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Ulrike Gayh

Process intensification of biological desulphurisation of biogas

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Humic substances may not be beautiful, but they do beautiful things
(Fritz Frimmel)

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Abstract

Biogas must be desulphurised before use to avoid corrosion and toxic concentrations. If the requirements for reliable purification performance increase in clean gas, external processes would be increasingly adopted. As conversion to biomethane becomes more important, the application of desulphurisation will evolve because of increasingly stringent purity requirements. The aim of this thesis was to develop a complete bio-scrubber system with high efficiency, i.e. high absorption capacity, good and cheap regeneration, no production of any waste with recovery of useful by-products. Operation of such a plant must be simple, stable and incurs little cost.

A bio-scrubber system containing humic substances as solubilising additives was found to be a solution. The system consists of a scrubber with downstream biological regeneration.

The optimisation of hydrogen sulphide removal by humic substances and the regeneration of the washing liquid were analysed in the laboratory. Equilibrium as well as continuous experiments showed an increase of the solubility of hydrogen sulphide by addition of humic substances in the liquid phase. This result was approved with experiments at a pilot plant. All experiments showed that the use of humic substances as solubility agents in the biogas treatment is effective.
Information about the biodegradation capacity of the sulphur bacteria as well as the influence of additives on the activity of sulphur bacteria was determined. A slight inhibition effect of humic substances on the activity of sulphur bacteria was observed. Nevertheless, the washing liquid can be regenerated by biological means. The optimum concentration of humic substances for a bio-scrubber system was determined at 2 - 4 wt-%.

As humic substances are a natural product their use in this process has clear advantages over the use of artificial solubilisers in optimising this treatment. In addition, humic substances improve the soil activity and can be used as agricultural fertiliser. This use of a by-product instead of removing it as waste is an advantage of the system, especially in comparison with chemical processes.

The costs of such a humic substances containing bio-scrubber-system are higher than for internal desulphurisation processes, but for plants with high gas flow rates or high hydrogen sulphide concentrations, a bio-scrubber system is recommended. This is especially for the conversion to bio-methane. Such a desulphurisation step is interesting because it has the advantage of the biogas not being diluted by air.

A model of the bio-scrubber system was developed. Different scenarios could be evaluated with the simulation of the absorption column using humic substances in the washing liquid.

In conclusion, biogas can be desulphurised efficiently and in an environmentally-friendly means by the addition of humic substances. The application of this bio-scrubber system in other industrial applications should be investigated in practice. For example, the removal of sulphur dioxide is one option.

Zusammenfassung

Entschwefelung von Biogas ist notwendig, um Korrosion sowie giftige Konzentrationen zu vermeiden. Wenn die Anforderungen an eine zuverlässige Reinigung im Reingas steigen, werden externe Verfahren bevorzugt. Da die Aufbereitung zu Biomethan fortschreitet, werden diese Reinigungsanforderungen an den Entschwefelungsprozess ebenfalls ansteigen. Das Ziel dieser Arbeit war es, ein komplettes Bio-Wäscher-System zu erhalten. Dieses soll sich durch hohe Effizienz, wie hohe Absorptionsfähigkeit, gute und einfache Regeneration sowie keinerlei Abfallproduktion auszeichnen. Das Betreiben dieses Prozesses soll einfach, zuverlässig und kostengünstig sein.

Die Lösung wurde mit einem Bio-Wäscher-System gefunden, welches Huminstoffe als Löslichkeitsvermittler einsetzt. Dieses System besteht aus einem Wäscher und einer nachgeschalteten biologischen Regeneration.

Mithilfe von Laborversuchen wurde die Verbesserung der Schwefelwasserstoffentfernung durch Huminstoffe sowie die Regeneration der Waschflüssigkeit durch Schwefelbakterien analysiert.
Durch Gleichgewichtsversuche sowie kontinuierlichen Laborversuchen wurde die Erhöhung der Löslichkeit von Schwefelwasserstoff durch die Zugabe von Huminstoffen in die Flüssigphase festgestellt. Dieses Ergebnis bestätigte sich auch durch Versuche an einer Pilotanlage. All diese Versuche zeigten, dass der Einsatz von Huminstoffen zur Schwefelwasserstoffentfernung sehr effektiv ist.
Des Weiteren wurden Informationen zum biologischen Abbau von Schwefelwasserstoff durch Schwefelbakterien sowie der Einfluss von Additiven auf die Aktivität der Bakterien im Labor bestimmt. Es wurde eine leichte Hemmwirkung der Huminstoffe auf die Schwefelbakterien festgestellt, jedoch ist eine biologische Regeneration trotzdem möglich.
Daraufhin wurde die optimale Huminstoffkonzentration in einem Bio-Wäscher-System von 2 bis 4 Gew.-% bestimmt.

Aufgrund ihres natürlichen Ursprungs haben die Huminstoffe Vorteile gegenüber künstlichen Additiven. Sie wirken als Bodenverbesserer und können somit zur Düngung eingesetzt werden. Die Nutzung dieses Nebenproduktes hat vor Allem gegenüber chemischen Verfahren Vorteile.

Die Kosten für ein externes Bio-Wäscher-System sind höher als bei internen Entschwefelungsprozessen. Dennoch ist es für Anlagen mit hohen Gasdurchsätzen oder hohen Schwefelwasserstoffkonzentrationen empfehlenswert. Vor Allem für die Entschwefelung bei Anlagen zur Herstellung von Biomethan ist dieses System interessant, da das Biogas nicht mit Luft verdünnt wird.

Es wurde ein Modell des Bio-Wäscher-Systems entwickelt. Durch die Simulation einer Absorptionskolonne unter Einsatz von Huminstoffen in der Waschflüssigkeit konnten unterschiedliche Szenarien bewertet werden.

Abschließend kann man sagen, dass Biogas effizient und umweltfreundlich durch den Einsatz von Huminstoffen entschwefelt werden kann. Dieses Bio-Wäscher-System ist auch für andere industrielle Anwendungen, z.B. zur Entfernung von Schwefeldioxid, interessant.

Résumé

La désulfuration du biogaz est nécessaire pour éviter la corrosion et déconcentrer les toxiques. Si l'exigence pour une purification fiable augmente, les procédés extérieurs seraient plus adaptés. La conversion au biomethane deviendra plus importante et ainsi les besoins en désulfuration changera à direction d'une meilleure performance de purification. L'objectif de cet ouvrage est d'obtenir un système de bio-laveur avec une efficacité élevée, c'est-à-dire une capacité d'absorption élevée, une régénération possible et bon marché sans production de déchets. L'opération de cette unité doit être simple, fiable et économique.

Le système de bio-laveur avec humines comme additif de solubilité est une option. Ce système est composé d'un laveur et d'une régénération biologique connectée en aval.

L'optimisation de l'absorption du sulfure d'hydrogène sur humines et la régénération des eaux de lavage étaient analysés dans le laboratoire. Par des essais d'équilibre et continues, l'augmentation de la solubilité du sulfure d'hydrogène par l'addition des humines dans la phase liquide est constatée. Ce résultat est confirmé par des essais à une installation pilote.
Le résultat des essais de laboratoires indiquent que l'usage des humines pour la purification de biogaz est effectif. L'information de désassimilation des bactéries sulfurées et l'influence des additifs ont aussi été déterminées. Une inhibition faible des humines sur l'activité des bactéries sulfurées ont été déterminée cependant une régénération biologique est possible. La concentration des humines optimales a été déterminée et doit être comprise entre 2 et 4 %massique.

Les humines sont naturelles, elles ont un avantage face à des additifs artificiels. Elles améliorent l'activité du sol et par conséquent elles pourraient être utilisées comme engrais. De plus ce produit secondaire est un avantage par rapport aux procédés chimiques.

Les coûts pour ce système de bio-laveur avec humines sont plus élevés que pour des procédés internes. Mais pour des installations avec des flux de gaz élevés ou des concentrations en sulfure d'hydrogène élevées, il est aussi recommandé. Dans le cadre d'une conversion au biomethane, ce système permet de ne pas diluer le gaz avec de l'air.

Un modèle de ce système de bio-laveur avec humines est développé. Plusieurs scénarios pouvaient être évalués avec la simulation d'une colonne d'absorption.

En résumé, le biogaz peut être désulfuré efficacement et écologiquement avec une addition d'humines. L'application de ce système de bio-laveur à d'autres procédés industriels pourrait être étudiée. Une option pourrait être la purification en dioxyde de soufre.

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Symbol	Definition	Dimension
Abs	Absorption	
ANOVA	Analysis of Variance	
b	Decay coefficient	h^{-1}
b	Equilibrium constant for linear equilibrium	
B	Biomass	
BTEX	Acronym for Benzene, Toluene, Ethylbenzene and Xylenes	
c	Concentration	$mg \cdot l^{-1}$
CHP	Combined Heat and Power plant	
DAPI	Fluorescent strain ($C_{16}H_{15}N_5$)	
DAE	Differential-Algebraic Equation	
DIN	Deutsches Institut für Normung (= German Institute for Standardization	
DOC	Dissolved Organic Carbon	$mg \cdot l^{-1}$
EEG	Erneuerbare Energien Gesetz (= German Renewable Energy Sources Act)	
EN	European Norm	
f	Function	
F	Ratio of "variation due to treatment" and "variation due to error"	
FISH	Fluorescent In Situ Hybridization	
G	Vapour, Gas flow rate	$mol \cdot h^{-1}$
GI	Germination index	%
h	Enthalpy	$J \cdot mol^{-1}$
H	Henry coefficient	Pa
HA	Humic acids	
HETP	Height Equivalent to one Theoretical Plate	m
HTU	Height of one Transfer Unit	m
k	Kinetic factor	
K	Dissociation constant	$mol \cdot (m^3)^{-1}$
K_m	Michaelis-Menten constant (= substrate concentration of half maximal growth rate)	$mg \cdot l^{-1}$
$KS_{4,3}$	Buffer capacity	$mmol \cdot l^{-1}$

K-HA	Potassium humate	
k_La	Gas liquid mass transfer coefficient	h^{-1}
L	Liquid flow rate	$mol \cdot h^{-1}$
LC-OCD	Liquid Chromatography - Organic Carbon Detection	
m	Local slope of equilibrium curve (y = m·x + b)	
M	Molecular weight	$g \cdot mol^{-1}$
n	Number of seeds germinated	
n	Stirrer rotation	rpm
NPK	Acronym for Nitrogen, Phosphorous and Potassium	
NTU	Number of Transfer Units	
NTU	Nephelometric Turbidity Unit	
OEL	Occupational Exposure Limit	
OC	Oxygen Consumption	$mg \cdot l^{-1} \cdot h^{-1}$
OUR	Oxygen Uptake Rate	$mg \cdot l^{-1} \cdot h^{-1}$
ORC	Organic Rankine Cycle	
p	Value for the statistical significance, exceedance probability	
P	Total pressure	bar
P	Product	
PID	Proportional-Integral-Derivative	
PLC	Programmable Logic Control	
Ppm	Parts per million	$ml \cdot m^{-3}$
Q	Volume flow	$l \cdot h^{-1}$; $ml \cdot min^{-1}$
r	Reaction rate	$mg \cdot l^{-1} \cdot h^{-1}$
R	Gas constant = 8.31447215	$J \cdot mol^{-1} \cdot K^{-1}$
R	Regeneration factor	
RSG	Relative Seed Germination	%
RRE	Relative Root Elongation	%
S	Substrate	
SS	Steady State	
t	Time	h
T	Temperature	°C ; K
TOC	Total Organic Carbon	$mg \cdot l^{-1}$
TN	Total Carbon	$mg \cdot l^{-1}$
UV	Ultraviolet	l

V	Volume	$l \cdot h^{-1}$
$\dot{V}$	Volume flow	$mg \cdot l^{-1}$
y	Gas concentration	$mol \cdot mol^{-1}$
Y	Gas loading	$g_{Pr} \cdot g_S^{-1}$
Y	Yield coefficient	$mg \cdot l^{-1}$
x	Liquid concentration	$mol \cdot mol^{-1}$
X	Liquid loading [mol/mol]	
Greek characters		
α	Temperature coefficient	
Δ	Delta, difference	
γ	Activity coefficient	
ε	Porosity	
η	Degree of reduction	%
λ	Stoichiometric oxygen sulphide relation	
μ	Specific growth rate	h^{-1}
φ	Process rate	$mg \cdot l^{-1} \cdot h^{-1}$
φ	Fugacity coefficient	
Indices		
*	Equilibrium condition, saturated	
Abs	Absorption	
aq	Aqueous	
avail	Available	
B	Biomass	
B	Bottom	
C	Control	
COD	Chemical Oxygen Demand	
cons	Consumed	
eq	Equilibrium	
G	Gas	
g	Gaseous	
HP	Potassium humate Humin-P	
i	Index	
I	Inhibition	
L	Liquid	

Max	Maximum
n	Number of seed germinated
O	Overall (based on the overall driving force)
opt	Optimum
Ox	Oxidation
P	Product
Pr	Proteins
R	Reaction
Red	Reduction
Ref	Reference
rl	Root length
S	Solid
S	Substrate
S	Sulphur
sol	Solution
T	Top
T	Test

Chemical formula

C	Carbon
CH_4	Methane
CH_4S	Methyl mercaptan
C_2H_6S	DMS (dimethyl sulphide)
$C_2H_6S_2$	DMDS (dimethyl disulfide)
C_2H_6OS	DMSO (dimethyl sulphoxide)
C_2H_7NO	MEA (monoethanolamine)
$C_4H_{11}NO_2$	DEA (diethanolamine)
$CH_3N(C_2H_4OH)_2$	MDEA (methyl diethanolamine)
$C_6H_{15}NO_3$	TEA (triethanolamine)
$C_{16}H_{15}N_5$	DAPI (4',6-diamidino-2-phenylindole)
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
COS	Carbonyl sulphide
CS_2	Carbon disulphide
Fe	Iron

$FeCl_3$	Ferric chloride, Iron (III) chloride
FeS	Iron sulphide
Fe_2S_3	Iron (III) sulphide
H (H_2)	Hydrogen
HCO_3^-	Hydrogen carbonate
H_2CO_3	Carbonic acid
HCl	Hydrogen chloride
H_2O	Water
HS^-	Sulphide
H_2S	Hydrogen sulphide
H_2SO_3	Sulphurous acid
H_2SO_4	Sulphuric acid
K	Potassium
N (N_2)	Nitrogen
Na	Sodium
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide
Na_2S	Sodium sulphide
Na_2SO_4	Sodium sulphate
$Na_2S_2O_3$	Sodium thiosulphate
NH_3	Ammonia
NH_4	Ammonium
$(NH_4)_2SO_4$	Ammonium sulphate
O (O_2)	Oxygen
OH^-	Hydroxide
P	Phosphorous
S	Sulphur
SCN^-	Thiocyanate
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SO_3^{2-}	Sulphite
SO_4^{2-}	Sulphate
$S_2O_3^{2-}$	Thiosulphate
$S_4O_6^{2-}$	Tetrathionate

1. Objective

Biogas production is gaining popularity in Germany. Today, there are more than 6,000 biogas plants installed in Germany [1]. In other countries like Sweden or China, biogas production has increased significantly. Before using the biogas the contained hydrogen sulphide (H_2S) has to be removed in order to avoid corrosive and toxic effects.
The objective of this thesis is to optimise the desulphurisation of biogas. A biological desulphurisation process is chosen, because biological processes are low-cost. The idea is to upgrade their efficiency to achieve better H_2S removal. A two-stage bio-scrubber system was selected. This system's advantages include a high purification capacity and no air dilution (see chapter 3.1.2). The disadvantages of such a system are that complex instruments are required, resulting in higher investment costs. Improving this system should result in lower costs and a stable and efficient H_2S removal. The optimisation of this process will be investigated in two ways: on the one hand by adding solubility agents and on the other hand by the variation and optimisation of process parameters (e.g. pH-value, oxygen (O_2) concentration). Figure 1 shows a flow diagram scheme of an improved bio-scrubber system. It contains a scrubber and downstream biological regeneration. H_2S is absorbed in the counter-current scrubber and the loaded washing liquid is regenerated by sulphur bacteria in the downstream bioreactor.

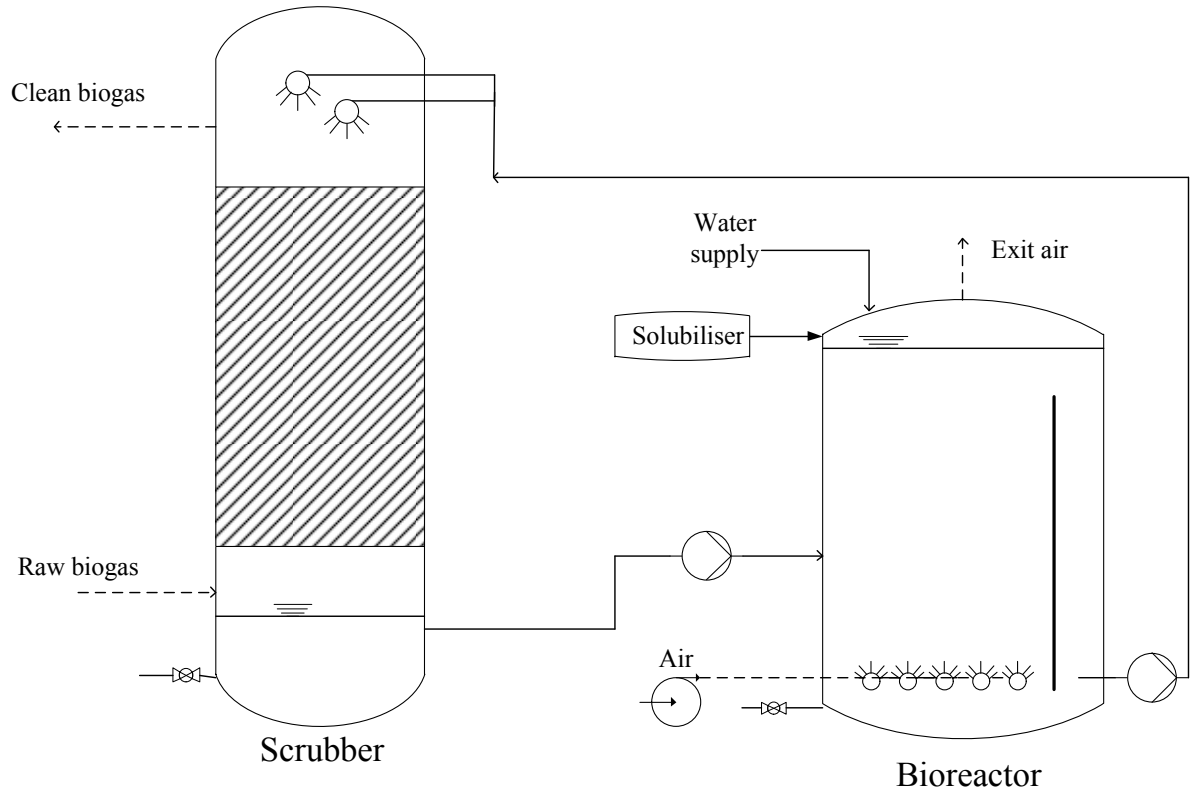

Figure 1: Flow scheme of a two-stage bio-scrubber system

The aim is to develop a complete bio-scrubber system with high efficiency, i.e. high absorption capacity, good and cheap regeneration and no waste production coupled with the gain of useful by-products. Operating such a plant should be easy, stable and of low cost.
By modelling the process the efficiency can be tested for different plants. This is investigated in different case studies. The cost and efficiency of the system is compared to other biological desulphurisation processes as well as chemical and physical desulphurisation processes.

2. Introduction

This introduction provides an outline of the chapters covered in this thesis. First, an overview of the basics of biogas and state of the art of the research topic is presented. The experimental chapters are divided into three parts, in which different sections of the bio-scrubber system are dealt with in separate chapters. The upgrade of the scrubber is described, analysed and evaluated in chapter 4. This chapter deals with optimising the removal of H_2S. Chapter 5 examines the regeneration of washing liquid. Information about the biodegradation capacity of sulphur bacteria as well as the influence of additives is also analysed. By-products, waste streams and exhaust air is detailed in chapter 6. This chapter mainly describes the possible use of washing liquid as agricultural fertiliser. Chapter 7 illustrates the modelling and simulation of the system and their individual components respectively. Costs are evaluated in chapter 8 and the practical application of the optimised bio-scrubber system is described in chapter 9 with some case studies. The thesis concludes with a summary of the results obtained and an outlook on further research options and applications.

3. Background and Basics

3.1. Biogas

Biogas is a renewable energy source. The produced biogas can be easily used for the generation of electricity and heat. Table 1 shows the components of biogas and their typical concentrations.

Table 1: Components of biogas [2]

Component	Concentration
Methane (CH_4)	50 - 75 %
Carbon dioxide (CO_2)	25 - 50 %
Oxygen (O_2)	< 2 %
Nitrogen (N_2)	0 - 5 %
Water vapour (H_2O)	1 - 5 %
Hydrogen sulphide (H_2S)	0 - 5000 ppm
Ammonia (NH_3)	0 - 500 ppm

The number of biogas plants has increased significantly in recent years. In Germany there were more than 4,000 biogas plants installed at the end of 2009. The main reasons for this are the amendments to the German Renewable Energy Sources Act (EEG) in 2004 and 2009. Now, there are more than 6,000 biogas plants. [1]
Biogas production has also increased in other countries, for example in China, which has the highest consumption of biogas in the world [3]. Electricity production worldwide from biogas was about 35 $Twh \cdot a^{-1}$ in 2009; the installed capacity was 7 GW. Specifically, the Europe 27 countries had an installed capacity of 5 GW with power generation of 25 $Twh \cdot a^{-1}$. [4]
In countries such as China, biogas is often produced in a biogas plant in the courtyard and directly used. China plans to have 20 % of rural households with biogas plants in their courtyard by 2020. In addition, some biogas plants with a capacity of 1 to 3 MW have been built and 90 projects with a plant capacity of over 1 MW are planned or under construction.[5]

Due to its characteristics, biogas can be used in applications other than in a combined heat and power plant (CHP). For example, biogas can be used as fuel for motor vehicles, fed into the natural gas grid or used for new technologies, including fuel cells, gas turbines, ORC (Organic Rankine Cycle) and refrigeration.

3.1.1. Production of biogas

Biogas is produced during the fermentation of organic matter by anaerobic microorganisms. After the disintegration of particulate biomass, the decomposition process is divided into four steps. Each step is carried out by different bacteria groups:

- Hydrolysis: Hydrolysing bacteria reconstruct high-molecular substances (protein, carbohydrates, fats, cellulose) by means of enzymes to low-molecular compounds like monosaccharides, amino acids, fatty acids and water.
- Acidogenesis: Fermentative bacteria produce carboxylic acids, alcohols and gases (e.g.: CO_2, H_2, H_2S).
- Acetogenesis: Acetogenic bacteria form the initial products for CH_4 formation from organic acids, namely acetic acid, CO_2 and H_2.
- Methanogenesis: Methanogenic bacteria form CH_4 and CO_2 in two parallel processes. 70 % of CH_4 is formed from acetic acid (decarboxylation) and 30 % from the reduction of CO_2.

Sulphur enters the process through the input of protein-rich substrates such as catering waste and dry chicken dung. The formation of H_2S during anaerobic fermentation is primarily divided into two processes [6,7]:

- Desulphuration: Sulphides are released during the anaerobic decomposition of organic protein compounds by hydrolysis and by fermentative bacteria, which results in the formation of H_2S.
- Desulphurication: The main product in this dissimilatory sulphate reduction process is H_2S. Sulphate reducing bacteria use sulphate (SO_4^{2-}) as their terminal electron acceptor during the oxidation of organic compounds.

Figure 2 demonstrates the different steps of anaerobic fermentation as well as the production of H_2S during this process.

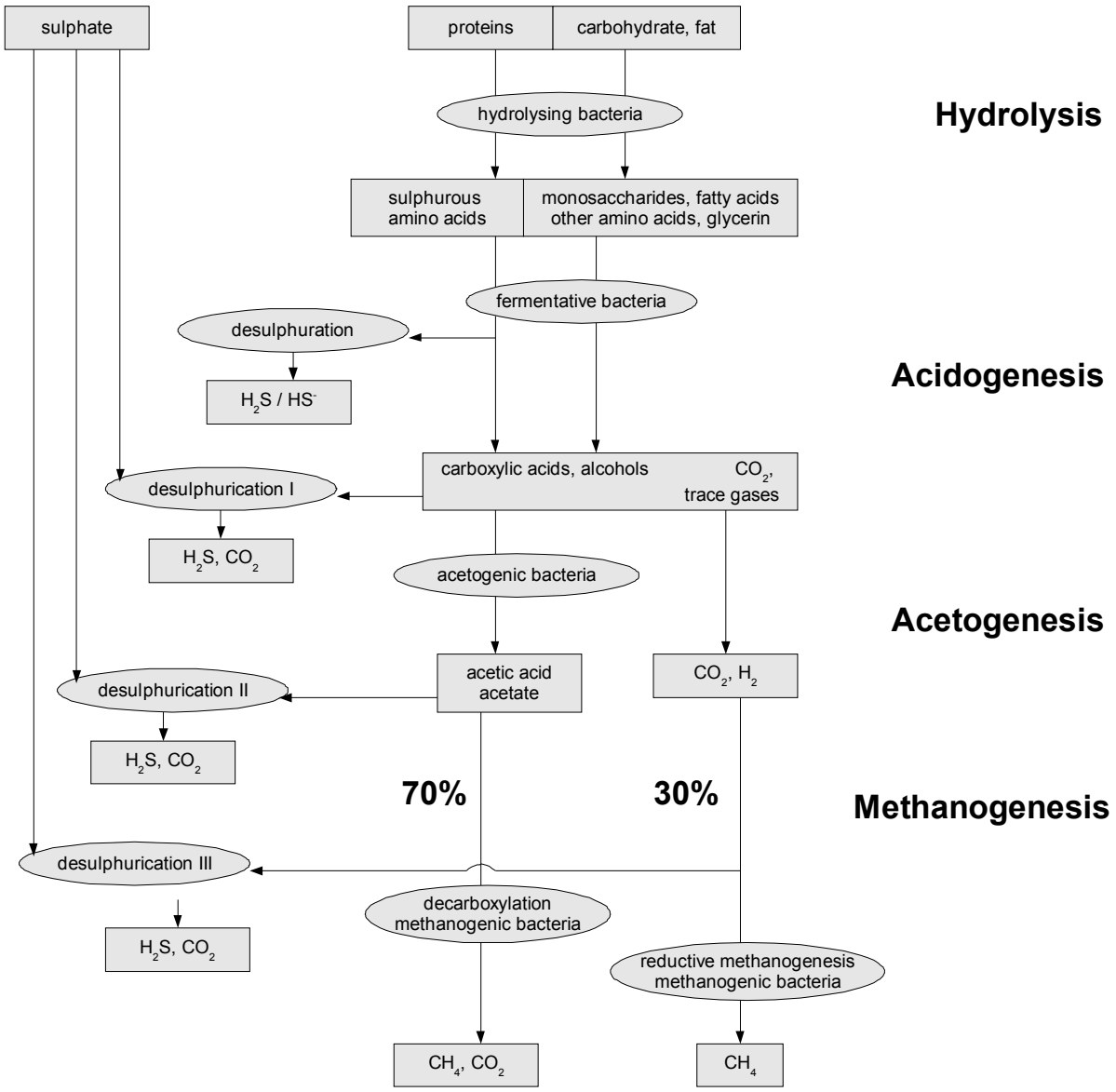

Figure 2: Production of H_2S during anaerobic fermentation [7]

The main production of CH_4 and H_2S occurs during methanogenesis. Elimination of H_2S-production in this step also means an inhibition of the production of CH_4. However, high concentrations of H_2S (>50 $mg \cdot l^{-1}$) inhibit the formation of CH_4 as well [8]. Further information regarding the inhibition of CH_4 production by H_2S is given in [9].

3.1.2. Desulphurisation

H_2S and organic sulphur compounds have to be removed before using biogas. H_2S is a very toxic gas (OEL = 10 ppm) and smells of rotten eggs [9]. The characteristics of H_2S are described in detail in table A3 and A4 in the annex. Desulphurisation of biogas is needed to prevent corrosion and avoid toxic concentrations. High concentrations of H_2S in biogas cause problems during the incineration process. When biogas is burned, sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are emitted, causing more severe air pollution than H_2S. The sulphurous acid (H_2SO_3) formed is highly corrosive. The acidified engine oil results in the need for frequent oil exchanges. Table 2 shows the service life of lubricating oils and ignition plugs in relation to H_2S concentrations. The oxidation catalyst for reducing the toxic content in exhaust gas reacts very sensitive to H_2S and decreases its efficiency. To convert biogas to biomethane several treatment processes also require an upstream desulphurisation step. The requirements on desulphurisation in relation to the recovery processes are shown in table 3. Biogas has typical H_2S concentrations of 1,000 to 3,000 ppm. There are different methods for the desulphurisation of biogas and an overview is given in table 4.

Table 2: Service life of lubricating oils and ignition plugs in relation to the H_2S concentration [10]

Concentration H_2S in biogas	**Operational restrictions**	**Service life of lubricating oils and ignitions plugs**
< 250 ppm	Optimum / unrestricted	800 - 1 000 operating hours
250 - 450 ppm	Increased maintenance	400 - 500 operating hours
> 450 ppm	High maintenance	Max. 300 operating hours

Table 3: Requirements for biogas desulphurisation [2,11]

Process	**Maximum H_2S concentration**
Gas combustion engine	200 - 250 ppm
Fuel	< 3.5 ppm
Pressure swing adsorption (CarboTech)	< 3.5 ppm
Pressure water scrubbing (Malmberg, Flotech)	500 - 2 000 ppm
Genosorb®-scrubbing (HAASE Energietechnik)	100 ppm
Amine scrubbing (MT Energie)	< 3.5 ppm
Fuel Cell	< 1 - 10 ppm

Table 4: Overview of desulphurisation methods [2]

Process	**Separation Effect**
Biological Oxidation	Microbial oxidation of H_2S with formation of S, SO_3^{2-}, $SO4^{2-}$
Adsorption	Adsorption of H_2S at molecular sieves or activated carbon
Chemical Adsorption	Chemical reaction of H_2S with iron oxide
Chemical Precipitation	Precipitation of H_2S as Fe_2S_3
Chemical Absorption	Chemical reaction of H_2S with NaOH
Separation by membranes	Permeability of H_2S higher than CH_4 and CO_2

Separation by biological means is a possible low-cost alternative. H_2S is transformed to an energy source during the metabolism of sulphur bacteria. Thiobacilli can then oxidise it to elemental sulphur (S) or SO_4^{2-}. In general, there are three different biological desulphurisation processes: internal biological desulphurisation, single-stage external biological desulphurisation and double-stage biological desulphurisation. Internal desulphurisation occurs during direct air injection into the fermenter where microbial oxidation takes place. Single-stage external desulphurisation happens mostly in a downstream trickling filter. In this counter current column the H_2S is absorbed in the washing liquid. Sulphur bacteria living on the packing material regenerate the washing liquid and form SO_4^{2-}. The conditions of this process are often acidic (about pH 1.5) because of the formation of SO_4^{2-} and sulphuric acid (H_2SO_4).
The double-stage bio-scrubber system contains a scrubber and downstream biological regeneration (see figure 1). H_2S is absorbed in a counter-current scrubber and the loaded washing liquid is regenerated by sulphur bacteria in the downstream bioreactor. Due to the aeration of the separately connected bioreactor, dilution of biogas is avoided and therefore also the reduction of the calorific value of the biogas.
The majority of biogas plants employ biological treatment, mostly using internal desulphurisation with air injection directly in the fermenter. Double-stage bio-scrubber systems are rarely selected. [12]
An example of a double-stage bio-scrubber system is the THIOPAQ® scrubber technology from the company Paques. THIOPAQ® is a biotechnological process which removes H_2S from gaseous streams and the microbial production of elemental sulphur from the absorbed sulphide. In 1991 the first THIOPAQ® installation for the removal of H_2S from biogas started operation. The THIOPAQ® process has a H_2S removal efficiency of 99.99 %. The gained elemental sulphur can be re-used for the production of H_2SO_4, H_2S and for agricultural applications. [13]

Table 5 demonstrates the advantages and disadvantages of the different biological desulphurisation processes as well as those of physical and chemical desulphurisation processes.

Table 5: Advantages and disadvantages of desulphurisation processes [14], [15]

Desulphurisation process	Advantages	Disadvantages
Internal	• Low effort • Low costs	• Unstable desulphurisation • Dilution of biogas resulting in a reduction of its calorific value • Explosion risk at incorrect air supply • Risk of corrosion in fermenter
External, single-stage	• High purification capacity • No corrosion problems in fermenter • Reliable	• Dilution of biogas resulting in a reduction of its calorific value • Clogging packed bed • High cost
External, two-stage	• High purification capacity • Low maintenance • Reliable • No dilution of biogas • No clogging in scrubber	• Complex process with a lot of components resulting in higher investment cost • Few practical experiences
Internal chemical desulphurisation (iron salts, iron hydroxide)	• Low investment costs • No dilution of biogas • Generally high purification capacity	• High operating costs
External chemical desulphurisation (iron hydroxide, iron chelates)	• Reliable • High purification capacity • High H_2S loadings • No dilution of biogas (iron chelates)	• High costs • Few practical experiences • Residue disposal • Dilution of biogas (iron hydroxide)
External activated carbon filters	• Very reliable • High purification capacity • Fine desulphurisation	• Only for low H_2S loadings efficient • High costs • Residue disposal • Dilution of biogas

3.2. Absorption

Absorption is a thermal separation process. During absorption one or more components of a gas stream are removed by being taken up in a non-volatile liquid.
Absorption can be physical or chemical. Physical and chemical scrubbing processes have different scrubbing mechanisms. In physical absorption the gas is removed because it has greater solubility in the solvent than other gases. There are no chemical reactions between the compound to be removed and the washing liquid. In chemical absorption the gas compound to be removed reacts with the solvent and remains in solution. In a chemical scrubbing process another substance is formed besides the washing liquid and the compound to be removed. Chemical scrubbers show better selectivity between various compounds while physical scrubbers can remove wide spectra of substances. [16]
Another difference is that a chemical scrubber reacts to the amount of the component to be removed and a physical scrubber reacts to the total gas amount. In addition, physical bonds are reversible while in chemical processes there are at least some irreversible by-products. [17]
The limit between physical absorption and absorption by chemical reaction often cannot be distinguished.

The basic equations to describe the process of absorption are (see chapter 7.1):

- Mass balance
- Energy balance
- Phase equilibrium equations

The general mass balance of a counter current absorber is stated in equation 3.1. Here, x_{H2S} is the concentration of H_2S in the liquid phase and y_{H2S} is the concentration of H_2S in the gas phase. L is the liquid flow and G is the gas flow. The indices T and B refer to top and bottom of the column respectively.

$$L_T \cdot x_{H_2S,T} + G_B \cdot y_{H_2S,B} = G_T \cdot y_{H_2S,T} + L_B \cdot x_{H_2S,B} \tag{3.1}$$

The energy balances consider enthalpy and heat balances. The stationary enthalpy balance without heat losses is as indicated in equation 3.2. In the equation, h_i refer to the enthalpies of the gas (G) and the liquid (L).

$$L_T \cdot h_{L,T} - G_T \cdot h_{G,T} - L_B \cdot h_{L,B} + G_B \cdot h_{G,B} = 0 \tag{3.2}$$

Phase equilibrium describes the solubility of gases (y) in liquids (x) and can be calculated using Henry's Law.

$$X_i \cdot \gamma_i^* \cdot H_i = Y_i \cdot \varphi_i \cdot p \tag{3.3}$$

The activity coefficient γ_i^* can be set to one for low mol fractions and the fugacity coefficient φ_i can be neglected for low pressures p ($\varphi_i = 1$). [18]
This means that the solubility of a gas in a liquid can be described mathematically according to Henry's Law as follows.

$$H_i = \frac{Y_i}{X_i} \cdot p \tag{3.4}$$

The Henry coefficient H is a common parameter to characterise the absorption capacity of a substance. Theoretically, the Henry coefficient of H_2S in water at a temperature of 25 °C is 560 bar [19].

The absorption of a gas in a liquid is based on mass transfer with the difference in concentration as the driving force. The concentration gradient describes an imbalance of phase equilibrium which results in mass transfer within and between the phases and through phase boundaries. The mass transfer depends mainly on the specific mass transfer coefficient. Figure 3 presents the idealised concentration profile of a substance vertically towards the phase boundary according to the two film theory. An increase of the phase boundary between liquid and gas increases the mass transfer.

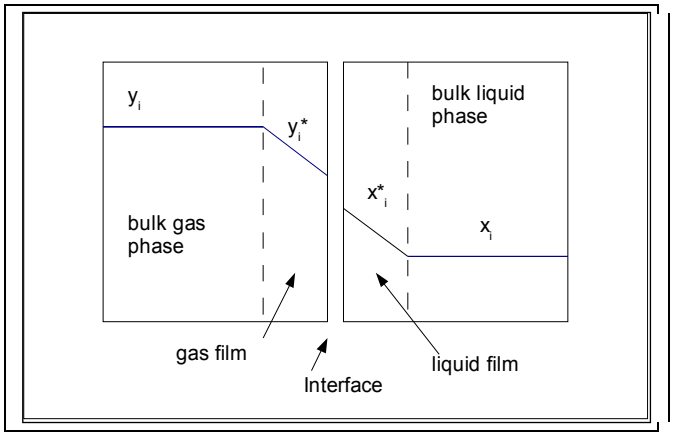

Figure 3: Concentration profile according to the two film theory

For describing the processes during absorption there are different methods, for example the method of theoretical stages (HETP method) and the method of transfer units (HTU-NTU concept) (see chapter 7.1).

3.2.1. Upgrade of solubility of H_2S

Improving the efficiency of gas scrubbers can be achieved by using adapted washing liquids. These washing liquids must satisfy certain requirements to ensure a safe, economic and environmentally-friendly absorption process. For application in biological desulphurisation, these solubilisers should offer, amongst others, the following characteristics:

- High selectivity for H_2S
- Water-soluble
- Non-toxic
- Non- or hardly biologically degradable
- Non-volatile
- Available
- Cost-effective

In the following paragraphs, possible solubilisers as well as known washing solutions are presented. Water is the most important solvent in physical absorption because of its availability at low cost. Therefore the effectiveness of other solvents is always compared to water. [20] Absorptive desulphurisation with sodium hydroxide (NaOH) solution (pH of about 8.5) is an existing process for industrial desulphurisation [14]. The desulphurisation with amines is efficiently used in natural gas treatment, but for the desulphurisation of biogas, it is not economically feasible [15]. Alkanolamines are often used as absorbents for acidic gases.

Triethanolamine (TEA) was used in early gas-treating plants and was the first commercially available alkanolamine. TEA has been replaced by monoethanolamine (MEA) and diethanolamine (DEA) which have proved to be of commercial interest. [20]

DMSO (dimethyl sulphoxide) is a polar aprotic solvent. It is often used in chemistry and industry. DMSO is also applied in scrubbing H_2S from fuel gas. [21]
DMSO, TEA and MEA are used as comparative solvents in laboratory tests (see chapter 4). Furthermore, normal tap water, as well as alkaline and acidic water, is used for comparative purposes.

Sulfa-Clear™ 8640 is a water-soluble sulphide converter from the company Weatherford. This product also fulfils the criteria as a solubiliser for application in biological desulphurisation. It is a 60 - 65 % active aqueous amine resin solution containing surfactants, designed as a H_2S scavenger for gas systems. Its application is mainly odour control in wastewater treatment. [22]
Sulfa-Clear™ 8640 has been proven to be a cost-effective alternative to other chemicals due to significantly lower treatment rates and better performance. The normal dosage required is 4 to 6 ppm per ppm of H_2S. Sulfa-Clear is a reddish-amber liquid which can be injected directly into the gas or liquid stream. The products do not foul or contaminate downstream operations. [23] The characteristics of Sulfa-Clear™ 8640 are listed in table 6.

Table 6: Characteristics of the Sulfa-Clear [22]

Trade name	Sulfa-Clear™ 8640
Chemical characterisation	Aqueous amine solution
Chemical state	Liquid
Colour	Reddish-Amber
pH-value	10.3 - 11.0
Flash point	66 °C
Pour Point	< -32 °C
Density	1 072 $kg \cdot m^{-3}$
Solubility in water	Soluble in water
Activity	60 - 65 %

Humic substances can also be used as solubiliser in this application. They are described in detail in chapter 3.3.

Table 7 presents some processes for the removal of H_2S (and CO_2) with industrially-adapted washing liquids.

Table 7: Absorption processes for the removal of H_2S and CO_2 [11]

Process	Washing liquid	Conditions
MDEA-process	Methyldiethanolamine 10 – 25 % in water	p > 10 bar T: 50 - 70 °C
DEA-scrubbing	2n -3n diethanolamine	p: 8 - 10 bar T: 20 - 55 °C
MEA-scrubbing	2.5n or 5n monoethanolamine	$p > p_{atm}$ T = 40 °C
Genosorb®-scrubbing	Tetraethylenglykoldimethylether	p < 7 bar T: 20 - 40 °C
Selexol®-scrubbing	Polyethylenglykoldimethylether	p < 20 - 30 bar T: 0 - 40 °C
Rektisol-scrubbing	Methanol	p > 20 bar T: -70 - -10 °C
Purisol-scrubbing	N-Methyl-2-pyrolidon	p > 20 bar T: -20 - 40 °C

3.3. Humic substances

Humic substances are a group of organic compounds either formed during the degradation of plants or other organic matter or are produced by bacteria, fungi and protozoa in soil, sediments and water. They consist of very high molecular weight compounds with undefined structures. The elemental composition of humic substances is carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S). These major elements are always present, regardless the origin of humic substances. According to their solubility in water they are divided into humin, humic acids and fulvic acids. Table A6 in the annex gives an overview of the main characteristics of humic substances.

Their major functional groups include carboxylic, phenolic, carbonyl, hydroxyl, amine, amide and aliphatic groups, among others. Humic acids are one of the most powerful chelating agents. Their zwitterionic character allows the interaction of anions with positively charged groups of humics and cations with negative charged groups of these substances. [24,25]

Due to a high number of donor sites humic substances form chemical reactions with a lot of natural and anthropogenic substances [26]. Humus-containing materials have already been utilised for sorbing gases. Their application includes, for example, the removal of waste gases from an animal-carcass rendering plant and the removal of H_2S and mercaptans from municipal gas supplies [24]. Furthermore, sodium humates can absorb SO_2 efficiently and to a high capacity [27]. It has been discovered that nitrohumic acid and its salts have excellent desulphurisation ability and can be used for industrial desulphurisation [28]. Since 2001, humates have also been used for the treatment of H_2S at a paper mill. The absorption capabilities of the humate molecule showed a rapid absorption of H_2S. Furthermore, humic-based materials are environmentally safe during handling, transport and disposal [29].

Another application of humic acids is as catalyst or with activated carbon for gas purification by means of H_2S oxidation [30]. Humic substances have also been identified as good solubilisers for odorous substances [31].
As they are natural substances, their purification process is cheaper than the synthesis of any other sorbent and they absorb more than absorbents used to date, such as active charcoal or clays [24]. Humic substances have a high storage capacity for SO_4^{2-}, S and H_2SO_4 [30].
Other applications of humic substances are, for example, agriculture, biomedicine and the removal of toxic metals [24]. Their benefit in agriculture is described in chapter 6.1. Detailed information about the structure, analysis and application of humic substances can be found in literature [24,32–35, 37].
Tested humic substances are mainly potassium humate (Humin-P) and sodium humate (Humin-S) from the company Humintech. Humates are the salts of humic acids; they consist of 70 - 80 % humic acids and are completely soluble in water. [36]
Figure 4 shows a photo of Humin-P and a potential molecule structure of humic acid. Its main characteristics are described in table 8.

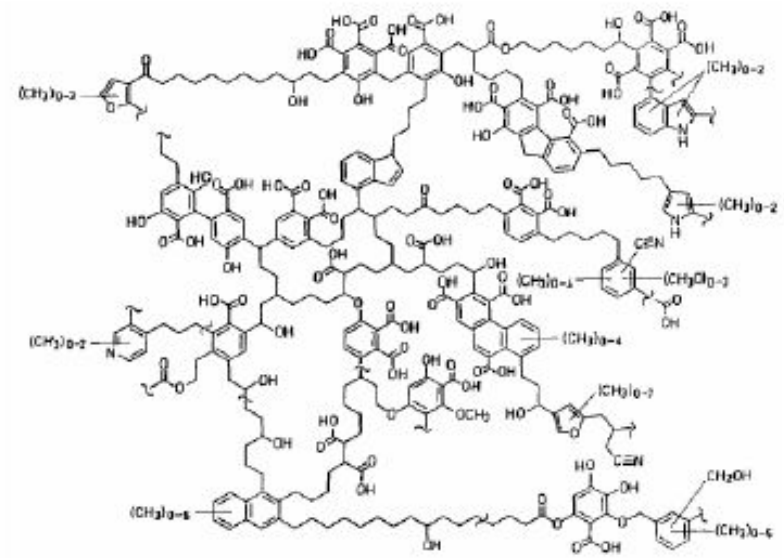

Figure 4: Photo of potassium humate and the molecular structure of humic acid [25]

Table 8: Characteristics of the potassium humate Humin-P [36]

Trade name	Humin-P 775
Article number	4 036964 003036
Chemical characterisation	Potassium salt of humic acids
CAS number	68514-28-3
Chemical state	Solid
Form	Flakes
Colour	Dark brown
Odour	Not distinguishable
pH-value (10 $g \cdot l^{-1}$, 20 °C)	9.0 - 10.0
Change in physical state	> 250 °C: destroyed to CO_2, H_2S and soot
Flash point	300 °C
Decomposition temperature	< 100 °C
Density, 20 °C	0.6 $g \cdot cm^{-3}$
Solubility in water, 20 °C	approx. 200 $g \cdot l^{-1}$

3.4. Biological sulphide oxidation

The biological oxidation of sulphide (HS^-) to sulphate (SO_4^{2-}) proceeds in two stages. First, the HS^- loses two electrons and polymeric sulphur compounds are formed. This elemental sulphur (S) is bound to the biomass [38]. In the second step, this S is oxidised to sulphite (SO_3^{2-}) and then to SO_4^{2-}. Intermediate products such as SO_3^{2-} or thiosulphate ($S_2O_3^{2-}$) are not secreted by the bacteria [39]. The following reactions occur in an aerobic sulphide removal system.

$$2 \cdot HS^- + O_2 \rightarrow 2 \cdot S + 2 \cdot OH^- \tag{3.5}$$

$$2 \cdot S + 2 \cdot OH^- + 3 \cdot O_2 \rightarrow 2 \cdot SO_4^{2-} + 2 \cdot H^+ \tag{3.6}$$

The first reaction proceeds faster than the second [38], but this is the energetically unfavoured reaction [40]. The microbiological H_2S-oxidation proceeds due to sulphur bacteria (Thiobazilli) which transform the H_2S in their metabolism. Biological H_2S oxidation proceeds faster than non-catalysed chemical oxidation [41]. Especially in highly loaded bioreactors, the chemical auto-oxidation of HS^- with the formation of $S_2O_3^{2-}$ occurs in addition [40].

$$2 \cdot HS^- + 2 \cdot O_2 \rightarrow H_2O + S_2O_3^{2-} \tag{3.7}$$

The incomplete oxidation of HS^- to elemental sulphur, followed by the separation of the water-insoluble elemental sulphur is an attractive method of reducing sulphur content [42]. An increase of the selectivity towards elemental sulphur can be effected only by kinetic control [39].
The formation of elemental sulphur instead of SO_4^{2-} has some clear advantages:

- Lower oxygen (O_2) demand resulting in less energy consumption
- Avoiding negative aspects of SO_4^{2-}, that is, the formation of sulphuric acid (H_2SO_4) (corrosive impact)
- Water-insoluble and easy to separate from the system [42]
- Fewer additives necessary for pH regulation [39]
- Formation of elemental sulphur is faster than the formation of SO_4^{2-} resulting in higher specific reduction rates [38]
- Higher efficiency of H_2S removal at higher pH values [43]
- Humates precipitate at pH values lower than 3 [44]

Furthermore, the recovery of elemental sulphur is an advantage, for instance to use as agricultural fertiliser.
SO_4^{2-} production rate can be suppressed by controlling the O_2 concentration. Furthermore, Buisman et al. [38] found that at high sulphide concentrations in the reactor, O_2 concentration should be increased in order to increase the sulphide oxidation rate. At low sulphide concentrations, the O_2 concentration should be kept low in order to suppress the oxidation of sulphur to SO_4^{2-}. This means that at low sulphide concentrations, O_2 concentration has a distinct influence on the amount of SO_4^{2-} formed. [38,42]
According to Stefess [42] the following variables are important for the control of sulphur formation:

- Sulphide load
- O_2 limitation
- Type of organism
- Growth history of organisms

3.4.1. Thiobazillus

Fundamental knowledge of the physiology of sulphur-producing Thiobazilli is important for process optimisation. The important point is that they can reduce sulphur compounds. Thiobazilli are small (0.3 - 0.5 · 0.7 - 4.9 µm), rod-shaped and Gram-negative bacteria. They can tolerate pH values from around 0 to above 8.5 with the optimum pH between 2 and 8. Their optimum temperature is between 20 and 50 °C. [45]
Schneider [39] determined that the microbiological degradation of sulphide is optimal at temperatures of about 30 °C.

Thiobazilli are further divided into three subgroups [42]:

- obligate chemolithoautotroph
- facultative chemolithoautotroph
- chemolithoheterotroph

Obligate chemolithoautotroph derive energy from the oxidation of reduced sulphur compounds and use carbon dioxide (CO_2) as their main source of carbon. Facultative chemolithoautotroph can grow autotrophically on reduced sulphur compounds and CO_2, and can also grow as heterotroph on organic compounds. Chemolithoheterotrophic Thiobazilli cannot grow autotrophically because they cannot fix CO_2, but their ability to oxidise reduced sulphur compounds can provide metabolically useful energy. Bacteria that do not show any benefit from the oxidation of reduced sulphur compounds are termed heterotrophic sulphur-oxidisers rather than chemolithoheterotrophs. These bacteria do not belong to Thiobazilli or colourless sulphur bacteria. [42]
Figure 5 shows a microscopic image of mixed culture consisting of different Thiobazilli.

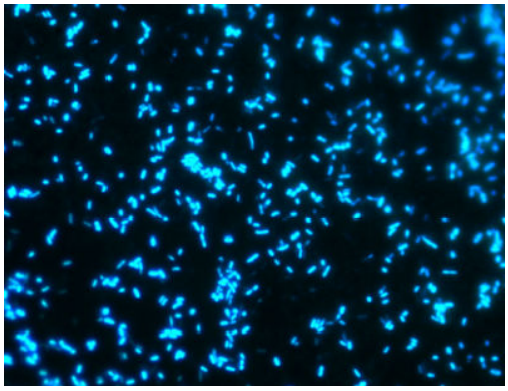

Figure 5: Microscopic image of Thiobazilli (DAPI colouring) [39]

Certain Thiobazilli can grow on sulphide and on sulphur. Janssen et al. [40] have proven that their change of metabolism from SO_4^{2-} to S production occurs within less than two hours, which is faster than their doubling time. Table 9 shows the growth conditions and optimum states of some species, which can degrade H_2S or other sulphur compounds.

Table 9: Overview of characteristics of sulphur bacteria [46]

Species	pH growth range [-]	Optimum pH [-]	Tempera-ture growth range [°C]	Optimum temperature [°C]	Energy source
Thiobacillus ferrooxidans	-	1.3 - 4.5	10 - 37	30 - 35	Fe^{2+}, $S_2O_3^{2-}$, S
Thiobacillus thiooxidans	0.5 - 6.0	2.0 - 3.5	10 - 37	28 - 30	H_2S, S, polithionates
Thiobacillus novellus	5.7 - 9.0	7.0	10 - 37	30	H_2S, CH_4S, C_2H_6S, $C_2H_6S_2$
Thiobacillus thioparus	5 - 9	7.5	-	28	$S_2O_3^{2-}$, S^{2-}
Thiobacillus denitrificans	-	6.8 - 7.4	-	28 - 32	S^{2-},$S_2O_3^{2-}$, S, $S_4O_6^{2-}$, SCN^-
Thermothrix azorensis	6.0 - 8.5	7.0 - 7.5	63 - 86	76 - 78	$S_2O_3^{2-}$, S, $S_4O_6^{2-}$, H_2S
Thioalkalispira microaerophila	8 - 10.4	10	-	-	$S_2O_3^{2-}$, S, S^{2-}, poly-sulfide
Thiomicrospra frisia	4.2 - 8.5	6.5	3.5 - 39	32 - 35	$S_2O_3^{2-}$, S, $S_4O_6^{2-}$, S^{2-}

3.4.2. Degradation kinetics

A series of mathematical models describe the growth of microorganisms. In kinetics, growth is defined as the irreversible increase of viable biomass. The Monod model is well-established for microbiological transformations. Here the concentration of the biomass is proportional to its growth rate, expressed by the specific growth rate μ. It is described analogously to the mathematical form of Michaelis-Menten kinetics. The concentration of the substrate is denoted by c_S.

$$\mu = \mu_{\max} \cdot \frac{c_s}{K_m + c_s} \tag{3.8}$$

Reaction-based parameters are the maximum growth rate μ_{max}, the Michaelis-Menten constant K_m (substrate concentration at half the maximum growth rate) and the yield coefficients Y_i described below. Here B refers to biomass, P to product and S to substrate. The reaction rate is denoted by r.

$$Y_{B/S} = \frac{\Delta B}{\Delta S} = \frac{dB}{dS} = \left|\frac{r_B}{r_S}\right|,\ Y_{P/S} = \frac{\Delta P}{\Delta S} = \frac{dP}{dS} = \left|\frac{r_P}{r_S}\right|,\ Y_{P/B} = \frac{\Delta P}{\Delta B} = \frac{dP}{dB} = \left|\frac{r_P}{r_B}\right| \tag{3.9) - (3.11}$$

All these kinetic parameters have to be determined experimentally. Methods include graphical determinations with the Lineweaver-Burk-plot or the Langmuir-plot.
With the determined kinetic parameters and the balance equation of the reactors in differential form, the concentrations of biomass, substrate and product can be determined numerically. A detailed description of these determinations and calculations can be found in chapter 5.
There are different possible inhibitions to the reaction rate. For example, the pH value, the O_2 concentration as well as a substrate surplus may have an inhibition effect.

According to Schneider [39] maximal growth rates occur at sulphide concentrations from 10 to 30 $mg \cdot l^{-1}$ and at a stoichiometric oxygen sulphide relation λ of two. The stoichiometric oxygen sulphide relation λ is defined as follows:

$$\lambda = \frac{\left(\frac{O_2}{H_2S}\right)_{real}}{\left(\frac{O_2}{H_2S}\right)_{stoichiometric}} \tag{3.12}$$

In literature, there is litter regarding growth kinetics and the production of elemental sulphur and/or SO_4^{2-} from the autotrophic sulphide oxidation by Thiobazilli. The maximum specific growth rate μ_{max} is around 0.33 - 0.36 h^{-1} [42,47,48]. The Michaelis-Menten constant K_m varied between 0.001 and 0.667 $mmol \cdot l^{-1}$ in the literature [39,42,49,50].
Schneider [39] and Stefess [42] described the oxidation of microbiological H_2S oxidation in their thesis. Gonzalez-Sanchez [49] also developed a model for microbiological H_2S oxidation. Chemical H_2S oxidation is described in detail in [40,41,51].

4. Upgrade of the scrubber

4.1. Materials and methods

4.1.1. Equilibrium experiments

First, the additives were analysed for their feasibility as potential solubilisers for the selective absorption of H_2S.

The effectiveness of these solubilisers was investigated in so-called equilibrium experiments. In these experiments the reduction of H_2S in the gas-phase was analysed according to the head space method. For equilibrium purposes a sample bag, filled with biogas and washing liquid, was stored for several hours in the laboratory at constant temperature. The samples of biogas were taken directly from the source at the biogas plant. Figure 6 illustrates the procedure of these experiments.

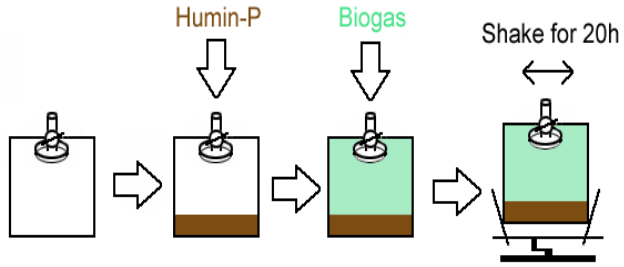

Figure 6: Procedure of equilibrium experiments

When the experiment was in equilibrium the concentration of H_2S in the gas phase was analysed and the degree of reduction η_{H2S} was calculated. This degree of reduction reflects the effect of the washing liquid on the reaction. It is calculated using the following formula:

$$\eta_{H_2S} = \frac{c_{H2S_{raw}} - c_{H2S_{eq}}}{c_{H2S_{raw}}} \cdot 100 \quad [\%] \tag{4.1}$$

c_{H2S_raw} refers to the concentration of H_2S in the biogas taken from the fermenter and c_{H2S_eq} refers to the equilibrium concentration.

The gas-phase measurements were carried out using three different methods:

1. Mass spectrometry
2. H_2S Data Logger OdaLog (electro-chemical detector) (App-Tek International Pty Ltd)
3. Dräger-test-tubes (Dräger Safety AG & Co. KGaA)

Figures 7 and 8 present different sample bags and their respective methods of analysis. Figure 7 demonstrates two types of gas bags (filled with biogas and Humin-P-solution). These bags were mainly analysed with the H_2S Data Logger OdaLog (photo on the right) and sometimes also with Dräger-test-tubes. The OdaLog measures H_2S in a range of zero to 200 ppm. In figure 8 five vials, filled with biogas and different amounts of Humin-P-solution, are shown, as well as their analysing device, the mass spectrometer. An example of the result screen of mass

spectrometer analysis is in figure A2 in the annex. The pressure in these gas bags and vials is assumed to be constant and is neglected in the evaluation of the experimental data.

Figure 7: Gas bags for analysing with the Data Logger OdaLog

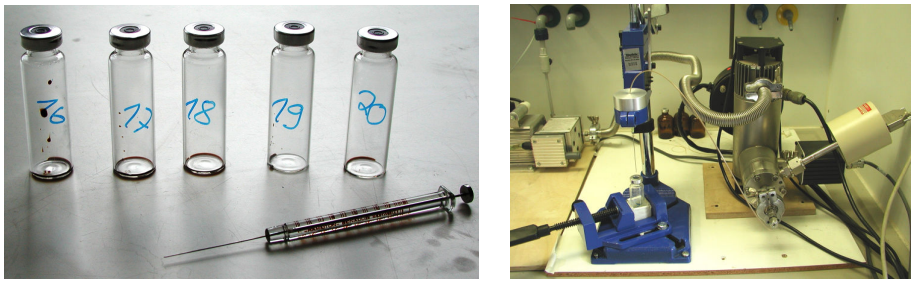

Figure 8: Sample vials for analysing with the mass spectrometer and mass spectrometer

Table 10 illustrates the liquid phase analyses. These measurements were taken before the experiments and in equilibrium state. Not all analyses were always conducted.

Table 10: Overview analyses - washing liquid

Parameters	Unit	Measuring method
pH	-	DIN 38404-5 with Microprocessor pH Meter (pH 196, WTW GmbH)
Redox potential	mV	DIN 38404-6 with Microprocessor pH Meter (pH 196, WTW GmbH)
Turbidity	NTU	EN ISO 7027 with portable Turbidimeter Model 2100P (Hach Lange GmbH)
Conductivity	$\mu S \cdot cm^{-1}$	Conductometer (LF 191, WTW GmbH)
TOC	$mg \cdot l^{-1}$	DIN EN 1484 with multi analyser N/C 3000 (Analytik Jena AG)
DOC	$mg \cdot l^{-1}$	DIN EN 1484 with liquid chromatography - organic carbon detection (LC-OCD)
TN	$mg \cdot l^{-1}$	EN 12260 with multi analyser N/C 3000 (Analytik Jena AG)
SO_4^{2-}	$mg \cdot l^{-1}$	Ion chromatography or sulphate cuvette tests, LCK 353 (Hach Lange GmbH)
Abs at 245 nm	-	Spectrophotometer (Modell Jasco V-550)
Abs at 550 nm	-	Spectrophotometer (Modell Jasco V-550)
Humic substances	$mg \cdot l^{-1}$	UV/VIS spectrometer Lambda 25 (Perkin Elmer)

Using the experimental set-up of the equilibrium experiments, the influence of different variables on the degree of reduction of H_2S was analysed. Table 11 presents the different series of equilibrium experiments with its variables. In table 12 the different additives tested are presented. Their characteristics are described in chapter 3.2.1 and 3.3.

Table 11: Parameters tested

Parameter	Range tested
Concentration of solubiliser	0.001 - 10 wt-%
Amount of washing liquid	0.1 - 200 $ml \cdot l^{-1}$
pH	3 - 12
Temperature	2 - 45 °C
Type of humic substances	Nature and company (see table 10)
H_2S concentration in biogas	100 – 7 000 ppm
Source of biogas	Renewable, waste, landfill, sewage
Sample storage method	Shaken, unshaken, for 6 - 40 hours
Repeated usage of washing liquid	

Table 12: Overview of additives analysed

Name of additive	Description	Company
Sulfa-Clear	Amine solution	Weatherford
TEA	Triethanolamine	Sigma-Aldrich
MEA	Monoethanolamine	Merck
DMSO	Dimethyl sulphoxide	Sigma-Aldrich
Humin-P	Potassium humate	Humintech GmbH
Humin-S	Sodium humate	Humintech GmbH
HA Fluka	Humic acid	Fluka, Sigma-Aldrich
HA Roth	Humic acid	Carl Roth
Humate Roth	Sodium humate	Carl Roth
POW	Potassium humate	Humintech GmbH
Nussbeize	Sodium humate	Bakelite AG
Water	Tab water (and distilled water) (acidified with HCl, alkalinised with NaOH)	

4.1.2. Continuous experiments

The effectiveness of humates was also analysed using a continuous laboratory experiment. Sodium sulphide (Na_2S) was dropped into a hydrochloric acid (HCl) solution to produce H_2S. The produced H_2S flowed continuously with the air into the humate solution, during which the outlet gas was analysed with the OdaLog. Figure 9 shows the schematic flow diagram and a photo of this set-up. With this set-up, the temperature and pH value could be varied easily. Their influence on the removal efficiency was analysed in a series of experiments. Temperatures between 20 and 70 °C and pH values between 3 and 11 were analysed. Furthermore the concentration of Humin-P in the liquid was varied between 0.1 and 10 wt-%. All results were compared with the experiments using water as well as using alkaline water. The average H_2S content in the inlet gas was 350 ppm. The liquid phase was analysed as well (see table 8).

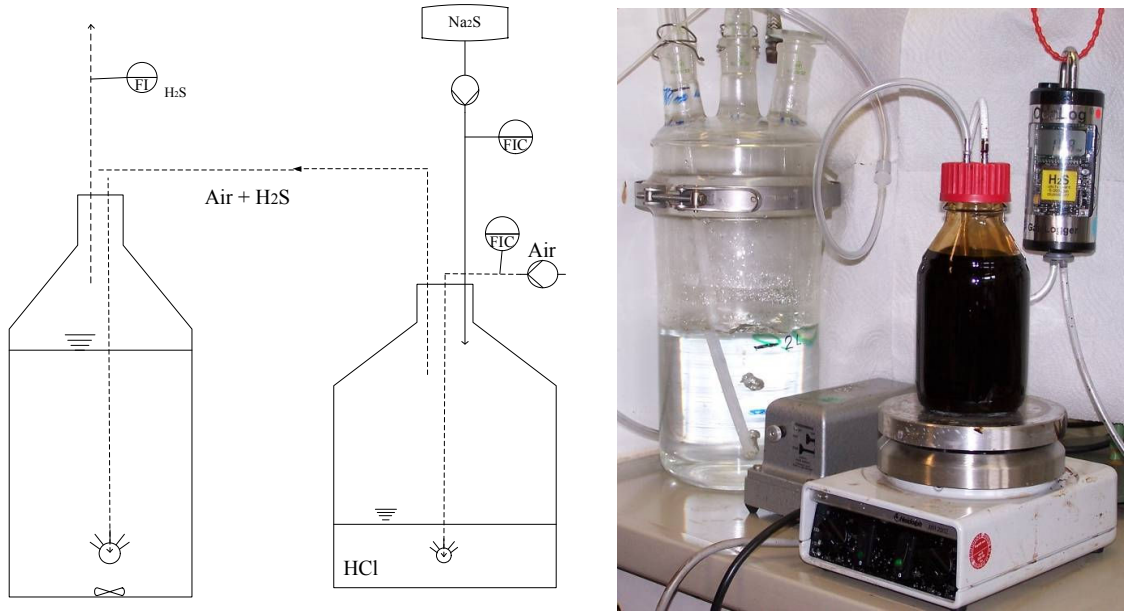

Figure 9: Schematic flow diagram and photo of continuous set-up

4.2. Results

4.2.1. Test of solubilisers

In the equilibrium experiments it turned out that only minimal amounts of humate solutions were necessary to achieve a reduction of more than 90 %. Due to different initial concentrations of biogas and different concentrations of the additive, the required amount alternated between 0.1 and 60 ml per litre of biogas.

Figure 10 compares the average reduction rates using different solubilisers and washing liquids.

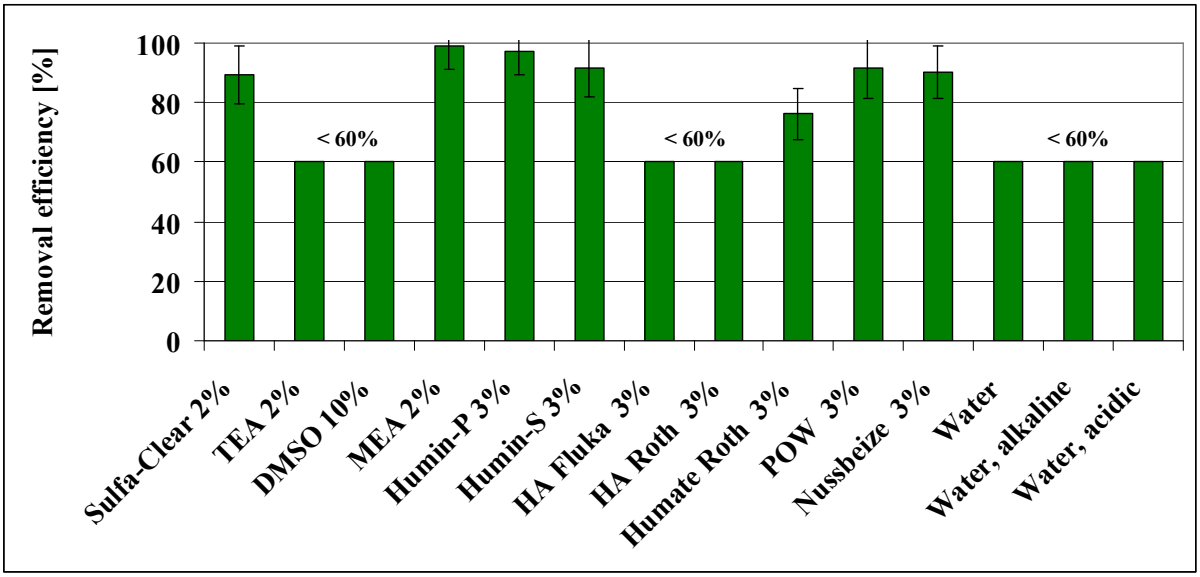

Figure 10: Comparison of different washing liquids

Figure 10 demonstrates that all humates, Sulfa-Clear and MEA were able to achieve high reduction rates. Almost all other solutions had reduction rates of less than 60 % which was below the detectable limit in this series of experiments.

The results indicated a high improvement in the absorption of H_2S by using humates. Pure humic acids did not achieve the good results of their salts. The reason for this is their lower pH value.

Even in comparison with alkaline water, humate solutions are much more efficient. The equilibrium experiments indicate that the absorption (chemisorption) of H_2S from biogas was improved. Figure 11 presents the degree of reduction based on the different wash volumes of a 3.5 wt-% humate solution. This example suggests that about 1 ml of washing liquid per litre of biogas is necessary to reduce H_2S in the gas phase to almost zero ppm. These results are similar to the results obtained with the established solubiliser Sulfa-Clear. Experiments with alkaline water show that more than 100 ml per litre biogas is required. This underscores the great effect of the humate solutions.

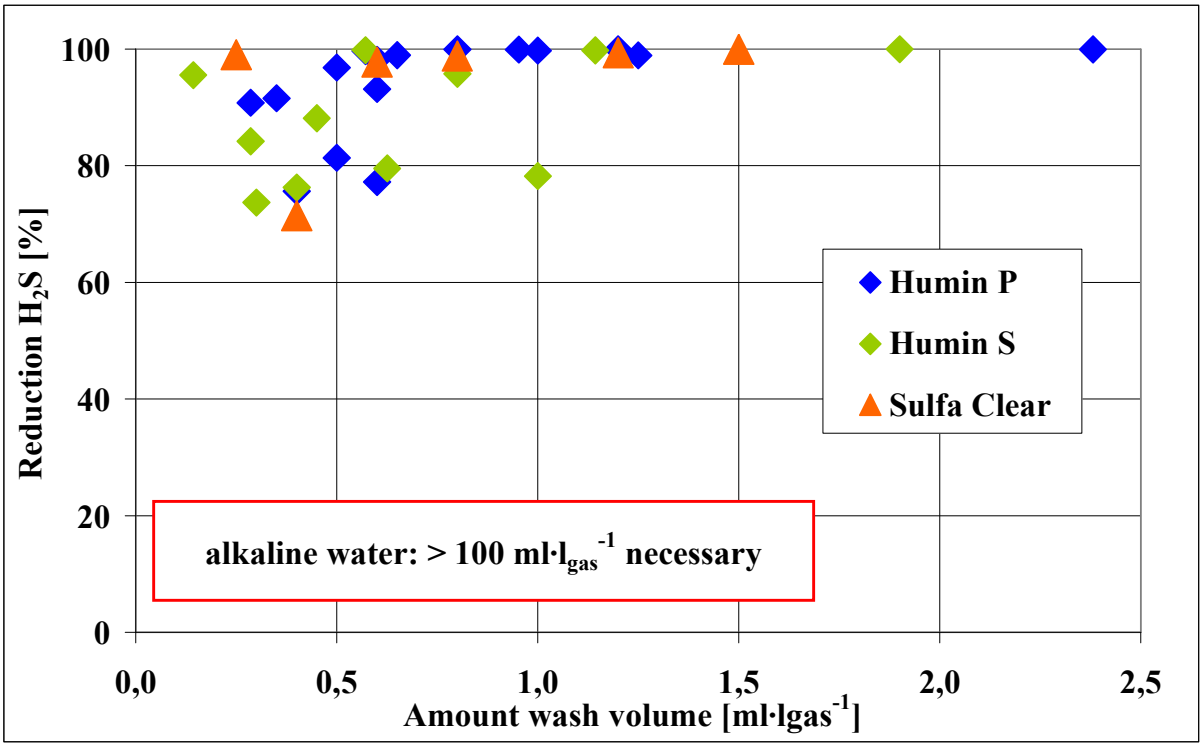

Figure 11: Reduction of H_2S with varying wash volumes

4.2.2. Influence of different parameters

Table 13 gives an overview of the results gained from the equilibrium experiments with humate solutions. Altogether, more than 1,000 gas bags were analysed over the series of experiments. Overall, more than 50 % of these bags were filled with humate solutions. 14.7 % were filled with Sulfa-Clear and 21 % with water, including alkaline and acidic water. Other bags were filled with other testing solutions for comparison purposes. The average concentration of H_2S in the biogas was about 1,000 ppm. A list of biogas plants where samples were taken is in table A7 in the annex.

Table 13: Overview of the results of the equilibrium experiments with humate solution

Parameter	Results
Concentration of humates	The higher the concentration, the higher the reduction of H_2S
Amount of washing liquid	Amount is dependent on the concentration of solubiliser and concentration of H_2S in the biogas
pH	Higher reduction rates at higher pH values. In addition, the reduction rate is also highly dependent on the concentration of humates
Temperature	Higher reduction rates at higher temperatures
Type of humic substances	All tested humates achieved high reduction rates.
H_2S concentration in biogas	At high H_2S concentrations, reduction to almost zero possible.
Source of biogas	No difference was detected
Storage of samples	Shaken samples achieved higher reduction rates, the influence of the duration of storage can be neglected after 10 hours.
Repeated usage of washing liquid	Even after 20 repetitions, the washing solution still achieved high reductions of H_2S.

In summary, the results in table 13 show again that humic substances can optimise the reduction of H_2S. Comparisons with Sulfa-Clear and water were carried out in each series of experiments. The results with Sulfa-Clear were alike the results with humates. For the comparison experiments with water mainly the temperature experiments were different.

Figure 12 demonstrates the relationship between the concentrations of the humates in the washing liquid with the amount of washing liquid required to achieve reduction rates of over 80 %. Even with only 0.5 wt-% Humin-P in the washing liquid the amount of washing liquid required is less than for an alkaline solution. Alkaline solutions with pH values between 8.5 and 13 were analysed.

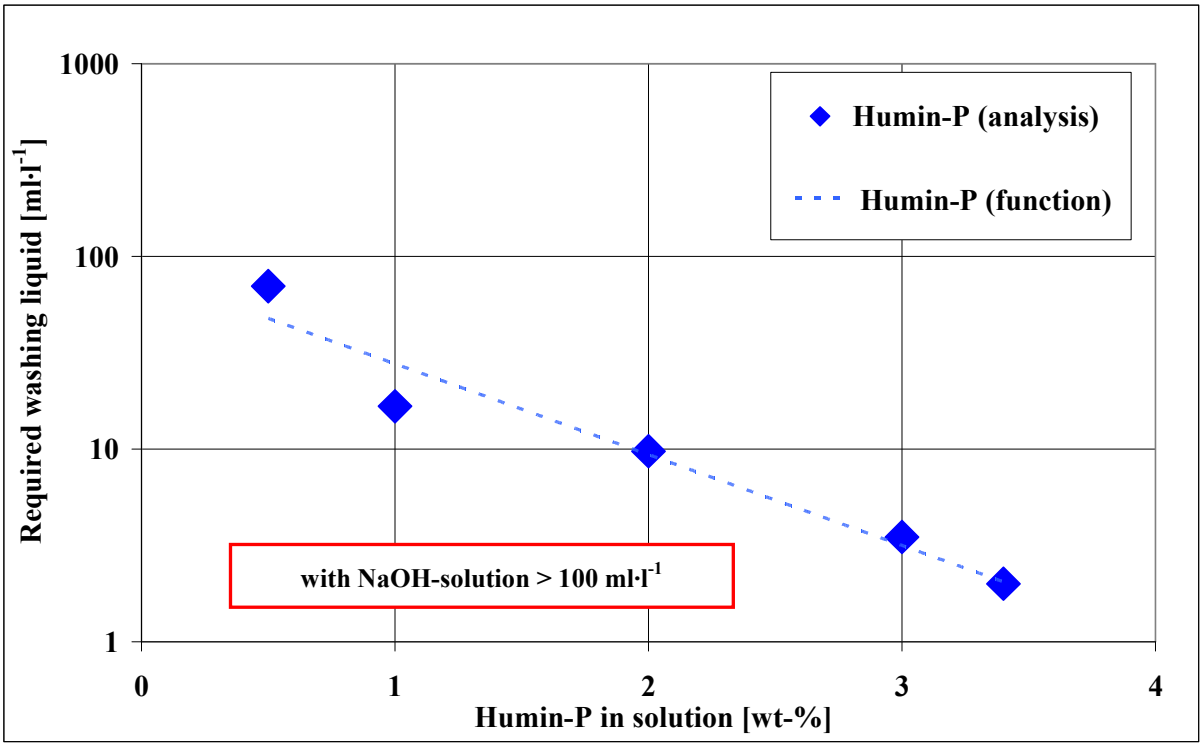

Figure 12: Influence of Humin-P concentration on the removal of H_2S

The most surprising result from the experiments was the influence of temperature. The removal of H_2S with humate solution is better at higher temperatures. This result indicates that other reactions occurred during the removal of H_2S by humates. In the comparison experiments with water, absorption capacity increased with lower temperatures, as expected. The considerable influence of Humin-P concentration, temperature and pH value was also determined during the continuous experiments. Figures 13 and 14 give an example of the continuous experiments where removal efficiency improved at higher temperatures and higher pH values. The removal of H_2S is calculated as mg H_2S per ml humate solution (1 wt-% Humin-P). Results of the equilibrium experiments with varying temperature and pH values are illustrated in the annex (figure A3 and A4). The increase with higher pH values is the cause of the dissociation of H_2S (see chapter 7.1.2). Figure 15 shows the improvement in removal efficiency with higher concentrations of Humin-P in the washing liquid. The effect of Humin-P on the removal of H_2S during the continuous experiments is linear.

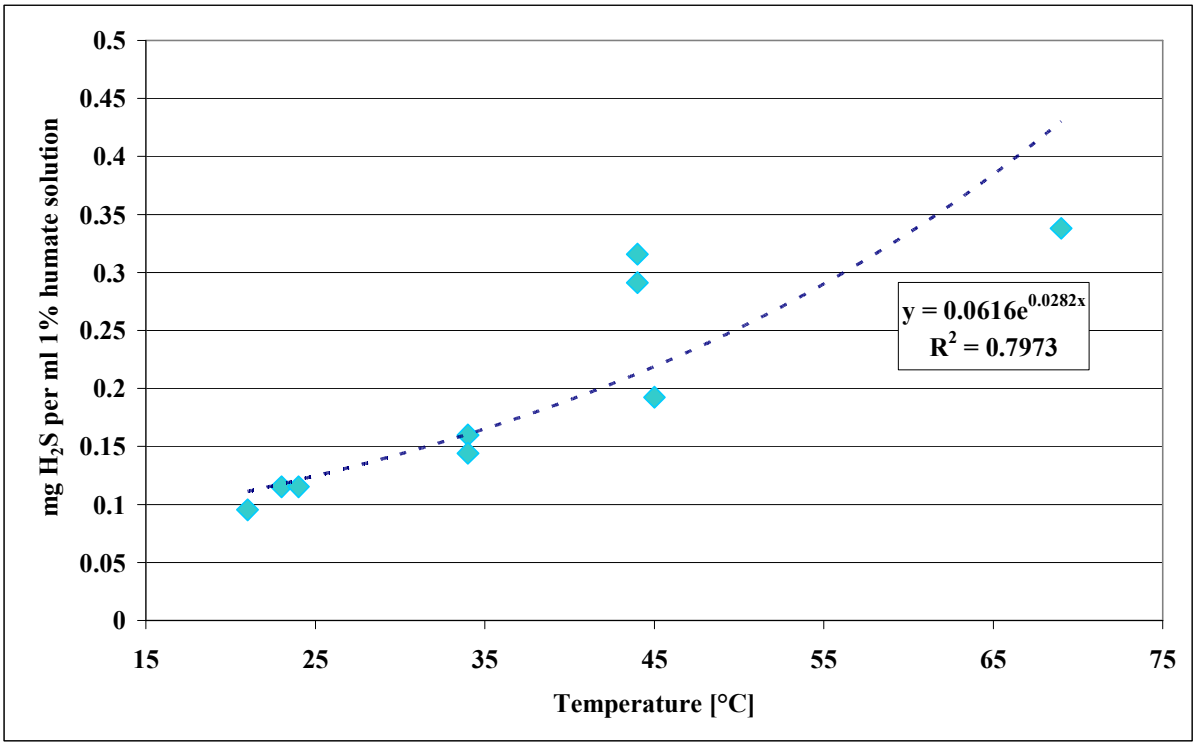

Figure 13: Effect of temperature on the removal of H_2S during the continuous experiment

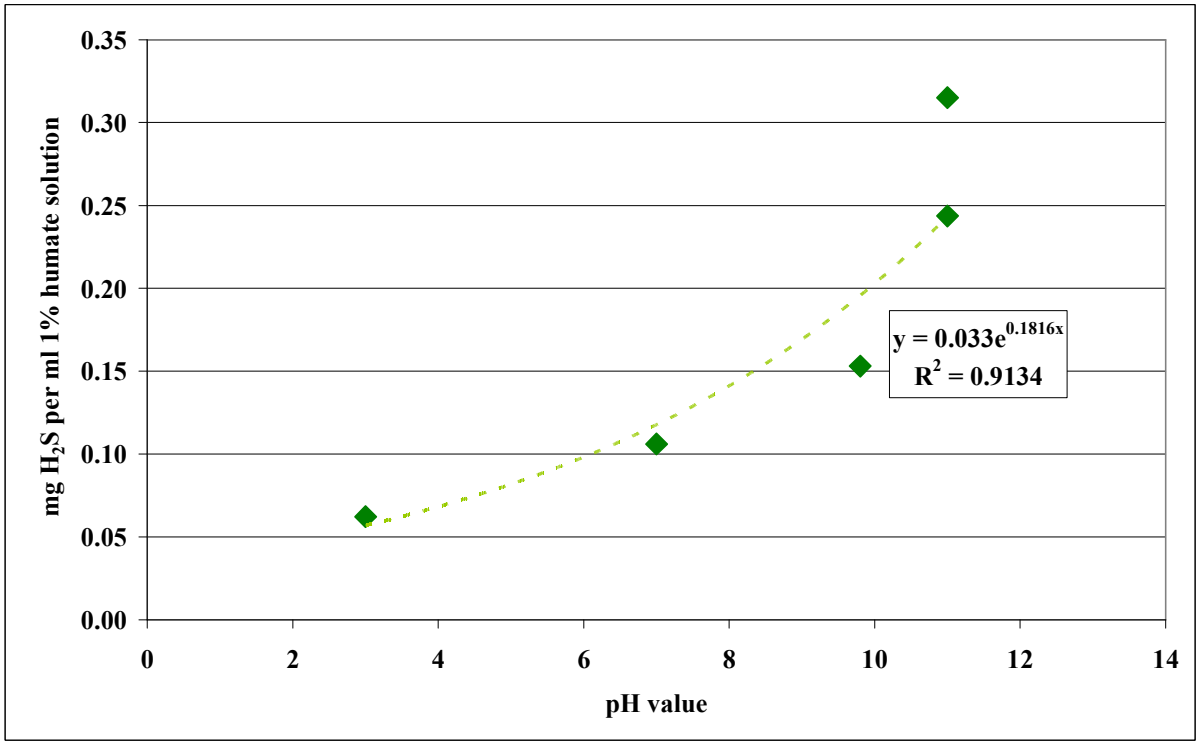

Figure 14: Effect of pH-value on the removal of H_2S during the continuous experiment

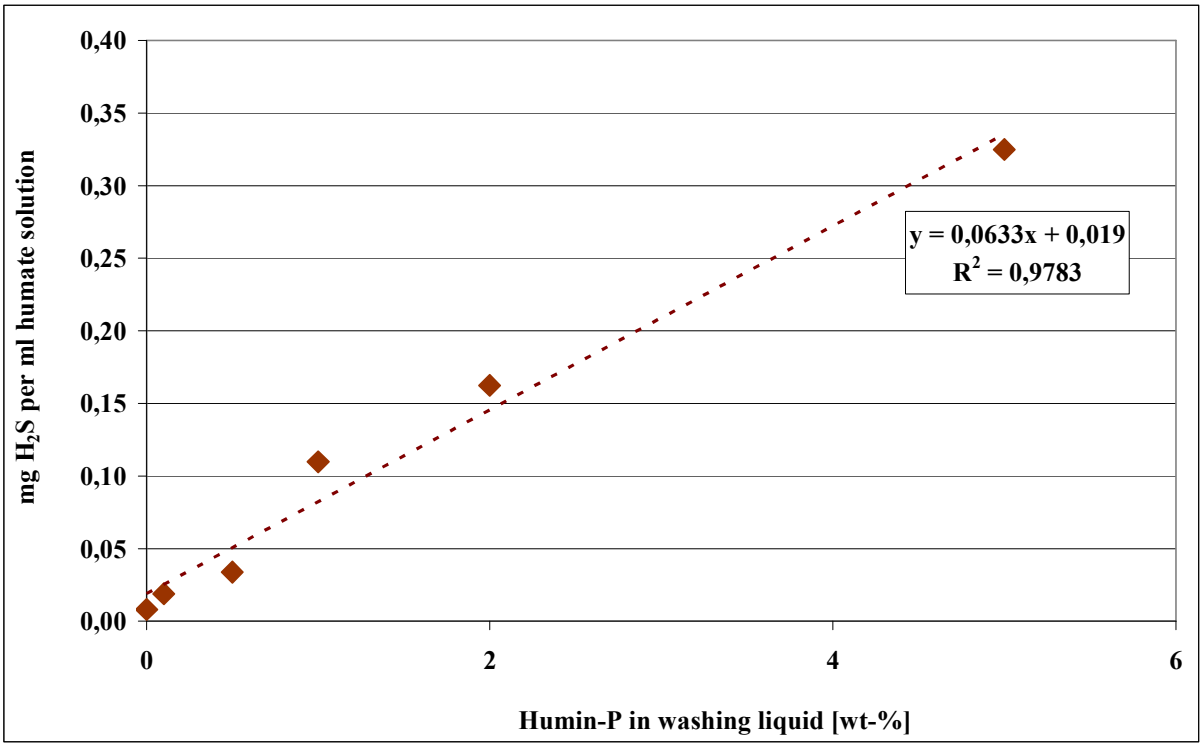

Figure 15: Effect of Humin-P on the removal of H_2S during the continuous experiment

Figure 13 to 15 show that the removal of H_2S by humate solution is best at high temperatures, high pH-values and with high concentrations of Humin-P.

4.2.3. Analysis of washing liquid

In addition to the change in H_2S in the gas phase, several other parameters in the washing liquid also change during contact and reaction with H_2S. Table 14 demonstrates the average difference in the washing liquid of a 2 wt-% Humin-P-solution before and after contact with biogas. The same parameters were analysed during the continuous experiments.

Table 14: Difference in parameters before and after contact with biogas

Parameter	Unit	Before	After
Redox potential	[mV]	-149.0	6.3
Humin-P	[%]	21.9	20.9
pH	[-]	9.8	6.1
SO_4^{2-}	[$mg \cdot l^{-1}$]	9.9	17.7
TN	[$mg \cdot l^{-1}$]	94.1	79.3
TOC	[$mg \cdot l^{-1}$]	432.1	391.9
Turbidity	[NTU]	3775	3295
Conductivity	[$\mu S \cdot cm^{-2}$]	3185	3115
H_2S in gas phase	[ppm]	1087	127

Due to the dissolving and dissociating of the acidic gas, pH values show a significant decrease after contact with H_2S. Figure A5 in the annex shows the differences of pH values of washing solutions before and after contact with H_2S. In summary, the analysis of the liquid phase shows that the pH value decreased by an average of about 3.7. In comparison, the pH of alkaline water during absorption with H_2S decreased by an average of 4.6. It is suggested that Humin-P has a pH buffer (see 5.2.3).
Electrical conductivity did not show a significant change during the reaction with H_2S. This shows that the total amount of ions in the Humin-P-solution did not vary. The reason for this could be that the sulphide ions and the hydroxide ions replaced one another.
The redox potential of the Humin-P-solution increased by an average of 150 mV during the reaction with H_2S. Due to the fact that these values were measured using a pH probe with a glass membrane rather than a redox probe with a metal electrode, inaccurate measurements could have caused the results. However, a change in the redox potential was measured and an electron transfer could have occurred during the reaction of Humin-P with H_2S.
The concentration of SO_4^{2-} increased during the reduction of H_2S. This shows that SO_4^{2-} is formed during chemical reactions. A slight increase in elemental sulphur was also detected.
Humates contain organic carbon (OC) and nitrogen (N). Therefore, Humin-P makes up the total content of total organic carbon (TOC) and total nitrogen (TN). There was a slight decrease in TOC and TN after the reaction with H_2S. Liquid chromatography with carbon detection (LC-OCD) was used to characterise the different organic fractions of Humin-P-solutions before and after contact with H_2S. No significant change in the OC signal before and after contact with H_2S was detected. It can be concluded that the structure and amount of Humin-P stayed constant during the reaction with H_2S. Figure 16 shows the results of the LC-OCD analysis.

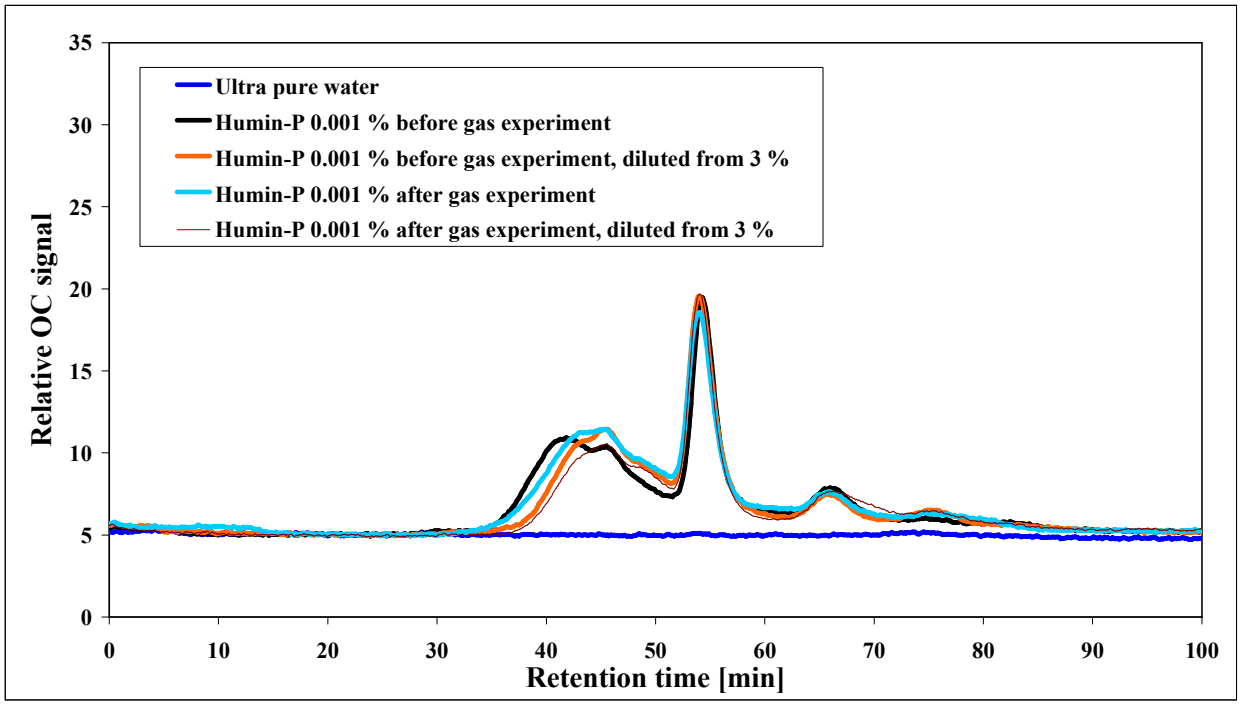

Figure 16: Results of LC-OCD analysis

4.2.4. Influence on other biogas components

In addition to the reduction of H_2S, the effect of washing liquid on the solubility of methane (CH_4), carbon dioxide (CO_2) and ammonia (NH_3) was determined.

The solubility of CH_4 in humate solution is very important for application in the desulphurisation of biogas. The dissolving of CO_2 could be another advantage of humate solutions in biogas treatment. To analyse the ability of the Humin-P-solution to absorb these two compounds, an analysis of CO_2 and CH_4 using gas chromatography and mass spectroscopy was carried out during the equilibrium experiments. These experiments showed that CH_4 was not soluble in Humin-P-solutions. Removal of CO_2 was negligible for humate solutions up to 5 wt-%. A 20 wt-% humate solution was able to remove up to 20 % of CO_2. Using humates to convert biogas to biomethane is not recommended. Solutions with 20 % MEA and solutions with 20 % NaOH achieved much higher removal rates than the humate solutions.

Figure A8 in the annex shows a diagram of the change in CH_4 and CO_2 for different washing solutions.

The concentration of NH_3 in biogas typically ranges from 10 - 180 ppm. The removal of ammonia gases occurs normally with acidic gas scrubbing. The parallel removal of H_2S and NH_3 in an alkaline scrubber-system is worse than under acidic conditions. This can be problematic at high ammonia loads. [15]

An analysis of NH_3 removal was performed during equilibrium experiments as well as during the continuous set-up. A NH_3 Data Logger OdaLog from the company App-Tek was used. In the continuous experiment, ammonium sulphate ($(NH_4)_2SO_4$) was used instead of Na_2S to produce NH_3. The results of both experimental set-ups show that NH_3 can be reduced with Humin-P-solutions. Reduction rates up to 99.8 % were achieved in the equilibrium experiments. This is in accordance with Ketrick [29] who also observed a significant reduction of ammonia by humates. With the continuous set-up, the results were similar to the results with water (see figure A9 in annex).

4.3. Discussion and conclusion

The results of the continuous experiments suggest that the ability of humate solutions to remove H_2S from biogas reaches levels of up to 50 mg H_2S per g Humin P-solution e.g. 0.3 mg per ml with a 1 wt-% humate solution with a pH of 11.
The equilibrium experiments with repeated applications of washing liquid determined that more than 1 g of H_2S per litre of a 2 wt-% Humin-P-solution could be removed (see figure A7 in annex). This means that per g of Humin-P, more than 82 mg H_2S can be removed.
The reaction between H_2S and Humin-P is a first-order reaction. The comparison of reduced H_2S ($c_{H2S,in} - c_{H2S,out}$) from laboratory continuous absorption experiment (see 4.1.2) with determined curve of first order kinetic is shown exemplary in figure A12 in the annex.

4.3.1. Influence of humates on removal rates

To evaluate the ability of solubilisers to remove H_2S, the Henry coefficients H were determined. The solubility of gas in a liquid can be described mathematically according to Henry's Law (see chapters 3.2 and 7.1):

$$H_i = \frac{Y_i}{X_i} \cdot p \tag{4.2}$$

The liquid molar loading X and the gas molar loading Y can be determined based on the H_2S concentration in equilibrium and the concentration of untreated biogas. To achieve the best possible accuracy the Henry coefficient must be determined at the limit value of $X_i = 0$ [18]. This value can be determined using a diagram where $Y \cdot X^{-1} \cdot p$ is plotted against X. The axis intercept $Y_{(X=0)}$ of a linear smoothing function shows the desired Henry coefficient H. For the determination of the Henry coefficient of humate solutions the weight concentrations [$g \cdot g^{-1}$] were used instead of molar loadings, because no molar weights were available.
When interpreting the Henry coefficients it must be kept in mind that the Henry coefficient is only valid for physisorption. In determining the Henry coefficient, the dissociation due to alkaline solutions is omitted. The Henry coefficients determined are therefore independent of the solution's alkaline pH value. In any case, a significant difference was obtained between the Henry coefficient of the system with H_2S/water and with H_2S/humate solution. The Henry coefficient for the system with H_2S/water was 550 bar. This value is in accordance with the literature [19]. For the system with H_2S/humate solution, the "Henry coefficients" were between 3 and 40 bar. These "Henry coefficients" are highly dependent on the concentration of humates in the solution (see chapter 7.1.5). Example diagrams demonstrating the determination of the Henry coefficient are shown in figure A10 and A11 in the annex. Due to this difference, reactions other than physisorption must occur. H_2S removal might proceed as follows:

- Absorption in accordance with Henry's Law
- Dissolved H_2S dissociates into HS^- and S^{2-}
- Reactions with Humin-P

Figure 17 illustrates the reactions of H_2S with Humin-P-solution. The reactions between sulphide and humates are described in detail in chapter 4.3.2.

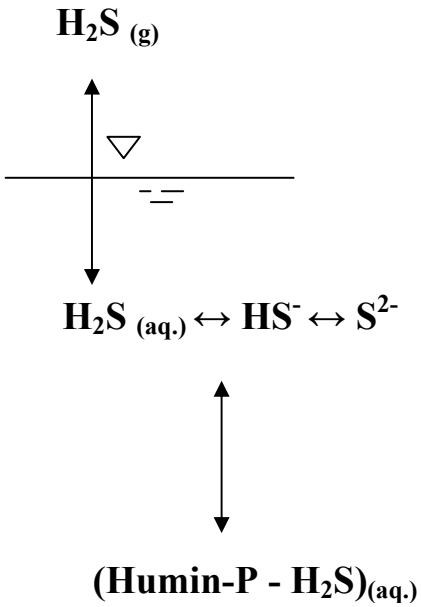

Figure 17: Reactions of H_2S with humate solution

With the Henry coefficient for H_2S (H = 557 bar for T = 30 °C) in water and the dissociation equations (see chapter 7.1.2, equation 7.7 and 7.8), the amount of H_2S which reacts with Humin-P can be calculated through balance equations. This calculation was performed with Modelica/Dymola. Important for this calculation are very exact results e.g. of the H_2S concentration and pH value. The obtained data from laboratory experiments are not precise enough but give an indication of the significant effect of Humin-P in chemisorption. They show that most of the H_2S is bound to Humin-P. This effect is mainly observable when simulating the experiments at lower pH values where the dissociation of H_2S has a lower influence. In this situation, the H_2S has to react with the humates.

4.3.2. Interaction between humates and H_2S

As described in chapter 3.3 humic substances have complex structures and contain many kinds of functional groups. Therefore, the interaction between Humin-P and H_2S is predicted to be multi-reaction. In this chapter, possible interactions are described and evaluated.

Generally, the removal of H_2S by humates is influenced by chemisorption. Apart from the dissociation of H_2S, the main reaction between H_2S and Humin-P is that between an acid and a base. The absorption capacity correlates well with the alkalinity of the humates solution. This is in accordance with Green and Manaham [27], who determined that the major mechanism of the absorption of SO_2 by sodium humates is an acid-base reaction.
Furthermore, oxidation-reduction reactions can occur. In the experiments only a small amount of elemental sulphur was detected after the reaction of Humin-P and H_2S. The insolubility of elemental sulphur in humate solutions was analysed to be equal to that in water.

The equations 4.13 to 4.5 show the reactions which may occur during the chemisorption of H_2S by a potassium humate K-HA (K=potassium, HA=humic acid).

$$H_2S_g \rightarrow HS^- + H^+ \tag{4.3}$$

$$K - HA_l + H_2S_g \rightarrow H - HA_S + HS^- + K^+ \tag{4.4}$$

$$HA_{Ox} + HS^- \rightarrow HA_{Red} + S + H^+ \tag{4.5}$$

In addition, humic substances have the ability to adsorb because of their large surface area resulting from their huge molecular size and porosity. The average molecular weight of Humin-P is 32,000 g·mol^{-1} [52]. It was determined in laboratory experiments that the adsorption effect is not one of the main reasons for the high reduction rates of H_2S by humates.

Another interaction could also be the complex or chelate formation of iron compounds in humates with H_2S. For example, Humin-P contains in average 8,000 mg·kg^{-1} iron (Fe). The detailed analysis of different compounds in potassium humate is in table A8 in the annex. The reaction of Fe with H_2S could proceed according to the equations 4.6 and 4.7:

$$Fe^{2+} + H_2S \rightarrow FeS + 2 \cdot H^+ \tag{4.6}$$

$$2 \cdot Fe^{3+} + 3 \cdot H_2S \rightarrow 2 \cdot FeS + S + 6 \cdot H^+ \tag{4.7}$$

If calculating with Fe concentration of 8,000 mg·kg^{-1}, all the H_2S could be bound to the Fe according to these reactions. Comparison experiments using an iron humate from the company Humintech (HUMIRON Fe WSP) showed that the iron humate did not have better removal efficiencies than the potassium humate Humin-P. It is likely that Fe might be a factor, but not a determining one, in the reaction.

One method of analysing the stability of sulphide in Humin-P-solution is through acidification. Hydrogen chloride (HCl) was added to the Humin-P-solution after its reaction with H_2S. During the process, the amount of H_2S in the gas phase was analysed by smell and detection using the OdaLog. Smelling was used in addition to the OdaLog because the human nose is a good measuring device due to the characteristic odour of H_2S. Very low concentrations can be detected immediately. Only a small amount was detected using 1 ml of 1 molar HCl. 2 ppm of H_2S was detected during acidification. This shows that H_2S is generally irreversibly bound to potassium humate. Humic substances have a high storage capacity for SO_4^{2-}, S and H_2SO_4. With sufficient O_2, H_2S is not released back into the gas phase. [30]
This could be one reason why desorption through acidification was not effective. A possible desorption effect by heat was not analysed.
Due to the complexity and undefined structures of the humic substances the reactions between H_2S and Humin-P could not be determined in detail.

5. Regeneration

The demanding requirements on the separation efficiency of gas treatment plants lead to the need for a high regeneration performance. Regeneration of the washing liquid reduces operational costs and costs for disposal. Therefore, one of the main selection criteria for the washing liquid is its ability to be regenerated and the effort involved in this regeneration.
Regeneration by microorganisms is a possible low cost method. The H_2S which is dissolved in the washing liquid will be transformed microbiologically to elemental sulphur which can be easily eliminated from the system.
The main objective of these laboratory experiments was to determine the kinetics of H_2S oxidation, as well as the effect of pH, O_2 concentration and solubilisers on the growth of the Thiobazilli, the degradation of sulphide and the formation of elemental sulphur.

5.1. Materials and methods

5.1.1. Experimental set-ups

The degradation of sulphide and the production of elemental sulphur by the species Thiobazilli was analysed using different laboratory bioreactors. The bioreactors were inoculated with a mixture of H_2S-oxidising bacteria from bioscrubbers of the biogas plants Albersdorf (Biokraft Albersdorf GmbH & Co KG) and Hamburg (Biowerk Hamburg GmbH & Co). By identifying different bacteria strains via DNA-analysis, a wide diversity of sulphur bacteria was found in these bioscrubbers.
The bacteria were fed with H_2S and sodium thiosulphate ($Na_2S_2O_3$) as the substrate. Thiosulphate ($S_2O_3^{2-}$) is often used as a replacement for sulphide, because it is not toxic, volatile or susceptible to chemical reactions [47]. With $S_2O_3^{2-}$ as substrate, the following reactions occur.

$$S_2O_3^{2-} + 0.5 \cdot O_2 \rightarrow S + SO_4^{2-} \tag{5.1}$$

$$S_2O_3^{2-} + 2 \cdot O_2 + H_2O \rightarrow 2 \cdot SO_4^{2-} + 2 \cdot H^+ \tag{5.2}$$

Guss C. Stefess [42] found that sulphide and $S_2O_3^{2-}$ were interchangeable substrates for a number of chemolithoautotrophic bcteria with respect to growth yields and various other characteristics. Patricia Cadenhead [53] also described that prior growth of $S_2O_3^{2-}$ was necessary to develop sufficient biomass in the reactors so that the biooxidation capabilities of the biomass were not exceeded when H_2S feeds were initiated.

In addition to the sulphurous substrate, a carbon-based nutrient solution was added. This nutrient solution contained an additional 3 % nitrogen (N), 2 % phosphorous (P), 5 % potassium (K) as well as trace elements. Experiments showed that the nutrient solution included a carbonate buffer. In the following paragraphs the different bioreactors used are described.

B. Braun Biostat bioreactors

The main reactors used were two B. Braun Biostat bioreactors with a culture volume of 2 litres. Figure 18 shows a schematic flow diagram and a photo of one Biostat reactor.

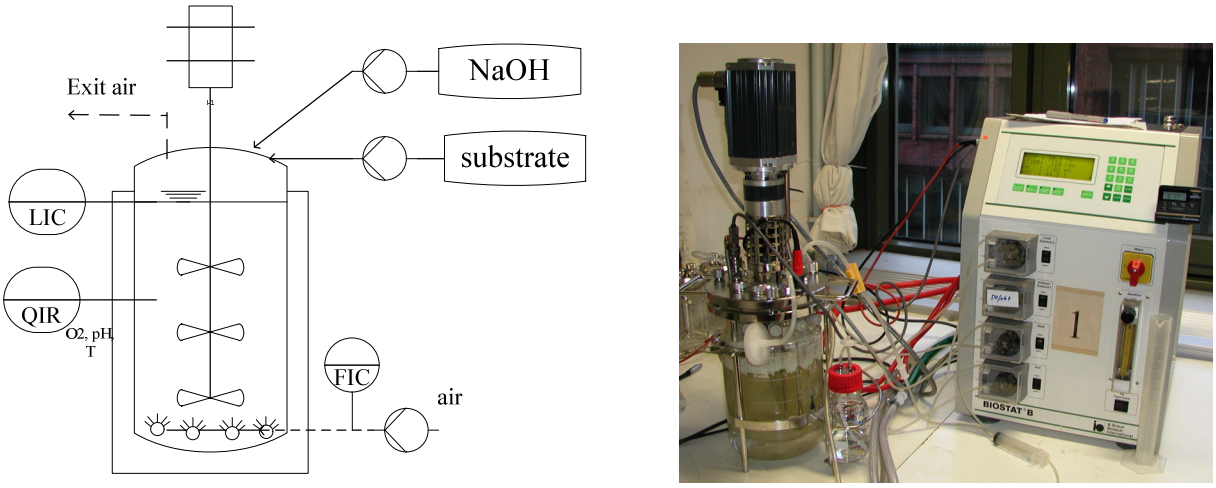

Figure 18: Schematic flow diagram and photo of laboratory B. Braun bioreactor

The bioreactors were stirred and aerated continuously. Controllable parameters were temperature, pH value, O_2 concentration as well as volume. These parameters were regulated with a PID controller.

The correlation between the transport coefficient of oxygen k_La [h^{-1}], the speed of stirrer rotation n [rpm] and the airflow Q_{air} [$ml \cdot min^{-1}$] was determined by:

$$k_l a = 0.0015 \cdot n^{0.7} \cdot Q_{air}^{0.2} \tag{5.3}$$

Different glass bottles as simple batch reactors

Closed glass bottles (in various volumes) were used for simple batch experiments. The solutions in the bottles were mixed thoroughly and aerated continuously. The temperature and pH-values were regulated depending on the experiment. In figure 19 a schematic flow diagram of this set-up as well as a photo is presented.

Figure 19: Schematic flow diagram and photo of glass bottles as simple batch reactors

Fixed-bed reactors

These reactors have a length of 50 cm, a diameter of 2 cm and are filled with expanded clay beads (ε = 0.6). The entire reactor with all the hollow spaces has a volume of 230 ml; the free volume of the fixed bed is only 90 ml. Diaphragm metering pumps pump the liquid from the storage tank through the reactor tubes. From the top of the reactor, the liquid flows back into the storage tank. The storage tank has a volume of 500 ml and was aerated continuously. A biofilm was formed on the fixed beds prior to the experiments. Figure 20 shows a schematic flow diagram and a photo of the four fixed-bed reactors.

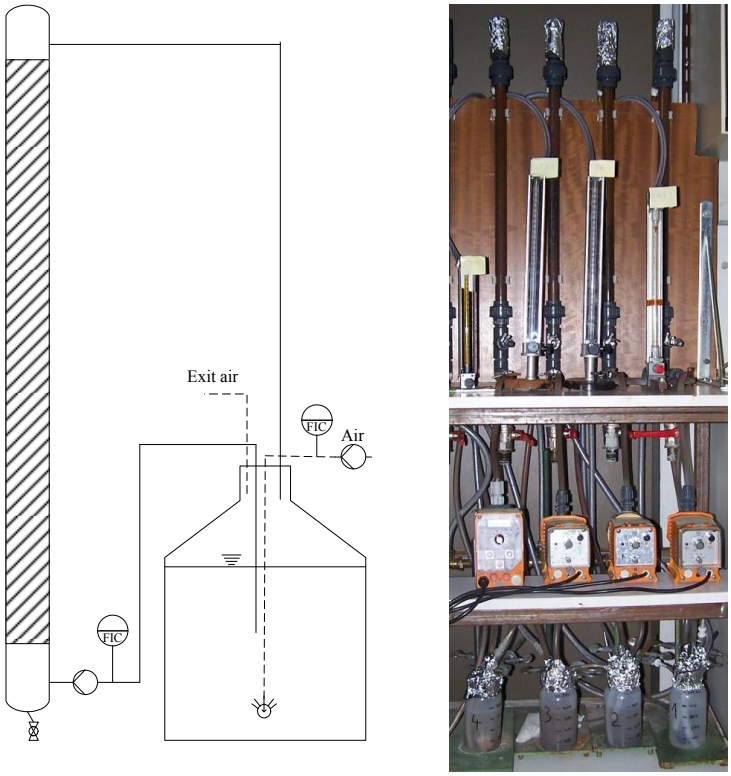

Figure 20: Schematic flow diagram and photo of fixed bed reactors

5.1.2. Analytics

One of the main problems during the experiments was the measurement of biomass, because it was impossible to separate the biomass and the sulphur completely. Elemental sulphur interferes strongly with most standard methods of biomass determination. These problems were also faced in experiments done by Buisman [38] and Stefess [42]. Another problem was the clogging of the biomass-sulphur-complex at the walls and tubes. When measuring the biomass the influence of humic substances also presents problems in some analyses. As a parameter of biomass, the concentration of proteins was utilised. Proteins are often used as parameters for biomass [42,49,54]. The protein measurement was conducted according to the Lowry method. This is a simple and reliable method to determine a multitude of proteins [55,56]. Detailed information on this protein analysis can be found in the literature [55,56]. With bovine serum albumin the relationship between extinction and protein concentration was determined. This relationship was verified by multiple determinations. Figure A13 in the annex shows the calibration line obtained.
The determination of proteins is independent of the pH value when ranging between 2 and 9. The dark colouring of Humin-P-solutions falsifies the absorption measurement in protein analysis. Figure 21 shows the dark colouring after a centrifugation step.

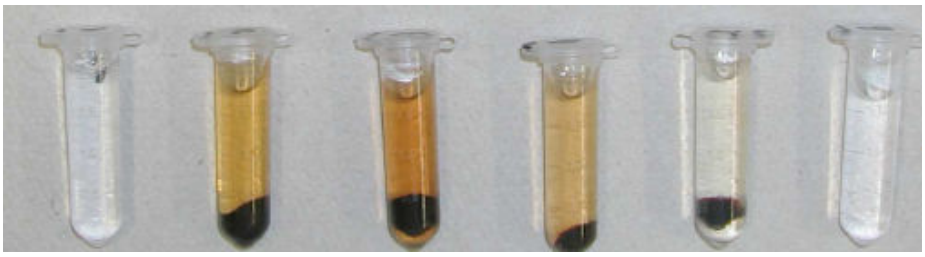

Figure 21: Photo of different samples after centrifugation

Furthermore, phenolic hydroxyl groups in humates can affect protein analysis. Proteins were analysed in distilled water with Humin-P. A relationship between the concentration of Humin-P and the concentration of protein can be determined. With equation 5.4, this relationship can be considered when determining the protein concentration. Figure A14 in the annex shows the determination of this relationship.

$$\text{Proteins } [\text{mg}\cdot\text{l}^{-1}] = 0.4998 \cdot \text{Humin-P } [\text{g}\cdot\text{l}^{-1}] \qquad (5.4)$$

Despite of the derived relationship between proteins and Humin-P, the exact protein content of the sulphur bacteria could not be determined due to a superposition of different factors during measurement. Furthermore, errors occurred during the measurement process due to a necessary dilution step.
When measuring the proteins, the biomass which settled and remained in the reactor by biofilm formation and sedimentation could not be analysed. This has to be considered in the results.
The determination of elemental sulphur is critical in the analysis of the kinetics of H_2S oxidation. There are several methods of analysis, such as color-forming reaction using pyridine [57] or different methods of UV-absorption [58,59]. In the Institute of Wastewater Management and Water Protection, iodometric titration is used. This method can be carried out without complex instruments and toxic substances. The disadvantage of this method is that it takes a

long time and that it is not an exact quantitative determination. Only the order of magnitude can be determined. The analysis is conducted according to the modified procedure by Jorgensen [59]. The analysis is not affected by humic substances or the product Sulfa-Clear in the samples. But, the filtration of samples containing humates takes a lot of time. More than one day is often necessary for one analysis of high concentrated humate solutions.
$S_2O_3^{2-}$, SO_4^{2-} and total sulphur are analysed using ion chromatography. The dry residue is analysed according EN 12880. Temperature and O_2 were analysed with a multi oxygen meter 3401 (WTW GmbH). In addition, the analyses described in table 8 were carried out.
Additionally, alkalinity was analysed according to DIN 38409-7 and the sedimentation of the settleable solids was determined according to DIN 38409-9.

The oxygen removal rate was analysed according to DIN 38408-22 with a multi oxygen meter 3401 (WTW GmbH). The respiratory activity OUR (oxygen uptake rate) [$mg_{O2} \cdot l^{-1} \cdot h^{-1}$] is defined as the change in O_2 concentration c_{O2} [$mg_{O2} \cdot l^{-1}$] over time t [h]:

$$OUR = \frac{dc_{O2}}{dt} \tag{5.5}$$

A picture of the oxygen consumption experimental set-up is shown in figure 22.

Figure 22: Set-up of oxygen consumption experiment

Reference measurements with distilled water were carried out. Higher oxygen consumption with the addition of humates was observed. Due to the lack of bacteria, oxygen consumption should not exist. The oxygen uptake rate OUR_{HP} [$mg_{O2} \cdot l^{-1} \cdot h^{-1}$] was highly dependent on the amount of humates c_{HP} [wt-%] in the sample. Equation 5.6 demonstrates this relation. Figure A15 in the annex shows an exemplary diagram of the oxygen consumption of distilled water with different humate concentrations.

$$OUR_{HP} = 27 \cdot c_{HP} + 190 \tag{5.6}$$

Other interactions with humates in the different analytic methods might occur as well. These possible interactions could not be determined and were therefore neglected.
The relationships between Humin-P and turbidity, conductivity, dry matter and carbon (C) concentrations are shown in figure A18 and A19 in the annex.

5.1.3. Series of experiments

Influence of different parameters

With all the reactors discussed, experiments with varying parameters were carried out. The parameters varied were temperature, pH, amount of substrate and O_2 concentration. The experiments were performed to obtain the optimum conditions for the production of elemental sulphur and the optimum conditions for the growth of the bacteria.
In these experiments reactors were always operated in parallel and the production of SO_4^{2-} and elemental sulphur, growth of bacteria or degradation of substrate were compared. All parameters mentioned were analysed regularly. The effect of temperature, pH and the amount of substrate on the activity of the sulphur bacteria was based on measurements of O_2 consumption.

Determination of kinetic parameters

The kinetic parameters were determined with the glass bottle reactors. These reactors were always inoculated with a consortium of sulphur bacteria. The analyses were carried out hourly in daily experiments and several times a day for long-term experiments. The determination of the kinetic parameters was analysed using the initial growth rates of different substrate concentrations. Substrate concentrations between 2.5 and 790 $mg \cdot l^{-1}$ were used. In all experiments the actual protein concentration was measured, so the cell lysis and mortality rate are already reflected in the growth rates. The growth rates can be plotted in a Monod-diagram. With the Langmuir-plot, μ_{max} and K_m can be easily read off. The determination with the Langmuir-plot is more precise than with the often used double reciprocally plot of Lineweaver and Burk because distortion is not as high. The determination of these values can also be carried out with the AQUASIM's parameter estimation (see chapter 7).
The yield coefficients were determined in these batch experiments as well as in experiments with other laboratory bioreactors.

Compatibility with solubilisers

The compatibility of humic substances with Thiobazilli is an important factor in the bioscrubber system. Only with compatibility can this system operate efficiently. To that effect the influence of humic substances on the microorganisms was analysed in the laboratory. Comparisons of laboratory bioreactors were arranged. The only difference with the parallel operated bioreactors was the addition of humates. The two B. Braun bioreactors, the glass bottle reactors as well as the continuous set-ups of the gas experiments (see chapter 5.1.1) were used. In addition, series of O_2 consumption measurements were carried out. So, bacterial activity with and without the addition of humates could be compared easily. The higher the OUR, the higher the activity of the microorganisms. The sedimentation of the washing liquid and its buffer capacity were analysed with and without addition of humates.

Regeneration

The continuous gas set-up (see chapter 4.1.2) was used to analyse the growth of bacteria in H_2S conditions. The removal of H_2S with and without bacteria as well as with and without Humin-P was analysed. To analyse regeneration efficiency with practical orientation, a laboratory bioscrubber was established. Therefore, one fixed bed reactor with a cultivated biofilm was combined with the H_2S production continuous gas set-up. Figure 23 shows a schematic flow diagram and photo of this set-up.

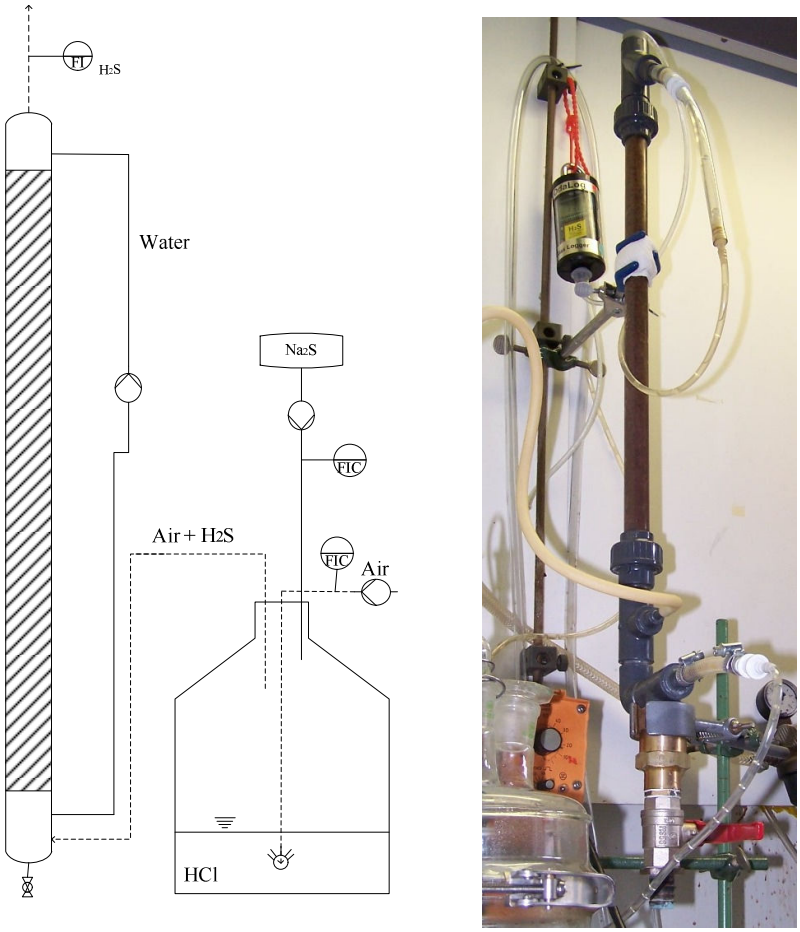

Figure 23: Schematic flow diagram and photo of laboratory bioscrubber set-up

The washing liquid was pumped continuously in a closed loop through the fixed bed reactor. The total volume of this liquid was 220 ml and its flow rate was about 8 $l \cdot h^{-1}$. The washing liquid flowed in counter current to the gas (H_2S and air). The gas flow rate was about 45 $l \cdot h^{-1}$. The outlet concentration of H_2S was measured continuously with the OdaLog H_2S data logger. The inlet concentration was between 250 and 500 ppm. The experiment was conducted with pure water as well as with Humin-P-solution. The sulphur bacteria were settled on the packed bed. This set-up mirrors the set-up of a real bioscrubber used in biogas treatment and so the regeneration of the sulphide loaded Humin-P-solution can be determined with practical orientation.

5.2. Results and Discussion

In the experiments with the laboratory bioreactor it was first successfully verified that the sulphur bacteria, living in acidic conditions, could adapt to a neutral pH environment.
A difficulty with the analysis of elemental sulphur as well as proteins, was the clogging on other surfaces of the reactors, the mixer and electrodes. Stefess [42] also had problems associated with sulphur production because of the loss of culture homogeneity due to the deposition of sulphur on the surfaces of the culture vessels. Cadenhead [53] talks about elemental sulphur clogging on the tubing and pumps, and that cells and sulphur agglomerate and accumulate at the air/liquid interface. This effect has to be considered when interpreting the results.

5.2.1. Determination of kinetics

In the batch experiments with glass bottle reactors the Monod kinetics was determined. Figure 24 shows the growth velocities obtained. These kinetics were attained with sodium thiosulphate ($Na_2S_2O_3$) as the substrate, a temperature of 30 °C and a pH of about 6.5. The maximum specific growth rate $\mu_{max} = 0.11\ h^{-1}$ was determined by evaluating and reading off a Langmuir-plot (see annex figure A17). The maximum specific growth rate μ_{max} determined is in accordance to the literature. Specialised chemolithotrophic Thiobazilli have high specific growth rates in a single substrate ($\mu_{max} = 0.35\ h^{-1}$). Versatiles Thiobazilli have low specific growth rates in a single substrate ($\mu_{max} = 0.10\ h^{-1}$). [48]

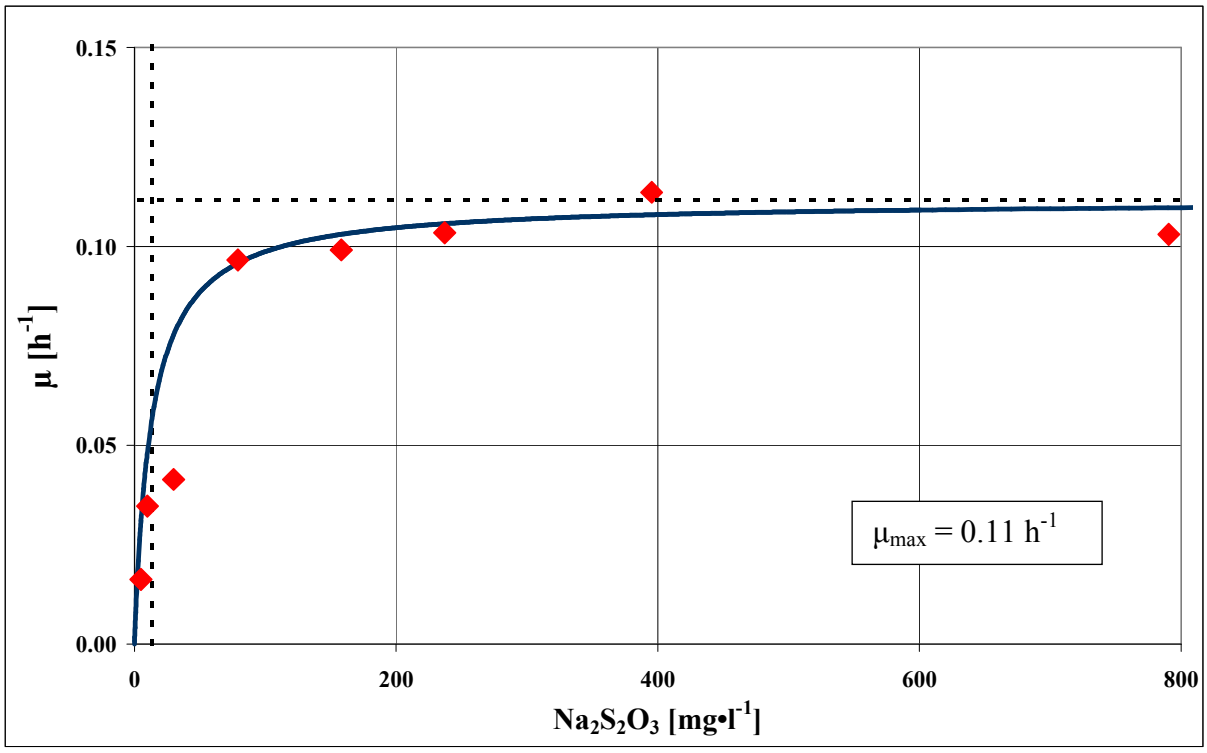

Figure 24: Determined Monod kinetics

The range of the K_m values determined was 10 - 15 $mg \cdot l^{-1}$. This range is in line with K_m values found in the literature (see chapter 3.4.2).
Figure 25 shows an example of experimental data in comparison with the kinetics obtained.

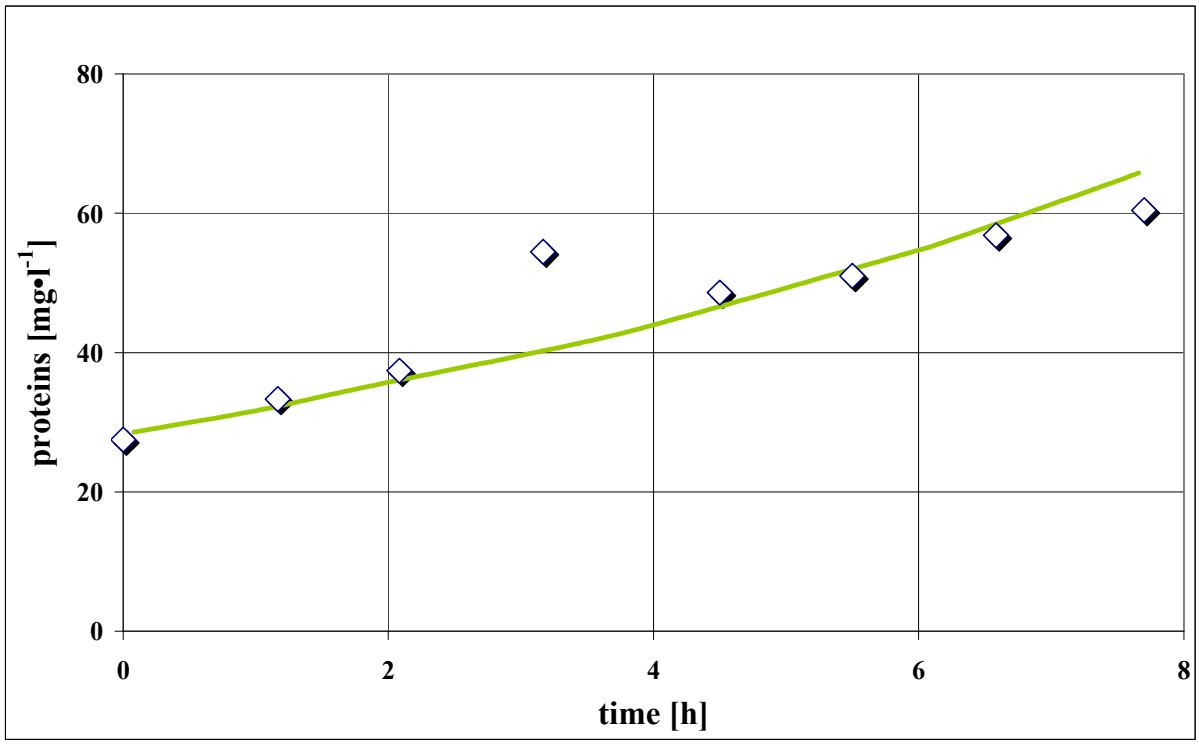

Figure 25: Comparison of experimental data with determined kinetic

The yield coefficient $Y_{B/S}$ could not be determined accurately. The values for $Y_{B/S}$ were found to range between 0.5 and 3.8 $g_{Pr} \cdot g_S^{-1}$. In simulations a value of 0.1 $g_{Pr} \cdot g_S^{-1}$ proved to be the most realistic. In experiments by Cadenhead [53] yield coefficients averaging 0.1 $g_{Pr} \cdot g_S^{-1}$ were obtained as well.

5.2.2. Influence of parameters

According to the reaction equations, the production of elemental sulphur should proceed at low O_2 concentrations. The accumulation of elemental sulphur at low O_2 supply was verified through analysis. In addition, elemental sulphur accumulates at saturation concentrations of O_2 with sufficient substrate supply. This means that the production of elemental sulphur does not depend on O_2 supply at high feed rates of H_2S or $S_2O_3^{2-}$. This is in accordance with Buisman [38]. With $S_2O_3^{2-}$ as a substrate, it was analysed that tetrathionate ($S_4O_6^{2-}$) is, in addition to SO_4^{2-} and elemental sulphur, another product of microbiological oxidation by Thiobazilli. Equation 5.7 shows this reaction.

$$2 \cdot S_2O_3^{2-} + 0.5 \cdot O_2 + H_2O \rightarrow S_4O_6^{2-} + 2 \cdot OH^- \qquad (5.7)$$

Figure 26 shows a diagram of the concentrations of elemental sulphur in two B.Braun Biostat bioreactors. In this case, bioreactor 1 is fed continuously with $Na_2S_2O_3$, so that there was a surplus of substrate. Bioreactor 2 was fed at the beginning of the experiment (4 $mmol \cdot l^{-1}$). In both reactors the initial elemental sulphur concentrations were the same. All other process conditions were equal and constant in the two bioreactors (V = 2 l, temperature = 30 °C, pH = 7, V_{O2} = 200 $ml \cdot min^{-1}$, n = 80 rpm).

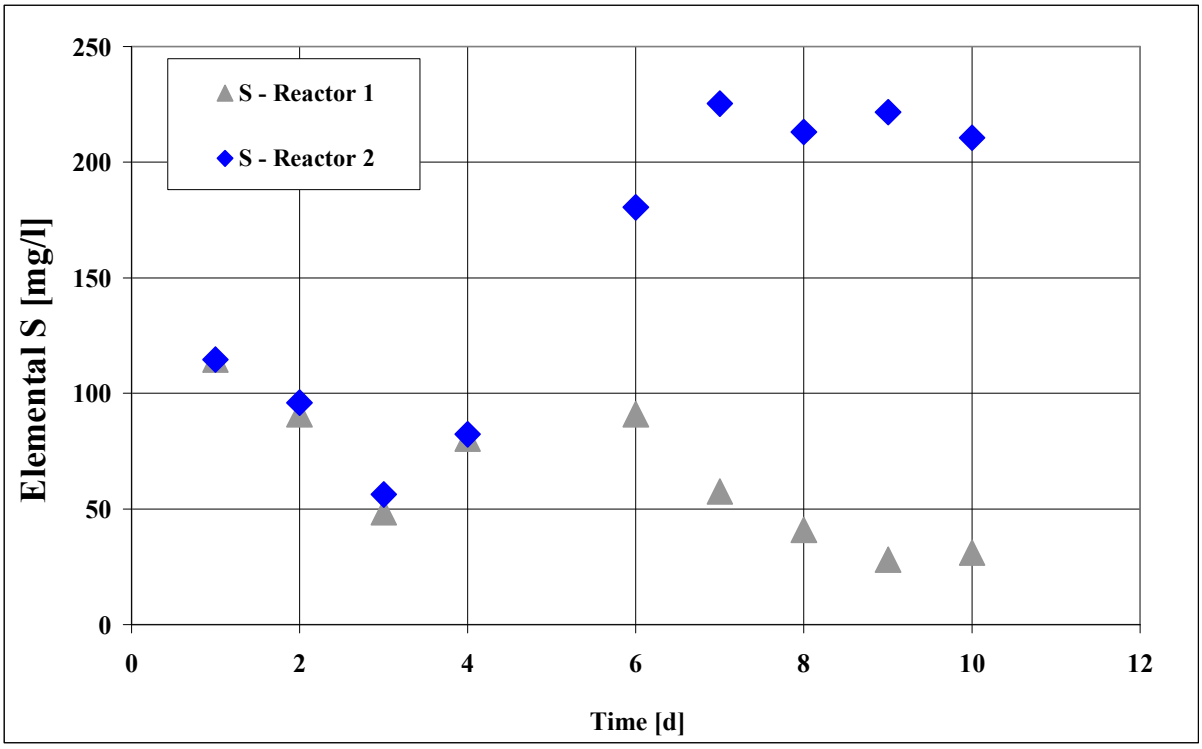

Figure 26: Elemental sulphur concentrations in bioreactor 1 and 2

It was determined that optimum growth conditions were at temperatures between 30 and 40 °C. This is in accordance with the literature [45]. pH values from 6 to 8 were the optimum range for the sulphur producing Thiobazilli [60]. This is in accordance with analysed bacteria strains in the liquid. For example, the contained "Thiomonas intermedia" has a temperature optimum of 30 °C and a pH optimum of 6 [61].

Experiments analysing O_2 consumption showed that the OUR is at an average of 0.4 $mg_{O2} \cdot mg_{Pr}^{-1} \cdot h^{-1}$ at a temperature of 30 °C.
This is equal to a value of 0.2 $mmol_{O2} \cdot g_{Pr}^{-1} \cdot min^{-1}$. Gonzalez [49] analysed average OUR values of 0.11 $mmol_{O2} \cdot g_{Pr}^{-1} \cdot min^{-1}$. The oxygen consumption experiments confirmed that the optimum temperature was about 30 °C. The OUR at this temperature was on average 25 % higher than at ambient temperature of 20 °C. An example experiment is shown in the annex, figure A16.

A difference in OUR at different pH values could not be determined because the bacteria can adapt to a wide range of pH values and so adaption to these pH values had a higher influence. The bacteria living in certain pH conditions always have a higher OUR than at changed pH conditions.

5.2.3. Compatibility with solubilisers

During the comparison experiments with different reactors, a marked difference in the growth of bacteria, the production of SO_4^{2-} and elemental sulphur and the degradation of $Na_2S_2O_3$ was noted upon the addition of humates. A change in existing bacteria with the addition of Humin-P was not found in the different reactors.
The concentration of $S_2O_3^{2-}$-S and SO_4^{2-}-S from one of the experiments is shown in figure 27. The pH of all solutions was about 7.5 (± 0.5), the O_2 concentrations were about 8 $mg \cdot l^{-1}$ and the temperature was 25 °C.

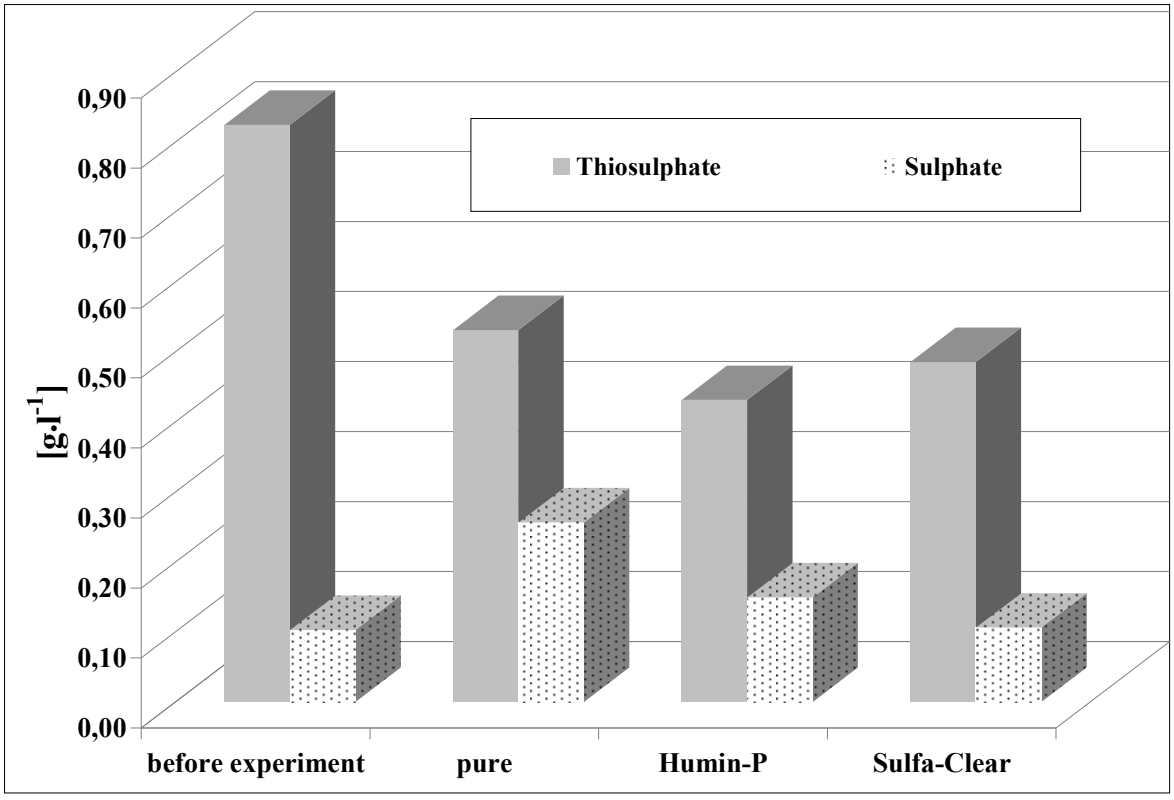

Figure 27: Sulphur concentrations with addition of Humin-P and Sulfa-Clear

Figure 27 shows a clear inhibition effect of Humin-P and Sulfa-Clear. These results were also observed in all other experiments. The inhibition effect of Sulfa-Clear is higher than of Humin-P. Without pH regulation of the alkaline solubilisers, an even higher inhibition on the degradation of $Na_2S_2O_3$ by the bacteria was observed.
A reason for the inhibition of the bacteria might be that the sulphur compounds are bound inside the humates and cannot be used by the bacteria. Humic acids can rearrange their structure permanently and also bring new functional groups outwards. Substances which were bound by chemisorption onto the humic acids may be enclosed by the structure of these humic acids [35]. The $S_2O_3^{2-}$ therefore stays in the humates.

With long-term fed-batch experiments at the Biostat bioreactors, average degradation rates of $Na_2S_2O_3$ were determined. The degradation rate was between 4 and 6 $g \cdot m^{-3} \cdot h^{-1}$. This value is lower than values found in the literature (see chapter 9.2). The reason for this might be the low temperature in the Biostat reactors which was an average 19 °C.

In these experiments, no influence from Humin-P was observed. Growth of sulphur bacteria could be found with and without the addition of humates in these long-term experiments as well.
Experiments with H_2S as a substrate showed a similar growth of bacteria in conditions with 2 wt-% Humin-P and without humates. This result shows that the chemical bound sulphide is probably available for the sulphur bacteria (see chapter 5.2.4).

Regarding the activity of the sulphur bacteria at humate conditions the OUR showed an inhibition of Humin-P. Figure 28 shows the dependence of the Humin-P concentration [wt-%] on OUR [$mg_{O2} \cdot mg_{prot}^{-1} \cdot h^{-1}$]. This dependency was determined by the AQUASIM's parameter estimation with equation 5.5. The maximum OUR in these experiments is determined to 0.83 [$mg_{O2} \cdot mg_{prot}^{-1} \cdot h^{-1}$], the constant K to 69.4 [wt-%] and n to 3.8.

$$OUR = OUR_{\max} \cdot \left(\frac{K}{K + c_{HP}^{n}} \right) \tag{5.5}$$

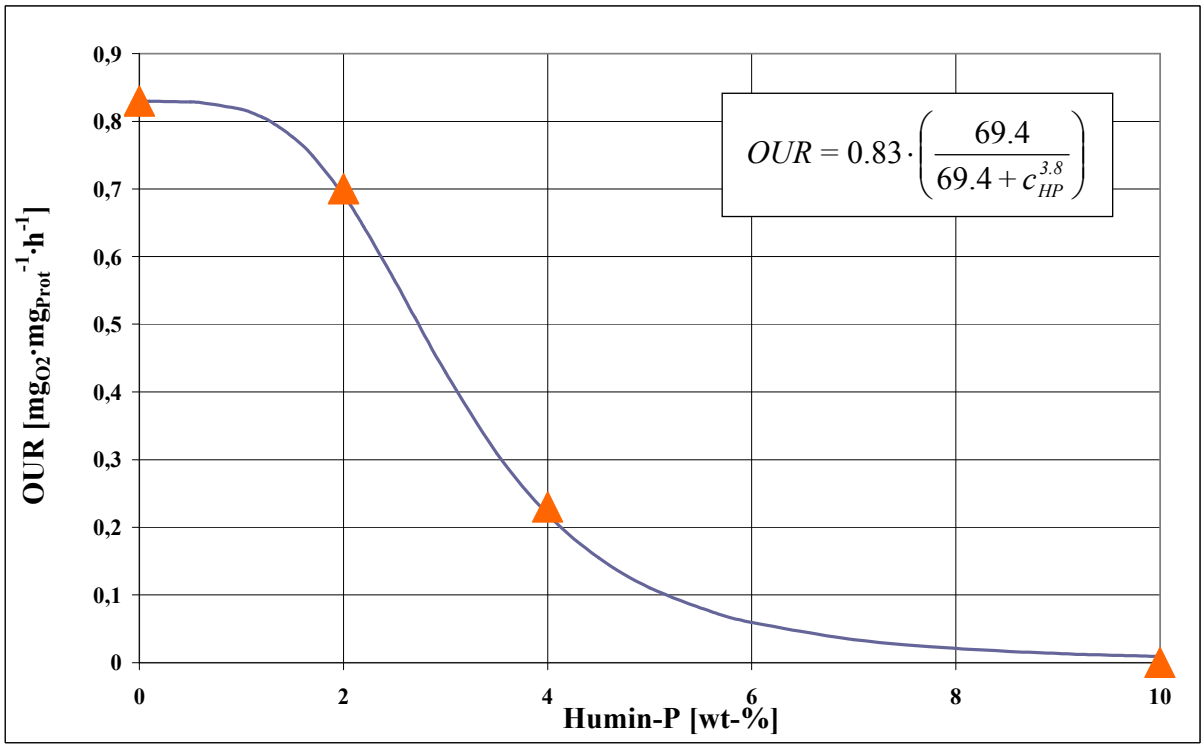

Figure 28: OUR of Thiobazilli and its relationship with Humin-P concentration

The rate of O_2 consumption is reduced by addition of humates. A Humin-P concentration of 10 wt-% has a high inhibition effect which showed also in the decay of protein concentration during the experiments. A high inhibition effect was also observed with the addition of Sulfa-Clear. It can be concluded that these additives have a negative effect on the activity of the sulphur bacteria.

Another negative effect of the addition of Humin-P is a slight foam formation. Foam formation increases with higher concentrations of Humin-P. Foam formation was also observed in experiments with Sulfa-Clear. A negative effect on the degradation and growth rates by several defoaming agents was observed in the experiments. Therefore, their use should not be excessive but be calculated properly.

The buffer effect of Humin-P was already observed in the gas experiments (see chapter 4.2.3). The high buffer capacity of humic substances is in accordance with the literature [33,68]. The buffer capacity $K_{S4.3}$ of a 2 wt-% Humin-P-solution is about 56 mmol $H^+ \cdot l^{-1}$. In comparison, the buffer capacity of sodium carbonate (Na_2CO_3) was determined to 22 mmol $H^+ \cdot l^{-1}$. As alkalinity is usually also given in "mg $CaCO_3 \cdot l^{-1}$", correspondingly, the 2 wt-% Humin-P-solution has an alkalinity of 2.8 $gCaCO_3 \cdot l^{-1}$.
$K_{S4.3}$ [mmol $H^+ \cdot l^{-1}$] is dependent on the concentration of humates [wt-%]. Its relationship with neutral Humin-P washing liquid is determined by:

$$K_{S4.3} = 1.5128 \cdot c_{HP} \tag{5.6}$$

Figure A20 in the annex shows a diagram of the dependence of Humin-P concentration on alkalinity.

In addition, the volume of settleable solids in the washing liquid was determined. In a pure 2 wt-% Humin-P-solution this value was about 2.55 ± 0.07 $ml \cdot l^{-1}$. In the washing liquid of a pilot plant the volume of settleable solids was about 1.71 ± 0.08 $ml \cdot l^{-1}$. Including 2 wt-% Humin-P this value increases to 3.45 ± 0.61 $ml \cdot l^{-1}$. This value is an indication of the sedimentation of humates. The pilot plant mentioned is described in chapter 9.1. A photo of a sedimentation experiment is shown in figure 29.

Figure 29: Comparison of sedimentation with and without humates

5.2.4. Regeneration

With the continuous gas set-up parallel experiments studying the removal efficiency of H_2S and growth of bacteria were determined. Figure 30 shows the saturation of the different liquids over one hour. It is evident that the addition of Humin-P increases the efficiency of the H_2S removal. This confirms further results. The presence of bacteria extends the time of H_2S reduction also.

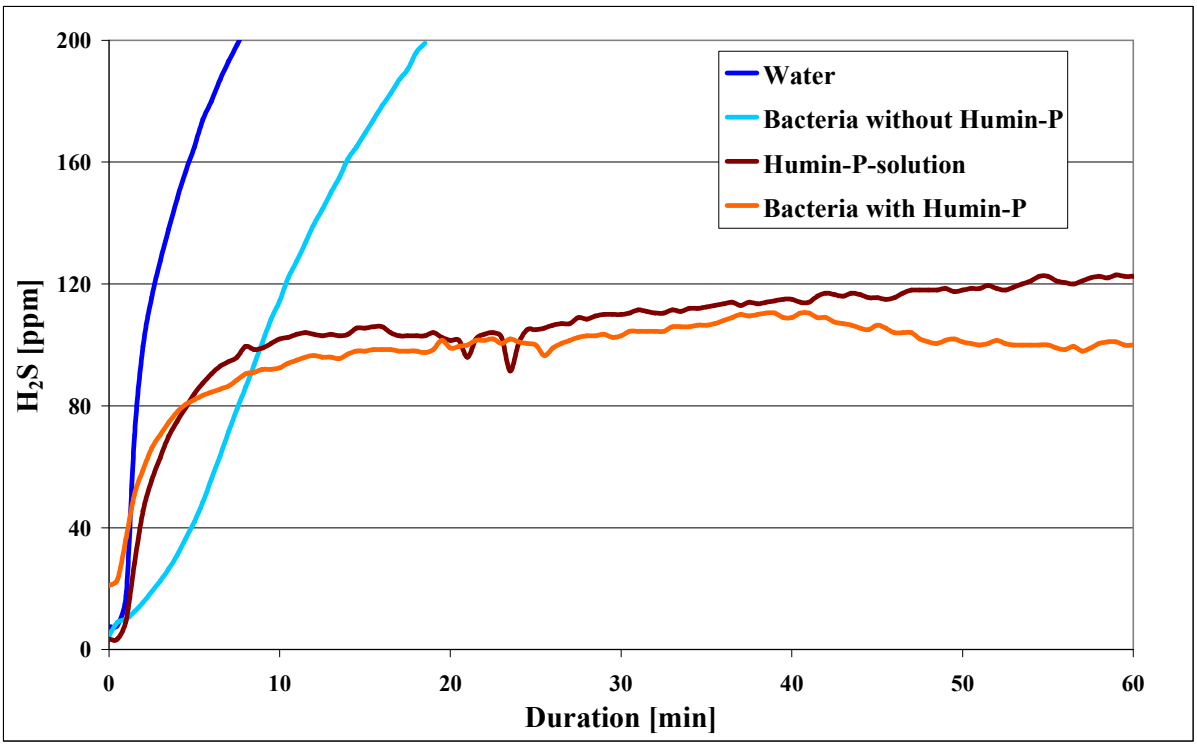

Figure 30: Time of saturation of washing liquids

The tests showed that Humin-P-solution can be regenerated by bacteria. Growth in bacteria with the addition of Humin-P was observed in all experiments. The chemical bound sulphide in the Humin-P is obviously also available to the bacteria. Even after 6 hours the solution of bacteria and Humin-P still removed H_2S - the outlet H_2S concentration measured was 100 ppm. Long-term experiments could not be arranged in the laboratory due to the set-up and safety reasons. The influence of Humin-P on H_2S absorption is described in chapter 4.2; the modelling of the regeneration is described in chapter 7.3.

The regeneration of the Humin-P-solution by microorganisms in a laboratory bioscrubber set-up was also successful. The outlet concentration of H_2S was much lower with a Humin-P-solution than in comparison experiments with water. These results are demonstrated in figure 31, based on a duration of five hours with an inlet H_2S concentration of about 250 - 500 ppm. Additionally, after 8 hours the concentrations of H_2S in the clean gas of the Humin-P experiment were the same as after one hour. Therefore, the results of this experiment further verify the efficiency of Humin-P as a solubiliser. Thiobazilli degrade H_2S and an inhibition effect of humates could not be detected in these experiments. This practical experiment validates the regeneration of humates by biological means and thus also their application in a bioscrubber. For the addition of Humin-P the relationship between the inhibition effect on bacteria and an increase in absorption capacity has to be determined (see chapter 7.2.1 and 7.3.1). Furthermore, other effects such as foam formation have to be considered.

Regarding the regeneration of Humin-P one question could not be answered by these experiments: can humates really be regenerated or does the dynamic structure of the humates replace the used functional groups with others inside the molecules. The sulphur compounds therefore stay in the humates. This effect may occur due to the inhibition of sulphur bacteria by humates, so that the sulphur compounds are bound inside the humates and cannot be used by the bacteria.

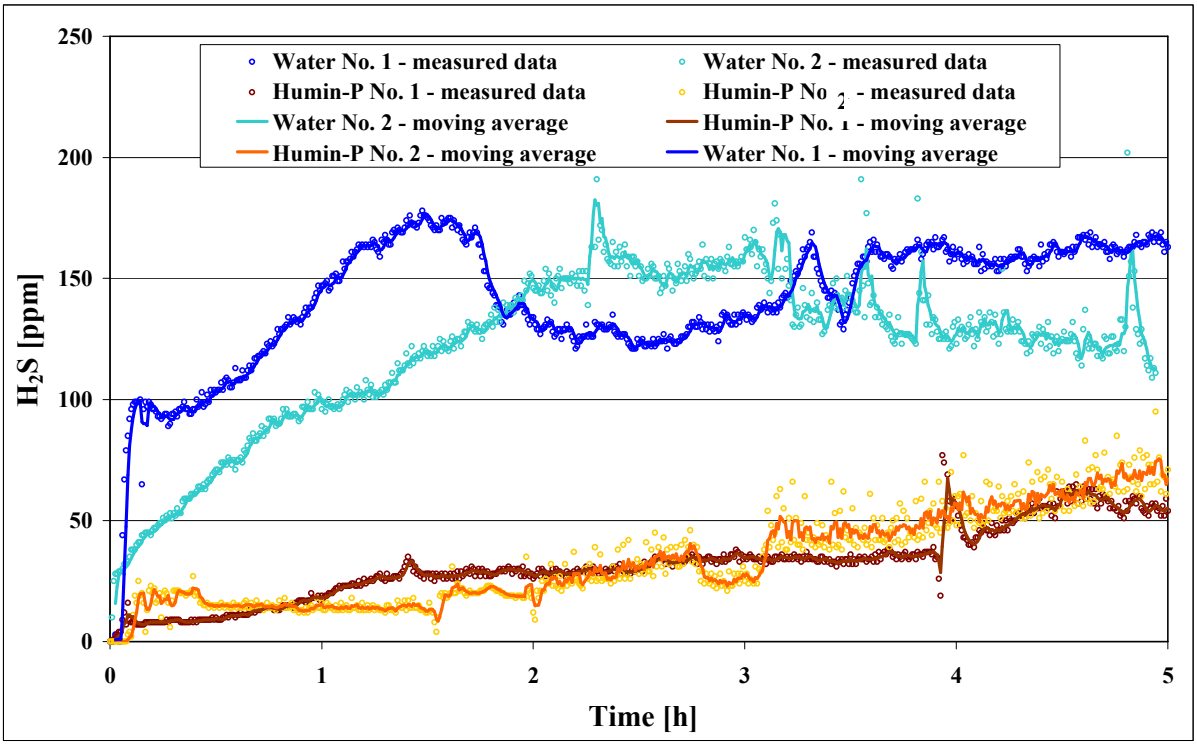

Figure 31: Outlet H_2S concentrations in laboratory bioscrubber

6. By-products and waste streams

This chapter deals with the two off streams of the bio-scrubber system (see figure 1). The present streams are the outflow of the bioreactor and the exit air of the bioreactor. The main issue dealt with is the liquid outflow because of its possible re-use e.g. as fertiliser.
The liquid outflow contains washing liquid with a high proportion of humic substances and elemental sulphur (as well as other sulphur compounds like SO_4^{2-}).
Humic substances are known to play an important role in soil fertility. They influence the quality and productivity of the soil. Humic substances assist in transferring micronutrients from the soil to the plant and also increase seed germination rates [24]. According to Müller-Wegener [32] there is a high increase in productivity in different cultivated plants such as tomatoes, potatoes and sugar beet, but there is also no effect on the productivity of sunflowers and pumpkin. In general, humic substances should increase biomass production. The main additive used is the potassium humates Humin-P. Potassium (K) is known as one of the more important fertilising elements.
Sulphur has to be fertilised more regularly in order to ensure a sufficient sulphur supply and crop productivity. The sulphur deficiency in agriculture is due to the declining atmospheric sulphur input. The sulphur dioxide (SO_2) emissions in Germany decreased enormous (see figure A22 in annex) [63]. Elemental sulphur has a better long-term effect than SO_4^{2-} [64]. Dissolved NH_3 in the washing liquid can also be used as nitrogen source. It is well known today that productive fertile soil is a non-renewable, endangered ecosystem.
The recovery of elemental sulphur for industrial purposes is another possible usage of the liquid outflow (see chapter 8.2).

6.1. Liquid outflow as fertiliser

In these experiments the quality of the liquid outflow of the bio-scrubber system as fertiliser was investigated. Therefore the influence of Humin-P and sulphur on plant growth was analysed. Rape and maize were considered for these plant experiments. Maize is one of the main substrates for biogas plants and rape is a very sulphur-dependent plant. To conduct the analyses, plant experiments with maize and rape as well as seed germination tests with maize were established.

6.1.1. Experimental set-up

Maize experiments

In these plant experiments the maize seeded in pots (diameter = 23 cm). The soil consisted only of bark mulch to ensure that existing nutrients in normal potting soil did not affect the data. One pot contained 3 seeds to ensure germination. After germination only one plant was kept in each pot. The pots were arranged in a randomized design in a greenhouse with a 12-hour lighting period. The plants were treated with a multi nutrient liquid fertiliser (NPK-fertilizer (7 % nitrogen (N), 7 % phosphorous (P), 5 % potassium (K)) and the potassium humate Humin-P. Table 15 lists the different treatments for the pots. Pre-experiments showed that a pure fertilisation with Humin-P and sulphur did not have positive effects, because of their lack of P and N. These experiments also showed that the alkaline pH value of Humin-P did not have a positive effect on the growth of maize and its fresh and dry weight. Therefore the Humin-P-solution used was slightly acidified.

The pH values of the used solution are in table 15. In the treatments with Humin-P the pots were irrigated with a 0.2 wt-% Humin-P-solution. In summary 7.5 g of Humin-P were applied in the pots after the 75 days of experiment.
The addition of NPK-fertiliser was calculated according to recommendations on maize fertilisation [65]. Nitrogen was taken as reference value for this calculation, and thus the fertilisation was conducted in three stages corresponding to the percentage distribution of nutrient uptake in relation to the development stages of maize: 2 % after germination, 85 % when there were four growing leaves and 13 % at the maturity of corncobs.

Table 15: Overview of treatments in maize experiments

Pot	Humin-P	NPK
1.1		
1.2		
1.3		
2.1	x (pH 8.7)	x
2.2	x (pH 8.7)	x
2.3	x (pH 8.7)	x
3.1	x (pH 7)	x
3.2	x (pH 7)	x
3.3	x (pH 7)	x
4.1		x
4.2		x
4.3		x

Rape experiments

The effect of sulphur as a fertiliser additive was analysed in experiments with rape seeds because rape is a very sulphur-dependent plant. The pots (diameter = 20 cm) with rape were standing in the laboratory in front of the window. The pots were filled with a mixture of bark mulch (65 %), sand (20 %) and potting soil (15 %). All plants were fertilised according to the recommendations on fertilisation [66] with a multi nutrient liquid fertiliser (12 % N, 12 % P, 17 % K). In addition, different amounts of sodium sulphate (Na_2SO_4) were added. According to the literature [66,67] the optimum addition of sulphur is 40 kg per hectare. Therefore sulphur dosages of 20 $kg \cdot ha^{-1}$, 40 $kg \cdot ha^{-1}$ and 60 $kg \cdot ha^{-1}$ were added to analyse the influence of sulphur fertilisation. In addition, one treatment with 40 $kg \cdot ha^{-1}$ sulphur and addition of Humin-P in granular form (2 g per pot) and one treatment without any addition were investigated. Each treatment experiment was replicated three times.

Seed germination test

The effect of different concentrations of the humate Humin-P on seed germination of maize was analysed with a seed germination test. This experiment was arranged in a completely randomized manner in a dark, aerated reservoir with a constant temperature of 30 °C. 10 maize seeds were germinated in Petri dishes filled with 0.5 g cotton wool and 60 ml liquid solution for seven days. Each treatment was replicated three times.

The following liquid solutions were used:

- pure tap water
- 0.01 wt-% Humin-P-solution, pH 7
- 0.01 wt-% Humin-P-solution, pH 10
- 0.04 wt-% Humin-P-solution, pH 10
- 0.1 wt-% Humin-P-solution, pH 7
- 0.1 wt-% Humin-P-solution, pH 10
- 0.4 wt-% Humin-P-solution, pH 10

6.1.2. Analysis

Plant experiments

During the plant experiments the parameters in table 16 were measured and calculated to quantify plant growth. Pictures were taken regularly to facilitate comparison of plant growth.

Table 16: Overview analyses - plant experiments

Parameters	**Unit**
Amount of leaves	-
Plant height	cm
Stem thickness	cm
Stem length	cm
Fresh weight	g
Dry weight	g

Seed germination test

To measure seed germination the radicles (root length > 5 mm) and the coleoptiles (root length > 2 cm) were counted at the end of the experiment.
Figure 32 shows two examples of germinated and ungerminated seeds.

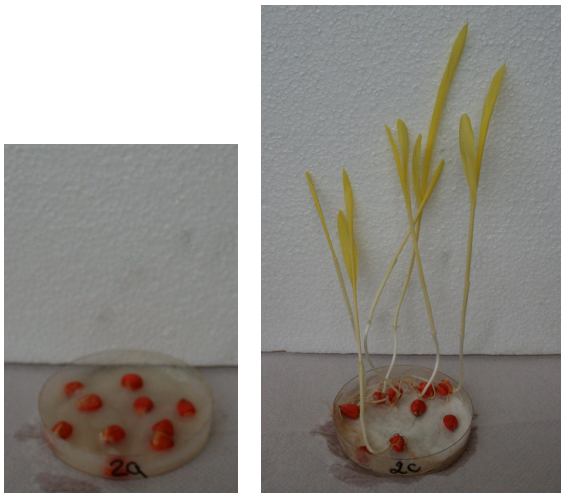

Figure 32: Left: Photo of ungerminated seed, right: Photo of germinated seed with their coleoptiles

To evaluate seed germination the germination index (GI) [%] is calculated.

$$GI = RSG \cdot RRE \cdot 100^{-1} \tag{6.1}$$

According to Singh [68] RSG is the relative seed germination and RRE the relative root elongation. They are calculated according the equations 6.2 and 6.3. Therein n refers to number of seeds germinated and rl to root length; the indices T refers to test and c to control. Germination is inhibited if the germination index is less than 60 % [69].

$$RSG = \frac{n_T}{n_C} \tag{6.2}$$

$$RRE = \frac{rl_T}{rl_C} \tag{6.3}$$

6.1.3. Results and Discussion

The results of these plant experiments showed that washing liquid is suitable as an additive to soil fertiliser. The liquid outflow of the humate containing biological desulphurisation process can enhance the efficiency of digestate as fertiliser. Together with the digestate of the biogas plants, fertilisation of plant substrates is efficient. Maize experiments with the digestate as additive showed that it is very suitable as a fertiliser.

In the following paragraphs the results of the different experiments are presented. The results of the plant experiments as well as of the seed germination test were evaluated additionally with the statistical program SPSS 15.0 using the analysis of variance (ANOVA). Differences were declared as significant at a p value smaller than 0.05. Thus, the p value represents the statistical significance. Tukey's post hoc test was used for all multiple comparisons. A positive effect of humates on plant growth, nutrient uptake and seed germination is in accordance with the literature [24,25,32].

Maize experiments

Figure 33 shows the average fresh and dry weight of the maize plants at the end of the experiment after 75 days.

The results of the fresh and dry weight clearly show the fertilisation effects of the NPK-fertiliser as well as the positive effects of adding Humin-P. When considering plant height the influence of the NPK-fertiliser is also evident. The plant height after 75 days is shown in figure 34.

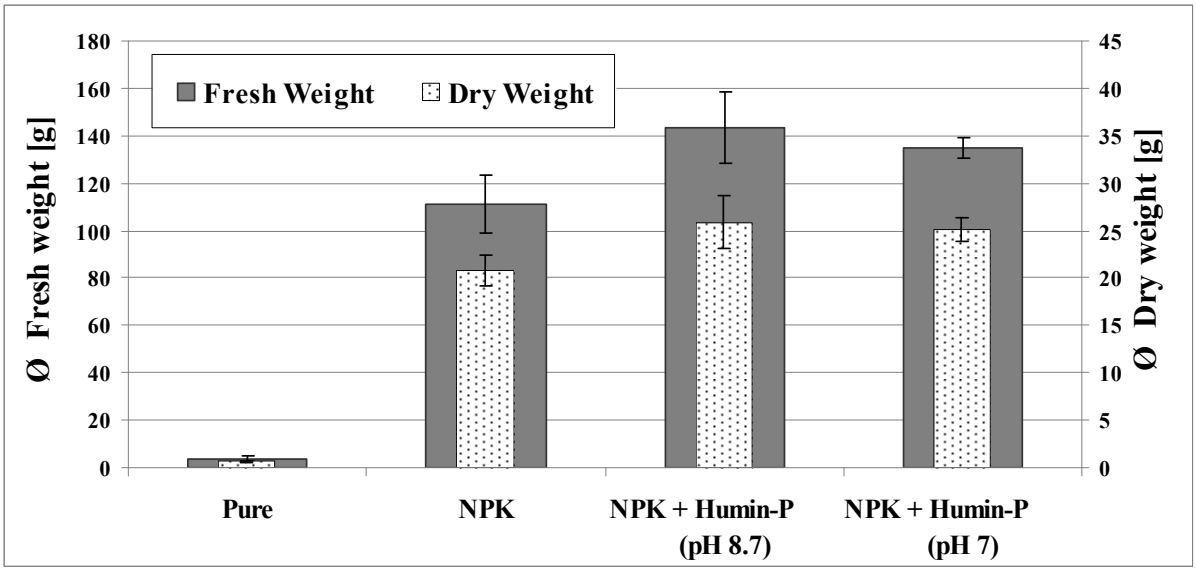

Figure 33: Average fresh and dry weight of maize

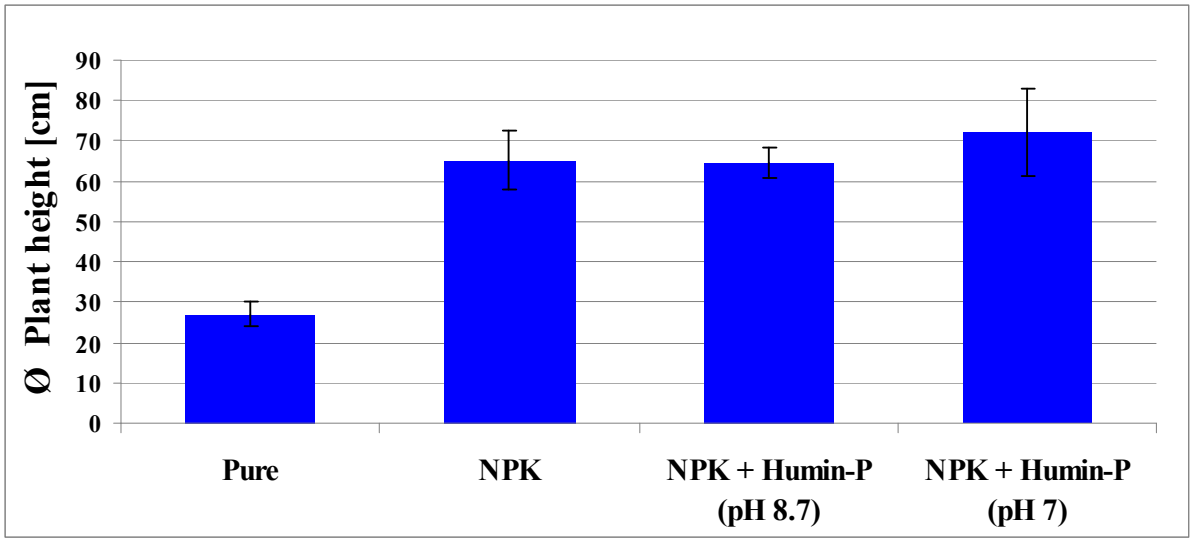

Figure 34: Average plant height of maize (until first knot)

A one-way between subjects ANOVA was conducted to compare the effect of Humin-P on maize in "pure", "NPK", "NPK + Humin-P (pH 8.7)" and "NPK + Humin-P (pH7)" conditions. There was a significant effect on maize growth at p value = 0.05 for the four conditions ($F(3,8) = 26.0$, $p = 0.0$). The F statistic value is the ratio of the variation due to treatment (variation between samples) and the variation due to error (variation within samples). The larger the F statistic value, the greater the possibility that the variances are different.
Also the effect on fresh weight and dry weight have a significant effect at the $p = 0.05$ level ($F(3,8) = 126.1$, $p = 0.0$); ($F(3,8) = 138.8$, $p = 0.0$). Tukey's post hoc test was used to compare each of the conditions investigated. This test showed that the "pure" condition is significantly different to all other treatments with regards to plant height, fresh and dry weight. All other treatments are not significantly different to each other except the fresh weight in "NPK" and "NPK + Humin-P (pH 8.7)" conditions ($p = 0.017$). This indicates that fertilisation using NPK is effective in general. Figure 34 shows that the addition of Humin P has an effect. Figure 35 shows examples of the maize plants under different treatments at the end of the experiment. It is evident that the stem of the Humin treated maize is thicker than those treated with NPK only. All these results suggest that Humin-P does have a positive effect on maize growth. This positive effect is in accordance with the literature [32].

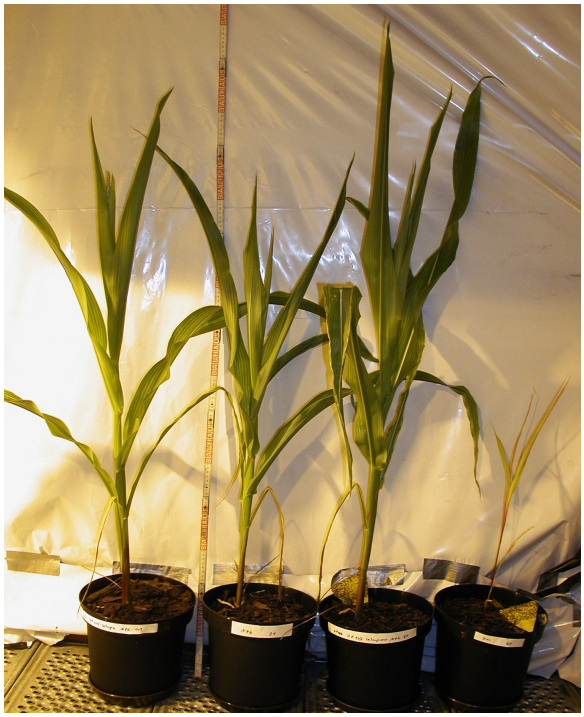

Figure 35: Photo of maize plants under each treatment ("NPK + Humin-P (pH 7)", "NPK", "NPK + Humin-P (pH 8.7)" and "pure"

Rape experiments

A one-way between subjects ANOVA was conducted to compare the effect of sulphur on rape in “pure NPK”, “20 kg·ha^{-1} sulphur supply”, “40 kg·ha^{-1} sulphur supply” and “60 kg·ha^{-1} sulphur supply” conditions. The influence of NPK-fertilizer is evident and was not determined further for this experiment. There is no significant effect of sulphur on rape growth at the $p = 0.05$ level for the four conditions ($F(3,7) = 0.62$, $p = 0.627$). Also fresh weight and dry weight have no significant differences at the $p = 0.05$ level ($F(3,7) = 1.75$, $p = 0.243$); $F(3,7) = 2.93$, $p = 0.109$). The number of leaves, stem thickness and stem height displayed no difference as well. Figure 36 shows photos of individual rape plants under different treatments before harvesting. The insignificant effect of sulphur addition is evident, but it showed good resistance against fungal infestations. This experience is in accordance with the literature which also recommends sulphur fertilisation because of this reason [67,70]. An influence of Humin-P was not determined in this experiment.

Pure | Pure NPK | 20 kg S·ha^{-1} | 40 kg S·ha^{-1} | 60 kg S·ha^{-1}

Figure 36: Photos of rape plants under different treatments

Seed germination test

Figure 37 shows the germination indices of the germination test and figure 38 shows the average values of germinated maize seeds.

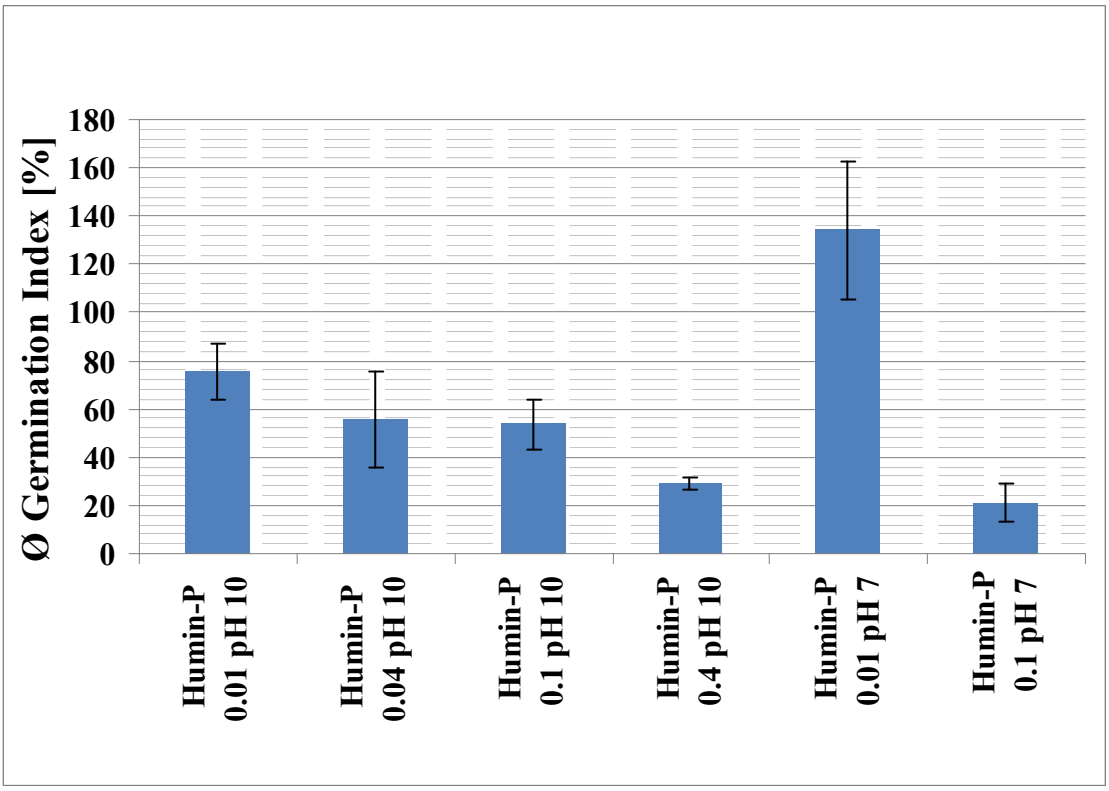

Figure 37: Average values of germination indices

Figure 37 demonstrates that only the treatments with "0.01 % Humin-P" have a germination index higher than 60 %, which is the threshold for the inhibition of seed germination. In particular, with a pH of 7 the solution shows a significant positive influence.
Figure 38 shows that for humate solutions with a pH value of 10, the higher the concentration of Humin-P, the more seeds are germinated. For humate solutions with a pH of 7, this is the other way around. The optimum treatment is with "0.01 % Humin-P, pH 7". With this treatment most of the seeds are germinated.

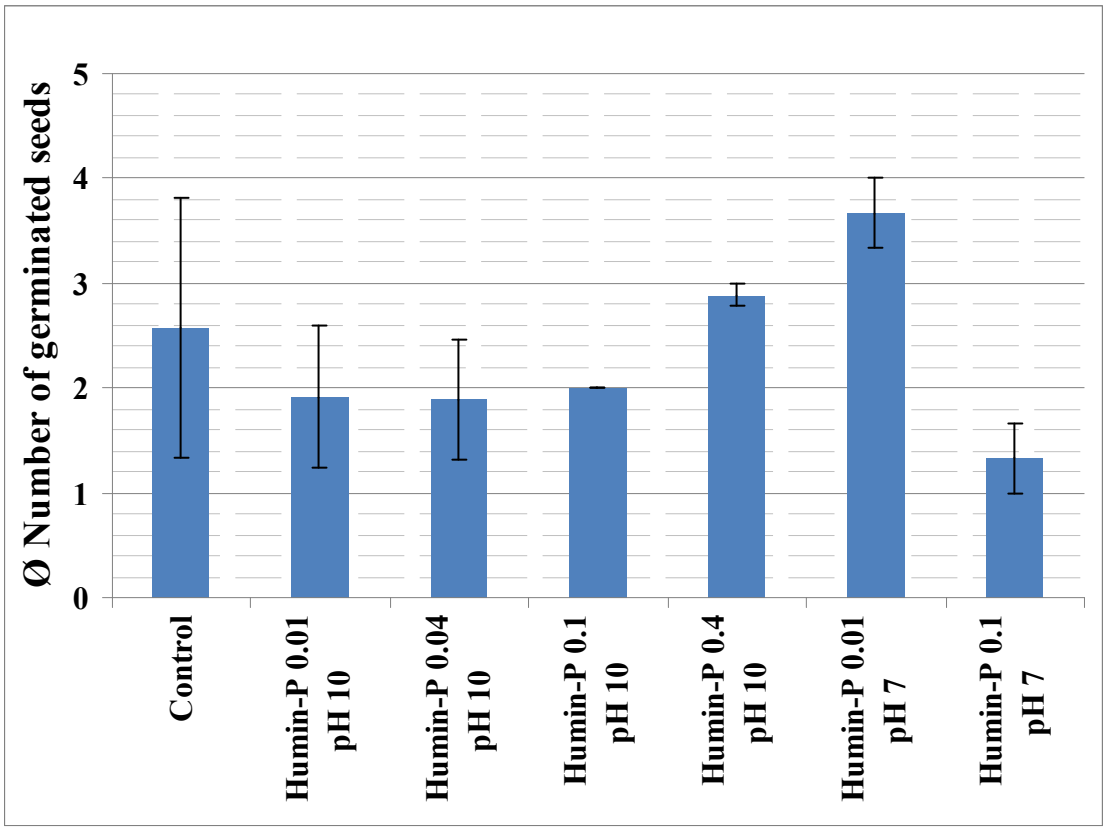

Figure 38: Average number of germinated maize seeds

A one-way between subjects ANOVA was conducted to compare the effect of Humin-P on seed germination in different Humin-P conditions. There is a significant effect of Humin-P on seed germination at the $p = 0.05$ level for the seven conditions ($F(6,14) = 2.99$, $p = 0.43$). With regards to the germination index, a significant effect was analysed ($F(5,12) = 6.57$, $p = 0.004$). It may be concluded that only the "0.01 % Humin-P, pH 7" treatment is significant to the other treatments. A pH regulated to 7 shows a positive influence on the seed germination.
Noticeable in these experiments was that maize seeds treated with water had longer coleoptiles but had shorter and thinner radicles. With the Humin-P treatment the coleoptiles were smaller, but the radicles were thicker, longer and in a higher quantity. Figure 39 shows the comparison of untreated and Humin-P treated maize seeds. It was observed that the higher the concentration of Humin-P, the smaller the coleoptiles.
Regarding the seed germination test, it is difficult to conclude whether the influence of Humin-P is negative or positive. It is analysed that with low concentrations of Humin-P and neutral pH value seed germination is optimised. Furthermore, it is observed that root formation is increased with the addition of Humin-P which was also found in other experiments [32]. An optimum dosage of humates has to be determined.

Figure 39: Comparison of treated and untreated maize seed (left: pure, middle: 0.01% Humin-P, right: comparison)

6.2. Exhaust air

The off gas of the bioreactor consists mainly of air (nitrogen (N_2) and oxygen (O_2)). Analysis of a two-stage bio-scrubber system at a pilot plant (see chapter 9.1) proved that this exhaust air might also contain harmful compounds of biogas, such as carbon dioxide (CO_2) and methane (CH_4). Their amount depends very much on the aeration. By analysing six samples of the exhaust air an extrapolation of the annual emission was calculated. This calculation indicates that the annual CO_2 emission is around 2.8 kg and the annual CH_4 emission is around 0.13 kg. These two values are far lower than the annual emission of CH_4 and CO_2 of one cow [71]. Due to the fact that the bio-scrubber system wants to gain elemental sulphur, which requires a low air supply, the harmful influence of the off gas would be lower than the above values and can therefore be neglected. If there are higher concentrations of CH_4 and CO_2 in the off gas, a downstream biofilter would be a solution against high emissions.

7. Mathematical modelling and simulation

In chemical processing technology, numerical process simulation is an established tool for modelling and evaluating the process of industrial plants. Based on mass and energy balances as well as phase equilibrium and reaction kinetics, process simulations are able to model the stationary and dynamic behaviour of chemical plants.
Simulations have the advantage of being generally safer, cheaper and more time-saving than real experiments. Furthermore, it is easy to manipulate the model and its parameters and suppress disturbances and second-order effects [72]. The disadvantages of simulations are that users may forget the limitations and conditions of the model and draw erroneous conclusions from the simulation. Therefore, it is very important to compare at least some of the simulation results with experimental results. [72]

Several simulation software for modelling chemical and microbiological processes are available. In this thesis the modelling language Modelica was used. Modelica is an object-oriented modelling language and is suitable for many specialised engineering fields. In Modelica, a physical model is described with differential-algebraic equations (DAEs). This model is translated into a mathematical model and solved with a solution algorithm. [73]
In this thesis, the programming environment Dymola from Dynasim was used. In this environment symbols are used for objects which can be linked with connectors. Other applications for Modelica include MathModelica, SimForge or OpenModelica.
Modelica was chosen because the absorption column and biological processes in the regeneration step could be easily combined. In typical modelling software for process engineering, such as ASPEN Plus, the modelling of biological processes cannot be applied satisfactorily. Furthermore, humic substances cannot be found in Aspen Plus data banks.
Some coefficients are also determined by modelling and simulation in AQUASIM. AQUASIM is used for the analysis and simulation of aquatic systems [74]. Parameter estimation in AQUASIM is a very useful tool, and is often used to determine certain coefficients from the experimental data.

The addition of Humin-P in the process was simulated by the model and the optimum amount of Humin-P to be added in the process was determined. Furthermore, the addition of Humin-P was compared to the system with water, so that, for example, the savings of washing water could be determined. The influence of Humin-P on behaviour of the sulphur bacteria in the bioreactor was simulated as well. A model of a humate containing bio-scrubber system was developed.

7.1. Modelling of scrubber

The scrubber is a device where counter current absorption occurs. Gas flows upwards through the column while washing liquid flows downwards. Contact between the gas and liquid is optimised e.g. with a packed column.
The required height H and the number of stages N of the packed column can be determined by the method of theoretical stages (HETP method) or the method of transfer units (HTU/NTU method). HETP refers to height equivalent to a theoretical plate and NTU the number of transfer units. The height H of the packed column is calculated as follows. The indices O refer to overall, G to gas and L to liquid.

$$H = N \cdot HETP \tag{7.1}$$

$$H = NTU_{O,G} \cdot HTU_{O,G} = NTU_{O,L} \cdot HTU_{O,L} \tag{7.2}$$

To determine the height and number of stages, the carrier gas flow, liquid flow, inlet concentrations and outlet concentrations have to be known.

In general the HTU value is not identical to the HETP value, but for simple reactions the following relationship is valid [75]. This equation was derived for straight operating and straight equilibrium lines, but is also approximately valid for curved operating and curved equilibrium lines.

$$HETP = HTU_{O,G} \cdot \frac{\ln\left(\frac{m \cdot G}{L}\right)}{\frac{m \cdot G}{L} - 1} \tag{7.3}$$

The HETP method is used for this model because of its simplicity. This equilibrium model is often used for the modelling of chemisorption processes although the interactions for mass transfer cannot be modelled [76].

The proposed model is based on the following general assumptions:

- The carrier gas (CO_2 and CH_4) is insoluble in washing liquid
- The solvent is non-volatile
- There is thermodynamic and mechanical equilibrium between material inflows and outflows
- The pressure dependence of all parameters is neglected because of the small pressure difference in the column
- The system is adiabatic
- There is thorough mixing of the phases
- There is no carrying away of liquid through counter flowing gas towards the next stage

Figure 40 shows the schematic flow scheme in Dymola. The package in Dymola contains one model which describes one equilibrium stage of the absorption column. The stage has four connectors for the gas and liquid flows to enter and leave the stage. For the connectors the individual stages are linked through programming using an array. By changing the length of the loop, the number of stages can be varied. The following chapters describe the equations considered in the one-stage model. The whole package also contains packages with units, calculations, symbols, connectors and reservoirs. The scenario to be simulated contains reservoirs for connectors which enter or leave the column, in addition to the column.

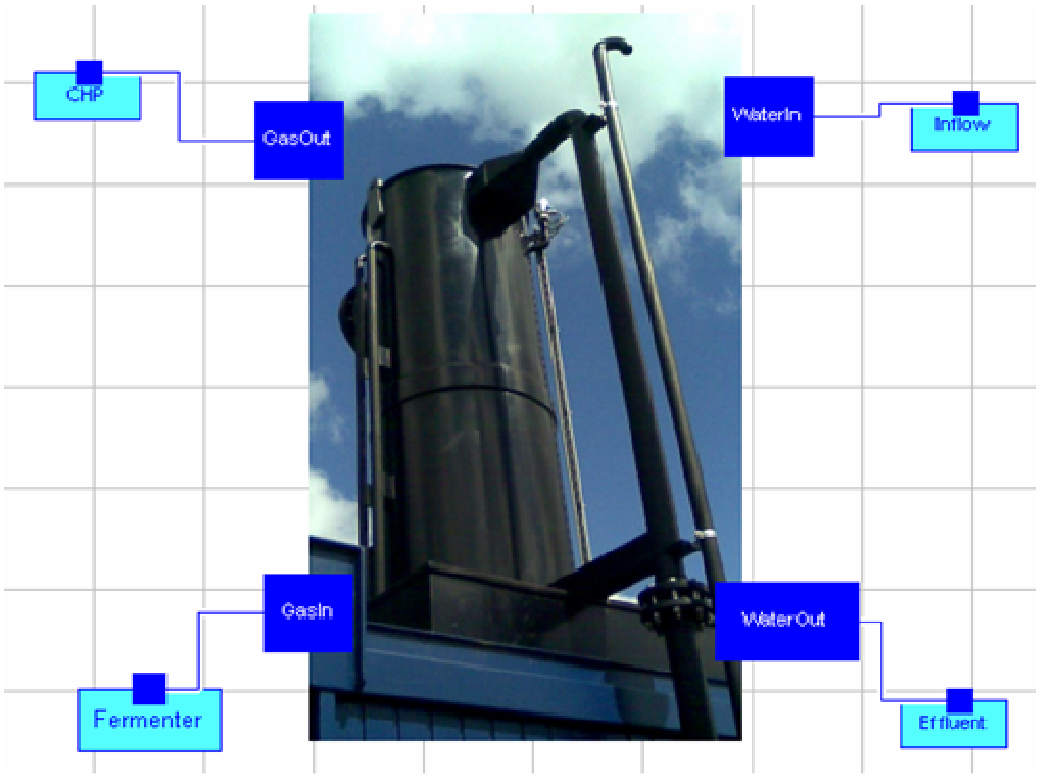

Figure 40: Scheme of scrubber in Dymola

7.1.1. Solubility of gas

The solubility of H_2S in washing liquid can be calculated using Henry's Law (see chapter 3.2).

$$H = \frac{Y}{X} \cdot p \tag{7.4}$$

The Henry coefficient H's dependence on the temperature [K] can be described as follows [19]:

$$H = H_{Ref} \cdot \exp\left(\frac{\Delta h_{sol}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right) \tag{7.5}$$

Here, the enthalpy of solution Δh_{Sol} is constant. At a temperature of 25 °C, $\frac{-\Delta h_{sol}}{R}$ is equal to 2100 K and H_{ref} is equal to 560 bar [19].

7.1.2. Mass balance

The flow of gas and liquid are constant over the column. So the input flow equals the output flow for liquid as well as for gas. G refers to gas flow, L to liquid flow, Y to gas loading and X to liquid loading. The indices B refer to bottom and T to top. The mass balance of H_2S when no reaction occurs is shown in equation 7.6.

$$Y_{H_2S,B} \cdot G + X_{H_2S,T} \cdot L = Y_{H_2S,T} \cdot G + X_{H_SS,B} \cdot L \tag{7.6}$$

7.1.3. Reaction equilibrium

Besides the mass balance, the dissociation of H_2S and HS^- has to be considered. The liquid flow L and the gas flow G are assumed to be constant over the column.

$$H_2S \overset{K_1}{\Leftrightarrow} HS^- + H^+ \tag{7.7}$$

$$HS^- \overset{K_2}{\Leftrightarrow} S^{2-} + H^+ \tag{7.8}$$

Figure A21 in the annex shows the aqueous H_2S in relation to the pH value. The equilibrium constants K_i [mol·l^{-1}] based on the temperature T [K] are defined as follows [77]:

$$\ln K_i = A + B \cdot T + \frac{C}{T} + D \cdot \ln T \tag{7.9}$$

With

- A = 218.599; B = 0; C = -12995.4; D = -33.5471 for equation 7.7
- A = -7.489; B = 0; C = -7211.2; D = 0 for equation 7.8

Balances including HS^- and S^{2-} according to equation 7.6 have to be inserted in the model as well.

7.1.4. Energy balance

The stages are adiabatic, so the heat produced in the chemical reactions and the absorption of H_2S is considered with the flows. The enthalpy balance is defined as follows.

$$\begin{aligned} &G \cdot h(T_{G,T}) + L \cdot h(T_{L,T}) - G \cdot h(T_{G,B}) - L \cdot h(T_{L,B}) \\ &+ L \cdot \Delta X_{H2S} \cdot \Delta h_{sol} + L \cdot \Delta X_{H2S} \cdot \Delta h_{R1} + L \cdot \Delta X_{H2S} \cdot \Delta h_{R2} = 0 \end{aligned} \tag{7.10}$$

The enthalpies of the ideal gas and the liquid (h_i) are dependent on temperature. They can be calculated using heat capacities and a reference enthalpy. This calculation together with the reaction enthalpies (Δh_{Ri}) and the enthalpy of solution (Δh_{sol}) is described in annex A1.
The temperature of the gas leaving the column is set equal as to the temperature of the liquid entering the column.

7.1.5. Reactions with Humin-P

Due to the complexity of the reaction between humates and H_2S, the description of these reactions is simplified with a box model. In this black box all reactions, for example ion exchange, complex formation and acid and base reactions occur. The effect of the reactions, described in chapter 4.3.1 and 4.3.2, is taken into account in the model with a modified Henry coefficient H_{HP}. This coefficient is calculated according to equation 7.11. Equation 7.11 is mainly based on equilibrium gas experiments at 30 °C. This temperature was chosen because it is the optimum temperature for sulphur bacteria. The equation is valid for Humin-P concentrations c_{HP} ranging between zero and 10 $g \cdot l^{-1}$.

$$H_{HP} = H \cdot \left(\frac{K_{HP}}{K_{HP} + c_{HP}} \right)^{n} \tag{7.11}$$

The kinetic constant K_{HP} and the exponential factor n were determined with AQUASIM's parameter estimation. The standard deviation was $2.231e^{-5}$.

$$K_{HP} = 8.52e^{-7} \quad [g \cdot l^{-1}] \tag{7.12}$$

$$n = 0.2765 \tag{7.13}$$

Temperature dependency has to be included in the model. The model is validated using equilibrium experiments. For a temperature $T_{30°C}$ of 30 °C, equation 7.11 is valid. 70 °C is the maximum temperature at which experiments were carried out.
The relationship with temperature is described according to Angelidaki [78]. K_{HP} is constant and the exponential factor n is dependent on temperature according to equation 7.14.

$$n(T) = n_{30°C} - \alpha \cdot (30 - T) \quad \text{for T} < 30\ °C \tag{7.14}$$

The temperature coefficient α is set as 0.004043. Activities at temperatures over 30 °C were neglected because the bacteria's optimum temperature is 30 °C and in winter only lower temperatures might be possible. The model is valid for temperatures ranging between zero and 30 °C.

The effect of pH on H_2S removal is considered in the dissociation reactions. Other effects of pH are neglected in this model.

Humin-P which reacts in this process has to be regenerated and is no more available. In all other processes and reactions it is assumed that Humin-P is inert and thus exerts no influence. Therefore, enthalpy changes due to the Humin-P are also neglected in this model. The humates which react with H_2S are consumed and their concentration is indicated as c_{HP_cons}. In the model it is assumed that 60 % of the available humates c_{HP_avail} are consumed in one stage of the column. Thus, the bonding sulphur at humates is included. The slight formation of SO_4^{2-} and S is also neglected in this model. Table 17 gives an overview of the constant parameters of the simulation. The following input parameters can be varied: volume flows of liquid L and gas G, their temperatures T, the H_2S concentration c_{H2S} of the gas entering the column as well as the pH of the washing liquid. The concentration of Humin-P c_{HP} can be varied as well. The model is valid for Humin-P concentrations of 0 to 10 wt-% and at ambient pressures.

Table 17: Overview of constants used in the model of the scrubber

α	0.004043
H_{ref}	$560 \cdot 10^5$ bar
K_{HP}	$8{,}52 \cdot 10^{-7}$ g·l^{-1}
n	0.2765
p	1 bar
T_{ref}	298 K
$T_{gas,in}$	298 K
x_{CH4}	0.65
x_{CO2}	0.35
Δh_{sol}	17459 J·mol^{-1}
Δh_{r1}	22200 J·mol^{-1}
Δh_{r2}	-15500 J·mol^{-1}

7.2. Simulation of scrubber

The simulation of the scrubber should demonstrate the practical applications of a scrubber. Therefore the scrubber is compared with the existing pilot plant to validate the model (see chapter 9.1). Figure 41 shows the H_2S clean gas concentration as result of simulating the scrubber. As input data the process-related parameters from the pilot plant were used in the model and 13 stages were simulated. The raw gas concentration of H_2S is set at 1,000 ppm. The temperature of the wash water is 30 °C and the pH is 6.5.

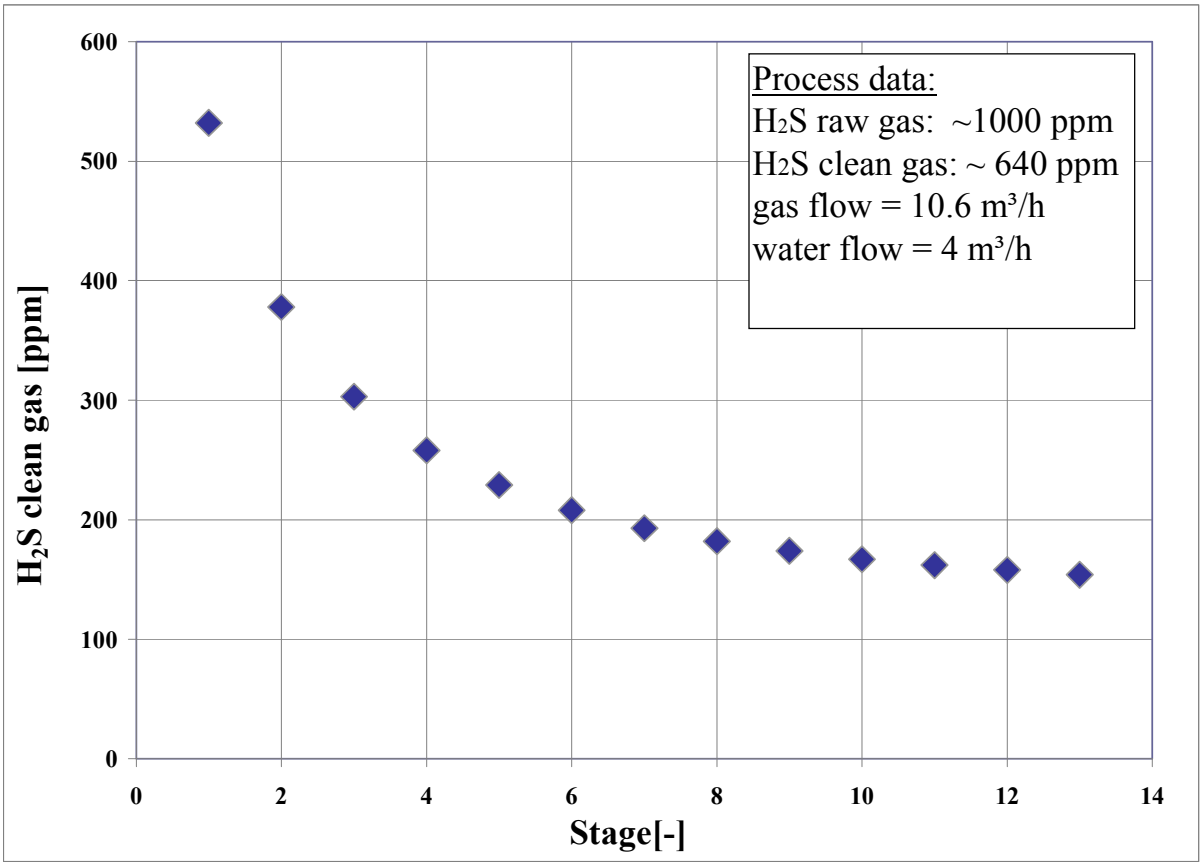

Figure 41: Results of simulating the scrubber from the pilot plant

The results of the simulation are not in line with the data obtained at the pilot plant. The HETP of the pilot plant can be determined using the height of the packing (H=2.2 m) and the defined number of stages. The H_2S clean gas concentration measured at the pilot plant was between 600 and 700 ppm in this scenario. These values are far higher than the H_2S clean gas concentrations obtained from simulation. The reason for that might be that there were too many problems in operating the pilot plant (see 9.1), so that no steady state in operating was achieved. The bacteria did not work well and the washing water might be partly saturated so that less H_2S may be absorbed in the liquid. Thus, the number of theoretical stages N in the pilot plant could not be determined and so the HETP either. If having data, the HETP for the pilot plant can be calculated with equation 7.15.

$$HETP = \frac{H}{N} \tag{7.15}$$

To validate used model ind Modelica/Dymola, it was compared to a model of a H_2S absorption column in Aspen Plus. Aspen Plus is one of the main process simulators used today in the processing industry. In Aspen Plus the absorption column is modelled with the radfrac model. With this model all types of multi-stage gas-liquid separation operations can be simulated. Considering the property method the ELECNRTL method is chosen. With sensitivity analysis different parameters and their influence can be easily simulated. The Henry coefficients are generated automatically in Aspen Plus. The comparison of the scrubber model developed in Dymola with the model developed in Aspen Plus shows that the Modelica resp. Dymola can be used for modelling absorption columns. The results obtained are similar to the simulation results of the absorption column modelled with Modelica. The model which was developed in chapter 7.1 deems to be valid.

The comparison of data obtained from the scrubber in the pilot plant with data obtained from the simulation is shown in figure 42. The number of theoretical stages is set at 5. The concentration of humates is 0.7 wt-% for the model with humates as well as for the measured data with humates.

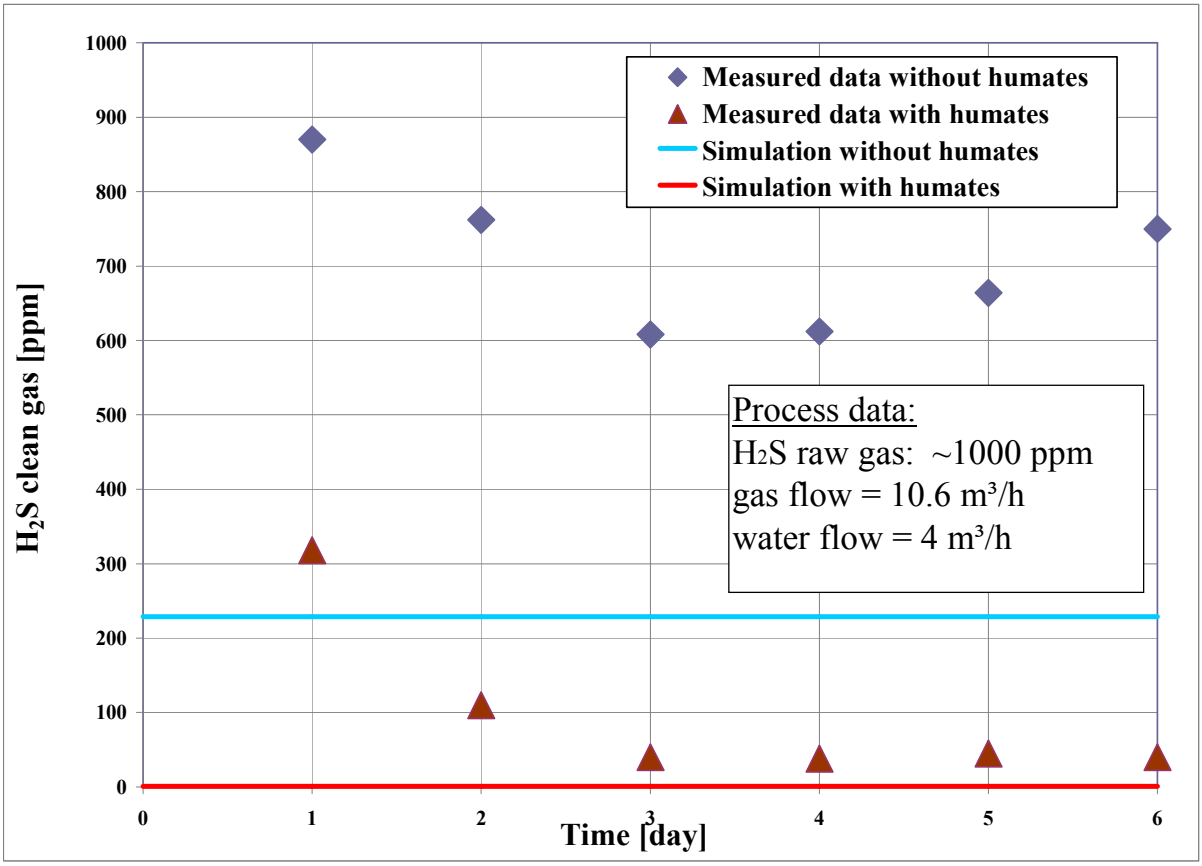

Figure 42: Comparison of the data from the simulation with the data from the pilot plant

The model is not able to display the data from the pilot plant without humates in the wash water. The reason for that was already described and is most likely due to problems in operating the pilot plant. The clean gas achieved in the simulation with humates had H_2S concentrations of 0 ppm. The pilot plant did not run longer than 5 days with humates, so it is possible that zero ppm may also be achieved in the pilot plant. In these 5 days the pilot plant operated well.

Using the model, the influence of temperature is determined. The influence of this parameter on the removal of H_2S is shown in figure 43 and 44. For the simulation in figure 43, a scrubber with a gas volume flow of 300 $m^3 \cdot h^{-1}$ and a water flow of 50 $m^3 \cdot h^{-1}$ is used. The raw gas concentration of the biogas is 1,000 ppm. The pH of the washing liquid is 6.5, its temperature is 30 °C. These two input parameters are prescribed in all following simulations conducted in this chapter. Other parameters are changed in the model before starting the simulation. The temperature range of the wash water for the simulation in figure 43 was between 5 and 40 °C. These are realistic values at which the plant can be operated. With a temperature less than 5 °C the risk of freezing is too high. Temperatures higher than 40 °C result in an even worse absorption and are not evaluated.

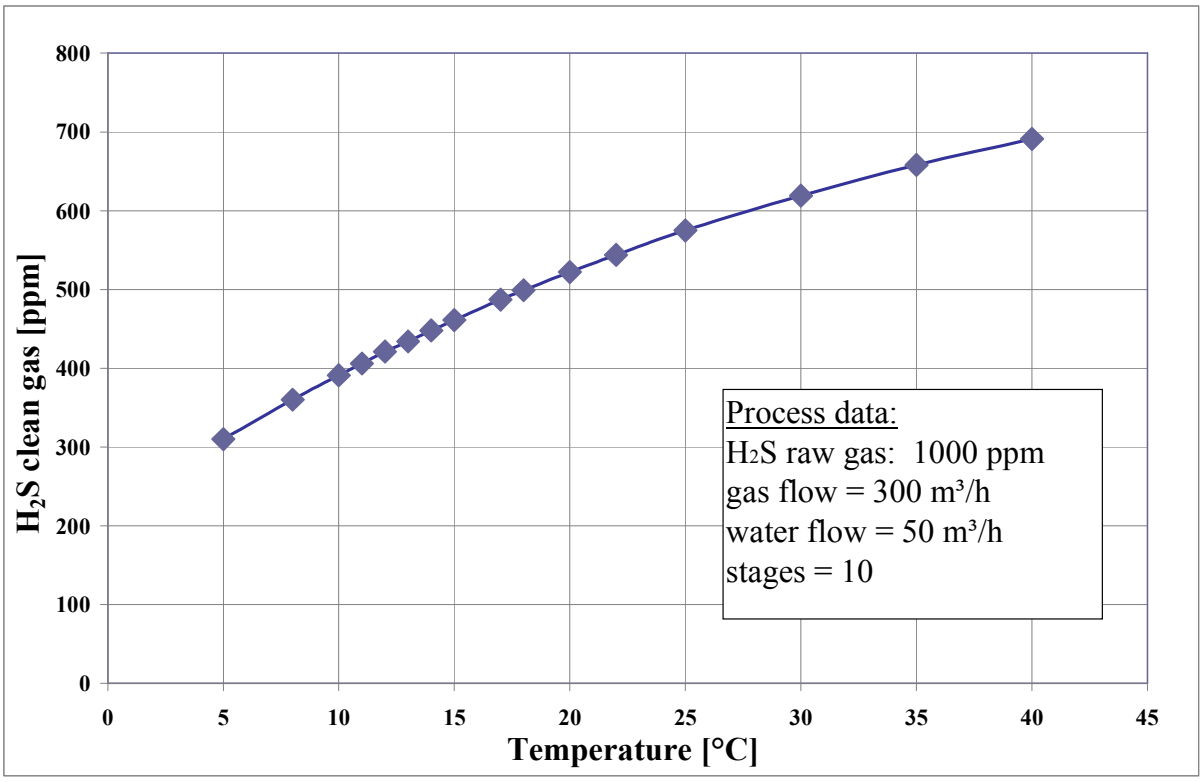

Figure 43: Dependence of temperature on clean gas concentration

For figure 44 the gas flow is 100 $m^3 \cdot h^{-1}$ and the raw gas concentration 1,000 ppm. In both diagrams (figure 43 and 44) it is evident that the absorption efficiency is better at lower temperatures of washing water. The temperature of the washing liquid is one of the most important parameters for absorption columns.

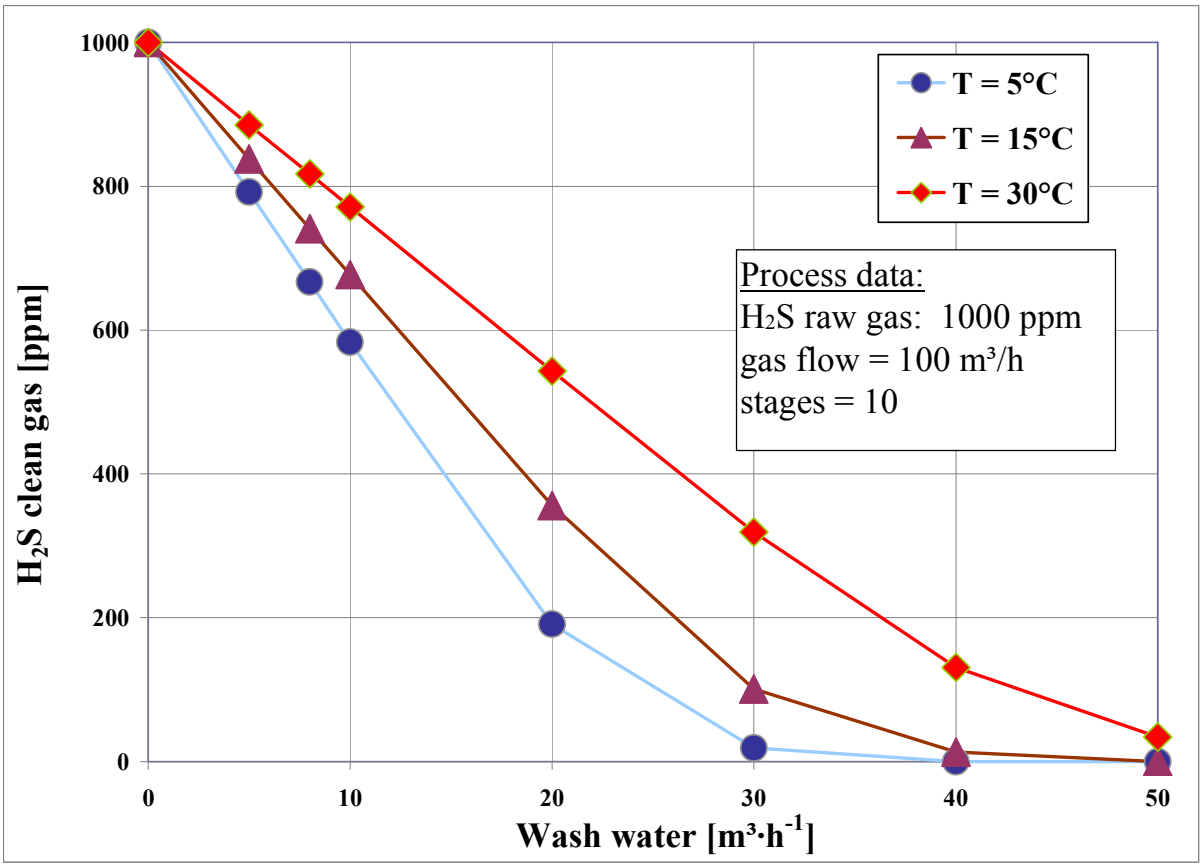

Figure 44: Dependence of temperature on clean gas concentration: Variation of water flow

When simulating the case illustrated in figure 44 with 2 wt-% Humin-P in the washing liquid, the clean gas concentration is lower than 10 ppm for water flows of 5 $m^3 \cdot h^{-1}$. Due to the influence of temperature on absorption with Humin-P-solution, with a 2 wt-% Humin-P-solution zero ppm H_2S in the clean gas is achieved at 30 °C. The significant effect of temperature determined in the laboratory experiments is reflected by the model.

The dependence of H_2S output concentration on the pH of the washing water is, in this simulation, only about 20 ppm in clean gas from low to high pH values of washing water. Simulating a variation of the gas temperature does not show a high influence.

The influence of the number of trays is determined as well and is shown in figure 45. For this simulation, a scrubber with a gas volume flow of 300 $m^3 \cdot h^{-1}$ and a water flow of 50 $m^3 \cdot h^{-1}$ is used. The raw gas concentration of the biogas is 1,000 ppm. When simulating with a 2 wt-% Humin-P-solution as washing water, concentrations of 26 ppm H_2S are obtained in the clean gas after one tray. Figure 45 shows that after 5 stages, the clean gas concentration does not decrease further. Due to the dissociation of H_2S, the washing liquid is saturated with H_2S.

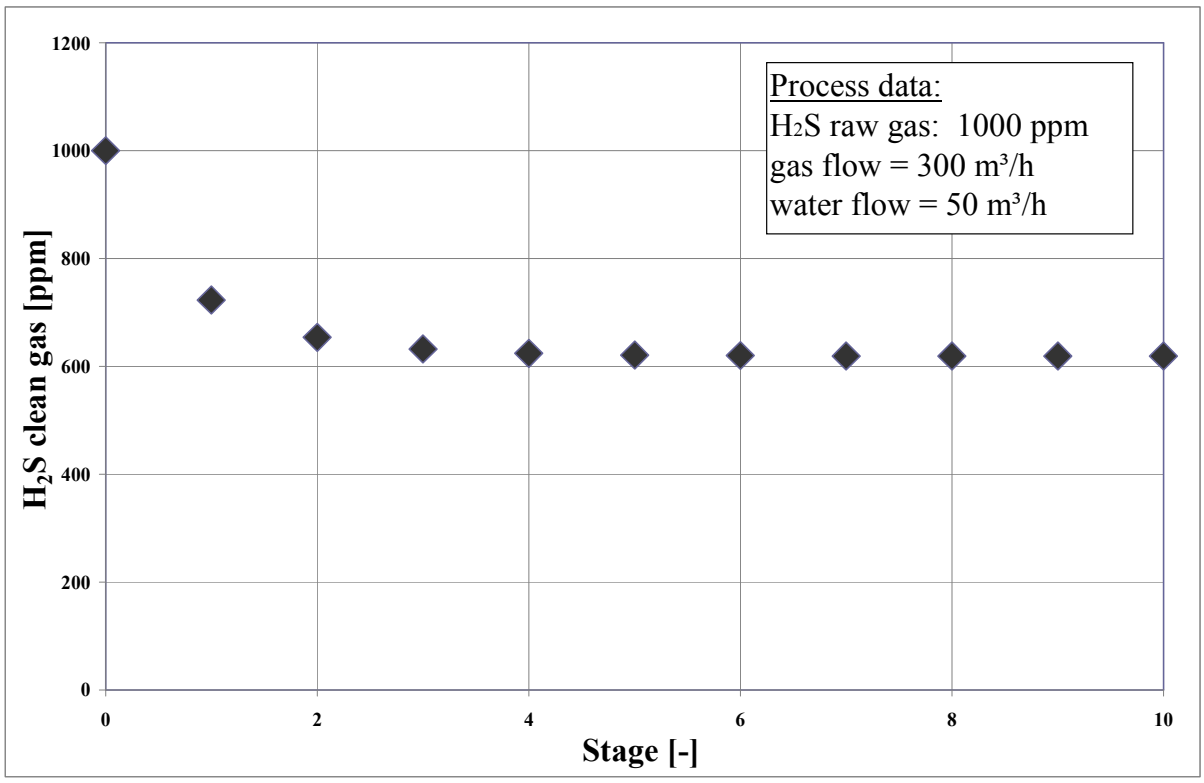

Figure 45: Relationship between trays and clean gas concentration

The variation of gas flow with constant water flow is shown in figure 46; figure 47 shows the variation of water flow with constant gas flow. For the data shown, the concentrations of H_2S in the clean gas with humates in the washing liquid are, in every case, zero ppm.
Figure 46 shows that more water would be necessary to achieve low clean gas concentrations at high gas flows. The water flow should be regulated in a scrubber depending on the clean gas concentration or the gas flow if its concentration is constant. Figure 47 highlights that increasing the wash water flow results in lower clean gas concentrations - a positive consequence.

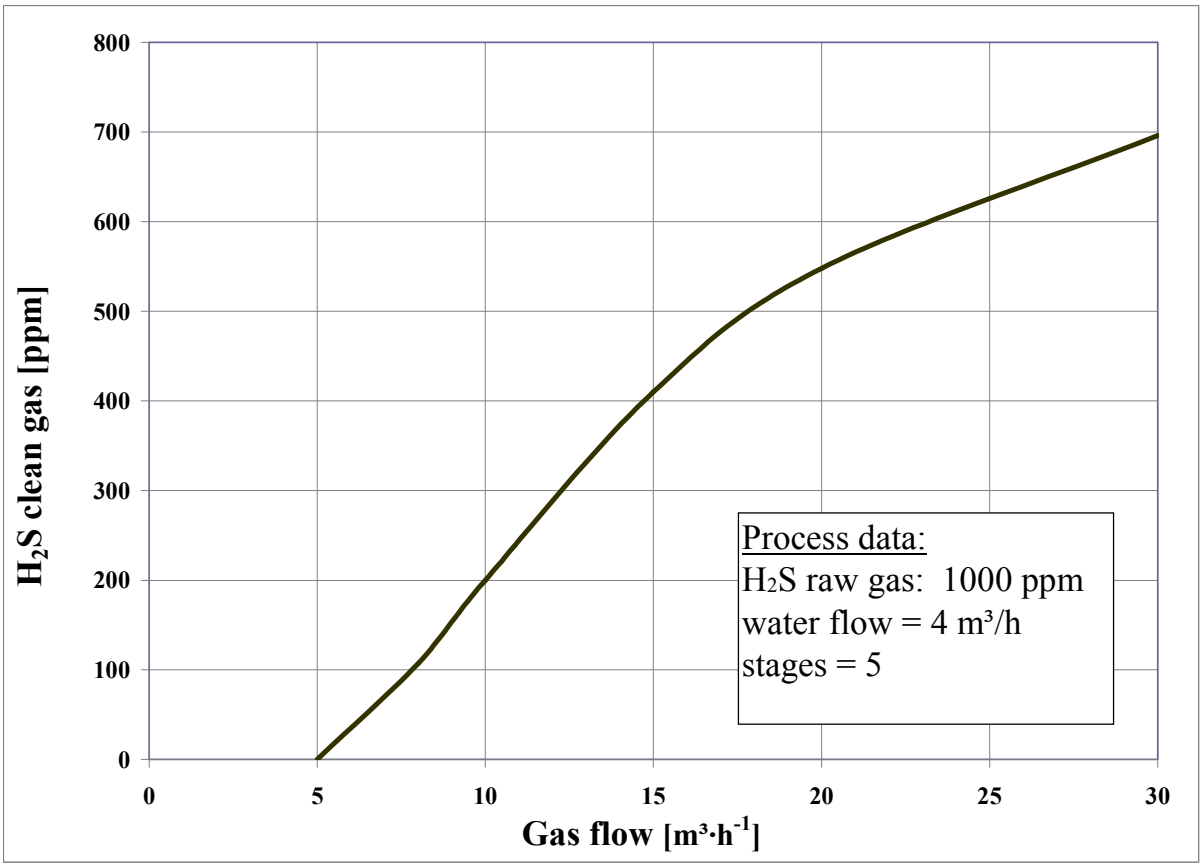

Figure 46: Variation of gas flow

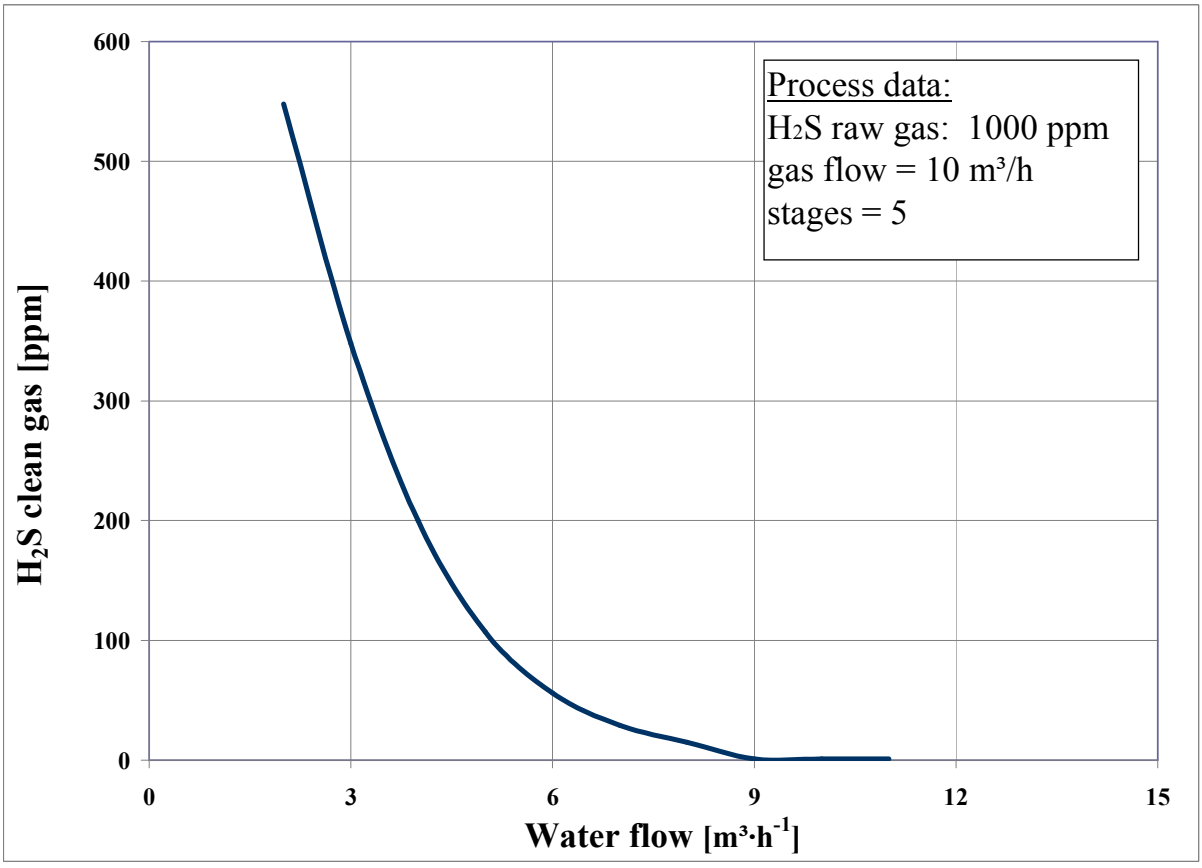

Figure 47: Variation of water flow

Figure 48 shows the H_2S clean gas concentration and its dependence on the raw gas concentration of the system with a gas volume flow of 300 $m^3 \cdot h^{-1}$ and variable water volume flows. Two cases without humates in the wash water (1,000 ppm respectively 2,000 ppm H_2S in the raw gas) and one case with 2 wt-% humates (2,000 ppm) were simulated.

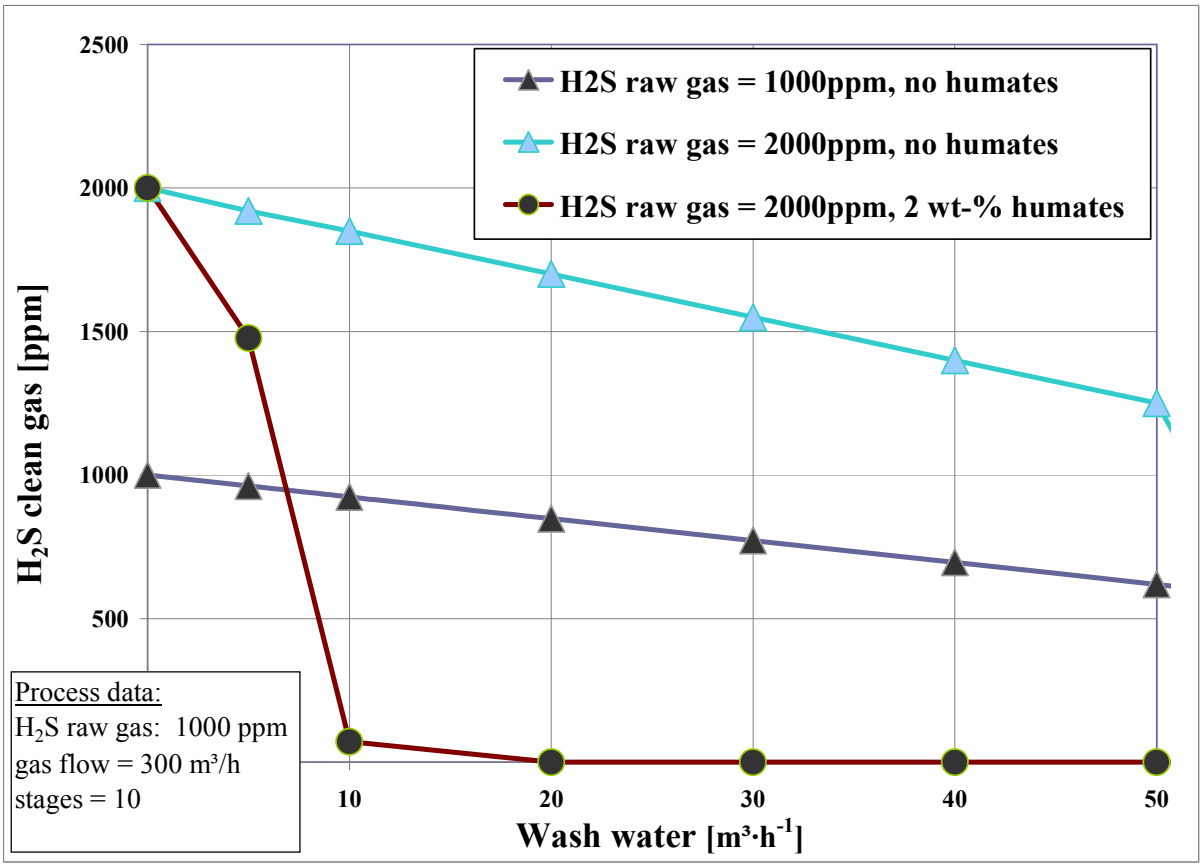

Figure 48: Influence of raw gas concentrations and Humin-P on clean gas concentrations

The influence of humates in wash water is evident. Without humates a much higher amount of wash water is necessary to achieve low clean gas concentrations. With an addition of 2 wt-% humates less than 50 % wash water is necessary.

Figure 49 shows the dependence of clean gas concentration on humate concentration. The input data is the same as above. The model clearly shows the positive effect of Humin-P on improving H_2S removal.

Optimum results are gained with a humate concentration of about 2 - 4 wt-% for a bioscrubber system when factoring in the inhibition by humates on the activity of bacteria (see chapter 7.4). The utilisation of the simulation of the scrubber is described in chapter 9.2.

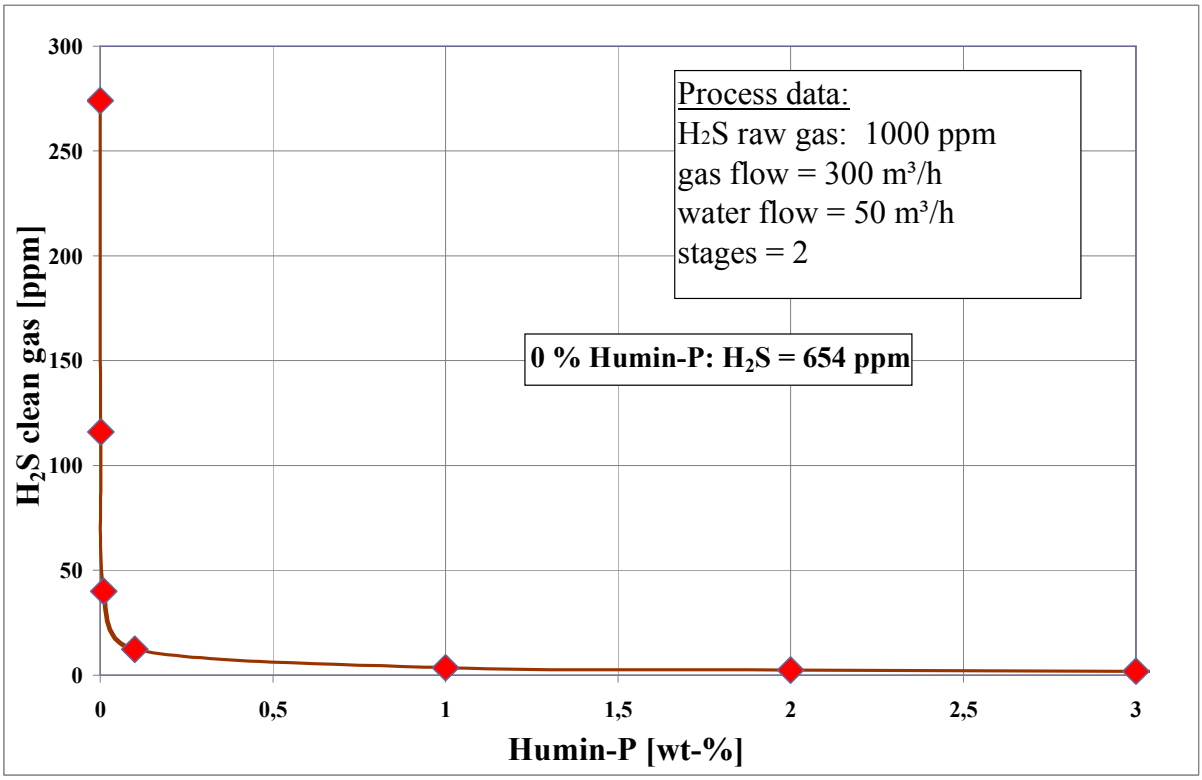

Figure 49: Dependence of humate concentration on clean gas concentration

7.3. Modelling of bioreactor

To model the bioreactor, biological as well as physical and chemical processes are considered. The bioreactor used in this model is a continuous stirred-tank reactor. The proposed kinetic model for aerobic and autotrophic H_2S oxidation is based on the following general assumptions:

- There is thorough mixing
- Microorganisms are distributed homogeneously
- The consumption of substrate obeys Monod kinetics. O_2 can limit degradation. Substrate inhibition is neglected.
- Only elemental sulphur (S) and sulphate (SO_4^{2-}), in accordance with equations 7.16 and 7.17, are products of the H_2S oxidation process
- No other O_2 is consumed other than those related to the H_2S oxidation and respiration of sulphur bacteria
- The system is isobaric and isothermal

The model is valid for temperatures ranging between 15 and 60 °C and for substrate concentrations up to 14 $mg \cdot l^{-1}$. These were the ranges in the laboratory experiments. The kinetic coefficients included in this program are obtained from the experiments with the laboratory bioreactors or from the literature. The model simulates the growth and decay of the bacteria, the aeration of the bioreactor and the dissociation of H_2S. The following two oxidation reactions occur in the bioreactor.

$$H_2S + 0.5 \cdot O_2 \rightarrow S + H_2O \tag{7.16}$$

$$S + H_2O + 1.5 \cdot O_2 \rightarrow SO_4^{2-} + 2 \cdot H^+ \tag{7.17}$$

As Thiobazilli can grow on sulphide and sulphur, two equations for the growth of the Thiobazilli (μ_1 and μ_2) have to be included in the model. The specific growth rate μ_1 for growth on H_2S and μ_2 for growth on S depend on the respective concentration (c_{H2S}, c_S) in the fluid:

$$\mu_1 = \mu_{max\_1} \cdot \frac{c_{H_2S}}{K_{m,H_2S} + c_{H_2S}} \cdot f_i \tag{7.18}$$

$$\mu_2 = \mu_{max\_2} \cdot \frac{c_s}{K_{m,S} + c_s} \cdot f_i \tag{7.19}$$

The bacteria can also grow without H_2S, and then only μ_2 is considered. The maximum growth rate μ_{max} is obtained through the determination of laboratory kinetics and is set to 0.11 h^{-1}. This μ_{max} is assumed to be equal to both μ_{max_2} and μ_{max_1}. The half saturation coefficient K_m is in the range of 10 - 15 $g \cdot m^{-3}$ which was determined in the kinetic experiments (see chapter 5.2.1). The oxidation to S is faster than the oxidation to SO_4^{2-} and therefore $K_{m,S}$ is set to 15 $g \cdot m^{-3}$ and $K_{m,H2S}$ to 10 $g \cdot m^{-3}$. The factor f_i represents all effects by other parameters. The yield coefficient Y is for both growth rates 0.1 $g_{Pr} \cdot g_S^{-1}$.

The influence of temperature and pH value is not considered in this model, because it is assumed that the optimum conditions are adjusted in the bioreactor. A possible way to take into account temperature or pH dependency is described in A2 in the annex. In this model the data obtained from the laboratory experiments are not sufficient for inclusion in the model aside from the fact that it is not required for the questions that the model is intended to answer.

The effect of O_2 concentration f_{O2} has to be taken into account in the growth kinetics. The following formula has to be included.

$$f_{O_2} = \frac{c_{O2}}{K_{O_2} + c_{O2}} \tag{7.20}$$

The O_2 constant K_{O2_1} for the growth on sulphide is 0.9 $g \cdot m^{-3}$ [49]. For the growth on sulphur this value is set lower to take into account the positive influence of O_2.

The rate of decay of bacteria is determined according to activated sludge model No. 1 [84]. The decay coefficient b_s was determined to be 0.08 d^{-1}. The process rate of decay of bacteria φ_{decay} is described in equation 7.21.

$$\varphi_{decay} = b \cdot c_B \tag{7.21}$$

The air supply of the gas phase into the liquid phase is described according to film-theory. The gas liquid mass transfer coefficient for oxygen k_La_{O2} can be calculated in accordance to the aeration system. Examples of such relationships are given by Wagner [80] and van't Riet [81]. According to Gonzalez-Sanchez [49], k_La_{O2} is set in this model to 200 d^{-1}. When modelling the bioreactor of the laboratory experiments, the correlation for k_La described in equation 5.3 is used for the process rate φ_{O2}.

$$\varphi_{O2} = k_L a_{O_2} \cdot \left(c^*_{O2} - c_{O2}\right) \tag{7.22}$$

The dissolved O_2 concentration in equilibrium c_{O2}^* (in $g \cdot m^{-3}$) under atmospheric conditions is mainly dependent on temperature (T in °C) and is calculated as follows [80]:

$$c^*_{O2} = \frac{2234.34}{(T + 45.93)^{1.31403}} \tag{7.23}$$

Dissociation reactions (equations 7.7-7.8) also occur in the bioreactor and have to be considered in the model. In addition, the dissociation of water (H_2O) has to be considered when varying the pH.

$$H_2O \overset{K_3}{\Leftrightarrow} OH^- + H^+ \tag{7.24}$$

The equilibrium constant K_3 based on the temperature T is defined in equation 7.9 with the following coefficients [77]:

A = 140.932; B = 0; C = -13445.9; D = -22.4773

When operating a continuous stirred-tank reactor, steady state is reached in a specific period of time after starting. When reaching the steady state, all concentrations stay constant.

The mass balance for each component is simplified as follows. In equation 7.25, c refers to concentration, t to time, F to flow, V to volume and φ to process rate.

$$\frac{dc_i}{dt} \equiv 0 = \frac{F}{V} \cdot \left(c_{i,in} - c_{i,out}\right) + \varphi_i \tag{7.25}$$

In the model, the complete differential equation is used, because the time to reach steady state is also calculated.

An overview of all the coefficients is demonstrated in table 18. The matrix of all reactions in the bioreactor is shown in table 19. The following input parameters can be varied:

Continuous bioreactor

- Volume flow F
- Concentrations c_i of the liquid entering the bioreactor (SO_4^{2-}, S, H_2S, HS^-,S^{2-}, O_2, H^+)
- Initial biomass c_B in the bioreactor
- Volume of the bioreactor V

Batch bioreactor

- Initial concentrations c_i in the bioreactor (SO_4^{2-}, S, H_2S, HS^-,S^{2-}, O_2, H^+)
- Initial biomass c_B in the bioreactor
- Air flow Q and stirrer rotation n for determining k_La for laboratory bioreactor

Table 18: Overview of constants used in the model of the bioreactor

b	0.0033 h^{-1}
k_La	200 d^{-1}
k_{H2S}	10^{10}
k_{HS}	10^{10}
k_{H2O}	10^{15}
$K_{O2,1}$	0.9 $mg \cdot l^{-1}$
$K_{O2,2}$	0.7 $mg \cdot l^{-1}$
$K_{m,S}$	15 $mg \cdot l^{-1}$
$K_{m,H2S}$	10 $mg \cdot l^{-1}$
m	3.8
p	1 bar
pH	6.5
T	303 K
Y_1	0.1 $g_{Pr} \cdot g_S^{-1}$
Y_2	0.1 $g_{Pr} \cdot g_S^{-1}$
μ_{max}	0.11 h^{-1}

Table 19: Matrix of reactions in bioreactor

Process	**B**	**O_2**	**S**	**SO_4^{2-}**	**H_2S**	**HS^-**	**S^{2-}**	**OH^-**	**H^+**	**Process rate φ**
Growth 1 Oxidation H_2S	+1	$-\frac{0.5}{Y_1}$	$+\frac{1}{Y_1}$	-	$-\frac{1}{Y_1}$	-	-	-	-	$\varphi_1 = \mu_1 \cdot c_B \cdot f_{O2}$
Growth 2 Oxidation S	+1	$-\frac{1.5}{Y_2}$	$-\frac{1}{Y_2}$	$+\frac{1}{Y_2}$	-	-	-	-	$+\frac{2}{32 \cdot Y_2}$	$\varphi_2 = \mu_2 \cdot c_B \cdot f_{O2}$
Decay	-1	-	-	-	-	-	-	-	-	$\varphi_4 = b \cdot c_B$
Aeration	-	+1	-	-	-	-	-	-	-	$\varphi_3 = k_L a_{O2} \cdot \left(c^*_{O2} - c_{O2}\right)$
Dissociation H_2S	-	-	-	-	-1	+1	-	-	$+\frac{1}{32}$	$\varphi_5 = k_{H2S}\left(K_1 \cdot c_{H2S} - c_{HS^-} \cdot c_{H^+}\right)$
Dissociation HS^-	-	-	-	-	-	-1	+1	-	$+\frac{1}{32}$	$\varphi_6 = k_{HS^-} \cdot \left(K_2 \cdot c_{HS^-} - c_{S^{2-}} \cdot c_{H^+}\right)$
Dissociation H_2O	-	-	-	-	-	-	-	+1	+1	$\varphi_7 = k_{H2O}\left(K_3 - c_{OH^-} \cdot c_{H^+}\right)$
Unit	$g_{COD} \cdot m^{-3}$		$g_S \cdot m^{-3}$					$mol \cdot m^{-3}$		

7.3.1. Reactions with Humin-P

As analysed in chapter 5.2.3, humates have an inhibitive effect on the activity of sulphur bacteria. Although no inhibition was observed in the long-term fed-batch experiments, an inhibitive effect of humates, especially at high humates concentrations, is probable. This effect has to be included in the model and is described as follows. The effect f_{HP} on the growth of the bacteria has to be considered in the equations of the specific growth rates (eq. 7.18 and 7.19).

$$f_{HP} = \frac{K_I}{K_I + c_{HP}^m} \tag{7.26}$$

The inhibition constant K_I and the exponential factor n were determined using laboratory experiments on respiratory activity and the batch experiments. It is assumed that inhibition of the activity of bacteria is similar to the inhibition on growth and sulphur production. Using parameter estimation in AQUASIM, K_I and m are estimated to be 69.4 and 3.8 respectively (see chapter 5.2.3). The concentration of Humin-P c_{HP} can be varied. The model is valid for Humin-P concentrations of 0 to 10 $g \cdot l^{-1}$.

The buffer capacity of humates is not considered in this model because it is not relevant to the modelling objectives. When the carbonate buffer of humates is included, the stripping of CO_2 and the dissociation of carbonic acid (H_2CO_3) have to be included as well. The procedure for this inclusion is described in annex A3.
The flow scheme of the continuous stirred bioreactor in Dymola is shown in figure 50. It consists of the bioreactor, the reservoirs of humates, effluent and inflow as well as aeration and off gas. The individual models of the equipment components are combined, using connectors, with the bioreactor model.

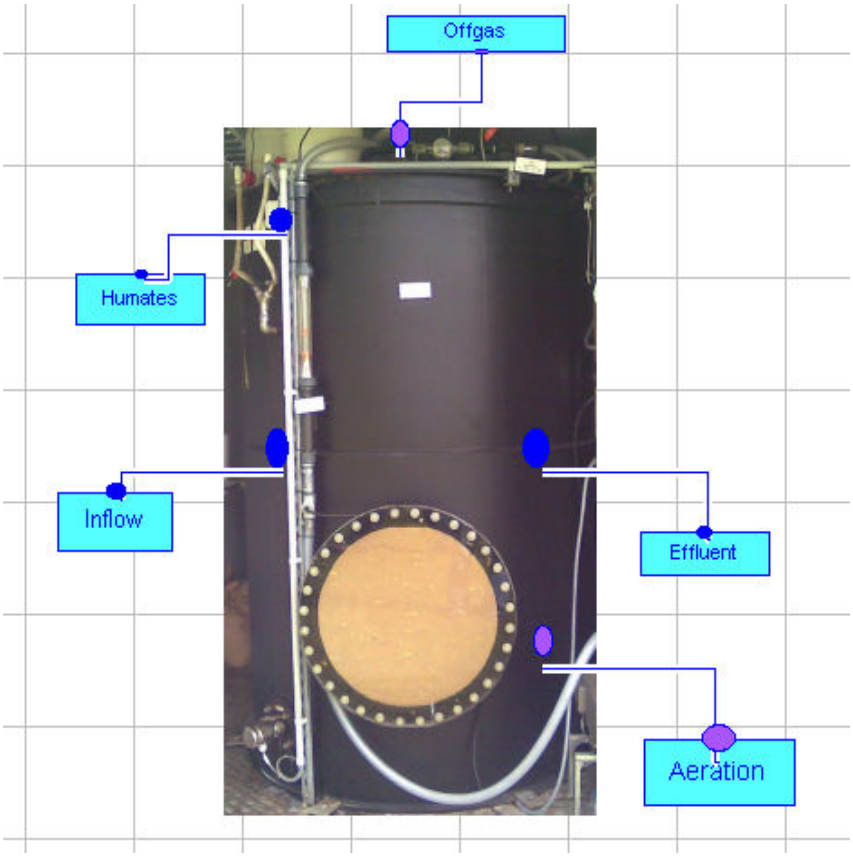

Figure 50: Scheme of bioreactor in Dymola

7.4. Simulation of bioreactor

The data for the coefficients used in the model of the bioreactor are obtained from the simple batch experiments (see chapter 5.2.1). The model is validated by comparing the results obtained from the long-term batch bioreactor experiments with the results obtained from the simulation.
The application of Aspen Plus to model microbiological H_2S oxidation is not recommended because the kinetics of the bacterial processes cannot be described sufficiently. Aspen Plus is not designed for microbiological processes. When using kinetic models such as POWERLAW or LHHW (Langmuir-Hinshelwood-Hougen-Watson), they refer to a reaction rate based model but they do not consider the effects of temperature or O_2 on the activity of the bacteria. A comparison of this model with the program AQUASIM is conducted. The results of this simulation and the simulation in Dymola are similar.
Figure 51 shows the results of the biomass concentration from the simulation in comparison with the data from one laboratory experiment. The biomass was measured in the laboratory experiments as proteins (see chapter 5.1.2) and so the biomass from the simulation is also represented by proteins. Furthermore, the concentrations of SO_4^{2-} and elemental S are displayed. On average, the data from the simulation reflect the data from the laboratory experiments and therefore the model of the bioreactor is deemed to be valid.

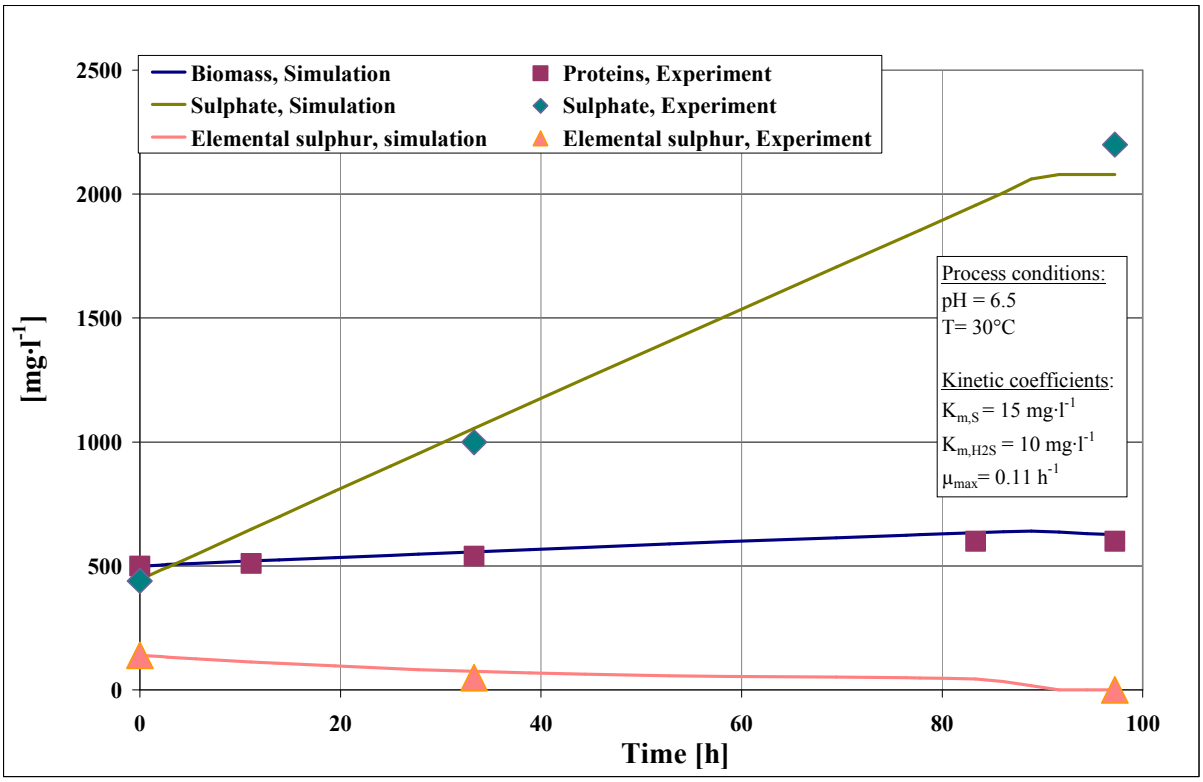

Figure 51: Comparison of results from the simulation with the long-term batch bioreactor experiments

Figure 52 compares the biomass concentration from the simulation with the results from one long-term batch bioreactor experiment with 2 wt-% Humin-P. Elemental S and SO_4^{2-} were only measured at the beginning and at the end of the experiments. These values can be represented by results from simulation.

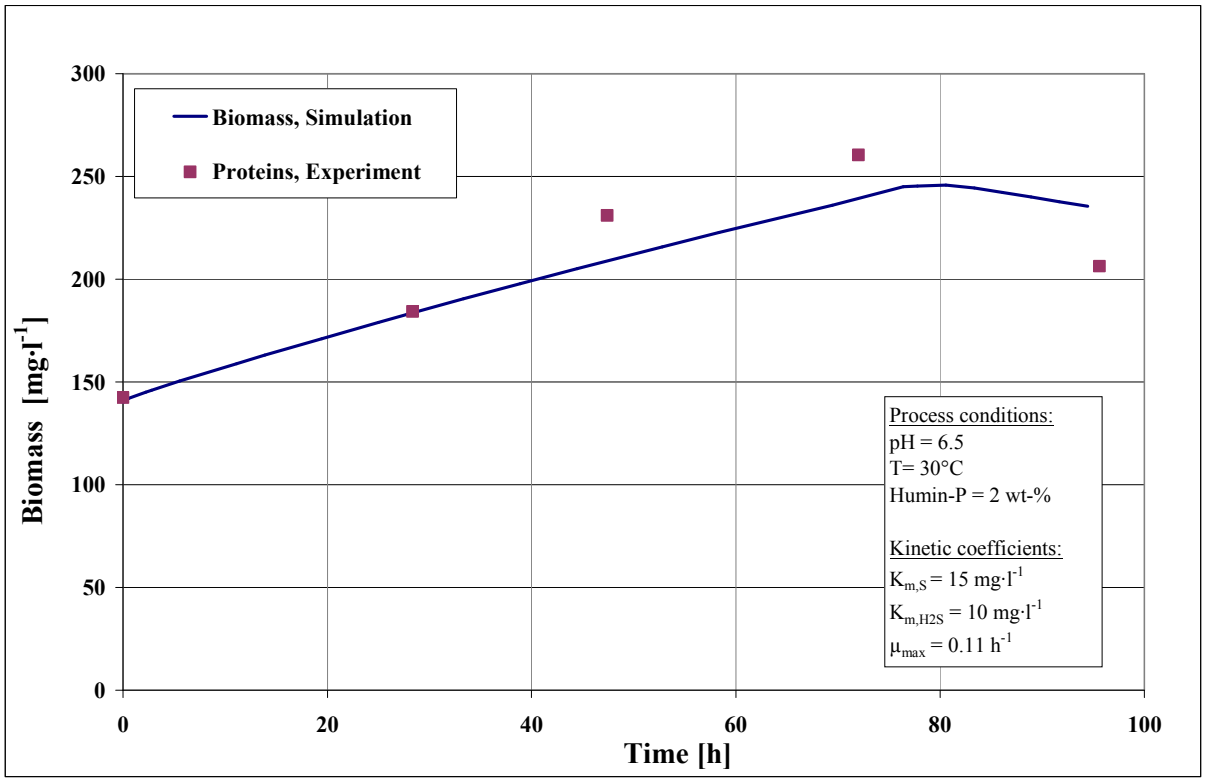

Figure 52: Comparison of results from the simulation with the long-term batch bioreactor experiments (2 wt-% Humin-P)

Figure 53 shows the dependence of biomass on Humin-P concentrations in the bioreactor based on the simulation. It is clear that the bacteria die in the presence of high concentration of humates. This was analysed in the laboratory experiments as well. Optimum Humin-P concentration are between 1 and 3 wt-%, an increase up to 5 wt-% Humin-P did not have significant negative impacts on the activity of the sulphur bacteria.

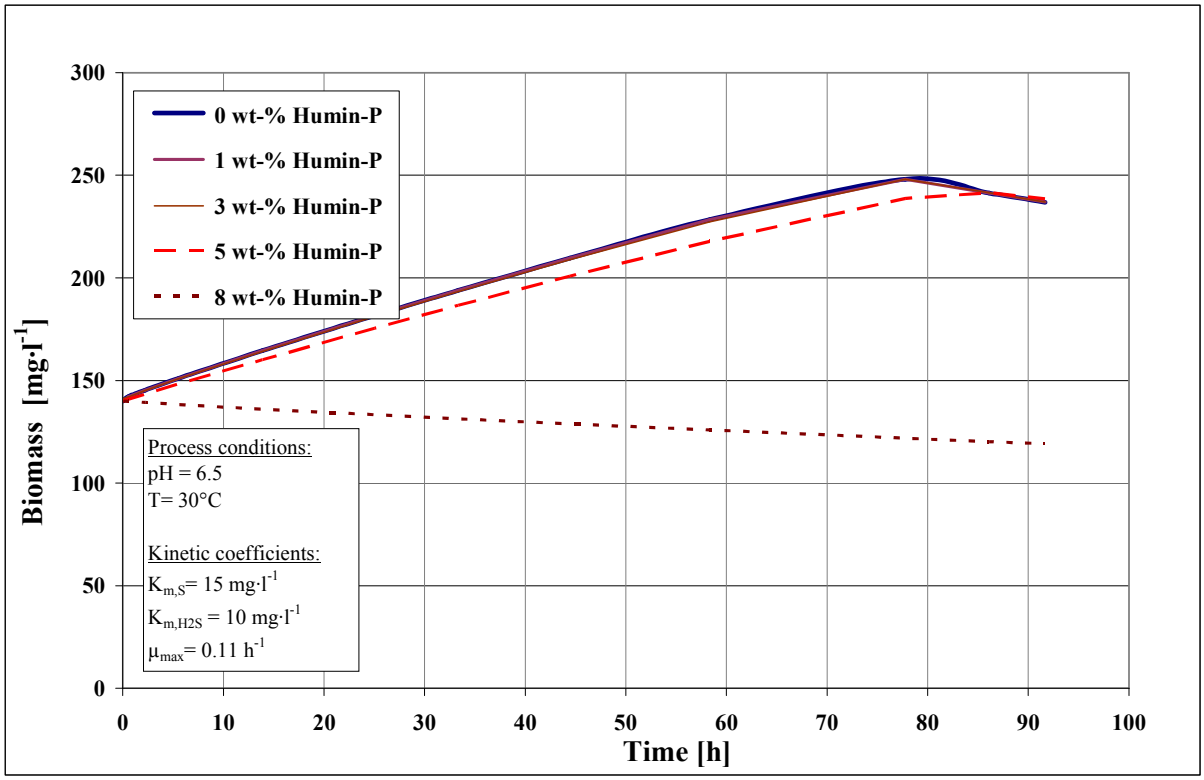

Figure 53: Simulation of the change in biomass in the batch bioreactor with different concentrations of Humin-P

The modelling of microbiological processes with Modelica is feasible and the obtained simulation results fits with the experimental results. Aside from the simulation of batch bioreactors, different scenarios in a continuous bioreactor, for example a continuous stirred tank reactor (see figure 50), can also be simulated.

7.5. Modelling of the bio-scrubber system

To model the bio-scrubber system the scrubber is combined with the bioreactor. The flow diagram of the model is shown in figure 54. The proposed kinetic model for the bio-scrubber system is based on the general assumptions described in chapter 7.1 and 7.3 which simplify the process.
The oxidation of sulphur compounds to elemental sulphur is mostly controlled by air injection into the bioreactor [82]. Therefore, O_2 concentration is controlled in this model by sulphide concentration and is calculated with an optimum stoichiometric oxygen sulphide relation λ of 2 (see chapter 3.4.2, equation 3.12). The pH range has to be kept constant, because each significant change in pH leads to a decrease of H_2S degradation in the bioreactor [39]. The pH is set to an optimum value of 7. In addition, temperature is regulated at 30 °C which is the optimum temperature for sulphur bacteria.
Figure 54 shows the scheme of the bio-scrubber system in Dymola. The inflow of gas into the scrubber comes from a fermenter where the biogas is produced. After the removal of H_2S the clean biogas goes into a combined heat and power plant (CHP). The washing water flows in a circuit through the scrubber and bioreactor. After the bioreactor a divider is included in the model which separates a part of the elemental sulphur formed from the washing liquid as well as some other ingredients. In order to replace the effluent with fresh water a water supply is also included in the model. The water inflow is mixed with the water from the scrubber. Aeration ensures the air supply in the bioreactor. Two unit converters are added in the model to connect different units of bioreactor and scrubber. Humates are added in the bioreactor as well as NaOH to maintain a constant pH value. It is assumed that the flows of these streams do not change the input feed stream into the bioreactor. Therefore, they do not influence other concentrations in the bioreactor.
The individual models of the equipment components are combined using connectors with the scrubber and the bioreactor or other equipment components.

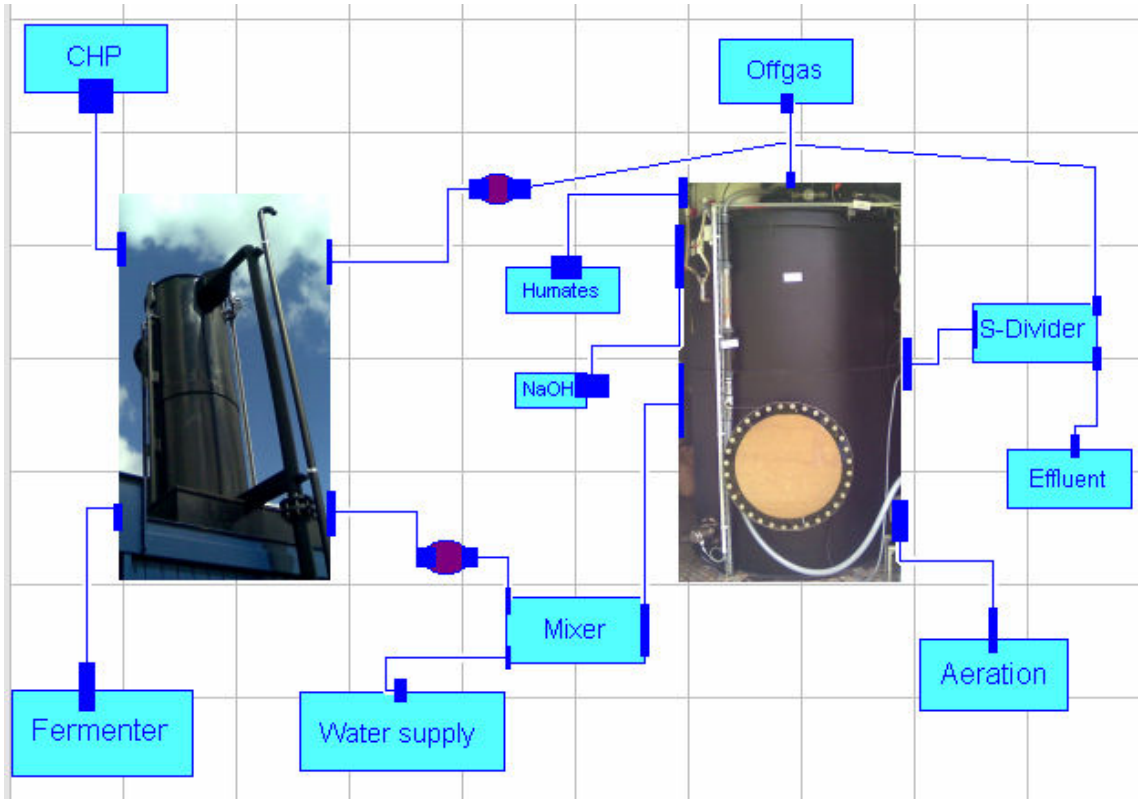

Figure 54: Scheme of bio-scrubber system in Dymola

In the model it is assumed that all other concentrations of the wash water stream coming from the bioreactor do not influence the process in the scrubber. Therefore, biomass, O_2, S and SO_4^{2-} are inert and bypass the scrubber. The water supply is controlled via the effluent leaving the system, so that that the wash water stream is always constant. The reflux ratio of the divider is set to 0.99. A higher reflux ratio leads to higher biomass in the bioreactor because the components stay longer in the system. If the reflux ratio is too small, the bacteria would be washed out because the retention time is too short for the growth of the bacteria. Simulation of the system showed that at higher reflux ratios the clean gas concentration is also lower.
At the divider it is assumed that 50 % of elemental sulphur is separated. Furthermore, 20 % of SO_4^{2-} and 10 % of Humin-P are separated. No experiments concerning the separation of elemental sulphur are conducted, so that the validated data is missing for this part of the simulation.
A pH regulation is inserted in the model. Due to a supply of NaOH, the pH is maintained at a value of 7. Equation 7.27 describes this regulation in the model. In this equation F_{NaOH} is the volume flow of the input stream of NaOH and $c_{OH,NaOH}$ its concentration of NaOH. The concentration of H^+ of the wash water stream coming from the scrubber and entering the bioreactor is $c_{H+,in}$. The reaction rate of H^+ in the bioreactor is based on the matrix of reactions in the bioreactor (see table 19) and is abbreviated as r_{H+}. V is the volume of the bioreactor.

$$0 = \frac{F_{NaOH}}{V} \cdot \left(c_{H^+,in} + c_{OH,NaOH}\right) + r_{H^+} \tag{7.27}$$

When adding the potassium humate Humin-P into the bio-scrubber system the additional reactions described in chapter 7.1.4 and 7.3.1 have to be considered. It is assumed that sulphur bacteria have access to all sulphide bound to humates.
In addition, the Thiobazilli regenerate the loaded humates by using the bound H_2S as a substrate. The humate concentration c_{HP_avail} which is available for the absorption of H_2S in the column is an input variable and is adjustable in the bioreactor model. Therefore, the addition of Humin-P is regulated in the bioreactor whereas the target concentration of Humin-P is adjustable. Both the consumed (c_{HP_cons}) and the remaining available humates enter the bioreactor and hinder the growth of Thiobazilli as described in chapter 7.2.1. The following equation is included in the bioreactor model.

$$c_{HP} = c_{HP,avail} + c_{HP,cons} \tag{7.28}$$

In the bioreactor the consumed humates are regenerated by the bacteria. The regeneration factor R is dependent on bacteria activity and their concentration. The possibility of repeated utilisation of consumed Humin-P is considered as well. In this model regeneration is assumed to be 80 %.

$$R = 0.8 \tag{7.29}$$

Detailed information to describe regeneration is missing. Long-term experiments are necessary to gain a satisfactory value and to describe the reaction of sulphur and humates with greater precision. With this simple inclusion of regeneration, the model can be used for simple calculations. The regeneration factor might be dependent on certain parameters which have to be identified in future experiments.
To achieve the target concentration of Humin-P, mass balances of Humin-P are set in the model in order to calculate the amount of Humin-P which has to be added in the bioreactor.

Equations 7.30 and 7.31 show these balances for the available (c_{HP_avail}) and the consumed humates (c_{HP_cons}). In these equations F is the wash water flow entering and respectively leaving the bioreactor and H the flow coming from the humates reservoir.

$$F_{out} \cdot c_{HP\_avail} = F_{in} \cdot (c_{In,HP\_avail} + c_{In,HP\_cons} \cdot R) + H \cdot c_{H,HP\_avail} \quad (7.30)$$

$$F_{out} \cdot c_{HP\_cons} = F_{In} \cdot (c_{In,HP\_cons} - c_{In,HP\_cons} \cdot R) \quad (7.31)$$

No data are available to validate the model because such a bio-scrubber system was not operated. The pilot plant (see chapter 9.1) was not in operation long enough so the bacteria could not adapt to their reactor and process conditions (see 7.2). This chapter showed how a model of such a bio-scrubber system can be built but experimental data are missing for a validation. A validation is necessary because no reliable data for the regeneration are present. The regeneration should be specified in more detail so that this can be modelled correctly. If all the parameters are available, simulations with the model can be conducted. Without this information and without a validation of the model, simulations are not recommendable.

Table 20 shows the process parameters of the bio-scrubber system with humates.

Table 20: Overview of constants used in the model of the bio-scrubber system

B	0.0033 h^{-1}
H_{ref}	$560 \cdot 10^5$ bar
k_La	200 d^{-1}
k_{H2S}	10^{10}
k_{HS}	10^{10}
k_{H2O}	10^{15}
K_I	69.4 $mg \cdot l^{-1}$
$K_{O2,1}$	0.9 $mg \cdot l^{-1}$
$K_{O2,2}$	0.7 $mg \cdot l^{-1}$
K_{HP}	$8{,}52 \cdot 10^{-7}$ $g \cdot l^{-1}$
$K_{m,S}$	15 $mg \cdot l^{-1}$
$K_{m,H2S}$	10 $mg \cdot l^{-1}$
M	3.8
N	0.2765
P	1 bar
pH	7
R	0.8
Reflux ratio	0.99
Separation of Humin-P	0.1
Separation of S	0.5
Separation of SO_4^{2-}	0.2
T_{ref}	298 K
T	303 K
x_{CH4}	0.65
x_{CO2}	0.35
Y_1	0.1 $g_{Pr} \cdot g_S^{-1}$
Y_2	0.1 $g_{Pr} \cdot g_S^{-1}$
α	0.004043
Δh_{sol}	17459 $J \cdot mol^{-1}$
Δh_{r1}	22200 $J \cdot mol^{-1}$
Δh_{r2}	-15500 $J \cdot mol^{-1}$
μ_{max}	0.11 h^{-1}

8. Evaluation of costs

Costs are typically divided into investment and operating costs. Investment costs are incurred during the construction of a plant and operating costs are incurred while operating the plant. Table 21 gives an overview of investment and operating costs. Maintenance costs were not examined.

Table 21: Overview of investment and operating cost [81]

Investment cost			**Operating cost**		
Cost of constructing a plant	Cost of implementation	Cost of purchasing work capital	General and administrative cost	Production cost	
				Indirect	Direct

8.1. Evaluation of investment costs

Investment costs comprise different components. Table 22 gives an overview of these components and their share of total investment costs. These data were combined and calculated from information given by Peters [83] and Hertel [84].

Table 22: Overview of investment costs

Component	Percentage
Individual components (e.g. bioreactor and scrubber)	17 %
Electrical systems and control	8 %
Aggregates and fittings	10 %
Piping and installation	17 %
Measuring technique (with explosion protection)	8 %
Service facilities	5 %
Engineering, supervision and commissioning	35 %

The percentage of service facilities costs increases when building the complete plant in a separate container which is not integrated to the biogas plant.
In general, the investment costs of a humate containing bio-scrubber system are similar to other bio-scrubber systems e.g. the Thiopaq process. For the humate containing bio-scrubber system additional investment costs for equipment to store and dose the humates are necessary. Because of the high absorption efficiency of a humate solution, scrubbers can be built smaller because fewer theoretical stages in the column are required.

Table 23 shows the investment costs required to install the humate containing bio-scrubber system based on data for the Thiopaq process (Gas flow: 500 $m^3 \cdot h^{-1}$) [85]. Costs such as engineering and supervision are not listed. The data for humates are obtained by the simulation.

The initial Humin-P concentration for high absorption capacity but only slight inhibition of bacterial activity is 2 wt-%. The volume of the bioreactor for such a plant is about 36 m³ (see 9.2.3). The initial Humin-P addition can be calculated and is about 710 kg.

Table 23: Investment costs for humate-process [85]

Component	Costs [€]
Bio-scrubber system	132 000
Compressor for air supply	4 000
Storage and dosing equipment	
• NaOH and nutrients	1 000
• Humates and Defoamer	1 000
Initial Humin-P addition	2 800
Insulation and frost protection	12 000
Transport and installation	10 000
Sum	**162 800**

8.2. Evaluation of operating costs

The main operating costs to be calculated are the costs for feedstock components and operating material. They are the result of mass balances in the process. The specific costs for the different operating material, and heat and electricity, have to be obtained from the suppliers. Personnel costs as well as general and administrative costs are equal to other desulphurisation plants and are therefore neglected. Most of the operating costs are equal to the operating costs in the Thiopaq process. With data provided by Ramesohl [85] the operating costs of the humates containing bio-scrubber system were determined.
The cost of Humin-P range between 3.6 €·kg^{-1} and 4.8 €·kg^{-1} depending upon the quantity required [86]. In comparison, the cost of the product Sulfa-Clear is about 2.5 €·kg^{-1}, including all local handling costs and duties [87].
Costs for the defoamer are not listed for the Thiopaq process. As the humates cause foam formation their costs are estimated. Furthermore, the amount of NaOH required is lower due to the buffer capacity. The costs are estimated by considering the costs for the Thiopaq-process.
The operating costs for the process are tabulated in table 24. These data are also based on a Thiopaq process with a volume flow of 500 m^3·h^{-1}[85]. The addition of humates for one year is estimated by simulating a similar plant and the costs are calculated with a price of humates at 4 €·kg^{-1}.

Table 24: Operating costs for humate-process

Component	Costs [€·a^{-1}]
Addition of NaOH	400
Addition of nutrients	750
Addition of humates	720
Addition of defoamer	200
Energy demand	4800
Process Water	1 200
Sum	**8 070**

The by-product elemental sulphur can be sold. In 2010 the prices of sulphur varied between 0.2 and 0.6 €·kg^{-1}. The use of this by-product as agricultural fertiliser would be another option, which is commonly practiced (chapter 6.1). According to Hansa Landhandel [88], the average price of sulphur fertiliser (including N and S) is 0.35 €·kg^{-1}. According to experiments carried out by Schneider [39] and Tomàs [89] the conversion of sulphide to elemental sulphur can be estimated to be an average of 70 %.

The value of sulphur yield determined is in the range of sulphur yield in the Thiopaq process (50 - 600 kg·d^{-1})[90]. A sulphur mass flow of 100 kg·h^{-1} is assumed to be definitely possible for a bio-scrubber system with humates. Therefore, revenues of about 7,000 €·a^{-1} are possible.

8.3. Comparison of costs with other processes

Table 25 gives an overview of the investment and operating costs for a single-stage bioscrubber, a double-stage bio-scrubber system according to Thiopaq and the system containing Humin-P. All costs are based on a biogas plant with gas flows of 500 $m^3 \cdot h^{-1}$. This gas flow rate is chosen because the literature has the most data available for plants with this flow rate.

Table 25: Cost comparison of external biological processes

Costs	Bioscrubber [96]	Thiopaq process [96]	Humate Process
Capital investment [€]	100 000	159 000	162 800
Operating costs [€·a^{-1}]	25 000	8 000	8 070

From table 25 it is clear that, from an economic point of view, the humate process is as efficient as the Thiopaq process.
In comparison to the internal desulphurisation process, external biological processes are much more expensive. Analysis of the Thiopaq process, done by Fraunhofer Institut Umsicht [11], showed that for biogas plants with H_2S concentrations of about 2,000 ppm and gas flows of 200 $m^3 \cdot h^{-1}$, the Thiopaq process was cheaper than dosing iron hydroxide. At lower H_2S concentrations (500 ppm), gas flows three times higher than stated above are necessary to achieve lower costs compared to the Thiopaq process. [11]
A cost comparison between the bioscrubber and internal chemical desulphurisation with ferric chloride ($FeCl_3$) carried out by Tomàs [89] indicated that biological treatment resulted in significant savings over the chemical process. These savings are due to the reduced use of chemicals. In table 26, the investment and operating costs of the different desulphurisation processes are summarised.

Table 26: Cost comparisons of other biogas desulphurisation processes for [85,91]

Treatment	Process	Investment costs [€]	Operating costs [€·a^{-1}]
Biological	Internal desulphurisation	~ 1 000	Negligible
	Single-stage bioscrubber	80 000 - 100 000	12 000
	Double-stage bio-scrubber system	~ 160 000	~ 8 000
Chemical	Iron containing purification compounds (intern)	10 000 - 15 000	2 000 - 30 000
	Column with iron hydroxide	~ 100 000	~ 1 200
Physical	Activated carbon filter	10 000 - 50 000	4 500 - 26 000

Investment and operating costs of other industrial physical and chemical desulphurisation processes are much higher than costs of the humate containing bio-scrubber system (see chapter 9.3).
In particular, compared to chemical processes, the humate system has the advantage that no waste is produced, so there are no costs for waste removal.

9. Application in practice

The application of a humate containing bio-scrubber system in desulphurisation is evaluated in this chapter. Different case studies were conducted to determine the scope of application. Its application in optimising existing biogas plants, in new biogas plants, and in preliminary treatment for the production of biomethane is analysed. These case studies are based on calculations and simulations using the model developed in chapter 7.1 as well as the cost evaluation performed in chapter 8. Experiences from a pilot plant are briefly described and their results were considered in the different case studies.
In addition, the application of the humate containing bio-scrubber system was analysed in other fields of application, for example in the removal of sulphur dioxide (SO_2). The evaluation in this chapter is based on literature research.

9.1. Experiences at pilot plant

This chapter describes the experiences during the operation of a double-stage bio-scrubber pilot plant. The results of the laboratory experiments were compared to the results from the pilot plant. Due to a high number of problems and malfunctions no long-term results could be obtained. Therefore the experiences were compared to the experiences described in literature to provide suggestions for the application of this process in practice. The pilot plant was built at the biogas power station site of the biogas plant in Albersdorf (see chapter 9.2.1). It contained a 2 m³ scrubber and a 3 m³ bioreactor according to the schematic flow diagram shown in figure 1. A complete flow diagram from the builder of the pilot plant, TIG Wessel Umwelttechnik GmbH, is shown in figure A1 in the annex. Figure 55 shows a photo of the pilot plant. The dimensions and design of the pilot plant, completed by Wessel Umwelttechnik, are described in annex A4.

Figure 55: Pilot plant in Albersdorf

The quality of the biogas was measured using different methods. The biogas was measured on-site using the following measuring devices. Raw and clean biogas were analysed regularly.

- Multi-channel measuring unit SSM 6000 (Pronova Analysentechnik GmbH & Co. KG)
- Multi-gas measuring device SR2-DO (Sewerin GmbH)
- Methane sensor BCP-CH_4 (Blue sens gas sensor GmbH)

In addition to these analyses, samples of biogas were taken and analysed in the laboratory using the following methods:

- Electro-chemical H_2S Data Logger OdaLog (App-Tek International Pty Ltd)
- Test-tubes (Dräger Safety AG & Co. KGaA)
- Gas chromatography
- Mass spectrometry

The liquid samples, which were taken from the scrubber and the bioreactor, were measured analogously to the samples of the laboratory bioreactor. Additionally, the pilot plant includes continuous and automatic recording of measurements for pH, temperature and O_2 concentration. Figure A24 in the annex shows a screen shot of this recording.

The addition of Humin-P into the bioreactor of the pilot plant started in spring 2010. The washing liquid contained 0.7 % Humin-P. Clean gas concentrations of 40 ppm were achieved. An overview of the operational parameters of the pilot plant during this time is shown in table 27. Unfortunately, the operation stopped in May 2010 because the space was required by the biogas plant Albersdorf. A long-term test of an operation with humates could not be carried out.

Table 27: Parameters during test operation with humates in spring 2010

Parameter	Value
Gas flow	10.6 $m^3 \cdot h^{-1}$
Water flow	4 $m^3 \cdot h^{-1}$
H_2S raw gas	1 100 ppm
H_2S clean gas	40 ppm
Temperature	20 °C
O_2 concentration	3.5 $mg \cdot l^{-1}$
pH value	6.5

The average O_2 concentration was, as shown in table 27, 3.5 $mg \cdot l^{-1}$. This value is similar to the optimum O_2 concentration calculated according to Schneider [39] (see chapter 3.4.3). With a λ of two and the data in table 27, the optimum O_2 concentration obtained was 3.7 $mg \cdot l^{-1}$. The air flow was an average of 0.5 $m^3 \cdot h^{-1}$. The disadvantage is that the air flow could only be regulated to a minimum of 1.3 $m^3 \cdot h^{-1}$. Throttling aeration is recommended because with the alternating mode used, high concentrations of O_2 can occur in a very short time. As described in chapter 3.4 and chapter 5.2.2, low O_2 concentrations are essential for the production of elemental sulphur.
The optimum temperature for sulphur bacteria is 30 °C (see chapter 5.2.2). However, the temperature was often below this value, except in summer. The operation in spring, autumn and winter showed that a good heating system was necessary. The heating of the pilot plant was carried out with a normal electrical heater which was independent of PLC (programmable logic control). Targeted control is recommended, especially for small plants where the turbulences due to higher volume flows are minimal. The heating could be realised simply with immersed dived heat exchangers.

The pH was controlled by the PLC which regulated the addition of NaOH. The buffer capacity of Humin-P was also analysed during the operation of the pilot plant when considering the amount of NaOH added during operation with and without Humin-P. An exact determination of the amount of NaOH added could not be carried out.
The experiences at the pilot plant clearly demonstrated a growth of sulphur bacteria at the walls and tubes. Figure 56 shows the biofilm of the sulphur bacteria on the sight glass of the bioreactor from the beginning to the end of the operation of the pilot plant. The photo on the left demonstrates the beginning of the operation without any biofilm. After some weeks a white biofilm is visible (second photo from the left). The two photos on the right show decolourisation due to humate addition. Other components also have biofilm. This is shown on selected pictures in figure A23 in the annex.
Due to biofilm formation, packing material in the bioreactor should be considered for such plants to provide the bacteria more volume for settling. The clogging of the packed bed has to be considered as well. During the one-year operation of the pilot plant, no problems due to clogging were encountered.

Figure 56: Photos of biofilm formation of sulphur bacteria on sight glass of bioreactor of pilot plant

Removing the washing liquid is necessary to remove sulphur from the system and prevent its agglomeration. This removal is dependent on the content of S and SO_4^{2-} as well as on the pressure drop in the column. The solids content in the liquid flow should not be too high (~ below 5 wt-%). A washing out of sulphur bacteria has to be avoided. When removing washing liquid, fresh water is brought in. The fresh water supply in the pilot plant was about 0.036 $m^3 \cdot d^{-1}$. For application in practice this value would be higher when more sulphur is produced and has to be removed. For the Thiopaq process with volume flows between 200 and 500 $m^3 \cdot h^{-1}$ this value is about 1 $m^3 \cdot d^{-1}$ [85].

The dosage of the nutrient solution and the defoamer was regulated manually. Operating the plant with humates resulted in a higher foam formation than operating the plant without humates. This foam formation was also observed in the laboratory experiments and in experiments carried out by Freudenthal [31]. Regulating defoamer addition should be considered for such a plant. Adding additional nutrient with a nutrient solution is necessary for sulphur bacteria. For a double-stage bio-scrubber system according to the Thiopaq process (gas flow: 500 $m^3 \cdot h^{-1}$) one litre per day of a mineral nutrient was added [85]. This value provides a guideline for practical application.

Protecting against explosions has to be considered when designing a biogas desulphurisation process. In the area around the scrubber, there should be no explosion risk. The control of raw gas pressure, to ensure no entry of O_2 into the gas tubes to avoid dangerous environments, was not found to be a good solution. In addition to the CH_4 sensor, an O_2 sensor in the raw gas stream is suggested.

9.2. Application at biogas plants

To evaluate the application at biogas plants different case studies were carried out. Two existing biogas plants and one new biogas plant with two options for using the biogas produced were studied.

The volume of the bioreactor V_R can be calculated using the H_2S loading ratio L_{H2S} and the degradation rate r of the sulphur bacteria.

$$V_R = \frac{L_{H_2S}}{r} \tag{9.1}$$

In laboratory experiments an average degradation rate of 5 $g \cdot m^{-3} \cdot h^{-1}$ was obtained (see chapter 5.2.3). This value is much lower than the values between 20 and 80 $g \cdot m^{-3} \cdot h^{-1}$ found in the literature [39,50,53]. Reason for that might be the lower temperature in the laboratory bioreactors (see chapter 5.2.3). Due to an operation of the bioreactor in practice with optimum temperature for the bacteria, the degradation rate of H_2S is assumed to be 20 $g \cdot m^{-3} \cdot h^{-1}$ for the calculations carried out in the different case studies.
The loading is dependent on the volume flow and the H_2S concentration in the liquid phase. The H_2S concentration in the liquid phase is dependent on the H_2S concentration in the gas phase, the absorption efficiency and chemical reactions e.g. dissociation. This value is obtained through simulation of the scrubber (see chapter 7).
The dimensions of the column are dependent on the gas flow and the H_2S concentration of the raw biogas. Desired clean gas concentrations of 50 ppm are assumed.

Important for the application of the bio-scrubber system at biogas plants is the consideration of explosion protection. Explosion protection is not evaluated for the individual plants in these case studies. The points described in chapter 9.1 should be considered in explosion protection.

9.2.1. Case Study: Albersdorf

For this case study the application of the bio-scrubber system as an alternative to the existing bioscrubber was conducted. The biogas plant in Albersdorf uses a normal counter current bioscrubber for desulphurisation (see chapter 3.1.2). Table 28 presents the main characteristics of the biogas plant in Albersdorf and figure 57 presents a photo of this plant.

Table 28: Characteristics of the biogas plant Albersdorf

Electrical output	836 kW
Thermal output	ca. 1 MW
Gas production	ca. 370 $m^3 \cdot h^{-1}$
Input (mainly cow manure)	ca. 86 000 $t \cdot a^{-1}$
Gas contents	CH_4: 60 - 65 % CO_2: 35 - 40 % H_2S: ca. 1 000 ppm (raw gas) H_2S: < 100 ppm (clean gas)

Figure 57: The biogas plant Albersdorf

The direct input of humates into such a single stage bioscrubber could not be carried out. The washing liquid of the bioscrubber has a pH of about 1.5. At these low pH values the humates precipitate. A neutral operation would aggravate clogging because of additional sulphur formation.

If installing a double-stage bio-scrubber system at the biogas plant in Albersdorf, their scrubber can be used and only an additional bioreactor is necessary. The bioscrubber in Albersdorf has a height of 12 m, a diameter of 3.2 m and contains about 70 m³ filling material.

With an optimum humate concentration of 2 wt-%, a volume flow of washing liquid of 15 $m^3 \cdot h^{-1}$ is necessary. The sulphide flow into the bioreactor is at maximum 525 $kg \cdot h^{-1}$ and so the bioreactor has to have a volume of 26 m³. In comparison to the actual bioscrubber, washing water is saved of more than 50 %. The outflow can be used as fertiliser.

If the investment in a bio-scrubber system is profitable for such an existing plant, it has to be evaluated with a more detailed cost estimation. For a new plant with such characteristics, a bio-scrubber system is recommended.

The biogas plant in Albersdorf plans to expand their plant and is building a new fermenter. Assuming that the H_2S concentration stays constant and the flow duplicates, they can still use their bioscrubber as scrubber in a humate containing bio-scrubber system. Only the additional bioreactor has to be bigger.

9.2.2. Case Study: Bargfeld-Stegen

For this case study the application of the bio-scrubber system in the existing biogas plant in Bargfeld-Stegen was conducted. The biogas plant in Bargfeld-Stegen actually has an internal biogas desulphurisation process (see chapter 3.1.2). The use of the humate containing bio-scrubber system was identified as alternative to this internal process. Table 29 presents the main characteristics of the biogas plant in Bargfeld-Stegen and figure 58 presents a photo of the plant.

Table 29: Characteristics of the biogas plant in Bargfeld-Stegen

Electrical output	ca. 110 kW
Thermal output	ca. 109 kW
Gas production	50 - 55 $m^3 \cdot h^{-1}$
Input	Maize silage: 1 460 $t \cdot a^{-1}$ Cow manure: 2 000 $m^3 \cdot a^{-1}$
Gas contents	CH_4: 50 - 52 % CO_2: 46 - 48 % H_2S: 50 - 150 ppm

Figure 58: Biogas plant Bargfeld-Stegen

Due to the substrate composition the H_2S concentration of the raw gas is estimated to be 800 ppm. The actual cost of internal desulphurisation is about 600 $€ \cdot a^{-1}$ [92]. With an optimum humate concentration of 2 wt-%, the amount of washing water necessary would be 4 $m^3 \cdot h^{-1}$ with 5 theoretical stages in the scrubber. The resulting volume of the bioreactor is 3.1 m^3.

The investment as well as the operating costs would be higher than the present costs. For small farm biogas plants the higher costs of external systems could not be recovered. Therefore, their application is only recommended for bigger biogas plants. In the literature a value of 200 kW_{el} is given as the value when the application of external desulphurisation processes becomes reasonable [93]. Due to the positive effects of H_2S removal a direct input of humates in the fermenter might be an option (see chapter 10). When implementing an additional fermenter an external desulphurisation process is recommend for the biogas plant in Bargfeld-Stegen. The bio-scrubber system can treat the biogas from both plants.

9.2.3. Conversion into biomethane

In this chapter, a case study was conducted to analyse the application of the bio-scrubber system for a new biogas plant. The desulphurisation process is included in the treatment to produce biomethane. Table 30 shows the characteristics of the biogas plant used for this case study.

Table 30: Characteristics of biogas plant

Gas production	500 $m^3 \cdot h^{-1}$
Gas contents	CH_4: 65 %
	CO_2: 35 %
	H_2S: 1 000 ppm

With 10 theoretical stages, a wash water stream of 20 $m^3 \cdot h^{-1}$ with a humate concentration of 2 wt-% is necessary. The bioreactor has a volume of 36 m^3. For the same scrubber without humates, a wash water stream of 250 $m^3 \cdot h^{-1}$ would be necessary. For a bioscrubber with biofilm in the column the wash water would be lower, but anyway the savings in wash water are enormous.
The humate containing bio-scrubber system is especially recommended for the desulphurisation step before the conversion into biomethane. Processes where the biogas is diluted are unsuitable for the application of production of biomethane. Consequently, normal bioscrubbers, for example, cannot be used because of the dilution with air. Therefore the calculated data has to be compared with other suitable processes, whereby the humate containing bio-scrubber system would be a good option. For the desulphurisation step before a combined heat and power plant the bio-scrubber system is also recommended if high gas volume flows are existent. It can also be used for biogas with high concentrations of H_2S. The savings in water are the best advantage in comparison to normal scrubbers.

9.3. Other fields of application

Due to the fact that humates achieve very high improvements in the removal of H_2S, their addition could also be used in other industrial gas purifications. For example, sulphur-containing gases have to be treated in paper mills, gas works, petrochemical plants and tanneries. The application of the removal of SO_2 is also an alternative to use the humates containing bioscrubber system. Green [27] has already analysed that sodium humates can absorb SO_2 efficiently and to a high capacity. The removal of SO_2 of exhaust gases, for example in power plants, may be an application. The purification of coke oven gas can be another application for the addition of humates. Coke oven gas contains 4 - 9 $g \cdot m^{-3}$ of NH_3 and 7 - 12 $g \cdot m^{-3}$ of H_2S and also amounts of carbon disulphide (CS_2) and carbon oxide sulphide (COS) [77]. Table 31 gives an overview about different sulphur-containing gases and their source.

Table 31: Overview of sulphur-containing gas compounds [85,94,95]

Gas compound	Chemical Formula	Examples of source
Hydrogen sulphide	H_2S	Landfill, biogas, sewage gas, natural gas
Sulphur dioxide	SO_2	Fuels from coal and crude oil, power plants, diesel exhaust gases, paper industry etc.
Sulphur trioxide	SO_3	Oxidation of H_2S and SO_2, production of H_2SO_4
Dimethyl sulphide	C_2H_6S	Boiling of different vegetables (e.g. cereals, cabbage)
Carbon disulphide	CS_2	Unclean natural gas, coke oven gas
Carbonyl sulphide	COS	Atmosphere, natural gas, volcanic gases, coke oven gas

For industrial desulphurisation, chemical and physical processes are mainly used, for example the limestone process, the Amasox-process or the Wellmann-Lord-process. The costs of these processes are much higher than the costs of biogas desulphurisation. [94]
The case studies for the application of the humate containing bio-scrubber process at biogas plants have shown that their application is recommended for biogas plants with volume flows higher than about 300 $m^3 \cdot h^{-1}$. Therefore an application of the humate containing bio-scrubber process is recommended for the removal of H_2S from natural gas where volume flows are higher. An efficient removal of H_2S from sewage and landfill gas with humate solution was analysed in laboratory experiments (see chapter 4.2.2), so the application in this two fields is suggested. The volume flows are also higher than in small biogas plants. Table 32 shows the average H_2S concentration of these gases.

Table 32: Overview of H_2S in different gases [2,9]

Gas	Concentration [ppm]
Biogas	0 – 5 000
Landfill gas	50 – 300
Sewage gas	10 - 40*
Natural Gas	0 – 35 000

* up to 2,000 ppm possible (dependent on substrate)

The treatment of natural gas with high concentrations of H_2S is an application of the humates containing bio-scrubber system. The application in landfills and waste water treatments plants is only recommended for high H_2S concentrations of more than 1,000 ppm.

10. Conclusion and outlook

In summary, the results of the laboratory experiments show that the use of humic substances as solubility agents in biogas treatment is effective. In the laboratory experiments, significant improvements were achieved in comparison to pure water as well as alkaline water as washing liquid. With regards to the activity of sulphur bacteria, the analysis demonstrated a difference upon the addition of Humin-P, but the washing liquid can be regenerated by biological means.
For the bio-scrubber system containing humates, optimum conditions are at temperatures between 30 and 40 °C and at neutral pH environments. Optimum humate concentration is between 2 and 4 wt-%. When operating the scrubber without biological systems even higher humate concentrations and higher pH values are possible and will improve the process.
As humates are a natural product their use in this process has clear advantages over the use of artificial solubilisers (e.g. MEA, Sulfa-Clear) in optimising the treatment. In addition, humic substances ameliorate soil activity and can be used in combination with the by-product elemental sulphur as agricultural fertiliser. The use of a by-product instead of removing it as waste is an advantage of the system, especially in comparison with chemical processes.
Altogether, biogas can be desulphurised efficiently and in an environmentally-friendly way through the addition of humates. Unfortunately, its application in a pilot plant could not be tested in detail. A preliminary test showed that Humin-P worked very well in practice and optimised the system. More practical tests with the addition of humic substances are recommended to verify the laboratory results in practice and to gain more information about the regeneration of humates.
The long-term behaviour of the humate solution should be analysed in detail. In particular, changes with regard to the microbiological degradation of sulphide, insufficient chemical stability and process-related wear have to be determined. The influence of the humate concentrations on the plant operation and process stability must also be analysed. An optimum dose of humates should be determined with regards to solubility, selectivity and conversion. In addition, the regeneration efficiency has to be further analysed in long-term experiments. Experiments at a pilot plant are necessary before implementing the process in practice. The regeneration of the humates should be determined in long term-experiments.
In general, this humate containing bio-scrubber system can only be efficiently used for bigger biogas plants where an internal desulphurisation step is not sufficient. The cost evaluation as well as the case studies showed that volume flows higher than 200 $m^3 \cdot h^{-1}$ should be feasible.
If the requirements for reliable purification performance increase up to a few ppms in clean gas, external processes would be increasingly adopted. As conversion to biomethane becomes more important, the application of desulphurisation will change because of the more stringent purity requirements.
The desire to remove formaldehyde and siloxanes is increasing. For example, hexamethyldisiloxane and octamethyltrisiloxane exist in landfill gas [96]. Sewage gas contains octamethycyclotetrasiloxane and decamethylcyclopentasiloxane [97]. The removal of siloxanes might be achieved with humates because of their characteristics e.g. huge molecular size and porosity. This should be analysed in further experiments, with a focus on the adsorption of siloxanes on humates.

The removal of H_2S by adding humic substances directly into the fermenter is an option. The adsorption effects and chemical reactions between humates and H_2S should also proceed directly in the fermenter. In this case the pH of the humates can be adjusted with sodium citrate or citric acid. The results of the interactions between H_2S and Humin-P justify such an application. But 30 years of studying the interactions between humic materials and microorganisms

showed that fermenting bacteria could reduce humic substances [24]. This study suggests that this application may not work well. Therefore, further studies should be completed before denying or applying it in practice.

To determine the biological behaviour further, the biomass or the cells can be analysed in detail using colourisation with DAPI and the FISH-technology. In a preliminary test, an effect on the bacteria consortium with and without humates was not observed. This effect on the cells by humates should be determined again in detail.
The influence of dosing nutrients on the microbiological degradation of sulphide and therefore on the purification potential of the scrubber has to be analysed. The optimum type and quantity have to be determined.

For more detailed analysis of the interactions between H_2S and Humin-P the zero point of charge of Humin-P can be determined through analysis of the zetapotential. The analysed isoelectric point helps to establish if compounds are attracted and at which point a difference may occur. From the charge obtained it can be determined if sulphide can be bound to the humates or if repulsive forces are present. Experiments with an ion selective electrode for sulphide measurements should also be carried out. The bounding of sulphide on iron compounds in the humate solution could be determined in detail using measurements of X-ray absorption fine structure (XAFS) [98]. Experiments to quantify the adsorption effects of H_2S on humates should be analysed as well.

The application of the humate containing bio-scrubber system in other industrial applications in practice should be analysed. For example, the removal of SO_2 can be analysed with laboratory experiments according to the head space method. The removal of other components can also be analysed. Chlorinated hydrocarbons, BTEX aromatics or organosulphur odorants as well as carbon disulphide (CS_2) and carbon oxide sulphide (COS) may also be removed by adding humic substances. The application of solubilisers for the removal of CO_2 can also be tested. Ionic liquids could be an efficient solubiliser for this application [99].

For the model of the bio-scrubber-system with humates, the regeneration efficiency should be specified more detailed so that this can be modelled correctly. The separation of elemental sulphur should be analysed in experiments in order to specify this part of the process in the model of the bio-scrubber system.
The column could also be modelled dynamically, so that start-up processes can be modelled. Furthermore, the calculation of the flooding point of the column could be integrated.
The model of the bio-scrubber system can be optimised with additional removal of other compounds, for example NH_3 or other soluble components. In addition, activities can be used instead of concentrations and the slight solubility of CO_2 and CH_4 can be integrated into the model. When including the buffer capacity of the humates, the amount of additional NaOH necessary can be determined. Therefore, the savings of NaOH in comparison to other bioscrubbers can be calculated. The addition of defoaming agents and nutrient solutions can also be added to complete the processes in the bioreactor. Also, the temporal removal of water when humates become over-accumulated should be inserted into the model.

In addition to the bio-scrubber system a single-stage bioscrubber can also be modelled. Here, microbial reactions occur directly in the scrubber. The bacteria live on the packing material and form a biofilm. The addition of Humin-P could be simulated as well. This scrubber exists more often in practice. The main problem is the clogging of the packing material. The addition of Humin-P can only be simulated. In practice this application is not recommended (see chapter 9.2.1). In the modelling of a single-stage bioscrubber, biofilm formation should be in-

cluded. This biofilm could also be included in the model of the double-stage bio-scrubber system.
Additionally, a cost calculation can also be incorporated into the model or can be modelled with another program such as Aspen Custom Modeller. The net present value, the internal rate of return and the payback period could be determined to obtain a more detailed overview of the cost with regards to the application of the humate containing bio-scrubber system.

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Annex

A1 Calculation of enthalpies

The enthalpies h for the biogas and the washing liquid are calculated according to equation A.1. The enthalpy h of the gas represents the enthalpy of the single gas components where the influence of H_2S is neglected because of its very low concentration. The heat capacity c_p is calculated according to equation A.2.

$$h(T) = h(T_0) + \int_{T_0}^{T} c_P(T)dt \tag{A.1}$$

$$c_P(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2} \tag{A.2}$$

Table A1 shows the coefficients for equation A.2.

Table A1: Constants for the calculation of heat capacities c_P of CH_4, CO_2 and H_2O [100,101]

	CH_4	CO_2	H_2O
a [$J \cdot mol^{-1} \cdot K^{-1}$]	2.23466	2.93296	$8.712 \cdot 10^{-2}$
b [$J \cdot mol^{-1} \cdot K^{-2}$]	$9.69265 \cdot 10^{-2}$	$3.99272 \cdot 10^{-2}$	$1.25 \cdot 10^{-3}$
c [$J \cdot mol^{-1} \cdot K^{-3}$]	$-2.60253 \cdot 10^{-5}$	$-1.47503 \cdot 10^{-5}$	$0.18 \cdot 10^{-6}$
d [$J \cdot K \cdot mol^{-1}$]	$6.10863 \cdot 10^{5}$	$-2.48862 \cdot 10^{5}$	0

The reaction enthalpies $\Delta h_{R,i}$ can be calculated with equation A.3.

$$\Delta h_{R,i} = \sum v_i \cdot \Delta h_{f,i} \tag{A.3}$$

The enthalpies of formation $\Delta h_{f,i}$ of the different compounds are listed in table A2.

Table A2: Enthalpies of formation [101]

$\Delta h_{f,H2S}$ [$kJ \cdot mol^{-1}$]	-39.7
$\Delta h_{f,HS-}$ [$J \cdot mol^{-1}$]	-17.5
$\Delta h_{f,H+}$ [$J \cdot mol^{-1}$]	0
$\Delta h_{f,S2-}$ [$J \cdot mol^{-1}$]	-33.0

The enthalpy of solution of H_2S Δh_{Sol} is assumed to be constant over the range of temperature considered and is set at 17459 $J \cdot mol^{-1}$[19].

A2 Inclusion of pH and temperature dependency in the bioreactor model

The dependence of maximum growth rates μ_{max} on temperature has to be estimated experimentally for a given range of temperature, e.g. 10 °C to 70 °C. According to Angelidaki [78] the following relation can be used. The temperature coefficient α can be estimated using AquaSim's parameter estimation. The optimum temperature was determined to 30 °C (see chapter 5.2.2).

$$\mu_{\max}(T) = \mu_{max,T_{opt}} - \alpha \cdot \left(T_{opt} - T\right) \quad \text{when } T < T_{opt} \tag{A.4}$$

$$\mu_{\max}(T) = \mu_{max,T_{opt}} \cdot \frac{\left(T_{\max} - T\right)}{\left(T_{\max} - T_{opt}\right)} \quad \text{when } T > T_{opt} \tag{A.5}$$

The influence of pH has to be incorporated into the growth kinetics. The following formula from Angelidaki [78] can be used.

$$f_{\mathrm{pH}} = \frac{1 + 2 \cdot 10^{0,5(pH_1 - pH_2)}}{1 + 10^{(pH - pH_2)} + 10^{(pH1 - pH)}} \tag{A.6}$$

In the Michaelis pH function, pH_1 and pH_2 are the lower and upper pH values respectively, where the growth rates are approximately 50 % of the uninhibited rate. It was determined that the activity of the bacteria is at its optimum at neutral pH values. pH_1 and pH_2 have to be determined through experiments.

A3 Inclusion of buffer capacity in the bioreactor model

The buffer capacity of the humates can be considered in the bioreactor. When considering the carbonate buffer of the humates, the stripping of CO_2 and the dissociation of carbonic acid (H_2CO_3) have to be included. The dissolved CO_2 and the gaseous CO_2 tend to be in equilibrium. The following dissociations reactions occur in addition to CO_2 stripping. H_2CO_3 is used to represent both H_2CO_3 and CO_2 in liquid phase. This is in accordance to Feng [102] who analysed that the error could be neglected.

$$\varphi_{CO_2} = k_L a_{CO_2} \cdot \left(H_{CO_2} \cdot p_{CO_2} - c_{H_2CO_3}\right) \tag{A.7}$$

$$\mathrm{H_2}\,CO_3 \overset{K_4}{\Leftrightarrow} HCO_3^- + \mathrm{H}^+ \tag{A.8}$$

$$\mathrm{H}\,CO_3^- \overset{K_5}{\Leftrightarrow} CO_3^{2-} + \mathrm{H}^+ \tag{A.9}$$

The partial pressure p_{CO2} can be calculated according to Daltons Law and the Henry constant H_{CO2} can be calculated according the following formula used by Behrendt [103]. The specific overall mass transfer coefficient k_La_{CO2} is calculated in correlation with k_La_{O2} and the diffusion coefficients D_{O2} (= 2.33·10-5 $cm^2 \cdot s^{-1}$) and D_{CO2} (= $1.60 \cdot 10^{-5}$ $cm^2 \cdot s^{-1}$) [104]. The concentration of the gaseous CO_2 is assumed to be constant in this model. When modelling the bio-

scrubber system, the concentration of the gaseous CO_2 in the bioreactor is higher than in the model for the bioreactor alone because of the CO_2 from the biogas which might be dissolved in the washing liquid.

$$p_{CO2} = c_{CO2} \cdot R \cdot T \tag{A.10}$$

$$\mathrm{H}_{CO2} = \exp\left(\frac{18980.723}{R \cdot T} - 0.316464\right) \tag{A.11}$$

$$\frac{k_L a_{O2}}{k_L a_{CO2}} = \left(\frac{D_{O2}}{D_{CO2}}\right)^{0.5} \tag{A.12}$$

The equilibrium constants K_i for the dependence of dissociations on temperature can be calculated with equation 7.9 using the following constants [77].

- A = 235.482; B = 0; C = -12092.1; D = -36.7816 for equation A8
- A = 220.067; B = 0; C = -12431.7; D = -35.4819 for equation A.9

Other buffer systems in the bioreactor such as a hydrogen phosphate buffer should be neglected because of low concentrations. The carbonate buffer of the nutrient solution can be neglected as well. Furthermore, it should be assumed that the amount and structure of the humates do not change in the bioreactor.

A4 Dimensions of the pilot plant

The pilot plant was designed by Wessel Umwelttechnik GmbH, Hamburg. The standard procedure for dimensioning a bioscrubber is described in the literature [105]. The scrubber of the pilot plant was dimensioned by downscaling an existing bioscrubber at the biogas plant in Albersdorf. The parameters used were the empty tube speed of the gas in the column to determine the diameter of the column and the residence time to determine the height of the packing material. The gas characteristics such as temperature and concentrations are known. For the packing material of the scrubber a huge packing (Hilfow® 90-7) was chosen. This has a smaller surface and therefore the separation efficiency is lower, but fast clogging resulting in a high pressure drop is prevented. Two full cone nozzles are used to regularly sprinkle washing water.
To dimension the bioreactor, the retention time is set at 45 minutes based on previous experiences. With a water flow of 4 $m^3 \cdot h^{-1}$, the volume of the bioreactor is determined to be 3 m^3. Normally, the volume V_R of the bioreactor is calculated using the ratio of loading L and the degradation rate r of the bacteria (see equation 9.1). The aeration is carried out by a membrane tube diffuser.
Figure A1 shows the flow sheet of the pilot plant built by Wessel Umwelttechnik GmbH.

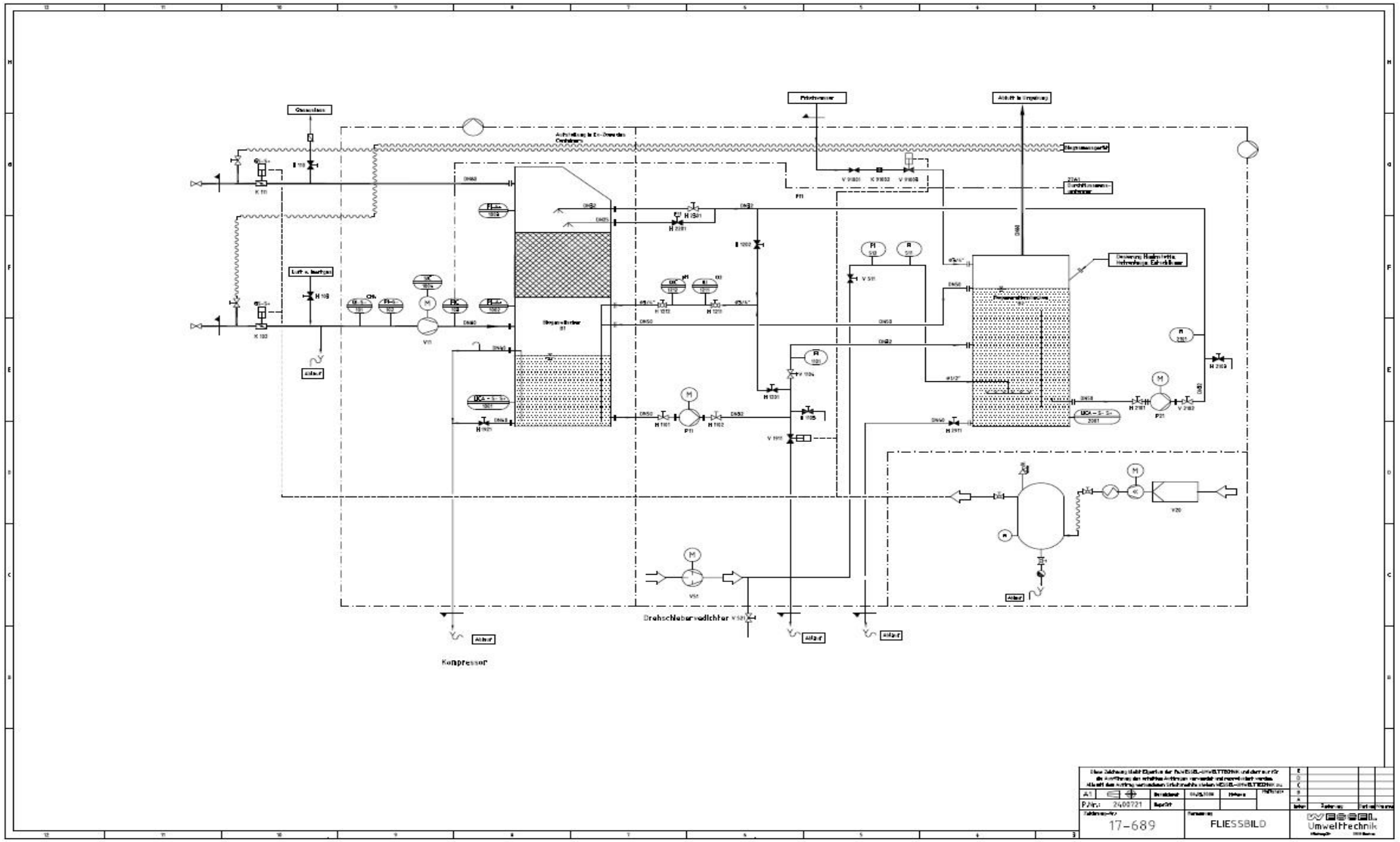

Figure A1: Flow sheet of pilot plant built by Wessel Umwelttechnik GmbH

A6 Tables

Table A3: Characteristics of the hydrogen sulphide (H_2S) [106,107]

Chemical formula	H_2S
Molecular mass	34.08 $g \cdot mol^{-1}$
CAS number	7783-06-4
Chemical state	Gaseous
Colour	Colourless
Odour	Rotten eggs
Odour threshold value	0.0014…0.0056 $mg \cdot m^{-3}$
Critical temperature	100.25 °C
Critical pressure	8.96 MPa
Critical density	347.63 $kg \cdot m^{-3}$
Flash point	100 °C
Ignition temperature	270 °C
Density, 0 °C	1.536 $g \cdot l^{-3}$
Solubility in water, 20 °C	2.61 $l \cdot l^{-1}$
Solubility in ethanol, 20 °C	approx. 11-12 $l \cdot l^{-1}$
OEL	10 ppm

Table A4: Acute toxic effects of H_2S in humans [107]

Concentration of H_2S	**Duration of exposure**			
[ppm]	**15 min**	**15 min - 1 h**	**1 h - 4 h**	**4 h - 8 h**
10				Eye irritation
50 - 100	Loss of olfactory perception	Eye irritation	Eye and bronchial irritation	Danger in case of continuous exposure
150 - 250	Loss of olfactory perception	Eye and bronchial irritation	Serious respiratory distress and asthenia	
300 - 400	Loss of olfactory perception, eye and bronchial irritation, asthenia	Severe respiratory distress, acute asthenia	Pulmonary edema and death	
500 – 1 000	Loss of consciousness, respiratory distress	Risk of pulmonary edema and death		
> 1 000	Immediate loss of consciousness and respiratory distress, risk of death			

Table A5: Oxidation numbers of selected sulphur compounds [108]

Oxidation number	**Sulphur compound**
- II	H_2S, HS^-, S^{2-}
0	S
+ II	$S_2O_3^{2-}$
+IV	SO_3^{2-}
+ VI	SO_4^{2-},SO_3

Table A6: Characteristics of humic substances [26]

Molecular weight	High molecular structure, several 100 up to 100 000 g·mol^{-1}
Element contents	**Element** / **Average value [%]** / **Variation [%]** C / 54 / ~ 10 O / 33 / ~ 8 H / 4,5 / ~ 3 N / 2,7 / ~ 2,6 S / ≤ 2 / - P / < 1 / -
Basic components	Aromatic and aliphatic structural elements, phenolic hydroxyl groups and ether groups
Acidity	Acidic character via -COOH and phenolic groups, capability for cation exchange
Polyelectrolyte	Humic substances are polyelectrolytes
Complexing agents	Due to different donor functions: complexing agent for metal ions; Trace amounts of reversibly or irreversibly bound metal ions are always present in humic substances; organic compounds are bound through hydrogen bonds or C-C-bonds.
Agglomerates	In solution: formation of reversible agglomerates, in dependence on surrounding in dynamic equilibrium
Surface activity	Surface activity due to hydrophobic and hydrophilic compounds
Spectroscopic properties	UV-Spectres decrease monotone; IR-Spectres have wide, little characteristic bands

Table A7: List of biogas plant where samples were taken

Biokraft Albersdorf in 25767 Albersdorf
Gut Stegen in 23863 Bargfeld-Stegen
BioEN Nord in 21357 Bardowiek
Bea Dithmarschen in 25693 Sankt Michaelisdonn
BioWerk Hamburg in 22525 Hamburg
Hof Steinberg in 21354 Bleckede
Schnapsbeckenhof in 79874 Breitnau
Gasthaus zum Strauß in 79874 Breitnau
Palmhof in 78199 Bräunlingen
Deponie Scheinberg in 79539 Lörrach
VERA Klärschlammverbrennung in 20457 Hamburg

Table A8: Detailed analysis of Humin-P

Ca	**Na**	**Fe**	**K**	**Mg**	**Al**	**P**	**S**	**Mn**	**Cu**	**Zn**
[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg]
4 150	673	7 600	108 000	542	6 270	< 250	2 220	12.1	26.5	10.5

A7 Figures

Figure A2: Example of result screen of mass spectrometer analysis

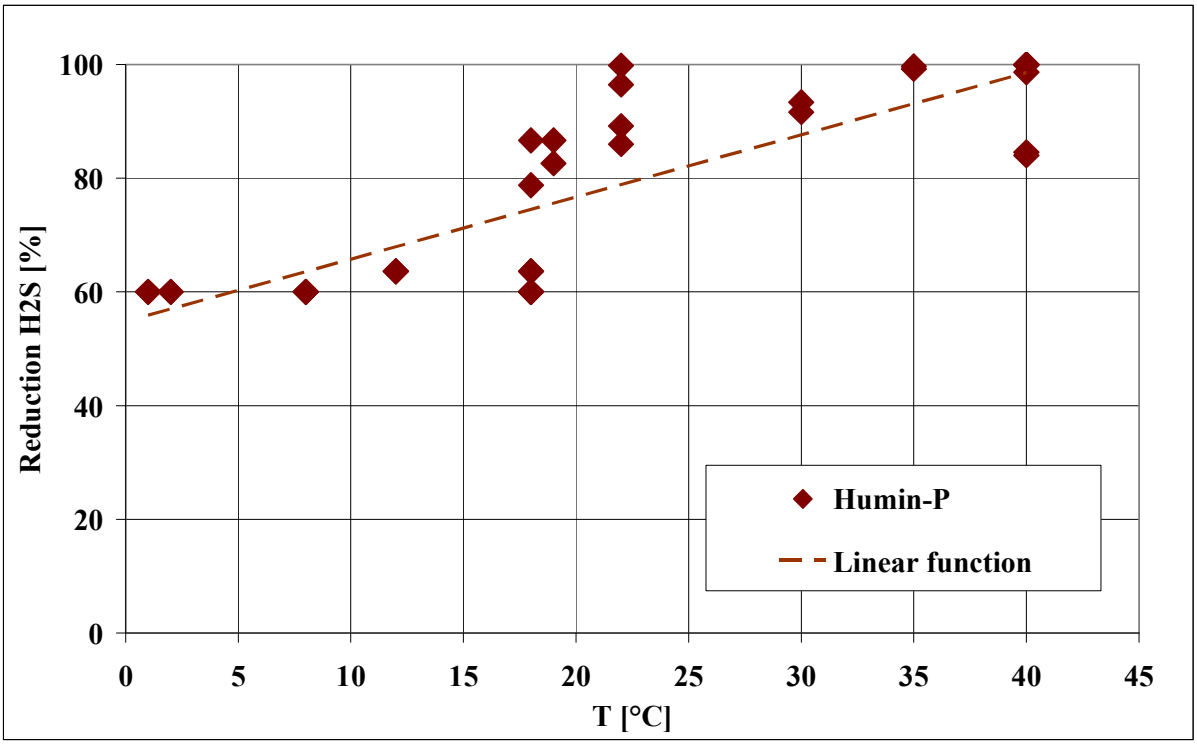

Figure A3: Influence of temperature in equilibrium experiments

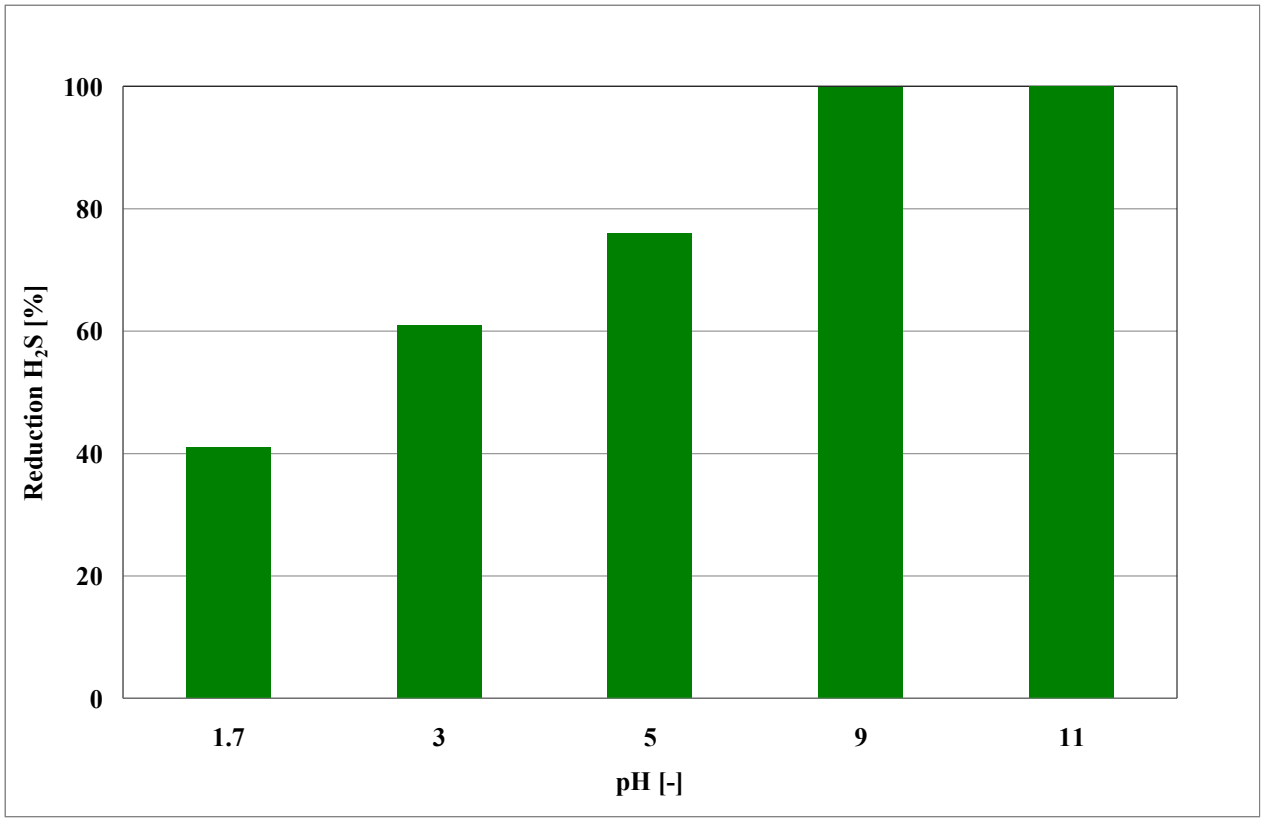

Figure A4: Influence of pH value in equilibrium experiments

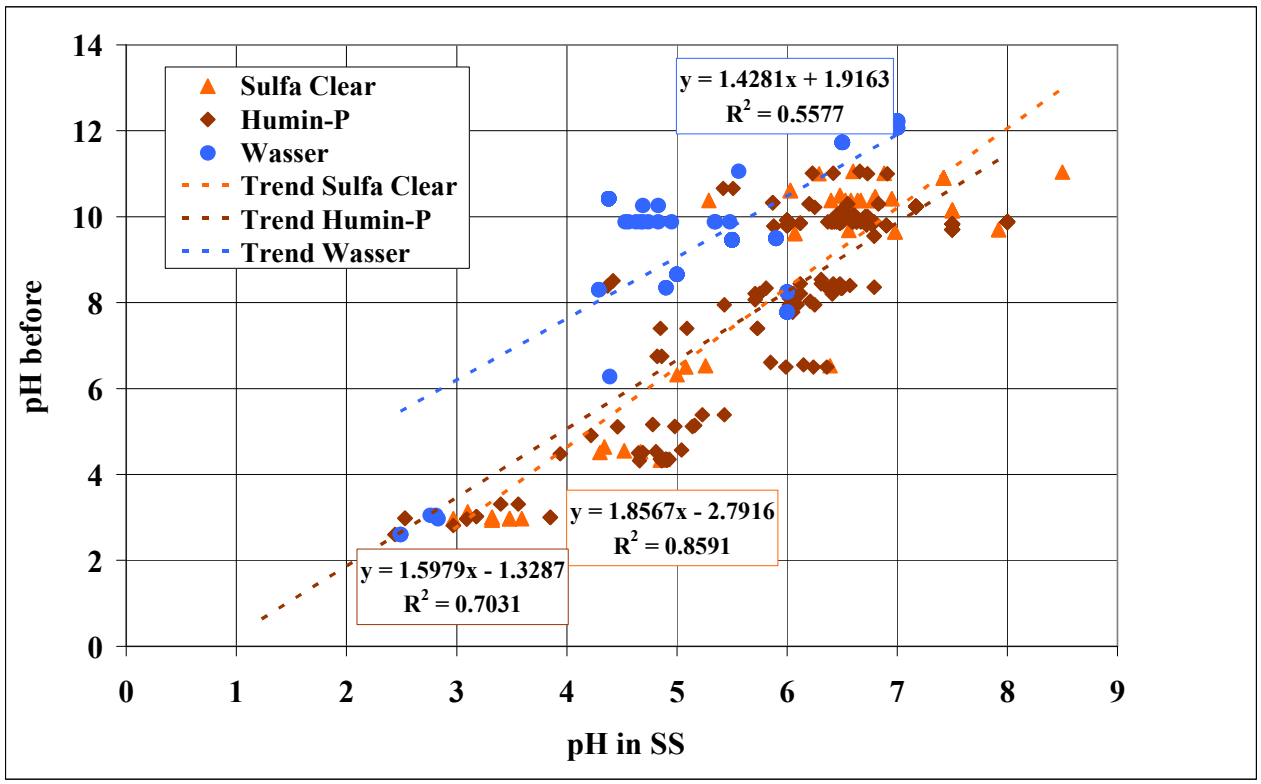

Figure A5: Difference of pH values of washing solution before and after contact with H_2S

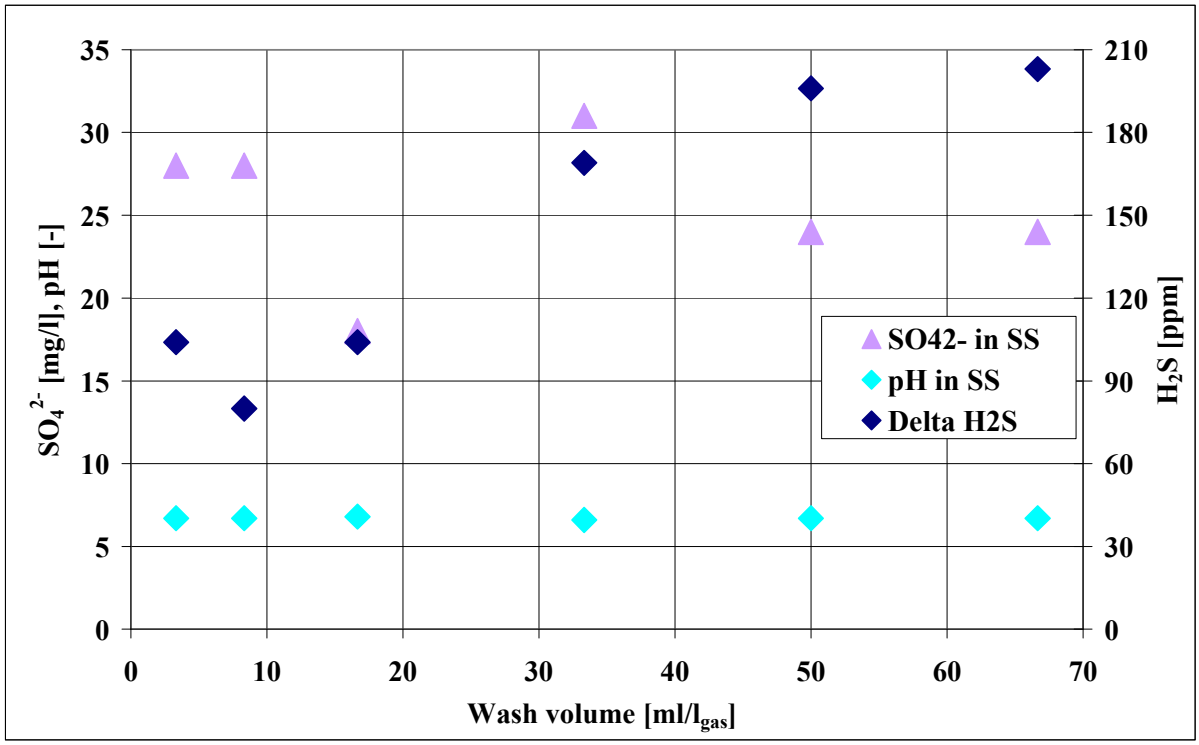

Figure A6: Concentrations of SO_4^{2-}, ΔH_2S_g and pH value in equilibrium experiments in dependence on the wash volume

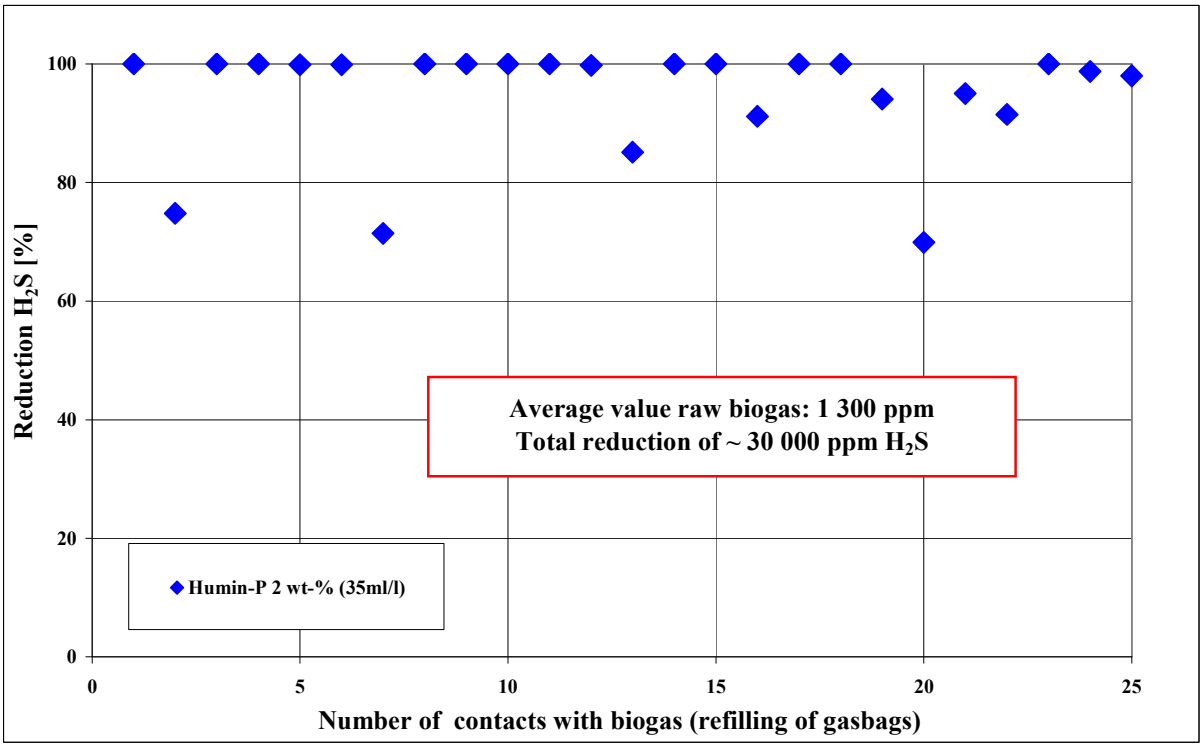

Figure A7: Results of repetition bags in a series of equilibrium experiments

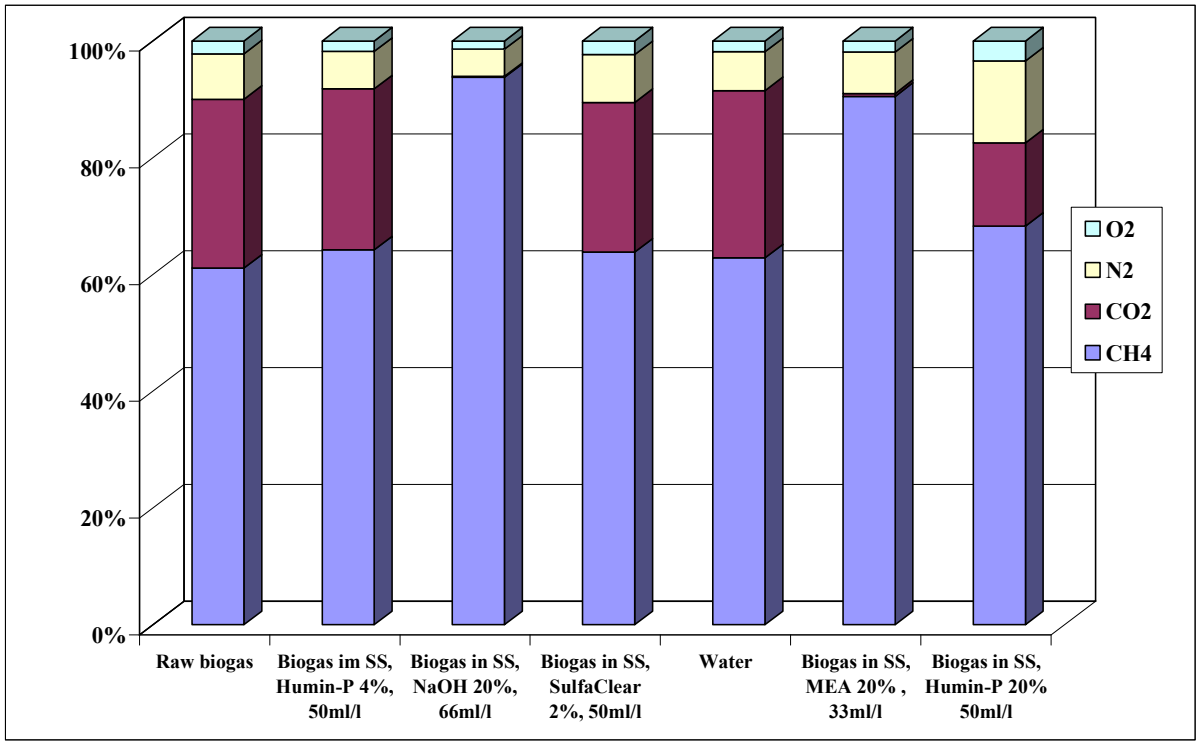

Figure A8: Influence on other biogas components in equilibrium experiments

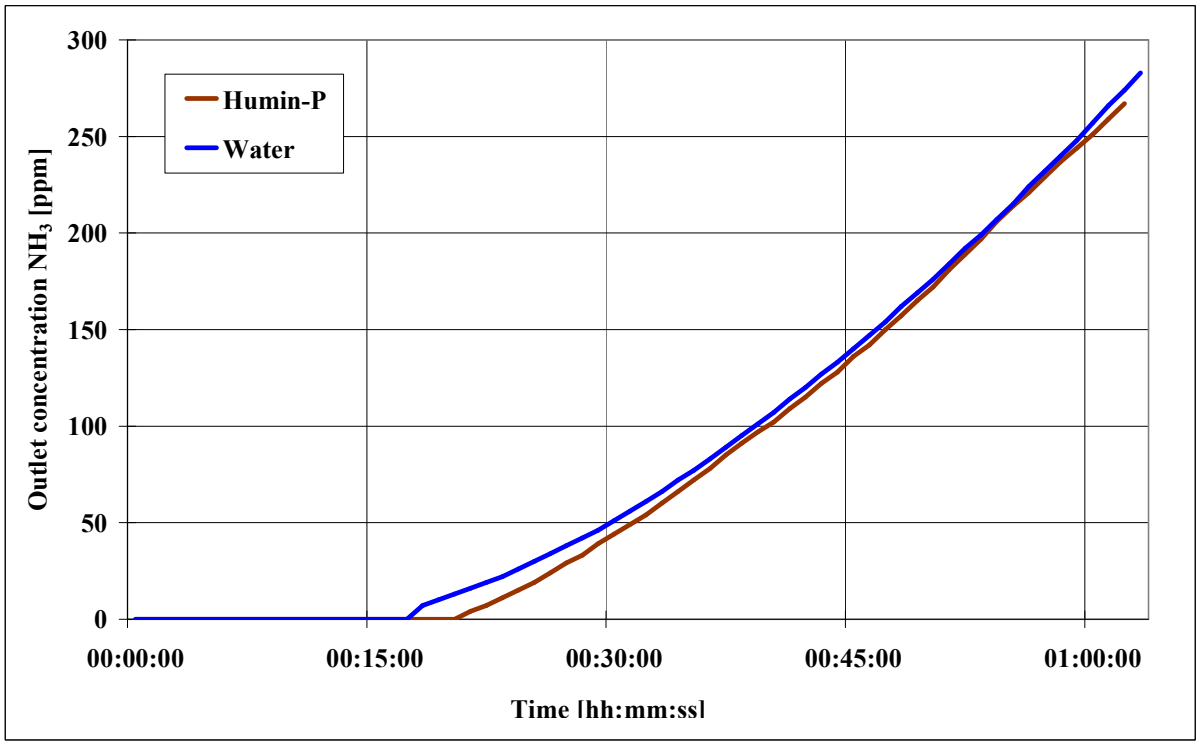

Figure A9: Continuous NH_3 experiment

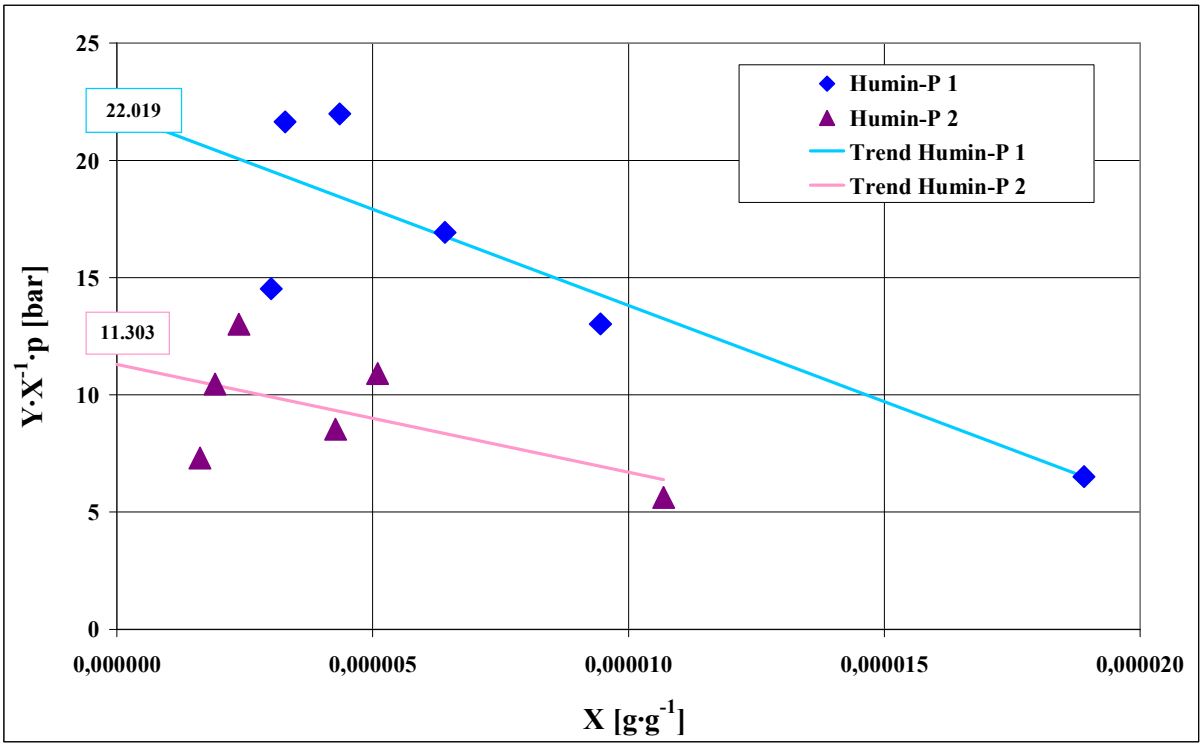

Figure A10: Example of determined "Henry coefficients" of Humin-P-solutions

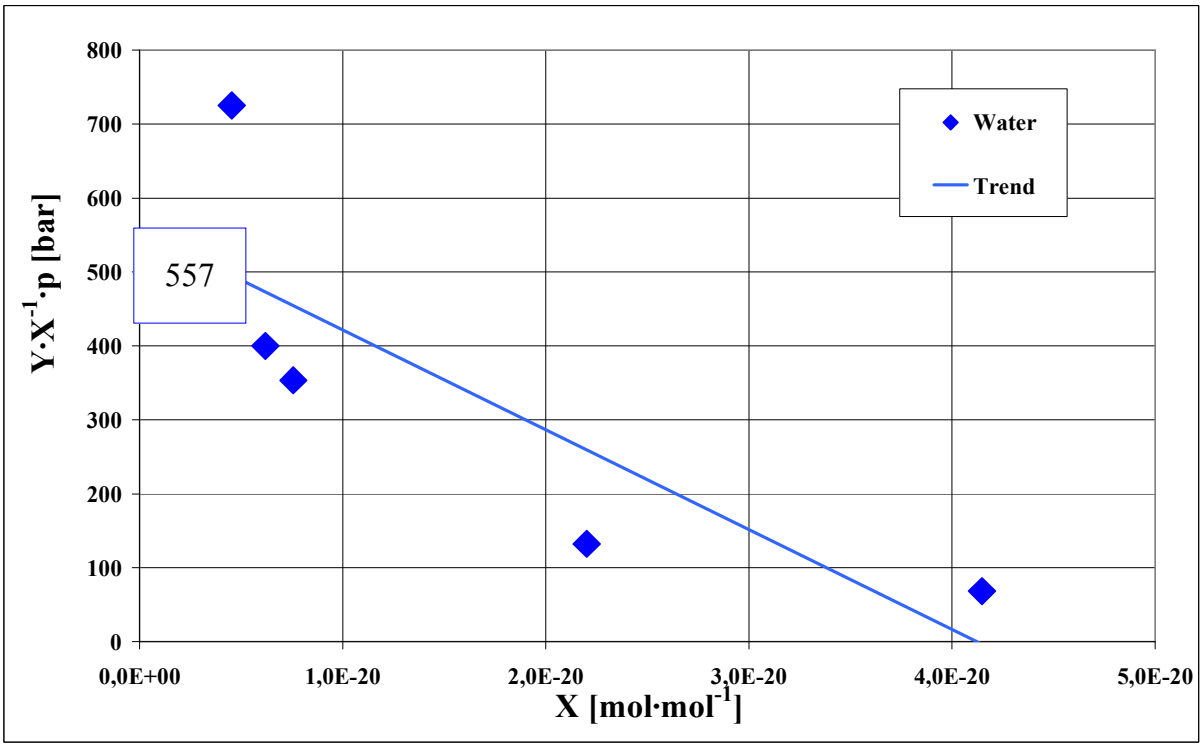

Figure A11: Determined Henry coefficient of water

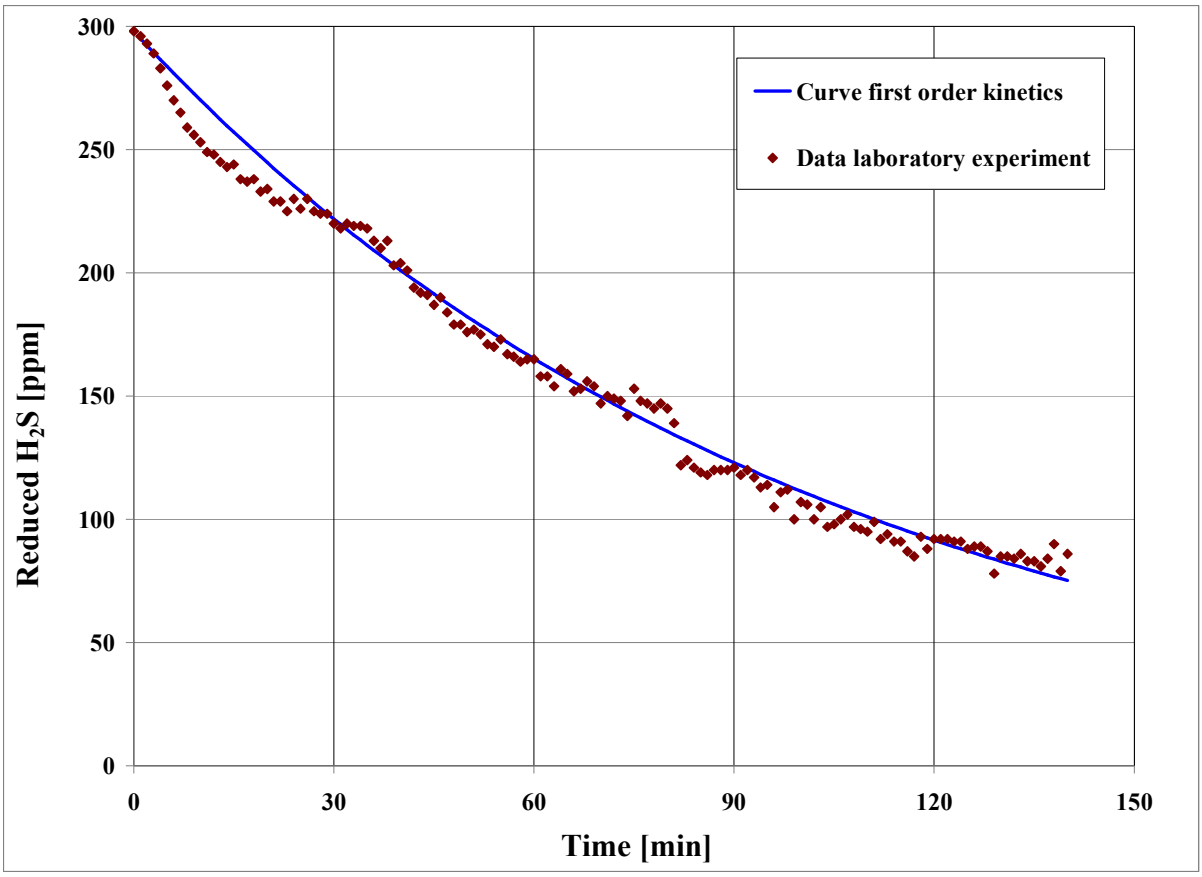

Figure A12: Comparison of reduced H_2S ($c_{H2S,in} - c_{H2S,out}$) from laboratory continuous absorption experiment (see 4.1.2) with determined curve of first order kinetic

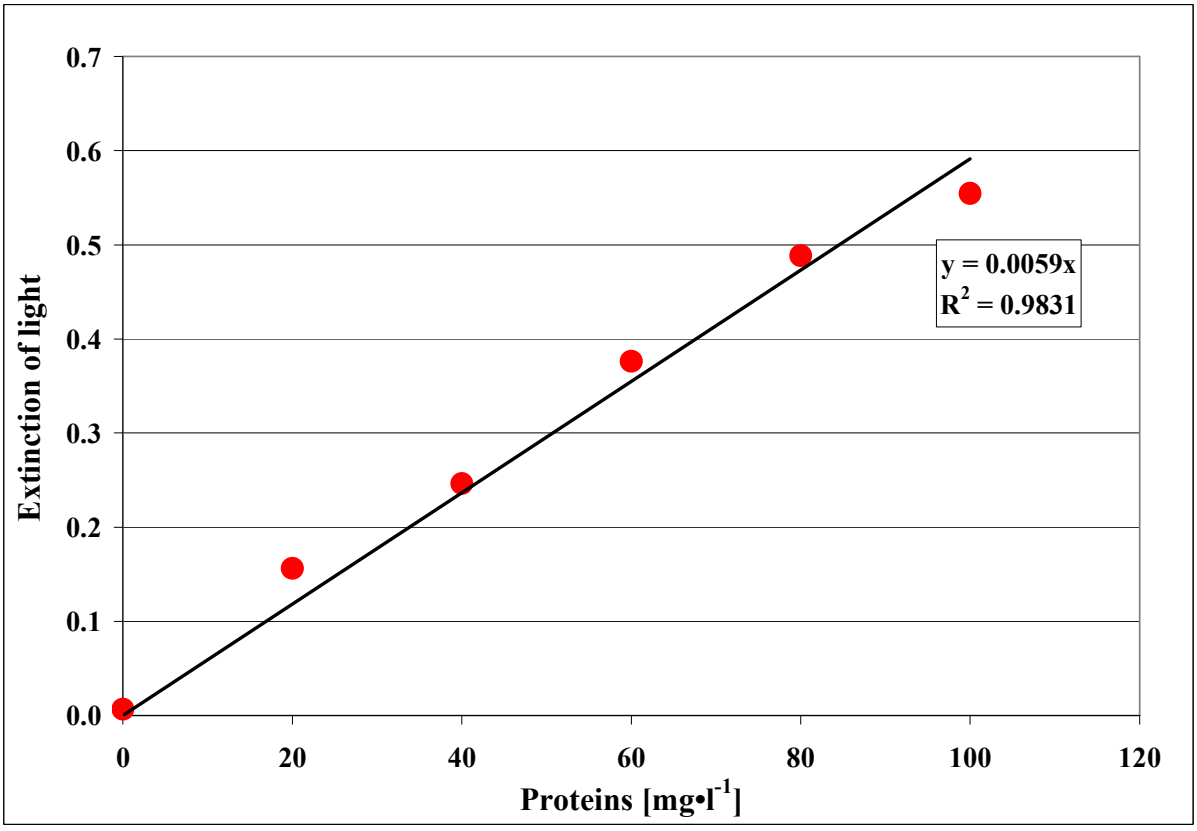

Figure A13: Calibration line for protein analysis

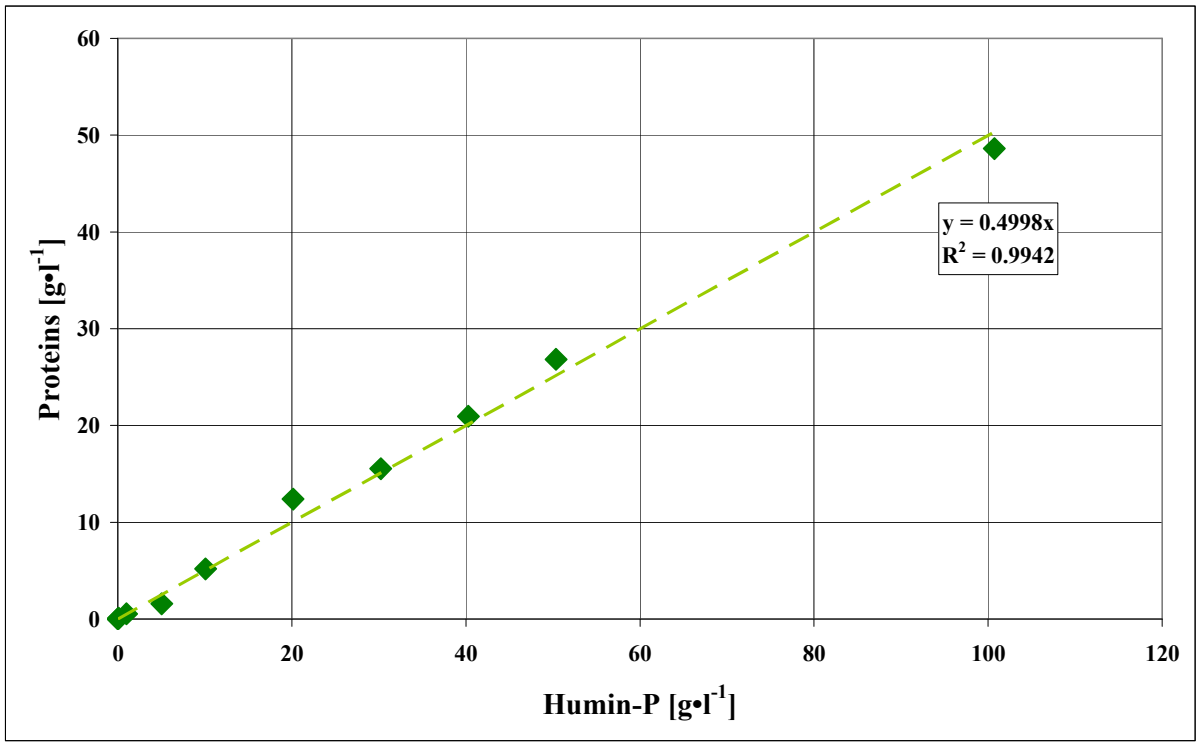

Figure A14: Dependene of Humin-P concentration on protein concentration

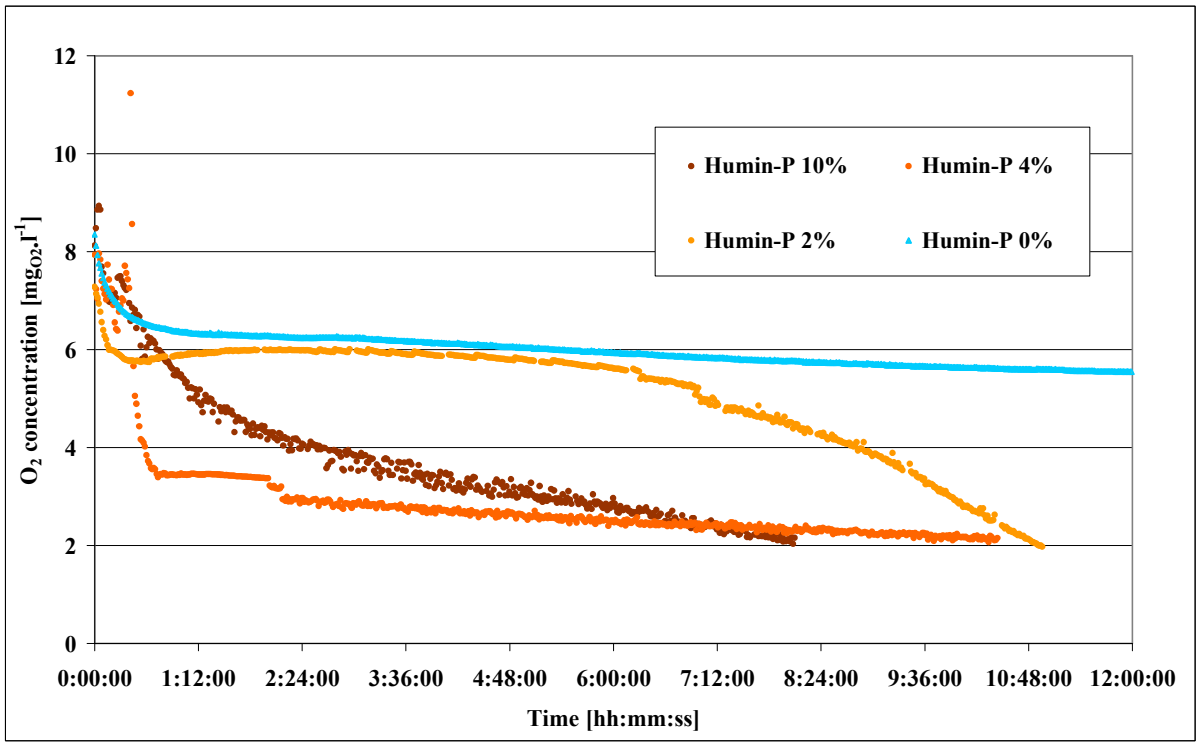

Figure A15: Oxygen (O_2) consumption of Humin-P-solutions

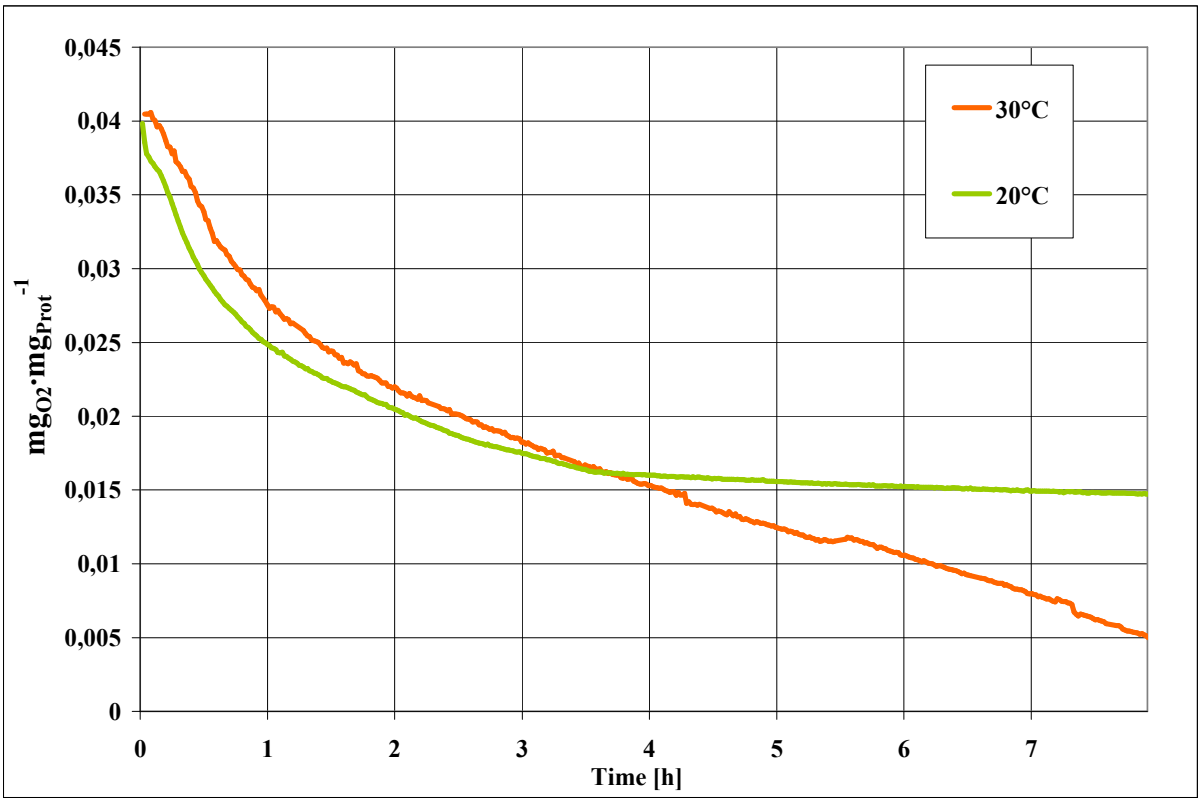

Figure A16: OUR at a temperature of 20 °C and 30 °C

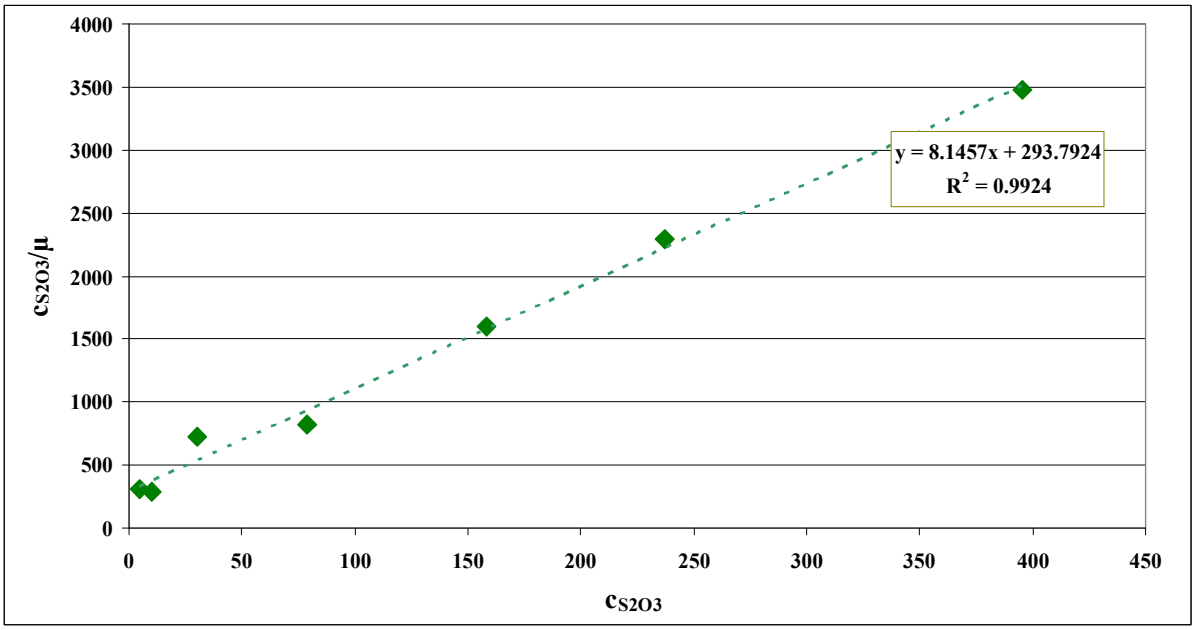

Figure A17: Example of Langmuir-plot for the determination of μ_{max} and K_m

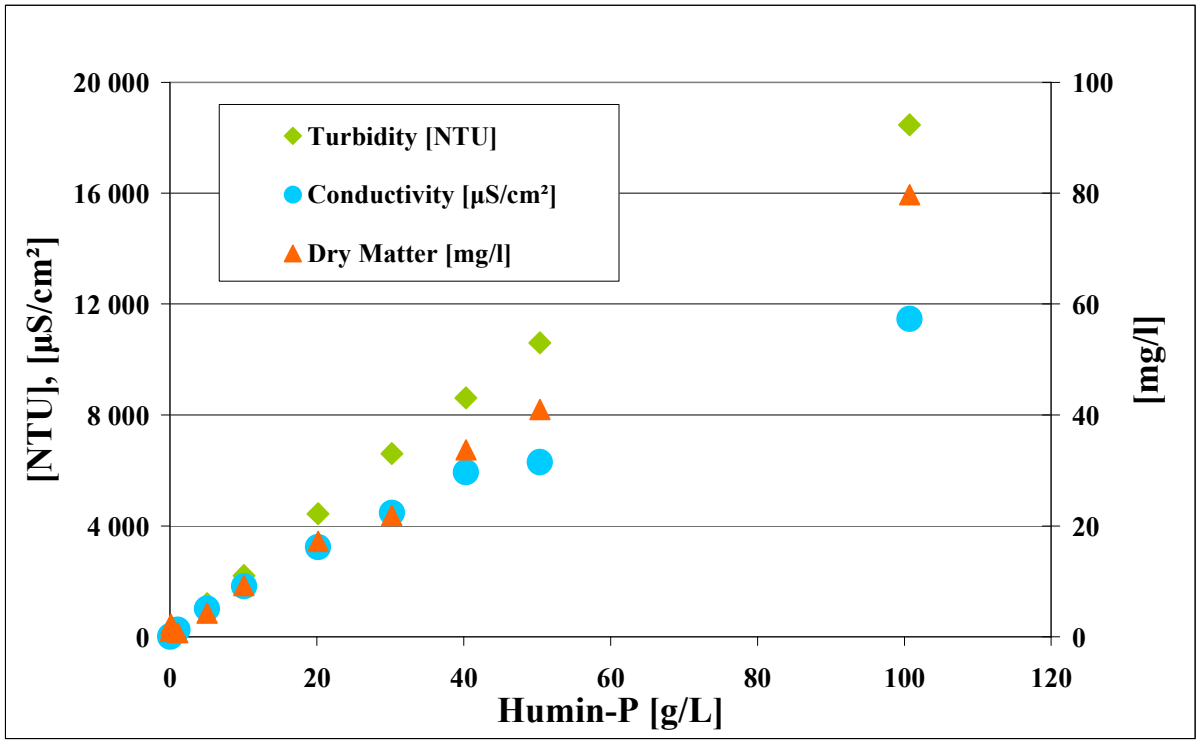

Figure A18: Relationship between Humin-P concentration and turbidity, conductivity and dry matter

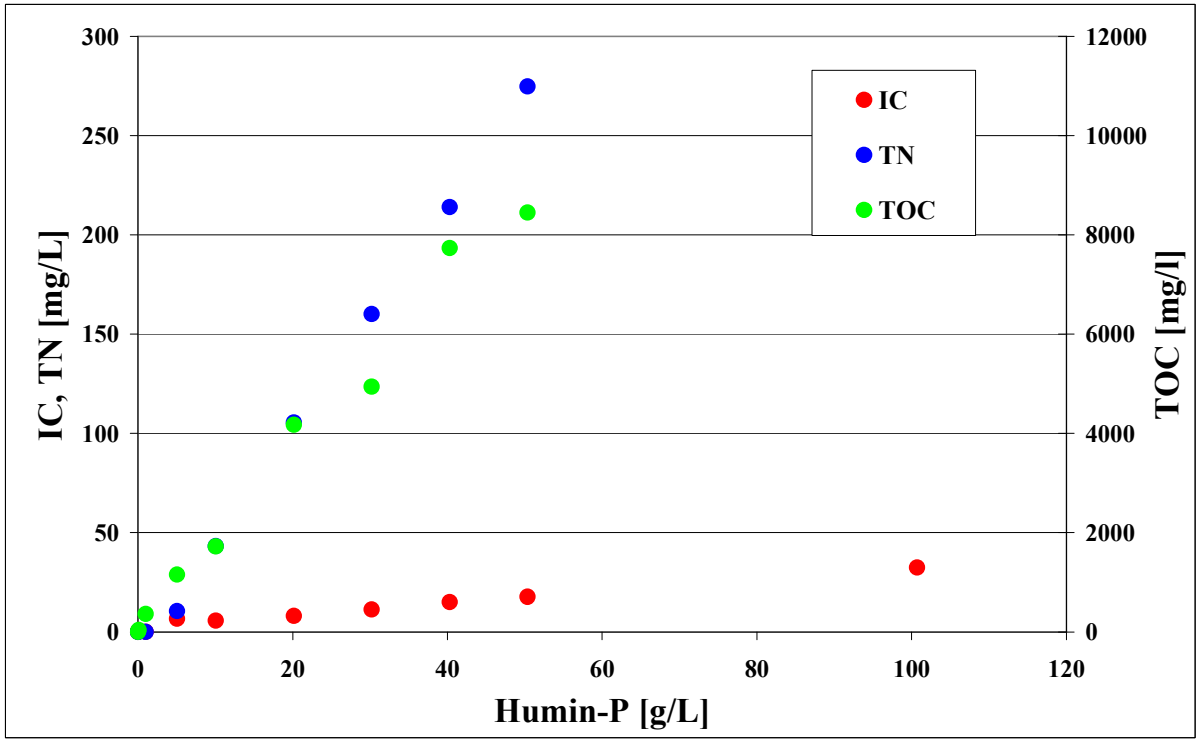

Figure A19: Relationship between Humin-P concentration and inorganic carbon (IC), total organic carbon (TOC) and total nitrogen (TN)

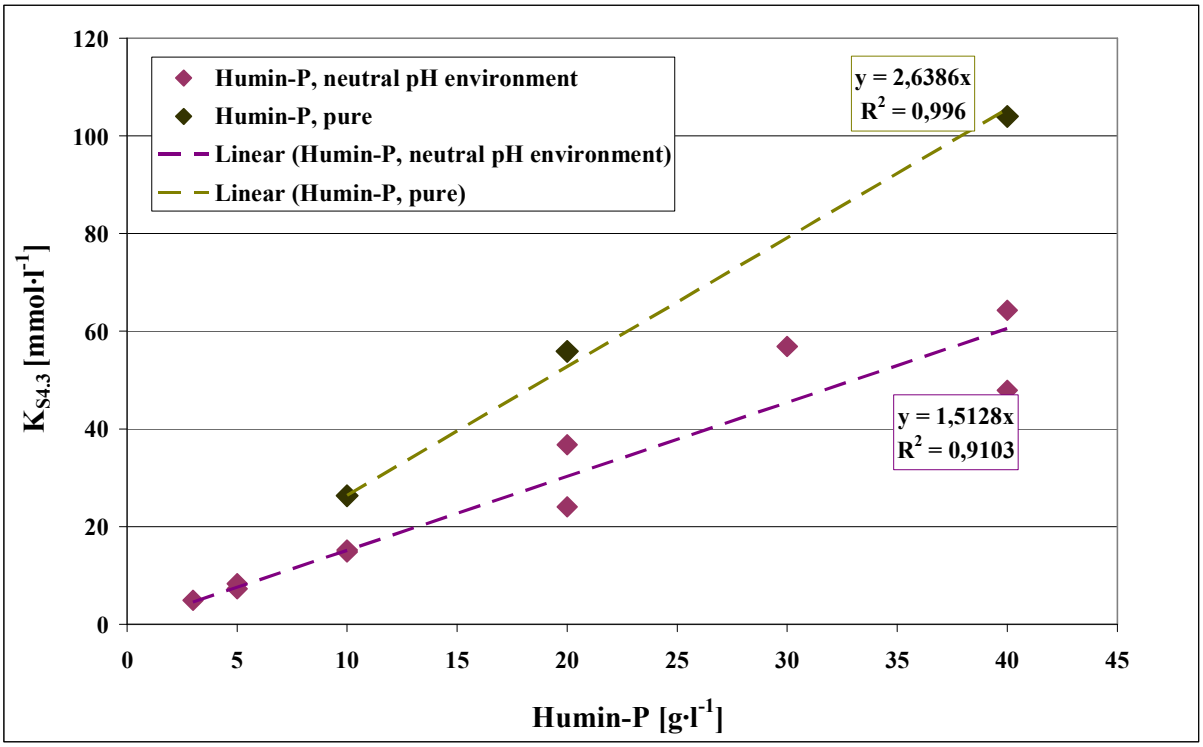

Figure A20: Buffer capacity $K_{S4.3}$ in dependence on Humin-P concentration

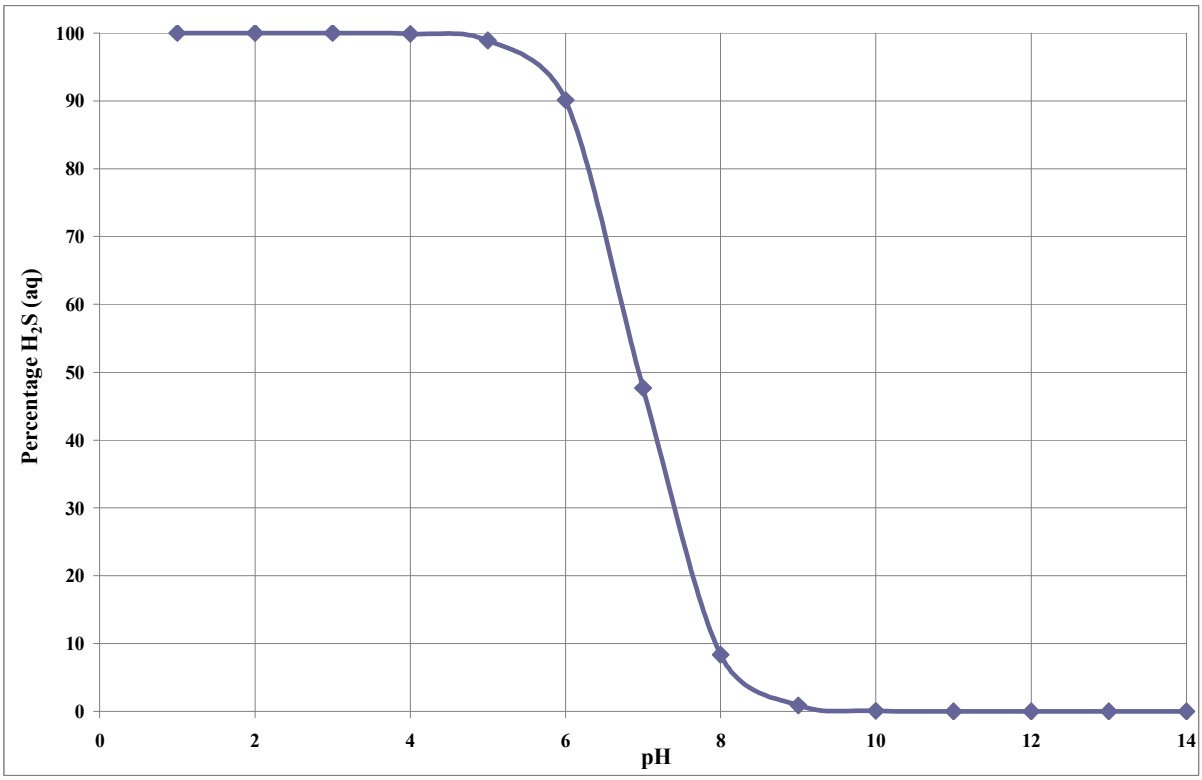

Figure A21: Aqueous H_2S in relation to the pH value

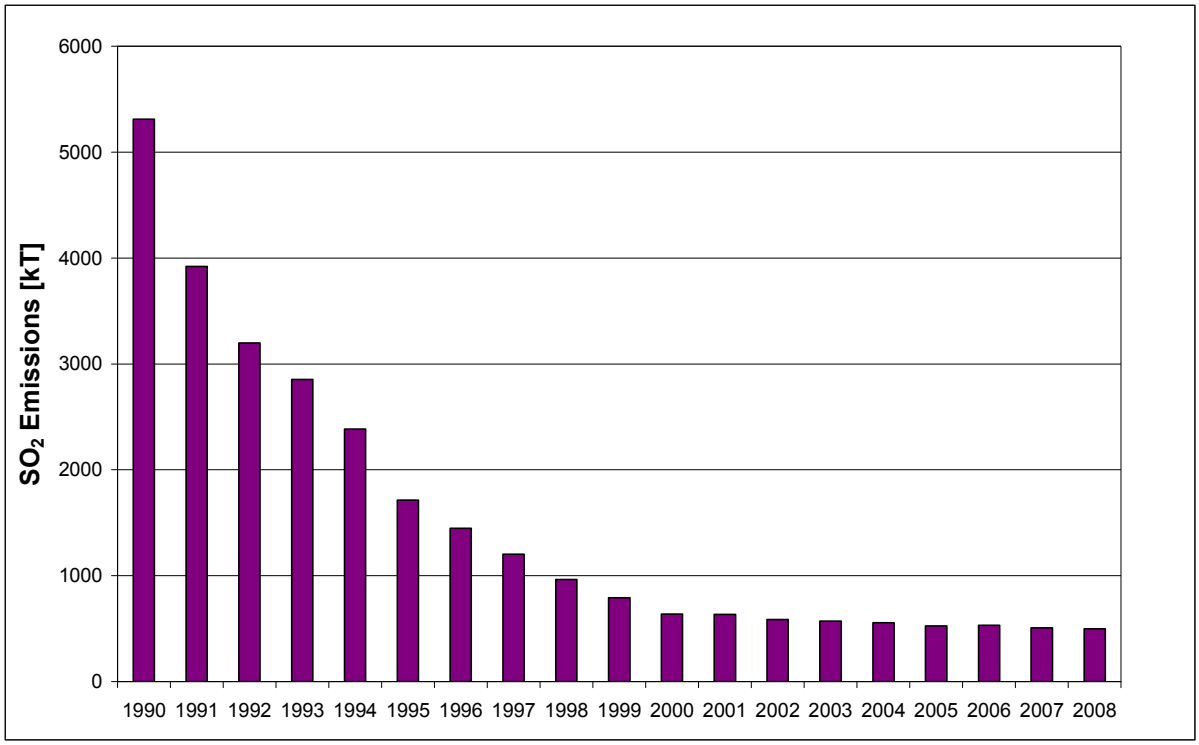

Figure A22: Emission Trends for Germany since 1990 (SO_2-Emission) [63]

Figure A23: Photos of biofilm formation of sulphur bacteria in pilot plant (from right to left: view in scrubber after the end of operation, view into flow sensor; outside view of flow sensor, sight glass of bioreactor)

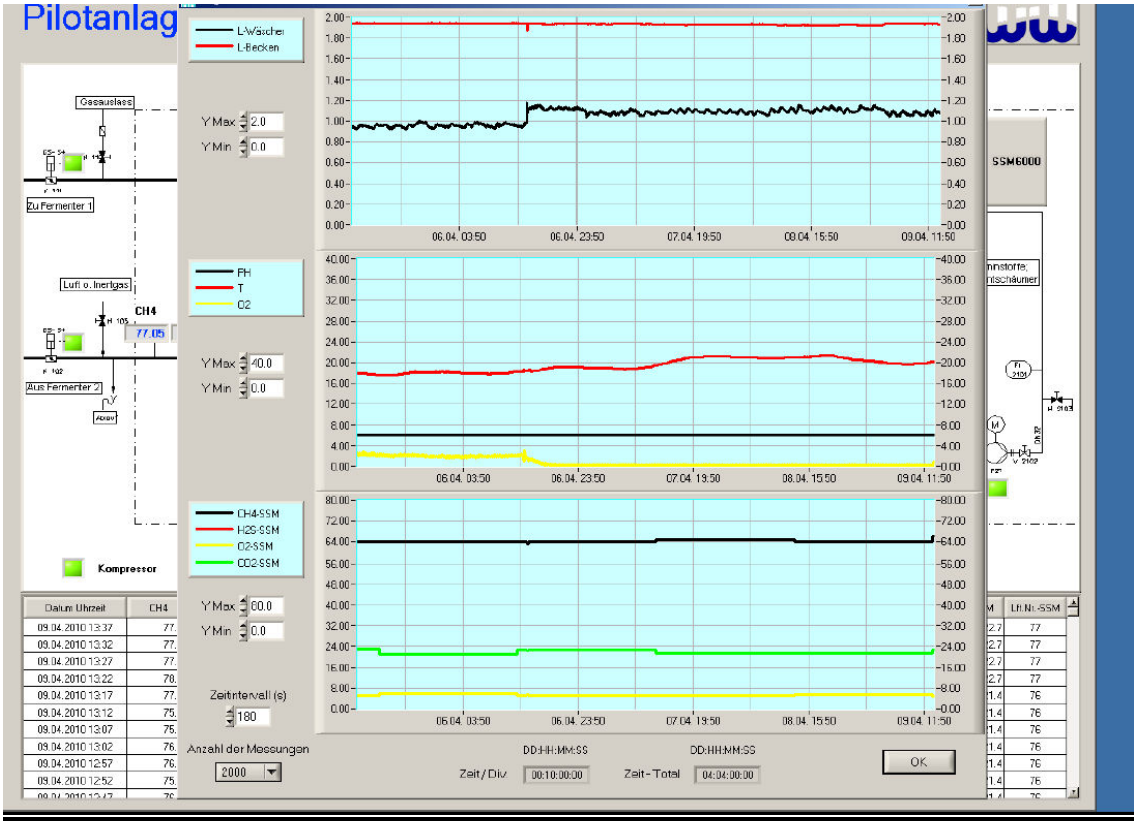

Figure A24: Screen shot of recording at pilot plant

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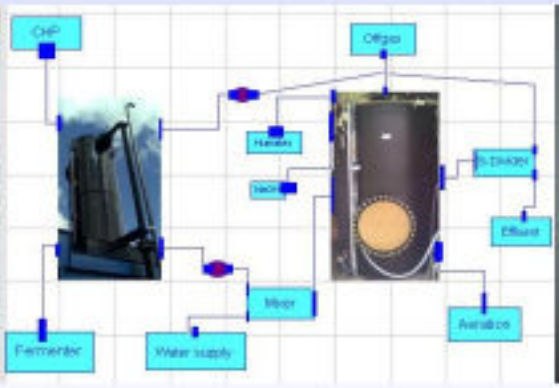
Hamburg University of Technology

The double stage biological desulphurisation, consisting of a scrubber with downstream biological regeneration, was improved using humic substances as solubilisers. The optimisation of H_2S removal by humic substances and the regeneration by sulphur bacteria of the washing liquid containing humic substances were analysed and evaluated. The experiments as well as the simulation of the scrubber showed that biogas can be desulphurised very efficiently by the addition of humic substances.



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