İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

CLEANING OF HYDROGEN SULPHIDE CONTAINING GASES : COMBINING SULPHUR AND NITROGEN CYCLES

M.Sc. Thesis by
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Department : **ENVIRONMENTAL ENGINEERING**

Programme: **ENVIRONMENTAL SCIENCES AND ENGINEERING**

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HİDROJEN SÜLFÜR İÇEREN GAZLARIN ARITILMASI : KÜKÜRT VE AZOT ÇEVRİMLERİNİN BİRLEŞTİRİLMESİ

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PREFACE

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ABBREVIATIONS

H_2S : Hydrogen Sulphide
SO_4^{2-} : Sulphate ion
NO_3^- : Nitrate ion
NO2- : Nitrite ion
CO_2 : Carbon Dioxide
S_{org} : Organic Sulphur
S^0 : Elemental sulphur
SO_2 : Sulphur dioxide
SO_3^{-2} : Sulphite ion
S^{-2} : Sulphide ion
HSO_4^- : Bisulphate
HS^- : Hydrosulphide anion
K_{H2S} : Equilibrium constant of solubility of H_2S in water
K_{HS-} : Equilibrium constant of solubility of HS^- in water
x_g : Mole fraction of gas within equilibrium of aqua phase
K_H : Henry Law constant
P_g : Partial pressure of gas
$S_2O_3^-$: Thiosulphate anion
(MEA) : Monothanolamine
(DEA) : Diethanolamine
(MDEA) : Methyldiethanloamine
(DIPA) : Disopropanolamine
NTA : Nitrilo acetic acid
EDTA : Ethylen diamine tetra acetic acid
Fe_20_3 : Iron Oxide
(LEDs) : Light emitting diodes
GSB : Green Sulphır Bacteria
ORP : Oxidation Reduction Potential
PLC : Programmable Logic Controller
HRT : Hydraulic Retention Time
EBRT : Empty Bed Retention Time
ΔG^o_m : Free Gibs' Energy
$Y_{SO4^{2-}/NO3^-}$: Yield value of used NO_3^- to produced SO_4^{2-} (mol/mol)
$Y_{SO4^{2-}/NO2^-}$: Yield value of used NO_2^- to produced SO_4^{2-} (mol/mol)
$Y_{S^0/NO3^-}$: Yield value of used NO_3^- to produced S^0 (mol/mol)
$Y_{S^0/NO2^-}$: Yield value of used NO_2^- to produced S^0 (mol/mol)
$Y_{SO4^{2-}/NO3^- + NO2^-}$: Yield value of used NO_3^- and NO_2^- produced SO_4^{2-} (mol/mol)
SS : Suspended Solids
VSS : Volatile Suspenden Solids
mV : milivolt

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CLEANING OF HYDROGEN SULPHIDE CONTAINING GASES : COMBINING SULPHUR AND NITROGEN CYCLES

SUMMARY

The oxidation of H_2S was carried out in continuous pilot scale absorption tower system using both nitrate and nitrite as electron acceptor in the presence of activated sludge. H_2S removal from biogas with autotrophic denitrification process by using nitrate and nitrite is an efficient process. Generally this process has been studied by labaratory scale experiments and wastewater is rarely prefered for this process. Specially synthetic nitrate and nitrite solutions are generally used in this process. And also, for autotrophic denitrification, this organisms are bioaugmented on activated sludge by using immobilized biofilters or other packing materials. In this study there is no sludge acclimation period, or there is no sludge recycle for sludge retention's expansion. Also there is no addition of trace and nutrient elements for growth of autotrophic denitrifiers. It is thought that all required chemical or biological necessities are supplied naturally from this industrial wastewater treatment plant. This thought is based on anaerobic reactor and biogas formation and also, activated sludge system for polishing treatment step by step.

The results of this study indicate that the potential of chemoautotrophic denitrification for the removal of hydrogen sulfide. The ratio of H_2S / NO_3 + NO_2 can be used to control the fate of sulfide oxidation to either elementel sulphur or sulphate.

Loading rates of wastewater and biogas and especially biogas/wastewater ratios are the main parameters to control the system for complete autotrophic denitrification. Specially, excessive H_2S loadings according to the stoichiometric relations cause an uncompleted denitrification reaction because of substrate inhibition. Also nitrite concentration in influent wastewater determines the reaction rate of nitrite and nitrate together. High nitrite concentrations force to H_2S reacts with nitrite instantly, and then nitrate removal starts

Products of anoxic sulphide oxidation were sulphate and elemental sulphur. Elemental sulphur is mainly the dominant end product of the reactions.

Oxidation Reduction Potential was the watching parameter on the system, and operating conditions could be controlled by this sensor. Sensitivity of this parameter gives an accurate observation on reactions.

These pioneering datas indicate that a simple and minimally managed system, comprised of absorption tower, biogas and wastewater feeding systems, can be effective in removing H_2S from biogas stream and also nitrate and nitrite removal with this autotrophic denitrification process. This study as a start-up work reveals some questions to be answered: Which conditions of study could be changed to reach higher removal rates of H_2S? Which sulphur products are formed? What are the limiting parameters?

HİDROJEN SÜLFÜR İÇEREN GAZLARIN ARITILMASI : KÜKÜRT VE AZOT ÇEVRİMLERİNİN BİRLEŞTİRİLMESİ

ÖZET

Bu çalışmada, biyogaz içerisindeki Hidrojen Sülfür'ün sürekli bir sistemde pilot ölçekli bir absorbsiyon kulesinde aktif çamur içerisinde elektron alıcısı olarak bulunan nitrat ve nitrit ile oksitlenmesi ele alınmıştır. Biyogaz içerisindeki Hidrojen Sülfür'ün nitrat ve nitrit ile ototrofik denitrifikasyon yolu ile giderilmesi etkili bir prosestir. Bu proses genellikle laboratuvar ölçekli sistemlerde çalışılmış, fakat bu çalışmalarda atıksu nadiren tercih edilmiştir. Özellikle sentetik nitrat ve nitrit çözeltileri bu proseslerde kullanılmaktadır. Ayrıca yapılan çalışmalarda ototrofik canlıların aktif çamur üzerinde çoğaltılması amacıyla canlıların üzerinde tutunabilmesini sağlayan dolgu malzemeleri ve biyofiltreler tercih edilmektedir. Yapılan bu çalışmada çamurun tutunma süresini artırmak için çamur geri devri veya çamurun ortama alıştırılması amacıyla herhangi bir sistem kullanılmamıştır. Ayrıca ototrofik organizmların geliştirilmesi amacıyla besi ve iz elementleri kullanılmamıştır. Bu çalışmada organizmların ihtiyacı olan tüm biyolojik ve kimyasal gereksinimlerin endüstriyel atıksu arıtma tesisinden karşılandığı kabul edilmiştir. Arıtma tesisinde bulunan anaerobik ve aerobik arıtma tesislerinin ve biyogaz oluşumunun doğal süreçler ışığında bu ihtiyaçları karşıladığı göz önüne alınmaktadır.

Bu çalışmanın sonuçları Hidrojen Sülfür'ün kemoototrofik denitrifikasyon yöntemi ile giderilebilirliğine işaret etmektedir. Sülfürün sülfat ve ya elementel kükürte oksidasyonunun H_2S / NO_3 + NO_2 oranları ile kontrol edilebileceği gösterilmeye çalışılmıştır.

Ototrofik denitrifikasyon prosesinin verimli çalışması bakımından atıksuyun ve biyogazın yükleme oranları en önemli parametreler olarak gözlemlenmiştir. Özellikle stokiyometrik oranlar dışındaki aşırı H_2S besleme oranlarında substrat inhibisyonundan dolayı denitrifikasyon reaksiyonun tam olarak gerçekleşmediği belirtilmiştir. Bununla beraber atıksu içerisindeki nitrit konsantrasyonu da nitrat ve nitritin reaksiyon oranlarını etkilemektedir. Yüksek nitrit konsantrasyonlarında H_2S öncelikle nitrit ile reaksiyona girmeye zorlanmış, daha sonra ise nitrat giderimi gözlenmiştir.

Anoksik sülfür oksidasyonunun reaksiyon ürünleri sülfat ve elementel kükürttür. Bu çalışmada elementel kükürtün son ürün olarak daha baskın olduğu gözlemlenmiştir.

Oksidasyon Redüksiyon Potansiyeli sistemdeki gözlem parametrelerinden biri olarak, işletme şartlarının belirlenmesinde bir kontrol parametresi olarak göze çarpmaktadır. Bu sensörün duyarlılığı reaksiyonların doğru bir şekilde gözlenmesinde etkili rol oynamaktadır.

Tüm bu öncü mahiyetindeki çalışmalar ve sonuçları, absorbsiyon kulesi, atıksu ve biyogaz besleme sistemlerinden oluşan kompakt bir sistem ile birlikte nitrat ve nitrit içeren atıksu ile ototrofik denitrifikasyon reaksiyonu sonucu biyogazdaki Hidrojen

Sülfür'ün etkili bir şekilde giderilmesinin basit ve masrafsız işletme koşullarıyla sağlanabileceğini göstermektedir.
Öncü bir çalışma olarak yapılan bu denemeler ışığında cevaplanması gereken bazı sorular ortaya çıkmaktadır: H_2S giderim oranlarının artırılması açısından hangi çalışma şartlarının değiştirilebileceği, son ürün olarak hangi sülfür türlerinin oluştuğu ve reaksiyon esnasında kısıtlayıcı faktörlerin neler olduğu?

1. INTRODUCTION

1.1 Meaning and Importance of This Study

Anaerobic treatment has successfully been used for many applications that have conclusively demonstrated its ability to recycle biogenic wastes. It has been successfully applied in industrial wastewater treatment, stabilisation of sewage sludge, landfill management and recycling of biowaste and agricultural wastes as organic fertilisers. Increasingly this treatment process is applied for degrading heavy organic pollutants such as chlorinated organic compounds or materials resistant to aerobic treatment.

Hydrogen sulfide is present in biogas produced during the anaerobic digestion of biodegradable substances. It is produced from the degradation of proteins and other sulfur containing compounds present in the organic feed stock to the digester [1]. Considerable amounts of hydrogen sulfide are also emitted from industrial activities such as petroleum refining, pulp and paper manufacturing, food processing, livestock farming [2]. It is also found in landfill biogas and is the principal odorous component in off-gases from wastewater collection and treatment facilities [3]. Biogas derived from these waste stabilization processes is not usually used as a renewable energy source, but rather flared off as excess gas when it is not used for space and process heating [4]. One of the biggest factors limiting the use of biogas is related to the hydrogen sulfide (H_2S) it contains, which is very corrosive to internal combustion engines [4].

This study deals with the integration of sulfur and nitrogen cycles to alleviate sulphur emissions. Combining sulfide removal with nitrate or nitrite allows not only to control H_2S in biogas but also improve nitrogen removal via autrotrophic denitrification without using extra carbon source.

1.2 Purpose and Scope of This Study

The purpose of this study is to control of the hydrogen sulphide in biogas with autotrophic denitrification process in an industrial wastewater treatment plant using a bubble type absorption tower fed with wastewater containing both nitrate and nitrite. By this process simultaneous H_2S oxidation to SO_4^{2-} and elemental sulphur and denitrification of nitrite and nitrate to N_2 gas is aimed. Specific objectives of this study described in this paper are;

- To determine the optimum operation conditions in this study with both nitrate and nitrite containing wastewater,
- to determine the allowable H_2S / NO_3^- + NO_2^- loading ratio that enables optimum hydrogen sulphide removal,
- to investigate the optimum biogas/wastewater ratio for maximum H_2S removal ratios,
- to investigate the stoichiometry of the microbial conversion of H_2S to sulfate and elementary sulphur using mass balance in a reactor under the studied conditions,
- to calculate the specific oxidation rate using nitrate and nitrite as an electron acceptor,
- to use ORP sensor as a controlling parameter to determine the H_2S removal efficiency comparing with NO_3 and NO_2 removal ratios.

In the scope of this study, wastewater and biogas loading rates are compared to obtain optimum removal efficiencies, different nitrite and nitrate concentrations and also different flowrates of wastewater and biogas are evaluated, pH and Oxidation Reduction Potential sensors are used to observe the electron transfer more accurately to lessen the control parameters in further researchs. By comparing stoichiometric relations of former studies, optimum experiment conditions are investigated.

2. LITERATURE REVIEW

2.1 Introduction

Anaerobic treatment has successfully been used for many applications that have conclusively demonstrated its ability to recycle biogenic wastes. It has been successfully applied in industrial wastewater treatment, stabilisation of sewage sludge, landfill management and recycling of biowaste and agricultural wastes as organic fertilisers. Increasingly this treatment process is applied for degrading heavy organic pollutants such as chlorinated organic compounds or materials resistant to aerobic treatment.

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Table 2.1: Requirements to remove gaseous components depending on the biogas utilisation [5]

Application	H_2S	CO_2	H_2O
Gas Heater (Boiler)	< 1000 ppm	no	no
Kitchen Stove	yes	no	no
Stationary Engine	< 1000 ppm	no	no condensation
Vehicle Fuel	yes	recommended	yes
Natural Gas Grid	yes	yes	yes

Boilers do not have a high gas quality requirement. Gas pressure usually has to be around 8 to 25 mbar. It is recommended to reduce the H_2S concentrations to values lower than 1.000 ppm which allows to maintain the dew point around 150°C. The sulphurous acid formed in the condensate leads to heavy corrosion. It is therefore recommended to use stainless steel for the chimneys or condensation burners and high temperature resistant plastic chimneys. Most of the modern boilers have tin-laminated brass heat exchangers which corrode even faster than iron chimneys [5]. Where possible, cast iron heat exchangers should be utilised. It is also advised to condense the water vapour in the raw gas. Water vapour can cause problems in the gas nozzles. Removal of water will also remove a large proportion of the H_2S, reducing the corrosion and stack gas dew point problems.

Gas engines do have comparable requirements for gas quality as boilers except that the H_2S should be lower to guarantee a reasonable operation time of the engine. Otto engines designed to run on petrol are far more susceptible to hydrogen sulphide than the more robust diesel engines. For large scale applications (> 60 kWel) diesel engines are therefore standard. Occasionally, organic silica compounds in the gas can create abrasive problems. If so, they should be removed [5]. Quality demands in different countries for utilisation of biogas as vehicle fuel are given in Table 2.2 [5].

Table 2.2: Quality demands in different countries for utilisation of biogas as vehicle fuel [5]

	Unit	France	Switzerland	Sweden
Wobbe index lower	MJ/nm^3			45,5
Wobbe index upper	MJ/nm^3			48,2
Water dewpoint	°C		5° lower than the lowest ambient temperature	
Energy content upper	kWh/nm^3	10.7		
Water content, maximum	mg/nm^3	100	5	32
Methane minimum	vol%		96	97
Carbon dioxide, maximum	vol%			3
Oxygen, maximum	vol%	3.5	0,5	1
Carbon dioxide, + oxygen + nitrogen, maximum	vol%	3	3	3
Hydrogen, maximum	vol%			0,5
Hydrogen sulphide, maximum	mg/nm^3	7	5	23
Total sulphure	mg/nm^3		14,3	
Particles or other solid contaminants, max. diameter	mm			5
Halogenated hydrocarbons	mg/m^3	1	0	

Currently, most commercial technologies for the removal of H_2S are chemically based and expensive to operate thereby negating all of the financial incentives associated with potential revenues from energy produced in a cogeneration plant [1].

2.2 Properties of Hydrogen Sulfide

2.2.1 Cycle of sulphur in nature

Hydrogen sulfide is one of the principal compounds involved in the natural cycle of sulfur in the environment. It occurs in volcanic gases and is produced by bacterial action during the decay of both plant and animal protein [6]. It can also be produced by bacteria through the direct reduction of sulfate. Significant concentrations of

hydrogen sulfide occur in some natural gas fields and in geothermally active areas [6]. Hydrogen sulfide can be formed whenever elemental sulfur or certain sulfur-containing compounds come into contact with organic materials at high temperatures. In industry, it is usually produced as an undesirable by-product, though it is an important reagent or intermediate in some processes. Hydrogen sulfide occurs as a by-product in: the production of coke from sulfur-containing coal, the refining of sulfur-containing crude oils, the production of carbon disulfide, the manufacture of viscose rayon, and in the Kraft process for producing wood pulp [6]. In Figure 2.1 biological sulphur cycle is shown [7].

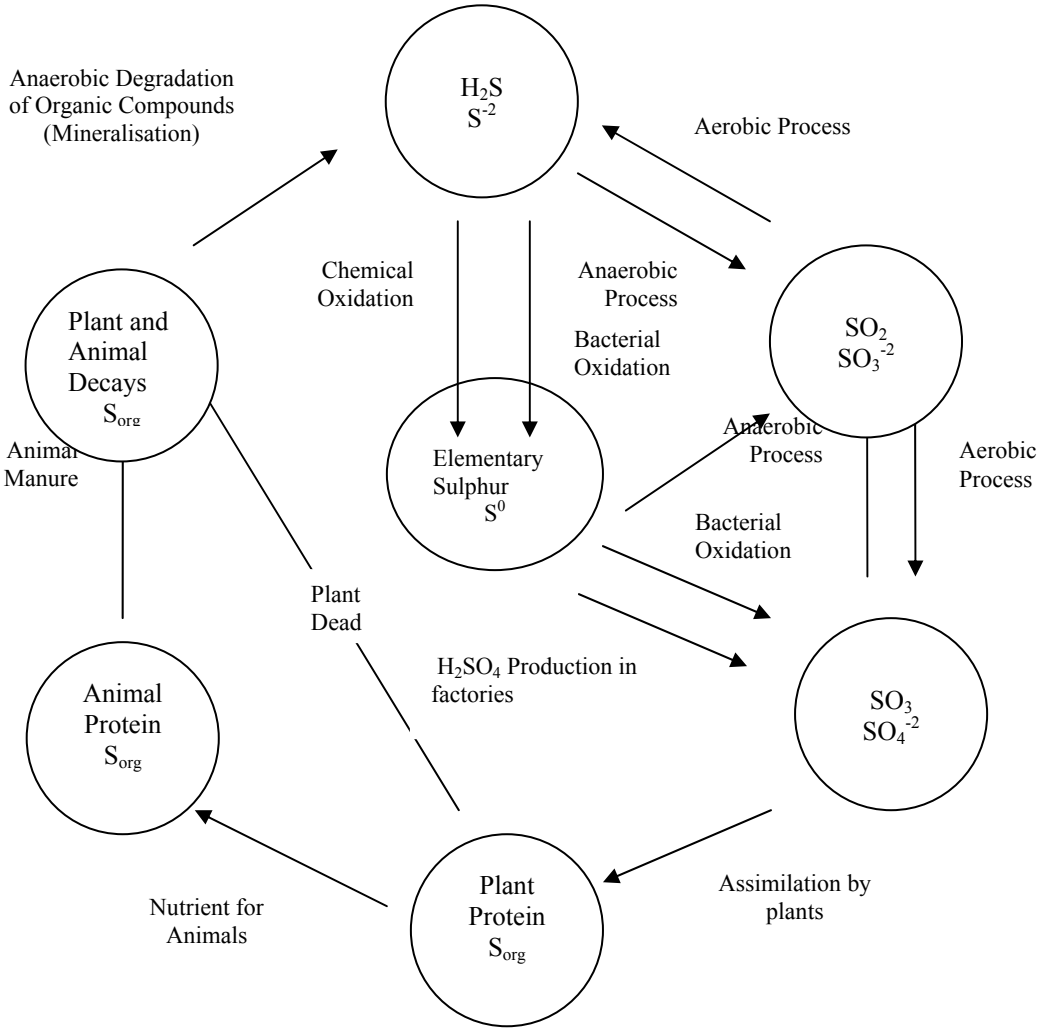

Figure 2.1: Sulphur Cycle in Nature [7]

2.2.2 Sulphur species in nature

There are lots of sulphur species in municipal and industrial wastewaters. At least number of 30 molecular inorganic and ionic sulphur compounds are present, but termodinamically just 6 of them are stable in room temperature [8]. These are; Bisulphate (HSO_4^-), sulphur (S^0), hydrogen sulfide (H_2S), bisulphide (HS^-), sulphate (SO_4^{-2}) and sulphide (S^{-2}). Tiosulphates, polysulphates and polythionates are present in nature and these compounds are instable and generally below threshold concentrations [8].

Sulphates (SO_4^{-2})

Sulphates are originated on the earth in the forms of mineral gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), epsomite ($MgSO_4.7H_2O$) and mirabylite ($Na_2SO_4.10H_2O$). Concentrations of sulphate ions on surface waters are 10-80 mg/L. Sulphates meet the surface water by from rocks, soils, other sulphur species' biochemical oxidations, atmospheric collapse, municipal and industrial discharges. Typical concentration of sulphate in municipal wastewater is 60-250 mg/L [8].

Sulphites (SO_3^{-2})

Sulphites are occured from wastewaters and SO_2 usage for dechloronization of treated water. In addition to this, it is present in boilers where addition of sodium sulphite to decrease the dissolved oxygen to prevent the corrosion. In high concentrations, sulphite decreases the pH and causes corrosion. As sulphite discharging is occured on the surface waters, it is oxidized to sulphates rapidly. If sulphite concentration in wastewater is high, oxygen is consumed and oxygen concentration in water decreases, so it effects the life in water badly [8].

Sulphides (S^{-2})

Sulphide ions on surface waters have low concentrations. Sulphide ions are originated from biochemical degradation of sulphate ions which formed in high concentration of organic matter in anaerobic conditions [8]. Sulphides come out from

various industrial facilities especially, tannery, pulp and paper, oil refining, coal and gas production, anaerobic treatment and petrochemical industries [8].

2.2.3 Chemical and physical properties of hydrogen sulphide

Hydrogen sulfide is a colourless gas with a characteristic odour that is soluble in various liquids including water, alcohol, ether, and solutions of amines, alkali carbonates, and bicarbonates. Hydrogen sulfide is a flammable colourless gas with the characteristic odour of rotten eggs. It burns in air with a pale blue flame and, when mixed with air, its explosive limits are 4.3% to 46% by volume. Its autoignition temperature is 260°C. The relative molecular mass of hydrogen sulfide is 34.08. Its density is 1.5392 g/litre at 0°C and 760 min. The ratio density of hydrogen sulfide compared with air is 1.19. One gram of hydrogen sulfide dissolves in 187 ml of water at 10°C, in 242 ml of water at 20°C, in 314 ml of water at 30°C, and in 405 ml of water at 40°C [6].

Hydrogen sulfide can undergo a large number of oxidation reactions, the type and rate of the reaction and the oxidation products depending on the nature and concentration of the oxidizing agent. The principal products of such reactions are sulfur dioxide, sulfuric acid, or elemental sulfur. Aqueous solutions of chlorine, bromine, and iodine may react with hydrogen sulfide to form elemental sulfur. In the presence of oxides of nitrogen, the oxidation of hydrogen sulfide in the gas phase may result in the formation of sulfur dioxide or sulfuric acid but, in aqueous solution (pH 5-9), the primary product is elemental sulfur [6].

Hydrogen sulfide dissociates in aqueous solution to form 2 dissociation states involving the hydrosulfide anion (HS^-) and the sulfide anion ($S^{=}$).

$$H_2S(aq) \Leftrightarrow HS^-(aq) + H^+(aq) \qquad \textbf{(2.1)}$$

$$HS^-(aq) \Leftrightarrow S^{-2}(aq) + H^+(aq) \qquad \textbf{(2.2)}$$

Equilibrium constants of reactions at 25 ^oC are given below [9].

$$K_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]} = 1x10^{-7} \quad \textbf{(2.3)}$$

$$K_{HS^-} = \frac{[S^{-2}][H^+]}{[HS^-]} = 1x10^{-13} \quad \textbf{(2.4)}$$

Hydrogen sulfide is relatively insoluble gas. Its solubility is explained by Henry Law

$$x_g = K_H P_g \quad \textbf{(2.5)}$$

In equation (2.5) x_g, mole fraction of gas within equilibrium of aqua phase; K_H, Henry Law constant ve P_g, explains partial pressure of gas [10].

Fraction of Hydrogen Sulfide in gas is given in equation (2.6)

$$\%H_2S = \frac{100}{1 + K_{H_2S}/[H^+]} \quad \textbf{(2.6)}$$

2.2.4 Environmental levels and exposures

Hydrogen sulfide is a very toxic gas. Within a few seconds, it can cause coma, fainting and death. Health effects of H_2S on people are given in Table 2.3.

Table 2.3: Health effects of H_2S on people [11]

H_2S (ppm)	Contact Time	Physiological Effects
100	Hours	Irritation on nose and eyes
200	60 minutes	Headache, conscious loss
500	30 minutes	Vomit, sleeplessness,
1000	-	conscious loss , death

Though concentrations of hydrogen sulfide in urban areas may occasionally be as high as 0.050 mg/m^3 (0.033 ppm) with averaging times of 30 min-1 h, they are generally (below 0.0015 mg/m^3 (0.001 ppm). Peak concentrations as high as 0.20

mg/m^3 (0.13 ppm) have been reported in the neighbourhood of point sources. In a geothermal area, 1-h mean concentrations of up to 2 mg/m^3 (1.4 ppm) have been observed [5]. When hydrogen sulfide was accidentally released in an incident in Poza Rica, Mexico, in 1950, the number of deaths that followed indicated that exposure levels probably exceeded 1500-3000 mg/m^3 (1000-2000 ppm) [6].

It is believed that workers are not usually exposed to hydrogen sulfide concentrations above the occupational exposure limits of 10-15 mg/m^3 (7-10 ppm) (8-h time-weighted average) adopted by many governments. There are, however, numerous reports of accidental exposures to concentrations that have ranged from 150 mg/m^3 (100 ppm) to as high as 18 000 mg/m^3 (12 000 ppm) [6]. Such massive exposures to hydrogen sulfide have resulted either from leaks in industrial gas streams containing high levels of hydrogen sulfide or from the slow, insidious accumulation of hydrogen sulfide in low-lying areas. The second case may arise when hydrogen sulfide of biogenic origin is generated from such sources as sewage disposal plants and cesspools [6].

Hydrogen Sulfide cause corrosion on mechanical parts made of iron, steel, cupper etc. It cause corrosion specially in treatment plants' equipments and canalisation pipes. So the equipments exposed to this gas should be chosen carefully [9].

2.3 H_2S removal technologies from biogas streams

Hydrogen Sulphide removal methods from biogas can be collected in two main groups. These are pyhsicochemical methods and biotechnological methods. These methods are shown in Figure 2.2. In this study, the principles of processes, application areas in industries and negative and positive sides of processes are evaluated.

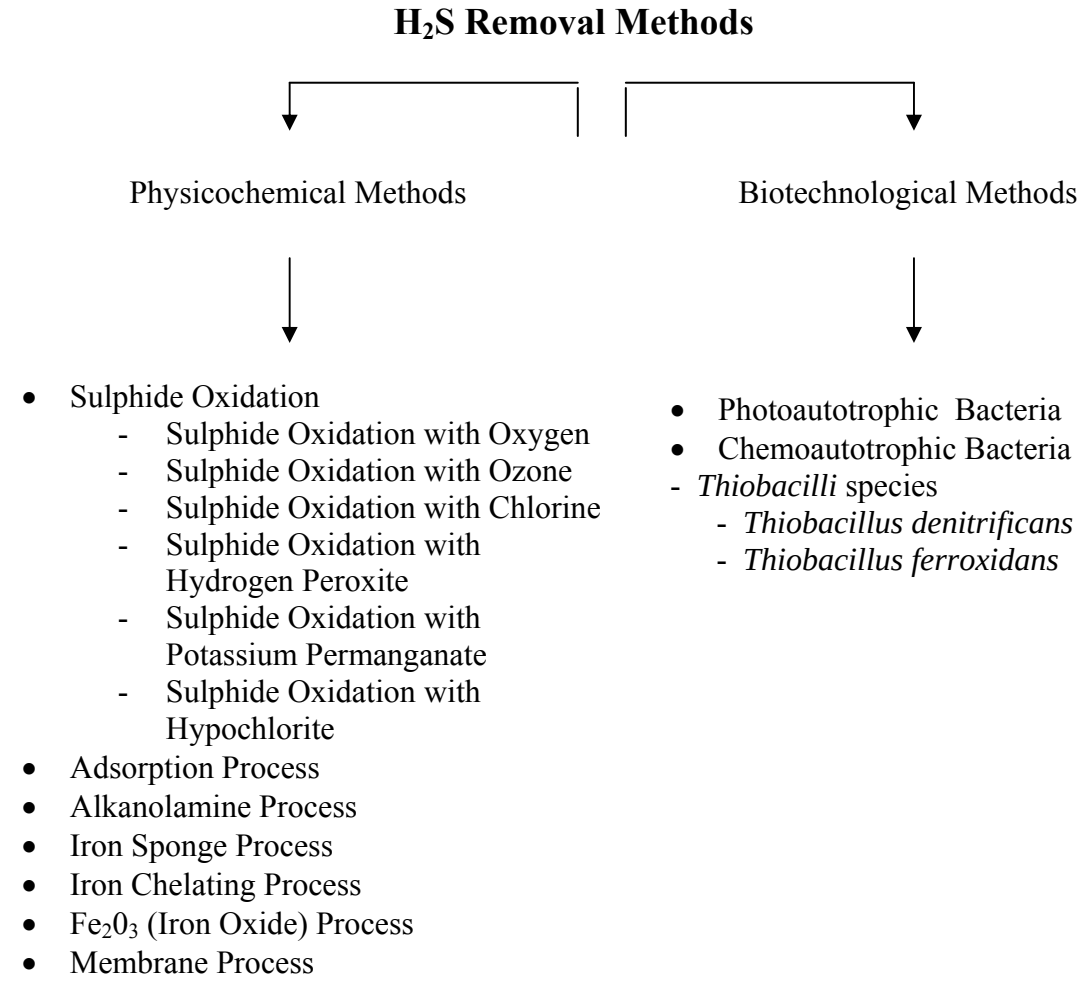

Figure 2.2: H_2S Removal Methods

2.3.1 Physicochemical methods

2.3.1.1 Sulphide oxidation

In chemical sulphide oxidation various oxidants can be used. These oxidants are; oxygen, chlorine, ozone, potassium per manganate, hydrogen peroxite and hypochlorite. The products formed by oxidation and necessity of oxidant material depend on pH and redox potential of solution [12].

Sulphide oxidation with oxygen

The principle of sulphide oxidation with oxygen is chemical transformation of sulphide to elemental sulphur or sulphate by oxygen. Sulphur compounds are oxidized in water phase by various ways.

H_2S is oxidized to; S^o, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-} . In these compounds valences of -2,0 and +6 are stable. The reactions of sulphide oxidation with oxygen are given below [13].

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad \textbf{(2.7)}$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{-2} + 2H^+ \quad \textbf{(2.8)}$$

Reaction mechanisms and nature of products are depended on pH of solution. On different pH values, reactions are given below.

Oxidation reactions in neutral, weak alkaline and weak acidic solutions are[14]:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad \textbf{(2.9)}$$

$$HS^- + (x-1)S \rightarrow H^+ + S_x^{-2} \quad \textbf{(2.10)}$$

Product S_x^{-2} is polysulphide and x values is 2-5 given. Polysulphides formed are reactive and give reaction with oxygen to build some products

Oxidation reactions in high alkaline solutions are[14]:

$$2HS^- + 3O_2 \rightarrow 2S0_3^{-2} + 2H^+ \quad \textbf{(2.11)}$$

$$2SO_3^{-2} + O_2 \rightarrow 2SO_4^{-2} \quad \textbf{(2.12)}$$

$$2SO_3^{-2} + 2HS^- + O_2 \rightarrow 2S_2O_3^{-2} + 2OH^- \quad \textbf{(2.13)}$$

As seen on the reactions, on high pH values Sulphur production is impossible. Also reaction is so slow on these pH values[14].

Sulphite, thiosulphate and sulphate are the most abundant products in sulphide oxidation processes. Elemental sulphur formation is depending on some special conditions. Additionally when bisulphide ions are dominant, sulphite, thiosulphate and sulphate are the main products occured [14]. The other factor that effects dispersion of reaction products is ratio of (S^{-2}/O_2). In high (S^{-2}/O_2) ratios elemental sulphur is dominant, in low (S^{-2}/O_2) ratios, sulphite, thiosulphate and sulphate are

formed[14]. When sulphide concentration is higher than 10^{-3} M, elemental sulphur is formed. In table 2.4 observed reaction products of different sulphide oxidation studies are given [9].

Table 2.4: Observed products in sulphide oxidation [9]

Researcher	pH	Reaction Solution	(S^{-2}/O_2) Ratio	Observed Products
Chen & Morris	6-5	Controlled	0.06-1.25	$S_x^{-2}, S^o, SO_3^{-2}, S_2O_3^{-2}, SO_4^{-2}$
Avrahami & Golding	11-14	Controlled	0.08-0.67	$S^o, S_2O_3^{-2}, SO_4^{-2}$
Cline & Richards	7-8	Sea Water	0.125-0.5	$SO_3^{-2}, S_2O_3^{-2}, SO_4^{-2}$
Skopintsev et al.	8.2	Sea Water	0.2-8.0	$SO_3^{-2}, S_2O_3^{-2}$
Demirjian	7-8.6	Controlled	0.03-5.0	$S^o, SO_3^{-2}, S_2O_3^{-2}, SO_4^{-2}$
Titova & Alferova	9-13	Controlled	20	$SO_3^{-2}, S_2O_3^{-2}, SO_4^{-2}$
O'Brien & Birkner	4-10.7	Controlled	1.0-1.37	$SO_3^{-2}, S_2O_3^{-2}, SO_4^{-2}$

Sulphide oxidation rates are depended on temperature, pH, induction period, sulphide ion concentration, oxygen concentration, neutral salt concentration, catalyzer abundance, microbial activity and presence of organic species [15].

Sulphide oxidation with ozone

Ozone is used to oxidize reduced sulphur compounds. Reaction stochiometry is given below [8].

$$S^{-2} + O_{3(g)} + H_2O \rightarrow S^0 + 2OH^- + O_2 \quad \textbf{(2.14)}$$

$$S^{-2} + 4O_{3(g)} \rightarrow SO_4^{-2} + 4O_2 \quad \textbf{(2.15)}$$

O_3 / S^{-2} molar ratio is 1:1 for elementary sulphur production. For sulphate production this ratio is 4:1 [8]

Sulphide oxidation with chlorine

Reduced sulphur compounds in aquatic solutions are oxidised with chlorine. Reaction stochiometry is given below [8]

$$Cl_2 + S^{-2} \rightarrow 2Cl^- + S^0 \quad \textbf{(2.16)}$$

$$4Cl_2 + S^{-2} + 4H_2O \rightarrow 8HCl + SO_4^{-2} \quad \textbf{(2.17)}$$

The reaction in these equations are occured very fast. When second reaction is dominant, system should be neutralised by adding alkalinity because of acid production. In experimental studies it was proved that, at high pH values more sulphur is produced. Good mixing, and slow chlorine dosage is needed for elementary sulphur production. In conditions of less chlorine addition and not enough mixing situation, oxidation products of thiosulphate, trithionate and sulphite are occured [8].

Sulphide Oxidation with Hydrogen Peroxite

Hydrogen Peroxite is an effective and powerful oxidant used for H_2S removal. Oxidation reaction is given below [7].

$$H_2S + H_2O_2 \rightarrow 1/xS_x + H_2O \quad \textbf{(2.18)}$$

x value is given 8 generally in this reaction.

Sulphide oxidation with potassium permanganate

Potassium permanganate is used successfully for removal H_2S from wastewater streams. Reaction stochiometry is given below [8].

$$8MnO_4^{-2} + 3S^{-2} + 4H_2O \rightarrow 8MnO_{2(s)} + 3SO_4^{-2} + 8OH^- \quad \textbf{(2.19)}$$

Sulphide oxidation with hypochlorite

Another method for removal of H_2S from biogas is alcaline hypochlorite treatment. In figure 2.3 this method is shown [11].

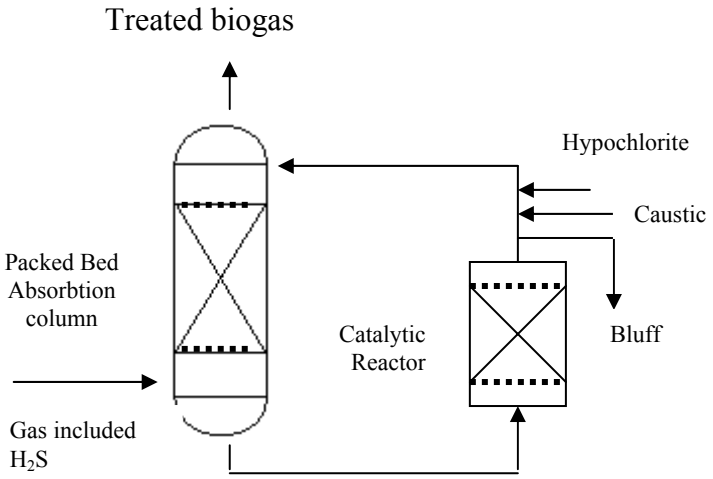

Figure 2.3: Hypochlorite oxidation to remove H_2S from biogas [11]

In this method, biogas including H_2S is given to the reactor from bottom and it is absorbed from alcaline hypoclorite solution given from top of the column. Liquid leaves the packed bed column sent to fixed bed reactor and in here H_2S is catalytically is oxidised by hypoclorite. After controlling pH and hypoclorite of liquid stream it is recycled to packed bed reactor [11].

According to the study that deals with chemical and biological technologies for hydrogen sulfide removal in sewer systems there is given a summary in Table 2.5 of literature related to chemical technologies for hydrogen sulfide emission control [12].

Table 2.5: Summary of literature related to chemical technologies for hydrogen sulfide emission control [12]

Chemicals	Ratio of chemicals to S (w/w)[a]	Scale and volume of reactor	Sulfide concentration in upstream ($mg\,S\,L^{-1}$)	Average elimination (%) of sulfide	Cost[b] (€ kg^{-1} S)
$FeCl_2 \cdot 4H_2O$	6.0–7.0:1	Plant scale, 59, 000 m^3[c]	More than 4.0	90	22.4–26.1
$FeSO_4 \cdot 7H_2O$	1.7:1	Plant scale, 25,000 $m^3 d^{-1}$	18.0–25.0	95–97	4.8
$FeClSO_4$	1.2:1	Plant scale, 25,000 $m^3 d^{-1}$	18.0–25.0	88–98	4.5
$FeCl_2$ and $FeCl_3$[d]	2.5:1	Plant scale, 75,000 $m^3 d^{-1}$	6.4	97	7.2
$FeCl_3$	1.5:1	Lab scale, 3.00 L	3.8	100	3.7
H_2O_2	4.0:1	Plant scale, 76,000 $m^3 d^{-1}$	15.0	85–90	10.6
H_2O_2	1.5–1.6:1	Plant scale, 2000 m^3[c]	8.5	90–95	4.0–4.2
H_2O_2	1.3:1	Plant scale, 25,000 $m^3 d^{-1}$	20.0	87–100	3.5
Cl_2	9.0:1	Plant scale, 90,000 $m^3 d^{-1}$	18.0	100	2.7
Cl_2	10.0–15.0:1	–	–	–	2.8–4.2
NaClO	2.0:1	Plant scale, 25,000 $m^3 d^{-1}$	20.0	96–100	2.6
$Ca(ClO)_2$	1.8:1	Plant scale, 25,000 $m^3 d^{-1}$	20.0	93–100	1.9
NaClO and NaOH[d]	1.0:1	Plant scale, 25,000 $m^3 d^{-1}$	18.2	100	1.9
$KMnO_4$	6.0–7.0:1	–	–	–	18.9–22.0
$NaNO_3$	6.7:1	Lab scale, 0.05 L	54.0	100	12.2
$NaNO_3$	0.18:1	Lab scale, 1.37 L	35.0	65	0.4

2.3.1.2 Adsorption Process

H_2S removal from gas streams can be done on various adsorbents depending on the temperature of the feed gas. In the case of a hot gas, inorganic adsorbents such as zinc oxide or new cerium-based materials were shown to be very efficient. When the process occurs at room temperature the catalytic reactions are less feasible and the combined factors of the porosity of adsorbents and their surface chemistry start to play an important role [13]. One group of porous adsorbents, which are often used for desulfurization at room temperature, are activated carbons. They have high surface area and developed porosity where small molecules of hydrogen sulfide or methyl mercaptan can be physically adsorbed [13]. Moreover, the carbon surface has catalytic properties owing to the presence of functional groups and free valences at the edges of graphene sheet. They take part in the oxidation of sulfur containing light

gases to elemental sulfur or sulfuric acid [13]. The latter is formed when water is present in the system. Unfortunately, due to the weak catalytic nature of activated carbon centers, only a relatively small amount of hydrogen sulfide can be retained on virgin, unmodified carbon [13]. To improve their performance, they are generally impregnated with caustic materials such as NaOH or KOH, or otherwise modified [14]. The presence of humidity facilitates the surface reaction of H_2S oxidation. The disadvantage of the application of caustic impregnated carbons is their low ignition temperature, which may result in self-ignition of a carbon bed [14]. This caused unmodified activated carbons to become attractive candidates to remove hydrogen sulfide, especially at low concentration in the ppm level. Generally, the process has been studied at two different conditions. One approach uses oxidation of hydrogen sulfide at temperature range from 100 to 250 ºC and dry conditions at low oxygen concentration, whereas another is based on oxidation at a room temperature in the presence of moist air [14]. The performance of activated carbons as hydrogen sulfide adsorbents depends on their porosity and surface chemistry. Pores act as storage space for oxidation products, which are mainly elemental sulfur, sulfur dioxide and/or sulfuric acid. Presence of chemical environment, favorable for dissociation of H_2S enhances adsorption by facilitating its dissociation to HS^- ions, which are further oxidized by active oxygen radicals to polysulfides and sulfur polymers [14].

2.3.1.3 Alkanolamine process

Amine processes constitute the largest portion of liquid-based gas purification technologies for removal of acid gases. They are attractive because they can be configured with high removal efficiencies, designed to be selective for H_2S or both CO_2 and H_2S, and are regenerable. Drawbacks of using an amine system, as with most liquid-based systems, are more complicated flow schemes, foaming problems, chemical losses, higher energy demands, and how to dispose of foul regeneration air [16].

Alkanolamines generally contain a hydroxl group on one end and an amino group on the other. The hydroxyl group lowers the vapor pressure and increases water

solubility, while the amine group provides the alkalinity required for absorption of acid gases [16]

The dominant chemical reactions occurring are as shown in equations [16]

$$H_2O = H^+ + OH^- \quad \textbf{(2.20)}$$

$$H_2S = H^+ + HS^- \quad \textbf{(2.21)}$$

$$CO_2 + H_2O = HCO_3^- + H^+ \quad \textbf{(2.22)}$$

$$RNH_2 + H^+ = RNH_3^+ \quad \textbf{(2.23)}$$

$$RNH_2 + CO_2 = RNHCOO^- + H^+ \quad \textbf{(2.24)}$$

Typically used amines include monothanolamine (MEA), diethanolamine (DEA), methyldiethanloamine (MDEA), and diisopropanolamine (DIPA). Adsorption is typically conducted at high pressures with heat regeneration in the stripper. The basic flow-scheme for an alkanolamine acid-gas removal process is depicted in Figure 2.4.

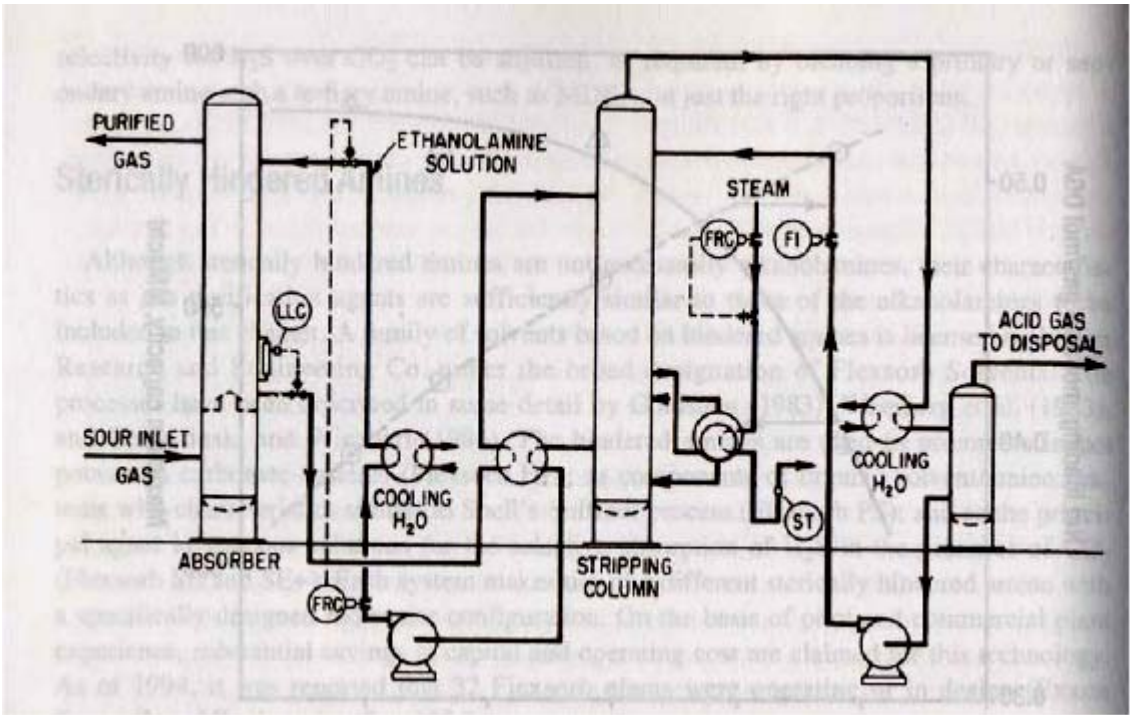

Figure 2.4: Flow Scheme for Alkanolamine Acid-gas Removal Processes [16]

In this process, H_2S containing gas is given to absorption tower from bottom, while rising it meets with amine solution in low concentration that is pumped on the top of the tower. H_2S and CO_2 is absorbed in lean amine solution. Enriched solution that

leaves the column crosses the heat exchanger (steam) and is heated by lean amine solution and posted to the top of stripping column. Treated gas leaves absorption tower. Heat in bottom of stripping tower is gained by using amine boiler and sour gases are aparted from enriched amine solution. Gas leaving the stripping column is cooled to condensate steam and pumped to column again [11].

Sour gas that leaves stripping column contains H_2S and CO_2. This gas is sent to Claus process directly to recover elementary sulphur. This gas is called Claus gas. In this process H_2S is sent to furnace by stochiometric rated air supply, and 1/3 ratio of H_2S is converted to SO_2 [11].

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \quad \Delta H = -518.5 \text{ kJ} \qquad \textbf{(2.25)}$$

H_2S and SO_2 reacts to form elementary sulphur in Claus reaction.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \quad \Delta H = -109.6 \text{ kJ} \qquad \textbf{(2.26)}$$

2.3.1.4 Iron sponge process

Iron Sponge method for removal H_2S from biogas is the oldest and unregenerated removal process. This method is generally is desirable for low flowrates of gases or ultimate cleaning process after treated gas streams in capacious facilities. In this process, H_2S containing gas is crossed flow through a tank that filled with iron oxide and sawdust according to the reaction [11].

$$Fe_2O_3xH_2O + 3H_2S \rightarrow Fe_2S_3 + (x+3)H_2O \qquad \textbf{(2.27)}$$

Air is added to gas instantly (%0.6-1.0 volume). Oxygen reacts with iron sulfide and iron oxide and elementary sulphur is occured.

$$2Fe_2S_3 + 3O_2 + xH_2O \rightarrow 2Fe_2O_3xH_2O + 6S \qquad \textbf{(2.28)}$$

When total sulphur amount reach to %50-90, reactant is disposed and freshed with new material. If gas contains CO_2, this process is so selective for H_2S [11].

Their surface to weight ratio is excellent thanks to the low density of wood. Roughly 20 grams of hydrogen sulphide can be bound per 100 grams of iron oxide chips. The application of wood chips is very popular particularly in the USA. It is a low cost product, however, particular care has to be taken that the temperature does not rise too high while regenerating the iron fitler [5].

2.3.1.5 Iron chelating process

This method is liquid redox process specially depended on iron. In figure 2.5 there is shown an iron-redox system. Process includes contactor, regenerator and filter. Gas is fed from bottom of the column and Fe^{+3} solution is given from top. While Fe^{+3} is reducing to Fe^{+2}, sulphur in H_2S is converted to elementary sulphur [11].

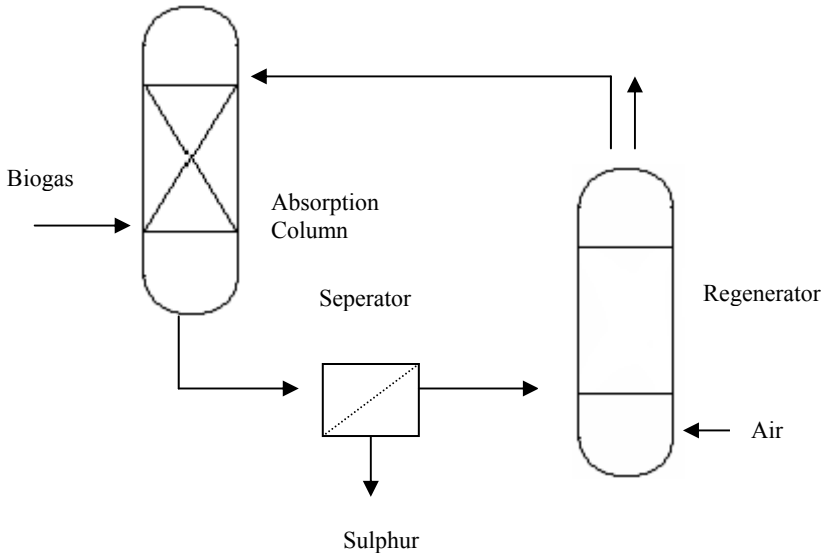

Figure 2.5: Iron-redox system

Liquid leaves the column from bottom is filtered, and sulphur is concentrated. Then it is disposed from system, and filtrate is recycled to the process. Iron used in process has a low solubility in solutions. To prevent this situation, it is retained by a chelate or ligand in the solution. Mostly used chelats are NTA (nitrilo acetic acid), EDTA

(ethylen diamine tetra acetic acid). Iron chelate concentration in solution is 10-1000 mol/m^3.

Fe^{+2} occured in absorption column is sent to regenerator and here it reacts with oxygen, and is oxidised to Fe^{+3}. After regeneration is completed Fe^{+3} solution is recycled to absorption column. Reaction is given in equation 2.29.

$$2Fe^{+3} + H_2S \rightarrow 2Fe^{+2} + S^0 + 2H^+ \qquad \textbf{(2.29)}$$

An industrial scaled system used for gas treatment by iron chelating is shown in Figure 2.6.

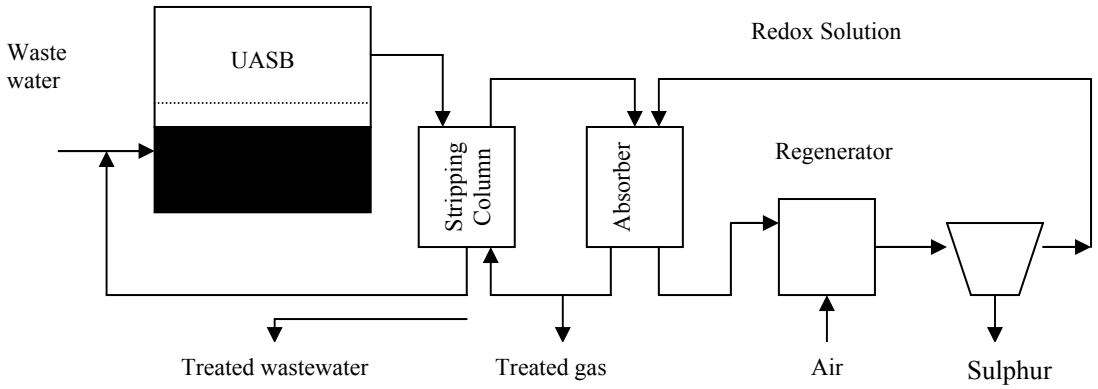

Figure 2.6: Iron-chelate system for H_2S removal [11]

Here, biogas meets with redox solution and H_2S converts to elementary sulphur. Some amount of treated biogas is recycled back to stripping column, and soluble sulfide in aquatic phase is passed through gas phase. So inhibition of sulfide in anaerobic reactor is decreased [11].

2.3.1.6. Fe_20_3 (iron oxide) process

Hydrogen sulphide reacts easily with iron hydroxides or oxides to iron sulphide. The reaction is slightly endothermic, a temperature minimum of approximately 12°C is therefore required to provide the necessary energy [5]. The reaction is optimal between 25 and 50°C. Since the reaction with iron oxide needs water the biogas should not be too dry. However, condensation should be avoided because the iron

oxide material (pellets, grains etc.) will stick together with water which reduces the reactive surface [5]. The iron sulphides formed can be oxidised with air, i. e. the iron oxide is recovered. The product is again iron oxide or hydroxide and elementary sulphur. The process is highly exothermic, i.e. a lot of heat is released during regeneration. Therefore, there is always a chance that the mass is self-ignited. The elementary sulphur formed remains on the surface and covers the active iron oxide surface. After a number of cycles depending on the hydrogen sulphide concentration the iron oxide or hydroxide bed has to be exchanged [5]. Usually an installation has two reaction beds. While the first is desulphurising the biogas, the second is regenerated with air. The desulphurisation process works with plain oil free steel wool covered with rust. However, the binding capacity for sulphide is relatively low due to the low surface area [5] .

Equation of reaction are given below.

$$H_2S + Fe^{+2} \rightarrow FeS + 2H^+ \quad \textbf{(2.30)}$$

$$3H_2S + 2Fe^{+3} \rightarrow Fe_2S_3 + 6H^+ \quad \textbf{(2.31)}$$

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad \textbf{(2.32)}$$

2.3.1.7 Membrane process

There are two basic systems of gas purification with membranes: a high pressure gas separation with gas phases on both sides of the membrane, and a low-pressure gas liquid absorption separation where a liquid absorbs the molecules diffusing through the membrane [5].

High pressure gas separation

Pressurised gas (36 bar) is first cleaned over for example an activated carbon bed to remove (halogenated) hydrocarbons and hydrogen sulphide from the raw gas as well as oil vapour from the compressors [5]. The carbon bed is followed by a particle filter and a heater. The membranes made of acetate-cellulose separate small polar molecules such as carbon dioxide, moisture and the remaining hydrogen sulphide. These membranes are not effective in separating nitrogen from methane. The raw gas

is upgraded in 3 stages to a clean gas with 96 % methane or more [5]. The waste gas from the first two stages is recycled and the methane can be recovered. The waste gas from stage 3 (and in part of stage 2) is flared or used in a steam boiler as it still contains 10 to 20 % methane [5]. First experiences have shown that the membranes can last up to 3 years which is comparable to the lifetime of membranes for natural gas purification - a primary market for membrane technology - which last typically two to five years. After 1½ years permeability has decreased by 30 % due to compaction. The clean gas is further compressed up to 3.600 psi (250 bar) and stored in steel cylinders in capacities of 276 m^3 divided in high, medium and low pressure banks [5]. The membranes are very specific for given molecules, i.e. H_2S and CO_2 are separated in different modules. The utilisation of hollow-fibre membranes allows the construction of very compact modules working in cross flow.

Gas-liquid absorption membranes

Gas-liquid absorption using membranes is a separation technique which was developed for biogas upgrading only recently [5]. The essential element is a microporous hydrophobic membrane separating the gaseous from the liquid phase. The molecules from the gas stream, flowing in one direction, which are able to diffuse through the membrane will be absorbed on the other side by the liquid flowing in counter current. The absorption membranes work at approx. atmospheric pressure (1 bar) which allows low-cost construction [5]. The removal of gaseous components is very efficient. At a temperature of 25 to 35°C the H_2S concentration in the raw gas of 2 % is reduced to less than 250 ppm [5]. The absorbent is either Coral or NaOH. H_2S saturated NaOH can be used in water treatment to remove heavy metals. The H_2S in Coral can be removed by heating. The concentrated H_2S is fed into a Claus reaction or oxidised to elementary sulphur. The Coral solution can then be recycled. CO_2 is removed by an amine solution. The biogas is upgraded very efficiently from 55% CH_4 (43 % CO_2) to more than 96% CH_4 [5]. The amine solution is regenerated by heating. The CO_2 released is pure and can be sold for industrial applications.

2.3.2 Biotechnological methods

To biologically address the problem of malodorous air, open-bed soil filters began to be used in the 1920's and industrial soil biofilters first appeared in the United States during the 1950's, but operation was not well understood [16]. Sulfur compounds are a major component of malodor in gases and are produced during biochemical reduction of inorganic or organic sulfur compounds. Many soils do exhibit a small chemical adsorption capacity for H_2S that is heavily dependent on the iron content of the soil [16]. It has since been determined that sustained effectiveness of soil or other biofiltration beds arises primarily from microbial oxidation of organic compounds, leading to biomass formation and nontoxic odorless products, or oxidation of inorganic compounds (such as sulfides), which supply energy to cells and produce odorless compounds like elemental sulfur and sulfate in the process [16].

Biologically active agents have since been used in a variety of process arrangements, such as biofilters, fixed-film bioscrubbers, and suspended-growth bioscrubbers [16]. These processes may also be effective at removing multiple contaminants from a gas stream, increasing their functionality. Fluidized-bed bioreactors have recently been tested for simultaneous removal of H_2S and NH_3 with promising results [17]. It is also possible to achieve co-treatment of volatile organic compounds and H_2S in the same biofilter [16].

2.3.2.1 Bacteria used in bioreactors

Figure 2.7 shows conversions of different species of sulfur by naturally occurring bacteria where a complete oxidation to elemental sulfur is occurring. Such a situation often occurs in nature and is called a sulfuretum. A typical example is a pond in autumn where fallen leaves are the source of organic matter [17]. Different bacteria tend to live in areas of the pond where their particular capabilities provide them with an ecological niche. Near the water surface, chemotrophic bacteria dominate where they can obtain their energy from the aerobic oxidation of H_2S and S^0 to form SO_4^{2-}. In the deep anaerobic zone, anaerobic decomposition of organic matter occurs and H_2S is produced. In the upper anaerobic zone where light can still penetrate and H_2S

is available, growth of phototrophic bacteria occurs. These bacteria find suitable conditions for growth only in a narrow zone of overlap since sulfide and light occur in opposite gradients. In these narrow layers, they obtain reducing electrons from either H_2S or S^0 [17]. The desirable bacteria to be used in a bioprocess to convert H_2S to S^0 should possess the following basic features: reliable capability of converting H_2S to S^0, minimum nutrient inputs, and easy separation of S^0 from the biomass. Relevant photoautotrophs and chemotrophs are discussed below.

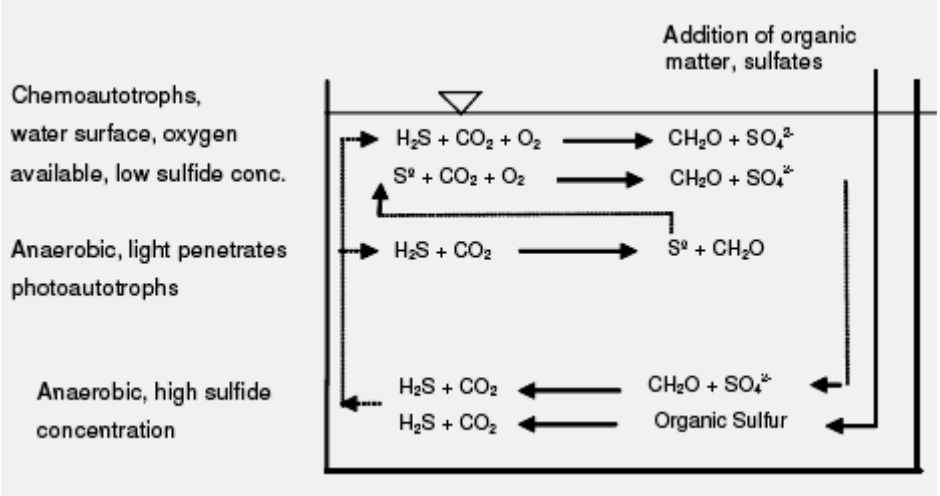

Figure 2.7: Cycling of sulfur in a sulfuretum [17]

Photoautotrophs

Studies on microbial ecology associated with phototrophic bacteria have shown that a species of green sulfur bacteria (GSB) *Cholorobium limicola* (originally called *Cholorobium limicola* forma *thiosulfatophilum* is the most suitable for sulfide removal and satisfies the criteria for a desirable bacterium [18]). *Cholorobium limicola* is capable of oxidizing sulfide to elemental sulfur, requires only light, CO_2, and inorganic nutrients for growth and is strictly anaerobic. GSB are nonmotile and deposit elemental sulfur extracellularly [18]. This feature makes GSB suitable where the recovery of elemental sulfur from sulfide-containing wastewater is desired. The overall photochemical reaction by which GSB oxidizes S^{2-} to S^0 while reducing CO_2 to carbohydrates is :[18]

$$2nH_2S + nCO_2 \xrightarrow{light\ energy} 2nS^0 + n(CH_2O) + nH_2O \quad \textbf{(2.33)}$$

Studies involving phototrophic bacteria are summarized in Table 2.6. Cork et al. (1985) introduced the concept of the "van Niel curve" by plotting the reactor feed rate as a function of irradiance (W/m^2) for their batch-fed reactor system [19] (Fig. 2.8). The curve describes the relationship between S^{2-} loading rate and light intensity (radiant flux). When light intensity and sulfide flow rate were adjusted to a point on the curve (balanced loading), all of the sulfide introduced to the reactor was oxidized to elemental sulfur without the formation of sulfate [19]. Under sulfide overloading conditions (to the right of the curve), light energy was not sufficient and sulfide accumulated in the reactor. When the reactor was in a sulfide underloading condition (to the left of the curve), the surplus light caused the formation of sulfate as shown by Eq. 2.34 [19].

$$nH_2S + 2nCO_2 + 2nH_2O \xrightarrow{light\ energy} nSO_4^{2-} + 2n(CH_2O) + 2nH^+ \quad \textbf{(2.34)}$$

Therefore, only when the bioreactor system is adjusted to operate "on the curve", sulfide removal is complete and a maximum amount of elemental sulfur is produced.

Table 2.6: Research conducted in hydrogen sulfide removal using photoautotrophs [19]

Reference	Configuration+	Volume* (L)	Influent (H_2S	S^{2-} loading (mg h^{-1} L^{-1})	Removal efficiency	Irradiance- (W/m^2)
Kobayashi et al. (1983)	FF, U	8	16 mg/L in liquid	0.59-1.27	81-92	NQ
Kobayashi et al. (1983)	FF, plug	0,1	19-24 mg/L in liquid	102-125	100	NQ
Cork et al. (1985)	SG, CSTR	0,8	Gas, concentration unknown	74-109	100	150-2000
Maka and Cork (1990)	SG, CSTR	0,8	1-2 mM in gas	32-64	90-100	139
Kim et al. (1991)	SG, CSTR	4	2.1 mM in gas	61	>99	1200
Kim et al. (1992)	SG, CSTR	4	2.1 mM in gas	64	100	1750
Kim et al. (1996)	SG, CSTR	11,9	1.45-1.87 mM in gas	14,6-19	99,8	15,2
Basu et al. (1996)	SG, CSTR	1,25	25,000 ppm in gas	94,4	>96,6	ID
Henshaw et al (1997)	SG, CSTR	13,7	90-550 mg/L in liquid	2,1-5,6	>90	258
Henshaw and Zhu (2001)	FF	0,02	141-380 mg/L in liquid	111-286	82-100	25,4
Syed and Henshaw (2003)	FF	0,0048	91-164 mg/L in liquid	1323-1451	100	152

+ CSTR = continuously stirred tank reactor; FF = fixed-film; SG = suspended-growth; U = upflow

* Volume = wet volume of reactor

- ID = insufficient data to calculate; NQ = not quantified

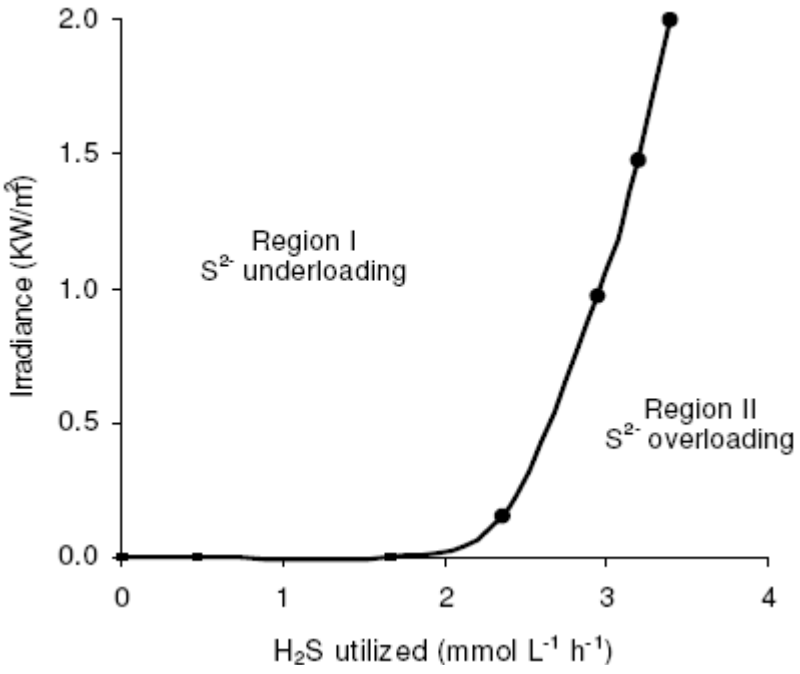

Fig. 2.8: van Niel Curve [19]

The *in vivo* light absorption spectrum of *C. limicola* exhibits light absorption between 350 and 850 nm with a peak at 760 nm [18]. The authors describe two different conditions under which the quality of light available is different. In shallow ponds, relatively rich in organic matter, except near the air-water interface, the water is oxygen-free allowing gren sulfur bacteria to grow close to the water surface. There they obtain light of long wavelength, which is transmitted through the overlying aerobic phototrophs, and the light, in the far red and near-infrared regions, used by the GSB for photosynthesis is almost entirely absorbed by bacteriochlorophylls [18]. The second environment occurs in lakes where a warmer, aerobic layer covers a stagnant layer that is cold and oxygen-free. GSB grow in a narrow horizontal band, situated just within the anaerobic layer. In this case, the overlying water column acts as a light filter, transmitting only green and blue-green light, of wavelengths between 450 and 550 nm [18]. Carotenoids become the dominant light harvesting pigments and the GSB in this environment typically contain a very high carotenoid content [18].

In another study, liquid batch cultures of *C. limicola* grew well, with the oxidation of all available sulphide, as indicated by the production of sulphur granules, residual sulphide concentrations below detection limits and further oxidation of the sulphur to

sulphate [20]. Additionally, batch cultures preserved well at 4 ºC for up to 2 months. Continuous cultures also converted nearly all the available sulphide supplied as sodium sulphide, with mass balance efficiencies >95% even when the culture biomass was declining. Further oxidation to sulphate resulted from sulphide limiting conditions and/or high light levels [24]. The oxidation of a gaseous sulphide source was highly efficient, in excess of 95% with a high biomass and a gas flow rate of 60 ml min^{-1} [20].

Chemoautotrophs

A number of chemotrophs are suitable for the biodegradation of H_2S. These bacteria grow and produce new cell material by using inorganic carbon (CO_2) as a carbon source and chemical energy from the oxidation of reduced inorganic compounds such as H_2S [21]. In the presence of reduced organic carbon sources (glucose, amino acids, etc.), some of these bacteria (so-called mixotrophic microorganisms) can grow heterotrophically, using the organic carbon as a carbon source and an inorganic compound as an energy source [21]. Biodegradation of H_2S by chemotrophs occurs in aerobic conditions with O_2 as an electron acceptor or in anaerobic conditions with alternative electron acceptors (e.g. nitrate), depending on the type of bacteria [21]. Examples of energy sources for representative chemotrophs are presented in Table 2.7 [21].

Table 2.7: Examples of energy sources for representative chemotrophs [21]

Bacteria	Electron Donor	Electron Acceptor	Carbon Source	Products
Thiobacilllus sp. (general)	S^0, H_2S, $S_2O_3^{2-}$	O_2	CO_2	SO_4^{2-}
Thiobacilllus denitrifcans	S^0, H_2S, $S_2O_3^{2-}$	O_2, NO_3^-	CO_2	SO_4^{2-}, N_2
Thiobacilllus ferrooxidans	Fe^{2+}, S^0, $S_2O_3^{2-}$	O_2	CO_2	Fe^{3+}, SO_4^{2-}

The metabolism of species such as *Thiobacillus, Thermothrix, Thiothrix, Beggiato* has been intensively studied for oxidation of inorganic (elemental sulfur, hydrogen sulfide, thiosulfate) or organic (methanethiol, dimethylsulfide, dimethyldisulfide) sulfur compounds [21]. These microorganisms grow in soil, aquatic habitats, activated sludge systems, etc. under aerobic, microaerophilic, and anaerobic conditions [21]. Characteristics of some of these microorganisms are presented in Table 2.8 [21].

Table 2.8: Characteristics of some microorganisms implicated in degradation of H_2S or other sulfur compounds [21].

Conditions	Microorganisms								
	Thiobacillus ferrooxidans	*Thiobacillus thiooxidans*	*Thiobacillus novellus*	*Thiobacillus thioparus*	*Thiobacillus denitrificans*	*Thermothrix azorensis*	*Thiothrix nivea*	*Thioalkalispira microaerophila*	*Thiomicrospra frisia*
pH growth range	-	0.5 - 6.0	[a]5.7 - 9.0	5 - 9	-	6.0 - 8.5	6 - 8.5	8 - 10.4	4.2 - 8.5
Optimum pH	1.3 - 4.5	2.0 - 3.5	7.0	7.5	6.8 - 7.4	7.0 - 7.5	-	10	6.5
Temperature growth range (°C)	10 - 37	10 - 37	[a]10 - 37	-	-	63 - 86 (thermophile)	-	-	3.5 - 39
Optimum temperature (°C)	30 - 35	28 - 30	30	28	28 - 32	76 - 78	15 - 30	-	32 - 35
* G+C content of DNA (mol%)	56 - 59	-	67.2	62	63	39.7	44 - 55	58.9	39.6
Cells type	Gram-negative	Gram-negative	[a]Gram-negative	Gram-negative	-	Gram-negative	Gram-negative or Gram-variable	Gram-negative	Gram-negative
Group	-	-	[a]α-2 Proteobacteria	β-Proteobacteria	β-Proteobacteria	β-Proteobacteria	[b]γ-Proteobacteria	γ-Proteobacteria	γ-Proteobacteria
Spore formation	None	None	None	-	-	None	-	-	-
Motility	0 to several polar or petrichous flagella	-	Non-motile	Motile	Motile by means of a polar flagellum	Motile	No flagella	Motile by means of a single polar flagellum	Motile
Shape	Rod, 0.5-1.0 µm	Rod, 0.5 x 1.1-2.0 µm	Rod, 0.4-0.8 x 0.8-2.0 µm	Rod, 0.9-1.8 µm	Rod, 0.5 x 1.0-3.0 µm	Rod, 0.3-0.8 x 2-5 µm	Rod, 0.7-2.6 x 0.7-5.0 µm	Spirillum, 0.3-0.45 x 1-4 µm	Bent-rod, 0.3-0.5 x 1.0-2.7 µm
Trophy	Obligate chemoautotroph	Obligate chemoautotroph	Mixotroph (faculative chemoautotroph)	Obligate chemoautotroph	Obligate chemoautotroph	Obligate chemoautotroph	Mixotroph (faculative chemoautroph)	Obligate chemoautotroph	Obligate chemoautotroph
Examples of energy source	Ferrous ion and reduced sulfur compounds	Hydrogen sulfide, polithionates, elemental sulfur	Hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide	Thiosulfate, sulfide	Thiosulfate, tetrathionate, thiocyanate, sulfide, elemental sulfur	Thiosulfate, tetrathionate, hydrogen sulfide, elemental sulfur	Inorganic sulfur compounds, simple organic compounds, sugars	Sulfide, polysulfide, elemental sulfur, thiosulfate	Thiosulfate, tetrathionate, sulfur, sulfide
Oxygen requirement	Facultative anaerobe **	Strictly aerobe	[a]Strictly aerobe	Strictly aerobe	Facultataive anaerobe ***	Strictly aerobe	Strictly aerobe and microaerophile	Strictly aerobe and microaerophile	Strictly aerobe
Sulfur deposit	-	-	-	Extracellular	-	Intracellular	Intracellular	Intracellular	Extracellular
Reference	Colorado School of Mines[¶]	Takano et al. (1997)	Cha et al. (1999) [a]Kelly et al. (2000)	Vlasceanu et al. (1997)	Kelly and Wood (2000)	Odintsova et al. (1996)	Howarth et al. (1999), [b]Prescott et al. (2003)	Sorokin et al. (2002)	Brinkhoff et al. (1999)

* G = guanine; C = cytosine
** Under anaerobic conditions, *T. ferrooxidans* can grow on elemental sulfur using ferric iron as an electron acceptor.
*** Grows as an anaerobic chemoautroph by using nitrate, nitrite, or nitrous oxide.

Thiobacillus sp. is widely used in studies of the conversion of H_2S and other sulfur compounds by biological processes [22]. These bacteria have the ability to grow under various environmental stress conditions such as oxygen deficiency, acid conditions, etc. Many *Thiobacillus sp.* (i.e. *T. thiooxidans*, *T. ferrooxidans*) have acidophilic characteristics and are able to develop in conditions of low pH (1-6). *Thiobacillus thiooxidans* has a great tolerance for acidic conditions and can grow at pH<1 [22]. Thiobacilli such as *T. thiooxidans* and *T. Ferrooxidans* are used in processing digested sludge or leaching lowgrade metal ores because of their ability to remove metals by microbial leaching [21]. Other *Thiobacillus* sp. (e.g. *T. thioparus, T. denitrificans, T. novellus*) develop in neutral medium (neutrophilic bacteria) at pH of 6-8 [22]. *Thiobacillus denitrificans* is able to grow facultatively on reduced sulfur compounds by reducing nitrate (NO_3^-) to nitrogen gas (N_2) [23]. *Thiobacillus novellus* is a mixotroph Thiobacilli because it can grow heterotrophically [24].

Other species are able to degrade sulfur compounds in neutrophilic, alkaline, or thermophilic conditions. *Thermothrix azorensis* and *Thiothrix nivea* are neutrophilic bacteria and develop well at pH of 6-8 [21]. Optimum growth temperature for *Thermothrix azorensis*, a thermophilic bacterium, is between 76 and 86ºC [21]. *Thioalkalispira microaerophila* is able to grow in alkaline conditions and attains optimum growth at pH 10 [21].

The reaction shown in Eq. 2.35 takes place in an aerobic sulfide removal system [21].

$$H_2S + CO_2 + nutrients + O_2 \xrightarrow{Chemetrophs} cells + S\ and/or\ SO_4^{2-} + H_2O \qquad \textbf{(2.35)}$$

Under oxygen limiting conditions, sulfur is the major end product, while sulfate is formed when sulfide is limited. Other relevant reactions are shown in Table 2.9 [1].

Table 2.9: Reactions involving chemotrophic bacteria [1].

Bacteria	Reaction mechanism	Reference
Thiobacillus thioparus	$2HS^- + O_2 \rightarrow 2S^0 + 2OH^-$ $2S^0 + 3O_2 + 2OH^- \rightarrow 2SO_4^{2-} + 2H^+$	Chung et al. (1996)
	$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$	Kim et al. (2002)
Thiobacillus denitrificans	$3HS^- + 3.9NO_3^- + 0.2NH_4^+ + HCO_3^- + 1.7H^+ \rightarrow CH_{1.8}O_{0.5}N_{0.2} + 1.9N_2 + 3SO_4^{2-} + 2.3H_2O$ $14.5HS^- + 5NO_3^- + 0.2NH_4^+ + HCO_3^- + 20.3H^+ \rightarrow CH_{1.8}O_{0.5}N_{0.2} + 2.5N_2 + 14.5S + 27.4H_2O$	Kleerebezem and Mendez (2002)
	$55S + 20CO_2 + 50NO_3^- + 38H_2O + 4NH_4^+ \rightarrow 4C_5H_7O_2N + 25N_2 + 55SO_4^{2-} + 64H^+$	Lampe and Zhang (1996)
	$5HS^- + 8NO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O$	McComas and Sublette (2001)
Thiobacillus ferrooxidans	$2FeSO_4 + H_2SO_4 + 1/2\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$	Mesa et al. (2002)
	$2FeS_2 + 7.5O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4$	Takano et al. (1997)

2.3.2.2 Bioreactors for H_2S removal involving phototrophic bacteria

Gas-fed batch reactor

Typically a gas fed batch reactor (Fig. 2.9) is a stirred tank type reactor, continuously or intermittently operated for the gas phase (the target flux) and cyclically operated for the liquid phase (nutritive solution). The microorganisms can be suspended in the solution or immobilized on different media [1].

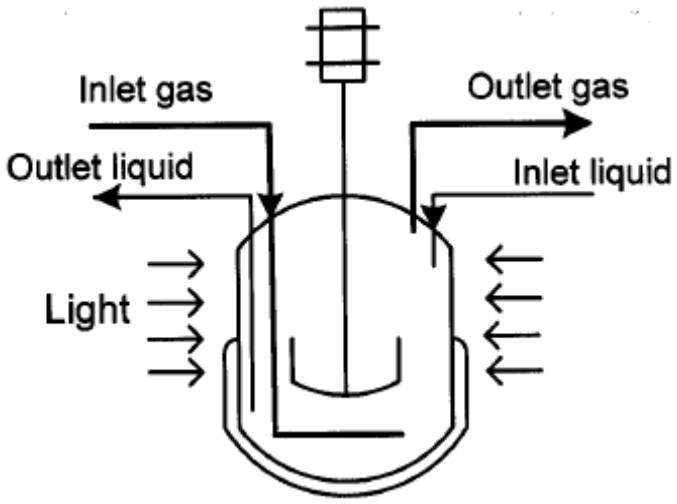

Figure 2.9: Fed-batch or continuous flow reactor.

Researchers studied the bioconversion of hydrogen sulfide to elemental sulfur by *C. limicola* in an immobilized-cell reactor and a sulfur settling tank with a free cell recycle reactor [25]. In the first reactor, cells were immobilized in strontium alginate beds and in the second reactor, the produced sulfur was removed by gravity settling and the medium was recycled to the fed-batch reactor. In comparison with the free cells, the immobilized cells required 30% less light energy at a H_2S removal rate of 68 mg h^{-1} L^{-1} initially but after 40 hours, the deterioration of the H_2S removal efficiency became significant due to the accumulation of sulfur in the beds [25]. Subsequently, in another study it was compared sulfide removal rates in 2-L and 4-L reactors [1]. The difference in sulfide removal rates between 2-L and 4-L reactors (0.11 and 0.07 mg H_2S/h per milligram of protein, respectively) was explained by the higher light attenuation in the larger reactor since light intensity decreased exponentially with the penetration depth. They also observed that the average diameter of sulfur aggregates was 10 times that of bacterial cells [1].

In a later study researcher used a continuous stirred tank reactor equipped with a sulfur separator to remove hydrogen sulfide from a gas stream containing 2.5% H_2S at 1 atmosphere pressure [26]. At a sulfide loading rate of 94.4 mg h^{-1} L^{-1}, H_2S conversion by *Chlorobium thiosulfatophilum* ranged from 53% at a gas retention time of 12.2 min to 100% at a gas retention time of 23.7 min [26]. The sulfur recovered from the process by gravity separation was 99.2% of the theoretical yield. The separation of elemental sulfur from the bioreactor contents is essential to realize its value as a chemical industry feedstock.

Later, light emitting diodes (LEDs) are used for these experiments. In 1996 researchers investigated the performance of LEDs in a plate type photo-bioreactor [27]. They observed that the maximum performance per unit luminous flux while using LEDs was 31 times that of an incandescent bulb. This efficiency was achieved by only supplying light within the wavelength range where absorption by bacteria was at a maximum [27].

Continuous-flow reactor

Using the effluent of a continuous-flow stirred-tank bioreactor, researchers tested separation of the sulfur by settling, settling at elevated pH, filtration, and centrifugation [28]. Centrifugation produced the best separation results; 90% of the elemental sulfur and 29% of the bacteria were removed from the suspension [28]. They noted that a continuous-flow suspendedgrowth bioreactor system for sulfide removal/sulfur recovery required two separation stages, one to separate S^0 from the bioreactor effluent and one to separate biomass from the liquid product of the first separator. A fixed-film reactor can eliminate or lessen the need for two separators since the biomass remains in the reactor.

Phototube reactors

Two types of phototube reactors are shown in Figs. 2.10a and 2.10b. These are tubular type reactors that are continuously operated. The reactor can be horizontally oriented (Fig. 2.10a) having several passes or spirals to improve the residence time in the reactor [29] or can be vertically oriented, as presented in Fig. 2.10b [18]. The material of the tube is transparent to light and impermeable to oxygen [18]. Bacteria develop on the inner wall of the tube reactor (fixed-film reactor).

There is used a “phototube” reactor in which a sulfide containing reactor was passed through a 12.8 m long, 3.2 mm ID Tygon tube which was immersed in an illuminated water bath [29]. The tube was able to achieve 95% sulfide removal in about 24.6 min while operated at a sulfide loading rate of 67 mg h^{-1} L^{-1}[29].

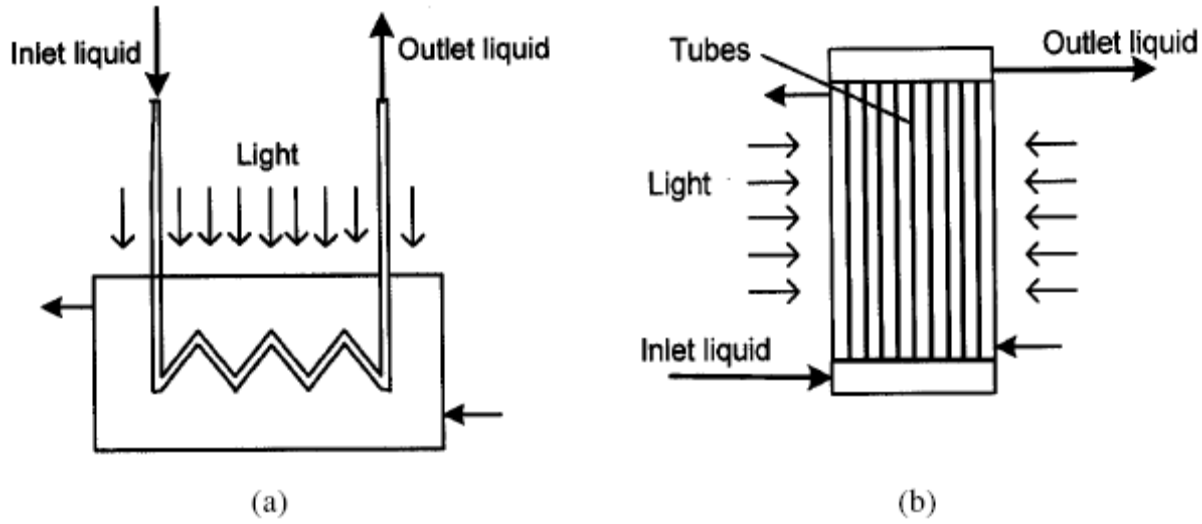

Figure 2.10: Phototube reactors: (a) horizontal; (b) vertical [18].

Using a fixed film, continuous-flow photobioreactor employing *C. limicola* and a infrared light source, it is succeeded in removing sulfide from synthetic wastewater at a sulfide loading rates of 111 to 286 mg h^{-1} L^{-1}, while 92 to 95% of the influent sulfide was converted to elemental sulfur [30]. A fixed-film reactor was selected because of its ability to retain biomass for further sulfide oxidation. In this process, light can easily be transmitted to the biomass adhering to the inside of the transparent tubes whereas in a suspended growth process, light can be considerably attenuated at the center of the reactor. In subsequent experiments, researchers investigated the effects of tube size and light quality on H_2S removal [1]. They observed that the smallest diameter tube reactor achieved the highest sulfide removal at the same light intensity (of infrared bulb and LEDs) [1]. A higher sulfide loading rate was achieved when LEDs providing light matching the peak absorption spectrum of GSB were the light source. The reactor system can be used for removal of gaseous H_2S after dissolving it in water.

2.3.2.3 Bioreactors for H_2S removal involving chemotrophic bacteria

Gas-fed batch reactors

In 1995 some researchers used two batch-fed reactors to study the oxidation of sulfide using a mixed culture of *Thiobacilli* [31]. Pure oxygen was supplied to the

reactors. The maximum sulfur production (73 ± 10%) occurred at an oxygen to sulfide ratio of 0.6 to 1.0 mol L^{-1} h^{-1}/ mol L^{-1} h^{-1}. At lower oxygen to sulfide ratios, the lower biological oxidation capacity resulted in the production of more thiosulfate. At higher oxygen to sulfide ratios, more sulfate was produced because more energy was consumed for bacterial growth than for the formation of elemental sulfur [31].

Continuous-flow reactors

In 1990 researchers tested three different continuous-flow reactor configurations: fixed-film CSTR, biorotor (a rotating cage containing reticulated polyurethane biomass support particles, partly immersed in the reactor liquid), and a fixed-film upflow reactor [32]. For the upflow and biorotor reactors, 95 to 100% sulfide removal efficiencies were achieved for loading rates up to 500 mg H_2S h^{-1} L^{-1}[32]. The removal efficiency decreased rapidly above this loading rate. At 938 mg h^{-1} L^{-1} (biorotor) and 1040 mg h^{-1} L^{-1} (upflow) loadings, sulfide removal efficiencies were 69 and 73%, respectively. At a 500 mg h^{-1} L^{-1} sulfide loading rate, the stirred-tank reactor's removal efficiency was approximately 62% [32].

Another study in 1987 reported on a continuous stirred-tank reactor (CSTR) system using *Thiobacillus denitrificans* to remove H_2S from gas streams. Ninety-seven percent of the H_2S bubbled was removed and oxidized to sulfate [33].

Biofiltration reactors

A biofilter consists of a filter-bed, traditionally composed of organic matter (peat, compost, sawdust, etc.), serving both as carrier for the active biomass and as nutrient source. While flowing through the filter-bed, contaminants present in the polluted air are degraded by the active biomass (Fig 2.11) [34]. One important characteristic of the process is the absence of a mobile liquid phase as a consequence of which biofilters are suitable to treat poorly water-soluble pollutants. Biofiltration is of interest for the treatment of pollutants having an air/water partition coefficient less than 1 [34]. Several examples of successful industrial applications can be found in

the literature and nowadays some industrial plants are treating gas flows of up to 200 000 m^3 h^{-1}.

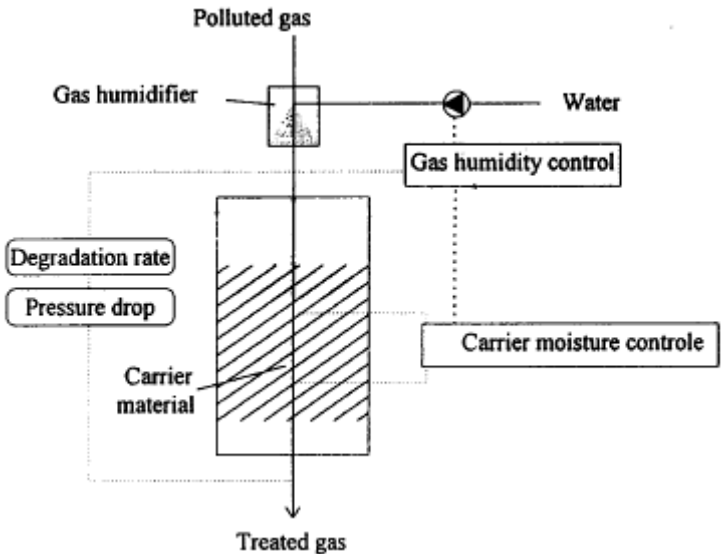

Figure 2.11: Biofilter design and control parameters.

Filter Bed:

Different filter-beds may be used in biofiltration. According to studies, almost any organic material presenting "a satisfactory structure and composition" could be used. It is listed important physical, chemical and biological characteristics for good biofilter media. The most important physical characteristics the carrier should present are [35] : (i) high surface area, for optimum microbial development, (ii) low bulk density for easiest and cheapest carrier operation and (iii) high void fraction to limit pressure drop and clogging problems. In addition to these physical characteristics, the presence of a large number of different bacteria naturally present in the carrier as well as a balanced chemical composition are of major concern in order to enhance microbial adaptation and activity inside the biofilter-bed [34].

A biofilter is a three phase bioreactor (gas, liquid, solid) made with a filter bed that has a high porosity, high buffer capacity, high nutrient availability, and high moisture retention capacity to ensure that the target microorganisms can grow on it [36]. The contaminated gas is continuously fed in the biofilter, while a nutrient solution is discontinuously added. Various types of biofilter media have been used by researchers. Representative cases are discussed below.

In a research made in 1996 researchers immobilized *Thiobacillus thioparus* CH11 with Ca-alginate producing pellet packing material for the biofilter [37]. At a 28 second optimal retention time, the H_2S removal efficiency was more than 98%. Elemental sulfur or sulfate was produced depending on the inlet H_2S concentration [37]. Another study in 1997, they used *Thiobacillus novellus* in a biofilter for H_2S oxidation under mixotrophic conditions [38]. A removal efficiency of 99.6% was achieved and the products were sulfate (83.6%) and sulfite (12.6%) [38]. Little conversion of sulfide to elemental sulfur was achieved. Later, in 2001 same research group used biofilters packed with co-immobilized cells *Pseudomonas putida* CH11 and *Arthobacter oxydans* CH8 for removal of H_2S and NH_3, respectively, which are often present in off-gases of a livestock farm [39]. In the 5-65 ppm range, H_2S and NH_3 removal efficiencies were greater than 96%. However, at higher concentrations, H_2S and NH_3 showed inhibitory effects on H_2S removal. They also assessed the environmental risk associated with the release of bacteria when treating large volumes of waste gases. The exhaust gas contained small amounts of bacteria (< 19 CFU/m^3 in all cases) and was considered safe [39].

A comparison between removal efficiencies of inorganic (H_2S) and organo-sulfur (methyl mercaptan, dimethyl sulfide, and dimethyl disulfide) odour compounds by immobilized *T. novellus* is presented in the study of made in 1999 [40]. They observed *T. novellus* can degrade H_2S > methyl mercaptan > dimethyl disulfide > dimethyl sulfide and the removal efficiency was 100% for H_2S and methyl mercaptan**,** 87% for dimethyl disulfide, and 73% for the dimethyl sulfide [40]. The final metabolic product was sulfate.

In an another study, researchers described the removal characteristics of H_2S and other reduced sulfur compounds emitted from kraft pulp mills using three different biofilter mediums: compost, hog-fuel (pulverized mixture of raw bark, wood waste, and other materials) and a mixture of compost and hog fuel at 1:1 (w/w) ratio [41]. Dolomitic lime was mixed with each medium to act as a pH buffer. No significant difference was observed in the H_2S elimination capacities of these three media. However, the pH of the media decreased significantly over an operating period of more than six months. At H_2S concentrations up to 250 ppmv, complete removal was observed [41]. The removal efficiency for inlet concentrations higher than 250 ppmv

was above 90%. Compost, hog-fuel, and the mixture media had maximum elimination capacities of 136, 137, and 138 g m^{-3} h^{-1}, respectively [41].

In 2002, some researchers reported the operation of a commercial biofilter for the treatment of an air stream containing hydrogen sulfide, ammonia, dimethyl sulfide, methanethiol, and ethylamine [42]. This proprietary wood-based (BIOMIX™) biofilter achieved 96.6% removal of H_2S at an inlet concentration of 1.07 mg/m^3 [42].

Another study in 2003 also performed an experiment involving H_2S and NH_3 using two laboratory scale biofilters packed with granulated digested sludge [43]. One unit was fed mainly with H_2S and the other unit with NH_3. Complete H_2S removal (100%) was obtained and no influence on NH_3 or H_2S removal was observed [43]. An 80% NH_3 removal efficiency was obtained, however, the authors concluded that the oxidation of high levels of H_2S might have a negative effect on the growth and activity of nitrifying bacteria [43].

Another research made in 2003 described the "BIO-Sulfex" biofilter to remove H_2S from biogas which uses thiobacteria attached on fixed bed material [44]. The biomass was aerated and the filter was flushed with nutrient containing liquid to remove sulfur from the system. Six BIO-Sulfex modules to treat biogas containing up to 5000 ppm H_2S were operated at flowrates of 10 to 350 m^3/h with 90% or more H_2S removal achieved [44].

Bioscrubbers

Bioscrubbing consists of the absorption of a pollutant in an aqueous phase, which is then treated biologically in a second stage in a liquid phase bioreactor (Fig 2.12) [34]. The effluent leaving the bioreactor is then recirculated to the absorption column. This technology allows for good gas cleaning when the gaseous pollutants are highly water soluble. The main advantage of this technology are : (i) removal of reaction products by washingout, avoiding their possible inhibitory e†ects, (ii) easy control of the biological process due to control of the liquid medium composition and

(iii) good adaptation capacity of the microbial biomass with reference to the composition of the gas to be cleaned [34].

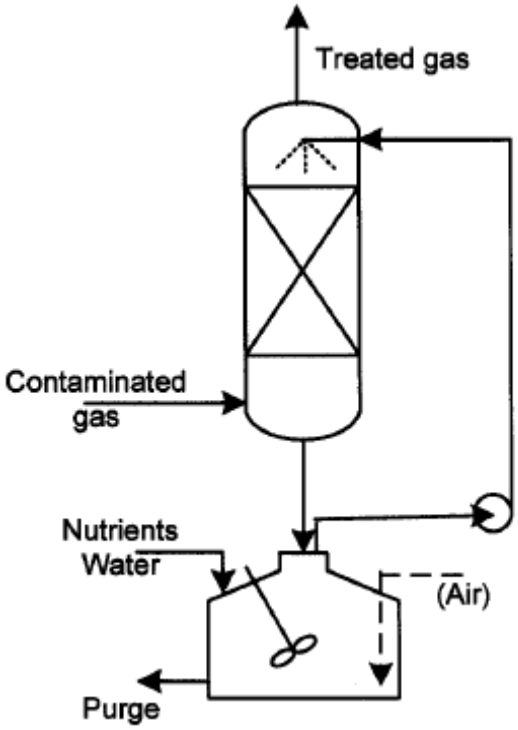

Figure 2.12: Bioscrubber [2]

Removal of H_2S using bioscrubbers involves a two stage process, firstly absorption of H_2S by a liquid followed by biological oxidation of H_2S in the liquid [1].

The major drawback of this technology is the necessity to dissolve the gaseous pollutants in an aqueous phase from which gas transfer problems may arise, taking into account the usually short residence time of the gas phase in the absorption column [34]. Bioscrubbing is therefore of interest for gaseous pollutants with a Henry's constant or partition coefficient of less than 0.01 [34]. This is of major importance since most of the target pollutants are volatile and poorly water soluble. This is probably one of the reasons why bioscrubbing is less popular than biofiltration, although several examples of successful applications have been reported. Nevertheless, recent developments indicate new interest in this technology since biological desulphurization of very large gas flow rates (up to $2x10^6$ m^3 h^{-1}) seems to be feasible in bioscrubbers and bioscrubbing is one of the very few examples of anaerobic waste gas treatment technology [34].

First experiments about this subject made in Japan in 1997, they used a multiple bubble-tray airtight contact tower (bioscrubber) to scrub hydrogen sulfide from the biogas produced by an anaerobic wastewater treatment process [45]. A two-reactor system (a gas-liquid contact tower and an aeration tank) were used to separate the oxidation process from the absorption process to prevent air from mixing with the biogas [45]. Mixed liquor from the activated sludge process was continuously fed to and withdrawn from the contact tower. In the contact tower, H_2S from the biogas was absorbed into the mixed liquor and subsequently oxidized to sulfate by sulfur oxidizing bacteria after returning to the aeration tank. Based on their preliminary results, a full scale plant treating potato processing wastewater was constructed. When treating 2000 ppm of H_2S in 40 m3/h of biogas, more than 99% removal efficiency was achieved [45].

A full scale plant located northeast of Brooks, Alberta, Canada uses Shell-Paques® process for natural gas desulfurization [46]. H_2S is removed from a gaseous stream by absorption into a sodium carbonate/bicarbonate solution. The sulfide containing scrubbing liquid is treated in the bioreactor where it is mostly converted biologically to elemental sulfur. The bioreactor is supplied with a nutrient stream, air, make-up water, and sodium hydroxide. It is reported that normally less than 3.5% of the sulfide is converted to sulfate and a continuous bleed stream is required to avoid accumulation of sulfate. A compost filter is used to treat the trace H_2S present in the spent air from the bioreactor. Less than 4 ppmv effluent H_2S concentration is achieved when treating natural gas containing 2000 ppmv H_2S.

In a research made in 2002 described a bioscrubber system which can be integrated into a system to remove H_2S from biogas by a combination of chemical and biological processes [47]. H_2S removal can be achieved by absorption in a ferric sulfate solution producing ferrous sulfate and elemental sulfur. Ferric sulfate can be regenerated by biological oxidation using *Acidithiobacillus ferrooxidans* [1]. Relevant reactions are shown in Table 2.10 [1]. The study investigated the oxidation of ferrous iron by *A. ferrooxidans* which was immobilized on a polyurethane foam support and the support particles placed in an aerated column. Ferric precipitates were accumulated on the support and on the air diffusers which necessitated periodic interruptions of the process for cleaning. Precipitation, air supply, and chemical cost

are the potential constraints for this process [47].

In 2006, new bacteria species were used in bioscrubbing system. The fixed-film bioscrubber was developed for hydrogen sulfide removal. Acinetobacter sp. and Alcaligenes faecalis are two new strains of microorganisms from the fixed-film bioscrubber systems found [48]. Under certain conditions, they exhibited more than 91% of hydrogen sulfide removal efficiency while a mixture of the two strains was capable of 98% hydrogen sulfide removal. Removal efficiency increased with decreasing inlet gas flow rates, increasing the height of packing and empty bed retention time [48]. During the operation, the pH decreased but did not fall below 6.4. Sulfate production increased when the removal efficiency increased due to the oxidation of hydrogen sulfide to sulfate. In addition, dissolved oxygen decreased during the same reaction.

Biotrickling filters

Waste gas treatment in trickling biofilters involves using a biological filter continuously fed with a liquid medium and packed with a synthetic carrier on which a biofilm grows. The polluted gas passes through the carrier material, co- or counter-currently to the mobile liquid phase which ensures nutrient supply to the microorganisms (Fig. 2.13) [1]. Fresh medium fed to the reactor may be mixed with drain water recirculated to the system. Carriers frequently used and reported in the literature include plastic or ceramic structured packings, unstructured celite, activated carbon or mixtures of different materials [34]. Trickling biofilters present similar advantages to bioscrubbers :

(i) easy elimination of reaction products by washing-out,
(ii) easy control of the biological process and
(iii) good adaptation capacity of the active biomass.

As with bioscrubbing, the major drawback of this technology is the problem of gas transfer arising from the necessity of dissolving the gaseous pollutants in an aqueous phase [34]. Nevertheless, this impediment seems to be less critical than in

bioscrubbers since trickling biofilters can efficiently be used for the treatment of compounds characterized by an air/water partition coefficient lower than 0.1 [49]. Lowering the feed rate of the aqueous medium can decrease the wetted area of the filter carrier which approximates to the active area. As a general rule, in a packed-bed reactor the wetted area represents less than half of the total specific area available. Removal efficiencies are thus expected to be higher with increasing liquid flow rates, although this will also increase operation costs. On the other hand, recent papers have shown that when reducing the liquid supply to the minimal microbial requirements better gas treatment efficiencies were reached. The liquid flow rate allowing the highest removal efficiency should be evaluated experimentally. Another possible problem, specific to trickling biofilters, is the excessive biofilm development on the carrier surface which progressively reduces the empty volume of the carrier and may cause unwanted increased pressure drop [50]. Biofilm development can lead to the complete clogging of the filter-bed although this does not always occur. This reinforces the importance of careful carrier design. Little is known about the factors that govern clogging or efficient ways to prevent it. Methods have been developed to restrict clogging including the limitation of biomass growth, regular filter-bed washing, or limitation of the liquid supply. Thus, with a reactor having a limited liquid supply there was no increased pressure drop nor clogging detected during a day operation period. However, the reduced liquid supply ultimately adversely affected microbial activity and reduced removal efficiency. Filter bed backwashing with medium fluidization twice a week for 1 h proved to be an efficient means for preventing excess biomass accumulation [49]. Biomass growth can be limited by reducing nutrient supply although this may slightly decrease reactor performance since growing organisms show higher substrate consumption rates than when in stationary phase. Carbon, hydrogen or oxygen are usually not limiting unless the contaminant load is highly variable, hence means are required to control biomass by the upplies of nitrogen, phosphorus, inert salts or trace elements. Biomass yield is a function of the nature of available nutrients, for example, as a source of nitrogen nitrate yields less biomass than ammonium. A good biofilm structure can be obtained by modifying ionic strength [50]. These observations indicate that it is important to find the optimum balance between limitation of biomass growth or clogging and removal efficiency. At present, no generalized rules

can be drawn and the best operating conditions must be determined experimentally for each specific case.

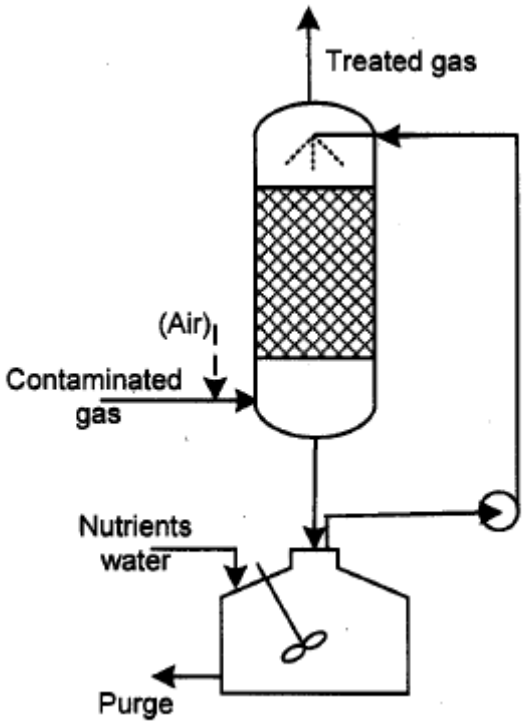

Figure 2.13: Biotrickling Filters [1]

The working principle of a biotrickling filter (Fig. 2.13) is the same as for a biofilter except that the packed bed is continuously trickled over by an aqueous phase nutritive solution [51].

In 2001, some researcher used two laboratory scale biotrickling filters made of polypropylene, inoculated with biomass from a toluene biodegrading filter operating at pHs of 7.0 and 4.5 to treat H_2S and toluene in a gas stream [51]. There was no significant difference between the performances of the two reactors in terms of H_2S removal. At an inlet concentration of approximately 50 ppmv, complete consumption of H_2S was observed. However, the removal efficiency decreased to 70- 80% when the inlet concentrations were raised to 170 ppmv [51].

In another research in 2005, researchers studied the aerobic removal of hydrogen sulfide using a biotrickling filter packed with 1L-polyethylene rings (73% volume

free) inoculated with *Acidithiobacillus thiooxidans* ATCC-19377 [52]. The inlet H_2S concentration was varied between 400 and 2000 ppm and the airflow rate was varied between 0.03 and 0.12 m^3/h. However, the system performance was not affected by changing the operational conditions and a maximal removal efficiency of 100% was obtained. During the experiment, the pH of the nutritive solution decreased to 2-3, but this did not affect the process performance [52].

High removal efficiency for H_2S, in comparison to other reduced sulfur compounds was obtained by the researchers using *Thiobacillus sp*. in a biotrickling filter [53]. For inlet H_2S concentrations as high as 30 ppmv, typical removal efficiency was 98%. Methyl mercaptan, carbonyl sulfide, and carbon disulfide removal efficiencies were 67, 44, and 35% at inlet concentrations of 67, 193, and 70 ppbv, respectively [53].

In another research made in 2005, they developed a laboratory-scale biotrickling system in order to remove H_2S from digester biogas under anaerobic conditions [54]. In these experiments, polypropylene balls inoculated with anaerobically digested sludge were used as packing material in the bioreactor (packing volume of 0.0062 m3, 90% volume free) [54]. Sodium sulfite was added in the nutritive solution as an oxygen scavenging agent. Nitrate was used as electron acceptor in the absence of oxygen. Removal efficiency greater than 85 % was achieved for an H_2S inlet concentration of 500 ppm and a gas flowrate of 0.05 m^3/h. Of particular interest, inhibition of the biological process by trace amounts of O_2 was noticed when a nitrate solution was used as the sole nitrogen/nutrient source [54].

There is given a summary for all biological methods processed for H_2S removal from biogas streams in Table 2.10 including bioscrubbers/biofilters or biotrickling filters.

Table 2.10: Researchs conducted on hydrogen sulfide removal using bioscrubbers/biofilters or biotrickling filters

Scale	Process type	Type bed	Bed volume	Pollutants treated and inlet gas concentration	Gas flow rate and empty bed residence time (EBRT)	Bacteria	Removal efficiency	Innoculation	Reference
Laboratory	Biofiltration	Cell-laden Ca-alginate	0.7 L	5-100 ppm H_2S, balance air	18-150 L/h	*T. thioparus*	85-99% (H_2S)	Immobilization of *T. thioparus* on Ca-alginate	Chung et al. (1996)
Full	Bioscrubbing: anerobic absorption + aerobic biooxidation	Activated sludge	3 m^3 (scrubber) 550 m^3 (aeration tank)	Biogas from waste-water treatment plant: 300-2000 ppm H_2S, 80% CH_4, 20% CO_2	40 m^3/h	Indigenous (*Thiobacillus sp.*, etc.)	>99% (H_2S)	-	Nishimura and Yoda (1997)
Laboratory	Biooxidataion in the bubble column reactor	Poly-4-vinylpyridine (PVP) matrix	6.3 L (reactor volume)	Mixed gas composed of 30 ppm H_2S, MM, DMS, and DMDS*	-	*T. novellus*	100% (H_2S) 100% (MM) 87% (DMDS) 73% (DMS)	Immobilization of *T. novellas* on PVP matrix)	Cha et al. (1999)
Laboratory	Biofiltration	Compost or compost/hog fuel	18 L	10-450 ppm H_2S, balance air	1.7 m^3/h 38s	Indigenous (in sludge)	90-100% (H_2S)	Yes (waste-activated sludge)	Wani et al (1999)
				10-450 ppm H_2S, 10.8 ppm DMS, 6.6 ppm DMDS, balance air			90-100% (H_2S) 30-35% (DMS) <30% (DMDS)		
Laboratory	Biofiltration	Cell-laden Ca-alginate	0.7 L	60-120 ppm H_2S, 60-120 ppm NH_3, balance air	36 L/h 72 s	*Pseudomonas putida* (for H_2S) *Anhrobacter oxydans* (for NH_3)	>90% (H_2S) >95% (NH_3)	Co-immobilization of *P. putida* and *A. oxydans* on Ca-aglinate	Chung et al. (2001)
Laboratory	Biotrickling	Polypropylene pall rings	10 L	170 ppm H_2S, 2.2 g/m^3 toluene, balance air	1 m^3/h 36 s	Toluene-degraders sulfide oxidizing bacteria	100% (H_2S) 25-75% (toluene)	Yes (biomass from a toluene-degrading biotrickling filter)	Cox and Deshusses (2001)
Laboratory	Biofiltration	Pig manure + sawdust	5.9 L	10-45 g H_2S m^{-3} h^{-1}, balance air	13.5-27 s	Indigenous	>90% (H_2S)	No	Elias et al. (2002)
Pilot	Biotrickling	-	3.8 m^3	Emissions from wastewater treatment plants: 10-50 ppm H_2S, 0-150 ppb VOC, traces of other compounds	650 m^3/h 21 s	-	98% (H_2S) 50-70% (VOC)	-	Cox and Deshusses (2002)
Full	Biotrickling	Structured plastic packing	51 m^3	Exhaust air from a cellophane plant 60-155 ppm H_2S, 35-100 mg/m^3 CS_2	44,200 m^3/h (total flow) 4-10 s	-	85-99% (H_2S) 40-70% (CS_2)	-	Cox and Deshusses (2002)

Table 2.10: continued

Full	Biotrickling/ Biofiltration	Polyurethane foam	500 m^3 (6 units)	Odors from tobacco company: 800-1200 OU	11 s	-	>90% (H_2S)	-	Cox and Deshusses (2002)
Laboratory	Biofiltration	Wood chips, granular activated carbon (GAC)	1 L	30-450 ppm H_2S, 35-200 ppm NH_3, balance air	60-180 L/h 20-60 s	*T. thioparus* Nitrifying bacteria	75-99% (H_2S) 30-92% (NH_3)	Yes (activated sludge from sewage water treatment plant + culture of *T. thioparus*)	Kim et al. (2002)
Laboratory	Biooxidation in the fixed film reactor	Polyurethane particles	1 L	Effluent from a gas lift reactor treating a sulfide nitrate mixture (2-20 mM as S-tot)	-	*T. tenitrificans* Nitrifying bacteria	>80% (S-tot)	-	Kleerebezem and Mendez (2002)
Full	Biosscrubbing (absorption +aerobic biooxidation) + separate biofiltration	Alkaline solution for scrubbing Compost for biofiltration	-	Natural gas: 2000 ppm H_2S	322,000 nm^3/d	Indigenous	>99.8% (H_2S)	-	Benschop et al. (2002)
Full	Biofiltration	Wood-based medium	Open bed biofilter	Odorous air from meat rendering plant (24,544 OU): 1.07 mg H_2S/m^3, 5.2 mg NH_3/m^3, 0.66 mg/m^3 methanethol, 1.2 mg/m^3 ethylamine, 775.25 mg/m^3 DMS	25485 m^3/h 30 s	Indigenous	>96% (all compounds, with exception of methanethiol, 70%)	No	Shareefdeen et al. (2002)
Full	Biotrickling	Polyurethane foam	7.3 m^3	Odorous air from wastewater treatment plant: 5-25 ppm H_2S, 67 ppb carbonyl sulfide, 192 ppb MM, 70 ppb CS_2 (4000 ppm CO_2)	1.6-2.3 s	*Thiobacillus sp.*	>97% (H_2S) 67% (MM) 44% (carbonyl sulfide) 35% (CS_2)	Yes (activated sludge from wastewater treatment plant)	Gabriel and Deshusses (2003)
Laboratory	Biofiltration	Granulated sludge	10 L (column)	170-680 g H_2S m^{-3} d^{-1}, 86-340 g NH_3 m^{-3} d^{-1}, balance air	-	Nitrifying bacteria, Sulfide oxidizing bacteria	100% (H_2) 80% (NH_3)	Yes (acclimatized sludge)	Malhautier et al. (2003)
Laboratory	Biofiltration	Mature compost	8 L	50 ppm H_2S, balance air	10 L/min	Indigenous	90-100% (H_2S)	No	Morgan-Sagastume et al. (2003)
Laboratory	Biofiltration	Peat	1 L	355-1400 ppm H_2S, balance air	30 L/h	*T. thioparus*	65-100% (H_2S)	Yes (culture of *T. thioparus*)	Oyarzún et al. (2003)
Full	Biofiltration	-	-	Biogas from anaerobic wastewater treatment plant (5000 ppm H_2S)	10-350 m^3/h	Thiobacteria *(Thiobacillus sp.)*	>90% (H_2S)	Yes (activated sludge from digester)	Schieder et al. (2003)

* MM = methyl mercaptan; DMS = dimethyl sulfide; DMDS = dimethyl disulfide

2.4 Research Statement

With integrated H_2S removal from biogas and denitrification of wastewater without organic carbon need, this research study will directly adress the relationship of nitrate/nitrite loading rates and biogas flowrates, and also optimum environmental conditions for cost effective solutions based on next years' progresses about this issue.

All experiments are conducted on the pilot scale absorption tower, and all system requirements, including wastewater, biogas, etc. are provided by the biological wastewater treatment system of fermentation industry.

All experiments are done within 6 months period especially within summer season. Influent wastewater temperatures were high depended on this situation This long-term experiments will be based on latter specific studies in this thesis work.

Because of dynamic operation present in activated slugde treatment plant, nitrate and nitrite concentrations especially in the sampling periods are changed day by day. So there is not smooth feed concentrations of wastewater. Also biogas composition and specially H_2S concentration in biogas changed depending of treatment plant's feed variation and operation conditions. According to this variation, loading rates of wastewater and biogas changed.

3 MATERIAL AND METHODS

3.1 Description of Pilot Scale Absorption Tower

All experiments for this study has been done on pilot scale absorption tower shown in Figure 3.1.

Figure 3.1: Pilot scale absorption tower

Specific details of absorption tower is given in Table 3.1.

Table 3.1: Specific details of absorption tower

Height: 5 m
Diameter: 80 cm
Feed pipes: Gas pipe at bottom including 50 holes, wastewater pipe on top including 200 holes
Material (inside/outside) : All material is stainless steel.
3 grill bars inside.

Beside the absorption tower, two pumps are used for wastewater piping, one of them is for influent wastewater, and other is for effluent wastewater. They have capacities of 15 m^3/h, and 14.5 meters head. For biogas, a blower is used for piping, and it has capacity of 100 m^3/h, and piping pressure is 0.6 bar. For wastewater, there is used a flowmeter and a pneumatic valve for adjusting the flowrates. For biogas, also a gas flowmeter and manual valve is used for controlling gas flowrates. All material's of pipelines and pumps are stainless steel to prevent corrosion on them.

There is established a Programmable Logic Controller (PLC) program on computer to control all the parameters including pumps, pneumatic valves, liquid heights, and also to watch the parameters added on the system:

* Temperature
* pH
* Oxidation-Reduction Potential (ORP) sensor
* Flowrates of wastewater and biogas
* Liquid heights

There is given a schematic view of control page of the system in Figure 3.2.

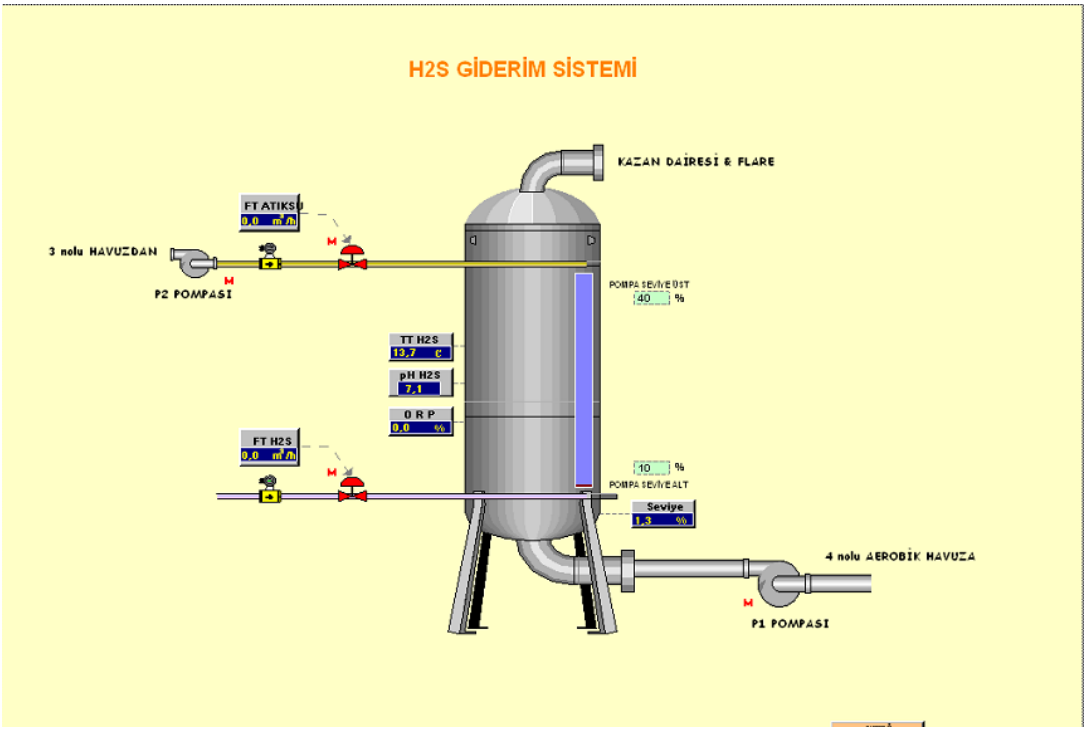

Figure 3.2: Schematic view of control page of the system

3.2 Operation of System

This study has been done at a biological wastewater treatment plant situated in a baker's yeast production factory. Wastewater treatment plant is comprised by anaerobic and aerobic reactors. Wastewater needed for this study is provided from aerobic reactors that used activated sludge system and also tertiary treatment: nitrification and denitrification for biological nitrogen removal. Activated sludge system has 4 pools on it. First pool is used as anoxic reactor and there is no oxygen transfer in this side. Other 3 pools are airated by air blowers by using piping system and recirculation lines on it. On the 4th pool there is a recirculation pump to recycle the effluent to the first anoxic reactor for nitrogen removal. In this study, wastewater is piped from third pool to the absorption tower, and effluent from the tower is discharged to the end of the plant.

Biogas is provided from anaerobic reactors in the plant. All biogas produced are stored in a big tank, and biogas is piped from here to the absorption tower by a compressor. Compressor and moisture trappers are shown in Figure 3.3.

Figure 3.3: Biogas compressor and Moisture trappers

3.2.1 Start-up phase

In start-up phase, firstly, biogas compressor and it's pressure values are determined. Pressure values are evaluated by liquid height in absorption tower and flare pipe's requirements. Start-up experiments showed that, at least 0.2 bar compressor pressure is necessary for breaking the hydraulic pressure of liquid height and flaring conditions on the pipe-way.

Secondly, moisture content of biogas is retained by two moisture trappers established at biogas feeding line and also biogas effluent line, because moisture is preventing combustion of biogas in flare.

Some of control sensors are placed on the absorption tower. pH meter, ORP sensor, temperature sensor, pressure sensor indicating liquid height in the tower, also, feeding and discharge pumps and biogas compressor are all control parameters loaded on the system. All of this parameters are pointed on a PLC program, so all

controls are watched from personal computer. Also all datas are saved on a data logger program. By using this program, saving periods and accuracy rates are determined in start-up phase.

Also, in start-up phase, there are some issues are watched. Firstly, clogging problems are occured on wastewater feeding pipe, and also in feeding holes. So, some precautions are taken to overcome this problem.

3.2.2 Reactor operation

Bubble type absorption tower is shown in Figure 3.4. As seen in the Figure 3.4, wastewater feed line is on the top, and there is a pneumatic valve to control the flowrate. Biogas feeding line is at bottom, and there is a manual valve on it. Flare is shown on the top cover. All sensors are also shown in Figure 3.4.

By using PLC programme, flowrates and liquid height can be determined. Discharge pump is logically controlled by liquid height set given, so to reach the set value, this pump works routinely in the values beetween.

Flare is automatically ignited by an ignitor when the biogas reaches the flare pipe, so it is watched periodically by the researcher if the flare works properly. If it does not work, it would cause pollution of air by crude H_2S.

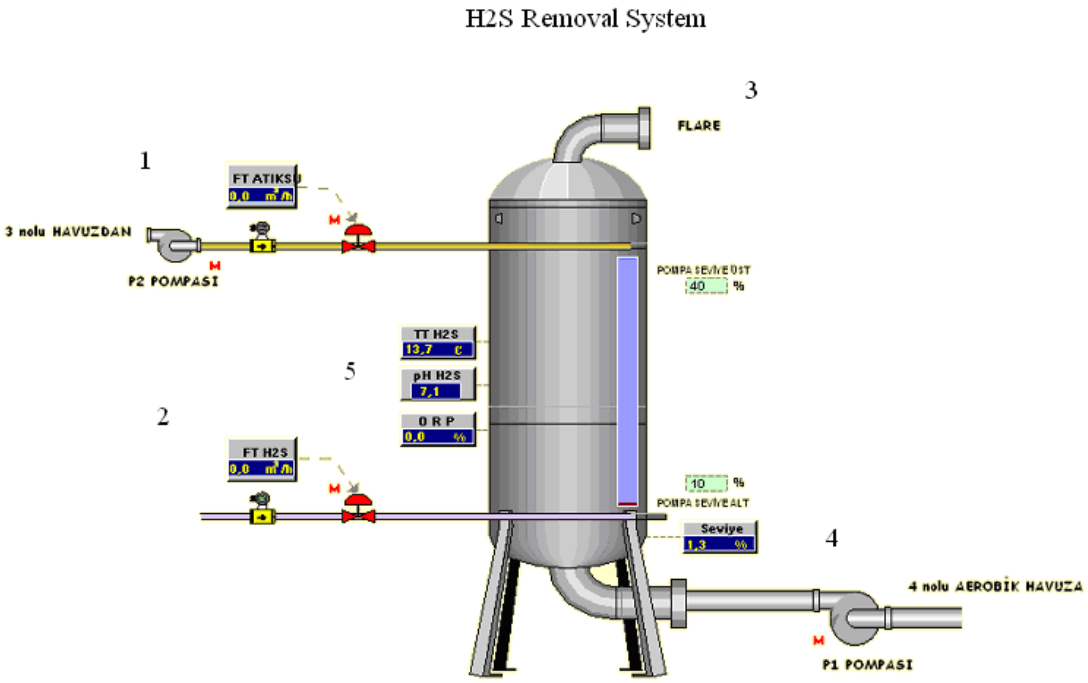

Figure 3.4: H_2S removal system (1- wastewater feeding, 2- Biogas feeding, 3- Treated biogas to flare, 4- Treated wastewater to aerobic pool, 5- pH, ORP, Temperatue, Liquid Height sensors)

Wastewater feed is obtained from 3rd pool in activated sludge system, so feed ORP and temperature values in activated sludge system are also watched in computer. This values are compared with the absorption tower's values to check the accuracy of the collected datas.

Wastewater discharge of absorption tower is given to 4th aerobic pool, but there is an option to discharge it to the effluent of the activated sludge system. If there is sludge bulking problem on the sedimentation tank, discharge is channelled to the effluent.

3.3 Sampling and Analytic Methods

3.3.1 Sampling

All feed wastewater samples are taken from 3rd aerobic pool by 500 ml plastic bottles. Samples in here are taken from the region that ORP sensor is so near from that point. So feed wastewater ORP values in absorption tower is almostly same in the activated sludge system. And also, it is important that, wastewater sample should not be taken from foamy side on the pool, it can cause errors on the samples.

All effluent wastewater samples are taken from discharge pump's sample line on it at the absorption tower. All samples are taken by waiting a few seconds by spilling some amount after. Samples are taken by 500 ml plastic bottles. All influent and effluent samples are directly forwarded to the laboratory and centrifuged instantly to avoid reaction's continuing in by contacting of sludge and wastewater.

All feed biogas samples are taken from a collector line of biogas from feed line coming from biogas tank. There is a sample line on this collector and biogas samples are taken by adjusting the valve to ensure that required biogas is taken from it. Biogas samples are taken by Accuro Type gas sucking pumps to the Drager Short-term sampling tubes. This pump is worked by the principle of vacuum process. Firstly, it is pressed by hand and the glass tube is placed on the sample point, when glass tube's top part is broken, biogas starts to fill in the pump, and the concentration value is read on the scales of the tube. The reaction in the tube is given in analytical methods. The important point in this sampling process is that, sucking pump should be carefully controlled and end of the reaction occurs in the tube should be watched carefully by the signal of sucking pump's.

3.3.2 Analytic methods

3.3.2.1 H_2S measurement

All H_2S measurements of biogas are done by Draeger Rohrchen Trade Mark, Hydrogen Sulfide Short-term tubes. This tubes are scaled in the range of 0.1 - 7 % volumetric content of biogas. And all samples are taken by Draeger Accuro suction pumps (Figure 3.5). In 2 minutes approximately, measured value could be read. Working principle of sample tubes are given by the reaction below:

Figure 3.5: Accuro suction pumps and Draeger Tubes

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \qquad \textbf{(3.1)}$$

In the reaction, Cu^{2+} reacts with H_2S and CuS is occured. CuS gives a black colour on the tube, and scale of this colour change gives the measured value of volumetric H_2S in the biogas.

As calculating the concentration values, this volumetric ratio is changed by ppm values in the given below:

% 1 v.v. H_2S = 10.000 ppm

To convert this value to mg/m^3 values, a calculation is needed:

In 20 ºC temperature and 1 atm atmospheric pressure,

1 ppm H_2S = 1.42 mg H_2S/m^3 **(3.2)**

So, all calculations in this study are done by using this equations.

3.3.2.2 SO_4^{2-} measurement

All SO_4 measurements are done by spectral-photometric method. By using ready SO_4 kits of Hach Lange Gmbh Cuvette Test tubes of LCK 153 type, SO_4 concentrations are read.

Dr. LANGE CADAS 30 S Spectral-photometer is used for measurements. In this method, firstly 5 minutes centrifuged sample by "Heraeus Labofuge Instruments 400 centrifuge tool in 3500 rpm" is diluted to measurable values of spectro-photometer by using distilled water. After this step, 5 ml sample is filled to test tube of SO_4 and shaked for a while. Then sample is saved as "Zero" on the spectro-photometer. After that, minor amount of $BaCl_2$ (Barium Cloride) is added to the sample. SO_4 in the sample reacts with $BaCl_2$ and $BaSO_4$ (Barium Sulphate) is occured at the end of the reaction. After two minutes waiting, sample is placed in the cuvette of photometer again, and measurement is done. Read value is multiplied by dilution factor if it is needed.

3.3.2.3 NO_3^--N measurement

All NO_3-N measurements are done by spectral-photometric method. By using ready NO_3-N kits of Hach Lange Gmbh Cuvette Test tubes of LCK 339 type, NO_3-N concentrations are read. Dr. LANGE CADAS 30 S Spectral-photometer is used for measurements. In this method, firstly 5 minutes centrifuged sample by "Heraeus Labofuge Instruments 400 centrifuge tool in 3500 rpm" is diluted to measurable values of spectro-photometer by using distilled water. After this step, 1 ml sample is filled to test tube of NO_3-N then, 0.2 ml A solution (prepared by Hach Lange) is added to the tube, then shaked for a while. After 15 minutes waiting, test tube is placed in the cuvette, and measurement is done automatically. Read value is multiplied by dilution factor if it is needed.

3.3.2.4 NO_2^--N measurement

All NO_2-N measurements are done by spectral-photometric method. By using ready NO_2-N kits of Hach Lange Gmbh Cuvette Test tubes of LCK 341 type, NO_3-N concentrations are read. Dr. LANGE CADAS 30 S Spectral-photometer is used for measurements. In this method, firstly 5 minutes centrifuged sample by "Heraeus Labofuge Instruments 400 centrifuge tool in 3500 rpm" is diluted to measurable values of spectro-photometer by using distilled water. After this step, 2 ml sample is filled to test tube of NO_2-N then, tap of the test tube is extracted and some amount of chemical powder in reverse tap is mixed with the sample by shaking it for a while. After 10 minutes waiting, test tube is placed in the cuvette, and measurement is done automatically. Read value is multiplied by dilution factor if it is needed.

3.3.2.5 Suspended (SS) and volatile suspended solids (VSS) measurement

All wastewater samples are filtered by Millipore Strain Set and fitler papers of Millipore AP40. Suspended solids (SS) and VSS values are measured according to the Standard Methods for the Examination of Water and Wastewater (1998) 20th addition. Sartorius LA 12005 type tare is used for measurements. For SS measurements, Nuve Dry Heat Sterilizer is used for 105 ºC heating and for VSS measurements Protherm Furnaces Type Furnace is used for 550 ºC igniting.

3.3.2.6 ORP, pH, temperature sensors

For online ORP measurements, Mettler Toledo ORP sensor is used. It's measurement range is between -500 to + 500 mV. For online pH measurements, Metler Toledo pH meter is used.

For determining ORP values of anoxic sulphide oxidation, an initial labaratory scale experiments are examined, and also another ORP sensor, pH meter are used. The results of this pre-study is given in results part.

3.4 Experimental Methodology

In the period of this study there is used an experimental methodology given in Table 3.2

Table 3.2: Experimental methodology

Parameter	Sampling Point	Measurement Method	Measurement Period
Temperature	In Absorption tower	Online	Continuous
pH	In Absorption tower	Online	Continuous
ORP	In Absorption tower	Online	Continuous
Liquid Height	In Absorption tower	Online	Continuous
VSS	Feed wastewater	2540 E Fixed and Volatile Solids Ignited at 550 ^{0}C	Start of feeding
SS	Feed wastewater	2540 D Total Suspended Solids Dried at 103-105 ^{0}C	Start of feeding
H_2S	Influent/Effluent Biogas	Short-term test tubes	1 hour period
NO_2-N	Influent/Effluent wastewater	Spectro-photometric	1 hour period
NO_3-N	Influent/Effluent wastewater	Spectro-photometric	1 hour period
SO_4^{-2}	Influent/Effluent	Spectro-photometric	1 hour period

According to the influent wastewater and biogas analysis, loading rates of wastewater and biogas are determined, hydraulic retention time (HRT) of wastewater, empty bed contact time (EBCT) for biogas, pressure of biogas, H_2S / NO_3^- and H_2S / NO_2^- ratios are evaluated, and all experiments are done by the light of this parameters. Mass transfer of H_2S content of biogas is thought that, all of H_2S is

transferred by feeding stream to the wastewater stream. Influent streams of wastewater and biogas are measured by one-time before feeding to the system. This values are thought that, they don't change in excessive amounts. Because influent wastewater and biogas are provided from continuous working treatment plant including activated sludge system of 4000 m^3 volume, and a biogas tank in huge dimensions. But concentrations of these streams could change according to the raw wastewater values fed to the anaerobic and aerobic reactors. So in every study period, feed measurements are done by occasionally.

Because of low HRT values, working and sampling periods of the system have not a necessity of lots of samplings and study period. In generally, below one hour working periods are sufficient for determining the removal rates.

4 RESULTS and DISCUSSION

H_2S removal from biogas with autotrophic denitrification process by using nitrate and nitrite is an efficient process. Generally this process has been studied by labaratory scale experiments and wastewater is rarely prefered for this process. Specially synthetic nitrate and nitrite solutions are generally used in this process. And also, for autotrophic denitrification, this organisms are bioaugmented on activated sludge by using immobilized biofilters or other packing materials. In this study there is no sludge acclimation period, or there is no sludge recycle for sludge retention's expansion. Also there is no addition of trace and nutrient elements for growth of autotrophic denitrifiers. It is thought that all required chemical or biological necessities are supplied naturally from this industrial wastewater treatment plant. This thought is based on anaerobic reactor and biogas formation and also, activated sludge system for polishing treatment step by step. In anaerobic treatment system wastewater has a high soluble sulphide concentration in equilibrium with H_2S in the gas form. This stream is fed to the aerobic treatment system sequentially. In this system nitrification and denitrification occurs simultaneously. Activated sludge system has 4 pools. Pre-denitrification system is processed in this system. So first pool is anoxic, there is no oxygen transfer in this region. Other 3 pools are aerated and there is sludge recycle from 4th pool to the first pool to denitrify the oxidized nitrogen forms to N_2 gas. Depending on all these process flow, autotrophic denitrifiers could be easily grown in this plant, and the wastewater taken from here to feed the absorption tower could be used for this autotrophic denitrification process.

H_2S removal rates from this process is basically depending on loading rates of wastewater and biogas, initial concentrations NO_3, NO_2 and H_2S in the streams, and stoichiometric relation defined in previous experimental studies.

4.1 Experimental Conditions

4.1.1 Volatile suspended solid (VSS) concentration profile

In all study period, the VSS concentration in raw wastewater differed according to the operation conditions of industrial wastewater treatment plant. In that case, the VSS concentration profile was between 2100 – 5100 mg/L, comparetively suspended solid concentrations were between 2800 – 6000 mg/L. In former studies, inoculum sludge was taken from different treatment plants and this sludge was acclimated with nitrite and nitrate solution. After a long period later, continuous sulphide feeding started and then since the steady state values were reached, sulphide removal efficiencies showed higher ratios [55-60]. In this study, there was no sludge acclimation or sludge retention period applicated. It was thought that, autotrophic organisms like *Thiobacilllus denitrificans* were present in activated sludge, and the mixed culture that responsible for anoxic sulphide oxidation were naturally acclimated by raw wastewater including nitrite, nitrate and sulphide concentration in it. In a similar study, different activated sludge concentrations were tried for sulphide removal [7]. Activated sludge concentrations in that study were between 7300 mg/L – 17000 mg/L, and increasing sludge concentrations resulted with higher sulphide removal ratios [7]. In this study there was not a distinctive increase on H_2S removal corresponding to activated sludge concentration increase. This situation mostly depend on very high volumetric H_2S loading rates and insufficient NO_3 and NO_2 concentrations in raw wastewater. As a result of limited NO_3 and NO_2 concentrations comparing to initial H_2S concentrations, elementary sulphur was predominantly end product of biochemical reaction. On the other hand, biomass production is comparatively less when limited NO_3 and NO_2 concentrations were used as electron acceptor. In all study period, there was not observed any biomass production, so this information also reveals that, there was not any heterotrophic growth while reduction of NO_3 and NO_2 to nitrogen gas occured in anoxic conditions.

4.1.2 pH and temperature

In all study period, influent pH values in raw wastewater were between 7,33 – 8,0. Comparetively, effluent pH values were between 6,58 – 7,3. In normal conditions, anoxic sulphide oxidation process consumes alkalinity and results with pH decrease. But in this study, pH decrease completely depend on CO_2 concentration in biogas. CO_2 concentration in biogas was almostly % 35 on a volume basis. CO_2 was absorbed within wastewater and dissolved in absorption tower resulting pH decrease on effluent wastewater. As seen from Figure 4.1, biogas/wastewater ratio was the main parameter to determine the pH change on the process. As seen from the graph, increasing biogas/wastewater ratio results in higher pH decrease in effluent wastewater. In former studies, different pH conditions were applicated for sulphide removal, and it was shown that, increasing pH values results decreasing H_2S removal efficiencies [55,56]. Especially, the pH range above 8,0 results inhibitive conditions for activated sludge samples for sulphide oxidation [7]. The optimum pH conditions for sulphide removal in that studies were between 6,5 – 7,5 [7]. In this study, influent pH values were higher according to the similar studies, but this situation completely depended on operation conditions in wastewater treatment plant. On the other hand, the influent alkalinity values were high and there was not any alkalinity limitation for autotrophic organisms.

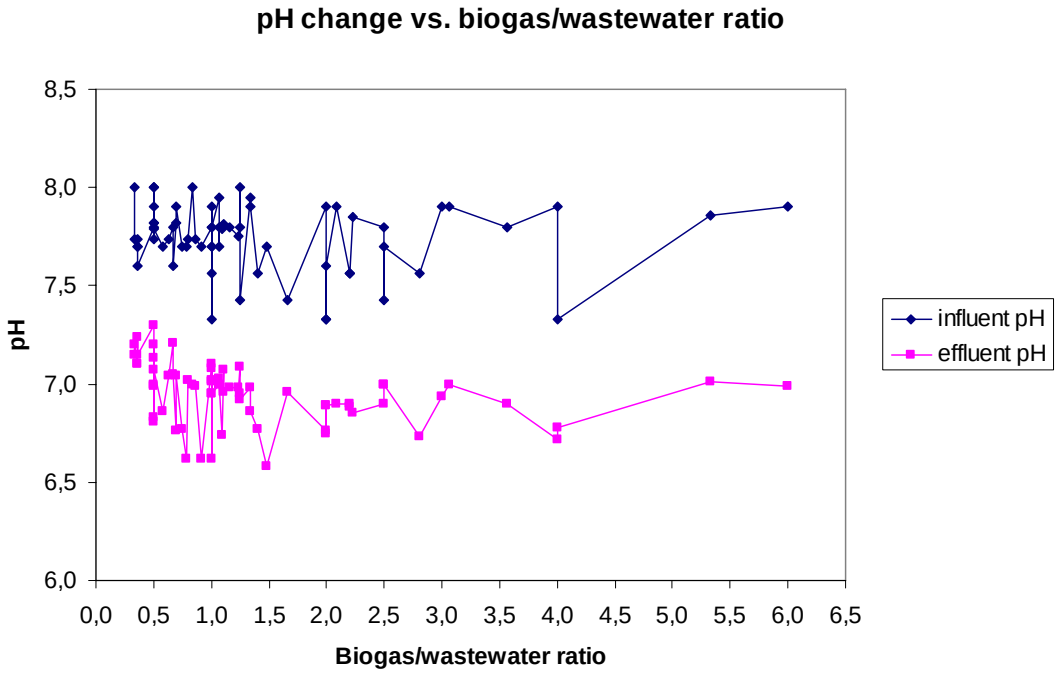

Figure 4.1: pH change vs. biogas/wastewater ratio

When pH and ORP values were evaluated together, it was seen that, pH decrease corresponds to ORP decrease in the absorption tower. As seen from Figure 4.2, increasing biogas flowrate were accelerating the absorption of biogas within wastewater and pH and ORP values were respectingly decreasing step by step

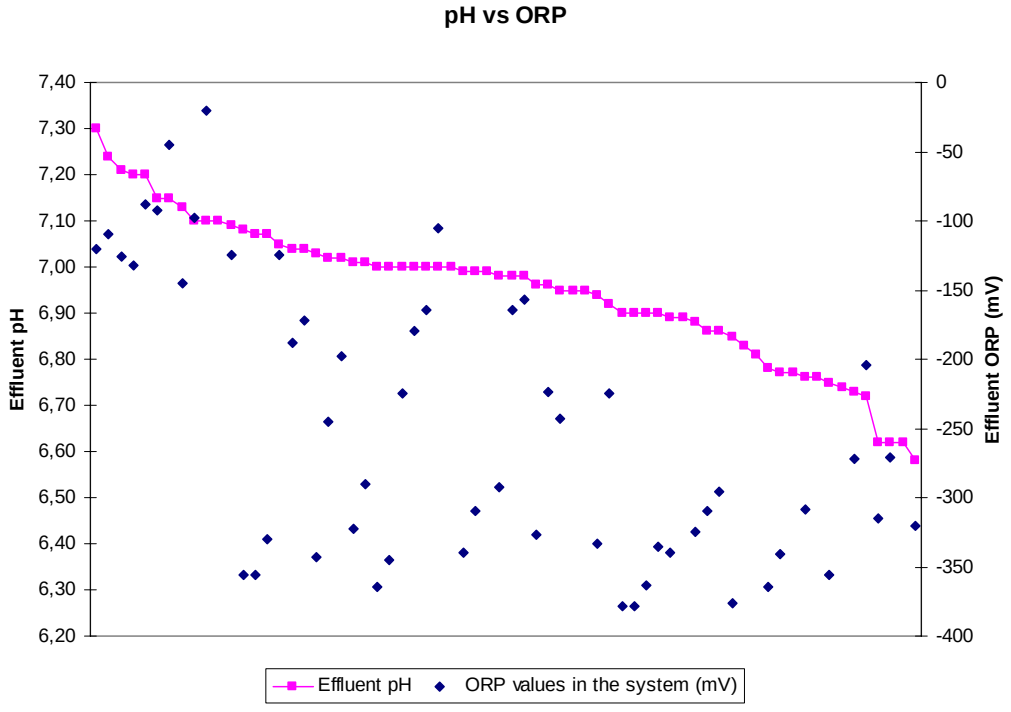

Figure 4.2: pH vs ORP

Temperature was another parameter investigated within all experiments. The influent temperature values in this study differed between 32 – 36 °C. These temperatures were relatively high according to the other studies. These high temperatures completely depended on anaerobic wastewater treatment plant's hot effluent stream reaching the aerobic ponds, and also other hot streams reaching aerobic ponds. Another factor to cause high temperatures in raw wastewater was high ambient air conditions respecting to hot summer months chosen for experiments. In similar studies, influent temperatures were chosen between 20 – 35 °C, but optimum growth conditions given for autotrophic organisms for anoxic sulphide oxidation were between 25 – 30 °C [7,56,58]. High temperatures in the ponds results with nitrite accumulation caused by inhibition of high temperatures for nitrite oxidizers in nitrification process. One of the reasons of higher nitrite concentrations according to the nitrate concentration in influent wastewater was based on this situation.

4.2 Loading Rates

4.2.1 H_2S loading rates

H_2S loading rates are one of the main parameters of this study. Because of daily fluctuations of feed biogas constituents, biogas flowrates are adjusted according to the influent H_2S concentrations in the biogas. H_2S content of biogas was changed between %1,3 - %3,7 on a volume basis. Influent SO_4 load to the anaerobic wastewater treatment system and pH are the main parameters effecting the inlet H_2S concentrations in biogas produced. Within all study period, various H_2S loading rates are examined. As seen from the graph there is loading interval between 92 g/h – 1100 g/h H_2S. Another parameter to compare the loading rates to the other experiments is volumetric H_2S loading rate. Volumetric loading rates are calculated according to the wet volume of absorbtion column setting the liquid height in it. In Figure 4.3, the volumetric loading rate interval is given.

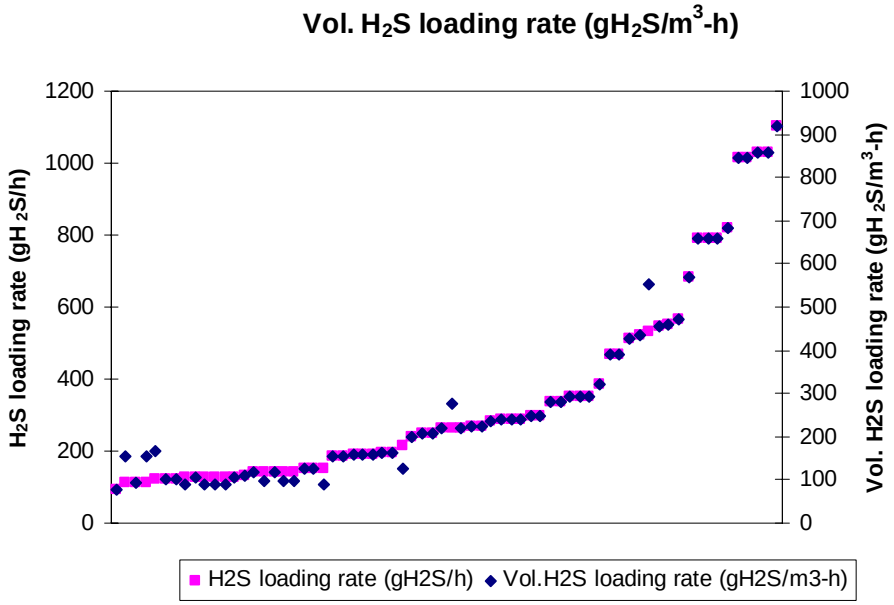

Figure 4.3: Volumetric H_2S loading rate

Volumetric H_2S loading rates in this study are the highest of the similar experiments done until this work. Comparing to the other pilot scaled experiments the volumetric loading of H_2S within biogas is nearly 10 times higher [53, 57, 58]. Maximum loading rate tried in those experiments was 917 g H_2S /m^3-day

4.2.2 NO_3 and NO_2 loading rates

NO_3 and NO_2 concentrations in the influent wastewater have showed fluctuations in the study period. Generally NO_2 concentrations was higher than NO_3 concentrations in the wastewater. There are some reasons to reveal this situation. First of all, the temperature in the aerobic treatment ponds are high (approximately 35°C). For nitrite oxidizer microorganisms, 30°C is the limited value gathered from early studies. And also the pH in the aerobic zone is high (approximately 7,9). For nitrite oxidizers this pH inhibitive [56]. Other parameters that can affect the complete nitrification of nitrite to nitrate could be limited aeration and lower sludge age [56]. In some periods, dissolved oxygen in the aerobic ponds are below 1 mg/L. And also sludge age sometimes was below the required limitations according to the sludge production in the ponds. Nitrite nitrogen and nitrate nitrogen concentrations in the influent wastewater was respectively between 0,2 – 127 mg/L and 6,4 – 70 mg/L. In Figure 4.4, influent NO_3-N and NO_2-N concentrations are given.

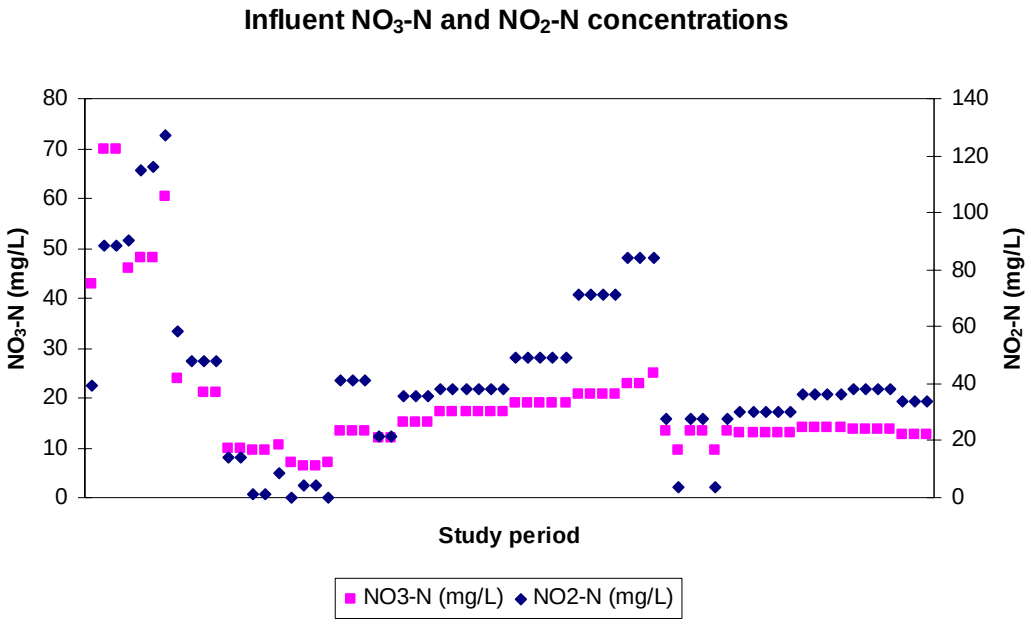

Figure 4.4: Influent NO_3-N and NO_2-N concentrations

Volumetric loading rates of NO_3 and NO_2 are the main parameters to determine the removal relationship of the components. These volumetric loading rates are the highest according to the other studies. Because of high influent H_2S loading rates, volumetric nitrate and nitrite loading rates should be kept higher considering the stoichiometric relationship of these compounds. In Figure 4.5, the volumetric loading rates are showed.

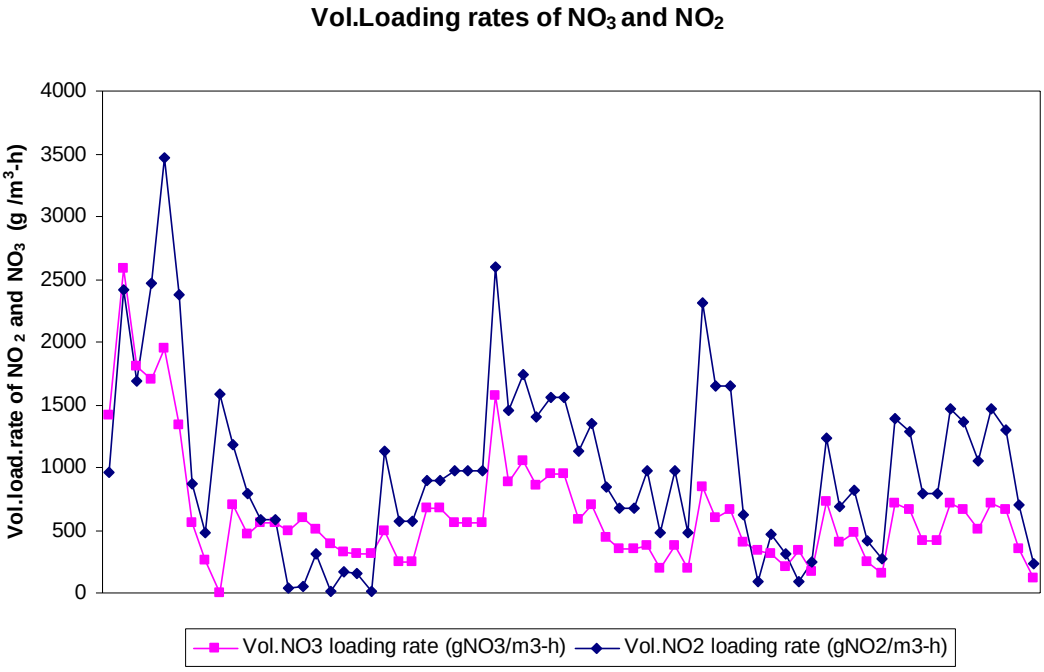

Figure 4.5: Volumetric loading of NO_3 and NO_2

4.3 Molar Loading Rates of H_2S to NO_3 and NO_2

During the anoxic sulfide oxidizing process (ASO process), the actual bio-chemical reactions are as follows [7,60]:

Sulphate production;

$$S^{-2} + 1.3984NO_3^- + 0{,}0504NH_4^+ + 0.201CO_2 + 0{,}0504HCO_3^- \rightarrow SO_4^{-2} + 0.0504C_5H_7NO_2 + 0{,}101H^+ + 1{,}728H_2O + 0.699N_2 \quad \textbf{(4.1)}$$

Elementary sulphur production;

$$S^{-2} + 0.3464NO_3^- + 0.0536CO_2 + 0{,}0134NH_4^+ + 0{,}8464H^+ + 0{,}0134HCO_3^- \rightarrow S^o + 0.0134C_5H_7NO_2 + 1.1622H_2O + 0.1732N_2 \quad \textbf{(4.2)}$$

According to standard Gibbs free energy change, the reaction shown in Eq. 4.1 takes place easily generating sulfate as the main product. However, to exercise the resource recovery, the reaction of Eq. 4.2 is preferable whereby elemental sulfur is

the main reaction product. Thus, it is obvious that the influent S/N ratio should be a key factor for simultaneous treatment of sulfides and nitrates.

Also there are some reactions given for oxidation with nitrite, The overall biochemical reactions during sulfide oxidation under different sulfide/nitrite molar ratios are shown in Eq. (4.3) and (4.4), indicating that reactions producing sulfate are thermodynamically more favored [60].

$$S^{-2} + 2{,}2976NO_2^{-2} + 0{,}2208CO_2 + 0{,}0552HCO_3^{-} + 0{,}0552NH_4^{+} + 2{,}2984H^{+} \rightarrow SO_4^{-2} + 0{,}0552C_5H_7NO_2 + 1{,}0936H_2O + 1{,}1488N_2 \quad \textbf{(4.3)}$$

$$S^{-2} + 0{,}5706NO_2^{-2} + 0{,}0576CO_2 + 0{,}0144HCO_3^{-} + 0{,}0144NH_4^{+} + 2{,}5706H^{+} \rightarrow S^{0} + 0{,}01444C_5H_7NO_2 + 1{,}2708H_2O + 0{,}2852N_2 \quad \textbf{(4.4)}$$

In this study, NO_3 and NO_2 are both present in the feed wastewater. So comparing the H_2S removal rates, molar loading rates should be calculated by taking NO_3 and NO_2 together into account. According to the stoichiometric relationship, theoretical molar ratios are given in Table 4.1

Table 4.1: Stoichiometric molar ratios

End product	S^{-2} / NO_3	S^{-2} / NO_2
Sulphate	0,72	0,44
Elementary sulphur	2,89	1,75

Considering that both nitrate and nitrite are present in the influent, so stoichiometric values should be between the values given in Table 4.1, H_2S / NO_3 + NO_2 molar ratio will be between 0,44 – 2,89. However in the experiments, because of high influent H_2S concentration and deficiency of nitrite and nitrate concentration enough in wastewater, generally this molar ratios are higher than the stochiometric values. In Figure 4.5, this situation is indicated.

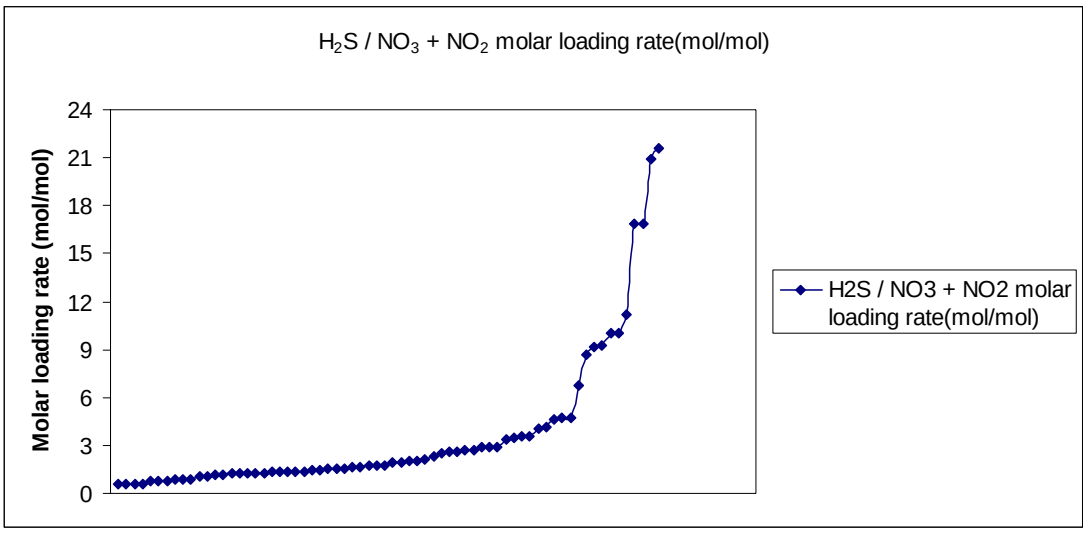

Figure 4.6: Molar loading ratio of H_2S / NO_3 + NO_2

As seen from the Figure 4.6, in this study it was worked with extreme molar ratio values. High H_2S concentration in inlet biogas and high feed flowrates of biogas comparing to low initial nitrate and nitrite concentrations in wastewater reveals this situation.

4.4 Biogas and Wastewater Flowrates

In all experimental study the biogas flowrates were between 5 – 25 m^3/h. Because of hydrostatic pressure in the absorbtion column depending on the liquid height, the inlet biogas pressure should be higher than this pressure to overcome the pressure loss. Actually, in study period, the liquid height is above 2 meters. So at least, 0,2 bar biogas pressure is needed to overcome the hydraustatic pressure within the column. 5 m^3/h biogas flowrate is supplying a 0,3 bar pressure above the hydrostatic load. Because of this situation there could not be reached smaller values. Biogas compressor has a 100 m^3/h flowrate capacity, but in this study 25 m^3/h biogas flowrates are sufficient to experiment the maximum substrate loads.

In all experimental study the wastewater flowrates were between 2,5 – 15 m^3/h. Required wastewater flowrates were adjusted automatically by pneumatic valve and also the liquid heights on the absorption tower were set automatically by effluent discharge pump. Most of the experiments were carried out on %50 liquid height of

absorption tower. This liquid height is chosen for two reasons. One of them is adequate inlet pressure required for head loss on the system, second one is to supply the appropiate hydraulic retention time in order to obtain the optimum reactions in the column.

Biogas / Wastewater ratio is one of the most important controlling parameters of complete sulphide oxidation process to determine the reaction and also end products of the reaction. In this study biogas/wastewater feed ratio was selected between 0,33 – 6. This ratio is absolutely depending on the required H_2S removal and biogas flowrate. In Figure 4.7, the distribution of biogas and wastewater flowrates against biogas/wastewater ratio is given.

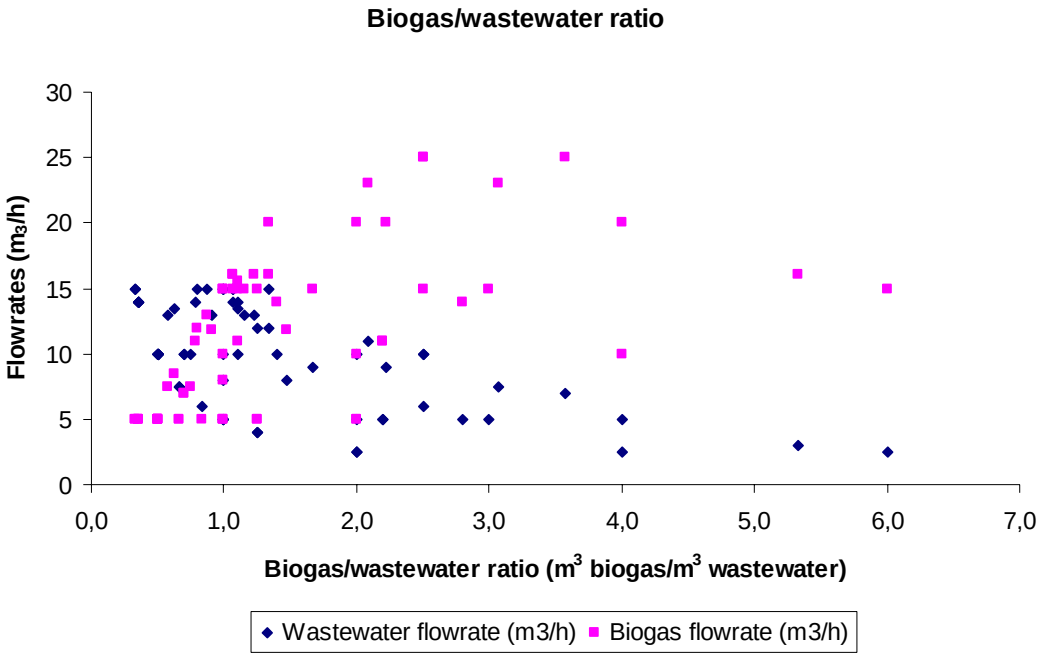

Figure 4.7: Biogas/wastewater ratio distribution respecting flowrates

4.5 H_2S Removal Ratio

In all experimental studies, H_2S removal ratios are varied between %48 - %96. This removal ratios depend on many parameters:

4.5.1 Effect of volumetric H_2S loading rate

H_2S removal is directly affected by volumetric loading rate of H_2S within biogas. Previous studies about this manner show that, in volumetric loading rates below 100 g/m^3-h, complete H_2S removal can be proceeded in anoxic sulphide oxidation reactors [53,57,58]. In this study, minimum volumetric H_2S loading rate is 70 g/m^3-h and it reaches to 900 g/m^3-h in the later experiments. This extreme operation conditions directly affect the H_2S removal rates. In Figure 4.8, H_2S removal change against vol. H_2S loading rate is shown.

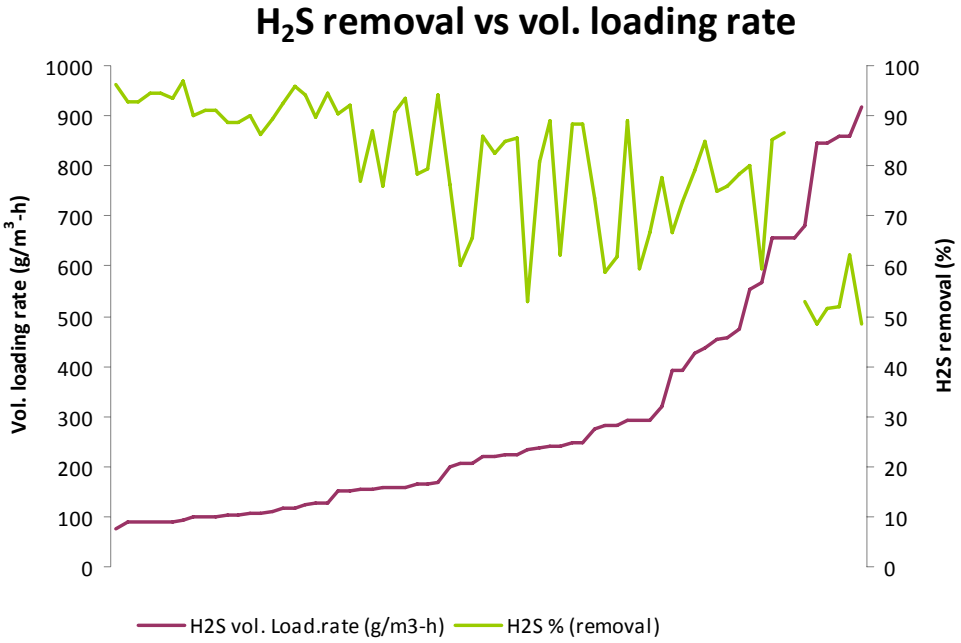

Figure 4.8: H_2S removal vs Vol. H_2S loading rate

As seen from the Figure 4.8, H_2S removal rates are declining against increasing volumetric H_2S loading rates. Maximum removal rates are encountered in the range of 70 - 150 g/m^3-h volumetric H_2S loading rates. As supporting this situation, minumum removal rates are come upon in the range of maximum volumetric H_2S loading rates.

Another H_2S removal parameter, "volumetric H_2S removal rate" puts forward another information about this subject. As seen from the Figure 4.9, increasing volumetric H_2S removal rate does not reflect to increasing H_2S removal rate.

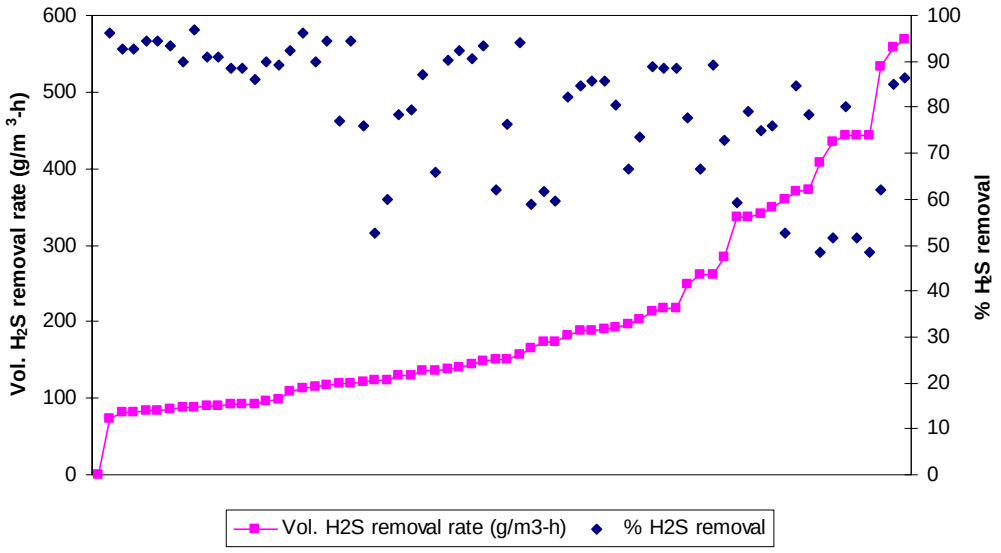

Figure 4.9: H_2S removal vs Volumetric H_2S removal rate

Another approach about this manner can be evaluated with influent and effluent % H_2S concentration in the system. While biogas/wastewater ratio increasing, the difference between inlet and outlet H_2S concentration is increasing too (Figure 4.10). In this period, also total H_2S removal from the system is increasing based on the Figure 4.11 given below.

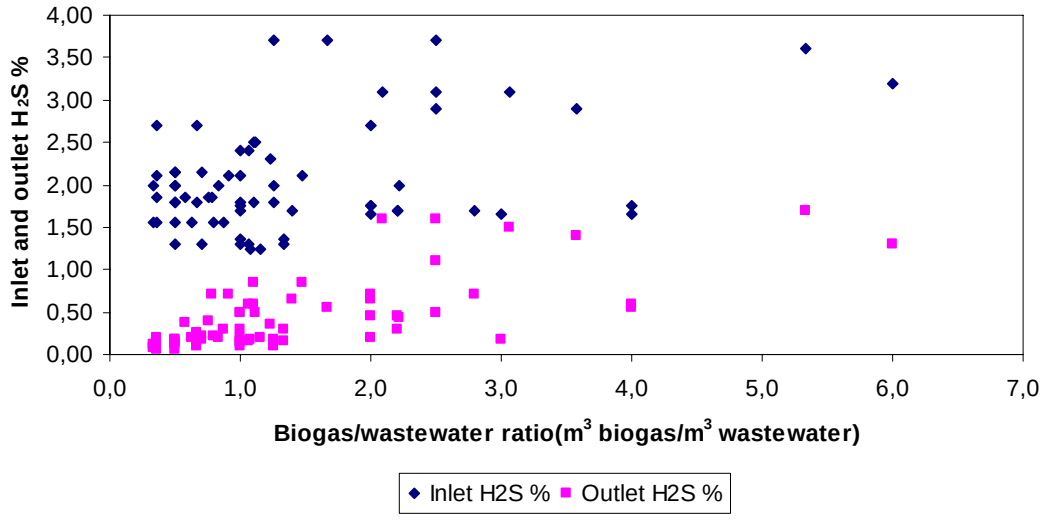

Figure 4.10: H_2S change vs. biogas/wastewater ratio

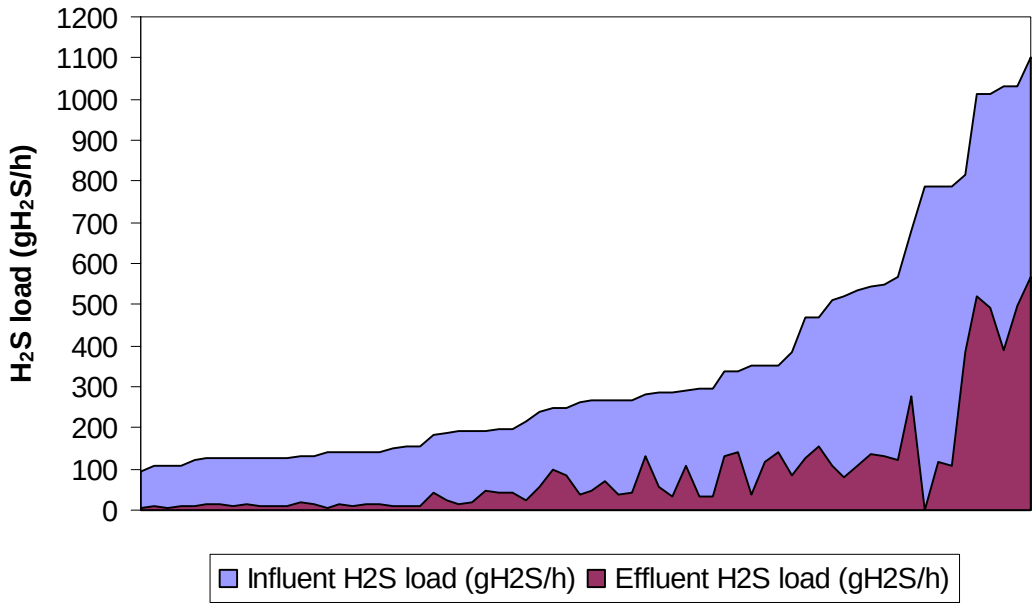

Figure 4.11: H_2S influent and effluent loads

4.5.2 Effect of biogas/wastewater ratio

H_2S removal efficiency strictly depends on biogas/wastewater ratio in this study. For maximum H_2S removal rates, 0,33 – 0,5 interval is the optimum biogas/wastewater ratio observed in this system. As seen from Figure 4.12, while this ratio is increasing H_2S removal percentages are declining meaningfully. In the experiments it can be concluded that, biogas flowrates between 5 – 7,5 m^3/h and on the other hand, wastewater flowrates between 10 – 15 m^3/h are taken the best place in order to get maximum H_2S removal percentages. Important point in here is the EBRT (Empty Bed Residence Time) for biogas in the absorption tower. EBRT for 10 - 20 minutes is responsing %90 - %96 H_2S removal ratio from biogas. Lower EBRT values come out with lower H_2S removal rates (Figure 4.13).

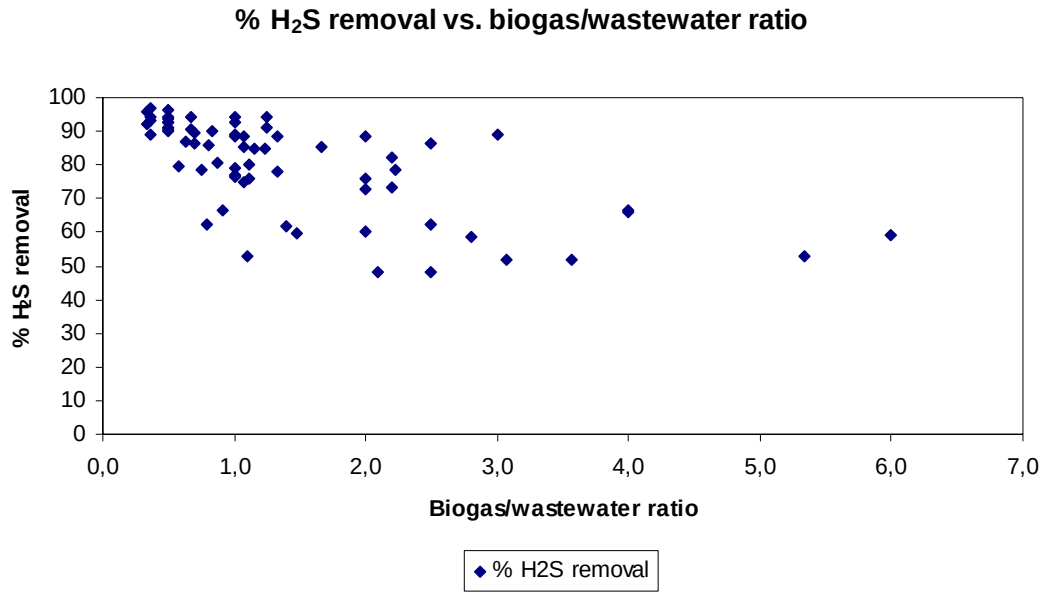

Figure 4.12: H_2S removal vs Biogas/wastewater ratio

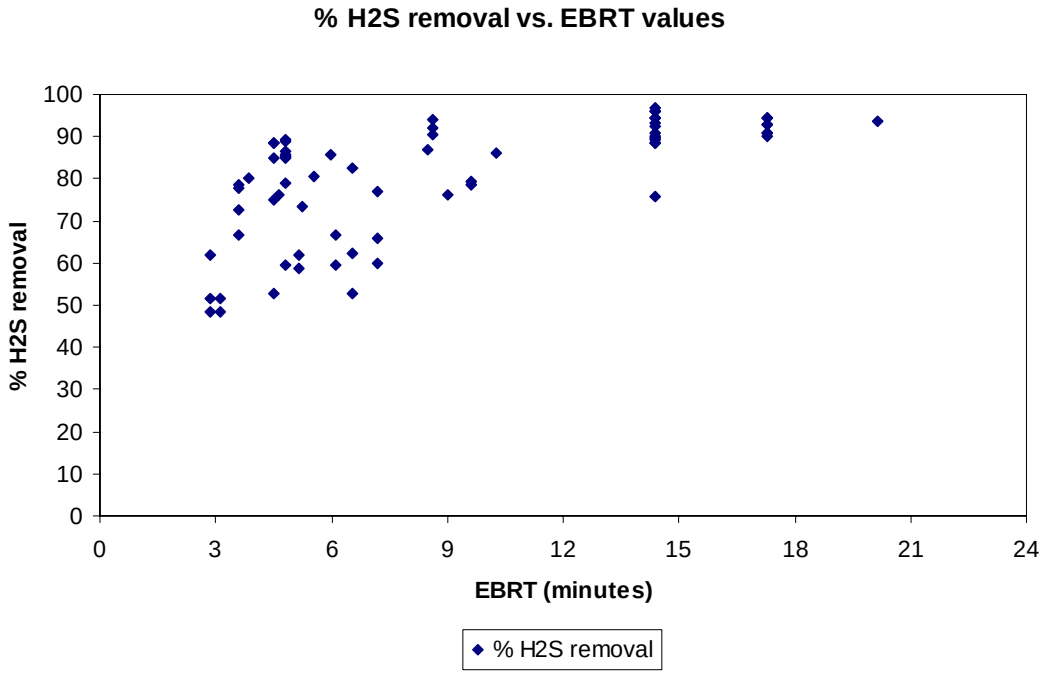

Figure 4.13: %H_2S removal vs. EBRT

While increasing the biogas/wastewater ratio, it is observed that the effluent H_2S concentration in biogas is raising, but on the other hand the difference between influent and effluent H_2S loads are increasing, so load based H_2S removal is increasing in these conditions (Figure 4.14).

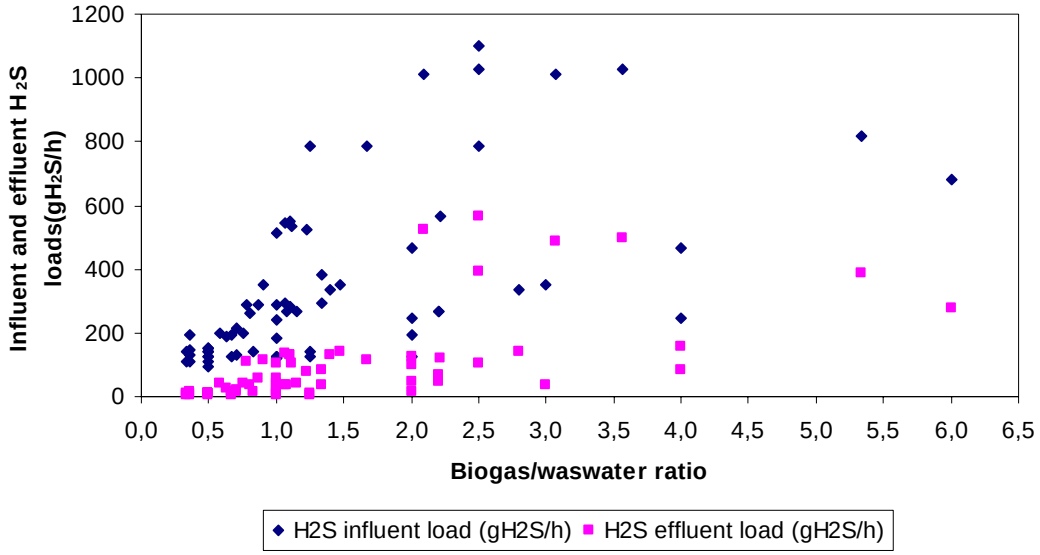

Figure 4.14: Effect of biogas/wastewater ratio vs influent effluent loads of H_2S

In Figure 4.15, biogas/wastewater ratio respecting biogas and wastewater flowrates are given. 5 m^3/h biogas flowrate and 15 m^3/h wastewater flowrate are repeated many times in order to reach the maximum H_2S removal rates in almostly same conditions.

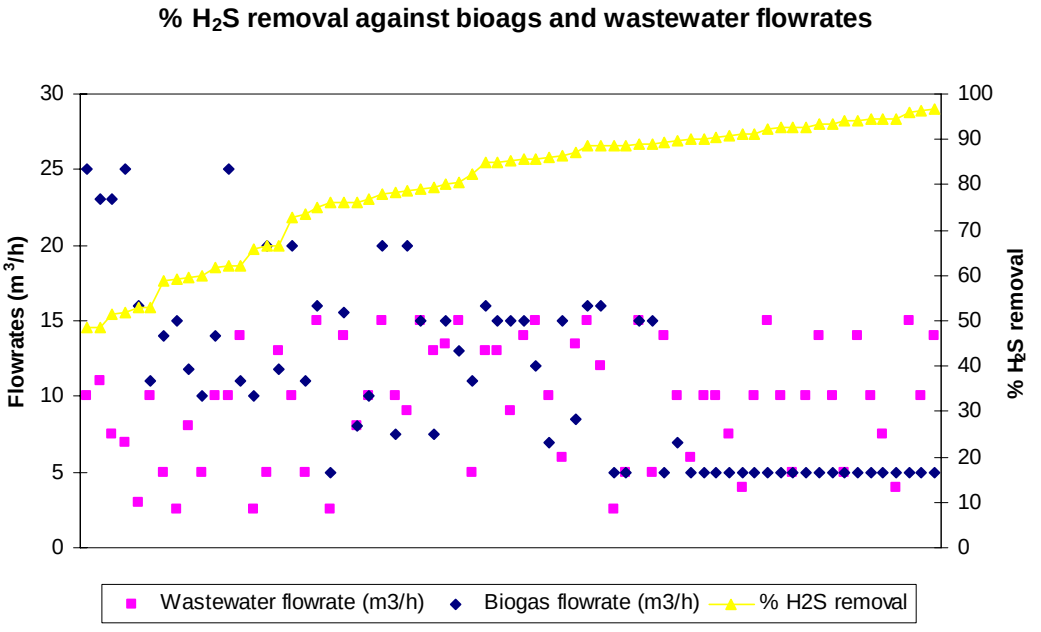

Figure 4.15: H_2S removal vs biogas and wastewater flowrates

4.5.3 Effect of molar loading rates of H_2S to NO_3 and NO_2

In former studies about anoxic sulphide oxidation process there were used S^- / NO_3^- and S^- / NO_2^- ratios seperately to interprete the autotrophic denitrification reaction and reaction efficiency [56,59,60]. In this study NO_3 and NO_2 are both present to oxidize H_2S in influent wastewater, so there will be a matrix about this stoichiometric relationship. This matrix can be defined as in Table 4.2

Table 4.2: Stoichiometric molar ratios with NO_3 and NO_2

End product	S^{-2} / NO_3	S^{-2} / NO_2	S^{-2} / NO_3 + NO_2
Sulphate	0,72	0,44	0,44 – 0,72
Elementary sulphur	2,89	1,75	1,75 – 2,89

In Figure 4.16, it is obviously seen that, maximum H_2S removal rates are eventuated in between 0 – 2 molar ratios of H_2S / NO_3 + NO_2.

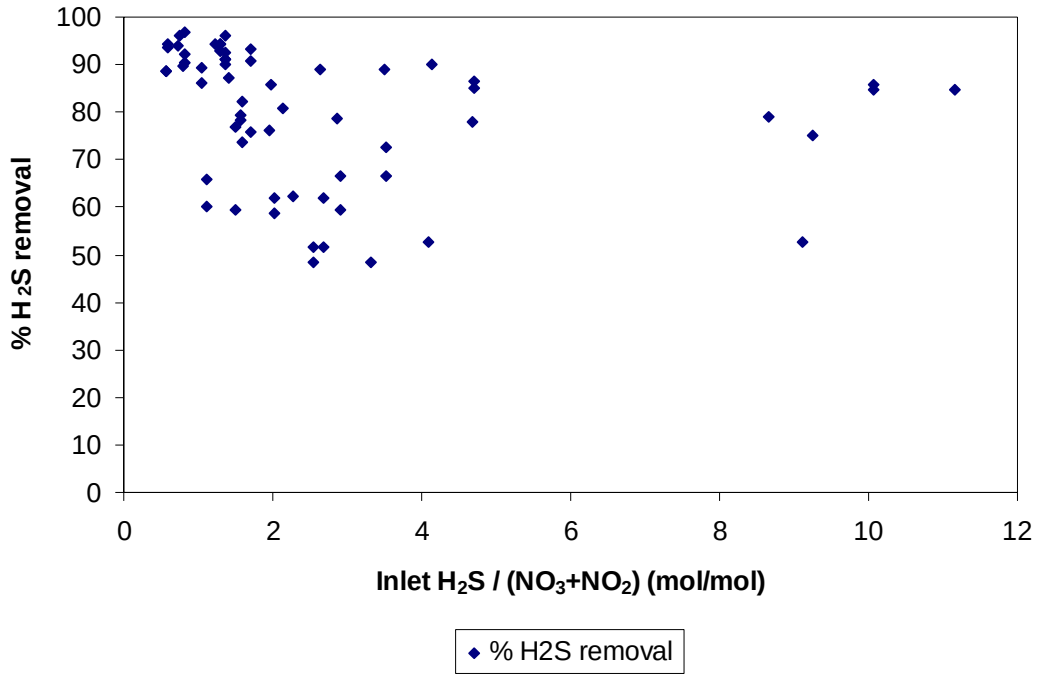

Figure 4.16: H_2S removal vs (H_2S /NO_3 + NO_2) ratio

4.6 NO_3 and NO_2 Removal Rates

In all experimental studies, NO_3 removal rates are varied between %7 - %63. NO_2 removal rates are varied between %10 - %98. NO_2 removal rates were mostly higher than NO_3 removal rates. This removal rates depend on many parameters:

4.6.1 Effect of volumetric H_2S loading rates

In this study, volumetric H_2S loading rates were varied between 76 – 917 gr/m^3-h. In all loading rates, NO_2 removal rates were higher than NO_3 removal rates. Former studies experienced that, nitrite removal rates were higher than nitrate removal rates in high volumetric H_2S loading rates above 40 g/m^3-h [59]. In those experiments, it is observed that, nitrite as electron acceptor were able to tolerate 1920 mg/L sulphide in influent wastewater, while nitrate were able to tolerate 580 mg/l sulphide concentration respecting 40-100 g/m^3-h vol.H_2S loading rate [56,59]. As seen in Figure 4.17, NO_2 removal rates are higher than NO_3 removal rates. NO_3 removal rates could reached maximum %63, but nitrite removal reached %98 specially in the vol. H_2S loading rates between 430 – 660 g/m^3-h (Figure 4.17). In this area, biogas flowrates are between 10-15 m^3/h and H_2S removal rates are between %48 - %75. These results show that, when increasing the biogas flowrate respecting high biogas/wastewater ratio, it helps absorption of biogas in wastewater more easily in the tower and subsequently the biochemical reaction rate of NO_2 and NO_3 with H_2S in biogas increases. But after that point, higher volumetric H_2S loading rates (650-917 g/m^3-h) and biogas/wastewater ratio cause substrate inhibition and consequently decrease the removal rates of NO_2 and NO_3 and also H_2S. Former studies support these results as while increasing the vol. H_2S loading rate from 10-40 g/m^3-h, nitrate removal rates decreased from %70-80 percentages to %20-25, but nitrite removal rates were still higher (%85-95).

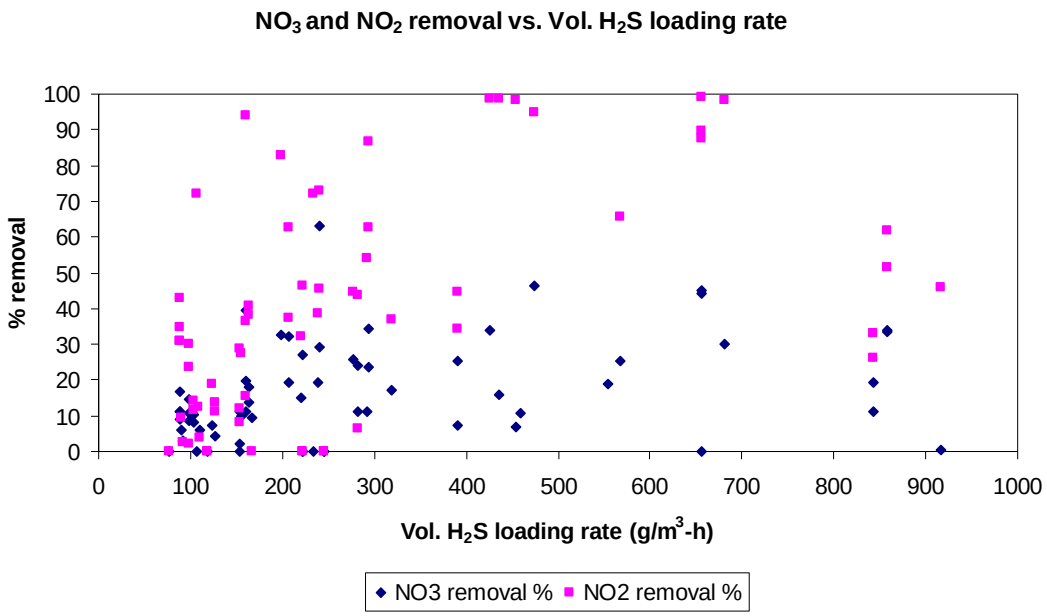

Figure 4.17: NO_3 and NO_2 removal rate vs Vol. H_2S loading rate

4.6.2 Effect of biogas/wastewater ratio

Biogas/wastewater ratio is one of the main parameters effecting the NO_3 and NO_2 removal rates. In collaboration with volumetric H_2S loading rate, biogas/wastewater rate specifies the NO_3 and NO_2 removal rates and also reaction end products. In Figure 4.18, the removal rates are given. As seen from the Figure 4.18, biogas/wastewater ratio between 0 – 1, the removal rates are under %80 and %40 respectively for nitrite and nitrate. In this region biogas flowrates are about 5 m^3/h, besides the inlet biogas pressure to the absorption tower is 0,3 bar which is the limit value to overcome the hydraulic pressure of liquid height on it. Similar results are supported by volumetric loading rate's effect on nitrate and nitrite removal rates. Volumetric loading rates between 70 – 430 g/m^3-h eventuated as low nitrite and nitrate removal rates respecting below %80 and %40. It means that, in absortion tower, NO_3 and NO_2 removal rates could not be observed very sensitively because of low biogas flowrates and initial pressure.

While increasing the Biogas/wastewater ratios between 1 – 2,5, nitrite and nitrate removal rates starts to increase, specially between 2 – 2,5, nitrite and nitrate removal rates reach to their maximum values. This situation exactly fits with the effect of volumetric loading rate in the range of maximum nitrite and nitrate removal rates.

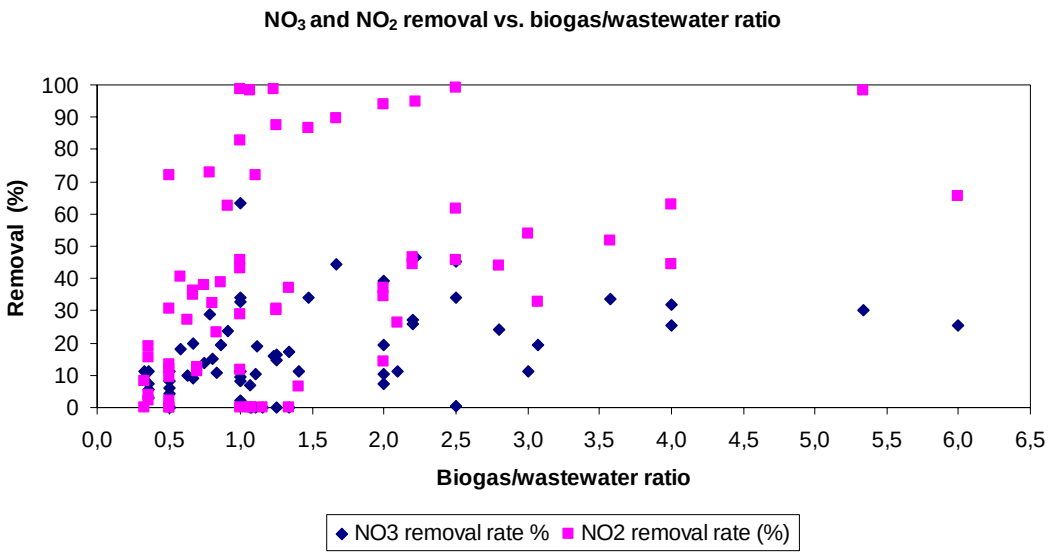

Figure 4.18: NO_3 and NO_2 removal vs. biogas/wastewater

4.6.3 Effect of molar loading rates of H_2S to NO_3 and NO_2

In Figure 4.19, it was showed that, interval of molar loading rates of H_2S to (NO_3 + NO_2) for maximum H_2S removal rate is 0 – 2. In this region, NO_3 and NO_2 removal rates are quite little according to the molar loading rates between 2 – 4. When looking to the stoichiometric relationship, it can be seen that 1,75 – 2,89 molar loading interval is favouring elementary sulphur production as end product. In this study, elementary sulphur production favours in the region above 2,5 molar loading ratio of H_2S to (NO_3+NO_2).

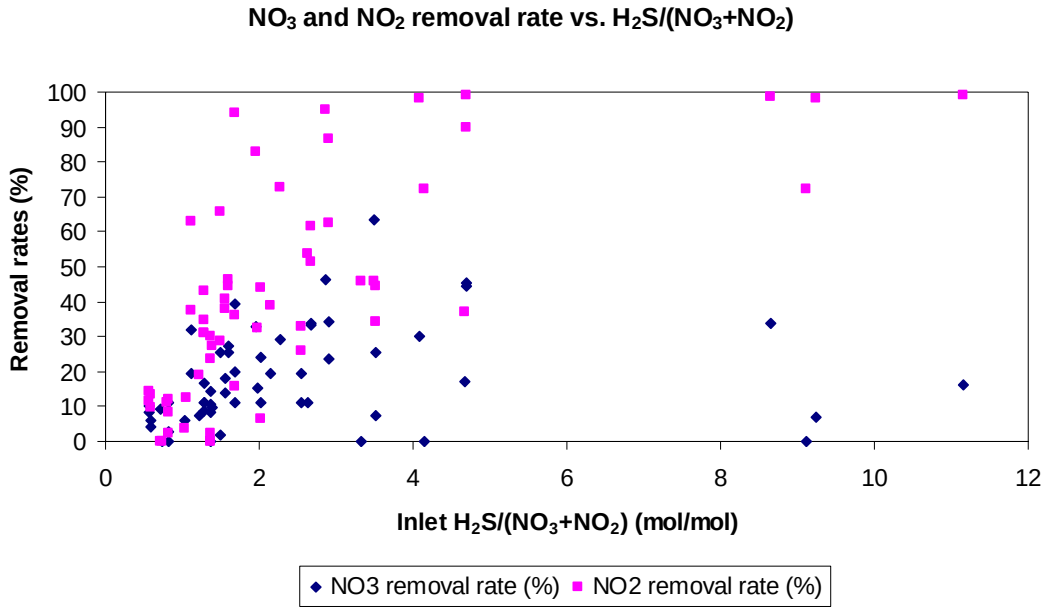

Figure 4.19: NO_3 and NO_2 removal rate vs. inlet H_2S / NO_3 + NO_2

Volumetric total N removal (Nitrite-N and Nitrate-N) against molar loading rate of H_2S/NO_3+NO_2 is another indicator to show the maximum removal rates of NO_3 and NO_2 in this region (Figure 4.20).

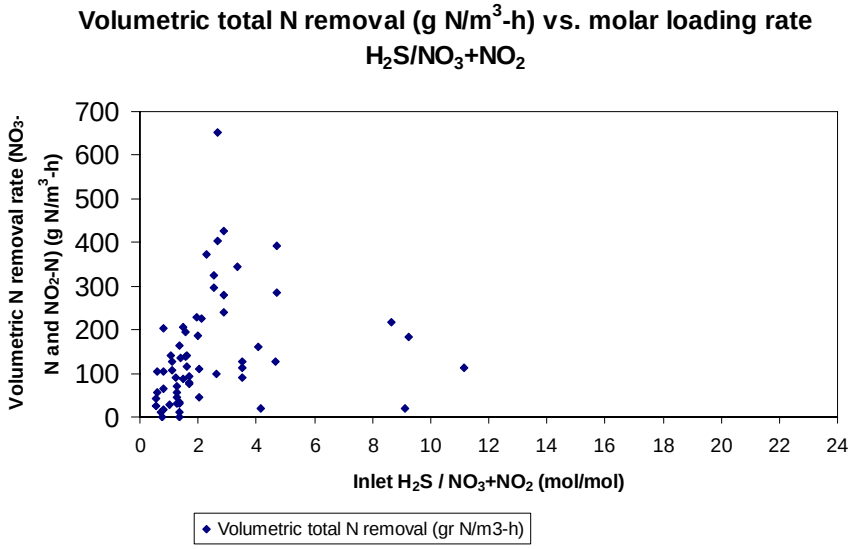

Figure 4.20: Vol. total N removal rate vs inlet H_2S /NO_3+NO_2

As seen from Figure 4.20, maximum volumetric total N removal was pointed in molar loading rate interval 2,5 – 3,5. In this area, H_2S removal was about %50 - %80, however, volumetric H_2S removal had reached maximum values in this area. In

Figure 4.21, it was shown that, increasing volumetric N removal responds to increasing volumetric H_2S removal. Especially, above 400 g/m^3-h volumetric N removal rates respecting 2,5 – 3,5 molar loading rates of (H_2S / NO_3+NO_2), answers maximum volumetric H_2S removal rates observed in the system.

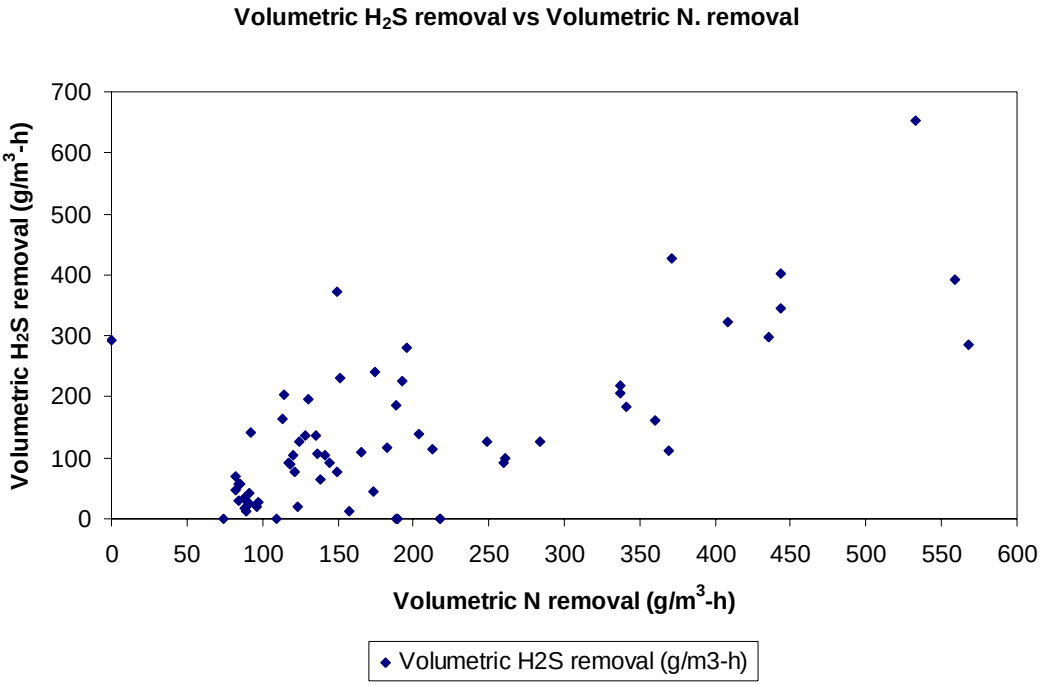

Figure 4.21: Volumetric H_2S removal vs. volumetric N removal

While examining yield value of H_2S / NO_3+NO_2 against inlet molar loading ratio of H_2S / NO_3+NO_2, it can be seen that, inlet molar loading ratio between 0 – 2 responds to very high yield values. It shows that, H_2S removal against initial molar loading ratio is very high in this region. Actually in this region, NO_3 and NO_2 removal rates could not be observed because of lower biogas flowrates. After inlet molar ratios reached between 2 – 10, yield values come close by theoretical value as seen in Figure 4.22.

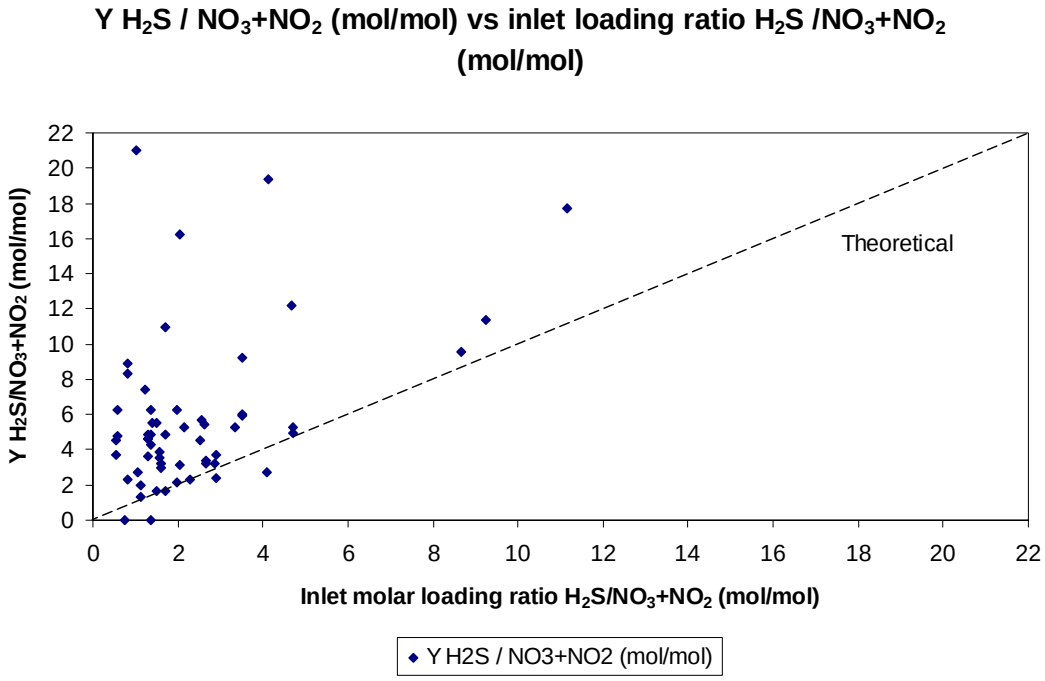

Figure 4.22: Y H_2S /NO_3+NO_2 vs inlet molar loading rate H_2S /NO_3+NO_2

4.7 Specific Sulphide Oxidation Rates (q_S^{-2})

Specific sulphide oxidation rate is one of the important parameters that indicate the efficiency of autotrophic denitrification process actualized within sludge. This value is calculated by g H_2S removal per g of unit volatile suspended solids in a hour period. In this study, specific sulphide oxidation rate reached 0,030 g H_2S / g VSS-h. Calculated specific sulphide oxidation rates in the process were between 0,001 – 0,030 g H_2S / g VSS-h.

When H_2S removal rates were analyzed, it can be seen that, removal percentages of H_2S between %80-95 were encountered by specific sulphide oxidation ratios between 0,001 – 0,01. In Figure 4.23, it is showed that, maximum specific sulphide oxidation values are obtained by maximum volumetric H_2S removal rates.

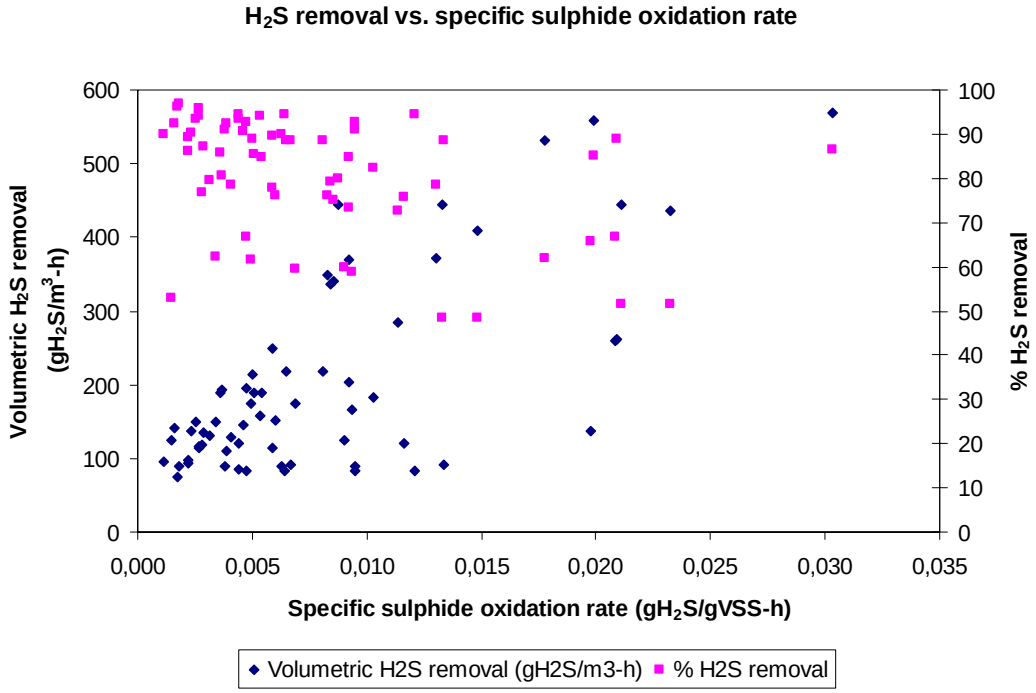

Figure 4.23: H_2S removal vs. specific sulphide oxidation rates

In similar studies, specific sulphide oxidation rates differed between 0,003 – 1,25 g H_2S /g VSS-h. In Table.. below, there is a summary of literature on sulphide oxidation rates [7]. In similar experiments worked with nitrite and nitrate, the specific sulphide oxidation rates are higher than this study. This situation completely depends on activated sludge used in this system. In other experiments, activated sludge was acclimated with high nitrite and nitrate concentrations in long periods, and also sludge is retained in the system within recirculation or immobilization with packed materials on the process. However in this study, sludge acclimation and sludge retention implementations did not executed. Raw wastewater including activated sludge is used in all experiments, and it is thought that, within industrial wastewater treatment system, activated sludge is naturally acclimated with wastewater including nitrite, nitrate and sulphide concentrations.

In this study, volumetric H_2S loading rate was higher than similar studies, especially in the experiments done before with nitrite, the volumetric loading rates are quite little comparetively. There is not enough study about H_2S removal from biogas with specially nitrite and nitrate. So given data in Table 4.3 generally compares the

present experiments done with synthetic wastewater including nitrite and nitrate solutions.

Table 4.3: Summary of literature on sulphide oxidation rates

Reference	Culture	Oxidation type	Electron acceptor	Volumetric loading rate (gS^{-2}/m^3-h)	Specific oxidation rates
Sublette and Sylvester, 1986	*T denitrificans*	Biological	Nitrate		0.17-0.242 g S^{-2}/ gN h
Ongcharit et al., 1990	*T denitrificans*	Biological	Nitrate	11350	-
Gommers et al., 1988	Yeast	Biological	Nitrate	83-125	-
Nishimura and Yoda, 1997	Activated sludge	Biological	Oxygen		0.008 g S^{-2}/ gVSS h
Barborosa et al., 2002	Activated sludge	Biological	Oxygen		0.003-0.0034 g S^{-2}/ gMLSS h
Takashima et al., 2000	*C limicola forma thiosulfatophilum*	Biological	Nitrate		0.012-0.003 g S^{-2}/ g N h
Vaiopoulou et al., 2005	Mixed culture	Biological	Nitrate	19,4	
Manconi et al., 2006	Activated sludge	Biological	Nitrate	6,3	
Yavuz et al., 2007	Activated sludge	Biological+Chemical	Oxygen	2286	0.062-0.234 g S^{-2}/ gVSS h
					1.62-1.8 g S^{-2}/ gN h
Yavuz et al., 2007	Activated sludge	Biological+Chemical	Nitrate	1975	0.047-0.22 g S^{-2}/ gVSS h
					1.55-1.76 g S^{-2}/ gN h
Cardoso et al., 2006	Mixed culture	Biological	Nitrate		1,25 g S^{-2}/ gVSS h
Can Dogan, 2008	Activated sludge	Biological+Chemical	Nitrate	58-83	0,11 g S^{-2}/ gVSS h
Can Dogan, 2008	Activated sludge	Biological+Chemical	Nitrite	20-90	0,04

					g S^{-2}/ gVSS h
Mahmood et al., 2007	Mixed culture	Biological+Chemical	Nitrate	60-135	0,018-0,028
Mahmood et al., 2007	Mixed culture	Biological+Chemical	Nitrite	12,5-40	0,011
Soreanu et al., 2005	Mixed culture	Biological+Chemical	Nitrate	5,7	
Soreanu et al., 2006	Mixed culture	Biological+Chemical	Nitrate	16-33	
This study	Activated sludge	Biological+Chemical	Nitrate and Nitrite	76-917	0,001 – 0,03 g S^{-2}/ gVSS h

4.8 Sulphide Oxidation End Products and Yield Values

While sulphide oxidation process was observed, it was seen that, sulphate and elementary sulphur were the end products formed in the process. Sulphate could be analyzed by spectrophotometric method, but elementary sulphur was defined by visual observation within by colour of wastewater samples and centrifuged sludge. The yellow colour and its tones in wastewater samples shows elementary sulphur production as end product. The equations 4.1 - 4.4 give the stoichiometric relationship of influent nitrite, nitrate and hydrogen sulphide yielding with end products of sulphate and elementary sulphur. Within this study, molar loading ratio of H_2S / NO_3 + NO_2 interval were between 0,5 – 12 Excessive H_2S loading were implemented in almostly every experiment because of high H_2S concentration in influent biogas, and also relatively high biogas flowrates. Comparing the stoichiometric relationship, this situation favours elementary sulphur production as end product (Table 4.4).

Table 4.4: Stoichiometric relation of sulphide oxidation with NO_3 and NO_2

End product	S^{-2} / NO_3	S^{-2} / NO_2	S^{-2} / NO_3 + NO_2
Sulphate	0,72	0,44	0,44 – 0,72
Elementary sulphur	2,89	1,75	1,75 – 2,89

For elementary sulphur production, theoretical H_2S / NO_3+NO_2 molar ratio should be between 1,75 – 2,89 according to the matrix above. For sulphate, this ratio should be between 0,44 – 0,72 respectively. While comparing the theoretical yield values against observed yield values, it is seen that, most of observed yield values are much higher than theoretical yield values for end products as both sulphate and elementary sulphur. As shown in Figure 4.24, observed yield values are above the dragged area for elementary sulphur production between 1,75 – 2,89, and also above the dragged area for sulphate production between 0,44 – 0,72.

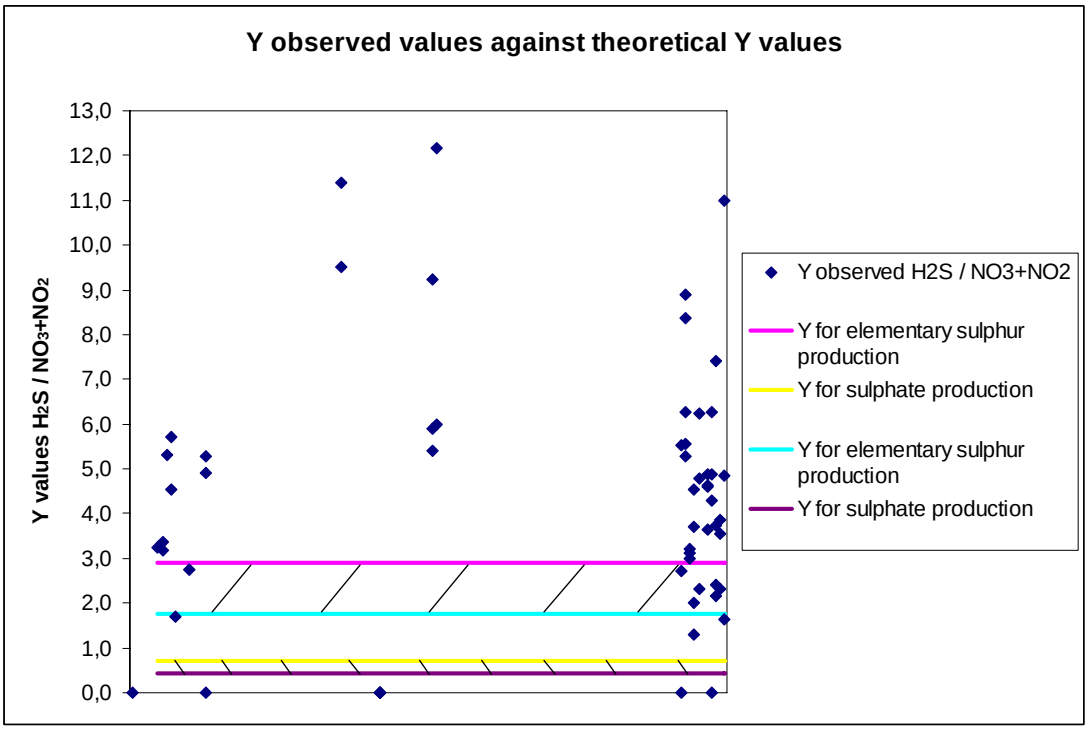

Figure 4.24: Y observed values against theoretical Y values

In Figure 4.25, inlet H_2S / NO_3+NO_2 values as against observed yield Y S / NO_3+NO_2 are given. As seen from the figure, the interval between 0 – 2,5 for inlet H_2S / NO_3+NO_2 molar ratio is replied with 0 – 2 molar ratio of Y SO_4 / NO_3+NO_2. After that point, when the H_2S/NO_3+NO_2 molar ratio increased, SO_4 production had no meaningful increase, so elementary sulphur production starts to increase, and the wastewater samples taken in this period show that, yellow and its tones are appeared to be an indication of elementary sulphur formed.

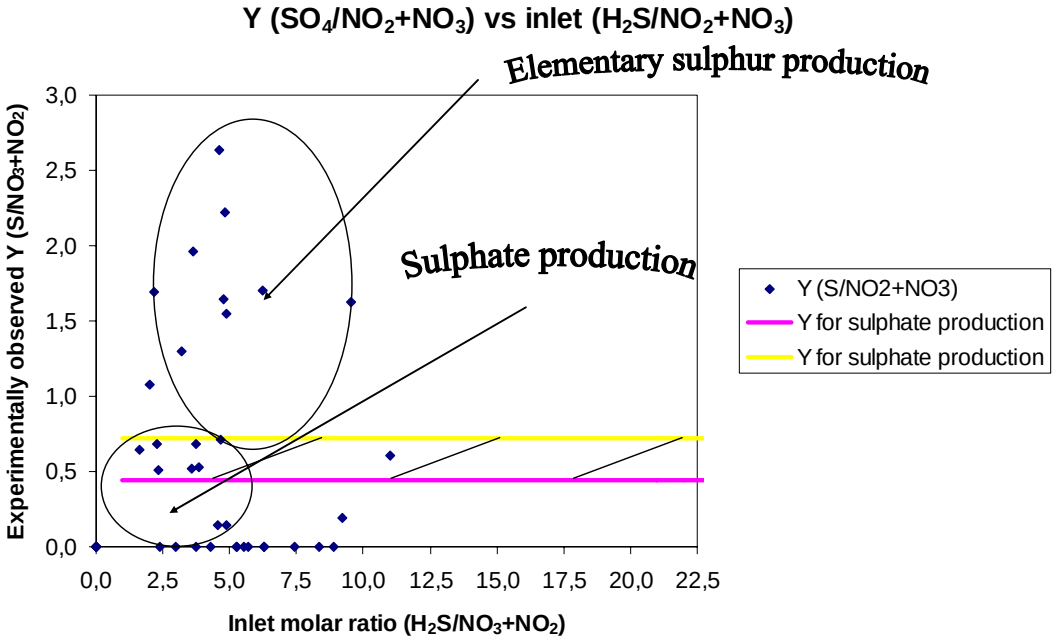

Figure 4.25: Y S / NO_3+NO_2 vs. Y H_2S / NO_3+NO_2

When the effect of biogas/wastewater ratio to SO_4 end product, it is seen that, the biogas/wastewater ratio between 0,5 – 1 favours SO_4 production, however higher values respond to elementary sulphur production.

4.9 Oxidation Reduction Potential (ORP) Values

Oxidation-reduction potential (ORP) is an important water chemistry parameter, providing a measurement of the oxidizing or reducing nature of the water. As pH is a measurement of proton activity and is used to assign a value to the acidity or alkalinity of a system, ORP is the analogous measurement for electron activity and is useful in assigning a value to oxidizing or reducing systems [61]. The oxidizing or reducing nature of water has implications in its ability to support (or not support) life, or the corrosiveness of the water, for example. ORP measurements have applications in the drinking water industry, monitoring the production/ destruction of chlorine or other oxidants; the wastewater industry, monitoring effluent for excess reductants or oxidants; the metal plating industry, monitoring the depletion of metal in the plating bath; and process systems, monitoring water chemistry [61]. The measurement of ORP is a direct potentiometric measurement of the equilibrium established between

all oxidized and reduced species in solution, and is governed by the Nernst equation [61]:

$$E = \mathrm{Eo} + 2.3RT / nF (\log Aox/Ared) \quad \textbf{(4.6)}$$

where E = potential developed at metal electrode surface, Eo = constant dependent on reference electrode, R = gas constant, T = temperature in degrees Kelvin, n = number of electrons transferred in process, F = Faraday constant, $Ao\ x$ = activity of oxidized species, and $Ared$ = activity of reduced species. The ORP reading should be reported versus the normal hydrogen electrode (NHE) as Eh and can be calculated from the measurement as follows:

$$Eh = Eobs + Eref \quad \textbf{(4.7)}$$

where Eh = measured ORP reported versus NHE, $Eo\ b\ s$ = observed ORP for electrode pair used, and $Ere\ f$ = ORP potential of the reference electrode versus NHE. The NHE has a potential of 0.0 V at all temperatures, at 1 atm of hydrogen partial pressure, and activity = 1. While the NHE has a number of ideal characteristics for a reference electrode, it is not a practical reference electrode for use in real life measurements. The more common reference electrodes used are the saturated calomel electrode (SCE) and the silver/silver chloride reference system. Platinum is the most commonly employed metal for most water systems [61]

The use of oxygen/air to control sulphide toxicity has been studied very recently [62,63]. The earlier studies used ORP as a controlling parameter to regulate the oxygen dosing. Since the ORP varies linearly with the logarithm of oxygen concentration, the intrusion of oxygen, even at a level beyond the detection limit of commercially available oxygen probe (0,1 mg/L), can be easily sensed by the ORP measurement. In this study ORP sensor is used as a controlling parameter of acceptable reducing environment in absorption tower for nitrite and nitrate removal within biogas including hydrogen sulphide as a biochemical reaction. In all study period, ORP values in influent wastewater stream and also ORP values realized in absoprtion tower were recorded online. Influent ORP measurements were an indicator of inlet NO_3 and NO_2 concentration of raw wastewater. ORP values in the

system were recorded as milivolt (mV), and in all study period the influent values changed between +0 - +77 mV. In Figure 4.26, the influent NO_3-N and NO_2-N concentrations against influent ORP values are given.

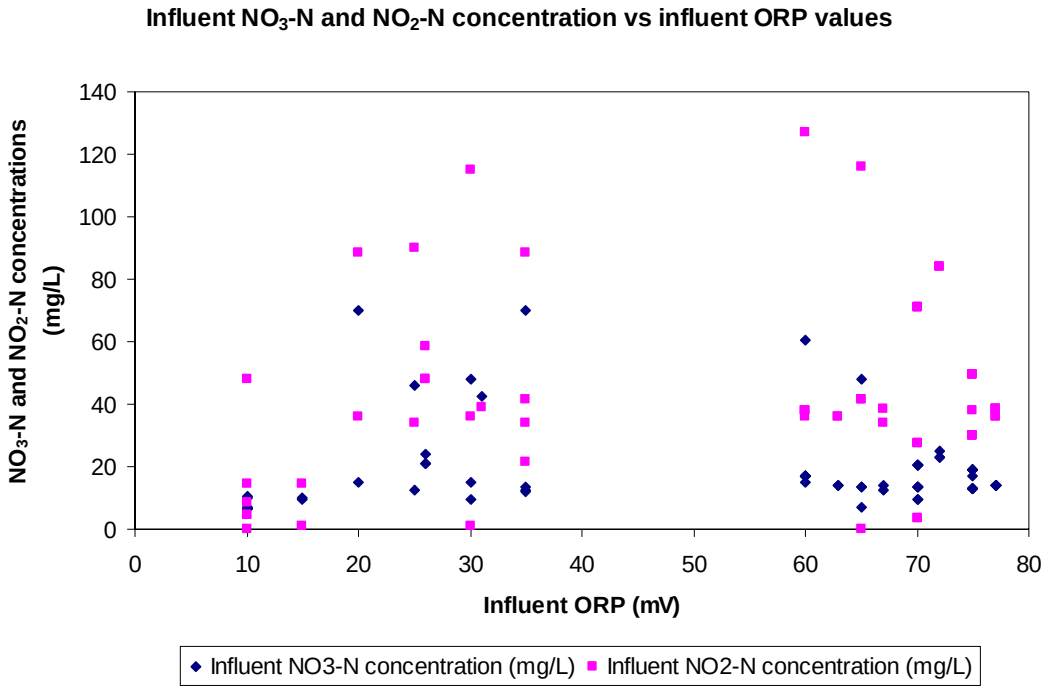

Figure 4.26: Influent NO_3-N and NO_2-N concentrations vs influent ORP value

As seen from Figure 4.26, there is not a smooth relation between initial NO_3-N and NO_2-N concentrations and influent ORP values. However, former studies show that negative (-) ORP values correspond to low nitrate and nitrite concentrations in raw wastewater. In this study inital ORP values were above 0 mV, and negative values have not been observed. In Figure 4.27, influent and effluent ORP values against initial biogas/wastewater ratio are shown. As seen from Figure, increasing biogas/wastewater ratio presents more reduction potential in the absorption column, at the end, effluent ORP values decrease to – 380 mV. In a research made in 2003, sulphide control was determined by ORP control by adding limited oxygen to the anaerobic reactor [64]. In that study, the target ORPs were maintained at elevated values of -230 and -180mV. These ORPs were selected arbitrarily (as no relevant literature was found to make a judgement) with a belief that the injected oxygen would be enough to eliminate the sulfide completely [64].

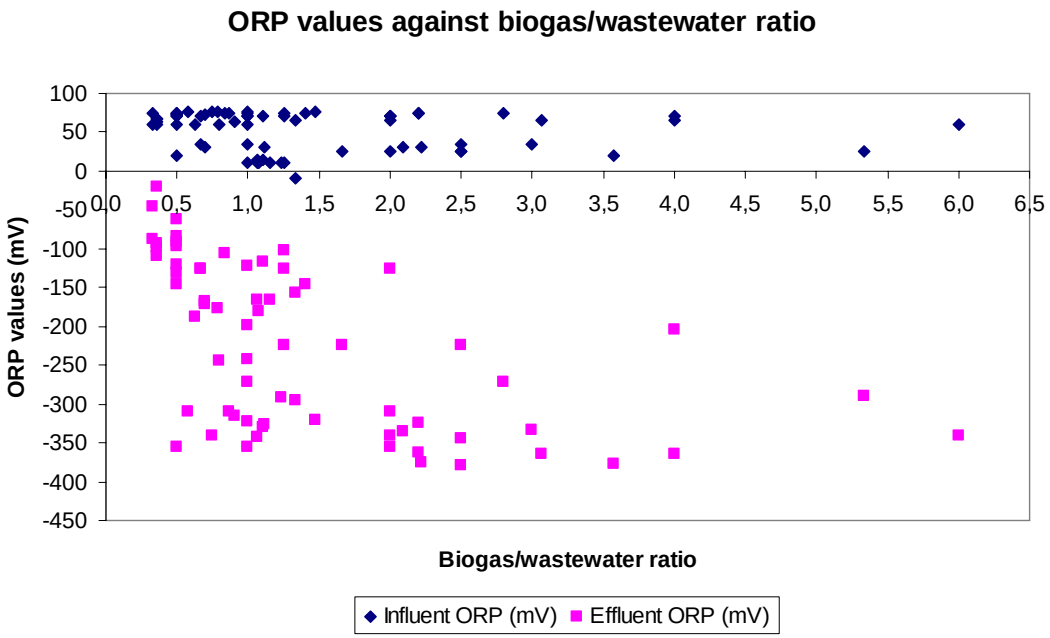

Figure 4.27: ORP values against biogas/wastewater ratio

The maximum H_2S removal efficiencies were obtained at biogas/wastewater ratios of 0,33 – 0,5 range. In this region effluent ORP values were between – 20mV – 50 mV. In the Figure 4.28, the optimum H_2S removal conditions against ORP values are given.

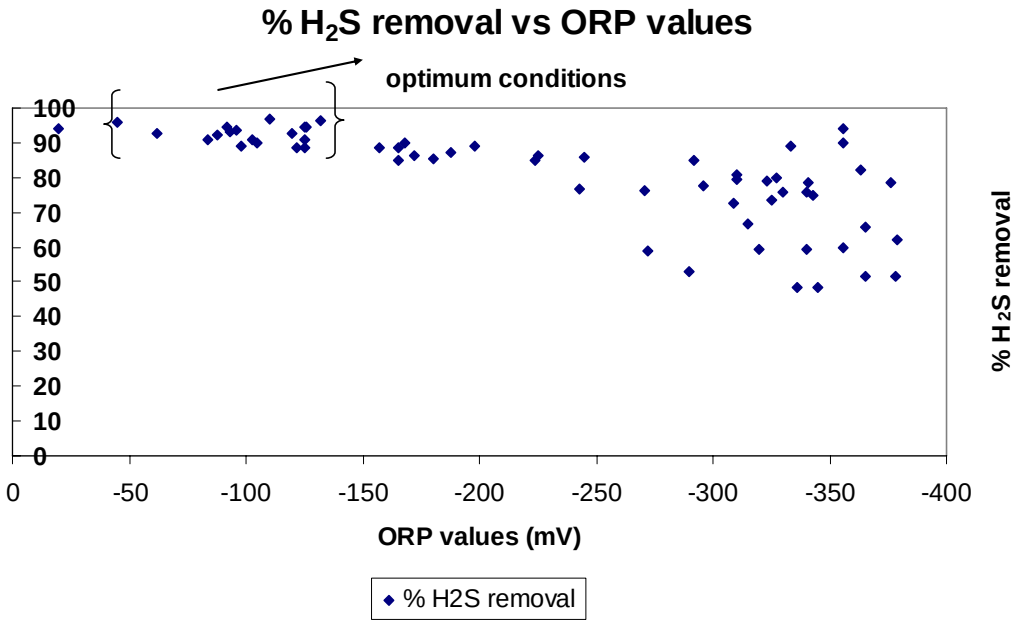

Figure 4.28: H_2S removal vs ORP values

As seen from Figure 4.27, H_2S removal ratio was above %90 in the ORP range of – 20mV – 50 mV.

When considering the specific ORP change in the reaction, it can be seen that, ORP values reach stable values after 20 minutes determining that the reaction of H_2S with NO_3 and NO_2 reaches steady state, and after 20 minutes there was not any significant change on these values. In Figure.. given below, ORP change within the process was given as a sample. As seen from Figure 4.29, steady state values were reached within 20 minutes in reaction period.

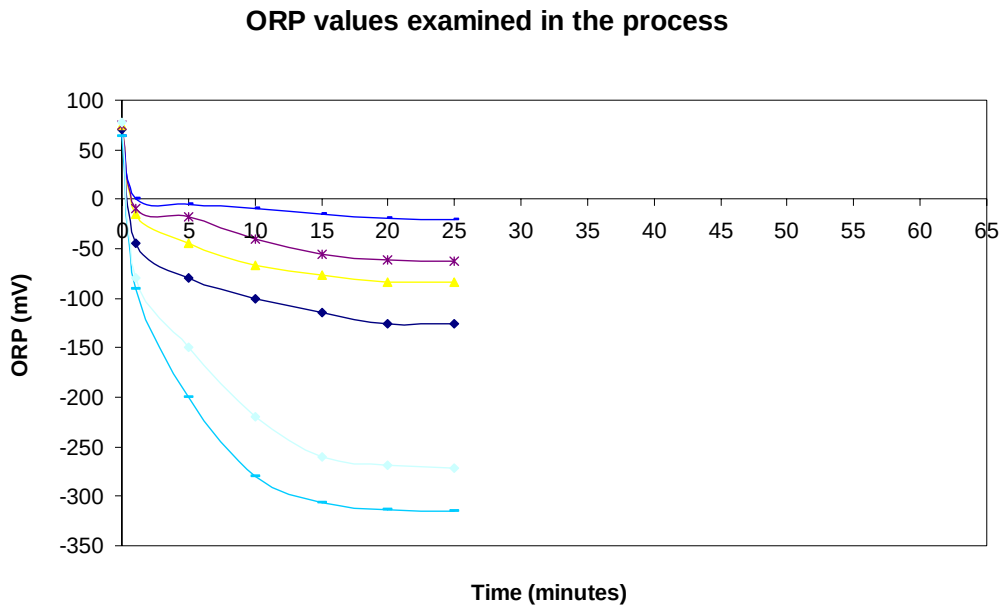

Figure 4.29: ORP values examined in the process

As seen from Figure 4.30, while biogas flowrate was fixed as 5 m^3/h and wastewater flowrate decreased step by step from 14 m^3/h to 2,5 m^3/h, ORP values started to decrease from + 67 mV respectively to – 93mV, -125 mV and -340 mV. Here, maximum H_2S removal realized on 14 m^3/h wastewater flowrate against fixed 5 m^3/h biogas flowrate. Decreasing wastewater flowrates correspond to lower H_2S removal ratios, however increasing biogas/wastewater ratios resulted in lower ORP values and higher reductive conditions. Specially, when the inlet biogas pressure were above 0,3 bar corresponding to > 5 m^3/h biogas flowrate, it is observed that elementary sulphur production is favoured as explained in end products section.

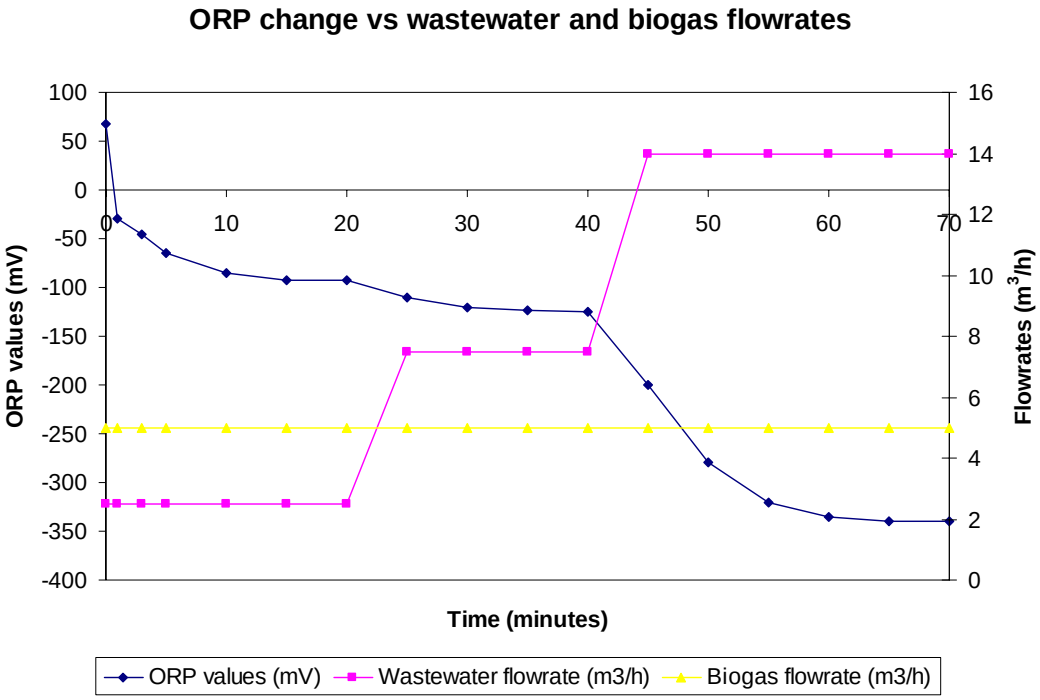

Figure 4.30: ORP change against fixed biogas flowrate (5 m^3/h) and increasing wastewater flowrate(2,5 m^3/h – 14 m^3/h)

As seen from Figure 4.31, while wastewater flowrate fixed as 10 m^3/h and biogas flowrate elevated step by step from 5 m^3/h to 10 m^3/h, ORP values starts to decrease from + 20 mV respectively to – 132mV, -172 mV and - 243 mV. Here, maximum H_2S removal realized on 5 m^3/h biogas flowrate against fixed 10 m^3/h biogas flowrate. Increasing biogas flowrates correspond to lower H_2S removal ratios because of substrate inhibition and also it is observed that, elementary sulphur production is favoured comparing to increasing biogas flowrates as explained in end products section.

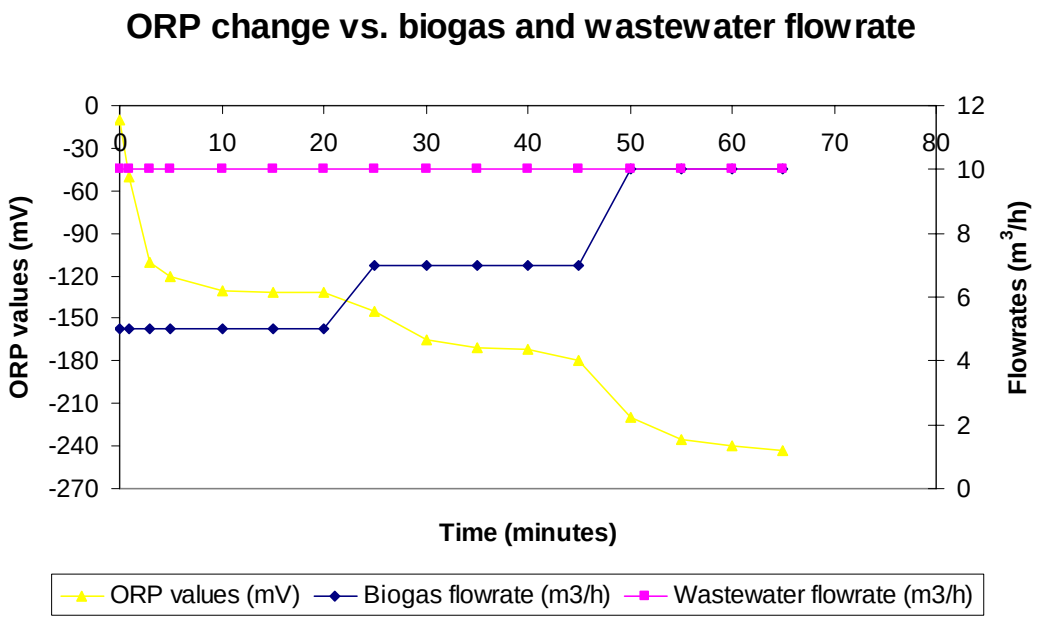

Figure 4.31: ORP change against fixed wastewater flowrate (10 m^3/h) and increasing biogas flowrate(5 m^3/h – 10 m^3/h)

4.10 Discussion

These pioneering datas indicate that a simple and minimally managed system, comprised of absorption tower, biogas and wastewater feeding systems, can be effective in removing H_2S from biogas stream and also nitrate and nitrite removal with this autotrophic denitrification process. Some online control parameters including ORP, pH are so effective to determine the reaction phase and period. In this study, influent wastewater and biogas characteristics force the study to work on different conditions to reach optimum removal rates. Specially high inlet concentrations of NO_2^- -N has a dominant effect on adjusting optimum operating conditions. High H_2S concentrations in feed biogas stream is another powerful phenomemon comparing to the similar studies done before. High H_2S loading rates and low EBRT values force this sytem to work in nonextensive study ranges. This study as a start-up work reveals some questions to be answered: Which conditions of study could be changed to reach higher removal rates of H_2S? Which sulphur products are formed? What are the limiting parameters?

5 CONCLUSIONS AND RECOMMENDATIONS

The oxidation of H_2S was carried out in continuous culture in absorption tower using both nitrate and nitrite as electron acceptor in the presence of activated sludge. This study showed that both nitrate and nitrite could be used to oxidize H_2S to sulfate or elementel sulfur depending on the ratio of nitrogen source to sulfide and both were now available in most wastewater treatment plants. H_2S removal ratios reached % 96 within biogas/wastewater ratio in the range of 0,33 – 0,5. Increasing biogas/wastewater ratios resulted in elementary sulphur production's predominance as end product. Volumetric loading rate of H_2S within the biogas was one the highest values tried in former studies, and at this extreme values could be tolerated by nitrite concentrations in raw wastewater. Higher removal rates of NO_2 according to the NO_3 showed that nitrite was more active in the process and more resistant to inhibitive substrate concentration of hydrogen sulphide. So the combining of anaerobic treatment, biogas production and biogas cleaning with aerobic treatment is now possible. This allows the integration of sulfur and nitrogen cycles to alleviate sulphur emissions. The oxygen has been used as electron acceptor in the same process to control sulfide emissions in practice. However nitrate and nitrit have not been used so far in industry. Combining sulfide removal with nitrate or nitrite allows not only to control H_2S but also improve nitrogen removal via autrotrophic denitrification without using carbon source [65].

Present study is for basis building for latter experiments of this new subject for H_2S removal from biogas. In this thesis study, further testing and verification of these results are necessary and the following experimental modifications are recommended:

* Measurement of gaseous sulfur compounds should be done via gas chromatography with a flame photometric detector for increased accuracy.

* The sulfur species in the medium and effluent gas, including sulfates and elemental sulfur, should be measured to account for sulfur reactions.

* A biological assessment of the major autotrophic denitrifier communities should be performed.

* Further long-term operation and bench-scale optimization are desired before scale-up to pilot and full scales. A life cycle assessment should then be conducted for determining overall economic and environmental benefits.

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