a more concentrated VOSCs for further treatment. However, there is currently no technology available to remove and recover sulfur in these smaller VOSCs streams. Technological progress should be made to avoid the disposal of spent solid scavengers into landfills or the injection of liquid scavengers in deep wells. These currently accepted solutions cannot be considered sustainable in the long run when considering the risks of leaching and VOSCs into the environment with the risk of contaminating drinking water supply sources and the increased importance of sulfur recovery.

The lack of suitable technologies combined with increasingly stringent legislation for VOSCs and sulfur dioxide emissions calls for new technological solutions. These new technologies should not merely focus on the detoxification of VOSCs but also on sulfur recovery, as sulfur will become a scarcer commodity with the declining fossil fuel extractions.

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Chapter 4

Microbial reduction of thiols and dimethyl disulfide at cathodes in bioelectrochemical systems

Abstract

Organosulfur compounds, present in e.g. the pulp and paper industry, biogas and natural gas, need to be removed as they potentially affect human health and harm the environment. The treatment of organosulfur compounds is a challenge, as an economically feasible technology is lacking. In this study, we demonstrate that organosulfur compounds can be degraded to sulfide in bioelectrochemical systems (BES). Methanethiol, ethanethiol, propanethiol and dimethyl disulfide were supplied separately to the biocathodes of BES, which were controlled at a constant current density of 2 A/m^2 and 4 A/m^2. The decrease of methanethiol in the gas phase was correlated to the increase of dissolved sulfide in the liquid phase. A sulfur recovery as sulfide of 64% was found over 5 days with an addition of 0.1 mM methanethiol. Sulfur recoveries over 22 days with a total organosulfur compound addition of 1.85 mM was 18% for methanethiol and ethanethiol, 17% for propanethiol and 22% for dimethyl disulfide. No sulfide was formed in electrochemical nor biological control experiments, demonstrating that both current and microorganisms are required for the conversion of organosulfur compounds. This new application of BES for degradation of organosulfur components may unlock alternative strategies for the abatement of anthropogenic organosulfur emissions.

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4.1 Introduction

Organosulfur compounds (OSCs) are naturally present in various environments, including oceans, marine estuaries, volcanos, salt marshes, and play an important role in the natural global sulfur cycle [1,2]. However, anthropogenic emissions of e.g. methanethiol and dimethyl disulfide account for 30% of the annual global emissions with 3222 GgS/year. Methanethiol, dimethyl disulfide and other compounds like ethanethiol and propanethiol, which do not play a major role in the natural sulfur cycle, are found in the pulp and paper industry, rayon and cellulose industry and (bio)gas streams [1]. Removal of organosulfur compounds from waste streams is required due to the low odor thresholds, high toxicity and their corrosive nature.

The state-of-the-art treatment strategy for conversion and removal of organosulfur compounds is the oxidation to insoluble disulfides. This process, known as the Merox process, is in many cases economically unfavorable due to complex processing schemes, high OPEX and CAPEX and low efficiencies [3]. In addition, this process requires chelating chemicals, which can harm the environment. Lacking a suitable treatment method, organosulfur compounds are typically incinerated contributing to SO_2 emissions. The emissions of SO_2 are strictly regulated and are becoming more stringent over the years. Therefore, new cost-effective, environmental friendly strategies for the removal of organosulfur compounds are desired.

In general, biological processes are considered environmentally friendly as they do not require chemical catalysts and require ambient temperatures and pressures. Methanethiol and dimethyl disulfide can be converted under aerobic conditions in bio trickling systems [4]. However, aerobic degradation only occurs at low concentrations and degradation rates are low. On the other hand, anaerobes, such as methanogenic archaea, are known to tolerate much higher thiol concentrations and, therefore, represent an alternative for the treatment of thiol containing waste streams. Several studies report successful biological reduction of methanethiol and dimethyl disulfide to methane and hydrogen sulfide by methylotrophic methanogens [5–7].

The degradation of ethanethiol and propanethiol appears to be much more challenging. Degradation in anaerobic bioreactor has, to the best of our knowledge, not been reported. Leerdam et al. was unable to convert these organosulfur compounds in anaerobic batch systems [8]. Only two studies report an enhanced production of ethane and propane in anoxic sediments when ethanethiol and propanethiol are supplied [9,10]. The conversion efficiencies were low, less than one percent of the added substrates, and Oremland et al. [9] suggested that conversions of ethanethiol were solely a result of co-metabolism and growth on ethanethiol as sole substrate was not possible. Nevertheless, these studies suggest that biological conversion mechanisms exist.

Bioelectrochemical systems (BESs) are an emerging biotechnology with a wide range of applications, e.g. electricity generation, metal recovery, chemicals synthesis, and wastewater treatment [11–14]. In bioelectrochemical systems, microorganisms catalyze anodic oxidation reactions or cathodic reduction reactions. Reaction rates can be manipulated by controlling electrode potential or current density. Complete reduction of organosulfur compounds at a biocathode would result in the formation of methane and sulfide. These products have as advantage that in the (bio)gas industry methane can be directly used and elemental sulfur can be recovered from the hydrogen sulfide with existing technologies. In this study, we demonstrate that methanethiol, ethanethiol, propanethiol and dimethyl disulfide can be converted at biocathodes, and that degradation requires both microorganisms and electricity.

4.2 Materials and methods

4.2.1 Bioelectrochemical cell setup

Bioelectrochemical experiments were performed in 4 identical anaerobic reactors (H cells [15]). Cells consisted of two 150 mL chambers separated by a cation exchange membrane (8.02 cm^2 CEM, fumasep®FTCM-E, Fumatech, Germany). The experiment was performed under continuous stirring at 350 RPM. Gas produced at the cathode was collected in 1 L gas bags (Cali-5-Bond™, Calibrated Instruments Inc., USA) with an initial gas volume of 35 mL. Graphite felt electrodes (0.4cm x 2cm x 15cm, CTG Carbon GmbH, Germany) connected to a platinum current collector were used as both anode and cathode electrodes. A 3M KCl Ag/AgCl reference electrode (+210mV vs SHE, Prosense, Oosterhout, the Netherlands) was inserted in the cathode chamber. The current was controlled with a potentiostat (Ivium, the Netherlands). Cells were operated at room temperature (22-25 °C).

4.2.2 Medium and inoculum

A bicarbonate medium similar to the medium used for biodesulfurization processes under haloalkaline conditions [16] was used during all experiments. The medium contained 49 g/L $NaHCO_3$, 4.42 g/L Na_2CO_3 and 0.1 mL/L nutrient solution containing N and P and trace elements (Paqell B.V., The Netherlands). The medium was flushed with N_2 for 20 minutes, resulting in a pH of 8.5. Anolyte contained the same carbonate buffer with 84.5 g/L potassium hexacyanoferrate(II)trihydrate. Hexacyanoferrate (II) is a typical substrate in bioelectrochemical system used as an electron donor in the anode to avoid the crossover of produced oxygen at the anode to the cathode when water is oxidized at the anode.

Cathode chambers were inoculated with a mixture of biomass selected based on their acclimation to anaerobic conditions, high salt concentrations, the presence of organosulfur compounds and the presence of methanogens. The inocula were obtained from (1) a chain elongation reactor fed with high methanol concentrations (250 mM)(total nitrogen (TN) 1.47 g/L) [17],(2) a granular anaerobic reactor operating at a high salt concentration (20 g Na/L)[18] (TN 4.3 g/L), (3) a digester for municipal wastewater treatment sludge (Ede, The Netherlands) combined with anaerobic sludge treating wastewater from paper industry (Eerbeek, The Netherlands)(4.4 g/L TCOD), and (4) sulfide oxidizing biomass adapted to the presence of 0.5-2.5 mM dimethyl disulfide (TN 0.6 g/L) [19]. The biomass mix was obtained by combining 2 mL of each of the different inocula. 1 mL of the biomass mix was added to the cells during startup.

4.2.3 Bioelectrochemical cell operation

For initial proof-of-principle experiments, sludge from the paper industry and municipal wastewater treatment plant was used to inoculate two cells. The reactors were started with 1 mM methanol (150 µmol) and 0.1 mM methanethiol (15 µmol) at the biocathodes and were operated for one week to stimulate initial growth and to acclimate the biomass. Subsequently, medium was replaced and methanol (150 µmol) and methanethiol (22.5 µmol to cell 1 and 15 µmol to cell 2) were supplied once. Cells were galvanostatically controlled at 2 mA (2 A/m^2 projected surface area of the graphite felt cathode). Gas phase concentrations of organosulfur compounds and sulfide concentration in solution was monitored for 5 days.

In the next experimental run, we studied the degradation of all four organosulfur compounds. Each organosulfur compound was supplied to a biocathode in a pre-experimental run 13 days prior to the start of the experimental run, allowing microorganisms to adapt to experimental conditions. 1 ml of biomass mix (see section 2.2) and 150 µmol methanol were added to all cells. Upon the detection of methane, indicating biological activity, 15 µmol of methanethiol, ethanethiol, propanethiol and dimethyl disulfide were added to individual cells every weekday. Cells were galvanostatically controlled at 2mA, obtaining a current density of 2 A/m^2 normalized to the projected surface area of the graphite felt electrode. Medium from the pre-experimental run was replaced at the start of the experimental run. Suspended biomass in the medium was collected by centrifuging for 15 minutes at 5000 rpm and was returned to the cells. Biomass mix (1 mL) and methanol (150 µmol) were added to the cells on day 0. Cells remained under galvanostatic control (2 mA/m^2) and 15 µmol of organosulfur compounds were added daily. After 12 days, organosulfur compound additions were doubled and current density was doubled to 4 A/m^2. The cells were operated in this mode for 10 days.

4.2.4 Electrochemical, biotic, and abiotic control experiments

Electrochemical control experiments were performed in the same electrochemical setup as described in 2.3 with a current density of $2 mA/m^2$. New graphite felt electrodes without microorganisms were used. Organosulfur compounds (15 µmol) were added individually to the cells, which were operated for 24 hours. Additional electrochemical experiments were performed with 15 µmol dimethyl disulfide, 150 µmol methanol and biomass from the different sources added to individual cells. The cells were operated until sulfide production was shown in each of the cells.

Biotic control experiments with hydrogen as electron donor were performed in 250 mL serum flasks. At the start of the experiment the headspace was replaced with a CO2/H2 (80:20) gas mixture at 1.3 bar. Flasks contained 150 mL medium, methanol (150 µmol) and were inoculated with 1 mL biomass mix. The start pH was between 7.7 and 8. Upon the production of methane, each serum flask was supplied with 15 µmol of one single organosulfur compound. Flasks were placed in an incubator and mixed at 150 RPM at 22-25°C for 30 days.

Abiotic control experiments with methanethiol were performed in 250 mL serum flasks under 100% nitrogen at atmospheric pressure. Individual flasks were filled with 150 mL medium and water and 0.1 mM methanethiol.

4.2.5 Analytical techniques and calculations

We used organosulfur gas phase analysis to validate the use of sulfide as indicator for organosulfur compound degradation. Gas phase concentrations of methanethiol and dimethyl disulfide were analyzed as described by Roman et al., 2015[20]. Analysis of organosulfur compounds to show their degradation is challenging as (i) organosulfur compound analyses are prone to errors due to their volatile nature, and (ii) a decrease in organosulfur concentrations does not necessarily indicate its conversion, as it could also indicate leakage of organosulfur from the system.

Total sulfide (S^{2-}, HS^- and H_2S) in the liquid was measured using the methylene blue method (Hach LCK 653), in which sulfide is converted to H_2S. To avoid measurement losses due to the alkaline nature of the samples, dilutions were performed with 0.5 M sulfuric acid. The method was tested for interference with organosulfur compounds by measuring solutions of sulfide with and without organosulfur compounds, and no interference was observed.

Sulfate and thiosulfate, were analyzed with Ion Chromatography (See SI-1). Gas chromatography was used to measure CH_4, N_2, O_2, CO_2 and H_2 using the methods described by Liu et al., 2017 [21].

Next Generation Sequencing was used to analyze the microbial community. The Powersoil DNA isolation kit was used for DNA extractions. DNA amplification via PCR and sequencing were performed as described by Takahashi et al.[22]

Coulombic efficiency was calculated as:

$$CE\ (\%) = \frac{V \times [OSC - S] \times n \times F}{\int_{t0}^{t} I\ dt} \times 100$$

Where V is the catholyte volume (0.15 L), [OSC-S] is the concentration of sulfur added (mol/L), n is the number of electrons for reduction of organosulfur compounds to CH_4 and HS^- (See eq 1-4), F is the Faraday constant (96485 C/mol), I is current (A) and t is time (s).

$$CH_3SH + H^+ + 2e^- \rightarrow CH_4 + HS^- \qquad \text{(eq. 1)}$$

$$C_2H_5SH + 3H^+ + 4e^- \rightarrow 2CH_4 + HS^- \qquad \text{(eq. 2)}$$

$$CH_7SH + 5H^+ + 6e^- \rightarrow 3CH_4 + HS^- \qquad \text{(eq. 3)}$$

$$C_2H_6S_2 + 4H^+ + 4e^- \rightarrow 2CH_4 + 2HS^- \qquad \text{(eq. 4)}$$

4.3 Results and discussion

4.3.1 Methanethiol degradation in BES

Gaseous methanethiol and its oxidation product dimethyl disulfide, expressed as organosulfur compounds, and dissolved sulfide were analyzed over time at the biocathodes of two BES cells. Organosulfur compounds were almost completely removed from the gas phase in 5 days. The gas phase concentration decreased with 95% starting with 0.13 µmol in cell 1 and with 82% in cell 2 starting with 0.19 µmol, while the sulfide in the liquid increased from <0.5 to 9.1 µmol (61 µM) in cell 1 and to 9.3 µmol (62 µM) in cell 2 (Figure 1). A considerable part of the supplied methanethiol was converted and recovered as sulfide. After 5 days: 41% of the 22.5 µmol (0.15 mM) methanethiol supplied in cell 1, and 64% of the 15 µmol (0.1 mM) methanethiol supplied to cell 2 was obtained as sulfide in the liquid phase. The fate of the remaining methanethiol fraction is unclear. However, there are several possible reasons why not all methanethiol was recovered as sulfide. First, a fraction of the methanethiol could be unconverted and still present in the liquid phase as there was still some methanethiol present in the gas phase. Second, methanethiol could be lost from the system through diffusion via or adsorption onto the membrane, tubing, electrodes and sampling ports. However, this was not quantified. Finally, the measured sulfide may underestimate the produced sulfide, since part of the sulfide could be used by microorganisms for growth. Abiotic controls, without electrical current, showed a minor decrease of gaseous organosulfur compounds of 1.1% in medium and 3.1% in Milli-Q (see SI-2) demonstrating that no degradation of methanethiol occurred in absence of bacteria and electrical current. Sulfide formation was used in further experiments to indicate organosulfur compound conversions, since sulfide formation provides a convincing proof that organosulfur compounds are converted.

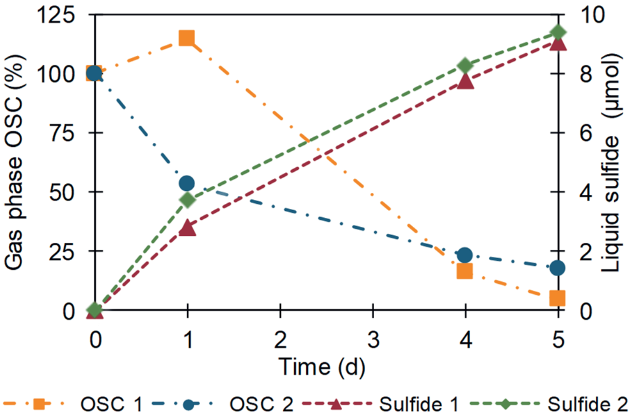

Figure 1 *Degradation of organosulfur compounds (OSC) at biocathodes. Decrease of organosulfur compounds in the gas phase, consisting of the sum of methanethiol and its oxidation product dimethyl disulfide, was related to the increase of sulfide in the liquid phase. The organosulfur compounds are shown as a percentage of the initial absolute amount present in the gas phase.*

4.3.2 Degradation of organosulfur compounds

Addition of organosulfur compounds over 22 days resulted in a total addition of 278 µmol (1.9 mM) sulfur for methanethiol, ethanethiol and propanethiol (Figure 2a) and 555 µmol (3.7 mM) sulfur for dimethyl disulfide (Figure 2b). Each biocathode, operating with different organosulfur compounds, showed a similar trend in the formation of sulfide. Sulfide was accumulating to 45 µmol (0.30 mM) for methanethiol, 44 µmol (0.29 mM) for ethanethiol, 42 µmol (0.28 mM) for propanethiol and 107 µmol (0.71 mM) for dimethyl disulfide during the experiment. The formation of sulfide in each of the biocathodes demonstrates that all organosulfur compounds were converted. Sulfide formation showed a faster increase with time after the current density and organosulfur compound additions were doubled, indicating that organosulfur compounds reduction continued at higher rates. The increased levels of organosulfur compounds did not inhibit the microbial community as sulfide production continued at an increased rate.

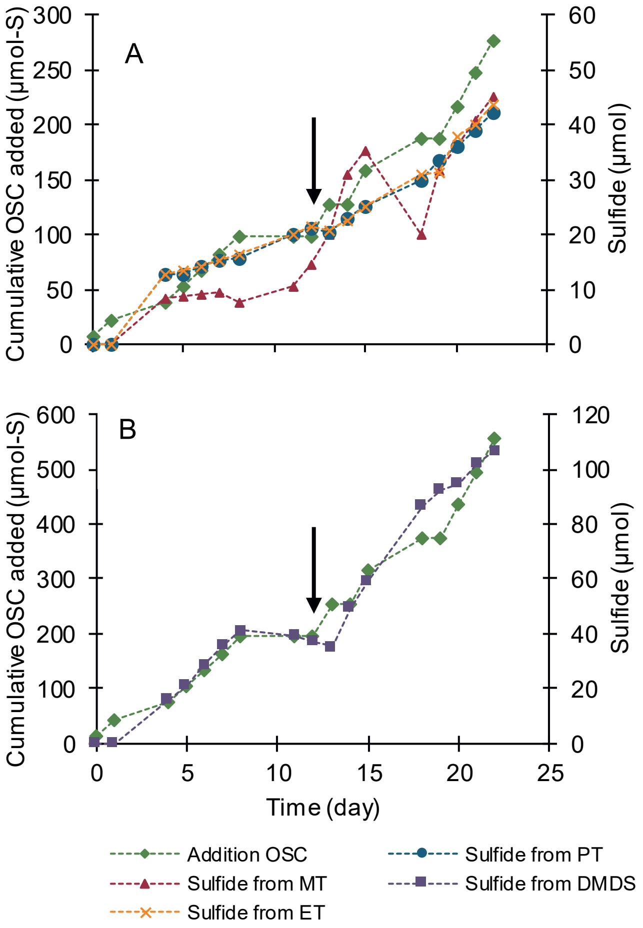

***Figure 2** Each organosulfur compound was converted into sulfide. Cumulative organosulfur (OSC) additions expressed as µmol S and sulfide measured in the liquid phase in cells with (A) methanethiol (MT), ethanethiol (ET), propanethiol (PT) and (B) dimethyl disulfide (DMDS). Arrows indicate the day at which organosulfur additions were increased from 15 µmol to 30 µmol and the increase of current density from 2mA to 4mA.*

Sulfur recoveries as sulfide were 18% for methanethiol, 18% for ethanethiol, 17% for propanethiol and 22% for dimethyl disulfide compared to total added sulfur in the form of organosulfur compounds. 17% of the sulfur added in the form of methanethiol was detected as sulfate, while sulfate recovery remained less than 5% in experiments with other organosulfur compounds. This is lower than the sulfur recovery obtained in the initial 5 day experiment with methanethiol (section 3.1), in which recoveries of 41% and 64% were obtained. It is likely that this difference in sulfur recovery is related to the difference in operation and experimental run time. For example, the longer experimental run (22 days) received 11 additions of methanethiol, whereas the 5 day experimental run received only one addition. A more detailed study to close sulfur balances will be needed in future studies.

The higher sulfate production for the methanethiol fed biocathode might be a result of some oxygen intrusion found at this cathode (See SI-3). The presence of oxygen in this cell may have influenced the conversion mechanisms, as strictly anaerobic conditions could not be maintained. However, with the measured cathode potentials lower than -1 V vs. Ag/AgCl, it is expected that oxygen was quickly reduced. The formation of methane within the cell indicates that anaerobic processes were still in place.

The cathode potentials in all tests were ranging between -1.15 to -1.43 V vs. Ag/AgCl and slowly decreased throughout the experiment, indicating that hydrogen formation took place. The main element of the medium consists of a carbonate/bicarbonate buffer. Under the operating conditions, methane can be formed biologically from this inorganic carbon source. Hydrogen and methane were also detected in the gas phase (SI-3).

The coulombic efficiency (part of the total charge used for organosulfur compound reduction) was 1.7% for methanethiol, 3.4% for ethanethiol and 5.0% for propanethiol and dimethyl disulfide, under the assumption that the available organosulfur compounds were completely reduced towards methane and sulfide (See eq 1-4). In our experiments, we did observe methane formation, but it is also possible that other products rather than methane, e.g. CO_2, ethane or propane were formed (not included for calculation of electron efficiency). Other electron sinks in this process were hydrogen and methane (See SI-3), and growth of biomass (not quantified). The effect of thiol concentration and current density on thiol degradation was not further studied in this manuscript and will be topic of further research.

4.3.3 Organosulfur degradation requires a combination of electricity and microorganisms

Electrochemical control experiments were performed to ensure that the degradation of organosulfur compounds was not merely a result of the applied current. The experiments showed no sulfide formation after 24 hours of operation and indicate that microbial activity is required for the conversion of the tested organosulfur compounds. Cathode potentials during the control experiments ranged between -1.10 and -1.34 V vs. Ag/AgCl, similar to the cathode potential in the bioelectrochemical runs.

During the bioelectrochemical experiments, hydrogen was produced at the cathode, which could be used as alternative electron donor for organosulfur compound degradation. Therefore, biotic control experiments were performed with 20% hydrogen in the gas phase, without electrodes. Surprisingly, during 30 days, no sulfide was detected, demonstrating that both current and biomass are required for the degradation of the organosulfur compounds. Even though bio-degradation of methanethiol[5–8,23,24] and dimethyl disulfide[6–8] in anaerobic environments has been frequently reported, this was not shown in our control experiments, and may be the result of different conditions, such as halo-alkaline medium, selected inocula and experimental run time. Oremland et al. studied the degradation of ethanethiol in the presence and absence of hydrogen, the obtained results were contradictory and showed both increased and decreased degradation under the presence of hydrogen[9]. The exact role of electrical current and potentially hydrogen in organosulfur degradation is still unclear and needs to be elucidated in further research.

4.3.4 Microbial composition in organosulfur compound degrading BES

Microbial community analyses were performed on the bioelectrodes collected at the end of the experiment (Section 3.2). A large similarity was found between cathodes fed with ethanethiol, propanethiol and dimethyl disulfide (Figure 3). Dominant families on the cathodes were *Halomonadaceae*, *Clostridiaceae* families *2* and *XIV*. The cathode fed with methanethiol showed a lower abundancy for the two families *Clostridiaceae 2* and *XIV,* while the presence of *Rhodobacteraceae* was increased. The difference in microbial community on this cathode compared to the others potentially resulted from oxygen intrusion into this cell (See SI-3). The members of the families *Halomonodaceae* and *Clostridiaceae 2,* dominant in all cells, were also observed in a haloalkaline sulfide oxidizing bioreactor in the presence of methanethiol, ethanethiol and propanethiol[25]. *Clostridium*, one of the genera within the family of *Clostridiaceae*, is well known to be electroactive[26]. Since a mixture of inocula were used to study organosulfur degradation, experiments were performed in the same bioelectrochemical test setup to evaluate whether each separate inoculum had the capacity to degrade organosulfur compounds. Here, dimethyl disulfide was used. The cell inoculated with a mix of paper industry sludge and municipal wastewater treatment plant sludge showed sulfide formation after 4 days. Sludge from the chain elongation reactor showed sulfide formation after 5 days, and, sludge from the high salinity reactor and sludge adapted to the presence of organosulfur compounds both showed sulfide formation after 18 days. Degradation of dimethyl disulfide was thus possible by all inoculum sources separately.

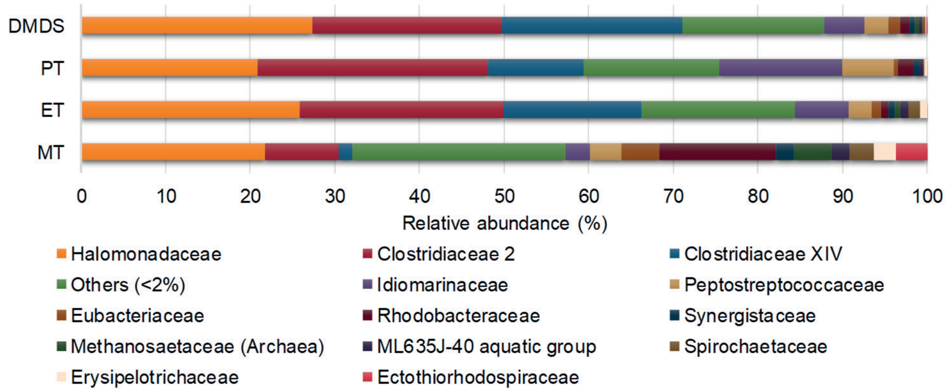

Figure 3 *Relative abundance of the microbial community for cells with methanethiol (MT), ethanethiol (ET), propanethiol (PT) and dimethyl disulfide (DMDS) based on 16S rRNA sequencing. A similar microbial composition was found in all cells with dominant species belonging to the families Halomonadaceae, Clostridiaceae families 2 XIV. Families with an abundancy <2% are summarized and shown as others.*

4.4 Outlook

Thiols and hydrogen sulfide are often both present in gaseous waste streams. Biodesulfurization technologies focused on the recovery of elemental sulfur from hydrogen sulfide suffer from the presence of organosulfur compounds[27]. The conversion of these organosulfur compounds towards hydrogen sulfide would in these cases be an advantage as this can then be detoxified together with the hydrogen sulfide and be removed in existing, well-known efficient treatment plants. This research presents a proof of principle for the reduction of methanethiol, ethanethiol propanethiol and dimethyl disulfide at biocathodes towards sulfide.

Various aspects need to be considered to further study and develop this new application of BES. Coulombic efficiencies in this experimental design were low and can be improved by limiting (i) the formation of methane resulting from carbon dioxide reduction and (ii) hydrogen formation at the electrode. When calculating the coulombic efficiency, we assumed a complete reduction towards methane, however, metabolic pathways and products were not further identified. Further design questions involve defining reaction kinetics, microbial growth rates, evaluating long-term process stability and the role of methanol as co-substrate. The economic feasibility of this system will largely depend on maximum attainable reduction rates and microbial toxicity limits. Regardless the remaining research questions, this application of BES demonstrated a new potential strategy to biologically convert organosulfur to sulfide, a product for which many efficient sulfur recovery technologies are available.

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Supporting information

SI-1 Ion chromatography method

Ion chromatography (Dionex ICS 2100 RFIC, Salt Lake City, USA) was used to determine the concentrations of sulphate and thiosulphate. An IonPac AS17C column 250x4mm was used at 30C with a flow rate of 1.0 ml per minute. The high carbonates were bypassed with a carbonate trap. The injection volume was 10µL. The eluent was generated by an eluent generator (EG40, Dionex, Salt Lake City, USA) equipped with a KOH cartridge, and carried by deionized water. Detection of the ions was based on conductivity; we used an ADRES 600 4mm suppressor to suppress eluent conductivity.

SI-2 OSC headspace concentrations in abiotic control of methanethiol degradation in BES

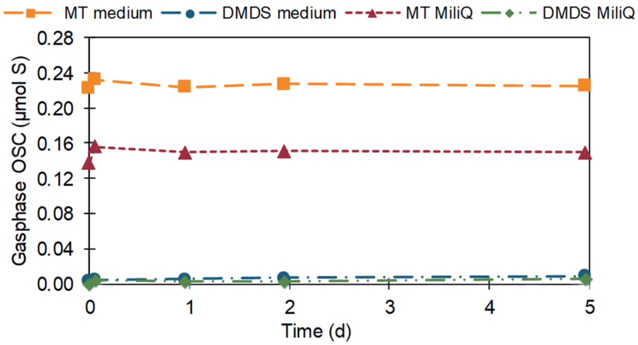

Figure SI-2 *Organosulfur compounds (OSC) present as methanethiol (MT) and its oxidation product dimethyl disulfide (DMDS)in the gas phase of anaerobic abiotic control experiments performed in medium and Milli-Q.*

SI-3 Gas phase composition coulombic efficiency CEs for degradation of organosulfur compounds experiment

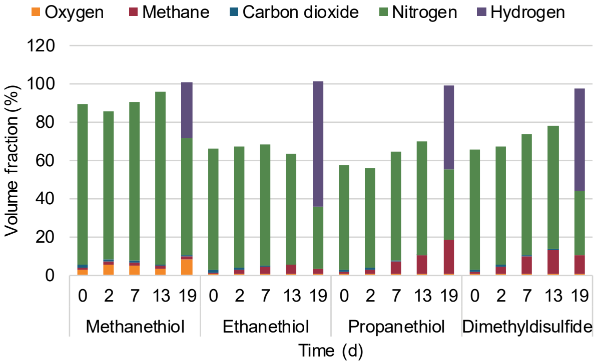

Figure SI-3 *Gas phase composition of cells fed with methanethiol, ethanethiol, propanethiol and dimethyl disulfude. Oxygen found in the methanethiol-fed cells are higher compared to the other cells and indicate oxygen intrusion into the system. Hydrogen was only measured at day 19.*

Hydrogen sulfide measurements were only performed at day 19 of the experiment. Since we have measured all other main components in the gas phase, we can make a rough calculation how much hydrogen would be present the other days. If we assume that the main components are methane, carbon dioxide, nitrogen and oxygen, hydrogen will be the remaining fraction of the headspace. Another issue is that we measured gas volumes only at the beginning and the end of the experiment, so we would need to assume a linear increase in gas production. We calculated the coulombic efficiency (CE) with these assumptions, and this shows that hydrogen was indeed one of the main electron sinks. The CE of these products are shown in table SI-3.

Table SI-3 *Coulombic efficiencies*

Cell operated with	Methane %*	Hydrogen %	Total %
Methanethiol	4.7	24.9	29.6
Ethanethiol	9.9	56.0	65.9
Propanethiol	61.4	37.6	99.0
Dimethyldisulfide	33.2	45.8	79.0

* We assume reduction of carbon dioxide to methane which requires 8 electrons.

Chapter 5

A simple method for routine measurement of organosulfur compounds in complex liquid and gaseous matrices

Abstract

The measurement of VOSCs in complex matrices is challenging due to their volatile and reactive nature. A straightforward method using headspace chromatography was developed for routine analyses of organosulfur compounds in a high saline liquid matrix with a pH of 8.4. Direct sample acidification with a 1M acetate buffer (pH 3.6) showed an increased response for methanethiol, ethanethiol, propanethiol, dimethyl sulfide, dimethyl disulfide and diethyl disulfide. A good quadratic fit (R^2 <0.995) was obtained for each compound over a calibration range of 5 µM-S until 125 µM-S (µmol sulfur/L). Gas standards were measured using the same chromatographic conditions over a calibration range of 0.08 µM-S until 1.85 µM-S (R^2 <0.999). Gas standards could also be used to calibrate the liquid phase with a response ratio of 105.2% for ET, 107% for DMS, 105.7% for PT, 108.9% for DMDS and 106% for DEDS. This alternative calibration strategy reduced the preparation time and does not rely on liquid standards, which were unstable over time. This method was used to determine Henry constants for the organosulfur compounds both in demineralized water and the high saline liquid matrix and to analyze samples from a bio electrochemical experiment that treated methanethiol. This new method allows for routine analysis of samples originating from natural gas desulfurization plants and can potentially also be used to analyze organosulfur compounds in other complex waste streams.

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5.1 Introduction

There is a widespread interest for reliable and simple methods to measure volatile organosulfur compounds (VOSCs) in both gaseous and liquid samples. Low weight organosulfur compounds, such as methanethiol (MT), ethanethiol (ET), propanethiol (PT) and hydrogen sulfide, are formed in industrial processes, including wastewater treatment plants [1–3], manure digestion [4], composting plants [5], paper [6,7] and rayon production [6–8] These organosulfur compounds and hydrogen sulfide are also present in natural gas and crude oil [9–11]. Furthermore, VOSCs play an important role in the global sulfur cycle [6,12–14]. Industrial VOSC emissions are strictly regulated as concentrations as low as 0.14 ppbv can already cause significant olfactory discomfort for the surrounding population and their potential toxicity at higher concentrations [15]. To develop efficient VOSC removal strategies and to comply with environmental safety regulations, reliable and simple measurement methods are required. However, accurate and straightforward measurement of these compounds remains a challenge. These challenges include the highly reactive nature of the VOSCs, the complex matrixes in which they are present and the accurate measurements at low concentrations.

The high volatility and reactivity of VOSCs puts a strain on sampling procedures, sample storage and complicates pretreatment steps [16]. The matrix in which the VOSCs are measured further complicates the measurement of VOSCs. The measurement of gaseous matrices is relatively straightforward as long as the samples are kept anaerobic and sorption to the sampling equipment is avoided. Liquid matrices, however, can also catalyze chemical reactions and may contain particles onto which VOSCs can adsorb [17]. In addition, microorganisms present in liquid samples may convert VOSCs [18]. One particularly difficult matrix containing VOSCs is found in the gas and oil industry, where H_2S and VOSCs are extracted using caustic or amine solutions [9,19]. These solutions typically have a high pH (10-12) and salinity (>0.5M Na^+) with a total sulfur content ranging from 0.1 to 4 wt% [20]. High pH values are known to increase reactivity of VOSCs and salt precipitation due to the high salinity in liquid samples may shortens the lifetime of analytical equipment. No straightforward method for routine measurement of VOSCs in this complex liquid matrix has been described so far.

Various techniques, including HPLC [21], spectrophotometry [22], voltammetry [23], have been developed to measure VOSCs in different liquid matrices. Unfortunately, these systems are unable to measure gaseous samples and would require a combination of methods to analyze both gas and liquid samples. Alternatively, gas chromatography (GC) can be used to measure VOSCs in both gas and liquid samples [24,25]. Various detectors can be used to measure sulfur compounds on a gas chromatograph. The Sulfur Chemiluminescence Detector (SCD) and the Flame Photometric Detector (FPD) are two detectors that have a high selectivity and sensitivity towards sulfur compounds [26,27]. High reproducibility and accuracy for gaseous samples can be obtained with both detectors. Even though the SCD has a higher sensitivity, FPD is more widely used due to its lower costs, low maintenance and overall robustness [26].

Another major challenge, in addition to analyze both gas and liquid samples, is measuring VOSCs at low concentrations which often requires preconcentration steps. Usually, concentration methods like purge and trap [28,29] or solid phase micro extraction [30–33]are applied to measure VOSCs at low concentrations. However, these methods obtained results with high standard deviations as the volatile and reactive nature of these compounds becomes an issue during these pre-treatment steps [16]. Furthermore, preconcentration steps are time consuming, require expensive equipment and are sensitive to losses due to dimerization and volatilization [31]. Direct injection of liquid samples in a GC may avoid the need for tedious preparation procedures and is applied in e.g. the analysis of volatile fatty acids [34,35]. A disadvantage of direct injection of liquid samples is that the equipment requires frequent maintenance especially with high saline matrices. Furthermore, the high salt concentrations increase the risk of VOSCs deposition in the injector as a sodium salt.

Direct measurement using a static headspace chromatography forms a potential solution for measuring VOSCs in high saline liquid matrices. This method requires minimal sample treatment and small sample volumes and was applied to analyze samples from municipal wastewater treatment plants [25]. With this method a recovery of 83% for methanethiol, 103% for dimethyl sulfide (DMS) and 102 for to 103% dimethyl disulfide (DMDS) was achieved in wastewater samples. However, the method included various pretreatment steps including acidification for sample storage and neutralization before analysis. Furthermore, the method was not specialized for highly saline samples with high pH values, and its applicability for ethanethiol, propanethiol, diethyl disulfide (DEDS) and hydrogen disulfide, was not evaluated.

In this work, a fast and straightforward method to measure VOSCs in the gas and the liquid phase using static headspace chromatography on a GC-FPD was developed. All samples were analyzed without preconcentration steps to minimize the risk of VOSCs losses and conversions during sample preparation. Different acidification strategies were evaluated to improve the chromatographic response for the liquid samples. The influence of different (bio) gas compositions in gas samples was evaluated. The calibration range, intermediate precision, quantification, and detection limits were evaluated. Additionally, the method was used to determine Henry coefficients in a high saline liquid matrix and in demineralized water.

5.2 Material and methods

5.2.1 Equipment

Gas chromatography was used to analyze gas and liquid samples. The gas chromatograph (Shimadzu Nexis GC-2030, Shimadzu, Germany) was equipped with a headspace autosampler (Shimadzu H20 plus, Shimadzu, Germany) increasing injection precision and minimizing physical presence. The incubation temperature of the autosampler was set at 60 °C with an equilibration time of 7 min. Additional mechanical shaking was applied for liquid samples during the incubation period. Following the incubation period, nitrogen gas was used to obtain an overpressure in the sample vials before sample injection (35 kPa for gas samples and 60 kPa for liquid samples). The split/splitless injector with a 250 µL loop was operated in spitless mode at 150°C. A total volume of 250 µL was injected. The sulfur compounds were separated on an intermediate polar capillary column (ZB-624PLUS, 30m length, 0.530 mm diameter, 3.0 µm film thickness, Phenomenex, UK) using nitrogen as a carrier gas with a flow of 2.54 mL/min. The oven temperature was programmed at 35°C and maintained for 3 minutes after injection. Thereafter a temperature ramp of 40 °C/min until 180°C was applied. The temperature was maintained at 180 °C for 4 minutes. The gas chromatograph was equipped with a flame photometric detector (FPD) using an optical sulfur filter (Optical filter ASSY (S) for FPD-2030 Shimadzu, Germany) and operated at 250°C with a 40 mL/min hydrogen and 60 mL/min air flow. Labsolutions 5.93 (Shimadzu, Germany) was used to operate the system and analyze the data.

5.2.2 Gas calibration standards

Amber glass vials (1.5 mL) were filled with liquid organosulfur compounds (purity >99.6%) and were used to prepare mixed gas standards. The vials were closed with PTFE lined caps (Septa N11 rubber/PTFE red hardness 45, shore A, MACHEREY-NAGEL, Germany). The equivalent of 1 mmol-S of ET, PT, DMS, DMDS and DEDS was transferred from the amber glass vials with a glass syringe (Hamilton, USA) to a 2.28 L glass bottle that was closed with a butyl rubber stopper (Bromobutyl rubber Stopper for GL 45, DWK Life Sciences GmbH, Germany) to prepare a mixed gas standard. Following preparation, the mixed gas standard was heated for 30 minutes at 50 °C to fully vaporize the organosulfur compounds before further gas dilutions were made. To obtain the final working stock, 5 mL of the mixed gas standard was transferred to a 120 mL serum flask resulting in a final concentration of 20 µM-S (µmol sulfur/L) for each compound. These working stocks were used for 2 weeks without changes in the gas composition and signal intensity. The calibration curve was obtained by diluting the working stock into 10 mL vials over a concentration range of 0.08 - 1.85 µM-S for each compound. All standard preparations were performed in an anaerobic chamber that was continuously flushed with nitrogen gas. Serum flasks and 10 mL vials were closed with 3mm PTFE lined butyl rubber crimp seal caps in a 100% nitrogen atmosphere (Septa butyl/PTFE Gray hardness 50, shore A, MACHEREY-NAGEL, Germany). H_2S and MT standards were prepared from a gas standard containing 207 ppmv H_2S and 206 ppmv MT in 100 %N_2 (Linde Gas Benelux B.V, The Netherlands)

The accuracy of the calibration is strongly influenced by the evaporation of the pure compounds used to prepare the mixed gas standard. Full vaporization of pure compounds was therefore evaluated by comparing the chromatographic response for mixed gas standards that were prepared at room temperature and subsequently heated for 30 minutes at 40, 50 and 60 degrees before working stocks with a final concentration of 0.223 µM and 0.372 µM were prepared.

5.2.3 Liquid headspace calibration standards for liquid samples

Liquid headspace calibration standards were prepared in a similar matrix (high salinity, high pH) that can be found in bio-desulfurization plants [20] and contained 4.42 g/L Na_2CO_3, 49 g/L $NaHCO_3$, 0.2 g/L $MgCl_2$ x 6 H_2O, 1 g/L KH_2PO_4, 0.01 g/L $CaCl_2$ 2 H_2O, 0.6 g/L CH_4N_2O, 1 g/L NaCl, with a final pH of 8.4.

Pure solutions (>99.6%) of ET, DMS, PT, DMDS and DEDS were used to prepare individual 10 mM stock solutions in methanol. A MT stock solution (10 mM) was prepared from its sodium salt in Milli-Q. Mixed working stock solutions were prepared in the high pH and highly saline matrix from the 10 mM standards obtaining a concentration of 125 µM-S for each compound. The working stock was further diluted with same matrix into the 10 mL vials creating the calibration standards over a range of 5 µM-S until 125 µM-S. The volume of the liquid standards in the 10 mL vials was 200 µL.

The influence of different acids on the exclusion of organosulfur compounds from the liquid phase was evaluated. The acids used to lower the pH of liquid samples were a glycine buffer (0.2 M glycine and 0.2 M HCl, pH 3), a HCl solution (0.5 M, pH 0.3) and an acetate buffer (1M, pH 3.6). Working solutions with a concentration of 50 µM-S following the procedure described in this manuscript were prepared. The 10 mL vials were filled with 200 µL of working solution and 200 µL of acid. The blank was prepared by adding 200 µL of working solution without VOSCs.

The use of gas standards to calibrate liquid samples was evaluated to shorten and ease the liquid calibration procedure. The 10 mL vials were filled with 200 µL of saline matrix and 200 µL of acetate buffer. Organosulfur compounds from the mixed gas standard were added with an air-tight syringe (Hamilton, USA). The response was compared with results obtained with liquid standards.

All standard preparations were, like gas standard preparations, performed in an anaerobic chamber that was continuously flushed with nitrogen and dilutions were made with gas tight glass syringes. Water, high pH saline matrix and buffer solutions were sparged with nitrogen for 20 minutes to ensure anaerobic conditions, before the addition of organosulfur compounds.

5.2.4 Assessment of chromatographic response

The chromatographic method was evaluated by comparing the results of 6 (MT and H_2S) and 10 (ET, PT, DMS, DMDS and DEDS) replicates of the calibration curve of gas and liquid standards. The peak separation was observed to assess the selectivity. The determination coefficient was used to evaluate linearity and the precision was evaluated by comparing the RSD values at the lowest calibration point. The limit of quantification (LOQ) and limit of detection (LOD) were calculated by using the calibration approach [36,37].

The chromatographic method was further evaluated by assessing the influence of incubation time and different (bio)gas compositions. The influence of incubation time was evaluated by injecting the headspace of a 10 μM-S ethanethiol liquid standard (gas standard for liquid calibration procedure) after an incubation time of 5, 7 minutes and with a gas standard containing 10 μM-S propanethiol and dimethyl disulfide after an incubation time of 5, 7, 10, 12 and 15 minutes. Additionally, the influence of (bio)gas composition was evaluated by preparing working stocks in 120 mL serum flasks with different gas compositions (Table1). Working stocks containing ethanethiol, dimethyl sulfide, propanethiol and dimethyl disulfide were diluted into the 10 mL vials to obtain a final concentration of 1 μM-S. The relative response at different conditions was calculated by dividing the natural logarithm of the response area (μV·min) by the natural logarithm of the response area obtained under a 100% nitrogen atmosphere.

Table 1 *Evaluated gas compositions for signal quenching*

Mixture	N_2 %	CO_2 %	CH_4 %
1	100	0	0
2	25	50	25
3	50	25	25
4	50	50	0
5	90	0	10
6	85	10	5
7	80	10	10

5.2.5 Method application

5.2.5.1 Henry coefficient determination

Henry coefficients were defined for MT, ET, PT, DMS, DMDS, and DEDS. The standard solutions, with a concentration of 3.8 mM-S for DEDS and 10 mM-S for all other evaluated compounds, were prepared in demineralized water under anaerobic conditions. The experiments were performed in 120 mL serum flasks that were sealed with PTFE lined butyl rubber crimp seal caps. The flasks were filled with 50 mL saline matrix or demineralized water and sparged with nitrogen gas for 20 minutes. The organosulfur compounds were injected from the standard solution into these vials resulting in the addition of 100 µmol-S. Flasks were stored at 25 °C during 24 hours before samples were taken from the gas phase. Henry coefficients were defined in triplicate for each compound in both saline matrix and demineralized water.

The Henry coefficient was calculated by the following equation:

$$Hc = \frac{c_L}{c_g} = \frac{\frac{V_L c_{in} - V_g c_g}{V_L}}{c_g}$$

With Hc (-) as the water-air partitioning coefficient, C_L (µM) as the concentration in the liquid phase, C_g (µM) concentration in the gas phase, C_{in} (µM) initial concentration of organosulfur, V_L (L) volume of the liquid phase in the serum flask and V_g (L) volume of the gas phase in the serum flask.

5.2.5.2 Samples of lab scale bioelectrochemical reactor treating MT

The conversion of VOSCs in lab scale bioelectrochemical systems treating methanethiol was analyzed using the developed method for gas phase measurements and the obtained Henry coefficients in the saline matrix. A bioelectrochemical systems was constructed as described by Elzinga et al., and the biocathode potential was controlled at – 800 mV vs Ag/AgCl [18]. The reactors were inoculated with biomass obtained from a papermill wastewater treatment plant (Eerbeek, the Netherlands) and at the start of the experiment 75 µmol MT was added to the reactor. Gas samples (1mL) were taken during the first 9 days and analyzed directly. The Henry coefficients that were defined in this manuscript were used to estimate the concentration in the liquid phase.

5.3 Results and discussion

5.3.1 Method development

The method parameters were varied to obtain a good chromatographic response. The chromatograms show a good peak separation and resolution (Figure 1) under the conditions described in the materials and methods. Each compound has a different response area, which is typical for FPD systems were the response is influenced by the molecular structure [38,39]. The background noise of the blank sample was small indicating a high sensitivity for the sulfur compounds typical for FPD detectors [39]. The method had a high selectivity as no detectible interference was observed in the blank chromatograms in both gas and liquid phase.

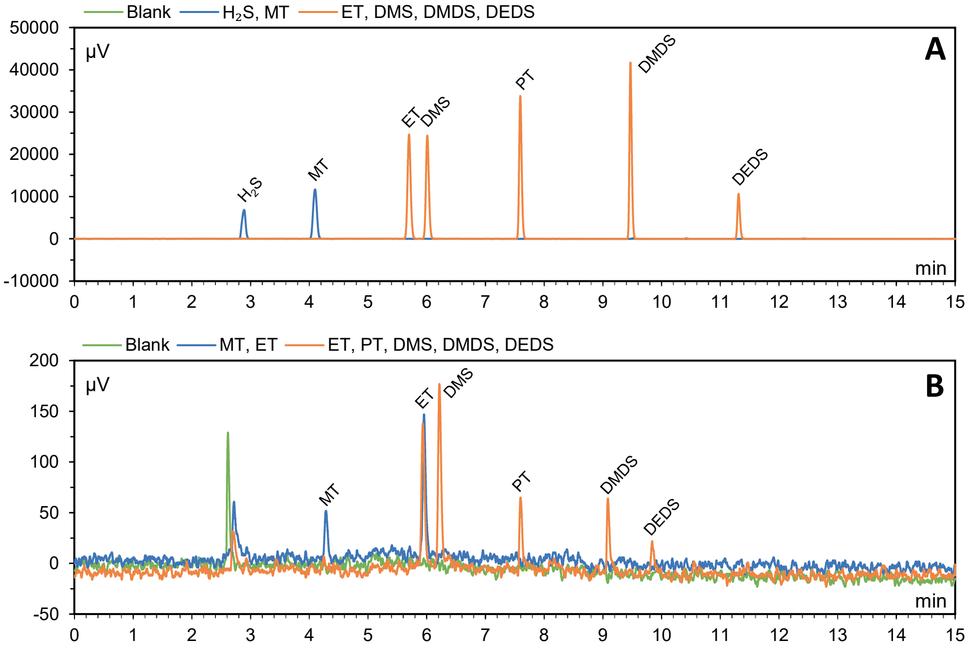

Figure 1 *Chromatogram showing a good peak separation of H2S, MT, ET, DMS, PT, DMDS and DEDS in the gas phase (A) and liquid phase (B) at the lowest gas calibration point.*

5.3.1.1 Equilibration time

The influence of the equilibration time in both the gas and liquid phase was evaluated by analyzing the response area after different equilibration times. The test showed a similar response area (SI-1) with RSD values of 0.29 % for ethanethiol in the liquid phase, and 0.35% for propanethiol and 0.46% for DMDS in the gas phase. The low variation between the different equilibration times shows sorption/desorption processes in the glass vials were finalized within 7 minutes for both propanethiol and

DMDS and that a gas-liquid equilibrium was obtained for ethanethiol within the same period. Similar behavior for the other organosulfur compounds was assumed. Therefore, a equilibration time of 7 minutes was considered sufficient to measure all compounds accurately.

5.3.1.2 Temperature gas standard preparation

The preparation of the mixed gas standard from pure liquids requires complete vaporization of these compounds towards the gas phase before further dilutions can be made to obtain the calibration line. Therefore, vaporization of the VOSCs was evaluated after heating the mixed gas standard to different temperatures. Full vaporization of thiols occurred at room temperature, whereas 30 minutes of heating at 50 °C was required for the full vaporization of disulfides (SI-2). This temperature was therefore used to prepare standards for further evaluation of the method.

5.3.1.3 Signal quenching

Signal quenching due to the coelution of hydrocarbon compounds is a well-known problem for flame photometric detectors [38,40,41]. The (bio)gas composition in industrial processes can vary substantially at different sites with varying concentrations of methane and carbon dioxide and may therefore influence the FPD response. Propanethiol and DMDS were used as model compounds to represent thiols and disulfides to evaluate the influence signal quenching (chromatograms can be found in SI-3). The response of PT and DMDS was close to 100% with increased carbon dioxide or methane concentrations (Figure 2). The results show a maximum response variation of 1.1 % for propanethiol and 1.6 % for DMDS compared to the 100% nitrogen reference. Therefore, the matrix effects and signal quenching due to the presence of methane and carbon dioxide were minimal under the evaluated conditions.

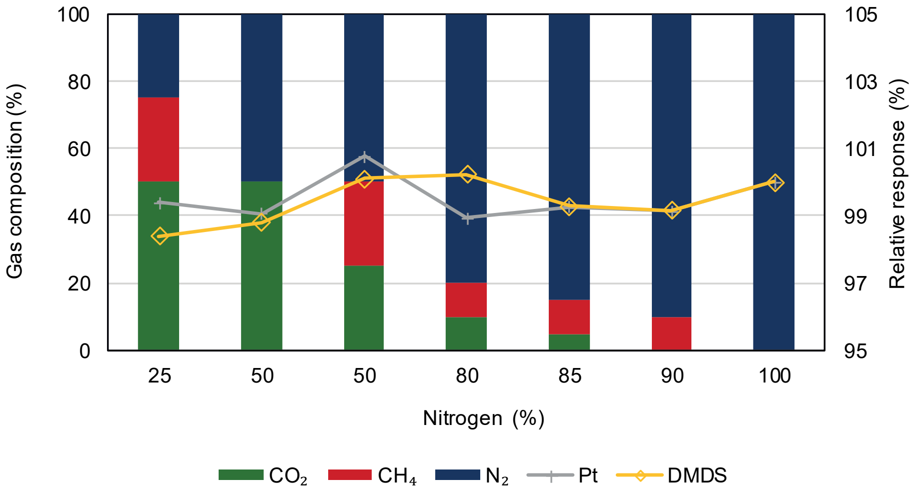

***Figure 2** The relative response of propanethiol (PT) and dimethyl disulfide (DMDS) at different gas compositions compared to the response under a 100% nitrogen atmosphere.*

Signal quenching in liquid samples due to the coelution of organic solvents e.g. methanol is another known phenomenon that can be limited by operating the injector in split mode [42]. However, the developed method was specified for a highly saline water solvent. VOSCs are more volatile compared to water and presence of water vapor was expected to have limited influence on the signal intensity and therefore not further evaluated.

5.3.1.4 Sample acidification and salting out effects

In general, organosulfur compounds oxidize faster at a high pH values [43] and acidification can be used as a strategy to minimize the oxidation and maintain sample integrity. Acidification of municipal wastewater samples with HCl in anaerobic vials was previously shown to suppress oxidation of methanethiol and samples remained stable for 24 hours [29]. Alternative strategies to avoid oxidation include the addition of Na_2SO_3 to a sample vial. Na_2SO_3 consumes the available oxygen and can limit oxidation. However, when added in excess, sodium sulfite can reduce DMDS to methanethiol, altering the concentrations of both components [29]. To maintain sample integrity, acidification was therefore preferred in this study.

The obtained response areas for acidified samples are presented in Table 2. The largest response area for each VOSCs was found when an acetate buffer was added to the samples. The response when HCl was used for acidification was 28 to 200 times smaller compared to the acetate buffer and samples acidified with a glycine and HCl showed almost no response for each of the organosulfur compounds. Interestingly, the solution with the highest pH after acidification showed the largest response area. A pH of 6.4 is sufficient to convert over 99% of thiols to their conjugate acid (i.e. pKa thiols >10 see SI-4), allowing them to transfer to the gas phase. Therefore, the acid formation did not form the main contribution for the increased exclusion of VOSCs from the liquid phase and the higher response areas that were found. This is also confirmed by the increased exclusion of disulfides which do not dissociate. The salting out effect on the other hand may have played a dominating role in the increased exclusion. The acetic acid buffer had the highest salinity and therefore might have the largest salting out effect. Which would also explain the increased exclusion of DMDS and DEDS.

Table 2 *Influence of acidification on pH and response area measured at an organosulfur concentration of 0.05 mM-S.*

		Response Area (µV*min)					
	pH	**MT**	**ET**	**DMS**	**PT**	**DMDS**	**DEDS**
No buffer	8.5	15	0	68	9	42	n.d[a]
0.2 M Glycine + 0.2 M HCl	4.7	30	24	79	22	0	0
0.5 M HCl	3.4	2.881	1.743	12.050	6.217	3.035	2.855
1 M Acetic acid	6.4	140.654	107.457	657.432	179.327	535.185	571.821

[a] *n.d = not detected.*

5.3.1.5 Simplification of liquid calibration procedure

Gas working standards were stable for 2 weeks after preparation when stored at 4 °C(See SI-5). Liquid working standards, however, did not remain stable and dimerization and oxidation reactions in the liquid resulted in various peaks in the chromatograms within 2 days after standard preparation (See SI-6). These peaks were not further identified, and liquid standards could thus only be used directly after preparation.

Gas standards were more stable compared to liquid standards and were therefore used to simplify the calibration procedure of the liquid phase. An average response ratio of 105.2 % for ET, 107.0 % for DMS, 105.7 % for PT, 108.9 % for DMDS and 106.0 % for DEDS was found (SI-7) when the use of gas standards to calibrate the liquid phase were compared to liquid standards. Therefore, the use of gas standards for liquid calibration under the applied conditions results in a slight underestimation of the actual concentration. However, we recommend the use of gas standards for liquid calibration for routine analyses, as it simplifies the calibration procedures and obtains good results to follow system dynamics and long-term trends.

5.3.2 Method validation

5.3.2.1 Linearity

Calibration lines for H_2S, MT, ET, PT, DMS, DMDS and DEDS for gas analyses were constructed over a concentration range of 0.074 - 1.85 µM. The calibration curves are presented in Figure 3a and 3b and the corresponding line equations can be found in Table 3. These calibration lines had exponential characteristics typical for FPD detectors. A linear relationship with determination coefficients $R^2 > 0.999$ for all compounds was obtained when analyzing the natural logarithm of the peak area and the natural logarithm of the sulfur concentration. Preliminary results showed that the concentration range could be extended to 10 µM without compromising the determination coefficients of the calibration line (results not shown). The extension of the calibration line was not further evaluated as gaseous samples can be diluted within the calibration range by adjusting the sample volume added to the 10 mL vials.

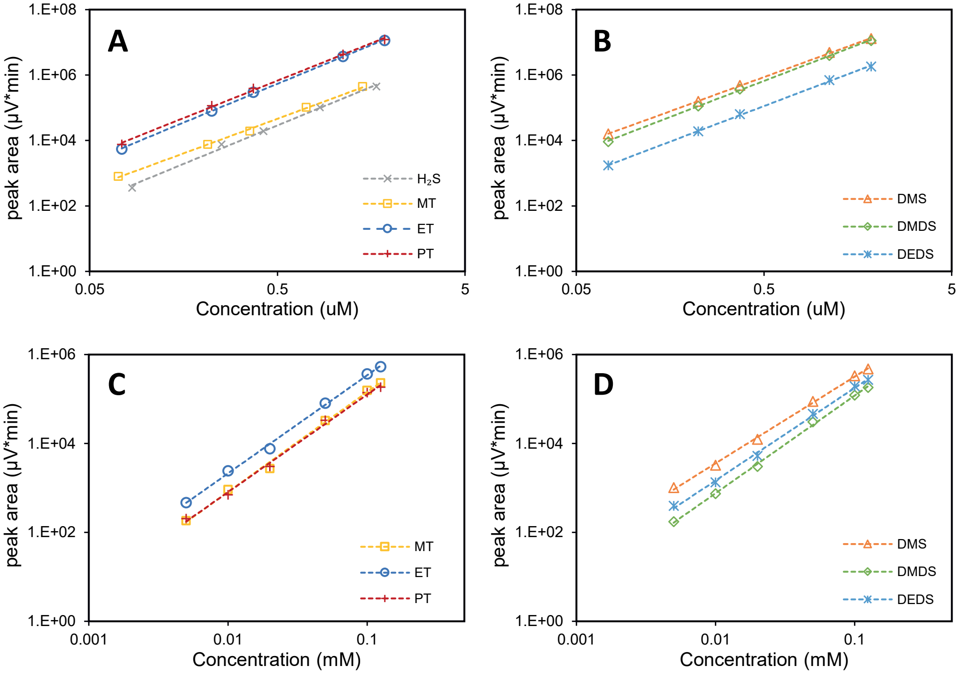

Figure 3. *Calibration curve and linearity of tested VOSCs in the gas phase (A and B) and liquid phase (C and D) using gas standards showing good linearity.*

The calibration lines for MT, ET, PT, DMS, DMDS and DEDS for liquid analyses were constructed over a calibration range of 5 - 125 µM (Figure 3c, 3d). Liquid samples with higher concentrations can be measured by decreasing the sample injection volume and addition of saline matrix reaching a total volume of 200 µL. The determination coefficient for liquid standards is slightly lower ($R^2 > 0.996$) than the determination coefficient for the gaseous standards and could be the result of the observed increased reactivity of organosulfur compounds in the liquid phase. Even though an increased reactivity in liquid standards was observed, the determination coefficients were still good. We observed an increased reactivity of the VOSCs standards when H_2S was added to the liquid standard (results not shown). When a calibration for H_2S in the liquid phase is required we recommend constructing separate calibration curves for H_2S and for VOSCs. For analyses of environmental samples containing both organosulfur compounds and H_2S in the liquid phase we recommend fast analyses to maintain sample integrity.

5.3.2.2 Reproducibility and detection limits.

Multiple gas calibration lines, produced over various days, indicated a high reproducibility with RSD values below 3.5% at the lowest calibration point (0.074μM) (Table 3). The liquid phase calibration lines showed lower RSD values ranging from 0.4% to 0.9% at the lowest calibration point (5μM). The increased reproducibility in liquid samples is likely related to the higher concentration at which the calibration of the liquid phase started. Cheng et al. measured organosulfur compounds in the liquid phase on a GC-MS and found RSD values in the same range with values varying between 0 and 8%. However, their method required a 25-min purge and trap pretreatment procedure [29], whereas the method described in this manuscript shows not only a higher reproducibility but is also based on direct measurement. Direct headspace analyses in wastewater samples was also performed by Sun et al., and showed a spiked sample recovery between 83 and 103% for MT, DMS and DMDS using a GC-SCD [25].

***Table 3** Overview of gas and liquid calibration parameters.*

Matrix	VOSCS	Calibration range μM	LOQ nM	LOD nM	Slope	Intercept	R^2	RSD %^{a}
Gas	H2S	0.084-1.68	10.05	4.22	2.114	12.200	0.999	1.85 (n=6)
	MT	0.071-1.42	16.2	7.07	2.114	12.200	0.999	1.35 (n=6)
	ET	0.074-1.85	5.76	3.72	2.372	14.838	0.999	3.08 (n=10)
	DMS	0.074-1.85	2.17	1.30	2.089	7.875	0.999	1.51 (n=10)
	PT	0.074-1.85	4.85	3.09	0.964	0.691	0.999	2.48 (n=10)
	DMDS	0.074-1.85	2.83	1.72	1.056	-1.034	0.999	2.70 (n=10)
	DEDS	0.074-1.85	4.83	2.90	0.951	-1.128	0.999	3.48 (n=10)
Liquid^b	MT	5-125	7.22	4.43	0.646	3.451	0.996	0.6 (n=10)
	ET	5-125	2.59	1.55	0.982	1.080	0.998	0.4 (n=10)
	DMS	5-125	2.01	1.18	1.126	-2.521	0.999	0.5 (n=10)
	PT	5-125	2.63	1.57	0.882	1.422	0.997	0.6 (n=10)
	DMDS	5-125	2.06	1.23	1.000	-0.053	0.999	0.5 (n=10)
	DEDS	5-125	14.02	7.66	0.948	1.004	0.998	0.9 (n=10)

^{a}RSD at for the lowest calibration point; 0.074 μM for gas and 5 μM for liquid standards; ^{b} Liquid calibration with gas standards

The limit of quantification for gas standards was between 2.17 nM and 16.2 nM and for liquid standards between 2.01 nM and 14.2 nM. Within the gas standards, the quantification limits were higher for the smaller molecules, i.e. hydrogen disulfide and methanethiol, whereas the limit of quantification in the liquid phase was especially high for DEDS. Indicative experiments (results not shown) demonstrated that the limit of quantification can be further increased by increasing the injection volume to the column for both gaseous and liquid analyses. The signal to noise ratio should be studied to further evaluate the limit of quantification when using larger injection volumes. Furthermore, the use of different split ratios may assist in avoiding loss of efficiency by overloading the column. Another strategy to increase the limit of quantification for liquid samples is to further explore the influence of acidification and salting out as these resulted in a higher VOSCs concentration in the headspace and an increased response area on the chromatograms. However, changes in matrix effect should be considered and further evaluated. Direct liquid injection is not preferred as the expansion volume of the water and the resulting pressure changes will limit the methods precision. Furthermore, the deposition of salts reduce the lifetime and efficiency of the column and requires frequent maintenance.

5.3.3 Method application

5.3.3.1 Henry coefficient determination

The Henry coefficient of ET, PT and DMS in demineralized water with our measurement method are similar to the Henry coefficients found in the literature (Table 4). However, the obtained Henry coefficients for DMDS and DEDS in this work are, in the same order of magnitude, but lower than previously reported Henry coefficients for reasons not well understood. Henry coefficients in the saline matrix are lower than coefficients obtained in demineralized water for each compound. This means that a larger fraction of the compounds was present in the gas phase. The salting out effect that drives thiols to the gas phase due to the high salinity and influences the Henry coefficient. The effect of increasing ionic strength resulting in lower Henry coefficients was also observed when comparing Henry coefficients obtained in demineralized water and sea water [44]. Another parameter that can influence the measured Henry coefficient is the acid base dissociation constant. The pKa of MT, ET and PT at 25°C is 10.33, 10.39, 10.44 respectively (SI-4) [45]. With a pH of 8.4 in the liquid matrix, only a small fraction <0.99% of the organosulfur is present as its conjugate base. Therefore, the pKa has a limited influence on the Henry coefficient and was not further considered.

Table 4. *Overview of the Henry coefficients for the five studied organosulfur compounds: ethanethiol, propanethiol, dimethyl sulfide, dimethyl disulfide, and diethyl disulfide, in demineralized water and saline matrix and their relative standard deviations.*

OSC	**Demineralized water** ***This study***	**Saline matrix** ***This study***	**Demineralized water** **[30]**	 **[32]**	 **[33]**
MT	11.93 ± 5.0	7.48 ± 1.0	9.88		
ET	5.90 ± 3.4	4.69 ± 0.4	6.88	5.45	
PT	5.03 ± 4.3	3.32 ± 1.0	5.99		
DMS	13.93 ± 5.2	9.46 ± 2.4	13.72	15.12	11.52
DMDS	13.53 ± 1.8	9.31 ± 2.7	22.22	20.58	14.38
DEDS	9.67 ± 2.6	6.24 ± 2.5	16.06	11.65	9.17

5.3.3.2 Samples of lab scale bioelectrochemical reactor treating MT

The results of the lab scale bioelectrochemical system treating methanethiol are presented in Figure 4. MT and DMDS were successfully measured with the developed method. No other organosulfur compounds nor H_2S were observed in the chromatograms (See SI-8 for an example chromatogram). The concentration of methanethiol decreased from 0.95 µM-S towards zero during the first 3 days of the experiment, while DMDS increased from 0 to 1.33 µM-S during the first two days. DMDS can be formed from methanethiol under microaerobic conditions in an autocatalytic or biocatalytic reaction. Not all MT was recovered in the form as DMDS which may be the results of microbial degradation, volatilization from the system or the formation of other, unknown, sulfur compounds. DMDS may also adsorb to the graphite felt electrode material, another reason why not al MT was recovered as DMDS. The applied chromatographic method can be used to further study the degradation kinetics and interaction of the organosulfur compounds with the electrode fur further development of this new technology. Furthermore, the method may also be used for the measurement of VOSCs in a full-scale bio-desulfurization plant that operates with a similar matrix.

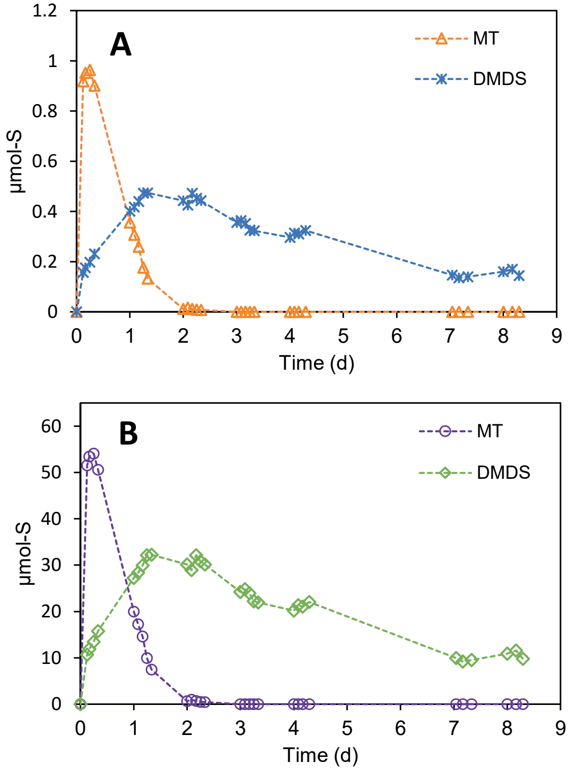

Figure 4 *Detected VOSCs in the gas (A) and liquid (B) phase of a bio electrochemical lab reactor treating methanethiol.*

5.4 Conclusion and outlook

A new method using GC-FPD was developed for routine analyses of VOSCs in complex liquid and gaseous samples. We demonstrated that apart from the more commonly measured compounds H2S, DMS and DMDS also PT, ET and DEDS could be measured accurately. VOSCs could be measured in a range from 5 µM-S to 125 µM-S for liquid and 0.08 - 1.85 µM-S for gaseous samples. Gas standards can be used to calibrate the liquid phase with response ratios between 105.2 - 108.9 % for the different VOSCs. Samples with higher concentrations could be easily diluted to fall within the calibration range. High reproducibility values with a relative standard deviation below 3.5% were found for both gas and liquid standards. The results show that signal quenching due to co-elution with carbon compounds in the gaseous phase was minimal under the tested concentrations. Henry coefficients were defined in both demineralized water and saline matrix and can be used to obtain a rapid indication of the concentrations in the liquid phase while only analyzing the static gas phase above the liquid. The method is suitable for routine analyses of highly saline samples with a high pH and can potentially be extended to other complex matrices.

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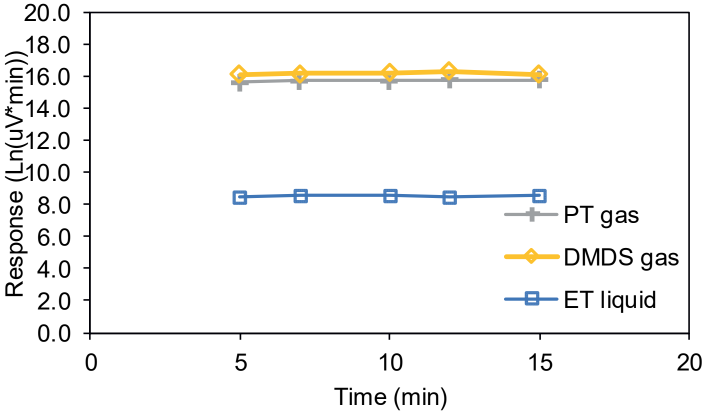
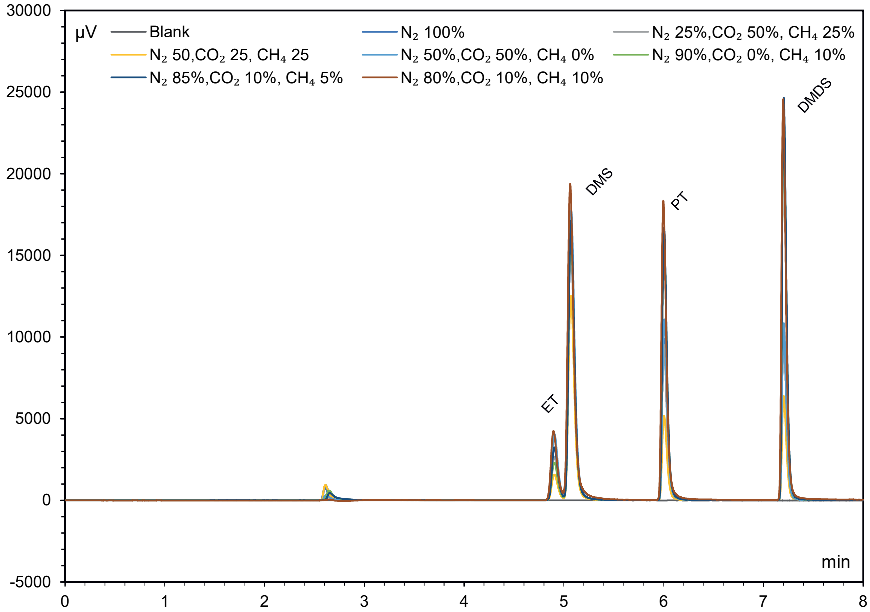
Supporting information



SI-1. *The response of a 10 µM-S standard in the liquid phase (ET) and gas phase (PT and DMDS) at different equilibration times.*

SI-2 *Effect of gas standard preparation temperature on the response area.*

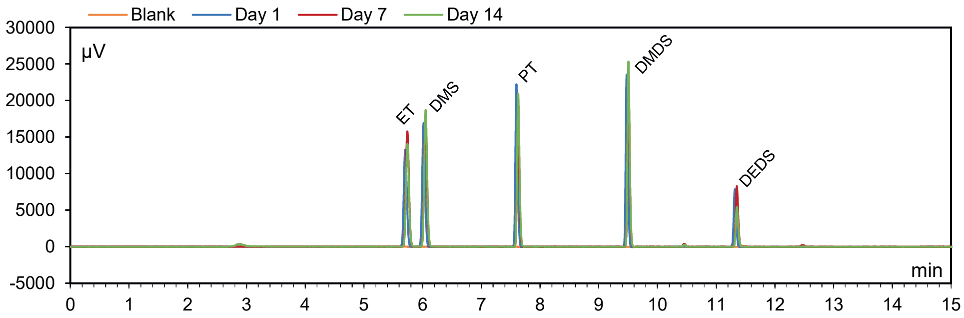
			Average Ln Area (µV*min)					**RSD %**				
Temp. (°C)	**Conc. (µM)**	**n**	**ET**	**PT**	**DMS**	**DMDS**	**DEDS**	**ET**	**PT**	**DMS**	**DMDS**	**DEDS**
20	0.223	5	11.8	12.0	12.1	11.8	9.66	0.575	0.568	0.425	2.01	4.32
20	0.372	5	15.3	15.4	15.5	15.2	13.1	0.626	0.620	0.323	1.31	3.59
40	0.223	3	12.1	12.2	12.3	12.2	11.6	0.748	0.737	0.701	0.836	1.60
40	0.372	3	15.4	15.6	15.6	15.6	14.8	0.455	0.449	0.449	0.523	1.38
50	0.223	3	11.9	12.1	11.4	12.2	11.1	0.765	0.748	1.21	0.808	1.57
50	0.372	3	15.2	15.5	15.5	15.6	14.5	0.249	0.244	0.282	0.482	1.17
60	0.223	3	12.0	12.2	12.3	12.4	12.4	0.292	0.287	0.308	0.486	1.25
60	0.372	3	15.3	15.6	15.5	15.7	15.7	0.371	0.366	0.393	0.461	1.34



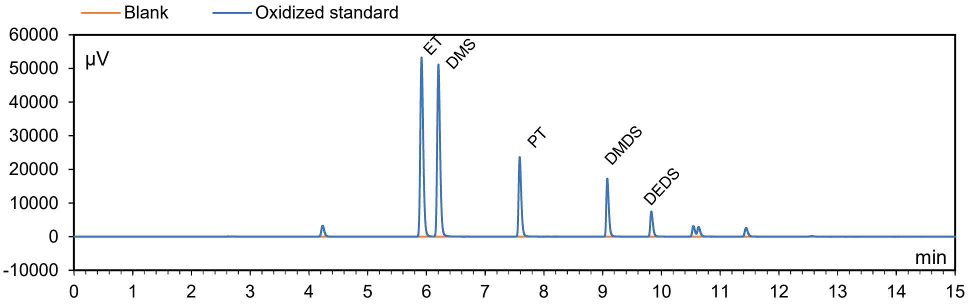
SI-3 *Chromatograms of ET, DMS, PT and DMDS in various synthetic biogas compositions.*

SI-4 *Properties of measured VOSCs*

VOSCs	**Solubility g/L in H₂O (25°C)**	**Boiling point °C**	**Vapor pressure kPa (25°C)**	**Acid dissociation pKa (25°C)**	**Log Pow**	**Reference**
H_2S	4.13	-60.3	1880 (20 °C)	6.90,12.92	0.11	[46,47]
MT	23.3	5.9	202 (26.1 °C)	10.30	0.54	[45,46,48]
ET	15.6	35.1	58.9 (20 °C)	10.39	1.27	[45,46,48]
PT	1.9	67.8	20.7	10.44	1.81	[45,46,49]
DMS	22.0	37.3	53.2	n.a.	0.84	[46,50]
DMDS	2.5	109.7	3.8	n.a.	1.77	[46,50]
DEDS	0.3	154.1	0.57	n.a.	1.77	[46,50]



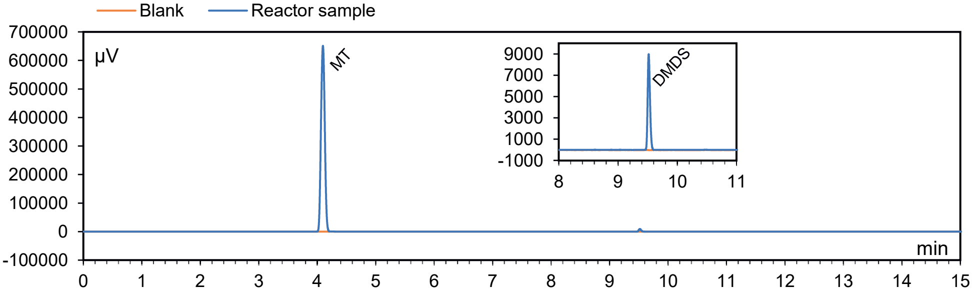
SI-5 Chromatograms of the lowest gas calibration standard at day 1, 7 and 14 after preparation.



SI-6 *Observed oxidation peaks in liquid standards after 2 days of storage.*

SI-7 *Recovery values using gas standards for liquid calibration*

Conc. µM-S	**n**	**ET**	**RSD**	**DMS**	**RSD**	**PT**	**RSD**	**DMDS**	**RSD**	**DEDS**	**RSD**
0.005	3	107.7	3.3	109.3	2.3	107.8	3.5	111.0	2.8		
0.035	3	105.2	0.3	107.1	0.3	104.3	0.2	107.9	0.2	106.9	0.6
0.065	3	104.3	0.6	106.2	0.6	103.7	0.5	106.9	0.6	105.8	0.8
0.095	3	104.8	0.6	106.7	0.6	104.2	0.7	107.3	0.5	106.4	0.6
0.125	3	104.1	1.2	105.8	1.0	103.5	1.1	106.2	1.0	104.9	1.1
Average		105.2		107.0		104.7		107.9		106.0	



SI-8 *Chromatogram of a gas sample obtained from a bio electrochemical system treating methanethiol.*

Chapter 6

Insights in ethanethiol degradation kinetics at biocathodes

Abstract

New technologies to remove organosulfur compounds from industrial sources should focus on the recovery of sulfur rather than incineration and sorption processes. The removal of organosulfur compounds using bio electrochemical systems might form a sustainable alternative. The aim of this study was to analyse ethanethiol degradation at biocathodes under anaerobic conditions. This was done by operating two cells at different loading rates for >360 days. We observed a stable removal efficiency of >70% with a maximum elimination capacity of 2.25 mM/d. Initially, ethanethiol was present in the effluent. However, over time, diethyl disulfide became the dominant organosulfur compound. Sulfate and thiosulfate were formed in small quantities in the biocathode. SEM imaging demonstrated the presence of crystalline structures with the typical bipyramid shape of elemental sulfur. The images also demonstrated the presence of a microbial community in a scattered biofilm on the electrode surface.

The biocathodes from the continuous experiments were used in the batch experiments to gain more insight in the degradation kinetics. No electron donor (other than ethanethiol) was added to these serum flasks. The experiments confirmed that the oxidation of ethanethiol into diethyl disulfide was mostly biocatalytic as ethanethiol oxidation rates were much lower in the controls. Dynamic modeling indicated that ethanethiol nor diethyl disulfide were further degraded under these conditions. We hypothesize that the oxidation of ethanethiol forms the first important step in the degradation of this compound and that diethyl disulfide can be further degraded under electrochemically controlled conditions.

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6.1 Introduction

Volatile organosulfur compounds (VOSCs) like methanethiol (MT), ethanethiol (ET) and their disulfides, dimethyl disulfide(DMDS) and diethyl disulfide (DEDS), are naturally present at low concentrations in various anaerobic environments [1–4]. However, in industrial processes, including the pulp and paper industry, wastewater treatment plants and natural oil and gas extraction sites, they are present at elevated concentrations[5–9]. Within the different industries a wide range of concentrations can be found. Typical observed concentrations may vary from 4 ppb(v) to <160 ppm(v) in the gas phase and from 30 to < 200 ppm(v) in the aqueous phase [10]. The VOSCs that are present in gas streams can be extracted to an aqueous phase via absorption. Adequate treatment of both gaseous and aqueous industrial product and waste streams containing VOSCs is required as: (1) the presence of VOSCs limits the removal efficiency of conventional biological and chemical desulfurization technologies, in which H_2S is removed and converted into re-usable elemental sulfur [11–13], (2) Thiols are highly reactive and the acidity of these compounds may cause severe corrosion problems in industrial installations [8], (3) the combustion of VOSCs will result in the formation of sulfur dioxide contributing to the formation of acid rain and dry acid deposition [14] and (4) VOSCs form a risk upon release into the environment as these compounds are hazardous to terrestrial and aquatic life at low concentrations [15].

Currently, the two main strategies for methanethiol and ethanethiol removal in the petroleum industry are focused on either oxidation to disulfides within the product streams or extraction into an aqueous phase coupled to oxidation [8]. The formation of disulfides lowers the toxicity and corrosivity of thiols. However, oxidation of thiols to their disulfides within the product stream does not change the total sulfur load [14]. The extraction into an aqueous phase coupled to oxidation results in a lower sulfur load and is typically performed via the Merox or Merichem process [8]. In the Merox and Merichem processes, the produced disulfides form an oily phase that can be separated from the aqueous phase. The disulfide fraction can be further processed in e.g., a hydro treating unit forming H_2S under high pressure and temperature or sold as chemical resource e.g. as food additives. The Merox or Merichem oxidation processes require prior removal of hydrogen sulfide to concentrations below 10 ppm to avoid an irreversible reaction between hydrogen sulfide and the caustic solution [8]. These technologies have high operational costs and are not applicable at small extraction sites with sulfur loads below 90 kg S-equivalent/d [8]. At these lower sulfur loads, organosulfur compounds are typically flared, which results in the formation of sulfur dioxide [14]. Alternatively, scrubbing or adsorption is applied for low sulfur loads which results in the production of non-regenerable aqueous and solid waste streams that needs to be disposed [8,16].

Biological treatment of waste streams has gained interest over the past decades. The low energy inputs, high selectivity and high efficiency of biological treatment processes make these an attractive alternative for chemical treatments in many fields [17–20]. Various attempts to degrade VOSCs in a biological anaerobic treatment systems showed that biodegradation is possible for methanethiol [21,22]. The degradation of ethanethiol, so far, has gained little research attention. The few studies focusing on biodegradation of ethanethiol were often unsuccessful or showed degradation at very low rates. For example, Leerdam et al., (2006) demonstrated the successful degradation of methanethiol and dimethyl disulfide in an UASB reactor but ethanethiol and propanethiol were not degraded [23]. The difficulty of anaerobic ethanethiol conversion was also shown by Xie et al., (2013). They reported an ethane formation yield from ethanethiol of 0.01% after 76 days of incubation in pre-cultured anoxic estuary sediments [24]. Slightly higher yields were obtained by Oremland et al., (1988) who found 0.6% ethane formation from ethanethiol in anoxic soda lake sediments [25]. Several studies focused on the anoxic and aerobic degradation of ET in bio-trickling filters [26–28]. The degradation of ET with nitrate as electron acceptor in an anoxic bio trickling filter reached elimination capacities of 9.57 mM/d and 29.04 mM/d. In these bio-trickling filters, elemental sulfur was formed as the main product [26,27]. An et al., (2010) found a maximum elimination capacity of 11.72 mM/d in an aerobic bio trickling filter and found sulfate as main sulfur product [28]. The aerobic conditions and the formation of sulfate in this technology are a disadvantage when applied for the treatment of natural gas since these limit the recovery of elemental sulfur from hydrogen sulfide [29].

The use of bio electrochemical systems (BESs) is an alternative strategy to remove VOSCs. In bio electrochemical systems, the combination of biofilm and electrode forms a biocathode or bioanode, and these can be used to selectively stimulate the conversion of thermodynamically unfavorable or complex reactions [30]. Recently, the degradation of methanethiol (0.013 mM/d), ethanethiol (0.015 mM/d), propanethiol (0.015 mM/d) and dimethyl disulfide (0.019 mM/d) towards sulfide was shown at a biocathode [31]. This approach has the potential of a new technology to convert VOSCs using electrons obtained from electrical current only. However, long term process stability, the influence of different control strategies, and organosulfur concentrations were not studied in these batch experiments. In this work, we evaluate the anaerobic degradation of ethanethiol in a continuous system for one year and evaluate the effect of different control strategies and VOSCs loading rates on the conversion and removal of ethanethiol. Insights in the kinetics of the process were obtained with batch experiments and modeling.

6.2 Materials and methods

6.2.1 Continuous system design and operation

Two bio electrochemical systems were constructed to evaluate the continuous reduction of ET at a biocathode (A schematic overview of the system design is provided in SI-1). The bio electrochemical cells consisted of a plexiglass anode flow compartment (33 cm^3) and a PEEK cathode flow compartment. PEEK was used for its chemical resistance and to minimize losses of volatile ethanethiol. The electrolytes in the two compartments were separated by a cation exchange membrane (Fumasep®FKB-PK-130), Fumatech, Germany) with a projected surface area of 22.3 cm^2. A titanium plate coated with Pt/IrO_2 (80:20) was used as anode and current collector. The cathode consisted of 5 layers of graphite felt (CTG Carbon GmbH, Germany) that was tightly packed between the membrane and the graphite plate current collector. Viton gaskets were used to seal the systems. The electrochemical cells were assembled between two Plexiglas support plates that were screwed tightly together with polyolefin coated screws. Fluran® F-5500-A tubing was used in inflow and recirculation pumps for its high chemical resistance and low gas permeability. PTFE tubes coated with gas resistant foil were used for recirculation flows. An Ag/AgCl reference electrode (+210 mV vs NHE, Prosense, Oosterhout, the Netherlands) was placed in the middle of the flow chamber on the surface of the graphite felt cathode with a capillary using a 3M KCl salt bridge. The electrochemical control was performed with a potentiostat (Ivium, the Netherlands). The systems were operated at room temperature (23 ± 1 °C). The anode compartment was continuously sparged with nitrogen (3.4 L/h) to remove oxygen.

The biocathodes were operated for 45 days prior to the start of the experiment, during which small improvements were made to the setup. At day 0 and day 107 the cathodes were inoculated. The biocathodes were subjected to changes both in electrochemical control strategy and loading rate during the 404 days of operation (see Table 1 for details). Until day 106, the cathodes were controlled at a constant current, which was stepwise changed between 2 and 6 A/m^2. This was followed by a potential controlled phase at -0.5 V vs Ag/AgCl. The biocathodes were temporarily operated at open circuit potential (OCP) from day 319 until day 340 in cell 1 and from day 296 to day 340 in cell 2 the biocathodes were operated at open circuit before they were returned to potential control. The volumetric loading rate (VLR) at the start of the biotic experiment was 1.8 mM/d and was lowered to 0.5 mM/d after 47 days. Thereafter the VLR was gradually increased up until 3 mM/d. The reactors were operated as duplicates and small VLR changes between the two reactors resulted from variations in the influent pump flow rate.

***Table 1** Overview of averaged operational conditions during the continuous operation of biocathodes fed with ethanethiol.*

Days	Electrochemical control	Infl. mM VOSC-S Cell 1	Infl. mM VOSC-S Cell 2	VLR mM VOSC-S/d Cell 1	VLR mM VOSC-S/d Cell 2	HRT d Cell 1	HRT d Cell 2
-44	OCP	4.0	4.0	0.5	0.5	8.0	8.0
-31	-2 A/m2	4.0	4.0	2.0	2.0	2.0	2.0
-8	-4 A/m2	4.0	4.0	2.0	2.0	2.0	2.0
0	-4 A/m2	4.0	4.0	1.8	1.8	2.2	2.2
44	-6 A/m2	4.0	4.0	1.8	1.8	2.1	2.1
47	-6 A/m2	1.1	1.1	0.5	0.5	2.1	2.1
53[a]	-4 A/m2	1.1	1.1	0.5	0.5	1.8	1.8
106[b]	-0.5 V vs. Ag/AgCl	1.0	1.0	0.5	0.5	1.9	1.9
142	-0.5 V vs. Ag/AgCl	1.0	1.0	0.4	0.4	2.2	2.2
148	-0.5 V vs. Ag/AgCl	2.2	2.1	1.0	0.9	2.3	2.3
188	-0.5 V vs. Ag/AgCl	2.6	2.8	1.3	1.4	2.1	2.0
203	-0.5 V vs. Ag/AgCl	2.7	2.8	1.7	1.7	1.7	1.6
286	-0.5 V vs. Ag/AgCl	2.8	2.8	2.1	2.1	1.4	1.4
296/319[c]	OCP	3.1	3.1	2.5	2.4	1.2	1.3
341	-0.5 V vs. Ag/AgCl	2.9	2.9	2.4	2.4	1.2	1.2
347	-0.5 V vs. Ag/AgCl	3.0	3.3	2.8	3.0	1.1	1.1

[a] No VOSC-S measurements were taken from day 70 to day 122; [b] Both biocathodes were reinoculated at day 107; [c] Cell 1 was in OCP from day 296 onwards and cell 2 from day 319 onwards.

6.2.2 Medium and inoculum

The catholyte had a high salinity and pH similar to biological desulfurization plants [32]. It contained 4.42 g/L Na_2CO_3, 49 g/L $NaHCO_3$, 0.2 g/L $MgCl_2$ x 6 H_2O, 1 g/L KH_2PO_4, 0.01 g/L $CaCl_2$ 2 H_2O, 0.6 g/L CH_4N_2O, 1 g/L NaCl, with a final pH of 8.4 and a conductivity of 40.3 mS/cm. The average pH in the catholyte was 8.77 and did not vary substantially with changes in loading rate or HRT because of the high carbonate concentration in the medium. Trace element stock solutions were prepared as described by Pfennig & Lippert (1966) [33] and were added with 1 mL/L. Additionally, 1 mL/L of a stock containing 30 mg/L $Na_2SeO_3 \cdot 3\ H_2O$ and 40 mg/L $Na_2WO_4 \cdot 2\ H_2O$ was added to stimulate growth of methanogenic archaea [34]. The medium was purged for 30 minutes with nitrogen gas before it was transferred to a 1 L multilayered influent bag (MediSense, Sense trading, The Netherlands). ET was added to the influent bag with a gas tight syringe (Hamilton, USA) with a final concentration of 1, 2, 2.8 and 4 mM-S. The anolyte consisted of a phosphate buffer with 5.0 g/L K_2HPO_4 and 67.0 g/L KH_2PO_4 with a final pH of 5.8.

The continuous reactors were inoculated with 2 mL biomass obtained from a mixture of (i) the anaerobic wastewater treatment plant at the papermill factory in Eerbeek, The Netherlands, and (ii) the sewer system of the Environmental Technology department of Wageningen University and Research, The Netherlands. Before inoculation, equal volumes of the biomass granules and sewer slurry were crushed with an immersion hand blender and washed 3 times. The washing procedure consisted of a centrifuging step at 5000 RPM, replacing of the supernatant with fresh medium and resuspension of the biomass.

6.2.3 Batch experiments

After the continuous operation of the biocathodes, the electrodes were taken from the cell and tested for their ET degradation activity (without additional electron donor) in serum flasks. Eight 120 mL serum flasks were filled with 50 mL medium and 2 cm^2 graphite felt. Clean graphite felt was used for the 2 controls, and pieces of felt from every layer of the biocathodes (0.4 cm^2) of cell 1 and cell 2 were used. These were tested in triplicate. The serum flasks were closed with chlorobutyl rubber stoppers (Chemglass CLS-4209-14, USA) , and the gas phase contained a CO_2:N_2 mixture at 20:80 with a final pressure of 1.4 bar. ET (25 µmol) was injected in each bottle from a 10 mM liquid standard. The serum flasks were incubated at room temperature and mixed at 150 RPM for 57 days.

6.2.4 Analytical techniques

The headspace of the recirculation liquid was sampled 3-5 times a week to measure the concentration of methanethiol, ethanethiol, propanethiol, dimethyl sulfide, dimethyl disulfide, and diethyl disulfide. These VOSCs were analyzed using a gas chromatograph (Shimadzu Nexis GC-2030, Shimadzu, Germany) equipped with a flame photometric detector (FPD) and a headspace autosampler (Shimadzu H20 plus, Shimadzu, Germany) as described by Elzinga et al., 2022 [35]. The concentration in the aqueous phase was calculated with the henry coefficients determined in the same matrix under the assumption that the gas and liquid phase were in equilibrium in batch and continuous experiments. The concentrations of CH_4, N_2, O_2, CO_2 and H_2 in the headspace were measured twice a week using gas chromatography according to the method described by Liu et al., 2007 [36]. Ion chromatography was used to measure sulfate and thiosulfate twice a week as described by Elzinga et al., 2020 [31] Lead acetate paper was used to determine if sulfide was present. Upon the detection of sulfide with lead acetate paper, spectrophotometry (LCK 653, Hach, Germany) was used to obtain the total sulfide (S^{2-}, HS^- and H_2S) concentration. Spectrophotometry was also used to analyze the concentrations of total and dissolved nitrogen (LCK 338, Hach, Germany). The microbial community was analyzed with Next Generation Sequencing.

6.2.5 Microbial community analysis

DNA samples were collected from the center of each graphite felt layer. The different pieces of graphite felt were cut in small pieces and combined to one sample for each cell. DNA was extracted with the QIAGEN Powersoil DNA isolation kit. PCR was used to amplify the V3-V4 region of the 16S-rRNA gene using the universal primer set described by Takahashi et al. (2014), Uni340F (5′-CCTACGGGNBGCASCAG-3′) and Uni806R (5′-GGACTACNNGGGTATCTAAT-3′)[37]. The sequencing was performed using Illumina Miseq 500. The taxonomic analysis was performed using QIIME 2 software. The tool Dada2 was used to join, de-noise and quality filter the reads. The tool feature-classifier was used to taxonomically classify the sequences based on Greengenes 13_8. The diversity analysis was performed using the qiime2 diversity tool. The tool computes several beta diversity metrics, and generated principal coordinates analysis (PCoA) plots using Emperor.

6.2.6 Model description

Matlab was used to write a kinetic model describing the chemical and microbial processes in the system[38]. The data from cell 1 and 2 were combined and treated as one data set for the model predictions. Chemical and microbial conversions were described with first-order kinetics and adsorption and desorption processes were described.

6.2.6.1 Mathematic description of batch experiments

An oxidation reaction (either chemical or biological) of ethanethiol towards diethyl disulfide was observed in the batch experiments. Furthermore, adsorption and desorption of DEDS was assumed. The following 3 reactions were considered to describe the batch experiments.

Oxidation reaction (biological or chemical):

$$2\,ET \rightarrow DEDS_L + 2H^+ + 2e^- \qquad \text{(eq. 1)}$$

Adsorption of DEDS to felt:

$$DEDS_L \rightarrow DEDS_{ad} \qquad \text{(eq. 2)}$$

Desorption of DEDS from felt:

$$DEDS_{ad} \rightarrow DEDS_L \qquad \text{(eq. 3)}$$

It was assumed that ethanethiol oxidation (eq. 1) follows first-order kinetics, according to:

$$R_{1,bio} = k_{ox,bio} \cdot [ET] \cdot A_{bio} \qquad \text{(eq. 4)}$$

$$R_{1,chem} = k_{ox,chem} \cdot [ET] \cdot A_{chem} \qquad \text{(eq. 5)}$$

Where $R_{1,bio}$ and $R_{1,chem}$ are first-order reaction rates (mM/day), $k_{ox,bio}$ and $k_{ox,chem}$ are the first-order reaction constants in the biological experiments and chemical controls, respectively (1/(day cm^2)), $[ET]$ is the concentration of ethanethiol in the solution (mM) and A is the surface area of the felt (cm^2). The subscript *bio* indicates that a biofilm is present and represents the combined chemical and biological rates in a biotic experiment. The subscript *chem* represents strictly chemical conversions. The adsorption of DEDS to the felt is based on the Langmuir adsorption kinetics, where the adsorption to the felt (R_2) and desorption to the felt (R_3) are described by:

$$R_2 = k_{ad} \cdot [DEDS_L] \cdot \frac{A}{V} \cdot \left(1 - \frac{[DEDS_{ad}]}{[{DEDS_{ad}}^{max}]}\right) \quad \text{(eq. 6)}$$

$$R_3 = k_d \cdot \frac{[DEDS_{ad}]}{V} \quad \text{(eq. 7)}$$

Where k_{ad} and k_{d} are constants of forward adsorption reaction and backward desorption reaction (L day^{-1} cm^{-2} and cm^2 day^{-1} respectively), $[DEDS_L]$ is the concentration of DEDS in the aqueous phase (mM), the term $\left(1 - \frac{[DEDS_{ad}]}{[{DEDS_{ad}}^{max}]}\right)$ represents the fraction of unoccupied surface area of the felt with $[DEDS_{ad}]$ as the absorbed DEDS concentration (mmol cm^{-2}), $[{DEDS_{ad}}^{max}]$ the maximum concentration of absorbed DEDS (mmol cm^{-2}) , A the surface area of the electrode (cm^2) and V the liquid volume of the batch bottle (L), For the parameter estimation, the following dynamic model was used:

$$\frac{d[ET]}{dt} = -R_1 \quad \text{(eq. 8)}$$

$$\frac{d[DEDS_L]}{dt} = R_1 - R_2 + R_3 \quad \text{(eq. 9)}$$

$$\frac{d[DEDS_{ad}]}{dt} = R_2 - R_3 \quad \text{(eq. 10)}$$

It should be noted that R_1 can be either the biological rate (eq. 4) or the chemical rate (eq. 5).

6.2.6.2 Model parameter estimation

The unknown parameters in the model, represented by parameter vector θ, are estimated using the experimental data of the batch experiments. Via a least square routine, the estimated parameter output vector ($\hat{\theta}$) is given by:

$$\hat{\theta} = argmin_{\theta \in D} \sum_{i=1}^{N} \varepsilon(\theta)^2 \qquad \text{(eq. 11)}$$

Where $\varepsilon(\theta) = y(i) - \hat{y}(\theta)$ is the output error at measurement index N, $y(i)$ the measured concentration (either $[ET]$ or $[DEDS_L]$) at time i, $\hat{y}(\theta)$ the predicted model output given with estimated θ, the concentration of organic sulfur component in the solution (mM) and D is the parameter domain. The measure for the model fit, error variance ${\sigma_\varepsilon}^2$, is given by:

$${\sigma_\varepsilon}^2 = \frac{\sum_{i=1}^{N} \varepsilon(\theta)^2}{N-p} \qquad \text{(eq. 12)}$$

With p the number of parameters. In case more than one parameter is estimated, the standard deviation for each parameter is found by the square root of the diagonal of the covariance matrix (COV), which is defined by:

$$COV = {\sigma_\varepsilon}^2 \cdot (SENS^T\ SENS) \qquad \text{(eq. 13)}$$

where $SENS$ is the (N x p) sensitivity matrix with elements $\frac{\partial \varepsilon(ORP_i | \theta)}{\partial \theta_j}$. The index $j=1,..,p$ represents the index of the estimated parameter.

6.2.6.3 Model Parameter Calibration and Validation

The unknown parameters $k_{ox,bio}$, $k_{ox,chem}$, k_{ad}, k_d and $[{DEDS_{ad}}^{max}]$ were calibrated in four subsequent steps. First, $k_{ox,bio}$ was estimated using the obtained data of the biological batch experiments. Subsequently, the parameters describing the absorption and desorption to the graphite felt were estimated i.e. k_{ad}, k_d and $[{DEDS_{ad}}^{max}]$. In addition to the same experimental data set, the calibrated parameter for $k_{ox,bio}$ was used to calibrate these parameters. Finally, $k_{ox,chem}$ was calibrated using the chemical batch experiments. In addition, the calibrated parameters for the absorption were validated.

6.3 Results and discussion

The bio electrochemical cells with continuous inflow of ET were operated over 360 days period to facilitate biofilm growth, reach stable operation, assess long term process stability, and study the removal efficiency under different ET loading rates and electrochemical control strategies. After ending the run, part of the cathode felt was harvested and controlled, dynamic batch experiments were performed to obtain better insight in the dominant kinetic parameters without external electron donor.

6.3.1 Biodegradation of ET without hydrogen or electricity

To study the dominant kinetics of ET degradation, several batch experiments were performed. In these experiments, no electron donor (hydrogen or electricity) other than ET was present. In these batch experiments, ET and DEDS concentrations were monitored in the presence of graphite felt, with and without biofilm. No other VOSCs or H_2S were observed in the chromatograms. In figure 1, the measured and modelled concentrations of ET and DEDS in the aqueous phase are presented. The serum flasks that contained graphite felt with biofilm show a substantially faster oxidation of ET to DEDS compared to the controls that contained clean graphite felt without biofilm. This indicates that the biofilm plays an important role in the conversion of ET to DEDS. An average ET removal of 94.6±3.4% in cell 1 and 98.4±2.3% in cell 2 was observed within 5 days, while the ET removal in the controls was 22.5% and 40.5% over the same time span.

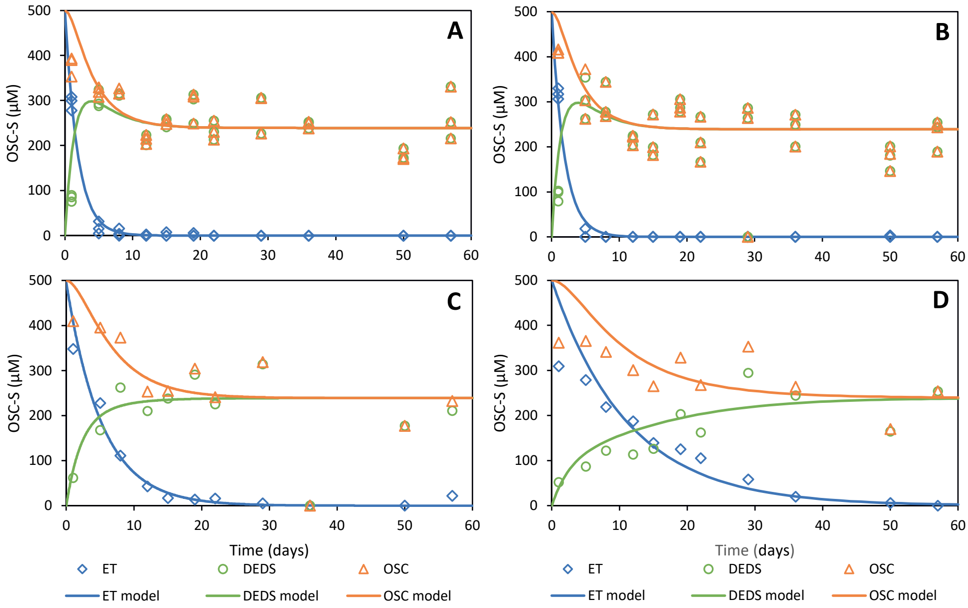

Figure 1 *Distribution of measured and modeled ethanethiol (ET) diethyl disulfide (DEDS) and total organosulfur (OSC) concentrations in the aqueous phase of serum flasks. The serum flasks were inoculated with graphite felt obtained from two continuously operated ethanethiol removing bio electrochemical systems (A and B) and clean graphite felt in the chemical controls (C and D).*

Not all sulfur from the removed ET was recovered as sulfur in DEDS, indicating that DEDS was partially converted or removed. The DEDS concentrations appear to stabilize during the experiment, which makes diffusion of DEDS out of the batch bottles unlikely. The formation of sulfide and sulfate, possible degradation products of ET and DEDS, in the serum flasks were monitored in time. No sulfide was observed in the serum flasks. While at the end of the experiment, sulfate accounted for 1.2 ±0.5% of the total sulfur added as ET at the start of the experiment in the controls and was similar (0.9 ± 0.3%) for the electrodes with biofilm. These low levels of sulfate indicate that sulfate is not the main degradation product under these conditions. Possibly, sulfur was one of the degradation products, and was indeed detected on the graphite felt (see figure 4).

The model parameters were calibrated based on the described procedure in the materials and methods. All experimental data for the electrodes with biofilm (in total 6 batch experiments) were clustered to obtain the biological kinetic parameters. The overall results of the parameter estimation are shown in Table 2. The model describing the conversion of ET to DEDS in both control and biotic experiments showed a good fit using first order kinetics, i.e. a relative small σ. In addition to the biological oxidation rates of ET to DEDS, the experimental data were used to calibrate the parameters for adsorption of DEDS to the graphite felt. The covariance matrix resulting from the estimation routine reveals that k_d and $[DEDS_{ad}{}^{max}]$ are strongly correlated, as can also be seen in the chosen model structure (see equation 6). These parameters are difficult to estimate individually, as shown by the relatively high standard deviation, and indicates that the desorption constant is strongly related to the maximum adsorption capacity of the graphite felt.

***Table 2**. Estimated parameters with corresponding standard deviations*

Parameter	**Unit**	**Estimate**	$\boldsymbol{\sigma}$
$\boldsymbol{k_{ox,bio}}$	day^{-1} cm^{-2}	2. 68 x 10^{-1}	1.24 x 10^{-2}
$\boldsymbol{k_{ox,chem,1}}$	day^{-1} cm^{-2}	9.52 x 10^{-2}	8.31 x 10^{-3}
$\boldsymbol{k_{ox,chem,2}}$	day^{-1} cm^{-2}	4.46 x 10^{-2}	5.57 x 10^{-3}
$\boldsymbol{k_{ad}}$	L day^{-1} cm^{-2}	5.55 x 10^{-3}	2.45 x 10^{-3}
$\boldsymbol{k_{d}}$	cm^{2} day^{-1}	3.52 x 10^{-3}	1.76 x 10^{-2}
$\boldsymbol{[DEDS_{ad}{}^{max}]}$	mmol cm^{-2}	3.99 x 10^{-1}	1.12

Two first-order chemical constants were estimated, because significant differences were found in the degradation rates for the two chemical control experiments. The substantially higher rate constant found for the experiments with biofilm confirms that the biofilm plays a dominant role in the conversion of ET, even though no additional electron donor was present. The calibrated parameters for absorption and desorption of DEDS were used to model the DEDS concentrations in the chemical batch experiments. As can be seen in figure 1, the model fits the data satisfactorily.

The stabilized DEDS concentration was lower than the amount of ET added in all experiments. This might indicate that part of the DEDS is adsorbed to the graphite felt. Therefore, adsorption and desorption kinetics, as described by equations 6 and 7, were used to describe the fate of DEDS in the solution. The adsorption of DEDS thus also seems to play a role in a bio electrochemical system with graphite felt as cathode material. Since the DEDS concentrations in these biological experiments stabilized with time, continuous conversion of DEDS to another degradation product with no alternative electron donor is unlikely to occur at reasonable rates (see SI-II for the obtained modeling results when assuming the continuous degradation of DEDS).

6.3.2 Biodegradation of ET at biocathodes

Two bio electrochemical systems were continuously fed with ET and were operated for over 360 days. During the operation, varying ET loading rates and electrochemical control strategies were applied.

6.3.2.1 Development of current and potential

During the first 107 days, the biocathodes were current controlled at -4, -6 and -2 A/m^2 (Figure 2A and 3A). The applied current resulted in a potential ranging between -1.4 and -1.0 V vs. Ag/AgCl in cell 1 and -1.2 and -1.0 V vs Ag/AgCl in cell 2. The cathode potentials decreased when the current was increased to -6 A/m^2 and increased again at the lower current of -2 A/m^2. The increase in cathode potential is typically shown in biocathodes during biofilm establishment. When the biocathodes were potential controlled, the current density was stable and did not increase over time.

In the first period, when current was controlled, the cathode potentials were lower than the theoretical hydrogen evolution potential (-0.729 V vs Ag/AgCl at pH 8.77 and a hydrogen pressure of 0.2 atm) and hydrogen was formed at the biocathodes (See SI-IV). From day 106 onwards, the biocathodes were potential controlled at -0.5 V vs Ag/AgCl and the resulting current density ranged between -0.2 A/m^2 and -0.4 A/m^2. At this potential of -0.5 V, electrochemical hydrogen production is unlikely and can only occur at extremely low hydrogen partial pressures ($<1.84 \cdot 10^{-8}$ atm). Indeed, only trace (<0.02%) amounts of hydrogen were detected in the headspace. Interestingly, even though the potential of -0.5 V was too low for hydrogen generation, still a reasonable current density of -0.2 to -0.4 A/m^2 was observed.

Cell 1

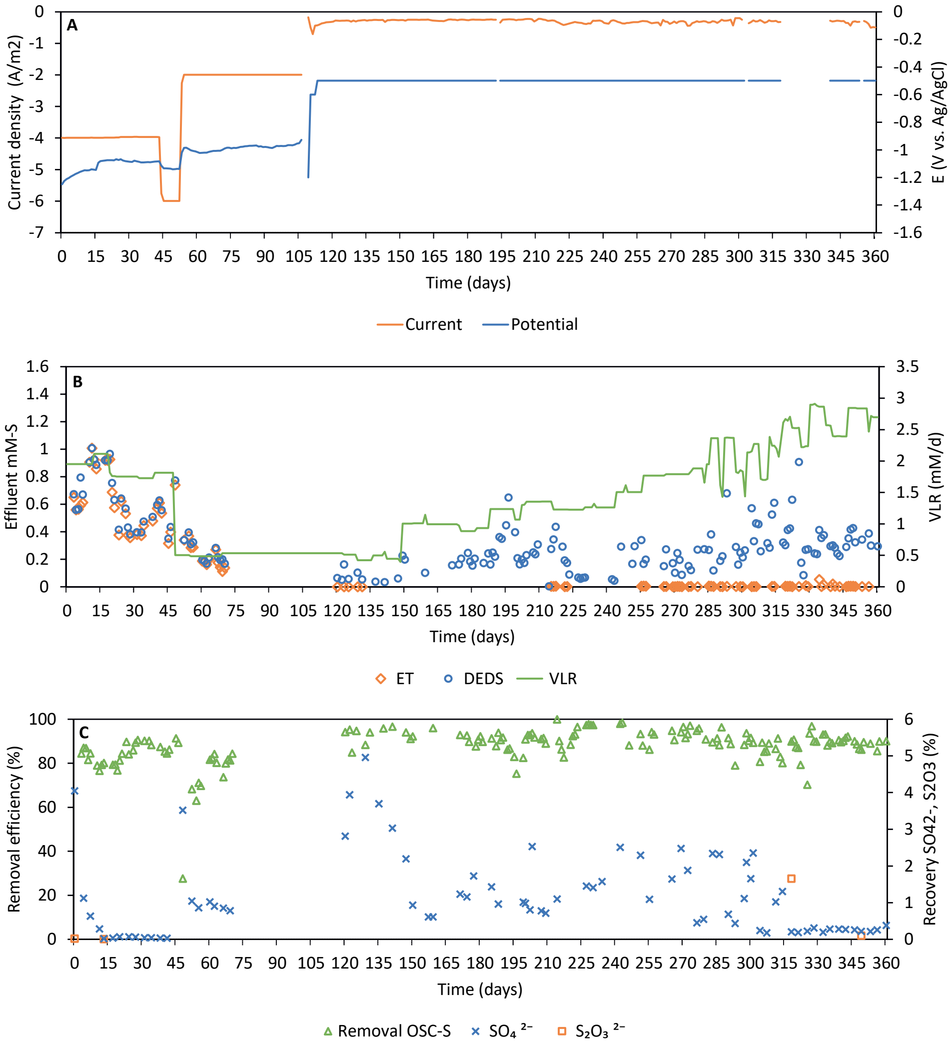

Figure 2. ***A*** *The development of current and potential,* ***B*** *volumetric loading rate and effluent organosulfur concentrations and* ***C*** *organosulfur removal efficiencies and sulfur recoveries at the biocathode of experiment 1. No VOSCs measurements were taken from day 70 till day 122.*

Cell 2

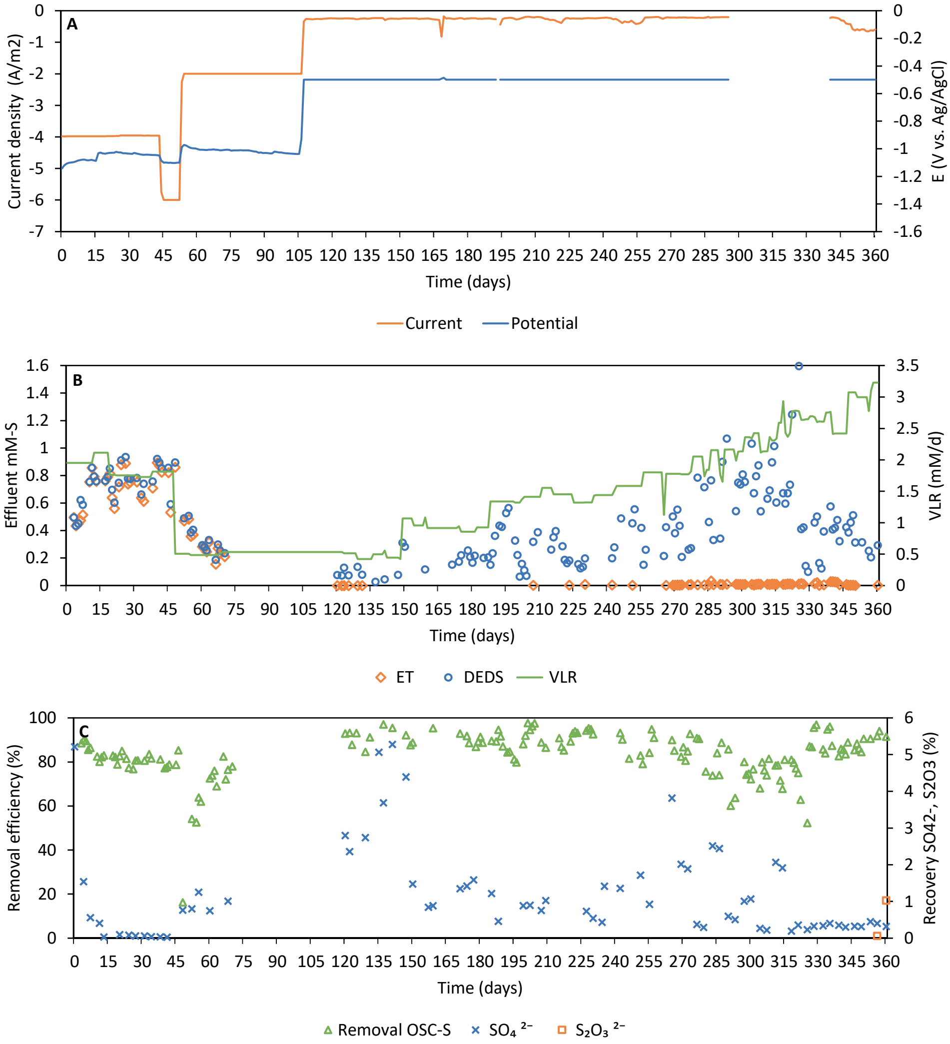

Figure 3 ***A*** *The development of current and potential,* ***B*** *volumetric loading rate and effluent organosulfur concentrations and* ***C*** *organosulfur removal efficiencies and sulfur recoveries at the biocathode of experiment 2. No VOSCs measurements were taken from day 70 till day 122.*

6.3.2.2 Ethanethiol removal at both biocathodes.

Figure 2B and 3B show the ethanethiol loading rate at the biocathodes and the organosulfur concentrations in the effluent of cell 1 and cell 2. The concentration of ET initially increased in both biocathodes. The ET levels in cell 1 started to decline 15 days after inoculation. Despite the reducing conditions at the cathode, we observed the oxidation product DEDS at concentrations between 15 and 65 μM-S. In cell 2, the effect of inoculation was less profound. ET levels started to decline only after the VLR was lowered from 4 to 0.5 mM/d. The DEDS concentrations were similar in both cells. After day 120, the main organosulfur compound found in both biocathodes was DEDS, while the concentration of ET remained mostly below 10 μM. The increase in loading rates after day 149, obtained by either altering the HRT or influent concentration, resulted in a gradual increase of DEDS in the effluent, while ET concentration remained low.

The biological oxidation of ET to DEDS under anaerobic conditions was also found in the batch experiments and modeling results. The model and the batch experiment results also demonstrated that further conversions of DEDS did not occur. Based on the model predictions, 52% of the DEDS was adsorbed to the graphite felt in the batch experiments. The obtained adsorption constants were extrapolated to the continuous setup (See SI-III). The results show that the graphite felt in the continuous experiment would be saturated after 15 days and that >90% of the ET fed to the biocathodes would be present as DEDS in the effluent after this period. However, DEDS recovery in the effluent was lower and therefore DEDS was further converted at the biocathodes (See SI-V). We postulate that adsorption may play a role (initially) in the continuous system but does not form the main removal mechanism. It seems that the combination of electricity and biofilm is essential for the continuous degradation of DEDS as no continuous degradation of DEDS occurred in batch experiments without external electron donor.

After more than 300 days of operation, there was a period of 35 and 45 days in which cell 1 and cell 2 were operated under open circuit. During this period, both the removal efficiency and the organosulfur speciation remained similar compared to the potential controlled period. It remains unclear why removal of DEDS continued during OCP. One potential mechanism would be adsorption of DEDS to the electrode and other reactor materials.

6.3.2.3 Stable high removal efficiency

The organosulfur removal efficiencies at the start of the experiment were close to 85% in both biocathodes (Figure 2C and 3C). Over the first 15 days, the removal efficiency decreased towards 75%. An increase in removal efficiency was observed in cell 1 between day 15 and 28, while the removal efficiency in cell 2 stabilized. At day 47, when the VLR was lowered to 0.5 mM/d, the removal efficiency dropped temporarily which is explained by the relatively high concentration in the system while the influent concentration was lowered. The removal efficiency was stable around 95% during the last 26 days under this loading rate. During the rest of the experimental run, while loading rates were increased, the removal efficiency remained high, between 85% and 95%, in cell 1. In cell 2, a larger variation in removal efficiency between 75 and 95% was observed with increasing loading rates. Interestingly, during the OCP period, the removal efficiency in cell 2 increased to values higher than 90%.

An average ET conversion rate of 0.015 mM/d was achieved in a proof-of-principle study that demonstrated bio electrochemical ethanethiol degradation [31]. In this research, the average conversion rate of the biocathodes during the last 50 days of the experiment, based on VLR and removal efficiency, was considerably higher with 2.25 mM/d in cell 1 and 2.21 mM/d in cell 2. These removal efficiencies were demonstrated for both biocathodes during long-term stable operation. Moreover, the increase in volumetric loading rate did not negatively affect the removal efficiency and a further increase of the loading rate should therefore be possible. The ET conversion rates observed in aerobic and anoxic biofilters are up to 12 times higher compared to the continuous ET conversion rates at biocathodes observed in this work [26–28]. However, in these systems alternative electron acceptors as nitrate and oxygen were present which may increase the microbial conversion rates and utilizes alternative metabolic pathways with elemental sulfur and sulfate as main product.

6.3.2.4 Biotic mediation of ET conversion to DEDS

The SEM pictures show that small clusters of biomass and crystals were present on the electrode surface (Figure 4). Typically, a dense biofilm can develop in biocathodes that operate continuously for a long time span [39]. However, such a dense biofilm was not observed, and growth rates in the microbial community might have been low. The lack of an alternative sulfur source, the toxicity of ET and DEDS and the high salinity of the matrix may have limited the microbial growth rates. Nevertheless, the microbial community played a key role in the conversion of ethanethiol. The batch flask experiments showed that microbial oxidation of ET to DEDS is substantially faster than chemical oxidation. Additionally, the ratio of ET and DEDS in the continuous cells were most likely also influenced by the development of the microbial community. Ethanethiol levels at the biocathodes were high at the start of the experiment and with time decreased to values that were below detection limit. It was previously postulated that the conversion of MT to DMDS under anaerobic conditions was the result of a detoxification mechanism and might not be energetically favorable [40]. A similar detoxification mechanism might also play a role in the currently observed oxidation of ET to DEDS, that was observed in the catholyte. Interestingly, thermodynamic calculations show that both ET and

DEDS can function not only as electron donor, but also as electron acceptor, yielding an energetically favorable reaction when, for example, the oxidation of ET to DEDS is coupled to the reduction of ET to sulfide and methane (See SI-VIII). Alternatively, we cannot exclude that trace levels of oxygen may have intruded into the biocathodes, and oxygen may have partly been the electron acceptor for ET oxidation. This would yield an energetically favorable reaction. However, a complete oxidation of ET to DEDS using oxygen as electron acceptor requires an ingress of approximately 14 mL air per day at the highest ET loading rate. Considering the small headspace volume of ~6 mL this high ingress of air was unlikely. Furthermore, diffusion of oxygen from the nitrogen flushed anode was assumed to be limited. Oxidation of ET to DEDS was thus not dominated by this route.

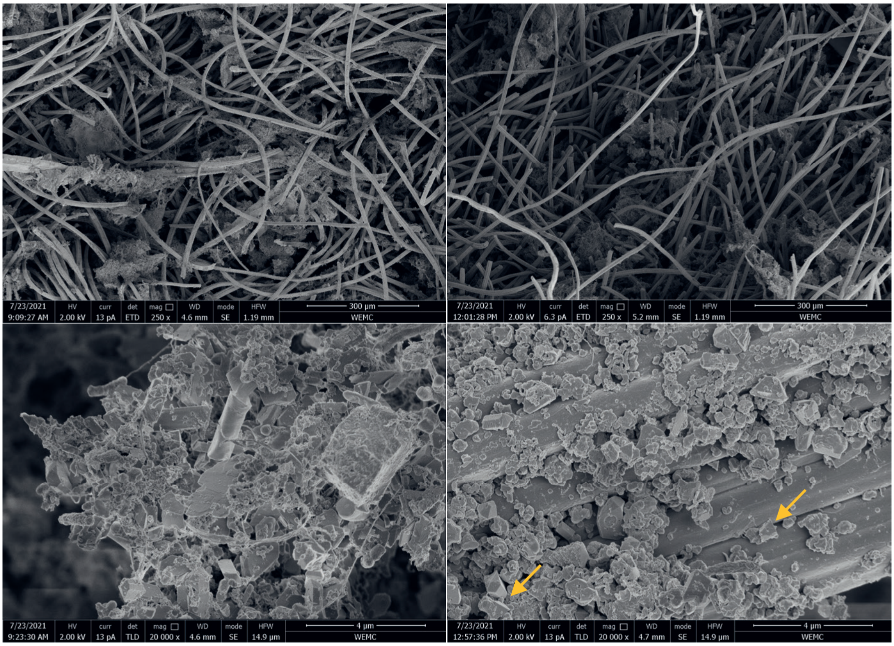

Figure 4 *SEM images showing the microbial distribution and crystal presence at the biocathodes at two different magnifications. The biomass and crystal clusters in cathode 1 (left) had a similar distribution over the graphite fibers in cathode 2 (right). The yellow arrows indicate the typical bipyramid shape of crystalline sulfur.*

The rRNA 16s sequencing data are presented in Figure 5. The biocathodes were mainly populated with members from the *Rhodobaca* and *Pseudomonas* genus. Species within the *Rhodobaca* genus are capable of anaerobic photoorganotrophic growth as well as aerobic chemoorganotrophic growth and were previously identified in hypersaline soda lakes [29]. The *Pseudomonas* genus contains many species with a wide range of metabolic strategies [41]. The *Pseudomonas* strain WL2 is capable of aerobic growth with ethanethiol as sole carbon and energy source with DEDS as major intermediate [42]. *Pseudomonas* are classified as aerobes and thus require oxygen for their metabolism [41,43]. However, some *Pseudomonas* species can grow anaerobically [44,45]. Even though aerobes formed the most dominant genera on the biocathodes the formation of methane (See SI-IV) and the presence of strict anaerobes e.g. *Methanobacteriaceae* indicates that local anaerobic conditions were maintained at the biocathodes as methanogenic archaea are inhibited by the presence of oxygen [46,47]. The families *Halomonadaceae*, *Idiomarinaceae*, *Methanosaetaceae* and *Rhodobacteraceae* were previously also found in bio electrochemical experiments that converted ethanethiol to sulfide and may have a high tolerance for ethanethiol and diethyl disulfide [31].

The Bray Curtis dissimilarity plot (See SI-IX) demonstrates that, despite the difference in relative abundance, the microbial communities of both biocathodes were similar to each other. The dissimilarity that was found between the biocathodes and the original inocula was higher compared to the dissimilarity between the two biocathodes, indicating a consistent selection pressure within both biocathodes. The ET removal efficiencies were similar in both biocathodes and the differences in relative abundance in the biocathodes might be related to a small difference in oxygen exposure favoring the growth of aerobes. These aerobic genera were not observed in previous work [31] . From these results it cannot be concluded which genera were responsible for the degradation of ET, since the dominant species enriched at the biocathodes might not be the key species performing this conversion.

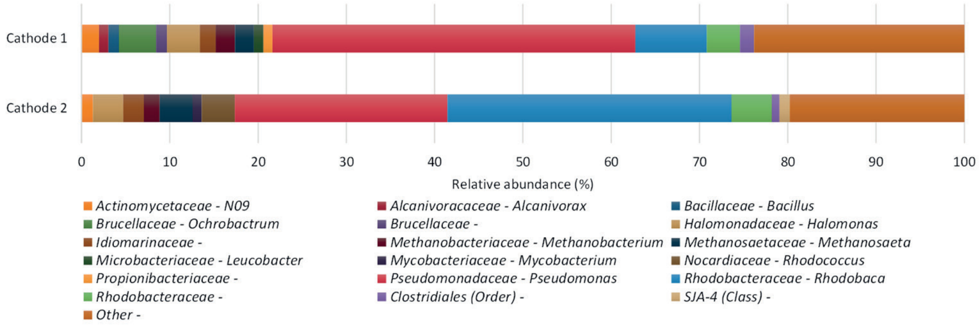

Figure 5 *Relative abundance of microbial community found at the biocathodes in cathode 1 and cathode 2. Taxa is shown as Family-Genera except when labeled differently. OTUs with a relative abundance <1% are represented as other.*

6.3.2.5 Sulfur balance and product formation

In a proof of principle study, sulfide was detected as the main product of ET degradation at biocathodes [31]. Surprisingly, in these continuous experiments, hardly any sulfide was detected throughout the >350 days of operation. There were differences between our current system design and the previous study: (i) continuous feed vs batch feed, (ii) control of current and potential vs current control, (iii) use of alternative oxidant at the anode (ferri/ferrocyanide vs oxygen evolution). These differences may have resulted in a different reaction mechanism. Furthermore, the longer duration of the experiment may have resulted in the development of alternative microbial communities with a higher affinity for sulfide or utilizing an alternative degradation pathway.

Figure 6 gives an overview of the different potential mechanisms for ET removal at the biocathodes together with the overall sulfur balance. We observed that the biological oxidation of ET to DEDS plays an important role in this system. A fraction of ethanethiol may have been directly reduced to hydrogen sulfide. The formed DEDS may also be reduced to sulfide directly. Alternatively, DEDS may be reduced to ET, as an intermediate, before the reduction towards of sulfide takes place. Similar to the known degradation pathway of dimethyl disulfide to sulfide via methanethiol [48,49]. The formation of sulfide may be followed by the well-known (bio) chemical oxidation of sulfide to elemental sulfur and sulfate under micro aerobic conditions [50]. Sulfate can also be formed from hydrogen sulfide via thiosulfate [50]. Under aerobic conditions DEDS may also be converted to elemental sulfur without hydrogen sulfide as an intermediate [42].

The sulfur balance could not be closed with the measured products. On average, only a small fraction (< 15 %) of the sulfur added as ethanethiol was recovered as DEDS, sulfate and thiosulfate (Figures 2 and 3). The maximum sulfur recovery as sulfate was 6% but remained mostly below 2% in both systems. Thiosulfate was observed occasionally at low concentrations at the cathodes, representing <1.7% of the sulfur balance. The presence of thiosulfate forms a strong indication that hydrogen sulfide was formed as an intermediate product even though hydrogen sulfide itself could not be detected [50]. Assuming that sulfide and methane were formed as (intermediate) products from ET degradation, the maximum coulombic efficiency, meaning which part of the electrons are used for the full reduction of ET at the biocathodes, at the biocathodes would be 4.7%. During the last 161 days of operation DMDS was observed occasionally at very low concentrations (<0.01%). No other VOSCs were detected. The extrapolation of the adsorption constants obtained in the model showed that the biocathodes would be saturated after 15 days (SI-III). Therefore, sorption of ET and DEDS plays a limited role in the sulfur balance after this initial period.

Biomass growth must have occurred on sulfur originating from ET as no other sulfur source was added to the influent. Based on the nitrogen removal in the system we estimate that, using a S:N ratio of 1:12, on average 2.5% of the sulfur present in the influent was incorporated into biomass (See SI-VI). Growth on ethanethiol as sole sulfur source is not widely studied. However, Basavapatna et al., (1986) found that various methanogens can use ethanethiol as sulfur source when very low levels of sulfide are present [51]. Furthermore Wang et al., (2015) found that ET can be used as sole sulfur source under aerobic conditions [42]. VOSC losses via the anode were also analyzed. The concentrations of DEDS found in the headspace of the anodes were low (<0.08 µM) and accounted for a maximum of 2.7 % of the overall sulfur balance with a removal rate of 7.1 µmol/day. Sulfate levels in the anolyte were between 0.28 mM and 0.89 mM and did not show an increase over the last 150 days of the experiment. Since the anodes were a closed loop, it is assumed that the formation of sulfate from VOSC originating from the cathode was limited. The presence of elemental sulfur at the anode was not analyzed. Diffusion from the biocathode to the surroundings may have played a role in the removal of VOSC-S. However, as the biocathode was not flushed actively with nitrogen we do not estimate the diffusion from the biocathode to be much larger than the losses from the bioanode.

The microbial growth and the measured sulfur products at the anode and cathode only accounted for a small fraction (on average 21%) of the sulfur balance. Therefore, other sulfur products were formed at the biocathode. SEM imaging (See figure 5) showed the presence of the typical bipyramid shape of crystalline sulfur [52]. A fraction of the elemental sulfur was likely removed from the system together with the effluent. SEM EDX performed on the graphite felt from the continuous experiments also revealed the presence of sulfur species on the biocathode (See SI-VI). The combination of elemental sulfur, sulfide and ethanethiol can yield polysulfides and diorgano polysulfanes [53,54]. These compounds were not measured in the current experiment and further chemical analyses are needed to provide more insight in the fate of sulfur in the biocathodes and close the sulfur balance.

The gas production rate at the biocathodes was low. Therefore, the gas flow rate could not be measured accurately. The observed methane levels varied over time and reached up to 3% in cell 1 and up to 0.4% in cell 2 (See SI-IV). Methane may be one of the degradation products of ET or a product of carbon dioxide reduction at the biocathodes. In the case of methane formation form ethanethiol, ethane or methane thiol would be expected intermediates. However, these were both not observed at our biocathode, and the carbon product form ET degradation remains unclear.

The formation of ethane as potential degradation product was analyzed occasionally but ethane was not detected.

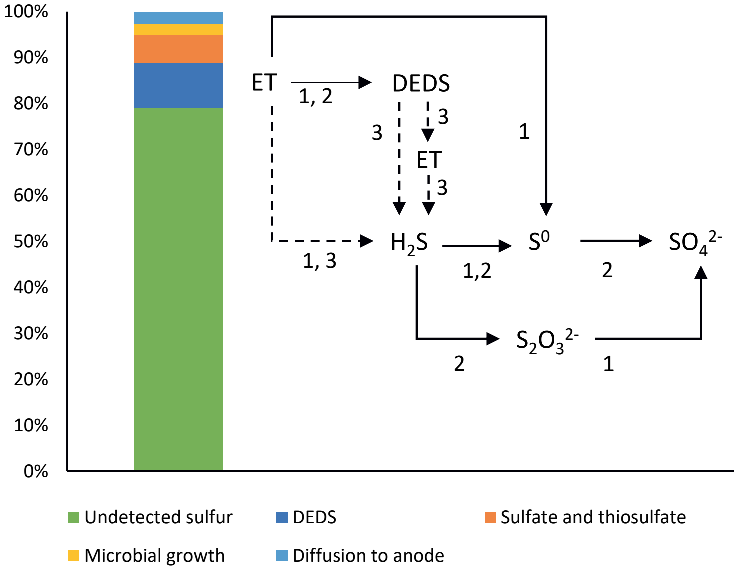

Figure 6 *Sulfur balance and potential reaction mechanisms for the (anaerobic) degradation of ET. Solid lines represent observed and known reactions and dotted lines represent potential reaction mechanisms. The numbers 1-3 represent a (1) biological reaction, (2) chemical reaction and (3) (bio) electrochemical reaction.*

6.4 Outlook

We showed the successful continuous degradation of ethanethiol in a BES. The oxidation of ET appeared in both batch and continuous experiments. The formed DEDS is hydrophobic, and adsorption/desorption kinetics was shown to be an important mechanism. Therefore, studying the sorption capacity to various (granular) electrode surfaces could benefit the development of future bio electrochemical systems for degradation of ET and DEDS. If this sorption is an advantage (higher availability close to the biofilm on the electrode) or a disadvantage (toxicity due to high local concentration) needs to be evaluated. To further understand the degradation pathway and whether the conversion of DEDS to H_2S proceeds with ET as intermediate can be studied in a similar experiment with only DEDS in the feed.

The role of supply of electricity at biocathodes, compared to the open circuit conditions and the batch experiments without electricity remains unclear. Electrochemical control may favor the formation of (bio)chemical catalysts and may enhance the selection of the microbial community for ET and DEDS degradation activity, as no other high microbial conversion rates of ET under anaerobic conditions have been reported. An advantage of a bio electrochemical system is that oxidation and reduction reactions can be separated at the anode and the cathode. Interestingly, we observed oxidation of ET at the cathode, under reducing conditions. The oxidation of ET to DEDS may be feasible at the anode, resulting in the release of electrons. The harvested electrons could then be used to facilitate the reduction of DEDS at the bio-cathode.

Typical waste streams containing ethanethiol also exhibit varying concentrations of hydrogen sulfide and other organosulfur compounds [5–9]. The interactions between these different compounds and potential toxicity of the combination of these compounds to the microbial community might alter the removal efficiency and product formation and should be studied further. While this research does not provide a complete understanding of the ethanethiol reduction pathway, the use of biocathodes shows potential to remove VOSCs in the future.

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Supporting information

SI-I Schematic overview of system design

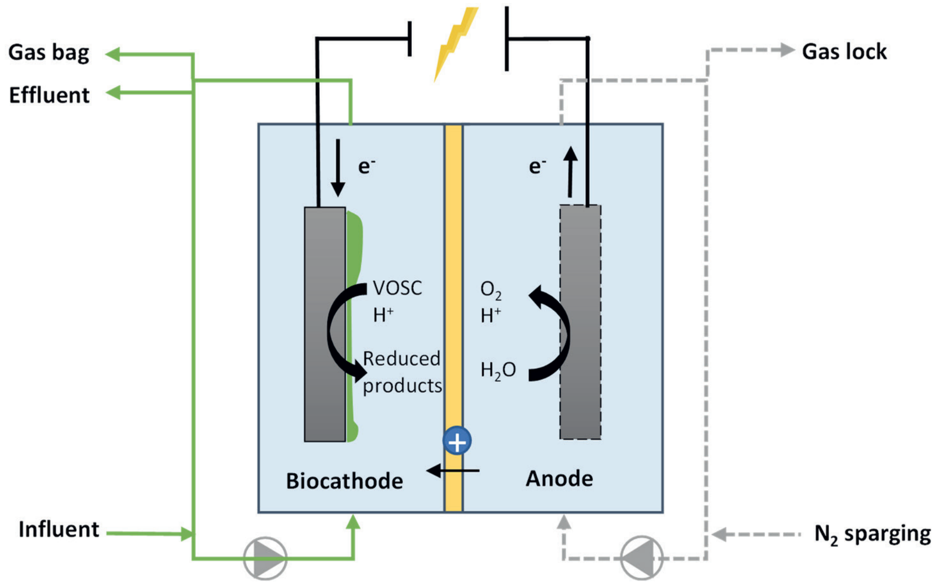

Figure SI-1 *Schematic overview of the continuously fed bio electrochemical system treating ethanethiol.*

SI-II Parameter estimation results of DEDS degradation

To verify whether DEDS was biologically converted in the Batch tests, the following model structure was calibrated:

$$R_{1,bio} = k_{ox,bio} \cdot [ET] \cdot A_{bio} \qquad \text{(SI-1)}$$

$$R_2 = k_2 \cdot [DEDS] \cdot A_{bio} \qquad \text{(SI-2)}$$

In table SI-1 the estimated parameters are presented, and in figure SI-2 model simulations are shown.

***Table SI-1** estimated parameters*

Parameter	Unit	Estimate	σ
$k_{ox,bio}$	day^{-1} cm^{-2}	2. 68 x 10^{-1}	1.24 x 10^{-2}
$k_{ox,chem,1}$	day^{-1} cm^{-2}	1.55 x 10^{-2}	1.41 x 10^{-3}

The results obtained with this model, including DEDS degradation, shows a poor fit with the experimental data (See figure SI-2). Here, while ET conversion still is described accurately with the model, the model predictions of DEDS and OSC shows a different behavior than the actual measurements. From the parameter estimation routine, the following error of variance ($\sigma_\varepsilon{}^2$), was obtained: $\sigma_\varepsilon{}^2$=1.08e-2. This error was significantly higher when compared the scenario assuming adsorption of DEDS (i.e. $\sigma_\varepsilon{}^2$=2.66e-3). Therefore, degradation of DEDS in the batch experiments without alternative electron donor is unlikely.

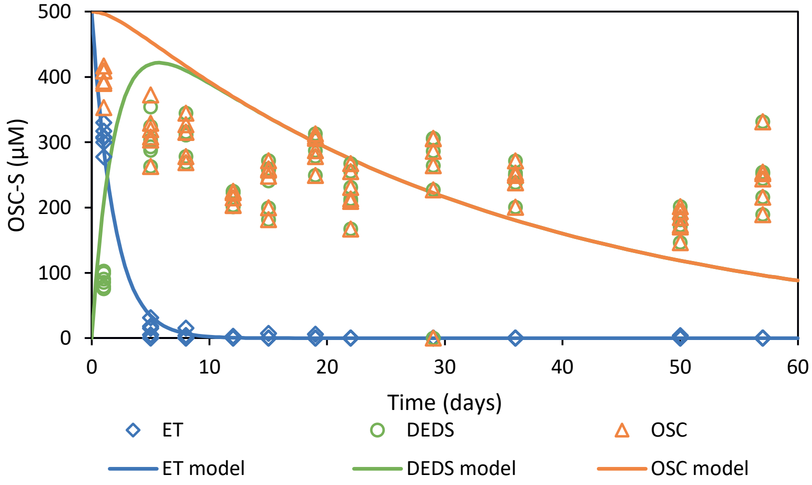

***Figure SI-2** Distribution of measured and modelled ethanethiol (ET) diethyl disulfide (DEDS) and total organosulfur (VOSC) concentrations in the aqueous phase of serum flasks experiments when assuming DEDS degradation.*

SI-III Model predictions of continuous operation under OCP

Mathematic description of continuous experiment

To model the OCP period in the continues BES system, the following dynamic model is proposed:

$$\frac{d[ET]}{dt} = \frac{[ET]_{feed} - [ET]}{HRT} - R_{1,bio} \quad (11)$$

$$\frac{d[DEDS{-}S_L]}{dt} = \frac{-[DEDS{-}S_L]}{HRT} + R_{1,bio} - R_2 + R_3 \quad (12)$$

$$\frac{d[DEDS{-}S_{ad}]}{dt} = R_2 - R_3 \quad (13)$$

Where $[ET]_{feed}$ is the concentration of ethanethiol in the feed solution to the BES reactor (mM) HRT is the liquid retention time of the BES reactor system (min).

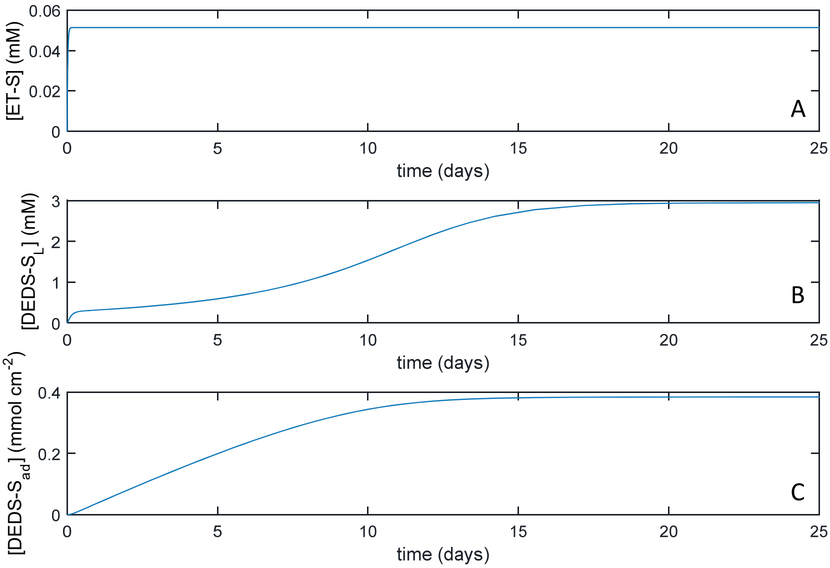

***Figure SI-3** Modeled concentrations of ET (A) and DEDS (B) in the aqueous phase and DEDS adsorption to the graphite felt (C) in continuous BES based on the kinetic parameters obtained in batch experiments.*

SI-IV Continuous reactor static gas phase composition

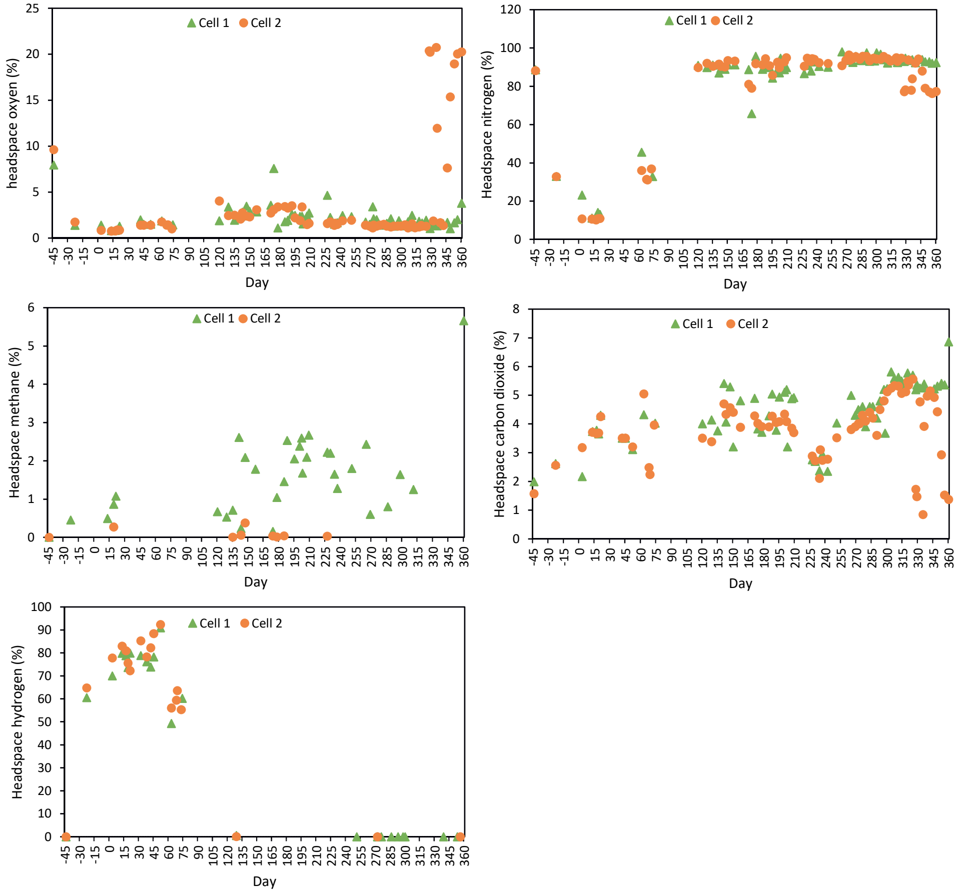

Figure SI-4. *Gas phase composition in the continuous experiment.*

SI-V ET and DEDS recovery in the effluent

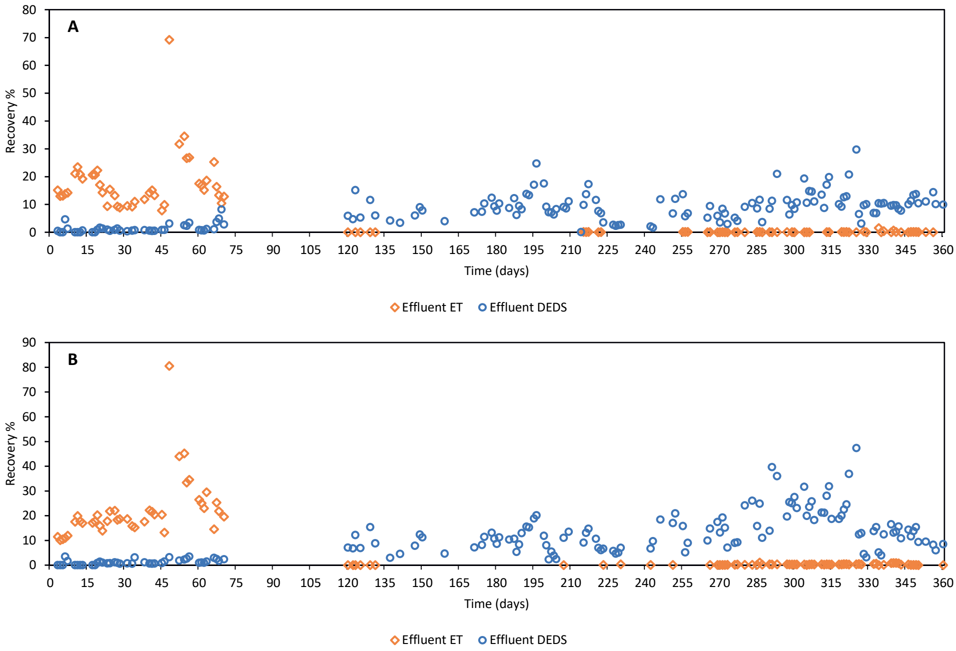

Figure SI-5 *The recovery of ET and DEDS in the effluent of cell 1(a) and cell 2(b) as a percentage of the influent concentration.*

Until day 75 between 10 to 50 percent of the ET added to the biocathodes was still present in the effluent as ET, while after day 150 between 5 and 50 percent of the ET fed to the system was present as DEDS in the effluent.

SI-VI Sulfur recovery in biomass

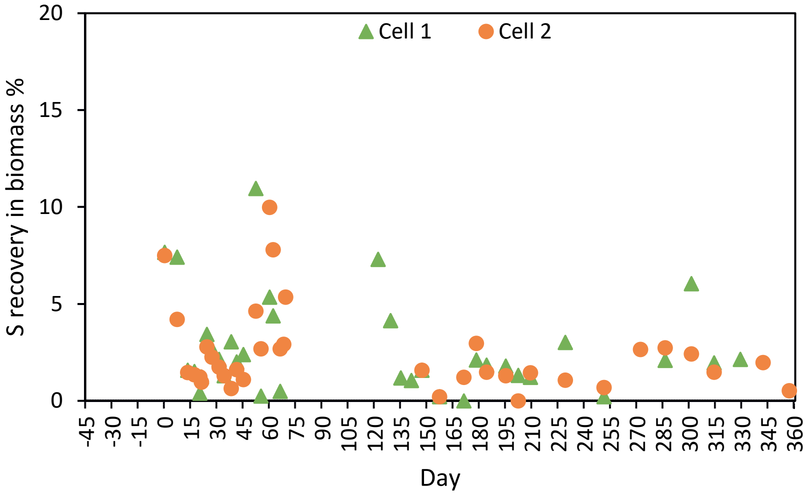

Figure SI-6 *Calculated sulfur recovery in the biomass based on the nitrogen removal in the continuous experiments using a N:S ratio of 12:1* [55].

SI-VII SEM EDX results

Element	**Full image wt%**	**Aggregate wt %**	**Fiber wt %**
C	70.37	36.05	85.27
O	19.67	34.27	8.82
Na		0.55	
Mg		0.71	
Al	0.76	3.87	
P	0.39	0.61	0.75
S	0.37	0.32	0.45
K		0.5	
Ca	8.43	20.89	4.71
Ti		2.23	

Figure SI-7 *SEM EDX imaging on the cathode of continuous experiment 1 demonstrates the presence of sulfur on the graphite fiber and the aggregate.*

SI-VIII Thermodynamic calculations

Table SI-2 *Thermodynamic calculations with ET and DEDS under nonstandard conditions.*

Reaction	Equation			ΔG’
Electron donor	$2\ C_2H_6S$	→	$C_4H_{10}S_2 + 2e^- + 2H^+$	-
	$C_4H_{10}S_2 + 12\ H_2O$	→	$4\ HCO_3^- + 2HS^- + 22e^- + 28\ H^+$	
Electron acceptor	$C_2H_6S + 4e^- + 3H^+$	→	$2\ CH_4 + HS^-$	-
	$C_4H_{10}S_2 + 2e^- + 2H^+$	→	$2\ C_2H_6S$	-
	$C_4H_{10}S_2 + 10e^- + 8H^+$	→	$4\ CH_4 + 2\ HS^-$	-
	$C_4H_{10}S_2 + 6e^- + 6H^+$	→	$4\ CH_4 + 2\ S^0$	-
Overall	$3\ C_2H_6S + 3\ H_2O$	→	$C_4H_{10}S_2 + CH_4 + HS^- + HCO_3^- + 8H^+$	-77 kJ/mol C_2H_6S
	$C_4H_{10}S_2 + 10\ C_2H_6S$	→	$5\ C_4H_{10}S + 4\ CH_4 + 2\ HS^- + 2H^+$	0.02 kJ/mol C_2H_6S
	$C_4H_{10}S_2 + 6\ C_2H_6S$	→	$3\ C_4H_{10}S_2 + 4\ CH_4 + 2S^0$	-30 kJ/mol C_2H_6S
	$C_4H_{10}S_2 + 5.5\ C_2H_6S + 12\ H_2O$	→	$11\ CH_4 + 4\ HCO_3^- + 7.5\ HS^- + 11.5H^+$	-116 kJ/mol C_2H_6S

The Gibbs free energy under nonstandard conditions was calculated at a temperature of 298.15K, at atmospheric pressure, a pH of 8.5, organosulfur compound and sulfide concentrations of 4 mM, a bicarbonate concentration of 0.5 M and a methane partial pressure of 5%.

SI-IX Bray Curtis dissimilarity plot

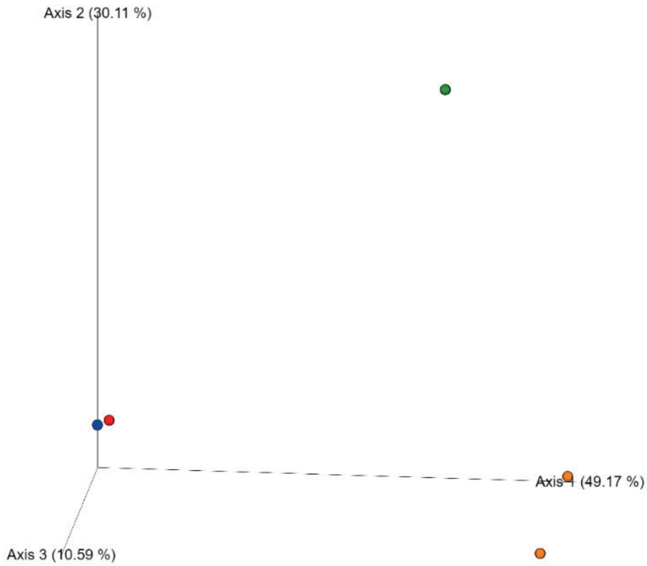

Figure SI-8 *Bray Curtis dissimilarity PCoA plot of biocathodes and inocula. The blue dot indicates cathode 1, the red dot cathode 2, the green dot inocula obtained from the sewer and the yellow dots the inocula obtained from paper mill wastewater. The maximum dissimilarity is shown on Axis 1 followed by axis 2 and 3. Samples from the biocathodes were highly similar whereas the inocula obtained from a paper mill wastewater treatment plant and the sewer system showed a large dissimilarity to the final microbial community composition found in the biocathodes.*

Chapter 7

General discussion

7.1 Introduction

Thiols must be removed from product and waste streams to prevent health issues and environmental damage. This damage can result directly from their toxicity or indirectly from the formation of sulfur dioxide upon combustion. A variety of technologies is available for the removal of thiols and the recovery of sulfur. These technologies are optimized for waste streams finding their origin in the oil and gas industry. The streams in this industry are characterized by their bulk size and high thiol concentrations. However, at low gas flows and low thiol concentrations, the removal of thiols and recovery of sulfur is a challenge. Due to the unfavorable feed for conventional technologies, scavenging technologies are generally applied. These non-specific strategies are associated with relatively high operational costs, waste production and do not recover sulfur. BES may offer a new strategy to convert thiols from these streams and may be able to convert thiols to sulfide and methane. Elemental sulfur can be recovered from the produced sulfide in established (bio)desulfurization technologies. Therefore, the main research question of this thesis was:

Can bioelectrochemical systems become a clean and circular technology for thiol removal and sulfur recovery?

To answer this research question, the requirements for thiol treating technologies and the desire for new technologies in the context of sustainable developments moving towards a Net Zero energy economy were explored in **chapter 2**. This chapter is complemented by **chapter 3,** which reviews the currently available technologies and their suitability to treat (current and future) thiol-containing waste and product streams. None of the currently available technologies are suitable for sulfur removal and recovery at a small scale, while industries produce more thiols containing waste streams at smaller decentralized scale, e.g., by treating biofuel waste streams or waste management plants. From these two chapters, we have concluded that there is a desire for small-scale and scalable technologies or technology combinations that can not only remove but also convert thiols into reusable sulfur compounds. Other important aspects, besides the potential for sulfur recovery, that could increase the competitive advantage of new technologies are (1) limited or no production of (toxic)waste streams, (2) low investment costs, and (3) low operational costs.

Chapter 4 provides the proof-of-principle for bioelectrochemical thiol reduction. This chapter describes the successful conversion of methanethiol (MT), ethanethiol (ET), propanethiol (PT), and dimethyl disulfide (DMDS) towards sulfide in current controlled biocathodes. Up to 64% of the sulfur added as methanethiol was recovered as sulfide within five days at the biocathode, whereas no sulfide was observed in electrochemical or biological control experiments. These experiments showed that both current and microorganisms were required to reduce organosulfur compounds toward sulfide. **Chapter 5** describes the development of a new gas chromatographic method to measure thiols and identify intermediate organosulfur compounds formed during the thiol degradation process. This method could measure methanethiol, ethanethiol, propanethiol, dimethyl disulfide, and diethyl disulfide (DEDS) in the gas and liquid phase. In addition, Henry coefficients in the saline medium were defined for these compounds. These coefficients could be used to calculate the concentration in the liquid phase based on gas samples. This new method was used to monitor the degradation and product formation in continuous ethanethiol degrading BESs (**chapter 6**). In these continuous experiments, ethanethiol was removed with a stable high removal efficiency (>70%) at loading rates up to 3 mM/d. In contrast to the proof of principle, sulfide was not found as a sulfur product. Instead, diethyl disulfide was observed as a major intermediate, while traces of sulfate, thiosulfate and elemental sulfur also accounted for a fraction of the formed sulfur products. Additional serum flask experiments showed that the formation of diethyl disulfide was bio-catalyzed and that no continuous degradation of diethyl disulfide occurred in the absence of an electrode.

In this chapter we will discuss whether BESs holds potential for full-scale implementation and merits further research. Two major topics, which are essential for maturation of the thiol converting BESs, will be discussed. Firstly, the results are compared to a theoretical thermodynamic framework to gain a further understanding of the observed reaction products. Secondly, we discuss the compatibility with the industrial biodesulfurization process and make a cost comparison between BESs and existing thiol removing technologies.

7.2 Reaction mechanisms and thermodynamics

7.2.1 Thiols can be degraded in bioelectrochemical systems

The introduction of this thesis describes the natural formation and degradation of thiols. While degradation pathways for methanethiol are known under both aerobic and anaerobic conditions, the degradation of ethanethiol and propanethiol appears to be much more complex and its degradation is not observed in nature nor achieved in laboratory experiments. Hence, practical applications implementing these natural degradation processes are limited to the degradation of methanethiol in, for example, UASB reactors or bio trickling filters, while ethanethiol and propanethiol remain unconverted [1,2]. Chapter 4 of this thesis provides a proof of principle for the degradation of thiols at biocathodes, including the conversion of ethanethiol and propanethiol. This chapter demonstrates that biodegradation of these compounds is possible in a bioelectrochemical system, with sulfide as one of the products of the reduction reaction at the cathode. In the follow-up continuous experiment (<360 days), ethanethiol was converted (Chapter 6). Rather than sulfide, other products, including diethyl disulfide, elemental sulfur, sulfate, and thiosulfate were observed as a product of ethanethiol degradation. The formation of these oxidized products at the biocathode was unexpected. The degradation pathway for thiol degradation in a bioelectrochemical system is yet to be identified. Furthermore, the sulfur and carbon balances could not be closed in these experiments. In the following section, we will compare the results to a thermodynamic framework to gain further insight into the possible degradation mechanisms.

7.2.2 Thermodynamic exploration of thiol conversions in a bioelectrochemical system

Various reactions of thiols and their disulfides can occur at a biocathode. Figure 1 presents the equilibrium potential of possible oxidation and reduction reactions for methanethiol, ethanethiol, dimethyl disulfide, and diethyl disulfide reactions. The formation intermediates, such as methane-ethanethiol (MTET) and dimethylsulfide (DMS), are also included in this figure. The arrows indicate the direction of the reduction reactions. The thermodynamics of overall reactions, without an electrode, are discussed in section 7.2.2.4. Furthermore, an overview of the half-reactions, their equilibrium potential, and possible side reactions is provided in the supporting information.

7.2.2.1 Equilibrium potential and pathways for thiol conversions

The calculated equilibrium potentials for the oxidation/reduction reactions of VOSCs presented in Figure 1 range from -0.32 to -0.42 V vs. Ag/AgCl. When the electrode potential is lower (more negative) than the equilibrium potential, the half-reactions can proceed as a reduction reaction. In this thesis, the biocathodes were operated at a potential of -0.5 V vs. Ag/AgCl or under current control resulting in cathode potentials below -1 V vs. Ag/AgCl. Therefore, all the reactions presented in Figure 1 can occur as reduction reactions at the biocathode. Their oxidation (e.g., ET to DEDS) is, therefore, not likely a result of the interaction with the electrode. Instead, an alternative electron acceptor is required to facilitate these oxidation reactions. It was previously suggested that the oxidation of thiols to their disulfides can proceed as a detoxification mechanism under anaerobic conditions and does not contribute to the energy metabolism of microorganisms [3]. It is important to note that the obtained equilibrium potentials are calculated for a sulfide concentration of 1 mM. However, increased sulfide concentrations in the liquid restrict the thermodynamic feasibility of this reduction reaction, and more negative potentials may be required to drive these reactions.

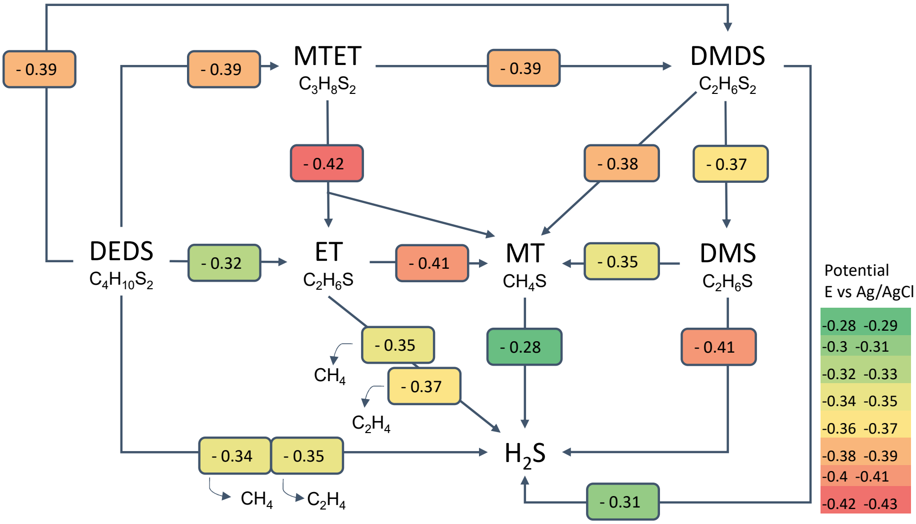

Figure 1 *Theoretical equilibrium potentials for the reduction/oxidation of VOSCs under actual conditions. The arrows indicate the direction of the reduction reaction. The equilibrium cathode potential was calculated based on a sulfur species concentration of 1 mM, a bicarbonate concentration of 0.6 M, a methane partial pressure of 0.2 atm, a pH of 8.5, and a temperature of 298.15 K. Two equilibrium potentials are presented for the reduction of DEDS and ET towards methane and ethane respectively.*

The reduction of ethanethiol towards bisulfide and methane is thermodynamically more favorable than the reduction towards methanethiol. Ethanethiol reduction towards bisulfide and methane can occur at a potential below -0.35 V vs. Ag/AgCl. At the conditions applied during the experiments (cathode potential of -0.5 V vs. Ag/AgCl), more energy is available for microbial growth or to overcome internal resistances of the BES in comparison to the reduction towards methanethiol (-0.41 V vs. Ag/AgCl) or ethane (-0.37 V vs. Ag/AgCl).

Ethanethiol can be oxidized to diethyl disulfide at potentials higher than -0.32 V vs. Ag/AgCl. Since this potential is higher than the applied potential of -0.5V vs. Ag/AgCl, the observed formation of diethyl disulfide in the continuous experiment (chapter 6) was likely not related to electron transfer with the electrode. Possible electron acceptors include thiols or oxygen (See section 7.2.2.4). The reduction of diethyl disulfide may occur via demethylation, resulting in the formation of methane ethane disulfide (MTET) or dimethyl disulfide. Both reactions are feasible at an electrode potential below -0.39 V vs. Ag/AgCl. In the continuous system, these compounds were not detected in the gas phase, meaning that these compounds were either not formed or directly converted. Alternatively, diethyl disulfide may be reduced to ethanethiol (-0.32 V vs. Ag/AgCl). This reduction reaction is thermodynamically more favorable compared to the one-step reduction of diethyl disulfide towards bisulfide and methane (-0.34 V vs. Ag/AgCl) or ethane (-0.35 V vs. Ag/AgCl). However, the consecutive reduction of ethanethiol to bisulfide and methane and ethane occurs at more negative potentials (-0.35 and -0.37 V vs. Ag/AgCl). Therefore, the direct reduction of diethyl disulfide to bisulfide in one step may be more beneficial for the microbial community as more energy is available to support microbial growth and overcome the internal resistances of the BES.

In the continuous ethanethiol degradation experiment, ethanethiol and diethyl disulfide could be measured in the reactor under current controlled conditions (<-1 V vs. Ag/AgCl) while under potential control (-0.5 V vs. Ag/Ag/Cl), only diethyl disulfide was observed. The absence of ethanethiol under potential controlled conditions may be explained by the growth and adaptation of the microbial community or by the applied electrochemical control strategy. The mode of operation (current vs. potential) may have influenced the conversion pathways. Under the current control regime, the selection pressure for the one-step reduction pathway from diethyl disulfide to sulfide may be lower as sufficient energy (a larger overpotential) is available to execute the direct or indirect reduction via ethanethiol towards bisulfide. In addition, the microbial oxidation of ethanethiol to diethyl disulfide may be limited under the current controlled strategy due to the more reducing conditions.

For methanethiol, a similar reduction pathway is thermodynamically most favorable. The oxidation to disulfides and methylation towards dimethyl sulfide is thermodynamically unlikely under experimental conditions. Yet, in the proof of principle and method development (chapters 4 and 5), dimethyl disulfide was observed in biocathodes spiked with methanethiol. In these experiments, methylation of methanethiol to dimethyl sulfide was not observed. The reduction of dimethyl disulfide to methanethiol gives a larger potential difference between the electrode and the equilibrium potential and may form an intermediate in the reduction pathway to bisulfide. However, the additional reduction step of methanethiol towards bisulfide and the involved energy losses may render the one-step reduction of diethyl disulfide towards bisulfide more favorable for microbial growth.

From a thermodynamic perspective, various products can be formed by methylation and de(m)ethylation of the thiols. However, not all these products were observed in the biocathodes. The availability of a metabolic pathway within the microorganisms, the activation energy, and the energy requirements for microbial growth determine which reactions occur at the biocathodes [4]. In addition, energy is also required to overcome the internal resistances of the bioelectrochemical system.

7.2.2.2 Equilibrium potential including microbial growth

All microorganisms produce ATP for cell maintenance and growth. The two main mechanisms to produce ATP include substrate level phosphorylation of ADP, requiring an energy input of 31.8 kJ/mol substrate under standard conditions, and ion gradient driven phosphorylation [5]. In ion gradient driven phosphorylation, the transport of a proton and an electron over the outer membrane creates a proton motive force driving ATP production. Therefore, the minimum energy requirement for one reaction is directly related to the energy required to translocate one ion across the outer membrane. The membrane potential was measured for various bacteria and archaea and can range from -100 mV to -210 mV [5,6]. Organisms that live under energy limited conditions, e.g., methanogens, tend to have a relatively low membrane potential [5]. If we assume a membrane potential of 150 mV, we can calculate the minimum required energy for a reaction to support microbial growth based on the relationship:

$$\Delta \mathrm{G} = -nFE$$

Under these assumptions, the minimum energy requirement to support microbial growth is 14.5 kJ/mol.

Figure 1 represents the equilibrium potentials of various VOSCs oxidation/reduction reactions. However, under these equilibrium conditions, no energy is available for microbial growth. Assuming that the minimum energy requirement for microbial growth is 14.5 kJ/mol, we can estimate the minimum overpotential and, thus, electrode potential to provide sufficient energy for growth. To sustain microbial growth, for the reactions presented in Figure 1, an additional overpotential of 15 to 74 mV is required (See supporting information). This overpotential is directly linked to the number of electrons in each reaction and decreases with reduction reactions that consume more electrons. The one-step reduction of diethyl disulfide to bisulfide occurs at a less negative potential (-0.36 V vs. Ag/AgCl) compared to the reduction of diethyl disulfide towards ethanethiol (-0.39 V vs. Ag/AgCl) when considering the energy for microbial growth. In contrast to the standard thermodynamic calculations, the one-step reduction to bisulfide is thermodynamically more favorable when considering the energy requirement for microbial growth. Therefore, including the microbial energy requirements in thermodynamic calculations may yield new insights when analyzing the thermodynamic feasibility of microbial reactions in bioelectrochemical systems.

7.2.2.3 Hydrogen as intermediate

The microbial processes and mechanisms involved in electron transfer at biocathodes are not fully understood yet. Indirect electron transfer via hydrogen or redox active compounds may occur, as well as direct electron transfer via membrane bound electron carriers [4,7,8]. In theory, direct electron transfer is more energy efficient than indirect electron transfer via, e.g., hydrogen, since lower overpotentials are required for the electron transfer from the electrode to the microorganism. However, hydrogen is commonly observed as an intermediate in bioelectrochemical systems and is shown in, for example, methane production from carbon dioxide [9,10].

From thermodynamic point of view, the reduction of thiols is possible with hydrogen as an electron donor (See section 7.2.2.4). Hydrogen formation was also observed in the current controlled biocathodes. Under potential controlled conditions (-0.5 V vs. Ag/AgCl), hydrogen can only be formed under extremely low partial pressures ($6.3 \cdot 10^{-8}$ atm) and was not detected. If hydrogen was present as an intermediate, it might have been consumed rapidly by the microbial community for thiol reduction or other reactions like methane formation. However, as ethanethiol degradation with hydrogen was studied but never observed in literature, it is unlikely that this formed a key pathway for thiol reduction at the biocathode. This is supported by the similar removal efficiency that was observed when switching ethanethiol treating biocathodes from current control to potential control, which indicates that hydrogen availability did not substantially impact the removal efficiency.

7.2.2.4 Thiol conversions without an electrode

In theory, thiols can also be degraded under anaerobic conditions without electrodes. For example, the reduction of thiols towards sulfide is thermodynamically favorable when coupled to water or hydrogen oxidation (See Table 1 *eq. 1, 3, 6 & 8*). These reactions are indeed observed in nature and laboratory experiments for methanethiol [1,11–14]. However, to the best of our knowledge, ethanethiol and propanethiol degradation with these electron donors was never observed.

Disulfides can be formed under anaerobic conditions resulting from disproportionation reactions (eq. 2,4,7 & 9). The disproportionation of thiols towards an oxidized disulfide and a reduced sulfide is thermodynamically feasible and yields an energetically favorable reaction. This reaction may be one of the mechanisms for the observed disulfide formation at the biocathode.

The reaction between methanethiol and elemental sulfur produces dimethyl disulfide, dimethyl trisulfide, and other diorgano-polysulfides [15,16]. Sulfur was also observed in the biocathode converting ethanethiol, and a similar reaction between elemental sulfur and ethanethiol may also have contributed to the formation of diethyl disulfide.

Table 1 *Gibbs free energy of theoretical thiol degradation reactions using water, hydrogen, or organosulfur compounds as an electron donor.*

Reaction		Equation			ΔG
MT	(1)	$4\ CH_4S + 3\ H_2O$	→	$3\ CH_4 + 4\ HS^- + HCO_3^- + 5\ H^+$	-51.1 kJ/mol CH_4S
	(2)	$4\ CH_4S + 3\ H_2O$	→	$C_2H_6S_2 + CH_4 + 2\ HS^- + HCO_3^- + 7\ H^+ + H_2$	-50.1 kJ/mol CH_4S
	(3)	$CH_4S + H_2$	→	$CH_4 + HS^- + H^+$	-96.6 kJ/mol CH_4S
	(4)	$3\ CH_4S$	→	$C_2H_6S_2 + CH_4 + HS^- + H^+$	-6.3 kJ/mol CH_4S
	(5)	$2\ CH_4S + 0.5\ O_2$	→	$C_2H_6S_2 + H_2O$	-86.9 kJ/mol CH_4S
ET	(6)	$2\ C_2H_6S + 3\ H_2O$	→	$3\ CH_4 + 2\ HS^- + HCO_3^- + 3\ H^+$	-75.6 kJ/mol C_2H_6S
	(7)	$3\ C_2H_6S + 3\ H_2O$	→	$C_4H_{10}S_2 + CH_4 + HS^- + HCO_3^- + 5\ H^+ + 1.5H_2$	-28.54kJ/mol C_2H_6S
	(8)	$C_2H_6S + 2\ H_2$	→	$2\ CH_4 + HS^- + H^+$	-132.5 kJ/mol C_2H_6S
	(9)	$3\ C_2H_6S + H_2$	→	$C_4H_{10}S_2 + 2\ CH_4 + HS^- + H^+$	-10.6 kJ/mol C_2H_6S
	(10)	$2\ C_2H_6S + 0.5\ O_2$	→	$C_4H_{10}S_2 + H_2O$	-80.7 kJ/mol C_2H_6S

The Gibbs free energy under nonstandard conditions was calculated with a sulfur species concentration of 1 mM, a bicarbonate concentration of 0.6M, a methane, hydrogen and oxygen partial pressure of 0.2 atm, a pH of 8.5, and a temperature of 298.15K.

7.2.3 Product formation in BES

7.2.3.1 Carbon products

The degradation of ethanethiol at biocathodes was studied in a continuous experiment for nearly a year. During this period, the formation of ethane was not observed, indicating that ethane was not a major final carbon product. Indeed, from the thermodynamic framework, it also becomes clear that the reduction towards methane and sulfide is energetically more favorable and may therefore be the dominant pathway of ethanethiol degradation. The formation of methane can also occur from the reduction of bicarbonate. However, at high pH values this reduction becomes less favorable. Potentials below -0.55 V vs. Ag/AgCl are required under a methane partial pressure of 0.2 atm and pH 8.5 (See supporting information). Therefore, it is likely that the methane observed in the ethanethiol conversion experiment under potential control (-0.5 V vs. Ag/AgCl) resulted from thiol degradation rather than carbon dioxide reduction.

7.2.3.2 Disulfide formation

As shown in chapter 6, disulfides are present as intermediates in the degradation of ethanethiol. In the proof of principle, dimethyl disulfide was also formed in the batch experiments. This oxidation reaction is shown in the degradation process, even though it is not yet clear if this reaction results from a disproportionation reaction or requires alternative electron acceptors.

7.2.3.3 Sulfur products

Closing the sulfur balance formed a challenge in this work. Whereas sulfide was detected as a major product in the proof-of-principle experiments, sulfide was not detected in the continuous ethanethiol degradation experiments. The change from hexacyanoferrate to water as an electron donor at the anode and changes in the reactor design may have altered the degradation pathway observed at the biocathodes. Even though sulfide was not detected in continuous experiments, sulfide was likely present as an intermediate since sulfate and thiosulfate were found at the biocathode. Sulfate and thiosulfate are both oxidation products of sulfide. Thiosulfate is formed by the chemical oxidation of sulfide when oxygen is present, whereas the biocatalyzed oxidation of sulfide forms sulfate with elemental sulfur as intermediate [17].

A more detailed analysis of the formed sulfur species is required to close the sulfur balance and understand the reaction mechanisms. Elemental sulfur was observed using SEM EDX but not quantified. In follow-up experiments, an ICP method can be developed to quantify total sulfur in the liquid phase of the biocathodes. However, the standard destruction procedure in ICP requires the acidification of samples and transfers thiols to their acid form, making them more volatile. Losses due to this volatilization should be accounted for when using ICP to close the sulfur balance. The developed method in chapter 5 can be adjusted to measure the presence of potential intermediates like methylethyldisulfide. However, no unidentified peaks were shown in the chromatograms. If these compounds are formed as intermediates, they are likely not present at detectable concentrations. Furthermore, the formation of (di-organo) polysulfides can be monitored with, for example, HPCL-UV [18].

7.3 Implications for application

BESs are an interesting technology for different fields. For instance, energy recovery from wastewater or the production of hydrogen and organic acids in BES are widely studied [19–21]. In these applications, BES must compete with established technologies. BES can form an environmentally friendly solution by using less energy and avoiding the use of expensive catalysts. However, the costs of BES application should decrease to compete with existing technologies from an economic perspective [22–24]. This makes BES especially an attractive platform for niche applications for which no solution is available, like thiol removal on small to medium scale (<500 kg S/d). Because no suitable solution exists, research efforts and investments to scale up BES for this type of application may be rewarding and result in new environmentally friendly solutions.

7.3.1 BES design considerations for thiol removal

7.3.1.1 Scalability of BES

The scaling up of BES from lab or bench scale to a full-scale technology is a crucial aspect for its technological application. However, research efforts remain predominantly at lab scale, focusing on improving efficiencies, deepening the understanding of underlying mechanisms, and investigating new applications, alternative reactor designs, and materials [25]. Various pilot projects were recently deployed, scaling up the lab scale BESs towards application [25]. These projects often focus on microbial fuel cells (MFCs, gaining energy from treating wastewater) and microbial electrolysis cells (MECs). Upscaling of biocathodes for electrosynthesis, e.g., methane and acetate production, is limited compared to MFCs and MECs.

The maturation of BESs technology in these pilot projects encounters various issues which require attention before BES can become a successful full-scale technology. For example, during scale-up, the distance between the electrodes is often larger, which results in increased internal resistance and energy losses. The pH gradients in these systems are important as they affect the internal resistance and microbial activity [26]. Therefore, the pH gradient should be minimized by optimizing the BES design. Techno economic assessments of a microbial electrosynthesis system indicated that the high costs of the anodes form a major CAPEX while the high electricity costs are indicated as the main OPEX. These high investment and operational costs form a large challenge for bioelectrochemical technologies [23]. Improving the energy efficiency is of key importance. This can be achieved by increasing the faradaic efficiency through limiting side reactions, and by lowering the required cell voltage through optimizing the cell design. Cell design can be optimized by, e.g., minimizing the distance between the electrodes, minimizing pH gradients, and optimizing the catalysts on the electrode. Using low-cost anode materials may reduce investment costs but may also reduce the anode's catalytic activity resulting in a higher energy input and higher operational costs.

7.3.1.2 Conversion rates of methanethiol and ethanethiol in a biocathode

We studied the degradation of ethanethiol under anaerobic conditions. However, little is described in literature about the anaerobic degradation of ethanethiol and propanethiol. Therefore, it is unique that ethanethiol and propanethiol degradation was observed at biocathodes, showing a promising potential for BES in this new application niche. The increase in ethanethiol loading rate resulted in stable conversion efficiencies, indicating that no inhibition occurred and that higher loading rates can still be achieved. The degradation rates for methanethiol and propanethiol were not investigated in continuous experiments. It is expected that methanethiol will also be degraded at stable conversion efficiencies. Possibly at higher loading rates as methanethiol is biodegradable in the natural environment.

The study of thiol conversion in the biocathode is analytically challenging. Therefore, in chapter 5, a method was developed to measure thiols and their corresponding disulfides in our process conditions. We excluded any other sulfur source at the biocathode to be able to quantify the product formation and limit side reactions (See Chapter 1). Interestingly, a biofilm developed on the cathode, meaning that part of the sulfur obtained from thiol conversion was used as a macronutrient for microbial growth. However, biofilm growth rates and, thus, thiol conversion rates might be improved using an easily accessible sulfur source such as sulfate and sulfur. However, these additional sulfur sources can be reduced at the biocathodes and may decrease the coulombic efficiency obtained in the system.

7.3.1.3 Energy efficiency

The energy efficiency of the system is defined by the required current and cell voltage. The obtained coulombic efficiencies at the biocathodes were up to 5% in the H-cells (chapter 4) and 4.7 % in the continuous cells that degraded ethanethiol (chapter 6). Increasing the coulombic efficiency would result in lower operational costs of this new thiol conversion technology. The coulombic efficiency may be improved by operating at a different electrode potential, limiting undesired side reactions, such as methane formation from carbon dioxide. The theoretical cell voltage for ethanethiol removal at biocathodes is 0.9 V (See chapter 1). However, the measured cell voltage under potential control was -1.7 V. In full-scale installations, a higher cell voltage is likely required due to the increased resistances inside the system by, for example, an increased pH and ion gradient over the membrane.

7.3.1.4 BES feed composition

The work in this thesis focused on the degradation of individual thiols in a BES. However, BES may be fed with streams that have different compositions. The mixture of various thiols and the presence of sulfide in the same stream may influence thiol degradation. Microbial conversions, chemical thiol-thiol, thiol-sulfide and thiol-sulfur interactions yield various products and can affect the conversion rates. The presence of various thiols, a high sulfide-to-thiol ratio, or chemically formed products may inhibit the degradation of thiols because of increased toxicity.

Ideally, the new bioelectrochemical technology will be able to treat a wide range of waste and product streams. These streams have specific properties and requirements. For instance, major differences are the sulfide and thiol concentrations and corresponding loading rates (See chapter 3). This work focused on aqueous thiol feeds (range 0.1-4 mM). However, BES can be applied as part of a gas desulfurization train, which uses an absorber. The design and operational performance of the absorber strongly impacts the feed composition of the thiol-converting BES. Co-absorption of, for example, sulfide can influence the BES performance. The degradation of thiols under these different conditions needs to be studied in more detail so that operational boundaries for maximum thiol loading rates and thiol and sulfide concentrations at the biocathodes can be defined.

7.3.1.5 Facilitating the adsorption of VOSCs in biocathodes may enhance reaction rates

Diethyl disulfide was an intermediate in the continuous ethanethiol degradation experiments. Because diethyl disulfide is hydrophobic, it can adsorb to the graphite felt electrode. This property can be applied to increase the removal rates and obtain deep removal of organo-sulfur components from the treated stream. The adsorbed disulfides are present in high concentrations on the electrode surface, in close vicinity of the microorganisms that can accept electrons from the electrode, which may increase the degradation rate of disulfides. Alternative conductive adsorption materials, such as granular activated carbon, can also be considered for the enhanced adsorption of diethyl disulfide. Graphite felt and granular activated carbon are also applied when treating micropollutants in BES, which benefit from the high adsorption capacity of these materials [27,28].

7.3.1.6 Reactor configuration

The differences in BES reactor types between the batch experiments (H-type cells) and continuous experiments (flow channel cells) may have resulted in different degradation mechanisms and final products. The H-type cells had, compared to the flow cells: (1) fewer connections, (2) a higher volume to surface ratio, (3) fewer seams to seal the reactor, (4) an alternative electron donor and (5) were easier to maintain under strictly anaerobic conditions compared to the flow channel cells. When scaling up bioelectrochemical systems, the contribution of oxygen diffusion over the membrane or through the tubing, and the diffusion of thiols from the reactor to the atmosphere, may be easier to avoid as the volume to surface ratio increases and alternative materials are used.

This study used cation exchange membranes to separate the anode and cathode compartments. Using a membraneless reactor would reduce possible mass transfer limitations over the membrane, construction costs, and may yield faster oxidation of thiols to disulfides resulting from microbial interactions with the anode or possibly from chemical oxidation reactions with the oxygen produced at the anode. A major drawback of membraneless design for thiol treating BES is the movement of produced sulfide at the cathode towards the anode. Sulfide can oxidize at the anode to elemental sulfur and deposit at the electrode. This deposition results in electrode passivation. The formation of sulfur at the anode may therefore be circumvented by operating at potentials below -0.4 V vs. Ag/AgCl [17]. This, however, eliminates oxygen evolution as anode reaction. Alternatively, thiol oxidation may be used as anode reaction (equilibrium potential -0.38 V vs. Ag/AgCl for MT to DMDs and -0.32 V vs. Ag/AgCl for ET to DEDS). However, more electrons are required for the reduction of disulfides to sulfide than available based on the oxidation of thiols to their disulfides, and an additional electron donor would be required at the anode.

In the experiments performed in this thesis, graphite felt was used to study the degradation of thiols. Using this porous material with a high surface area supports microbial growth and facilitates microbial community interactions. However, this material also influences removal rates in the startup phase due to adsorption. Therefore, experiments focusing on further elucidating thiol degradation kinetics, conversion mechanisms, and product formation should be performed with alternative electrode materials for which the effect of adsorption can be well defined.

7.3.1.7 The potential benefit of thiol oxidation at the anode

We observed the oxidation of ethanethiol to diethyl disulfide in the cathode of continuous ethanethiol degrading experiments (chapter 6). However, the oxidation of thiols at the biocathodes in the performed experiments was thermodynamically unfavorable (See section 7.2.1) Bioanodes may form a new opportunity in case these oxidation reactions form a rate limiting step in upscaled biocathodes. These oxidation reactions may be stimulated at bioanodes, and as a result energy can be harvested. For example, a recent study showed the formation of dipropanethiol disulfide as an intermediate in propanethiol oxidation to sulfate [29]. This demonstrates that bio-catalyzed disulfide formation at the anode is possible. The achieved removal rates were up to 6 mM/d with a maximum power output of 72.5 mW/m^2 [29]. These conversion rates at these bioanodes were 3 times higher than those obtained at our ethanethiol treating biocathodes [29–31].

The oxidation of thiols to their disulfides at the anode, could be followed by a consecutive reduction of the obtained disulfides at biocathodes, and could be done by sequential flow of the organosulfur containing stream through the anode and the cathode or by alternating the electrode potentials between oxidizing and reducing potentials. The effect of this alternating current on the biofilm should be carefully examined and may form a limiting factor. Furthermore, the produced sulfide at the biocathode may be oxidized to elemental sulfur at the anode resulting in anode passivation. In addition, when treating thiol containing sulfide rich streams, sulfide should be removed before thiol oxidation at the anode. Therefore, the potential benefit of faster oxidation rates and energy harvest at the anode may not outcompete the technological limitations when treating sulfide rich streams.

7.3.2 Applicability of BES in biodesulfurization processes

Thiols are typically present in combination with hydrogen sulfide in desulfurization feed streams. The compatibility of BES with desulfurization processes is essential for the successful implementation of this new technology. BES can be integrated in the biodesulfurization process or operated as stand-alone technology, forming sulfide that can be recovered with alternative desulfurization techniques. The compatibility with physicochemical hydrogen sulfide removal and sulfur recovery technologies is not further discussed in this work.

The Thiopaq biodesulfurization processes can desulfurize gas streams on a small to medium scale (up to 70 tS/day) [32]. However, the biodesulfurization process is inhibited by the presence of thiols at concentrations above 1 μM under a sulfide-to-methanethiol ratio of 200 and limits the sulfur recovery [15]. The presence of thiols interferes with the oxygen reduction potential (ORP) measurement, which is used as a control parameter to regulate the air inflow into the aerobic reactor[33]. The disturbance of this ORP measurement results in the inefficient dosing of oxygen to the bioreactor and affects process performance. Therefore, if BES can be applied to reduce the thiol concentrations in the process solution, the application range of the biological desulfurization process can be extended. Figure 2 shows a typical biodesulfurization process scheme and indicates potential locations where BES can be implemented.

The first step in the biodesulfurization process is the absorption of hydrogen sulfide, present in, e.g., natural gas, into the halo alkaline medium that contains sulfide oxidizing bacteria (pH 7.5-10.0 and 1.0-1.5 M Na^+) [17]. When thiols are present, they are partially absorbed into the halo alkaline medium and adsorbed onto the present elemental sulfur [33]. The so-called rich solution is directed from the absorber to the anaerobic reactor. From the anaerobic reactor, the rich solution flows to the aerobic reactor, where oxygen (air) is supplied to the sulfide oxidizing bacteria which oxidize hydrogen sulfide into elemental sulfur. The regenerated lean solution, e.g., free of dissolved sulfide, is recirculated to the top of the absorber. The produced elemental sulfur is removed from the process by a decanter. The formed sulfur cake can be used as a resource, and the liquid is reused in the biodesulfurization process. This centrate contains a low sulfur concentration. Two gas streams leave this process: the first is the treated gas low in hydrogen sulfide (<25 ppm), collected at the head of the absorber, and the second is the vent air from the aerated reactor. This vent air contains depleted air and does not contain sulfide or oxygen. However, when the feed gas stream contains components other than sulfide, such as thiols and carbon dioxide, they are co-absorbed into the medium and stripped from the solution in the aerated reactor. Hence, in case the feed gas contains thiols, the vent air of the bioreactor also contains thiols and their oxidation products.

Figure 2 presents three main scenarios for the implementation of biocathodes to remove thiols. These include (1) pretreatment of the feed gas going into the absorber, (2) simultaneous treatment with hydrogen sulfide removal in (a side-stream of) (2a) the rich solution of the anaerobic reactor, (2b) the lean solution of the aerobic reactor and (2c) the centrate from the decanter, or (3) posttreatment of the treated gas and vent air. Each of these scenarios has its own benefits and potential drawbacks, summarized in Table 2. Each reactor compartment contains different sulfur species due to the different process conditions in the desulfurization process. For example, when thiols are present in the feed gas, these are oxidized in the aerobic reactor to disulfides [34].

Implementing a BES as a pretreatment step has the advantage that only small quantities of thiols will be present in the feed gas to the biodesulfurization process. Thiols are converted to sulfide in the pretreatment step, and the formed sulfide is oxidized to elemental sulfur in the consecutive biodesulfurization process. As thiols do not enter this process, they will not affect the biodesulfurization process in terms of stability and sulfur recovery. A downside of this configuration are the additional

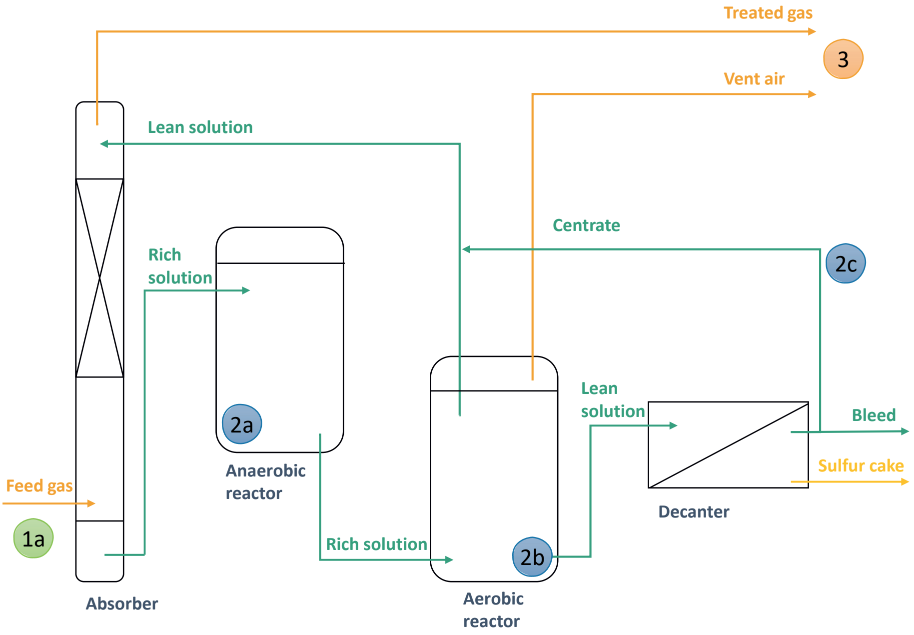

Figure 2 *Biodesulfurization process with possible locations for BES implementation; 1 pretreatment of the biodesulfurization feed gas; 2a treatment in (a side stream of) the anaerobic reactor, 2b treatment in (a side stream of) the aerobic reactor, 2c treatment in the lean centrate returning from the decanter, and 3 posttreatment of the sulfide free gas stream.*

***Table 2** Potential benefits of organosulfur conversion in different compartments of the biodesulfurization process.*

	1 Pre-treatment	2a Anaerobic reactor	2b Aerobic reactor	2c Centrate	3 Post-treatment
Stable biodesulfurization	+	+-	+-	+-	-
Presence of disulfides	-	+-	+	+	+-
Minimized reactions with sulfur	+	-	-	+	+
Avoids additional absorber	-	+	+	+	-
Low sulfide concentrations	-	-	+	+	+-
Coulombic efficiency	+	+	+	-	+

investment costs. An additional absorber is required to remove thiols from the feed gas before the absorbed thiols can be degraded in the BES. Thiols will likely be absorbed with hydrogen sulfide in the first absorber, leading to inefficiencies in thiol absorption. Furthermore, the presence of sulfide in the BES may limit the efficiency of thiol conversion, as thiol reduction is thermodynamically less favorable under high sulfide loads.

The second option entails the implementation of BES in the biodesulfurization process. This can occur in the anaerobic reactor, the aerobic reactor, or the centrate obtained during the decanting process. In this scenario, no additional absorption step is required since the absorber will absorb both sulfide and thiols. In the anaerobic reactor, thiols and sulfide remain unconverted, while sulfide oxidizes to elemental sulfur in the aerobic reactor. Sulfide is, therefore, not present at measurable concentrations in the liquid phase. In the aerated reactor, thiols are oxidized to disulfides [34]. The formation of disulfides in the aerobic reactor may benefit the biodegradation of thiols in the BES, as the formation of disulfides was also shown as an important intermediate in the continuous degradation of ethanethiol.

However, the treatment of thiols in the bioreactor has potential drawbacks. The thiol concentration in the biodesulfurization reactor should be low to maintain process stability of the biodesulfurization reactor. In addition, part of the thiols (and disulfides) will be stripped from the liquid phase due to the aeration in the aerobic reactor and end up in the vent gas. Lastly, the presence of elemental sulfur in the reactor solution forms a potential downside of BES application in the biodesulfurization liquid stream. The treatment of thiols in the biodesulfurization liquid can form polysulfides and diorganopolysulfides due to the reactions between thiols and elemental sulfur (See **chapter 1**). The formed products can affect the properties of the elemental sulfur and its settleability and limit the recovery of sulfur [34]. Alternative operational strategies of the biodesulfurization process may alleviate the negative effects of thiols, for instance stripping of thiols from the process solution [33] or applying an alternative oxygen supply strategy [35]. However, these strategies will still result in the emission of thiols as thiols are distributed throughout the biological desulfurization system.

In addition, sulfur present in the biodesulfurization liquid may have adverse effects on the BES performance. Sulfur clogging on the graphite felt and unwanted side reactions such as sulfur reduction form possible challenges when operating inside the biodesulfurization liquid stream. The BES design should be optimized to minimize these potential drawbacks.

If future studies reveal that sulfur indeed affects the BES performance and pretreatment cannot be applied, the BES may be placed in the return liquid stream of the decanter. This stream contains low concentrations of sulfur, and the advantage is that sulfur deposition on the electrode may be limited. However, thiols are not yet removed from the processing liquid before it is sent to the decanter. Thiols can attach to the sulfur resulting in a sulfur cake that is polluted with thiols and requires additional treatment. Furthermore, the decanter may introduce oxygen into the liquid phase. This would result in the reduction of oxygen at the biocathode, consumes electrons, and will lead to lower energy efficiencies.

Lastly, BES can also be implemented as a posttreatment step for the vent gas and the treated gas. In this case, an additional step, e.g., an absorber, is required to remove organosulfur compounds from the gas stream. The vent gas contains mostly disulfides. These disulfides are more hydrophobic than thiols and harder to absorb in alkaline solutions. When sulfur particles are present adsorption to sulfur particles will enhance the removal of thiols and disulfides from the gas streams[34]. The low sour component in the gas is a major benefit of the posttreatment option, i.e., the efforts of thiol absorption from the treated gas are relatively small compared to a gas stream containing more sulfide and carbon dioxide. The BES effluent, containing sulfide, needs further treatment. For example, an additional sulfide treatment step or a recirculation loop to one of the biodesulfurization compartments. In the latter case, elemental sulfur will be present in the BES medium which causes side reactions between organosulfur compounds and elemental sulfur.

To sum up, the optimal location for BES implementation depends on several factors, such as process specific conditions, feed gas composition, size of installation, and final gas stream requirements. BES may be suitable as a stand-alone pre-treatment step, as an integrated process in for example the biodesulfurization process or as posttreatment to remove residual organosulfur compounds and meet the required sulfur demands in the off gas.

7.3.3 Cost estimation for a thiol converting BES

Bioelectrochemical systems are not widely implemented yet. Therefore, the costs of full-scale installations are currently unknown. The capital costs of pilot scale (1-22.5 m^3 reactor volume) microbial electrochemical systems treating wastewater at the anode can range from 735 $/$m^3$ to 36000 $/$m^3$[36]. The costs for a bioelectrochemical system treating ethanethiol were estimated based on the parameters presented in Table 3. The cost estimate was based on the current performance using the results obtained in the laboratory. Additionally, an improved performance scenario assuming improved conversion rates and low-cost materials was calculated.

Table 3 *Parameters used for the cost estimation of a BES treating thiols.*

Variable	Current performance	Improved performance
Removal efficiency (%)	80	80
Removal rate (kg-S/m^3/d)	0.22	2.20
Faradaic efficiency (%)	4.7	47
Cell voltage (V)	2.5	2.5
Electricity costs (€/kWh)	0.32	0.32
Anode costs (€/m^2)	500	100
Cathode costs (€/m^2)	155	60
Current collector costs (€/m^2)	27.5	27.5
Membrane costs (€/m^2)	235	100
Reactor frame costs (€/m^3)	4000	4000
Lifetime reactor (Years)	20	20
Lifetime others (years)	5	5

The required energy input was calculated assuming a coulombic efficiency of 4.7% (Chapter 6), a cell voltage of -2.5V, and an electricity price of 0.32 €/kWh. The removal efficiency was set at 80% with an overall removal rate of 0.22 kg/m^3/d and was based on the ethanethiol removal rate considering the cathode volume (Chapter 6). In the improved performance scenario, the coulombic efficiency and the removal rate increased by a factor of 10. The cost of the Pt/Ir coated titanium mesh anode was estimated at 500 €/m^2 [23]. In the experimental design, the projected surface area of the anode and cathode were equal. However, the current densities that can be achieved with this state-of-the-art noble metal-coated anode are up to 450 times higher than the required current densities for the cathode [23]. Therefore, a cathode-anode ratio of 450:1 was used in these calculations. The costs of the cathode carbon felt were set at 155 €/m^2 [23]. A low-cost anode using a coated stainless-steel electrode of 100 €/m^2 and low-cost graphite felt cathode of 60 €/m^2 were used for the improved performance scenario. The costs for current collectors were set at 27.5 €/m^2 [23]. The membrane prices were set at 235 €/m^2 in the current performance scenario and replaced by a low-cost membrane of 100 €/m^2 in the improved performance scenario. The reactor frame, including, amongst others, the costs for reactor casing and pumps, was estimated at 4000/m3 [37]. A lifetime of 20 years for the reactor frame and a lifetime of 5 years for the membranes and electrodes were incorporated in the calculations. Additional costs for maintenance, labor, and energy for pumps, were not included in this calculation but will increase the overall costs per kg/S removed. The price for the recovered sulfur was also not included because additional technologies are required to recover the sulfur from this bioelectrochemical technology.

Using the parameters provided in Table 3, the overall investment costs of the reactor in the current performance scenario were estimated at 16500/m3, comparable to pilot scale prices mentioned in the literature [36]. The costs per kg sulfur removed were 39.95 €/kg-S in the current performance scenario and lowered to 2.50 €/kg-S in the improved performance scenario (Figure 3).

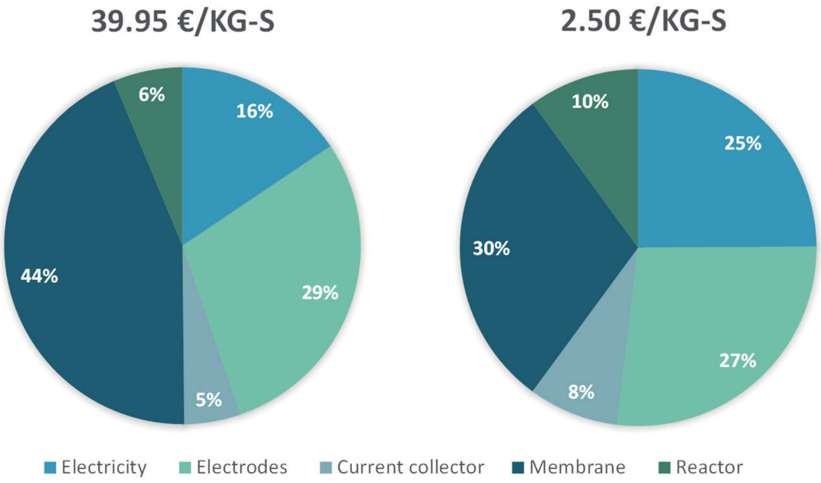

Figure 3 *Cost breakdown of thiol treating BES in the current performance scenario (a) and the improved performance scenario (b).*

The low conversion rates are the primary factor attributing to the high costs for thiol removal in BES. Increasing thiol removal rates with a factor of ten reduces the overall investment per kg sulfur removed by 90%. The required reactor size reduces significantly if the conversion rates increase. The maximum removal rate of ethanethiol was not yet achieved and enhancing the removal rate is likely possible by increasing the influent flow. Furthermore, higher removal rates are expected for methanethiol than for ethanethiol.

Changing the reactor materials and overall reactor design also substantially influences the costs for thiol removal. The membranes form the largest expense for this BES in both scenarios. The use of low-cost membranes decreases reactor investment costs by 24%. However, these low-cost membranes may contribute to increased internal resistances with lower proton transfer efficiencies and can potentially decrease thiol reduction rates. In addition, the increased oxygen crossover from the anode attributes to lower coulombic efficiencies and higher energy input. A membraneless reactor is most likely not desirable, as discussed in section 7.3.1.

Electrodes make up for 29% and 27% of the sulfur removal costs in the two scenarios. The titanium Pt/IR coated anode electrode is expensive. Each anode can be coupled to a cathode on either side in a stacked cell design. Alternatively, cheaper anode materials, e.g., carbon materials [24] or coated stainless steel electrodes, can be implemented to lower the electrode costs. However, using these alternative electrode materials increases the required energy input, translating into higher operational costs [24].

Finally, Improving the coulombic efficiency to 47% can reduce the energy costs from 6.22 to 0.62 €/kg-S. With energy prices rising globally, high energy efficiencies are essential for this technology to be viable. The coulombic efficiencies can increase by operating at a potential that is close to the minimum required potential for thiol conversion, avoiding side reactions such as methane formation from bicarbonate or sulfur reduction. Furthermore, optimizing the reactor design can limit energy losses related to oxygen ingress.

7.3.4 Comparison BES with thiol removal technologies

BES must compete with commercially available technologies for thiol removal. The BES removal rates should be sufficiently high, and costs should be comparable to or lower than those of commercially available technologies. The ability to recover sulfur and the low waste production associated with this application are two significant advantages of a BES. The comparison between BES and these established technologies is complex as limited data is publicly available on their performance and large-scale application of BES is still in its infancy. Table 4 presents some key performance parameters of bioelectrochemical systems and other technologies to remove thiols.

Table 4 *BES comparison with established thiol removal strategies.*

Process	**Treated compounds**	**Products formed**	**Rate kg S/ m³/d**	**Efficiency %**	**Ref.**
BES cathode	MT, ET, PT	H_2S, RSSR, SO_4^{2}, S^0, CH_4	0.22[a]	70-95	[38,39]
BES anode	PT	RSSR, S^0, H_2S, SO_4^{2}	0.46	91	[29]
BES anode	DMDS	MT, S^0, H_2S, SO_4^{2-}, CO_2	0.51	<76.6	[30]
SuperClaus[b]	H_2S, MT, ET, PT	S°, CO_2	n.a.[c]	99.9	[40,41]
Merox, Thiolex	MT, ET, PT	RSSR	n.a.[c]	n.a.[c]	[42,43]
Solid scavenger[d]	H_2S, MT, ET, PT	FeS_2(R)	37.3	n.a.[c]	[44]
Liquid scavenger[e]	H_2S, MT, ET, PT	NaS(R) Dithiazine-RSH	n.a.[c]	n.a.[c]	[44–46]
LO-CAT	H_2S	S^0	n.a.[c]	99.9	[44]
SulFerox	H_2S	S^0	500	>99.9	[44,47]
Flare	H_2S, MT, ET, PT	SO_2, CO_2	n.a.[c]	100	[48]
UASB[f]	MT	H_2S, CO_2, CH_4	1.56	100	[12,49]
UASB[g]	MT	H_2S, CO_2, CH_4	1.16	>95	[13,49]
UASB[h]	MT	H_2S, CO_2, CH_4	0.41	100	[49,50]
Biotrickling filter	MT	SO_4^{2-}	2.05	96.6	[51,52]
Biotrickling filter	ET	SO_4^{2-}, S^0, CO_2	0.87	91	[51,53]

[a] rate based on ET; [b] based on 140 TS/d; [c] *not available;* [d] iron oxide; [e] NaOH, or dithiazine; [f] pH>7.5 Na^+, 0.03M; [g] pH<8 Na^+, 0.5 M; [h] pH<10Na^+, 0.8 M.

The BES removal rates are based on the degradation of ethanethiol described in chapter 6. These rates underestimate the capacity of the BES because the maximum degradation rate was not yet achieved. In addition, higher removal rates for methanethiol in BES are expected, as this is already a biodegradable substrate under anaerobic conditions. The obtained degradation rates of ethanethiol in this thesis are lower than the degradation rate of methanethiol in UASB reactors and biofilters. However, it is important to note that these processes can only convert methanethiol [54–56]. The capacity to degrade ethanethiol and propanethiol in BES provides a significant advantage over alternative biodegradation processes. The removal rates of chemical thiol conversion processes are not readily available in literature as it highly depends on the processed streams. However, the chemical rates are substantially higher than those reported for UASB reactors. The low degradation rate in biological systems requires a large area and is an important factor in the limited applicability of these reactors [13].

Currently, chemical processes to remove thiols outcompete the performance of bioelectrochemical systems regarding removal rate and cost per ton of sulfur removed. The Claus or Superclaus process has the lowest cost per ton of sulfur removed. However, the estimated costs are based on a hydrogen sulfide treatment process in which thiols are removed by co-combustion. A stream dominated by thiols or with a hydrogen sulfide load lower than 3 ton S/day is incompatible with the Claus process [57]. Alternatively, the merox™, thiolex™, and solid and liquid scavengers are compatible with thiol-rich streams and operate at small to medium scales. The costs of iron-based scavengers are estimated at 5200 € per ton of sulfur removed

[44]. At these costs, scavengers are 7.5-18 times cheaper compared to the BES in the current performance scenario [44–46]. Within the improved BES scenario, BES can economically compete with scavengers and have the advantage of potential sulfur recovery, which is typically not applied for scavengers. It should be noted that these costs do not include the disposal of the toxic waste produced with scavengers or the further processing of sulfide from the BES.

The Low-Cat® technology treats hydrogen sulfide at an estimated cost of 300-900 € per ton sulfur removed [44] Low-Cat is a liquid redox process which utilizes an iron-based catalyst. The Merox and Thiolex processes are also liquid redox processes but utilize a cobalt phthalocyanine complex as catalyst for the oxidation of thiols [45]. Assuming similar costs for Low-Cat and the Thiolex and Merox processes, these thiol treating processes have lower costs per ton of sulfur removed compared to the BES. It should be noted that these costs do not include the disposal of toxic disulfides or hydrotreatment of the formed disulfides to hydrogen sulfide; the overall costs for thiol removal are thus higher. Nonetheless, these technologies form the main competitors in the future, where thiols will be produced on a decentralized scale.

The BES process has a competitive advantage when looking at the products that are formed in this process. At least when assuming sulfide is an important intermediate, this technology can be applied to recover sulfur. Bioelectrochemical systems can regrow its own catalyst, while in the merox and thiolex process, the catalyst needs to be replaced. A complete cost comparison, including waste disposal, operational and maintenance costs, is required to accurately compare BES with existing technologies.

Whether BES can compete with existing technologies depends largely on the economic aspects. In addition, the removal rates of BES should increase to become competitive with chemical processes. Low removal rates require large reactors and are render this technology unfeasible for high thiol loads.

7.4 Final considerations

This chapter described the feasibility of BES becoming a future technology for thiol removal. In BES, oxidation and reduction reactions can be separated from each other, and the energy levels at the electrodes can be set at a specific value. BES forms a unique strategy that facilitates microbial conversions. This thesis showed that ethanethiol could be degraded at a biocathode, while natural biodegradation processes under anaerobic conditions are unknown for this compound.

The work in this thesis demonstrates that BES may become a suitable low-cost and low-waste technology for thiol removal. To achieve this, degradation rates should increase, and the investment costs of a BES should be reduced considerably. Using a

BES avoids the production of toxic waste streams, and sulfur from thiols can be recovered when combined with a desulfurization process.

The compatibility of BES with other technologies forming a suitable treatment train should be evaluated. Before scaling up this technology, more insight into the product formation, reaction mechanism, and inhibition concentrations is required. Furthermore, to effectively implement a new technology and solve an environmental issue, governments should implement legislation that empowers innovations that contribute to less waste generation, lowers energy use, and prevents environmental damage.

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Supporting information

Table SI-1: *Theoretical equilibrium potentials under actual conditions and electrode potentials including the minimum required overpotential to sustain 14.5 kJ/mol for microbial growth.*

	Eq. potential V vs. Ag/AgCl	**14.5 kJ/mol Potential V vs. Ag/AgCl**	**Half reaction**
Methanethiol	-0.28	-0.36	$CH_4S + H^+ + 2e^- \leftrightarrow CH_4 + HS^-$
Ethanethiol	-0.35	-0.39	$C_2H_6S + 3H^+ + 4e^- \leftrightarrow 2CH_4 + HS^-$
	-0.37	-0.45	$C_2H_6S + 1H^+ + 2e^- \leftrightarrow C_2H_6 + HS^-$
	-0.41	-0.49	$C_2H_6S + 2H^+ + 2e^- \leftrightarrow CH_4 + CH_4S$
Dimethylsulfide	-0.35	-0.43	$C_2H_6S + 2H^+ + 2e^- \leftrightarrow CH_4S + CH_4$
	-0.41	-0.45	$C_2H_6S + 4H^+ + 4e^- \leftrightarrow CH_4 + HS^-$
Dimethyl disulfide	-0.31	-0.34	$C_2H_6S_2 + 4H^+ + 6e^- \leftrightarrow 2CH_4 + 2HS^-$
	-0.37	-0.43	$C_2H_6S_2 + H^+ + 2e^- \leftrightarrow C_2H_6S + HS^-$
	-0.38	-0.45	$C_2H_6S_2 + 4H^+ + 6e^- \leftrightarrow 2CH_4S$
Diethyl disulfide	-0.32	-0.39	$C_4H_{10}S_2 + 2H^+ + 2e^- \leftrightarrow 2\ C_2H_6S$
	-0.34	-0.36	$C_4H_{10}S_2 + 8H^+ + 10e^- \leftrightarrow 4CH_4 + 2HS^-$
	-0.35	-0.38	$C_4H_{10}S_2 + 4H^+ + 6e^- \leftrightarrow 2C_2H_6 + 2HS^-$
	-0.39	-0.46	$C_4H_{10}S_2 + 2H^+ + 2e^- \leftrightarrow C_3H_8S_2 + CH_4$
	-0.39	-0.42	$C_4H_{10}S_2 + 2H^+ + 2e^- \leftrightarrow C_2H_6S_2 + 2CH_4$
MT ET disulfide	-0.39	-0.46	$C_3H_8S_2 + 2H^+ + 2e^- \leftrightarrow C_2H_6S_2 + CH_4$
	-0.42	-0.49	$C_3H_8S_2 + 2H^+ + 2e^- \leftrightarrow C_2H_6S + CH_4S$
Bicarbonate	- 0.63	-0.66	$HCO_3^- + 8H^+ + 6e^- + HS^- \leftrightarrow CH_4S + 3H_2O$
	- 0.61	-0.62	$2HCO_3^- + 15H^+ + 12e^- + HS^- \leftrightarrow C_2H_4S + 6H_2O$
Side reactions	+0.51		$O_2 + 4H^+ + 4\ e^- \leftrightarrow 2\ H_2O$
	- 0.41	-0.43	$SO_3^{2-} + 6H^+ + 7e^- \leftrightarrow HS^- + 3H_2O$
	- 0.51	-0.53	$SO_4^{2-} + 8H^+ + 9e^- \leftrightarrow HS^- + 4H_2O$
	-0.52	-0.67	$S^0 + H^+ 2e^- \leftrightarrow HS^-$
	- 0.55	-0.56	$HCO_3^- + 9H^+ + 8e^- \leftrightarrow CH_4 + 3H_2O$
	- 0.77	-0.84	$2H^+ + 2e^- \leftrightarrow H_2$

The equilibrium potential was calculated based on a sulfur species concentration of 1 mM, a bicarbonate concentration of 0.6 M, a methane partial pressure of 0.2 atm, a pH of 8.5, and a temperature of 298.15 K.

Summary

The degradation of thiols using bioelectrochemical systems was explored in this thesis.

Thiols, also known as mercaptans, are toxic organosulfur compounds with a low odor threshold. These compounds are naturally formed in anaerobic degradation processes. However, anthropogenic activities like natural gas extraction or renewable fuel production increase the natural flux of these organosulfur compounds. These compounds must be removed from fuels before combustion to avoid the formation of sulfur dioxide, which attributes to acid rain and dry acid deposition. Hydrogen sulfide and thiols are typically extracted from these sources with amine or caustic solutions which require further treatment. Hydrogen sulfide can be converted to elemental sulfur in various (bio)desulfurization processes. However, the presence of thiols limits the sulfur removal and recovery in these processes. Thus, adequate treatment of thiols is required.

New challenges and opportunities for waste streams produced in a net zero energy market are discussed in chapter 2. These upcoming streams contain pollutants such as thiols, ammonia, benzene, toluene, and xylene, and require treatment. The sulfur, nitrogen, and carbon dioxide can be recovered and can contribute to a circular economy. However, to achieve this, new technologies need to be developed. Chapter 3 provides an overview of the current and anticipated thiol-producing markets and the available techniques for thiol removal and sulfur recovery. Current thiol-producing markets include, aside from the fossil fuel industry, the pulp and paper industry, wastewater treatment plants, landfills, rayon and viscose production, and metal mining. New thiol producing markets include hydrogen stored in former fossil fuel wells, biogas production and treatment, syngas production, and biofuel production. The currently available thiol removal and recovery techniques are tailor-made for the fossil fuel industry, characterized by high and stable flows. At the same time, the future markets will require more flexible techniques, dealing with lower and fluctuating sulfur loading rates. Furthermore, the recovery of sulfur will become increasingly important with the decline of sulfur recovery from fossil fuels. Therefore, new technologies should aim to convert thiols and recover the sulfur.

Bioelectrochemical systems (BES), combining microorganisms and electrodes, may offer a new strategy to convert thiols towards hydrogen sulfide. We show that thiols can be reduced towards hydrogen sulfide at a biocathode. Chapter 4 demonstrates that methanethiol, ethanethiol, propanethiol, and dimethyl disulfide were reduced to hydrogen sulfide in current-controlled (2A/m^2 and 4 A/m^2) biocathodes. A sulfur recovery from methanethiol of 64% was found within 5 days after the addition of 0.1 mM methanethiol. Moreover, in a 22-day fed-batch experiment, sulfur recoveries as

sulfide of 18% for methanethiol and ethanethiol, 17% for propanethiol, and 22% for dimethyl disulfide were found.

Chapter 5 describes a new method to measure thiols and their related organosulfur compounds in complex matrixes. The saline matrix, useful for the absorption of thiols from gaseous streams, and the reactivity and volatility of thiols complicate their detection. Headspace chromatography was used to analyze liquid samples. The direct acidification of samples with 1 M acetate buffer (pH 3.6) allowed the measurement of organosulfur compounds over a calibration range of 5 µM-S till 125 µM-S (R^2 <0.999). Liquid standards deteriorated rapidly due to the reactivity of the thiols in this matrix. As an alternative, gas standards were used to calibrate the liquid phase. After equilibration, gas standards obtained a response of 105.2% for ET, 107% for DMS, 105.7% for PT, 108.9% for DMDS and 106% for DEDS in comparison to the liquid standards. Gas samples were measured using the same chromatographic conditions over a calibration range of 0.08 µM-S until 1.85 µM-S (R^2 <0.999) and were used to define henry constants in demineralized water and the saline liquid matrix. Using gas standards for liquid calibration or coefficients allows for the routine sampling and analysis of thiols in this complex matrix.

Chapter 6 describes the continuous degradation (>360 days) of ethanethiol at a biocathode under current controlled (ranging from -2 to -6 A/m^2) and potential controlled (-0.5 V vs. Ag/AgCl) conditions. The removal efficiencies were stable (<70%-99%), and the maximum obtained removal capacity was 2.25 mM/d. Higher removal rates may be obtained by further increasing the thiol loading rate. The dominating organosulfur compound in the effluent changed from ethanethiol towards diethyldisulfide, an oxidation product of ethanethiol. Furthermore, sulfate and thiosulfate, and elemental sulfur were found at the cathode. Batch bottle experiments with no other electron donor than ethanethiol demonstrated that the oxidation of ethanethiol to diethyldisulfide was dominantly catalyzed by microorganisms, even under anaerobic conditions. Modeling demonstrated that diethyldisulfide nor ethanethiol was further degraded in absence of an electrode. Therefore, the oxidation of ethanethiol may form the initial step in its degradation and diethyldisulfide can be converted to hydrogen sulfide at biocathodes.

In Chapter 7, the results of all chapters are combined. First, the observed reaction products are linked to a thermodynamic framework. In theory, thiols can be reduced to hydrogen sulfide with hydrogen as electron donor. However, hydrogen was unlikely an intermediate in ethanethiol degradation, as the hydrogen availability was limited under potential control. When considering a minimum energy requirement of 14.5 kJ/mol for microbial conversions, the one-step degradation of DEDS towards hydrogen sulfide is more favorable than the degradation via ethanethiol.

There are various options for the implementation of a thiol converting BES in the biological biodesulfurization process. We discuss that the BES may be integrated within the biodesulfurization process or installed as a stand-alone pre- or post-treatment process. The best location for the BES and the successful implementation in the biodesulfurization process depends on various factors, such as the maximum thiol concentrations, the effect of high sulfide concentrations on thiol degradation, the effect of thiols on the sulfur crystallization, and the feed composition. Each of these aspects should be carefully evaluated when further developing a thiol converting BES.

The costs for thiol treatment in a BES system were estimated at 2.50 €/kg-S in the improved performance scenario. When these rates and costs are achieved, BES can compete with scavenger technologies and can become a new technology for the conversions of thiols, while recovering sulfur.

Abbreviations

AEGL	acute exposure guideline level
AGRU	acid gas removal unit
BTX	benzene toluene xylene
BES	bioelectrochemical system
CE	coulombic efficiency
CEM	cation exchange membrane
CAPEX	capital expenditure
DEDS	diethyl disulfide
DMDS	dimethyl disulfide
DMS	dimethyl sulfide
DMSO	dimethyl sulfoxide
DMSP	dimethylsulfoniopropionate
ET	ethanethiol
FPD	flame photometric detector
GC	gas chromatograph
HEFA	hydro processed esters and fatty acids
HPLC	high pressure liquid chromatography
HVO	hydrotreated vegetable oil
ICP-OES	Inductively Coupled Plasma Optical Emission spectroscopy
IEA	international energy agency
IPCC	intergovernmental panel on climate change
LD-50	median lethal dose
LOD	limit of detection
LOQ	limit of quantification
MEC	microbial electrolysis cell
MFC	microbial fuel cell
MT	methanethiol
MTET	methane ethane disulfide
OCP	open cell potential
OPEX	operating expense
ORP	oxygen reduction potential
OSC	organosulfur compound
PEEK	polyetheretherketone
PT	propanethiol
PTFE	polytetrafluoroethylene
rRNA	ribosomal ribonucleic acid
RSH	thiol
SAF	sustainable aviation fuel

SCD	sulfur chemiluminescence detector
SEM	scanning electron microscope
SEM EDX	scanning electron microscopy-energy dispersive X-ray
SHE	standard hydrogen electrode
SRU	sulfur recovery unit
TCOD	total chemical oxygen demand
TLV-TWA	threshold limit value – time weighted average
TN	total nitrogen
UASB	upflow anaerobic sludge blanket
VLR	volumetric loading rate
VOC	volatile organic compound
VOSC	volatile organosulfur compound

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Margo

About the author

Margo Elzinga was born on September 9th in Groningen, the Netherlands. She grew up with her siblings in a small town filled with opportunities and freedom to explore the world around her. Learning has always been a great source of joy to Margo. Her enthusiasm to learn, explore and discover was further fueled during her BSc. in Environmental sciences, where she specialized in water technology. She performed her internship at the federal university of Viçosa, Brazil, where she worked on identifying toxic compounds in municipal wastewater. During her bachelor thesis at Paques on UASB reactors, she realized that there was much more to learn, prompting her to apply for the Wetsus Academy. Joining Wetsus academy, she received a grant from the Waterboard Vallei en Veluwe where she also performed her internship. During this internship, she studied different waste streams and their biogas production potential. She completed her MSc thesis in Wetsus, centre of excellence for sustainable water technology, where she studied the microbial rechargeable battery.

Exploring the world around her was not limited to universities and the laboratory. After obtaining her BSc and MSc, she travelled to South America, immersing herself in different cultures and communities, enjoying an off-grid, slow-paced lifestyle. Returning to the Netherlands, she worked as a research assistant at Wageningen University and studied thiol reduction in bioelectrochemical systems. During this period, a proof of principle was established, eventually resulting in a PhD position in a partnership between the Environmental Technology department at Wageningen University and Research and Paqell B.V. She engaged in this new learning opportunity and the results of this work are presented in this dissertation.

Author's patents and publications

Elzinga, M., de Haan, D., Buisman, C. J. N., ter Heijne, A., & Klok, J. B. M. (2023). Nutrient recovery and pollutant removal during renewable fuel production: opportunities and challenges. Trends in Biotechnology. https://doi.org/10.1016/J.TIBTECH.2022.12.016

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- Research in context activity: 'Course development Microbial Electrochemical Technologies' (2022)

Other PhD and Advanced MSc Courses

- Competence assessment, Wageningen Graduate Schools (2018)
- Bath electrochemistry winter school, University of Bath, United Kingdom (2019)
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- Scientific writing, Wageningen Graduate Schools (2020)
- Presenting with impact, Wageningen Graduate Schools (2020)
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- Structure and Reactivity, Wageningen University (2021)
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- *Insights in ethanethiol degradation at biocathodes*. ISMET 8 Global Conference, 19-22 September 2022, Chania, Greece
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