MARMARA UNIVERSITY

INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES

DESULFURIZATION OF BIOGAS USING A MEMBRANE BIO-SCRUBBER

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Ph.D. THESIS

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ÖZET

BİYO-MEMBRAN GAZ SIYIRICI İLE BIYOGAZDAN HİDROJEN SÜLFÜR GAZININ UZAKLAŞTIRILMASI

Biyogaz bünyesinde bulunan H_2S gazı yanma motorlarında metal aksamların aşınmasına sebep oldugundan kojenerasyon performansını olumsuz yönde etkilemektedir. Bu çalışmada, biyogaz üretimi sırasında açığa çıkan biyogazın olumsuz etkilerini azaltmak üzere biyolojik ve biyolojik olmayan gaz–sıvı membran kontaktörler geliştirilmiş ve bunların seçici sülfür giderim verimleri incelenmiştir.

Çalışmanın ilk aşamasında; farklı pH, gaz debisi, sıcaklık ve membran duvar kalınlıklarında laboratuvar ölçekli abiyotik polidimetilsiloksan (PDMS) membran kontaktörün H_2S absorpsiyon performansı incelenmişir. Sonuçlar, en düşük sülfür yükleme hızında (91 mg $H_2S/m^2.h$) H_2S'in ve CO_2'in sırasıyla %98 ve %59'dan yüksek bir performansta absorplandığını göstermiştir. Böylece biyogazdaki metan içeriği sadece %5 kayıpla %60'dan %80 mertebesine ulaşmıştır. Artan pH (7-10) ve sülfür yükleme hızları (91–355 mg $H_2S/m^2.h$) H_2S absorpsiyon kapasitesini arttırmıştır. Hidrojen sülfürün karbondioksite ve metana göre seçicilik faktörü (H_2S/CO_2 ve H_2S/CH_4) sırasıyla 2,5 ve 58 olarak hesaplanmıştır. Benzer bir şekilde, membran duvar kalınlığı 1mm'den 2mm'ye çıkarıldığında, hidrojen sülfürün seçiciliğinin arttığı gözlenmiştir. Ayrıca prosesde sıcaklık da anahtar rol oynamaktadır. Düşük sıcaklıklarda H_2S absorpsiyon verimini arttığı gözlenmiştir. SEM-EDS analizleri membran üzerinde Ca, Mg, S, ve Si gibi inorganiklerin biriktiğini göstermiştir. Ancak, çalışma boyunca herhangi bir membran tıkanma olayına rastlanmamıştır. En yüksek H_2S akısı pH 10 ve 7'de sırasıyla 4 g/m^2.gün and 1,8g/m^2.gün ve kütle transferi ise 6.91×10^{-6} ve 4.99×10^{-6} m/s olarak hesaplanmıştır.

Çalışmanın ikinci aşamasında literatürde ilk defa bir hibrit PDMS membran biyo-sıyırıcı (MBS) ile biyogazdan hidrojen sülfür giderimi araştırılmıştır. Absorpsiyon sıvısının pH'sı, biyogaz debisi ve çözünmüş oksijen konsantrasyonunun, seçici H_2S giderimi ve sülfür oksidasyonu üzerine etkileri incelenmiştir. H_2S giderim kapasitesi ve seçicilik göz önüne alındığında proses performansının pH 7'de pH 8.5'e göre daha iyi olduğu gözlenmiştir. Sülfürün karbondioksit (H_2S/CO_2) ve metana (H_2S/CH_4) göre

seçiciliği gaz debisinin arttırılmasıyla (32/gün) sırasıyla 3,5 ve 63'e yükselmiştir. Metan içeriğinin %21 oranında artması ile birlikte biyogazın kalorifik değerinde anlamlı bir artış meydana gelmiştir. Uzun soluklu işletim sırasında membrandan biyogaza hava girişi gözlenmemiştir. Hacimsel yükleme oranının 148 g H_2S/m^3gün ve çözünmüş oksijen konsantrasyonunun 1 mg/l'nin altında olduğu durumda, H_2S'in neredeyse tamamı (%97) giderilmiş ve giderilen H_2S in %74'ü elementel kükürte oksitlenmiştir. Sülfürün elementel kükürte kısmi oksidasyonu, sülfata tam oksidasyonundan ziyade, kostik sarfiyatını yarıya indirmiştir. MBS'lerde SEM-EDS analizleri sonucu membran yüzeyinde elementel kükürt ve diğer inorganik maddeler gözlemlenmesine rağmen herhangi bir tıkanma problemi yaşanmamıştır.

Anahtar sözcükler: Biyogaz, CH_4 zenginleştirme, hidrojen sülfür giderimi, inorganik madde birikimi, membran kontaktör, polidimetil siloksan membran

ABSTRACT

DESULFURIZATION OF BIOGAS USING A MEMBRANE BIO-SCRUBBER

The hydrogen sulfide (H_2S) in biogas affects the co-generation performance adversely by corroding the metal components within the engine. In this thesis study, to reduce the negative effects of H_2S gas, a hybrid, physical-chemical and biological desulfurization process using gas-liquid membrane contactor was developed and its effectiveness on selective biogas desulfurization was investigated.

In the first part of the study, the absorption performance of a laboratory scale abiotic polydimethylsiloxane (PDMS) membrane gas-liquid contactor was evaluated at different absorption liquid pH, biogas flowrate, membrane thickness and temperature. The results revealed that at the lowest loading rate (91 mg $H_2S/m^2.h$), more than 98% H_2S and 59% CO_2 absorption efficiencies were achieved. The CH_4 content in the treated biogas increased from 60 to 80% with only 5% CH_4 loss. Increasing the pH (7-10) and loading rate (91–355 mg $H_2S/m^2.h$) enhanced the H_2S absorption capacity and the maximum H_2S/CO_2 and H_2S/CH_4 selectivity factors were 2.5 and 58, respectively. Similarly, a higher biogas desulfurization selectivity was observed when the membrane thickness raised from 1 mm to 2 mm. The temperature also played a key role in the process and at lower temperatures higher H_2S absorption efficiencies were obtained. The SEM-EDS analysis confirmed the deposition of inorganics such as Ca, Mg, S and Si on the membrane surface. However, any membrane clogging and fouling problem was not observed. The highest H_2S fluxes at pH 10 and 7 were 3.4 $g/m^2.d$ and 1.8 $g/m^2.d$ with overall mass transfer coefficients of 6.91×10^{-6} and 4.99×10^{-6} m/s, respectively.

Secondly, a hybrid PDMS memrane bio-scrubber (MBS) was tested to remove the H_2S from biogas. The effect of absorbing liquid pH, biogas flowrate and DO concentration on H_2S selectivity, sulfide oxidation oxidation performance and the sulfide oxidation products were investigated. The process performance at pH 7.0 was better than at pH 8.5 in terms of H_2S oxidation capacity and selectivity. Desulfurization selectivity of H_2S/CO_2 and H_2S/CH_4 increased with rising gas flowrate (up to 32 l/d) and reached a maximum of 3.5 and 63, respectively. The calorific value of the biogas significantly increased due to the increased CH_4 content by 21%. During the long-term operation, air

diffusion through the membrane into the biogas was not observed due to hydrophobic nature of the membrane. Almost complete H_2S oxidation (>97%) and its conversion into elemental sulfur (>74%) were achieved when volumetric loading rate and DO concentration were kept below 148 g H_2S/m^3d and 1 mg/l, respectively. Partial oxidation of sulfide to elemental sulfur (at DO 1 mg/l) rather than sulfate (at DO 4 mg/l) reduced the caustic consumption by half. In the MBS, even though elemental sulfur and other inorganics were detected on the membrane surface with SEM-EDS analysis, no fouling and clogging problem was observed.

Keywords: Biogas, CH_4 enrichment, hydrogen sulfide removal, inorganics deposition, membrane contactor, polydimethylsiloxane membrane

CLAIM FOR ORIGINALITY

In this thesis study, the performance of a gas-liquid membrane contactor for selective removal of H_2S from the biogas was investigated experimentally.

In the literature, there were several studies about the removal of H_2S from biogas and most of them focused on conventional physico-chemical or biological methods under different operational conditions. There is also some membrane based desulfurization studies in which microporous membrane contactors were used as an alternative technology for desulfurization of biogas. However, the performance of porous membranes significantly declines when they are operated for long time, owing to penetration of solvent through the pores of wetted membranes. Therefore, generally non-porous dense polymeric membranes were preferred in biogas desulfurization studies to eliminate the membrane wetting problem. The major drawback of biogas desulfurization using dense membranes such as glassy polymeric is its poor H_2S selectivity than CO_2, because absorption in glassy polymers is controlled by the size of the molecule and diffusion coefficient. Significant amount of CO_2 in biogas can pass through the membrane and decreases the pH of receving solution, as a result cost of the process increases due to high caustic consumption. Therefore, in this thesis study a rubbery polymeric PDMS membrane having high H_2S/CH_4 and moderate CO_2/CH_4 selectivities were used. To increase the H_2S driving from the gas phase into the liquid phase mildly alkaline solution was also used.

Unlike numerous reports in the literature, a novel approach was developed for desulfurization of highly H_2S loaded synthetic biogas. In this thesis, the selective biogas desulfurization performance of a hybrid, physical-chemical and biological desulfurization process using gas-liquid membrane contactor processes were tested and evaluated for the first time.

Ebrahim Tilahun MOHAMMED **Prof. Dr. Barış ÇALLI**

Prof. Dr. Erkan ŞAHİNKAYA

SYMBOLS

%	: Percent
α	: Selectivity
A_i	: Internal Area
A_e	: External Area
Au	: Gold
µm	: Micrometer
µS	: Micro siemens
C	: Carbon
Ca	: Calcium
CO_3^{2-}	: Carbonate
$Ca(OH)_2$	: Calcium hydroxide
CH_4	: Methane
cm	: Centimeter
CO	: Carbon monoxide
CH_3COOH	Acetic acid
CH_3CH_2OH	: Ethanol
CH_3CH_2OOH	: propanoic
CO_2	: Carbon dioxide
Cu	: Copper
CuS	: Copper sulfide
$CuSO_4$	: Copper sulfate
d	: Day
Fe	: Iron
Fe^{2+}	: Ferrous ion
Fe^{3+}	: Ferric ion
$FeCl_2$	: Iron chloride
Fe_2O_3	: Iron oxide
$Fe(OH)_3$	: Iron(III) oxide-hydoxide
FeS	: Iron sulfide
g	: Gram

h	: Hour
H_2	: Hydrogen
HCO_3^-	: Bicarbonate
H_2S	: Hydrogen sulfide
H_2SO_4	: Sulfuric acid
K	: Potassium
KI	: Potassium iodine
KOH	: Potassium hydroxide
kg	: Kilogram
l	: Liter
M	: Molar
m^2	: Meter square
m^3	: Meter cube
mg	: Miligram
Na_2CO_3	: Sodium carbonate
$NaHCO_3$	: Sodium hydrogen carbonate
Na_2S	: Sodium sulfide
NaHS	: Sodium hydrosulfide
Mg	: Magnesium
mm	: milimeter
$KMnO_4$	: Potassium permanganate
N_2	: Nitrogen
N	: Normal
Na	: Sodium
NaOH	: Sodium hydroxide
NH_3	: Ammonia
NH_4^+	: Ammonium
O_2	: Oxygen
^{o}	: Degree
^oC	: Degree celcius
OH^-	: Hydroxide
P	: Phosphorus

Pd	: Palladium
pH	: Activity of hydrogen ion
pKa	: Ionization constant
rpm	: Revolutions per minute
s	: Second
S	: Sulfur
S^o	: Elemental sulfur
Si	: Silicon
SO_2	: Sulfur dioxide
SO_4^{2-}	: Sulfate
Zn	: Zinc
ZnO	: Zinc oxide
ZnS	: Zinc sulfide
ΔG	: Gibb's free energy

ABBREVIATIONS

AC	: Activated carbon
AMS	: Abiotic membrane scrubber
ASB	: Alkaliphilic sulfoxidizing bacteria
BTF	: Biotrickling filter
CHP	: Combined heat and power
DEA	: Diethanolamine
DO	: Dissolved oxygen
EBRT	: Empty bed retention time
EC	: Elimination capacity
EDTA	: Ethylenediamine tetraacetic acid
EDS	: Energy Dispersive X-ray Spectroscopy
Eq	: Equation
ePTFE	: Expended polytetrafluoroethylene
HFMC	: Hollow fiber membrane contactors
GC	: Gas chromatography
GRT	: Gas retention time
inf	: Influent
kpa	: kilopascal
MBS	: Membrane bioscrubber
MDEA	: Methyldiethylamine
MEA	: Monoethanolamine
min	: Minute
ORP	: Oxidation reduction potential
out	: Outlet
PAN	: Polyacrylonitrile
PDMS	: Polydimethylsiloxane
PE	: Polyethylene
ppmv	: Parts Per Million by Volume
PP	: Polyproplene
PSf	: Polysulfone

PTFE	: Polytetrafluoroethylene
PVC	: Polyvinyl chloride
PVDF	: Polyvinylidene difluoride
RE	: Removal efficiency
SEM	: Scanning Electron Microscopy
SOB	: Sulfide oxidizing bacteria
SRB	: Sulfate reducing bacteria
TCD	: Thermal conductivity detector
TKN	: Total Kjeldahl nitrogen
TSR	: Total sulfide removal efficiency
UNFCCC	: United Nations Framework Convention on Climate Change
VFAs	: Volatile fatty acids
VLR	: Volumetric loading rate
VSRR	: Volumetric sulfide removal rate
XRD	: X-ray diffraction

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1. INTRODUCTION

Among emerging alternative energy sources, waste biomass has a great potential and is a better choice for sustaining the demand and assurance of forthcoming energy supply in a viable manner primarily through physicochemical, biochemical, thermochemical transformations and conventional combustion (Corro et al., 2013). Moreover, it is more promising, cost effective and ever available, and the application of waste biomass-based energy is getting bigger public and scientific attention owing to its inherent green potential (Akhtar and Amin, 2011). As alternative energy source, biomass-based energy has several advantages over fossil fuel, because bioenergy which resulted from different biomass sources are readily available and is almost greenhouse gas neutral substitute for fossil fuels because of its abundance in nature, widely applicable and renewable characteristics (Haberl et al., 2012; Raheem et al., 2015). The energy from waste biomass can be utilized by direct burning or conversion to gas. Biogas is the gas produced from organic biomass through process of anaerobic digestion.

Recently, the preparation and development of alternative energy sources such as biogas have been extensively studied (Bohutskyi and Bouwer, 2013; Esen and Yuksel, 2013; Mussgnug et al., 2010). Biogas is a combustible gas created by biological degradation of organic compounds by an assortment of microorganisms under oxygen free conditions. The common biogas sources include a wide range of feedstocks for instance agricultural, municipal, and industrial wastes (Kapdi et al., 2005; Yadvika et al., 2004). Hence, by proper disposal of waste materials it is possible to resolve the environmental pollution problems, for example environmental sanitation, offensive odor and flies. Biogas formation processes could also offer economically feasible and renewable source for meeting energy needs as well as contributing to resource and environmental conservation of fossil resources (e.g. natural gas, oil or coal) (Deublein et al., 2008; Holm-Nielsen et al., 2009). In anaerobic fermentation the chemical composition of the biogas is determined by the applied operational conditions and the nature of the raw materials used. Biogas largely comprises of methane (CH_4) and carbon dioxide (CO_2), but also trace amount of H_2S and other impurities (Frigon and Guiot, 2010; Truong and Abatzoglou, 2005). Methane (CH_4) is the combustible component of biogas, which able to used for mutable energy sources for heating, power, vehicle fuel and may possibly

replace roughly 20-30% of the natural gas utilization (Khanal, 2009; Lantz et al., 2007). Additional benefit of biogas generation is decreasing natural CH_4 emissions, due to the self-decomposition of organic chemical compounds, which encourages the conservation of extensive traditional uses of the ecosystems. The global warming potential of CH_4 is estimated to be more than 20 times greater than that of CO_2 effect (Rutz and Janssen, 2008; UNFCCC, 1998). The anaerobic digestion process enables to capture and utilize CH_4 for energy creation, and its purity is greatly affected by the existence of pollutants in small or higher amounts (De Baere, 2000). During biogas production process the inorganic and organic sulfur contained in the feedstocks will be reduced into hydrogen sulfide (H_2S) which can be transferred to the biogas (Stefanie et al., 1994; Mackie et al., 1998). H_2S has corrosive properties damaging the engine and metal parts of the equipment, as well as bad smell and toxic effects in the work place (Appels et al., 2008). For trouble free operation of CHP installations most manufacturers recommended H_2S concentration in biogas should be lower than 300 ppmv. In addition, combustion of H_2S generates sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) which are harmful for the environment. Excess H_2S may also inhibit microorganisms due to its toxic effects or by precipitating trace metals required for enzymatic activities (Chen et al., 2008; Lopes et al., 2010; van der Veen et al., 2007). Thus, H_2S have to be removed prior to further application of biogas. H_2S removal can be done at different levels for instance (i) by controlling the feedstocks fed to the anaerobic digester, (ii) during the anaerobic digestion process, (iii) by treating the produced biogas. Section 2.4 presents a comprehensive overview of various technologies used for removal of H_2S from biogas.

2. LITERATURE REVIEW/BACKGROUND

2.1. Anaerobic Digestion Process

Anaerobic digestion is usually deemed to be a complicated process that takes place under anaerobic environment via consecutive biochemical breakdown of polymers mainly to CH_4 and CO_2 while sulfates are converted into H_2S (Krzysztof Ziemiński, 2012; Themelis and Ulloa, 2007). As displayed in Figure 2.1, the conversion of the organic portion of the waste occurs in four basic steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis.

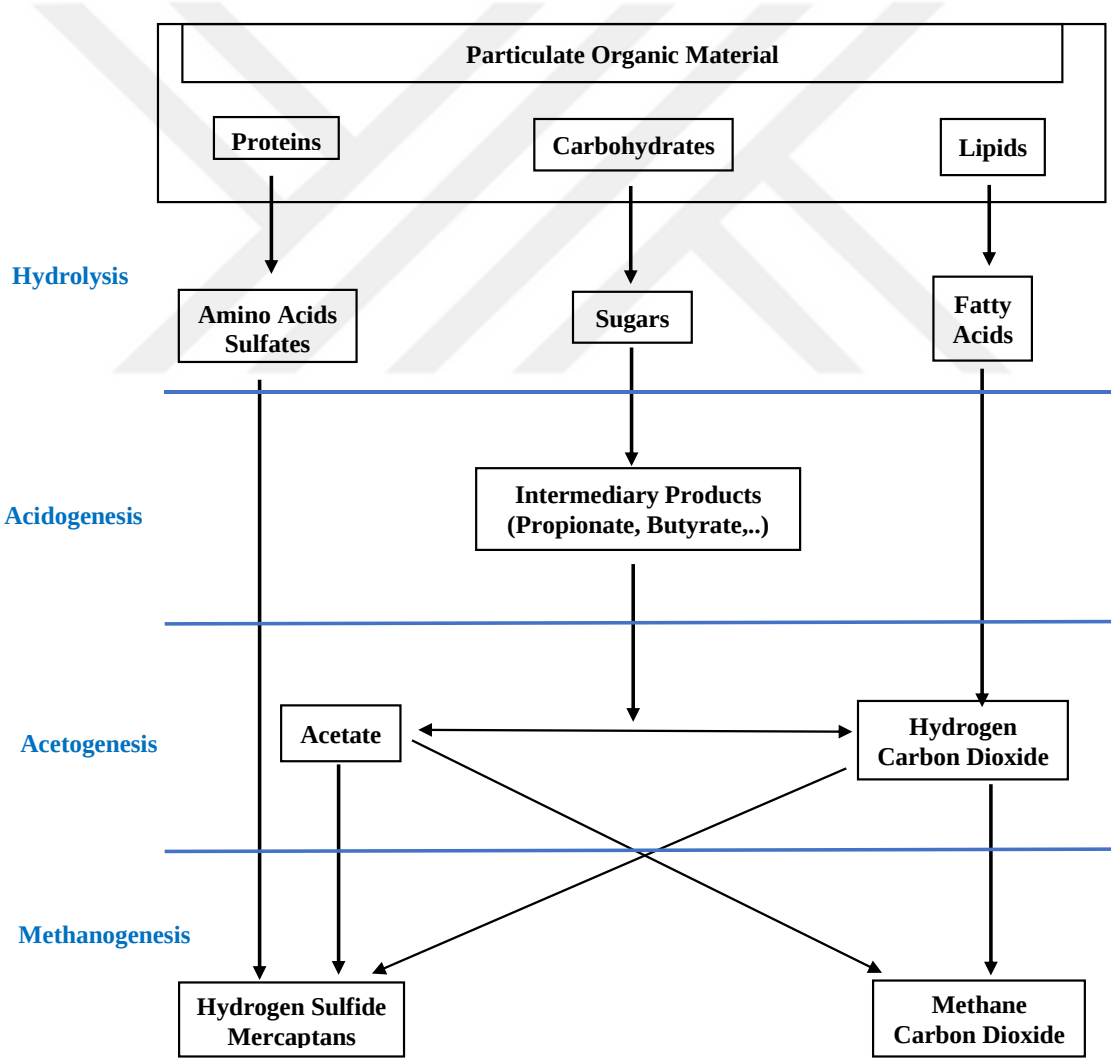


Figure 2.1 The key process stages of anaerobic digestion (Bailón and Hinge, 2012)

The individual conversion stage is performed by numerous groups of microorganisms working together (Demirel and Scherer, 2008; Jäckel et al., 2005; Yadvika et al., 2004). Biomass is mainly made up of larger organic compounds and the anaerobic digestion process begins with bacterial hydrolysis of these compounds. The breaking of particulate organic material into small constituent parts by addition of water is hydrolysis process (Figure 2.1). As shown in Figure 2.1, hydrolysis is the initial step, and involves the enzyme-mediated conversion of complex organic matters for instance proteins broken down into smaller molecules of amino acids, likewise fats into fatty acids, and carbohydrates converted into simple sugars which are soluble organic compounds and suitable to be used as source of energy and carbon. Some of the products which are produced in the first steps of anaerobic fermentation, such as hydrogen and acetate can be utilized by methanogens. The remaining large molecules should be further broken down in the following stages to be used by microorganisms as source of food. For the whole anaerobic digestion of large organic materials, hydrolysis is relatively slow and energy consuming process and it is mostly deemed as the rate limiting step but may differ depending on the substrate composition used (Gallert and Winter, 2005). In this particular step, facultative anaerobes or anaerobes are responsible to carry out the biodegradation of larger molecules and use them as a source of energy and nutrition (Merlin Christy et al., 2014).

The second stage of anaerobic digestion is acidogenesis, where acidogenic bacteria further breakdown the remaining biomass and organic products after hydrolysis phases (Figure 2.1). The soluble organic compounds for example sugars, fatty acids and amino acids resulted from the first step is then degraded by a great assortment of facultative anaerobes and anaerobes, and produced various intermediate products such as CO_2, H_2, alcohols, organic acids, some other organic nitrogen and sulfur compounds, besides trace quantities of other byproducts including formation of new bacteria cells (Gerardi, 2003). The most important organic acids formed in this stage is acetate since it can be immediately used as a food source by methanogens. The content of H_2 formation as an intermediary product effects the type of end product created in the digestion procedure. For instance, if the H_2 partial pressure is too high, it would reduce the amount of acetate formation while other volatile fatty acids (VFAs) could be generated. The VFAs such as butyrate and propionate may not be directly used as substrate by methanogens, hence it

should be converted into acetate and/or hydrogen gas.

The third step in anaerobic fermentation is acetogenesis. As presented in Figure 2.1, simple molecules which formed in the acidogenesis step is farther processed by acetogens. Acetogens break down the relatively long chain VFAs to acetate and hydrogen gas, which can be utilized for methane generation. In this step, acetogenic bacteria convert lots of organic acids and alcohols that produced in the acidogenesis into acetate and hydrogen gas, which are used as substrates by methanogens (Gerardi, 2003; Seadi et al., 2008). This transformation can only be thermodynamically preferential if the hydrogen partial pressure is remained low, that explicates the importance of collaboration with the methanogens, as it can continually consume hydrogen to creat methane (Figure 2.2). Thus during this symbiotic relationship effective elimination of hydrogen transfer occurs (Chandra et al., 2012; Gerardi, 2003; Schink, 1997).

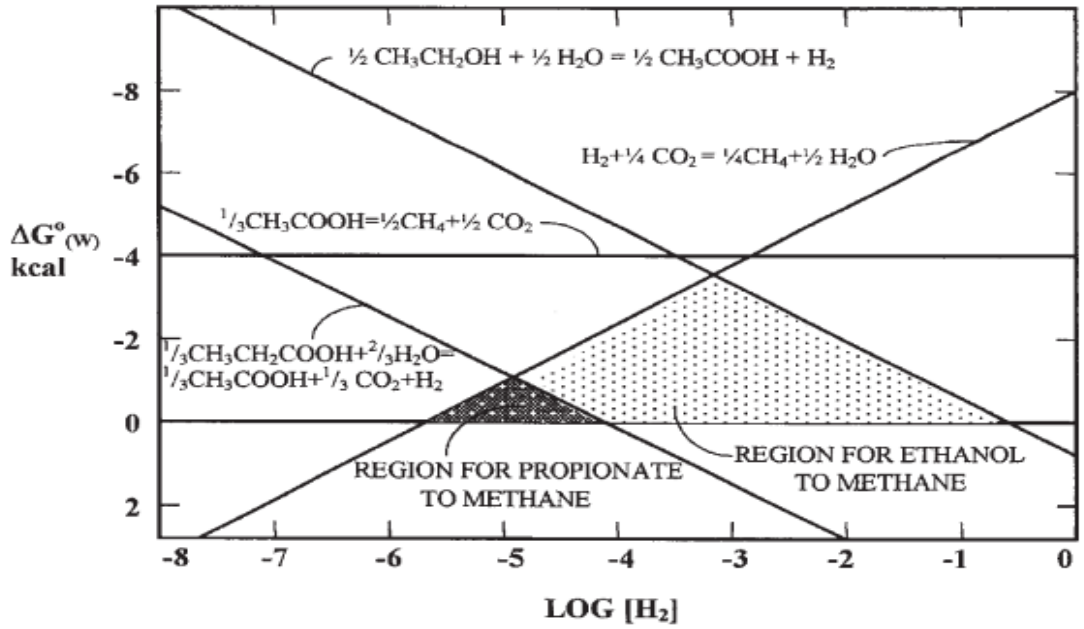


Figure 2.2 The importance of hydrogen partial pressure on acetate and methane formation

This final step in anaerobic breakdown of organic compounds is methanogenesis (Figure 2.1). Methanogens, classified as archaea not bacteria, utilize the ultimate products of the acetogenesis and some intermediate output of the preceding stages (i.e. hydrolysis and acidogenesis) and convert these products into CH_4, CO_2, and water (Aslanzadeh, 2014). It is also sensitive to both higher and lower pHs values and mostly occurs in the ranges from pH 6.5 to pH 8. Therefore, CH_4 and CO_2 make up the

majority of the biogas composition created in anaerobic digesters. There are two primary pathways for the production of CH_4; the first is the conversion of acetic acid into CH_4 (around 66%) and CO_2, and the second is the reduction of CO_2 with hydrogen, which produces CH_4 around (about 34%) and water as shown by (Eq. 1 and 2) (Thauer, 1998).

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2)$$

Specifically, the methanogens using hydrogen may be liable at lower hydrogen partial pressures inside the digesters (Figure 2.2). Hence, it is crucial to create best situations for acetogenic bacteria to break down the hydrolyzed organic matters into easily usable substrates for methanogens (Tchobanoglous et al., 2003). Many of alcohols, acids and other organic nitrogen compounds may not be utilized immediately with methanogens, consequently these components accumulate inside the anaerobic digester (Gerardi, 2003). The residual non-digestible substances which cannot be used up by microorganisms and any dead bacterial remaining makes up the liquid digestate.

When the substrate fed into the anaerobic reactor contains sulfate, the sulfate reducing bacteria (SRB) compete against the methanogens for similar substrate such as acetate and hydrogen, and can produce hydrogen sulfide (H_2S) in the digester (Figure 2.3). SRB usually win the competition (Figure 2.3) due to many interacting factors: (i) in anaerobic respiration, in comparison with CO_2, utilization of sulfate as the source of ultimate electron acceptor produces more energy for growth, (ii) the higher affinity of SRB for both H_2 and acetate, allowing SRB to use up these substrates than methanogens (Rabus et al., 2013), and (iii) usually the specific growth rate of SRB is also higher than that of methanogens (Stefanie. et al., 1994). Hence, under low acetate concentrations, where the ratio of substrate to sulfate is less than 2, SRB can obtain both hydrogen and acetate easier than methanogens. When the ratio of substrate to sulfate is in between 2 and 3, the competition is mainly more intense. As the ratio of the substrate to sulfate is greater than 3, the methanogens can easily acquire H_2 and acetate (Gerardi, 2003).

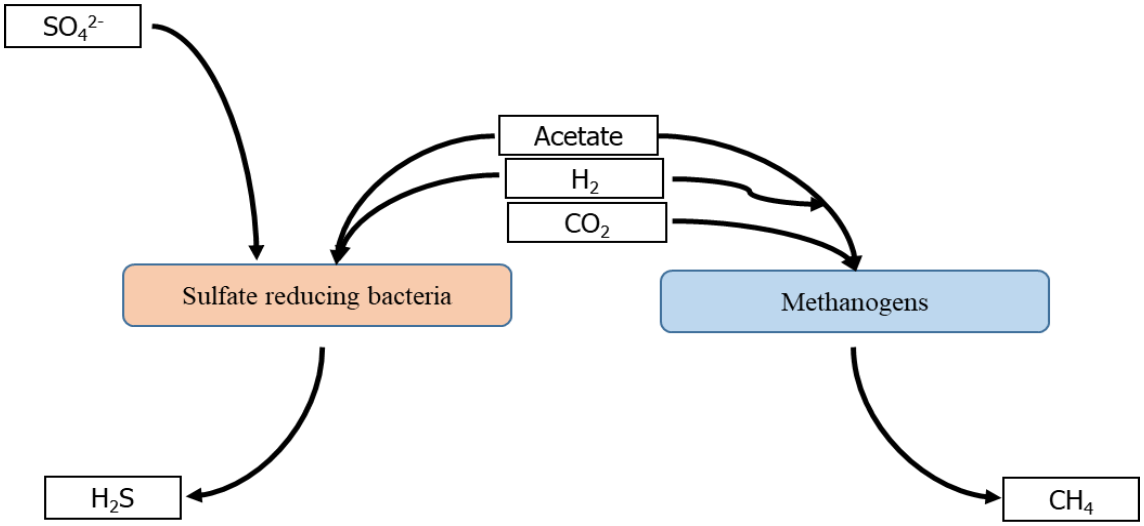


Figure 2.3 The competition among SRB and methanogens for acetate and H_2 (Gerardi, 2003)

2.2. Biogas Composition

Biogas compositions intrinsically differ depending on the type and the concentration of organic material used, operational conditions (pH, alkalinity, temperature and others), the presence of sulfur and nitrogen comprising wastes, and the type of technology adapted for the digestion process (Jönsson et al., 2003). Raw biogas obtained in anaerobic digestion of sewage sludge, livestock residues, and agro-industrial waste is a complex mixture typically containing CH_4 (45–70%), and CO_2 (30–45%) (Table 2.1). Other minor contaminants and by-products that make difficulties in biogas production and utilized are the following contaminants; H_2S, N_2, H_2, O_2, CO, NH_3, halogenated hydrocarbons and siloxanes (Table 2.1). Other organic compounds such as aromatic hydrocarbons also rarely exist, besides if biogas saturated with water vapor it may hold dust particles depending on the feedstock and process conditions (Ajhar et al., 2010; Bailón and Hinge, 2012; Bauer et al., 2013; Ryckebosch et al., 2011; Soreanu et al., 2011). Typical composition of the biogas is presented in Table 2.1 (Deublein D, 2008).

CO_2 constitutes the major contaminant of biogas, reducing its specific heating value and thus its Wobbe index, but it is not toxic and corrosive like H_2S (Ryckebosch et al., 2011). H_2S is of prime concern because it is an odorous, poisonous, and highly corrosive gas. Moreover, high amount of H_2S in combination with condensate water result in corrosion of metallic components of pumps, compressors, pipelines, gas

storage tanks and engines that can decrease the lifespan equipments (Huertas et al., 2014).

Table 2.1 Typical composition of biogas (Deublein D, 2008)

Biogas components	Contents
Methane, CH_4 (%)	45-70
Carbon dioxide, CO_2 (%)	30-45
Nitrogen, N_2 (%)	0-5
Hydrogen, H_2 (%)	0-1
Hydrogen sulfide, H_2S (%)	0-2
Carbon monoxide	<0.6
Water (%)	0-5
Oxygen, O_2 (%)	0-2
Ammonia, NH_3 (%)	0-0.5
Siloxanes, mg/m^3	0-50

During combustion process, H_2S gas will also release as sulfur dioxide, contributing to atmospheric pollution. Furthermore, depending on the concentration of H_2S and its exposure time, H_2S can cause many problems to human health (Table 2.2). Likewise, during combustion ammonia and halogenated hydrocarbons have corrosive properties, which can harshly harm metallic parts of engines and pipelines (Petersson and Wellinger, 2009). High content of O_2 in biogas mixture can be the cause of explosion risks. Finally, combustion of methyl siloxanes creats silicone oxide and its residues in cogenerator, result in overheating, malfunctioning and abrasion effects (Abatzoglou and Boivin, 2009). On the other hand, CH_4 is lighter in comparison with air, because the gas density of CH_4 is 0.55 relative to air. Thus, if CH_4 leaks, it may not stay on the ground instead leave to atmosphere (Noyola et al., 2006).

Table 2.2 The characteristics of H_2S gas

Molecular weight	34.08
Specific gravity (relative to air)	1.192
Auto ignition temperature	250^oC
Explosive range in air	4.5 to 45.5%
Odor threshold	0.47 ppb
8 hour time exposure limit	10 ppm
15 minute short term exposure limit	15 ppm
Immediately dangerous to life of health	300 ppm

2.3. Biogas Utilization

Anaerobic digestion is a viable method for waste treatment that can provide energy recovery by converting waste biomass to biogas and it is stored in gas holders and then used as a possible source of energy. Biogas can be used for space heating, drying, in simple gas stoves for cooking, water heating, and lighting in remote rural areas. It may also be used to generate both heat and electricity (Andriani et al., 2014; Daniela Thrän et al., 2014). Conversion of biogas into electrical energy is convenient, but it needs extra management and capital expense. In some cases, biogas has been more upgraded to produce a transportation fuel and it can substitute natural gas, as well as being injected to the grid line for domestic and industrial applications. The energy potential of biogas is nearly 2/3 of natural gas, due to its great CO_2 content (Table 2.3). Thus, the fuel value of biogas containing 60% CH_4 and 40% CO_2 contents are 5340 kcal/m^3 and 4800 kcal/m^3, for the gross (higher heating values) and net (lower heating values), respectively (Balsam and Ryan, 2006). The Kyoto Protocol also well-defined CH_4 as one of the six crucial greenhouse gases where its global warming potential is beyond 20 times higher than that of CO_2 (UNFCCC, 1998). As a result, the running of CH_4 for energy generation not only provide as power source but also lower its release to the atmosphere. It is also deemed as carbon neutral, since the carbon contained in the biogas is captured from atmospheric CO_2 upon relative short timescale. The residue, nutrient-rich liquid digestate, is another beneficial by-product of anaerobic fermentation processes and utilized in soil amendments, organic fertilizer to enhance agricultural productivity (Balsam and Ryan, 2006).

Table 2.3 Characteristics of biogas versus natural gas

Parameter	Unit	Natural gas	Biogas (60% CH_4, 38% CO_2, 2% others)
Calorific value (lower)	MJ/m^3	36.14	21.48
Density	Kg/m^3	0.82	1.21
Wobbe index (lower)	MJ/m^3	39.9	19.5
Maximum ignition velocity	m/s	0.39	0.25
Theoretical air requirement	m^3 air/m^3 gas	9.53	5.71
Dew point	ºC	59	60 – 160

The various components in the biogas has negative effect on its ultimate utilization. Gas purification is necessary to ensure proper functioning of cogeneration units, extending the life of biogas processing equipment, and increasing energy potential of the gas. The generated biogas might be used in conventional gas burners for cooking. While the usage of biogas in boilers does not require a high gas quality, and it can withstand up to 1000 ppmv H_2S concentrations (Bailón and Hinge, 2012; Wheeler et al., 1999). The utilization of biogas in internal combustion engines, for CHP, work better when H_2S concentration is kept under 300 ppmv, depending on the manufacturer. Turbines and micro-turbines are more H_2S tolerant, and they can withstand high concentrations up to 10,000 ppmv and 70,000 ppmv, respectively (Table 2.4) (Bailón and Hinge, 2012; Soreanu et al., 2011). Fuel cells usually desire significant H_2S reduction to very low levels in ranges of 20 ppmv to 1 ppmv depending on the applied technology (Xenergy, 2002). The most strict biogas quality is obligatory when it directly injected to gas grids line and for utilization in a vehicle fuel, which regularly needs greater than 95% CH_4 and less than 2% CO_2 contents (Marsh et al., 2005; Muñoz et al., 2015a), H_2S concentration must be reduced to less than 4 ppmv (Table 4) (Kohl and Nielsen, 1997). Also the substantial quantity of CO_2 reduces the calorific value of the biogas, enlarging compression and conveyance costs of biogas, can restrict economic feasibility to use biogas at the place of production. The biogas utilization technologies as well as H_2S requirements was presented in Table 2.4 (Persson et al., 2006; Petersson and Wellinger, 2009).

Table 2.4 Biogas utilization technologies and H_2S requirements

Technology	H_2S tolerance (ppmv)
Boilers	< 1000
Kitchen stoves	< 10
Internal combustion engines	< 500
Turbines	< 10,000
Micro-turbines	< 70,000
Fuel cells	< 20
Natural gas grid	< 4

2.4. Biogas Desulfurization Technologies

The most commonly used physicochemical and biological technologies for the removal of H_2S from biogas was reviewed in following sections.

2.4.1. Physical/chemical H_2S removal technologies

2.4.1.1. Physical absorption

The removal of H_2S from biogas using conventional gas–liquid contacting systems, for example packed bed or spray towers, can be performed through physical absorption of H_2S by using only water and/or organic solvents (Schomaker et al., 2000). Whereas, physical H_2S removal can be applied by either single pass or regeneration steps, however huge water consumption is required if there is no regeneration step involved (Jönsson, 2003). The advantage of this process is, high H_2S removal efficiency (up to 99%), small footprint and capability to manage a wide range of contaminants. H_2S solubility in water is not as high as in other liquids, but it has the advantages of availability and low cost. H_2S has a slightly higher solubility than CO_2, nevertheless cost related with selective H_2S removal by water scrubbing process have not yet been revealed competitive with other techniques. This is due to its huge water consumption and large power requirement associated with pumping. Thus, it would only be considered for simultaneous removal of both CO_2 and H_2S (Figure 2.4). If wastewater is used as a source of absorption water, it can cause problems in pipes, vessels, and on packing materials of the system owing to the growth of microorganism (Ryckebosch et

al., 2011). In this case, cleaning has to be done many times either internally washing the column using detergent or by withdrawing the packing materials and washing it outside the column. In addition, the effluent water (used) needs proper treatment before disposing into the environment.

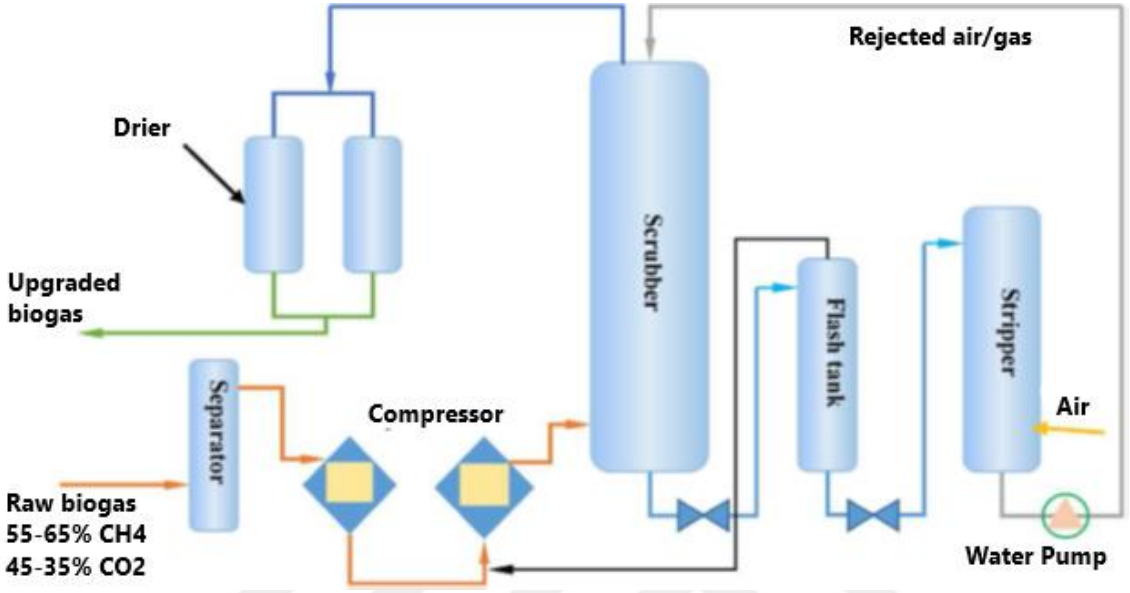


Figure 2.4 Biogas desulfurization by water scrubbing (Awe et al., 2017)

Organic solvents such as mix of dimethyl ethers of polyethylene glycol (Selexol® process), which have five times higher affinity for H_2S than water can also be used for physical absorption of H_2S (Figure 2.5). Compared to water, scrubbing with the selexol process need less amount of water, compact size and need regeneration step (Ryckebosch et al., 2011). Alike water scrubbing, the cost of selective H_2S removal with selexol method not competitive, however the selexol method presumably applied for improving the biogas to relatively pure CH_4 level. Besides, it can be economically visible if large gas flows treated. Overall, only water and organic solvent based absorption processes are proper for cleaning of gas containing low level H_2S, and only competitive if it applied for removal of both H_2S and CO_2 simultaneously (Kapdi et al., 2005; Wheeler et al., 1999).

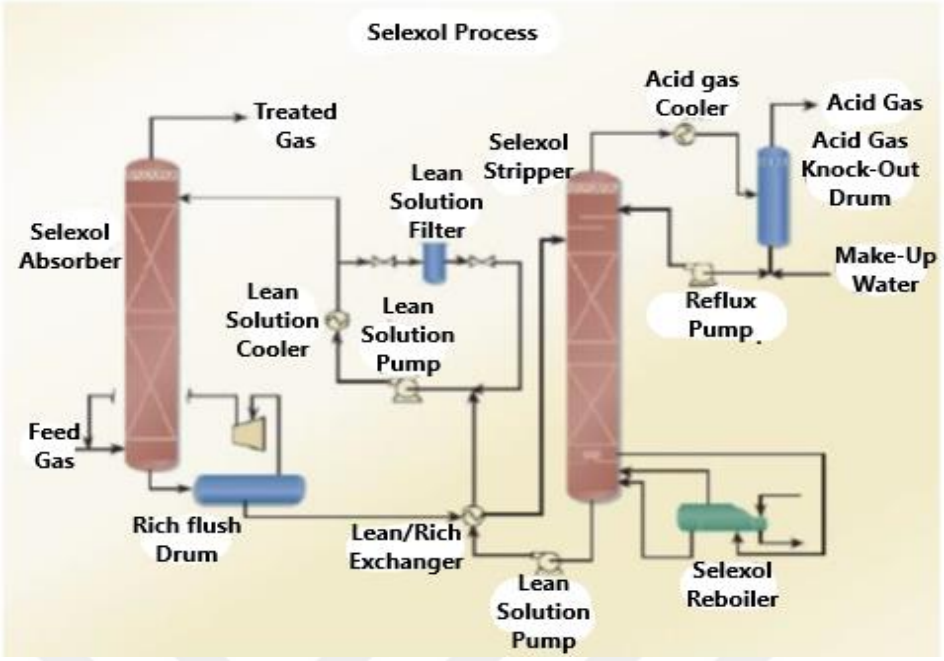


Figure 2.5 Biogas desulfurization with the Selexol process (Electrigaz Technologies Inc, 2008)

2.4.1.2. Chemical absorption

One of the eminent method for gas desulfurization is the absorption with chemically active liquids. In chemically supported physical abosption of H_2S, first the required gas components are dissolved and then it reacts with the chemical added in the absorption liquids. Chemical assisted absorption liquids perform better than only physical based absorption liquids, hence it enhanced the water absorption capacity by lowering water and energy consumption and reducing pumping costs (Ryckebosch et al., 2011). Chemical scrubbing methods largely display high H_2S removal efficiencies (90% to almost 100%), thus after treatment the H_2S concentration drop to remarkably low level even at varying pollutant loads (Schiavon et al., 2014). The main shortcomings of this method are its higher specific costs and obligation to handle chemicals. The most common chemical draw on the absorption liquids are NaOH, $Ca(OH)_2$, $FeCl_2$, $Fe(OH)_3$, $Fe^{3+}/CuSO_4$, ethylenediaminetetra acetate (Fe^{3+}/EDTA) and monoethanolamine (MEA) (Persson et al., 2006; Petersson and Wellinger, 2009; Tippayawong and Thanompongchart, 2010). The quick chemical reactions with these alkaline solutions can favor a higher H_2S gradient from gas phase to liquid, and also reduce gas/liquid ratio desired for effective mass transference of H_2S (Abatzoglou and Boivin, 2009;

Ryckebosch et al., 2011; Sun et al., 2015). The NaOH reacts with the H_2S and form soluble salt such as Na_2S or NaHS, where the salts formed in this method non-regenerative and it desires to be disposed. To avoid salt precipitation in the system, spent caustic need to be taken out from the reactor regularly. The NaOH solution absorbs not only H_2S but also absorbs CO_2, so this method favored elimination of both CO_2 and H_2S simultaneously, however CO_2 absorption of significantly increases chemical requirements. But, due to its great skill necessity to handle the alkaline liquid, this technic only practiced for cleaning of biogas containing large amount of H_2S or when huge gas flowrates are treated (Petersson and Wellinger, 2009). Similarly, the combination of $Ca(OH)_2$ and sulfur compounds resulted sulfur containing salts which is not also regenerative and needs to be disposed. The same is true for $FeCl_2$ solution, which results in the creation of insoluble FeS which is not regenerative and needs to be disposed. Another gas desulfurization method for the formation of intermediate nonsoluble sulfide salt was initially settled by (Broekhuis et al., 1992), they used $CuSO_4$ solution and Fe^{3+}, besides the system was operated with gas contact times of 16–22 s and with temperature of 60 ^oC. In this process, H_2S is transformed into CuS as shown in Eq. 3, and it is further converted to elemental sulfur according to Eq. 4. Fe^{3+} can be regenerated with oxygen or air in a column reactor as described by (Eq. 5).

$$Cu^{2+} + H_2S + 2SO_4^{2-} \rightarrow Cu + 2HSO_4^- \quad (3)$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+} + S \quad (4)$$

$$2Fe^{2+} + 0.5O_2 + 2HSO_4^- \rightarrow 2Fe^{3+} + H_2O + 2SO_4^{2-} \quad (5)$$

Moreover, the use of $Fe(OH)_3$ able to remove H_2S and result in the creation of the insoluble salts Fe_2S_3, and by using either oxygen or air regeneration is possible (Ryckebosch et al., 2011; Schomaker et al., 2000). Chemical absorption by iron and zinc oxide has been generally replaced by the most efficient chelated-iron Fe^{3+}/EDTA (0.2 mol) based H_2S removal processes. Horikawa et al. (2004) studied removal of H_2S using catalyst solution containing Fe(III)-EDTA, hence H_2S was first dissolved and then catalytically reduced by a chelated iron solution. In this process hydrogen sulfide is oxidized to elemental sulfur while ferric chelated iron (Fe^{3+}) reduced into ferrous chelated iron (Fe^{2+}) according to Eqs. 6.

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S \quad (6)$$

$$2Fe^{2+} + 0.5O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \quad (7)$$

The generated sulfur element can be simply recovered or separated by sedimentation before regeneration of the Fe-EDTA-solution. Using this method H_2S removal efficiencies of 99% or greater can be attained, but plugging of the units and foaming are the main problems (Bailon and Hinge, 2014). The chelating agents are used to avoid the iron sulfide deposition in which the reduced iron (Fe^{2+}) is able to re-oxidize into its active form ferric iron (Fe^{3+}) with air according to Eq. 7 (Demmink and Beenackers, 1998; Neumann and Lynn, 1984). Chelated iron (Fe^{3+}) is used as a catalyst during H_2S absorption process; while in lack of catalytic agent the chemical supported oxidation of H_2S by dissolved oxygen proceeds at a barely slow rate. Consumption of huge amount of chemical is prevented owing to the regeneration of Fe^{3+}/EDTA solution. This method can be run at room temperature and precise for H_2S removal, whereas the remaining gas constituents such as CH_4 and CO_2 remain nearly the same. Besides, H_2S reduction from 90% to 100% can be attained for biogas having 2.2% of H_2S with gas flowrate of 1 dm^3/min and liquid flowrate of 83.6 cm^3/min, also the pressure of the gas kept at 220 kPa (Ryckebosch et al., 2011). At lower flow of catalytic solution, lesser H_2S removal efficiency was attained, while by feeding less concentrated H_2S higher removal efficiency can be achieved. Therefore, the total H_2S removal depends on adequate use of gas to liquid ratio and flowrates. It was also stated that the iron-chelated method can eliminate 50% to 90% of the mercaptans existing in biogas with insignificant removal of CO_2 (Abatzoglou and Boivin, 2009; Hosseini and Wahid, 2014). The available materials for chelated and non-chelated Fe^{3+} catalytic scrubbing are LO-Cat®, SulFerox®, and Sulfothane®, MINI-CAT®, (Bailón and Hinge, 2012).

2.4.1.3. Adsorption using metal oxide/hydroxide

The oldest method still in practice is theadsorption of H_2S on the surface of metal oxides and hydroxides. It is a commonly used technology because of its simplicity, high efficacy, quick kinetics of oxidation (Petersson and Wellinger, 2009; Ryckebosch et al., 2011). This process used parallel adsorbent columns and packed with iron oxide, iron hydroxide, zinc oxide, copper oxide, and working with adsorption and regeneration mode or by replacing of the adsorbent pattern (Ryckebosch et al., 2011). In the adsorption of H_2S with metal oxides, sulfur is bound and form metal sulfide (e.g. iron

sulfide (FeS) or zinc sulfide (ZnS)) and water is released. The adsorption and regeneration of the adsorbent material shown in Eqs. 8–10.

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (8)$$

$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O \quad (9)$$

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S + Heat \quad (10)$$

The materials commonly used for immobilizing of reagents are steel wool (covered with rust), wood chips or pellets made of red mud (a waste from aluminum manufacture) and enhanced the adsorbent surface area (Hosseini and Wahid, 2014; Persson et al., 2006). Thus, the surface area is a key parameter for the whole performance of the all adsorption systems. The relative small surface area of steel wool resulted in low binding capacity of sulfide. In this method wood chips impregnated and iron oxide have been used frequently, due to its greater surface over volume ratio than plain steel and low-cost (Svensson, 2014). The oxide or hydroxide of iron could be bound on the surface of pellets prepared from red mud, with these pellets it is possible to enlarge the surface to volume ratio (Marsh et al., 2005). In the purification step (Eqs. 8 and 9) the reaction is marginally endothermic, least temperature of around 12 ^{o}C needed for providing the required amount of energy. To achieve optimal reaction a temperature of 25 to 50 °C applied, meanwhile this reaction also desires water so the gas stream ought not be excessively dehydrated. Conversely, condensation must be prevented since iron oxides will stick together with water, and it might decline the reactive surface area.

As shown in Eq. 10, the reaction during adsorbent regeneration is exothermic and consequently during regeneration a huge amount of heat is released (Eq. 10). This might precede to self-ignition of the wood chips, unless temperature and air flowrate were not properly regulated. It may be run only one to two times due to practical reduction of its adsorption capacity, nearly 33%, with on each regeneration step (Abatzoglou and Boivin, 2009). This technology is simple and effective (more than 99%), which makes the technology right and proper to act as a final desulfurization step for highly pure CH_4 formation, particularly for introduction into the grid line (Miltner et al., 2012). However, the high cost comes from regeneration and replacement of the adsorption materials restricts to apply it on either small or medium level reactor. The adsorption capacity of commercial adsorbents exhibits 0.2 grams of H_2S per each gram of iron

wood chips or 1.8–2.5 gram of H_2S per each gram of Fe_2O_3 in a continual mode of operations, besides inorder to permit an internal adsorbent restoration 2-3% of air was supplemented (Kapdi et al., 2005; Kohl and Nielsen, 1997). The overall shortcomings of this method are vastly chemical requirement, high adsorbent costs and replacement frequency, and spent hazardous waste (Ryckebosch et al., 2011). Besides, direct regeneration automation is difficult and problematic unless the heat during the regeneration is dissipated prudently. Rather than the common adsorbent, lately a numbers of materials, such as Sulphur-Rite®, SulfaTreat®, SOXSIA®, Meda-G2®, and Sulfa-Bind® have been suggested as better choices to the conventional ones. The capital expenses only considered the adsorption component, i.e. the commercial brands of the material used in the time of operation the system (Bailon and Hinge, 2014; Petersson and Wellinger, 2009).

2.4.1.4. Adsorption on activated carbon

The removal of H_2S can be performed by adsorbing on non-impregnated (virgin), catalytic-impregnated, and impregnated activated carbons (AC), the latter two activate the conversion of H_2S into elemental sulfur and water better than the virgin activated carbon (Hosseini and Wahid, 2014; Persson et al., 2006). H_2S adsorption in AC is performed at high pressure between 7 and 8 bar and temperature from 50°C to 70°C. As in biological desulfurization, the adsorption of H_2S on AC usually done with addition of oxygen (4–6 %) to help the conversion of H_2S to elemental sulfur and water and to bind it stronger to the surface (Petersson and Wellinger, 2009; Ryckebosch et al., 2011). It is possible to conduct catalytic impregnation through treating the carbon with ammonia, whereas ordinary impregnation needs mixing of the carbon with alkaline or oxide (before, during or after activation). Thus, it boosts the H_2S removal capacity from 10–20 kg H_2S/m^3 (virgin carbon) to 120–140 kg H_2S/m^3 (impregnated carbon) (Bailón and Hinge, 2012). Without oxygen addition the partial oxidation of H_2S can be supported by only KI or $KMnO_4$ impregnation (Petersson and Wellinger, 2009), which is highly desired option for desulfurization, and after treatment the resulted biomethane able to injected into gas grids or vehicle fuel utilization (Petersson and Wellinger, 2009). Even though spent adsorbent regeneration is technologically possible, it is unusual for biogas treatment applications. In other meaning, at high temperatures the adsorbed elemental

sulfur can be desorbed, however ordinarily replacement of the saturated AC bed commonly used instead of regeneration (Rutledge, 2005). The H_2S oxidation mechanisms are very susceptible to the surface of AC and its chemical properties. Acidic surfaces endorsing the oxidation of H_2S into sulfur dioxide and sulfuric acid, while alkaline surfaces enhancing elemental sulfur formation (Bandosz, 2002). The disadvantages of adsorption with AC are high operation costs for replacement of bed material, oxygen residual in the system, and difficulties of waste material disposal. Furthermore, before treatment of AC the attached dust and water should be removed (Cosoli et al., 2008; Muñoz et al., 2015b).

2.4.1.5. Iron chloride dosing into the digester (In-situ H_2S precipitation)

Various divalent or trivalent iron salts such as $FeCl_2$, $FeCl_3$, can be dosed either into the feedstocks, in the pre-storage tank prior to adding to the digester, or directly injected into the digester. $FeCl_2$ (in liquid form) is the most commonly used chemical reagent (Persson et al., 2006). Thus, by in-situ reacting of H_2S with iron salts, stripping of H_2S can be controlled and leading to insoluble iron salt (FeS) formation and precipitation as described in Eqs. 11 and 12.

$$Fe^{2+} + S^{2-} \rightarrow FeS \quad (11)$$

$$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S \quad (12)$$

The precipitated FeS salt can be removed from the digester with the digestate. The digestate can be spread on land and used as source of fertilizer. In this technology, not only hydrogen sulfide but also removal of ammonia from biogas can be attained. Although this method is suitable for in-situ removal of high H_2S concentrations, however less effective to reduce H_2S concentration to very low level for injecting to the gas grid line demands. Reductions of H_2S concentrations in the biogas below 100–200 ppmv have been described, depending on the amount of iron chloride supplemented (Bailon and Hinge, 2014; Persson et al., 2006). This technic is relatively cheap because it only requires a tank for storing iron salt and dosing pump as a main capital cost. Moreover, anaerobic digestion plants can be operated, monitored and handled easily, whereas the degree of H_2S removal is difficult to control and to take pro-active actions. Additionally, the main weakness of this technology is the use of excessive chemical and

the corresponding operating costs when anaerobic digester feed with protein or sulfur rich substrates. The general advantages and disadvantages of the various H_2S removal techniques are presented in Table 2.5.

Table 2.5 Physical/chemical techniques used for H_2S removal (Tilahun et al., 2018)

Technologies	Methods	Efficiency (%)	Advantages	Disadvantages
In-situ H_2S precipitation	$FeCl_2$, $FeCl_3$ and $FeSO_4$ into the liquid phase of the digester	_	- Effective in reducing high H_2S concentration (200-100 ppmv) - Low investment costs -Simple operation and maintenance	- High operating costs - Difficulty in dossing of chemicals - Degree of desulfurization is difficult to control
Adsorption of hydroxide or metal oxides	Fe_2O_3, $Fe(OH)_3$, ZnO	upto 99%	- Simple process - Fast oxidation kinetics - Efficient to reduce high H_2S concentrations	- Expensive operating costs (regeneration and replacement of the adsorbent Material) - Reagent disposal
Physical absorption	Water or organic solvents	> 99%	-Cheap when water is available -No additional compression requirement	- Suitable for removal of low H_2S concentrations - High initial investment cost - High water, pressure and energy consumption
Chemical absorption	Aqueous solution of NaOH, $Ca(OH)_2$, $FeCl_2$, $Fe(OH)_3$, monoethanolamine (MEA)	90 to 100%	-Can be used with medium or high H_2S concentrations -Can treated H_2S with high load fluctuation -Low electricity requirements	- Higher Specific Costs - Needs proper chemicals handling - Create a contaminated liquid stream
Membrane separation (gas-liquid contactor)	Hydrophobic Microporous (polypropylene (PP), polyvinylidene fluoride (PVDF), polyethylene(PE))	Up to 98%	- High mass-transfer capacity -Low energy consumption - High compactness - Operational flexibility to scale up or down - Easy to operate	- Wetted membrane led to an increase of membrane resistance - Long operation affected the membrane morphology, pore size and porosity, and resulted in a deterioration of the membrane performance
	Hydrophobic Nonporous (dense) PDMS	> 97%	- Higher H_2S selectivity - Flexible operation without wetting problem - High compactness - Scaling is straightforward - Low investment and operation costs	-Mass transfer limitation due to significant membrane resistance -More efficient on H_2S removal at higher pH of scrubbing solution (When pH >8.5)

2.4.2. Biological H_2S removal technologies

2.4.2.1. In-situ micro-aerobic H_2S removal (Dosing of air/oxygen into anaerobic digester)

In-situ desulfurization is one of the oldest method used for controlling of H_2S in the digester itself. It was performed by injecting a limited amount of either oxygen or air to the gas or liquid phase of the digesters (Ryckebosch et al., 2011). In this method H_2S can be aerobically oxidized into elemental sulfur and CO_2 is also used as a carbon source by a group of specific autotrophic bacteria (*Thiobacillus spp*.) (Miltner et al., 2012). Depending on H_2S concentration limited amount of O_2 (2-6%) injected into the digester. The following reaction takes place in the digester (Díaz et al., 2011b, 2010; Kobayashi et al., 2012; Madigan et al., 2009).

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (13)$$

Without the requirement of inoculation, the sulfide oxidation bacteria (SOB) grow on the surface of the head space wall and ceiling which creating overlaid laminas of elemental sulfur that can be used as support material. Also it offers the necessary nutrients for microbial growth and at the same time facilitate O_2 mass transfer (Díaz et al., 2011b; Kobayashi et al., 2012). Despite the reliability, simplicity and economical efficiencies of this method, elemental sulfur deposition might negatively affect H_2S removal efficiency over long operation period by decreasing the gas retention time, headspace overpressure, and O_2 transfer rate to the microorganisms. As a result, periodical cleaning is inevitable to avoid clogging problems and minimize any reductions in the H_2S removal efficiency, while it adds extra costs to the total operational cost of the process (Díaz and Fdz-Polanco, 2012; Ramos et al., 2014b).

Several factors have been presented as essential parameters on the evaluation of in-situ biogas desulfurization performance such as, gas residence time, amount of air/oxygen, dosing point, location of oxidation process, recirculation, reactor configuration, and temperature. As mentioned earlier, either air or oxygen can be introduced into the digesters as source of oxygen. Although air supply is often an inexpensive alternative, however the residual O_2 and N_2 contents decrease heating value of biogas, which ultimately reduce the combustion engine efficiency. This is particularly challenging

when biogas CH_4 content is relatively low (about 50%), because minor dilution of biogas may affect negatively its final applications (Chandra et al., 2012). Krayzelova et al. (2015) reported that desulfurization of biogas having extremely high H_2S concentrations (about 12,000 ppmv) with the mentioned method increases the content of N_2 in the biogas increased up to 20% and decreases the CH_4 content below 50%, which is too low to use for most cogeneration units. To reduce the dilution effect of N_2, pure O_2 can be injected, but O_2 supplementation is rather expensive. Thus, the other alternative is on-site O_2 generation which required a lower operation cost and irregularly applied in large scale biogas treatment plants (Díaz et al., 2015). However, we should avoid overdosing of oxygen (6-12%) which is highly explosive and might inhibit the anaerobic digestion process (Persson et al., 2006; Petersson and Wellinger, 2009). But, when limited air or O_2 is given into liquid portion of the digester, sulfide concentration in the liquid decreases that have a positive effect in reduction of sulfide toxicity towards the hydrolysis of organic matter and methanogenic activity or CH_4 productivity (Díaz et al., 2011a, 2010; P. Jenicek et al., 2010; Krayzelova et al., 2014a; van der Zee et al., 2007; Zhou et al., 2007).

In spite of dosing point, most researchers reported that sulfide oxidation mainly took place on the walls of the headspace, also there are a few works indicating partial or even no accumulation of elemental sulfur on the headspace of digester (Díaz et al., 2011a; Kobayashi et al., 2012; Ramos et al., 2014c). The study performed by (Ramos et al., 2014a) found out that by enlarging the digester headspace from 0.3 to 25 L, the SOB can be grow on the extended area of the digester headspace (walls) and the microbial mat formed on enlarged area acted as a biofilter, so the H_2S removal process was improved considerably. From this result it is understood that large-scale biogas digester may have large headspaces to store biogas and it provides enough biogas retention time to reach acceptable removal efficiency.

As presented in Table 2.6, when operating at a gas residence times higher than 5 h over 97% H_2S RE was achieved. On the contrary, Ramos et al. (2013) demonstrated a successful removal efficiency of 96% under variable gas retention time ranging from 1 h to 1.5 h, this happened owing to oscillating of H_2S concentration and the amount of sulfur compound (substrate) added into the digester in the time of feeding (Table 2.6).

Table 2.6 The impacts of gas residence time on H_2S removal efficiency

Biogas residence time (h)	Removal efficiency (%)	Reference
5 - 8	99	Fdz.-Polanco et al. (2009)
5.3	99	Díaz et al. (2010)
6.6	97.5	Díaz et al. (2010)
6.3	98	Díaz et al. (2011c)
7.1 – 8.6	97	Díaz et al. (2011a)
2.4	72	Rodríguez et al. (2012)
1.4	68	Kobayashi et al. (2012)
6	90	Ramos and Fdz-Polanco (2013)
8	99	Ramos and Fdz-Polanco (2014)
10	99	Ramos et al. (2014b)
-	73	Krayzelova et al. (2014b)
13	99	Nghiem et al. (2014)

According to literatures the type of the reactor in which the H_2S removal process takes place have not major impacts on the system performance. Although the type of reactor has little impact on the H_2S removal process as stated, but few researchers revealed that some modification made in the common reactors could support to achieve better performances (Fernández et al., 2007; Montalvo et al., 2014).

2.4.2.2. Bioreactors for H_2S removal

There are three categories of common bioreactors used for biogas desulfurization: bioscrubbers, biofilters, and biotrickling filters (Figure 2.6 and 2.7). Bioscrubber includes two separate units, the primary unit is absorption, followed by a biological unit in which a microbial strain is suspended in the liquid part of the bioreactor, besides for proper growth of microorganism vital nutrients are supplied periodically (Delhoménie and Heitz, 2005). Shell-Paques/THIOPAQ™ is a common bioscrubber process used for removal of H_2S from gaseous stream (Figure 2.6). Using this process, it is possible to achieve more than 99.5% H_2S removal efficiency. Thus, THIOPAQ™ was used for removal of H_2S from biogas containing 80% CH_4, 18% CO_2, 2% H_2S, and achieved to

reduce H_2S concentration down to a level of 100 to 10 ppmv (Cline et al., 2003). Despite 95% to 98% of sulfide was converted into elemental sulfur, fouling or blocking problem was insignificant, presumably due to hydrophilic nature of the generated sulfur compound. However, the remaining sulfide is completely oxidized to sulfate, so to avoid accumulation of sulfate ions, liquid stream should be continuously removed or refreshed to take out unwanted products from the bioreactor. As a result, it requires large amounts of make-up water and caustic solution as well, in addition, its smaller gas to liquid surface area is the other weakness (Potivichayanon et al., 2006).

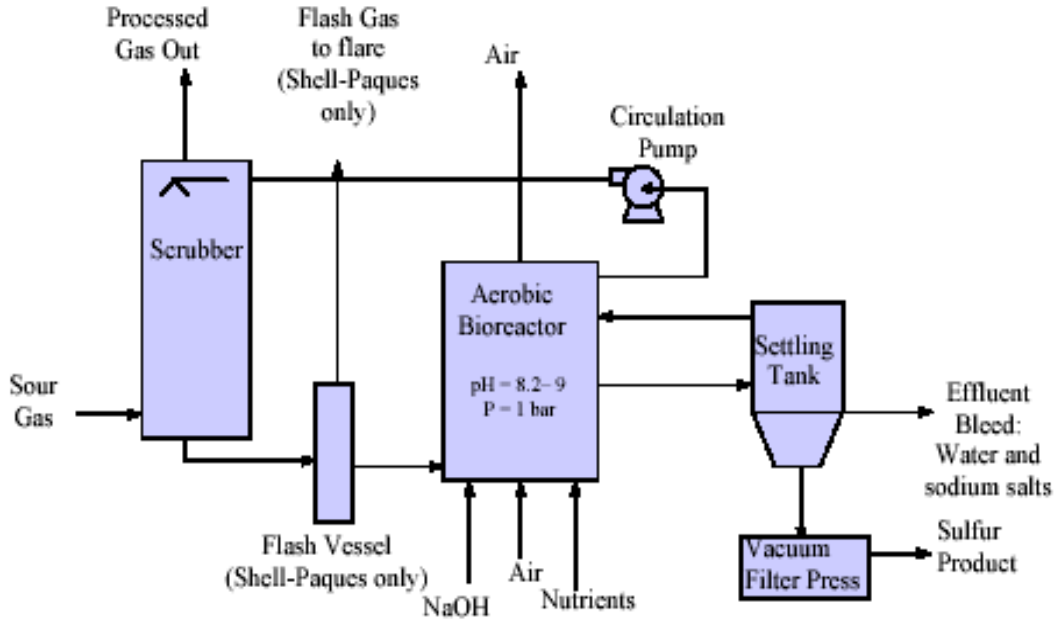
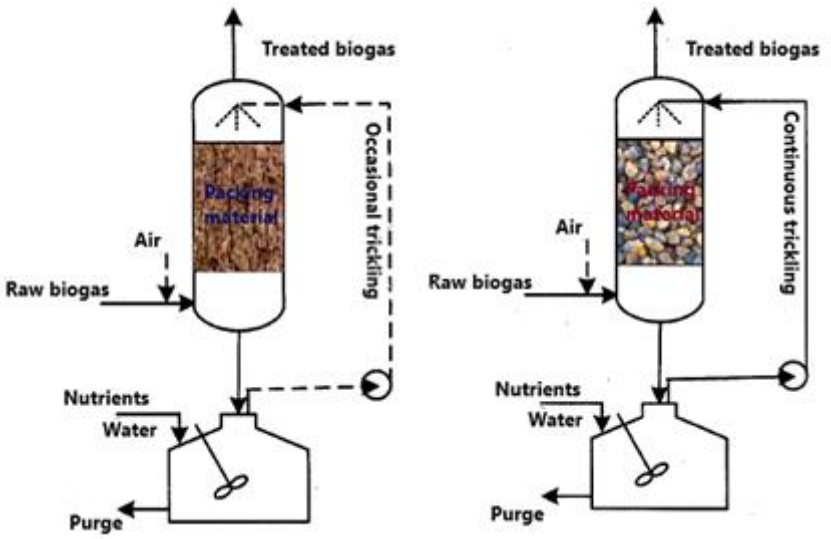


Figure 2.6 THIOPAQ™ and Shell-Paques System Schematic (Beil, 2010)

Biofilters are vessels that commonly involve a gas pre-humidity facility as well as its bed packed by organic materials, in which a diverse culture of microorganisms immobilized as a biofilm for degrading of H_2S (Figure 2.7a). The H_2S gas will be conveyed into the biofilm through the packed bed or liquid phase and subsequently biologically oxidized into less harmful substances (elemental sulfur or sulfate). The laboratory and pilot scale findings revealed that organic and inorganic sulfur compounds in the biogas can be effectively treated with this technologies (Ho et al., 2008; Morales et al., 2012). In biotrickling filters, H_2S can also trapped and solubilized in a reactor packed with humid inert (inorganic) materials immobilized with sulfide-

oxidizing bacteria (SOB), which is constantly trickled and recirculated with a liquid comprising necessary nutrients that can be used by the SOB during degradation process (Figure 2.7b). In these bioreactors oxygen or nitrate can be used as a source electron for oxidation of H_2S (500 ppmv - 12,000 ppmv) and it is possible to remove 80 to 100% (Fortuny et al., 2008; Persson et al., 2006; Tomas et al., 2009).



(a) (b)

Figure 2.7 Systems for removal of H_2S: (a) biofilter; (b) biotrickling filter (syed et al 2006).

Several studies have been carried out to optimize the key parameters for biological oxidation of H_2S such as, packing materials, type of microorganisms involved, reactor configuration and other operating conditions (pH, empty bed retention time (EBRT), recirculation rate etc.), which determine whether a partial (elemental sulfur) or complete oxidization (sulfate) is taking place while formation of sulfite and thiosulfate is occasionally detected (Chaiprapat et al., 2015; Estrada et al., 2012; Gabriel et al., 2013; González-Sánchez and Revah, 2007; Li et al., 2008; Mora et al., 2014; Muñoz et al., 2015b).

In the different bioreactor process pH is an important physicochemical parameter, because it does not only affect the biochemical reactions for removal of impurities but also interfere the microbial activity in the system (Table 2.7). As indicated in Table 2.7, several studies indicate that during H_2S oxidation *Acidithiobacillus thiooxidans* or *Acidithiobacillus* and *Thiobacillus thioparus* are the most commonly used sulfide-

oxidizing bacteria (SOB) at acidic and neutral pH conditions, respectively (Oyarzún et al., 2003; Ramírez et al., 2011; Robertson and Kuenen, 2006; Yamanaka, 2008). With acidic pH (pH 1-4) the removal of low and high H_2S loading rates have been successfully employed in a bioreactor (Aroca et al., 2007; Lee et al., 2006; Sercu et al., 2005). Few SOB for instance *Acidithiobacillus* species can live in extremely low pHs (Dolan, 2006). Charnnok et al. (2013a) also described operation of a biotricking filter at pH ranges 1.8–2.5 which could attain greater H_2S EC of 393 $gH_2S/m^3/h$ compared to neutral pH range 5.5 – 7.0 with EC of 15 $gH_2S/m^3/h$. Namgung et al. (2012) also stated both the microbial activity and the filter performance improved when the pH fallen from 6.5 to 1.5. It was reported that while treating greater H_2S concentration the pH decrease significantly (Chaiprapat et al., 2011a). The drop in pH is related to excess H_2S oxidation by the microorganism that produce H^+ and SO_4^{2-} ions, and when sulfate ion reacts with water sulfuric acid (H_2SO_4) is generated. Consequently, it is understood that pH started to drop as the microorganisms are adapted to high H_2S concentrations. It is very important from economic perspective since the bioreactor does not need any expensive buffer solutions and materials. Besides, working at low pH might reduce CH_4 oxidizing bacteria which cause CH_4 loss in several bioreactor process (Chaiprapat et al., 2011a). Conversely, Jin et al. (2005a) assessed the influence of pH on H_2S removal, and they stated that RE stayed high, more than 95% at pH ranges of 4 to 7, and then fallen to 94% and 87% when the pH dropped to 3 and 2, respectively. Similarly, Omri et al. (2011) observed a decline in H_2S removal from 99 to 90% as the system pH decreased from 7.0 to 2.5. While, Fortuny et al. (2011) reported that drop of pH from 6.5 to 2.5 did not influence H_2S RE. Nevertheless, after decreasing the pH they observed 25% decline on generation of sulfate, presumably owing to a reduction in the biological activities.

Despite biological filter benefits from acidic conditions due to lower operation cost to keep pH against the acidifying condition, drops in pH to very low values resulting from the formation of sulfuric acid might decrease the process efficiency. At low pH values, the solubility of H_2S decreases in which the dissociation of H_2S is nearly insignificant, which in turn slows down sulfide transportation as mass transfer is not ideal at lower pH. In other words, the lower the H_2S mass transfer, the lower desulfurization efficiency. Moreover, under strict acidic conditions, the activity of microorganisms might be inhibited (Chitwood et al., 1999; Jin et al., 2005). Hence to avoid such

drawbacks other studies use buffer solutions in the packed bed and recirculation liquid to enhance the reactor performance when acidification occurred.

Table 2.7 The effects of pH and residence time on H_2S removal efficiency

Inlet H_2S concentration (ppmv)	pH of liquid medium	Gas residence time (min)	H_2S removal efficiency (%)	Elimination capacity ($gH_2S/m^3.h$)	Reference
2107 ± 151	1.7	3.8–5.9	99 ±2	54± 13	Rodriguez et al. (2014)
2000	6 to 6.5	3	99	52	Montebello et al. (2012)
2000	6 to 6.5	2–3	98	55–82	Fortuny et al. (2011)
2000–10,000	2.5	2.1	80–100	52–223	Montebelloa et al. (2014)
1250–4750	2.7	1.9–9.7	99	50	Tomas et al. (2009)
500–1500	6.5	5–16	93–96	177–182	Soreanu et al. (2009)
12,300	3.5–7.0	2.8	>90	280	Fortuny et al. (2008a)
2235 ± 92	1.0–4.0	0.66	82 ± 4	114 ± 10	Chaiprapat et al. (2011b)
6395 ± 2309	0.5–4.0	3	97	150	Charnnok et al. (2013a)
10,000	1.6–3.6	4.8	97	169	Aita et al. (2016)
450	6.5–7.5	0.33 - 1	100	75	Kim et al. (2002)
-	7.3–7.5	2.4	99	130	Fernández et al. (2014)
900	8.2–9.2	-	99	428	Cho et al. (2000)

To do that, two different approaches were used to control the pH of the liquid medium; i.e. replacing low pH medium with fresh medium and/or adding buffering solution (Table 2.8). Thus, by keeping the pH stable and higher, H_2S solubility is enhanced and it can reduce gas to liquid mass transfer restriction. Consequently, the amount of H_2S gas transferable to the liquid boosted as the pH increased.

As shown in Eqs 14-16, the chemical equilibrium towards sulfide species affected by pH, for example hydrosulfide (HS^-) formed when p*K*a = 7.0 or sulfide (S^{2-}) at p*K*a = 12.8 when temperature is fix at 30 ◦C (Dean, 1999). It also reported that the solubility saturation of Na_2S was 186 g per liter of water (i.e. 2.38 M) at temperature of 20 ◦C, whereas the saturation solubility of H_2S in aqueous solution at pH < 4, ambient pressure

and, temperature of 30 ^{o}C is only 0.12 M (4.08 g/l) (Dean, 1999).

Table 2.8 pH adjustment of the liquid medium some bioreactors to remove H_2S from biogas

Method of pH adjustment	pH of the liquid medium	References
Fresh medium	0.5 to 4	Chaiprapat et al. (2015)
Alkaline nutrient	6.8 to 7.4	Almenglo et al. (2016)
Sodium bicarbonate	2 to 6.8	Jin et al. (2005a)
Sodium hydroxide	6 to 6.5	López et al. (2016a)
Sodium hydroxide	6 to 6.5	Fortuny et al. (2011)
Sodium hydroxide/Hydrochloric acid	6.5 to 7	López et al. (2016b)
Sodium bicarbonate	2 to 7	Jin et al. (2005b)

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \quad (14)$$

$$H_2S_{aq} + OH^- \leftrightarrow HS^- + H^+ \quad (pKa=7.0) \quad (15)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (pKa=12.8) \quad (16)$$

Sorokin et al. (2001) used alkaline solution (pH >9) to increase mass transfer and the reaction rate of H_2S. They also reported that, alkaliphilic sulfoxidizing bacteria (ASB) can be used for oxidation of H_2S, the ASB able to grow in higher pH (9-11) and can efficiently oxidize the reduced sulfur compounds (Sorokin et al., 2001). Currently, some biotechnological uses of ASB presented and they described that the oxidation of sulfide speed up when the pH values increased (Chen and Morris, 1972; Cline et al., 2003; Millero et al., 1987). Besides, the abiotic chemical oxidation of sulfide elevated at greater concentrations of the reacting species (when pH > 9). However, accumulation of excess dissolved sulfide resulted due to higher pH can adversely affect the activity of the sulfide oxidizer. Fortuny et al. (2011) also stated a substantial slowdown of the biological activity plus a shift in the metabolism take place, a shift from sulfate to thiosulfate, as a result of the higher pH (up to pH of 9.5). Other work by van den Bosch et al. (2008) revealed that at high pH, even if the biological oxidation negatively affected, H_2S removal only gradually dropped to around 95%, because physico-

chemical conversion of sulfide to thiosulfate and (poly)sulfide are favored at alkaline pHs. This process need greater operation cost to keep the solution alkaline and becomes a big hindrance for treatment of large scale biogas plants (González-Sánchez et al., 2008). Hence to minimize the drawback of extremely acid and alkaline pH, several studies operated their reactors using neutral pHs of 6–8 (Awe et al., 2017; Fernández et al., 2014; Fortuny et al., 2011; Montebello et al., 2012).

The other two limiting factors having significant impacts on biological filter performance are oxygen availability and mass transfer. It can be ascribed to the low solubility of oxygen in water, i.e., 8.24 mg/L at 25 °C (Colt, 1984). Besides, uneven distribution of both oxygen and H_2S along the height of the bioreactor also restrict the complete oxidation because the reactions cannot evenly proceed throughout the reactor. Rodriguez et al. (2012) described that by using Venturi-type gas diffusers, higher oxygenation capabilities can be achieved than of conventional diffusers for intensive gas–liquid mass transfer. If high amount of oxygen supplied, in which air is commonly used as a source of electron acceptor due to its free availability, the CH_4 content will be diluted with nitrogen and oxygen (Chaiprapat et al., 2011a). To resolve such problem supplying of DO into recirculating liquid was suggested by Rodriguez et al. (2014). By this approach (recirculating) CH_4 dilution in biogas can be reduced, also it enhanced the supply of moisture and nutrients to the SOB, whereas it might remove the microbial metabolic products from the bioreactor (Charnnok et al., 2013b).

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad \Delta G = -129.5\ kj/mol \qquad (17)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad \Delta G = -732\ kj/mol \qquad (18)$$

On other hand, elemental sulfur could be generated during desulfurization process if a partial oxidation takes place. As shown in Eq. 17, by generating alkalinity during partial oxidation of H_2S, it is possible to lower operating cost against the lowering pH. Partial H_2S oxidation also requires one-fourth of O_2 needed for complete oxidation (Eqs. 17 and 18). However, the formation of elemental sulfur gradually increases the pressure drop and eventually clogs the filters, entailing higher operating costs for packing media cleaning or replacement, constitutes the key operational restrictions of partial oxidation (Burgess et al., 2001; Rodriguez et al., 2014). One way to solve the clogging problem is to shut down filtration systems to withdraw the accumulated solids from the filter.

Tomas et al. (2009) also reported 95% solid elemental sulfur deposition on the packing materials due to low oxygen availability for the microorganism activity.

Like other biochemical processes longer gas retention within the packed media gives time for gas to be effectively absorbed into the liquid film and where the bio-oxidation of dissolved sulfide (substrate) with microorganisms took place (Chaiprapat et al., 2011b). Chaiprapat et al. (2015) also indicated that a greater removal efficiency was attained at higher EBRT tested. However, increasing EBRT leads to increased efficiency of sulfuric acid generation due to higher oxygen delivery into the filter promote a complete oxidation of H_2S to sulfate, but it may have resulted in a greater dilution of CH_4 which can limit its further applications as energy source. Montebello et al. (2014) reported the enhancement of H_2S RE from 50–60% to 90–100% when the gas retention time was increased from 0.5 to 2 minutes. Montebello et al. (2013) worked on BTF with neutral pH and they reported increasing EBRT from half to one minute could improve H_2S RE from 30% to 65%. Similarly, Chaiprapat et al. (2011b) reported an increase in H_2S RE from 30–40% to 80–90% when the gas retention time was increased from 1.3 to 5.2 minutes in a BTF treating a biogas produced from a full-scale anaerobic digester. In general, the longer the EBRT, the higher the desulfurization efficiency. However, larger reactors and as a consequence higher investment costs are required. Keeping the recirculation velocity at optimum level can assist to compensate the lower EBRT, but increasing liquid recirculation velocity above the optimal points could result in excessive liquid content of the bioreactor and reduce the medium porosity.

Packing materials also play a pivotal role in bioreactors because SOB are stabilized inside the bed materials, thereby, the reactions between DO and H_2S occur in this part of the filters. Several kinds of packing materials have been tested for H_2S removal inside biological filters (Table 2.9). High specific area and porosity, high chemical stability and structural strength, suitable surface for bacterial attachment and growth, low weight and cost are among the important features which a good packing material should have to perform in better order. Table 2.9 tabulates some of the important packing materials used in the bioreactors.

Table 2.9 Some of Packing materials used in bioreactors

Type of inoculum	Packing material	References
Acidithiobacillus thiooxidans	Wood chips	Aita et al. (2016)
Mixed culture	Polyurethane foam	Fernández et al. (2014)
Mixed culture	Plastic rings and coconut fiber	Charnnok et al. (2013a)
Mixed culture	Coconut fiber	Chaiprapat et al. (2011b)
Mixed culture	Polyurethane foam	Fortuny et al. (2008b)
Thiobacillus thioparus	Peat	Oyarzún et al. (2003)
Acidithiobacillus thiooxidans	Porous ceramics	Lee et al. (2006)
Thiobacillus thioparus	Wood chips	Kim et al. (2002)
Mixed culture	Polypropylene Pall rings	Jin et al. (2005b)

2.4.3. Gas-liquid membrane for H_2S removal

Absorption of both H_2S and CO_2 by conventional processes have been widely studied by several researchers experimentally and theoretically (Karoor and Sirkar, 1993; Li et al., 1998). Using alkaline absorption solution for example NaOH, Na_2CO_3, MEA, DEA favors not only to absorb the H_2S, but also it reacts with H_2S to enhance the system performance, by this it is possible to improve H_2S selectivity in the column that also reported to be in the range of 10–30 (D. Wang et al., 2004). However, the conventional absorption processes suffer from several shortcomings for instance channeling, flooding, foaming, entrainment and significant operating cost and capital cost. As a result, several researchers explored alternative method to boost the removal efficiency of the conventional absorption processes. Recently, use of hollow fiber membrane contactors (HFMC) for removal of acid gases (i.e. H_2S, CO_2) catch the attention of numerous scholars as a new technics for gas purification (Feron and Jansen, 2002; Kreulen et al., 1993b; Kumara et al., 2003; Mansourizadeh and Ismail, 2009; R. Wang et al., 2004; Yeon et al., 2003). The gas liquid membrane contactor offers many practical benefits than conventional contacting reactors. It includes great surface area per unit contactor volume, gas and liquid flowrates can be controlled independently, a known and constant gas liquid interfacial area, modularity and simple to be scaled, low operational and capital cost. In addition, membrane contactors can eliminate working difficulties like foaming or weeping, flooding, entrainment (Gabelman and Hwang,

1999; Kreulen et al., 1993a; Li and Chen, 2005). Even though the membrane wall introduces extra resistance which did not occur in classical absorption processes, while greater surface area can offer greater amount of mass transfer and higher selectivity (Klaassen et al., 2008). This technology also allows different components to come into direct contact with each other and favor mass transfer without dispersion of one phase into the other phase. Moreover, the gas flows in one side of a membrane whereas the liquid part flows in the other side, where gas diffuses through the membrane and goes into the gas–liquid interface and absorbed in the liquid phases.

Qi and Cussler (1985) grew the concept of the hollow fiber membrane for the first time in order to absorb acid gas with a polypropylene membrane in which NaOH solution was used as an absorbent liquid. Since then most of the researchers have been mainly worked on CO_2 elimination from gas streams (Feron and Jansen, 2002; Mansourizadeh and Ismail, 2009; Ren et al., 2006). The absorption of low H_2S concentrations by membrane contactors in which water is the only absorbent liquid was well described by Boucif et al. (2008). Earlier studies also performed removal of H_2S from gas streams by gas-liquid membrane processes (Li et al., 1999; Marzouk et al., 2010; D. Wang et al., 2004; Wang et al., 2002). Besides, mathematical models for removal of both H_2S and CO_2 using HFMC processes and MEA and carbonate solutions was described by (Faiz and Al-Marzouqi, 2011, 2009). Lately, Hedayat et al. (2011) experimentally examined the reduction of both CO_2 and H_2S by PVDF and PSf (Polysulfone) membrane contactors, as well as aqueous amine solutions used as an absorbent liquid. Besides the membranes characteristics, reactor working situations like solution pressure have important role for membrane supported gas absorption performance (Karoor and Sirkar, 1993; Poddar et al., 1996). As stated by Poddar et al. (1996) and Malek et al. (1997), the operating pressure in the liquid side have to maintained marginally greater than gas side pressure to avoid dispersion of gas bubbles into the liquid to minimize gas loss and keep stable operation. On the contrary, maintaining of a great pressure at the liquid side for long operation period might result in membrane wetting or partial wetting problems by the liquid absorbent (Malek et al., 1997; Mavroudi et al., 2006). Lu et al. (2008) tested wetting mechanism of hydrophobic membranes theoretically as well as experimentally while removing CO_2, and they indicated the liquid side pressure have a substantial impact on membrane pore wetting. The use of organic compounds as liquid absorbent,

such as amine solutions, may reduce the liquid surface tension and lead to partial wetting of membranes. Al-Marzouqi et al. (2008) and Atchariyawut et al. (2007) also examined CO_2 removal using hollow fiber membrane contactors and aqueous solution of MEA and NaOH and they observed membrane wetting problems. Keshavarz et al. (2008) carried out the impacts of wetting and operational parameters on simultaneous removal of H_2S and CO_2 and they reported that wetting and DEA concentration have a significant influence on removal of CO_2 in comparison with removal of H_2S. In another study, Faiz and Al-Marzouqi (2009) used polytetrafluoroethylene (PTFE) hollow fiber membranes contactors with MEA as an absorption liquid and they reported lower amount of MEA is effective for entire H_2S absorption, whereas increasing of MEA enhanced the RE of CO_2. Thus, to avoid CO_2 absorption and reduce operation cost (caustic consumption) few studies focused on selective H_2S removal. Kreulen et al. (1992) experimentally tested selective H_2S removal from a gas mixtures containing CO_2 and N_2 using polypropylene (non-wetted) and nylon 66 horizontal (wetted) flat sheet membranes as well as MDEA (Methyldiethylamine) absorption liquid, and they stated when the membrane was in non-wetted condition lower H_2S selectivity recorded. D. Wang et al. (2004) worked on the selective removal of H_2S using a tailor made PVDF membrane and aqueous solution of Na_2CO_3, and they reported mass transfer of H_2S increased at high gas/liquid flow ratio, thereby H_2S selectivity enhanced. Recent studies displayed that with short gas resident time and high gas to liquid flow ratio, hollow fiber membrane modules favor selective H_2S removal (Li et al., 1999, 1998). It is obvious that like selectivity, mass transfer capacity of membrane contactor was taken as another performance indicator of the process efficiency. Kreulen et al. (1992) examined selective passage of H_2S using flat-sheet microporous membranes, and reported an overall H_2S mass transfer coefficient of about 1.9 cm/s (Table 2.10). Li et al. (1999) also investigated the H_2S removal through PVDF microporous hollow fibre membranes and they found mass transfer coefficients of up to 7.2 cm/s, that is four times greater comparing with the result described by Kreulen et al. (1992). However, the gas removal capacity of microporous membrane declined when the membrane gets wetted. To testify this fact, Kreulen et al. (1993c) examined the mass transfer rates in wetted as well as non-wetted situations, and they revealed mass transfer reduces significantly in wetted condition. Similarly, Zhang et al. (2008) stated that, if 10% of the membrane length is

wetted, the resistance of the membrane might increase by 10% to 70%. Therefore, the membrane gas transfer capacity would greatly reduce owing to wetting or partial wetting problem. It was reported that a completely wetted hydrophobic membrane may have lower efficiency compared to a conventional absorption processes (Karoor and Sirkar, 1993; Kreulen et al., 1993b). The mass transfer coefficients of different materials are tabulated in Table 2.10.

Table 2.10 Mass transfer coefficient of different membrane materials

Membrane type	Mass transfer coefficient, (m/s)	References
Symmetric polypropylene Microporous	0.0073	Qi and Cussler, (1985)
Symmetric polypropylene Microporous	0.019	Kreulen et al. (1992)
Asymmetric polysulfone Microporous	0.0125 – 0.025	Li et al. (1998)
Asymmetric polysulfone Dense	5×10^{-4}	Li et al. (1998)
Asymmetric PVDF Microporous	0.012 – 0.072	Li et al. (1999)
asymmetric PVDF Porous	0.0096 – 0.012	D. Wang et al. (2004)
PVDF Microfiltration	$2.38 – 3.43\times10^{-4}$	Hedayat et al. (2011)
Polysulfone Microfiltration	$1.82 – 2.55\times10^{-4}$	Hedayat et al. (2011)
ePTFE Microporous	$1.08 – 1.3\times10^{-6}$	Marzouk et al. (2012)
PFA Microporous	$1.0 – 1.1\times10^{-5}$	Marzouk et al. (2012)
Polypropylene Microporous	$1.0 – 1.7\times10^{-3}$	Esquiroz-Molina et al. (2013)
polypropylene Microporous	$1.0 – 25x10^{-4}$	Jefferson et al. (2005)

Alternatively, membrane bioscrubbers (MBS) are a potential substitute for controlling of reduced sulfur compound and other gas impurities (Debus, 1995; Debus and Wanner, 1992; J. et al., 2000; Wilderer, 1995). Membrane based bioscrubber integrates the advantages of membrane as well as biological treatment process (Kumar et al., 2008). In addition, the membrane acts as a support for the growth of microorganisms and offers a great gas to liquid surface area for mass transport of impurities (H_2S) as well. Thus, the gaseous impurities diffuse across the membrane and then degraded with microbial population (biofilm) (De Bo et al., 2002; Ergas et al., 1999; Van Langenhove et al., 2004). In MBS process different configurations, i.e. tubular, flat sheet and spiral wound, have been studied for waste gases treatment (Fitch, 2005). Similar to physicochemical membrane process, the membrane materials in MBS can be porous, microporous, dense or composite. In microporous membrane contactor, the pollutants are transported to the actively metabolizing biofilms, and favorable results are obtained at low loading rates. But, at greater loading rates the pore of the membrane tends to be blocked with biomass (Ergas et al., 1999; J. et al., 2000; Reij et al., 1998). Therefore, plugging of pores with biomass may have contributed to deterioration of the system performance and require continual cleaning (Kennes and Thalasso, 1998). Although microporous materials are more permeable but susceptible for significant wetting of the membrane tubes after long operation time which possibly caused mass transfer performance problems. To avoid the drawbacks of microporous membrane, the dense (nonporous) membrane contactor which are commonly composed of silicone rubber tubing or plates have also been examined for the removal of unwanted gas streams and shown promising results (Attaway et al., 2001; Freitas Santos et al., 1995). Dense membrane mass transfer coefficient governed by pollutant solubility and diffusivity through membrane, and by selecting membrane material carefully, the pollutant can be removed selectively (Reij et al., 1998, 1995). The dense membranes are able to operate at high gas pressure, and it is resistant to chemicals and mechanical abrasion (Stephenson et al., 2000). Besides, it is also more resistant to biofouling than microporous membranes, probably owing to the hydrophobic nature of the membranes that prevent the microbial attachment on membrane surface (Kumar et al., 2008). Thus, the nonporous membrane showed no deterioration in its performance for long operation time, in comparison with the microporous system, and it requires no continual cleaning to remove pore blockage

(Attaway et al., 2002). However, a limited number of studies reported that the nonporous silicone membranes could not provide sufficient mass transfer compared to microporous membranes. Besides, their long term operational stability has to be determined (Al-Marzouqi et al., 2009; Al-saffar et al., 1997).

2.5. Scope of the Thesis Study

Biogas produced from anaerobic fermentation of organic wastes is a sustainable energy source that plays a vital role in the emerging renewable energy market, because of its substrate flexibility and energy yield (Holm-Nielsen et al., 2009). Biogas composition primarily depends on the type of raw materials and operational conditions used in digestion processes. During biogas production process the inorganic and organic sulfur contained in the feedstock is reduced into H_2S which can be transferred to the biogas (Mackie et al., 1998). H_2S is one of the most common trace compounds in biogas and its concentration fluctuates widely depending on the type of feedstock from 0.1% to 2% v/v or (1000 ppmv – 20,000 ppmv) (Abatzoglou and Boivin, 2009). Hence. the existence of H_2S needs special attention due to its unpleasant odor, toxicity and serious corrosion problems and thus limit plant lifetime (Appels et al., 2008; Panza and Belgiorno, 2010; Tang et al., 2009). Moreover, during combustion the H_2S in biogas generates sulfur oxides (SO_2) which is an acid rain precursor and causes serious health and environmental problems (Chaiprapat et al., 2011a). Therefore, cleaning of H_2S from the biogas is required prior to its use in any commercial or long-term application. For trouble free operation of CHP, most manufacturers recommended the maximum allowable H_2S concentration levels below 300 ppmv (Peu et al., 2012; Rodriguez et al., 2014; Ramos and Fdz-Polanco, 2014). The major presence of CO_2 in biogas also considerably reduces the calorific value and increases the compression, storage and transportation costs restricting its use at the point of production (Marzouk et al., 2012; Poloncarzova et al., 2011). Thus, along with the removal of H_2S fractional reduction of CO_2 is importance for technological and economic feasibility of the whole biogas cleaning process. Therefore, by applying different technologies H_2S level should to be controlled to prevent the damage and fulfill the quality standards required for different applications. So far, many studies investigated the effects of different liquid absorbents and membrane materials for removal of H_2S and CO_2, however, studies evaluating the

effects of different operating parameters on the selective H_2S removal using membrane contactor was very limited.

In the first part of this thesis study, the performance of abiotic gas-liquid membrane contactor was tested for selective removal of H_2S and partially absorption of CO_2 from biogas for the first time under varying operational conditions and the results obtained were reported in section 4.1. Due to its high H_2S/CH_4 and moderate CO_2/CH_4 selectivity, absolutely impermeability to the liquid permeation, a rubbery dense polymeric membrane such as PDMS looks more suitable for biogas cleaning. In order to increase the mass transfer of H_2S through the membrane and increase its selective removal, a slightly alkaline solution was used. From alkaline compounds NaOH was chosen due to its low cost and rapid reaction rate with the dissolved H_2S. In addition to using a slightly alkaline solution, the process operated at atmospheric pressure and ambient room temperature to minimize the operational cost of desulfurization. However, the frequent liquid replacement and caustic requirement of this process increased the operating costs associated with chemicals as well as water consumption, and also generate byproduct which needs treatment before discharge (Muñoz et al., 2015; Petersson and Wellinger, 2009). To overcome these inconsistencies, the conventional biological treatments (i.e. conventional bioscrubber (CBS)) was tested as a convenient substitute for treating H_2S from biogas because of its eco-friendliness (section 4.3). However, there are also problems during operation of these technologies, such as, significant dilution of biogas, risk of explosion, difficulty in control of the operational parameters and high operational cost due large alkaline consumption. Hence, further studies on biogas desulfurization is required to develop novel technologies, capable of making biogas technically suitable, economically viable, and ecologically appropriate source of energy.

Thus, in the next part of the study a hybrid system coupling the gas-liquid PDMS membrane contactor and bio-oxidation process were developed. During the hybrid process, H_2S is first selectively diffused and dissolved into an aqueous absorption liquid and then bio-oxidation of H_2S occurred in the bioscrubber. To maintain a high H_2S diffusion rate, mildly alkaline solution is generally used. The route of H_2S oxidation is dependent on the concentration of oxygen, i.e., it is oxidized to elemental sulfur (S^o) or sulfate under oxygen limiting and non-limiting conditions, respectively. A novel

approach for continuous removal of H_2S from the biogas established in this study demonstrated feasibility of the MBS process for selective desulfurization of biogas without dilution and explosive risks. In addition, the effects of the absorption liquid pH, gas flowrate (loading) and DO concentration on biogas desulfurization performance were discussed and the results obtained are described in section 4.2. The specific aim of the study is, selective removal of H_2S from biogas with less operational cost using a membrane integrated gas-liquid absorption processes. Figure 2.8 also shows the structure of the study.

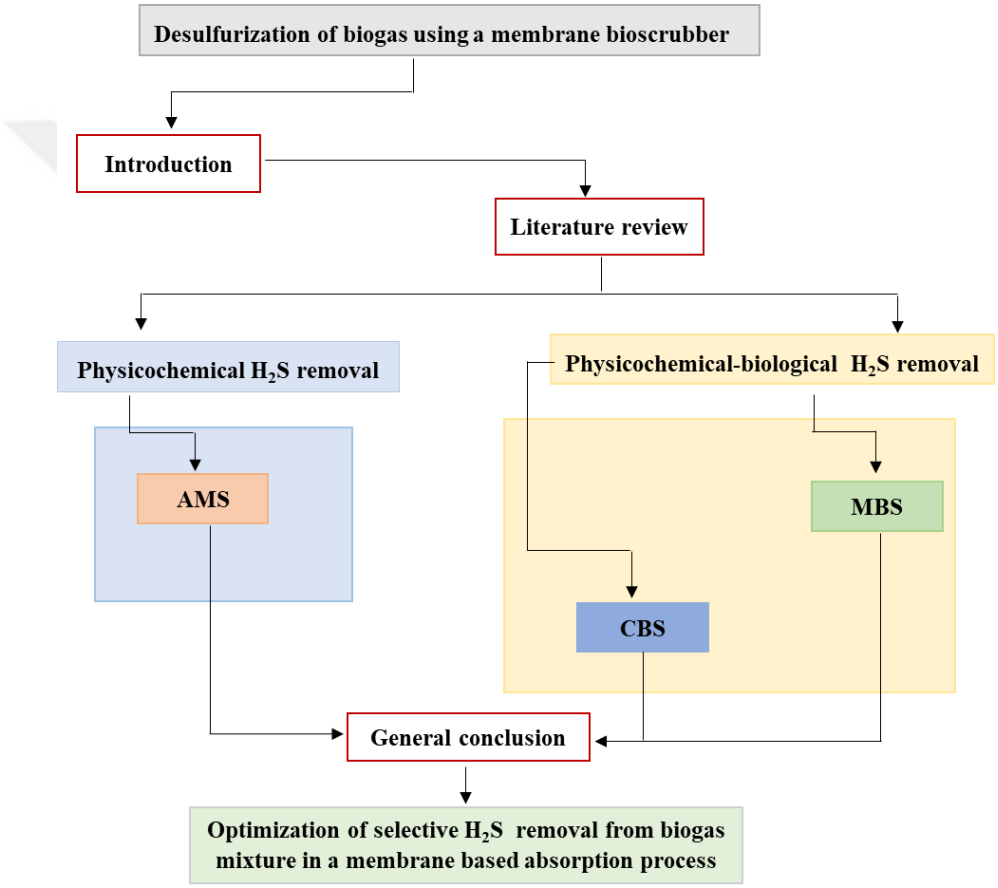


Figure 2.8 The structure of this study.

3. MATERIALS AND METHODS

3.1. Abiotic Gas-Liquid Membrane Contactor for H_2S Removal from Biogas

In this part of the thesis, the performance of abiotic PDMS membrane contactor process for selective H_2S removal from the biogas was investigated for long time in a lab-scale reactor. Besides, the effects of different operational parameters on process performance were evaluated.

3.1.1. Materials

A synthetic gas mixture consisting of H_2S (10,000 ppmv, which is 1% of the biogas), CO_2 (39%) and CH_4 (60%) and simulating a typical biogas was purchased from Hat Industrial Gases PLC, Kocaeli, Turkey. Tap water was used as absorption solution and its pH was adjusted to 7.0, 8.5 and 10.0 with 1M NaOH solution using a pH transmitter and a dosing pump (Seko, PR 40/Q). NaOH was purchased from a local supplier (TEKKİM Kimya Sanayi, Bursa, Turkey) and the stock alkaline solution was prepared by using distilled water as required. Commercially available PDMS membrane (Silicone tube) was used in the study. The PDMS membrane having 1mm thickness was purchased from EUROFLEX (Germany), while 1.5 mm and 2 mm were purchased from DEUTSCH & NEUMANN (Germany) and other properties are summarized in Table 3.1.

Table 3.1 Characteristics of PDMS membrane

Number of module	1
Effective length, m	3
Thickness, mm	1, 1.5, 2
Inner diameter, mm	7
Outer diameter, mm	9
Internal Area (A_i), m^2	0.066
External Area (A_e), m^2	0.085

3.1.2. Experimental methods

A laboratory scale gas-liquid membrane contactor was designed and manufactured to perform biogas desulfurization experiments under different operational conditions. The bench scale experimental setup and image of the gas-liquid membrane contactor were displayed in Figure 3.1 and 3.2.

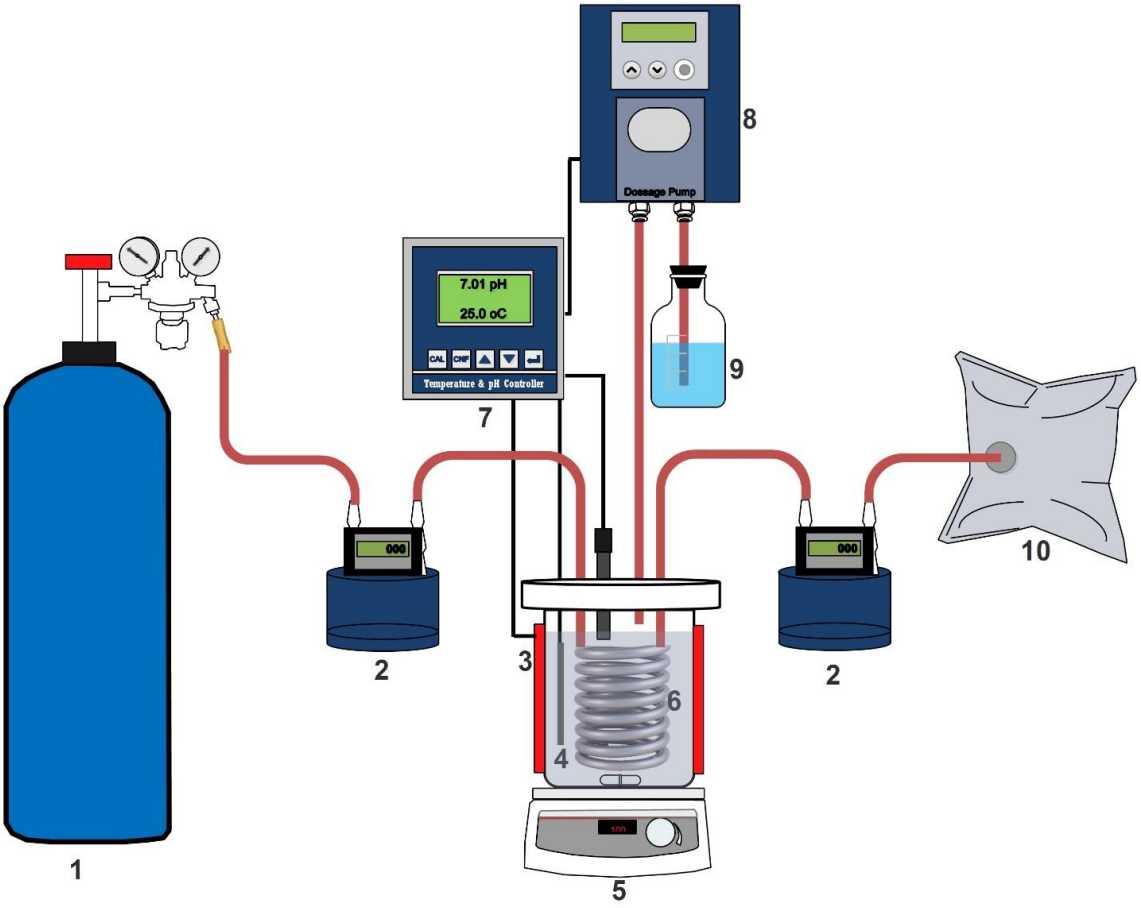


Figure 3.1 Schematic diagram of abiotic experimental setup: (1) synthetic biogas cylinder, (2) milligas counter, (3) heating blanket, (4) temperature sensor, (5) magnetic stirrer, (6) tubular PDMS membrane, (7) pH transmitter, (8) NaOH dosage pump (9) NaOH solution (10) effluent biogas bag (Tilahun et al., 2017)

The absorption vessel is a pyrex glass cylinder of 120 mm wide and 200 mm high, the total volume and the liquid volume of the reactor (i.e., excluding the membrane volume) were 1.69 L and 1.5 L, respectively. In the experiments, the synthetic biogas was continuously fed to the tubular membrane placed folded into the absorption vessel filled with tap water. The inflow biogas was controlled by a gas flow gauge at different flowrates and counted by digital gas counters (MGC, Ritter, Germany) before entering and after exiting the tubular membrane.



Figure 3.2 Image of abiotic experimental set up

Almost the whole H_2S and some of CO_2 were removed from the simulated biogas mixture, where it diffused across the membrane and then absorbed/reacted with mildly alkaline solution. During each experiment the vessel was completely filled with liquid to minimize volatilization of sulfur compounds. To reduce O_2 concentration the abiotic reactor was flushed with N_2. Due to the high toxicity of H_2S, all experiments were performed in a fume hood to confine any accidental leakage of H_2S gas. For uniform distribution and complete mixing of the biogas with mildly alkaline solution in the reactor magnetic stirrer (550 rpm) was used throughout the experiment. In the liquid phases online pH monitoring was performed using a sensitive glass electrode combined with temperature sensor. Periodic calibration was also performed with pH buffers of 7 and 10 units, assuring for the proper operation of the probe. The temperature of the absorption solution was controlled at different levels with an electrical heating blanket wrapped on the wall of the glass vessel to assess the effect of temperature on the process performance. The conductivity, oxidation reduction potential (ORP) and dissolved oxygen (DO) were monitored on-line using a digital multimeter electrodes (Multi 9430, WTW, Germany).

The abiotic experiments were carried out at different gas flowrates, temperatures and pH values of absorption solution to determine the optimum CO_2 and H_2S fluxes (Table 3.2). Each test lasted about 4 h and biogas samples were taken from the exit once every hour and analyzed. The average values were used in evaluating the system performance. Table 3.2 summarizes the operational conditions of the reactor.

Table 3.2 Operating conditions of the abiotic membrane contactor set-up

Parameters	Run-1	Run-2	Run-3	Run-4
Temperature (^oC)	21	21	21	10-45
Gas flow rate (L/h)	0.54-2.1	0.54-2.1	0.54-2.1	0.54
pH	7	8.5	10	10
Gas velocity (cm/s)	0.39-1.52	0.39-1.52	0.39-1.52	0.39
H_2S loading rate (mg/m^2-membrane.h))	91-355	91-355	91-355	91

3.1.3. Analytical methods

Sulfide concentration was measured spectrometrically (WTW PhotoLab 6100VIS) following the method described by Cord-Ruwisch (1985). Sulfate (4500-SO_4^{2-} E) concentration was determined as per standard methods (APHA et al., 2005). For offline gas quantification gas sample was first collected at the exit of reactor with about five-liter aluminum foil gas collecting bag. By taking gas sample at gas inlet and gas exit port of the main reactor and H_2S, CO_2 and CH_4 contents were analyzed by a gas chromatography (GC, Shimadzu, Tokyo, Japan) equipped with a thermal conductivity detector (TCD) and Restek MS-13X stainless steel column (Restek MS-13X 45/60, 2.74 m length internal diameter of 2 mm). The temperatures of injection port, column and detector were 150 °C, 40 °C, and 150°C, correspondingly. Argon gas was used as the carrier gas. When H_2S concentration in the exit of the reactor was under the detection limit (less than 250 ppm) of GC-TCD, a second absorption solution of 0.5% NaOH was used to absorb and determine it before venting. The detail of second absorption system was explained in our previous work (Bayrakdar et al., 2016). In that case, the concentration of the absorbed HS^- (mg/L) is measured spectrophotometrically as mentioned above, which was used to calculate the H_2S concentration in the exit. Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-

EDS) analyses were carried out at Yildiz Technical University Science and Technology Application and Research Center (Istanbul, Turkey). The changing morphologies of the membrane were directly observed using a SEM after Au–Pd coating. The semi quantitative elemental analyses of the inorganics deposited on the external surface of the membrane were performed using an EDS coupled with SEM at the end of the experiment. All samples were collected and analyzed in triplicate following each change in the process operation conditions and the averages were reported.

3.1.4. Basic mechanisms and reactions

The basic mechanisms and reactions involved in the diffusion/dissolution of H_2S occurs according to Eqs. 19-21. In the process, H_2S first dissolved in the absorption liquid as shown in reaction 19, after that two dissociation reactions occurred (Eqs. 20 and 21). To keep a high H_2S diffusion rate, overall a mildly basic solution is used. From alkaline compounds NaOH had been chosen due to its low cost and rapid reaction rate with the dissolved H_2S. The more the NaOH concentration the better the H_2S mass transfer.

At the interface:

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \quad (19)$$

In the liquid phase:

$$H_2S_{aq} + OH^- \leftrightarrow HS^- + H_2O \qquad (pKa=7.0) \quad (20)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \qquad (pKa=12.9) \quad (21)$$

If oxygen available in the reactors, the dissolved HS^- will be biologically oxidized by SOB either to elemental sulfur or sulfate under oxygen limiting and non-limiting conditions, respectively. Hence, the aerobic biological oxidation of H_2S indicated in Eqs. 22 and 23.

$$HS^- + \frac{1}{2}O_2 \Rightarrow S^o + OH^- \qquad (\Delta G^o=-169.35\ kJ.mol^{-1}) \quad (22)$$

$$HS^- + 2O_2 \Rightarrow {SO_4}^{-2} + H^+ \qquad (\Delta G^o=-732.58\ kJ.mol^{-1}) \quad (23)$$

CO_2 is major impurity in biogas, it is an acid gas whose mass transfer is also increased when alkaline scrubbing solution is used. Depending on the pH values absorption of CO_2 takes place in accordance with Eqs. 24-27.

At the interface:

$$CO_{2\ gas} \leftrightarrow CO_{2\ aq} \quad (24)$$

In the liquid phase:

$$CO_{2\ aq} + H_2O \leftrightarrow H_2CO_{3\ aq} \quad (25)$$

$$CO_{2\ aq} + OH^- \leftrightarrow HCO_3^- + H_2O \quad (pKa=6.4) \quad (26)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (pKa=10.3) \quad (27)$$

H_2S absorption occurs faster than CO_2 absorption because CO_2 goes through a slow hydrolyzing step (Kohl and Nielsen, 1997). It is clear that the concentration of CO_2 in biogas is much greater than H_2S, and both have similar acidic behavior. CO_2 and H_2S can both be absorbed in an alkaline solution (Miltner et al., 2017; Ryckebosch et al., 2011). Absorption, hydrolysis as well as dissociation of CO_2 in alkaline solutions are indicated in reactions 24-27. Hence the removal of CO_2 generates additional H^+ that can decrease the pH of the absorption liquid according to reactions 26 and 27. To maintain a high H_2S removal efficiency, pH of the absorption liquid needs to be high; therefore, extra alkali solution should be supplemented, while the operational costs becomes greater. Hence, the CO_2 removal should be minimized to reduce the alkali chemical consumption, which can be achieved by using dense PDMS membrane due to its higher selectivity towards H_2S compared to CO_2 (Montoya, 2010).

3.1.5. Evaluation of the system performance

In this study, the H_2S or CO_2 removal efficiencies (RE) and methane loss were calculated according to Eqs.28.

$$(\mathrm{RE}) = (([\text{gas inlet}] - [\text{gas out let}])/[\text{gas inlet}]) \times 100 \quad (28)$$

Where,

RE - removal efficiency of CO_2 or H_2S, and methane loss,

gas inlet - the inlet gas concentration, and

gas outlet - the outlet gas concentration

The selectivity factor has been generally used to indicate the performance of membrane gas separation processes. Usually, in the gas–liquid membrane contacting process, the permeate gas was the preferred component. Thus, the permeate selectivity can describe the process performance. The selectivity factor (α) of H_2S over CO_2 is the mole fractions of the gasses in the liquid and feed gas phases (Eqs. 29). Similarly, the H_2S selectivity over CH_4 was calculated according to Eqs.30. The process was considered selective for H_2S, if α is greater than 1.

$$\alpha = \frac{xH2S/xCO2}{yH2S/yCO2} \quad (29)$$

$$\alpha = \frac{xH2S/xCH4}{yH2S/yCH4} \quad (30)$$

Where,

x - refer to the mole fraction of each gas in the liquid phase and

y - refer to the mole fraction of each gas in the feed gas.

Flux is another performance indicator and estimated by using Eq.31:

$$J = \frac{Q(S_o - S)}{A} \quad (31)$$

Where,

J is the flux of the gas diffused from gas phase into the absorption solution ($g/m^2.d$),

Q is the flowrate of feed gas (L/d),

S_o is concentrations of each gas component in the feed gas (g/L),

S is concentrations of each gas component in the effluent (g/L) and

A is the membrane surface area (m^2).

In the membrane based gas absorption technics, transfer of impurities from gas to liquid phase involves three steps. Each step of mass transfer is related to a mass transfer

resistance in series, i.e.: gas phase boundary layer resistance, membrane resistance and liquid boundary layer resistance. Compared with the specific mass transfer coefficients, the overall mass transfer coefficient can be more conveniently evaluated (Kreulen et al., 1993). It can be determined by the experimental results as follows in Eqs. 32.

$$K_G = \frac{Q_G}{A} \ln\left(\frac{C_{in}}{C_{out}}\right) \quad (32)$$

Where,

K_G is the overall mass transfer coefficient,

Q_G is flow rate of the feed gas (m^3/s),

A is total outer surface area of the membrane (m^2),

C_{in} and C_{out} are gas concentration in the gas phase at the inlet and outlet of the membrane contactor, respectively.

3.2. Biotic Gas-Liquid Membrane Contactors for H_2S Removal from Biogas

In this part of the thesis, a membrane integrated gas absorption and bio-oxidation process for the removal of H_2S from biogas was investigated.

3.2.1. Experimental set-up and operation

The laboratory scale hybrid membrane bio-scrubber contactor setup image used in this study was shown in Figure 3.3 and 3.4. It was consisted of a cylindrical glass reactor with 120 mm diameter and 200 mm depth and working volume of 1.5 l. The glass reactor was filled completely with tap water to minimize the volatilization of the sulfur compounds. A simulated biogas mixture, containing of 60% (v/v) CH_4, 39% (v/v) CO_2, and 1% (v/v) (10,000 ppmv) H_2S (Hat Industrial Gases PLC, Kocaeli, Turkey), was supplied with mass flow controllers and fed into the system from the bottom of the reactor. The flowrate of the biogas was adjusted and controlled by using mass flow controller at exit of the biogas cylinder and measured by gas counters (MGC, Ritter) both in the influent and effluent of the membrane contactor. The commercial tubular PDMS membrane (EUROFLEX GmbH, Germany) had an internal diameter of 7.0 mm, wall thickness of 1.0 mm and length of 3 m, corresponding to a total surface area of

about 9.2 dm^2 (Figure 3.5). The membrane was folded and fully submerged into the liquid portion of the system.

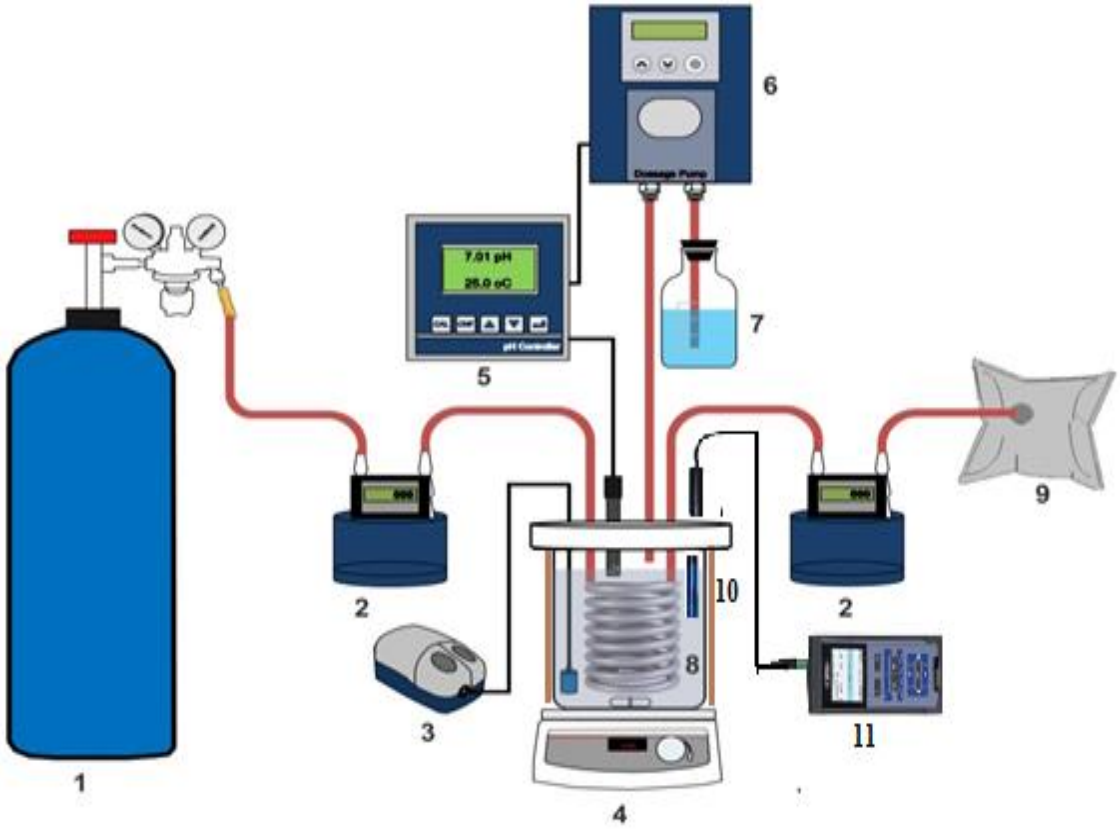


Figure 3.3 Schematic diagram of biotic experimental setup: (1) synthetic biogas cylinder, (2) milligas counter, (3) air pump, (4) magnetic stirrer, (5) pH transmitter and temperature sensor, (6) NaOH dosage pump, (7) NaOH solution, (8) tubular PDMS membrane, (9) effluent biogas bag, (10) heating blanket, (11) Multi probes meter (Tilahun et al., 2018)

The pH of the liquid in the bioreactor was automatically controlled and on-line monitored by addition of NaOH (1N) directly into the referred absorption unit using a pH transmitter and a dosing pump (Seko, PR 40/Q). To avoid excess accumulation of anions and cations, which resulted in higher conductivity (over 7mS/cm), could affect the bacterial activity, hence about 2/3 of the supernatant was periodically withdrawn from the bioreactor and replaced with fresh medium.



Figure 3.4 Image of biotic experimental set up

Liquid sample of 20 ml was daily withdrawn from the mixed liquor portion of the MBS, and filtered through a 0.45 µm size filter was used prior to sulfur compounds determination. Tap water was daily supplied to the systems to replace the liquid taken for analysis and water losses due to evaporation.



Figure 3.5 Membrane used before and after

The liquid in the reactor was continuously stirred with a magnetic stirrer at 550 rpm to achieve complete mixing and to control the attachment of biomass on the membrane surface. The operating temperature in the bioreactor was kept at 30±1 ^{o}C using an

electric heating pad wrapped around it. During the experiments, conductivity ORP and DO in the liquid phases were monitored online using a digital multimeter (Multi 9430, WTW GmbH, Germany). Detailed of the hybrid membrane bio-scrubber (MBS) operating parameters were shown in Table 3.3.

Table 3.3 MBS operating parameters

Parameters	Unit	Period I	Period II
Operation duration	d	105	75
Biogas flowrate	l/d	8 - 32	14
DO concentration	mg/l	4	1 - 4
ORP	mV	80 - 100	100 to -300
Conductivity	mS/cm	2 - 7	2 - 7
pH of absorption liquid		7 - 8.5	7
Inlet surface H_2S loading	$g/m^2.d$	1.29 – 5.1	2.3
Inlet volumetric H_2S loading	$g/m^3.d$	79 - 316	140
Temperature of absorption liquid	^oC	30	30
Operating absolute pressure	pa	$\approx 10^5$	$\approx 10^5$

3.2.2. Substrate and inoculum

The bioreactor was inoculated with 200 ml of autotrophic sulfide oxidizer bacteria, in particular *Thiobacillus* spp. and *Thioalkalivibrio sulfidiphilus* with the sludge taken from a laboratory scale aerobic membrane bioreactor treating sulfide containing textile wastewater (Yurtsever et al., 2017). During the operation, dry air was supplied manually, used as electron acceptor by sulfide oxidizing bacteria, using peristatic pump into the bottom of the system and bubbled via a fine bubble flexible diffuser. Pictures of the flexible diffusor used during the long time operation were shown in Figure 3.6.

The liquid medium was composed of (g/l): K_2HPO_4 2.0, NH_4Cl 0.4, $MgCl_2.6H_2O$ 0.2, $CaCl_2.2H_2O$ 0.1 and tap water, was prepared and supplied periodically. During biogas separation most of the H_2S and some of CO_2 was permeated through the membrane, and dissociated into sulfide (H_2S_{aq}, HS^-, S^{2-}) and bicarbonate ion (HCO_3^-). The scrubbed sulfide and bicarbonate was used as electron donor and inorganic carbon source by autotrophic H_2S oxidizing bacteria, respectively. In addition, because of the low cost and its effectiveness, NaOH was used as alkaline chemical (Jegatheesan et al., 2015).



Figure 3.6 Pictures of the flexible diffusor before and after experiments

3.2.3. Analytical methods

For the purpose of analysis, samples were collected and all the determinations were performed in duplicate to examine the reproducibility of the data. For the analysis of CO_2, H_2S and CH_4 gas compositions in the inlet and outlet of the membrane bioreactor 10 ml of gas sample was taken and injected into a gas chromatograph (Shimadzu GC-2014, Japan) equipped with thermal conductivity detector (TCD) (Reddy et al., 2016). As a carrier gas argon was used. The concentration of sulfide in liquid was determined spectrometrically (DR/2800, HACH, USA) following the methylene blue method described by Standard Methods (APHA/AWWA/WEF, 2012). In the MBS liquor samples, following 0.45 µm filtration, sulfate, thiosulfate and sulfite concentrations were off-line analyzed using an ion chromatography. All chemicals used were of analytical grade and employed without further purification. Biomass concentration in the bioreactor was estimated by measuring Total Kjeldahl (TKN) according to standard methods (APHA/AWWA/WEF, 2012). Before analyzing TKN, the liquid sample was centrifuged and the biomass was washed 3 times with deionized water to remove dissolved nitrogen compounds.

Table 3.4 The sampling points, analysis frequency and type of analysis performed in MBS

Sampling point of MBS			Performed analysis	Analysis frequency
Inlet gas phase	Inside liquid phase	Outlet gas phase		
×		×	H_2S, CO_2, CH_4 gases	Daily
	×		Sulfide	Daily
	×		Sulfate	Daily
	×		pH, ORP, DO, Conductivity	Continuously
	×		NH4-N, TKN	1 time/each operational period
	×		SEM	1 time/each operational period
	×		SEM-EDS	1 time/each operational period
	×		XRD	1 time/each operational period

3.2.4. XRD, SEM-EDS experiments

To determine the structural characterization of the absorption solution and the suspended biofilms whether any compounds were formed other than elemental sulfur, the absorption solution was dried and prepared for analysis using X-ray diffractometer (XRD) (Rigaku D-Max/2200PC). During preparation the sample was placed into a 60° drying oven overnight to avoid any remaining water. Then the obtained sample was put into a desiccator to cool to room temperature. Finally, as shown in Figure 3.7, the dried sample pulverized to produce a fine-sized powder for analysis.



Figure 3.7 Dried sample used for XRD experiment

At the end of each experimental period, scanning electron microscopy (SEM) was also used to determine the surface morphology of the clean and used membrane surface. In addition, Energy Dispersive X-ray Spectroscopy (EDS) was conducted for semi-quantitative elemental analysis of inorganic deposited (S^o, Si, Mg, Ca, Na, K, Na, P etc.) on the external surface area of the membrane. Samples were well-kept in the refrigerator under temperature of 4 ^{0}C to use until 24 h and freezer at -20 ^{0}C to store for longer periods.

3.2.5. Calculations

In this study, the CO_2 or H_2S gas phase removal efficiencies (RE) and CH_4 loss were calculated according to Eq. 33.

$$\text{RE } (\%) = \frac{(Q_g in * C_g in) - (Q_g out * C_g out)}{(Q_g in * C_g in)} * 100 \quad (33)$$

Where,

RE- gas phase removal efficiencies,

Q_g^{in} – inlet biogas flowrate (m^3/d),

Q_g^{out} – outlet biogas flowrate (m^3/d),

C_g^{in} - inlet gas concentrations (mg/l),

C_g^{out} - outlet gas concentrations (mg/l)

In biotic gas purification processes the performance of the system can be indicated also by computing the selectivity factor. Selectivity of the gas-liquid-membrane contacting system for H_2S may be defined as the ratio of H_2S over CO_2 concentrations in the liquid phase to that in the gas phase (Eq. 34). Likewise, the selectivity of H_2S over CH_4 was calculated according to Eq. 35.

$$\alpha(H_2S/CO_2) = \frac{(xH_2S/xCO_2)}{(yH_2S/yCO_2)} \quad (34)$$

$$\alpha(H_2S/CH_4) = \frac{(xH_2S/xCH_4)}{(yH_2S/yCH_4)} \quad (35)$$

Where,

α is dimensionless which represents the selectivity factor,

x - denotes the mole fraction of the biogas components absorbed in the liquid phase and

y - denotes the mole fraction of the biogas components in the feed gas.

Surface removal rate or absorption flux (J) of the membrane contactor is another performance indicator, which can be estimated as Eq. 36.

$$J = \frac{(Q_g in * C_g in) - (Q_g out * C_g out)}{A} \quad (36)$$

Where,

J - flux of the gas components ($g/m^2.d$) and

Q_g^{in} – inlet biogas flowrate (m^3/d),

Q_g^{out} – outlet biogas flowrate (m^3/d),

C_g^{in} - inlet gas concentrations (mg/l),

C_g^{out} - outlet gas concentrations (mg/l)

A is the membrane surface area (m^2)

The total H_2S removal efficiency (*TSR*) of the system was calculated according to Eq. 37.

$$TSR\ (\%) = \frac{\left(Q_g in * C_g in(H_2S)\right) - \left(Q_g out * C_g out(H_2S)\right) - (Q_L out * C_L out(H_2S))}{\left(Q_g in * C_g in(H_2S)\right)} * 100 \quad (37)$$

Where:

Q_g^{in} – inlet biogas flowrate (m^3/d),

Q_g^{out} – outlet biogas flowrate (m^3/d),

C_g^{in} (H_2S)- inlet H_2S gas concentrations (mg/l),

C_g^{out} (H_2S)- outlet H_2S gas concentrations (mg/l)

Q_L^{out} – outlet liquid flowrate (m^3/d),

C_L^{out} (H_2S)- H_2S concentrations in the outlet liquid (mg/l).

The process capacity for H_2S removal was also calculated as volumetric removal rate (*VSRR*) according to Eq. 38.

$$\text{VSRR } (\text{g/m}^3.\text{d}) = \frac{\left(\text{Q}_\text{g}\text{in} * \text{C}_\text{g}\text{in}(\text{H}_2\text{S})\right) - \left(\text{Q}_\text{g}\text{out} * \text{C}_\text{g}\text{out}(\text{H}_2\text{S})\right) - \left(\text{Q}_\text{L}\text{out} * \text{C}_\text{L}\text{out}(\text{H}_2\text{S})\right)}{\text{V}} \quad (38)$$

Where:

Q_g^{in} – inlet biogas flowrate (m^3/d),

Q_g^{out} – outlet biogas flowrate (m^3/d),

C_g^{in} (H_2S)- inlet H_2S gas concentrations (mg/l),

C_g^{out} (H_2S)- outlet H_2S gas concentrations (mg/l)

Q_L^{out} – outlet liquid flowrate (m^3/d),

C_L^{out} (H_2S)- H_2S concentrations in the outlet liquid (mg/l)

V is the active volume of the reactor (m^3).

The quantity of elemental sulfur (S^o) produced can be estimated theoretically by subtracting the aqueous sulfur species that exist in the absorption liquid. Since the concentrations of thiosulfate and sulfite were below the detection limit throughout the study, the mass balance calculation was performed according to Eq. 39.

$$\text{Q}_\text{g}\text{in} * \text{C}_\text{g}\text{in}(\text{S} - \text{H}_2\text{S}) = \text{Q}_\text{g}\text{out} * \text{C}_\text{g}\text{out}(\text{S} - \text{H}_2\text{S}) + \text{Q}_\text{L}\text{out} * \text{C}_\text{L}\text{out}\left[(\text{S} - \text{HS}^-) + \left(\text{S} - \text{SO}_4^{-2}\right) + (\text{S} - \text{S}^\text{o})\right] \quad (16)$$

Where:

Q_g^{in} – inlet biogas flowrate (m^3/d),

Q_g^{out} – outlet biogas flowrate (m^3/d),

C_g^{in} (H_2S)- inlet H_2S gas concentrations (mg/l),

C_g^{out} (H_2S)- outlet H_2S gas concentrations (mg/l)

Q_L^{out} – outlet liquid flowrate (m^3/d),

C_L^{out} (H_2S)- H_2S concentrations in the outlet liquid (mg/l)

(S-S^o) is the concentration of S^o produced (g S^o/1),

(S-H_2S) is the concentration of H_2S in the gas phase (g S-H_2S/l),

(S–SO_4^{-2}) is the concentration of SO_4^{-2} generation (g S–SO_4^{-2}/1) and

(S–HS^-) is the concentration of non-oxidized sulfide ion in the liquid (g S–HS^-/1).

3.3. Conventional Bioscrubber (CBS) for H_2S Removal from Biogas

3.3.1. Experimental set-up and operating procedures

The set-up of a conventional bioscrubber was similar with schematic shown in Figure 3.3, however membrane was not used. The CBS was made of plexiglass cylinder and having total working volume of about 1.7 L (internal diameter 120 mm, height 200 mm). It was only filled by alkaline aqueous solution and continuously stirred with magnetic stirrer in order to mix the liquid and gas uniformly. It was operated under mesophilic conditions at a constant temperature of (30 ± 1 ^oC). The pH of the liquid also automatically controlled with a pH transmitter and a dosing pump by addition of NaOH (0.5N) solution directly into the referred absorption unit. The synthetic biogas mixture contains H_2S (1%), CO_2 (39%) and CH_4 (60%) was purchased from local supplier (TEKKİM Kimya Sanayi, Bursa, Turkey). The gas mixture was supplied with mass flow controllers and directly fed into the bottom part of the bioscrubber. Dry air was supplied manually using peristatic pump into the bottom of the bioscrubber and bubbled via a fine bubble diffuser. Both dry air and biogas directly contacted with the liquid part of the bioscrubber. Due to the direct contact between biogas and the liquid most of the H_2S and CO_2 has a chance to be absorbed and dissociated into sulfide (H_2S_{aq}, HS^-, S^{2-}) and bicarbonate ion (HCO_3^-). The scrubbed sulfide and bicarbonate was used as electron donor and inorganic carbon source by autotrophic H_2S oxidizing bacteria, respectively. The system was inoculated with 200 ml of autotrophic sulfide oxidizer biomass, in particular *Thiobacillus spp.,* with the sludge taken from a laboratory scale aerobic membrane bioreactor treating sulfide containing textile wastewater. The composition of the medium: 2 g/l K_2HPO_4, 0.4 g/l NH_4Cl, 0.2 g/l $MgCl_2.6H_2O$, 0.1 g/l $CaCl_2.2H_2O$ and tap water, was prepared and supplied periodically. The liquid phase of the CBS was suited with on-line monitoring of conductivity, oxidation–reduction potential (ORP) and dissolved oxygen (DO) (Multi probe, WTW, Germany). Also, pH was on-line monitored during experiments by integrating with automated pumping of NaOH solution into the liquid part of the system. The H_2S removal performance of the CBS was evaluated with different operating parameters, gas residence time (5 min-20 min), pH (7-8.5). The sulfide oxidation to either sulfate or elemental sulfur were also examined, while throughout the CBS test the DO concentration was kept above 4 mg/l.

To avoid excess accumulation of anions and cations, which can affect the bacterial activity, more than half of the supernatant was periodically withdrawn from the CBS and replaced with fresh medium. Liquid sample of about 20 ml was daily withdrawn from the mixed liquor portion of CBS and filtered through a 0.45 mm filter before analyzing the sulfur compounds concentrations. Moreover, tap water was daily supplied to the systems to replace the liquid taken for analysis and water losses due to evaporation.

3.3.2. Analytical methods

To determine the concentration of H_2S, CO_2, and CH_4, gas sample was daily taken at the enterance and exit sampling ports of CBS and injected into GC equipped with TCD and stainless steel column (Restek MS-13X 45/60 mesh, 2.74 m length, 2 mm internal diameter) (Tilahun et al., 2017). The pH of the liquid media was measured using a pH/ ^{o}C meter (Seko, PR 40/Q). After the liquid samples filtered through 0.45μm filters, sulfate was off-line examined according to standard methods for the Examination of Water and Wastewater (APHA/AWWA/WEF, 2012). Sulfide was determined spectrometrically (WTW PhotoLab 6100VIS) following the way described by Cord-Ruwisch, (Cord-Ruwisch, 1985).

4. RESULTS AND DISCUSSION

4.1. Abiotic Gas-Liquid Membrane Contactor for H_2S Removal from Biogas

4.1.1. The effect of biogas and pH on CO_2 and H_2S removal efficiencies and CH_4 loss

The effect of biogas flowrate on the removal efficiencies of CO_2, H_2S and CH_4 loss is illustrated in Figure 4.1. As a general trend, H_2S removal efficiency declined with increasing biogas flowrate. For example, at pH 10, the H_2S removal efficiency decreased from 98±1% to 41±1.8%, while the CO_2 absorption efficiency dropped from 59±0.8 to 16±0.5%, when the feed biogas flowrate increased from 9 to 35ml/min, respectively. At the lowest biogas flow rate, the volumetric calorific value of the biogas increased around 25% due to 60% CO_2 removal and the H_2S concentration reduced from 10000 ppm to 200 ppm in the effluent, which is an acceptable level for co-generation units (Ramos and Fdz-Polanco, 2014). This result reveals that the absorption efficiency of H_2S is much higher than that of CO_2, due to the instantaneous reaction of H_2S with NaOH, which is in agreement with the findings of Keshavarz et al. (2008). As expected, the H_2S removal efficiency reduced at higher gas flowrates due to decreasing contact time, which restricted the reaction of the acid gases with NaOH. Therefore, the evaluated process combining the benefits of membrane and absorptive capacity of alkaline solution, was found highly effective particularly at low gas flowrates. It was in accordance with other studies in literature (Al-Marzouqi et al., 2009; Marzouk et al., 2010b), in which less H_2S removal was reported as the gas pressure and flowrate increased. Besides, Marzouk et al. (2010a) revealed that the removal of H_2S decreased from 100 to 74% as the gas flowrate increased from 400 to 1000 ml/min, while the H_2S fluxes increased from 5.76 to 10.8 mol/m^2.d when distilled water was used as receiving solution at feed gas pressures of 50 bars. The CH_4 content in the outlet reached up to 80% with 5.2 ±0.3% CH_4 loss at the lowest flowrate (9 ml/min). While the biogas flowrate rose up, the CH_4 loss dropped below 1%. In this study, the CH_4 losses remained quite small as a result of low CH_4 transfer through the PDMS membrane in comparison with CO_2 and H_2S.

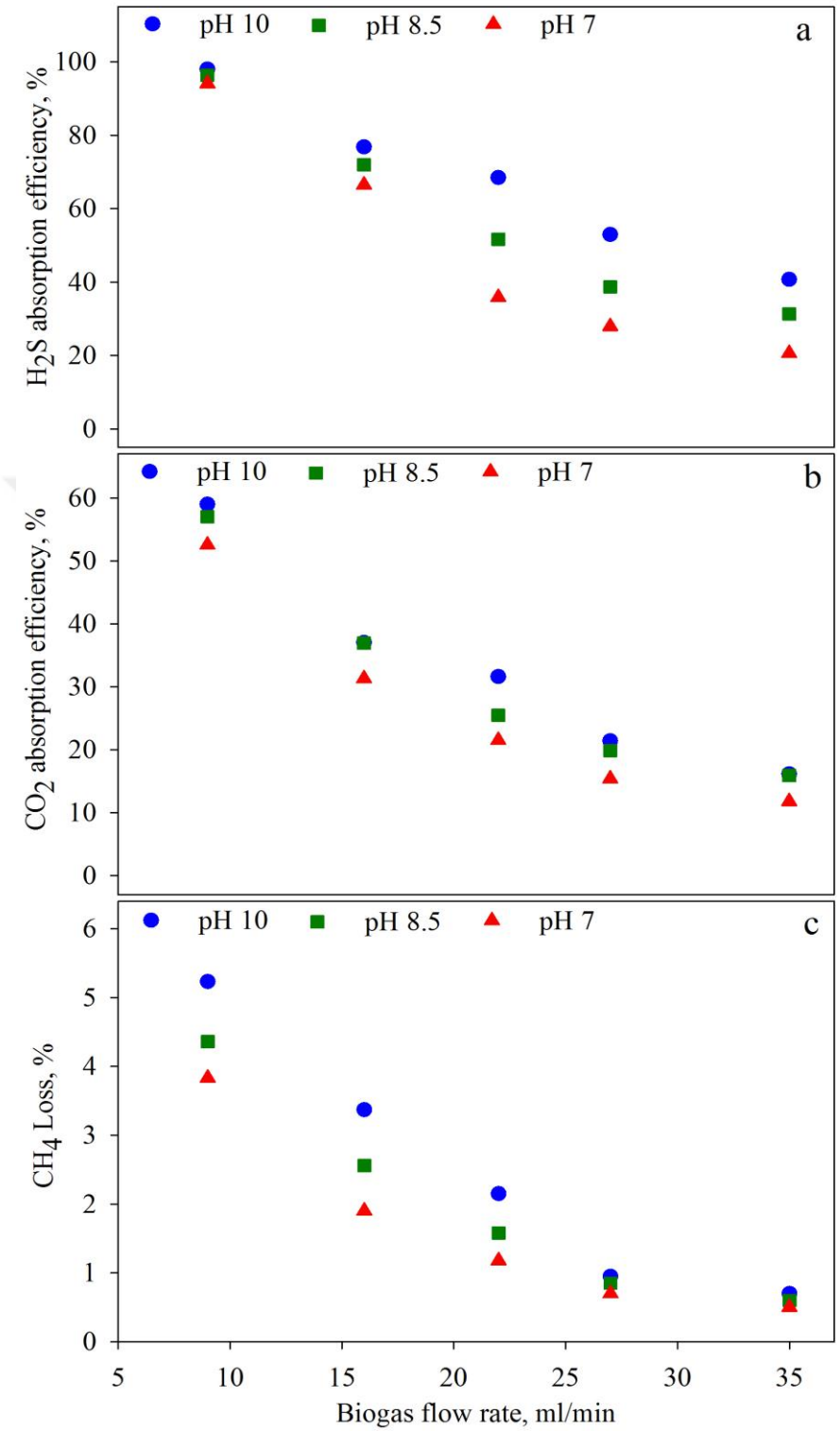


Figure 4.1 The effect of pH and biogas flow rate on, (a) H_2S removal efficiencies, (b) CO_2 removal efficiencies and (c) CH_4 loss

At pH 8.5 and 7.0, the H_2S removal efficiencies decreased from 96.3±0.1% to 31.3±2%

and from 94.0±0.5 to 20.6±0.6%, respectively, while the CO_2 absorption efficiencies dropped from 57.0±0.1 to 15.9±0.2% and from 52.5±1.2 to 11.8±0.1%, correspondingly, with increasing flow rate from 9 to 35 ml/min (Figure 4.1). Similarly, at these pH values, the volumetric calorific value of the biogas increased by about 23 and 21% at lowest gas flowrate, respectively. The impact of biogas flowrate on the removal efficiency was intensified at lower pHs, the effluent H_2S concentration at pH 8 was 400ppm, whereas at pH 7 was 600ppm (at 9 ml/min) which is two times more than the maximum allowed threshold content for heating generator (Ramos and Fdz-Polanco, 2014). As a result, the effluent biogas could not be fed to co-generators without further treatment, thus requiring more surface area to meet the treatment objective. In this experiment with the lowest pH, more than 75% CH_4 content could be obtained at low flowrates. Other studies also indicated that due to its considerably lower solubility, CH_4 absorption was lower compared to CO_2 and H_2S (Dolejš et al., 2014). In general, the obtained order of H_2S and CO_2 removal efficiencies were pH 10 > pH 8.5 > pH 7. The main disadvantage of using alkaline solution was the difficulty or impossibility of alkalinity reuse. Even though, it is a relatively low cost chemical, significant amount would be required, for complete H_2S removal. Compared to conventional chemical absorption processes, the use of PDMS membrane contactor has an advantage of being able to selectively remove H_2S using less alkali solution. For that reason, the suggested membrane-based desulfurization process may offer cheaper possibilities in comparison with the conventional processes used for simultaneous removal of H_2S and CO_2 by water and/or alkaline scrubbing (Basu et al., 2010).

4.1.2. The effect of pH and flowrate on selectivity

The effects of gas flowrate and pH on the selectivity factor were shown in Figure 4.2. An increase in the biogas flowrate has a positive effect on selectivity. Thus, at pH 10 and 8.5 the selectivity factor of H_2S/CO_2 increased from 1.7 to 2.5 and 1.7 to 2.0, respectively. Whereas at pH 7, the selectivity decreased from 1.8 to 1.7 with less fluctuation at the corresponding flowrate. The result revealed that at lower pH values, a physical absorption dominates and H_2S saturates quickly in the absorbent solution. Hence H_2S absorption at lower pH suffers from the low separation efficiency compared to higher pH absorption process, agrees with other studies (Atchariyawut et al., 2007).

Similar conclusions were reported by others who reported that rising the gas flowrate improves the absorption selectivity (Lu et al., 2006; Mandal et al., 2004). Bontozoglou and Karabelas (1993) reported that the selectivity of H_2S increased by minimizing the contact time between the gas and liquid phases due to the faster absorption of H_2S than CO_2. The weakness of this process is that the selectivity is inversely proportional to H_2S removal efficiency. Therefore, an optimum point should be determined to have acceptable amount of H_2S in the treated biogas with minimum CH_4 loss. According to the results in Figure 4.2, at pH 10, 8.5 and 7, the selectivity factor of H_2S/CH_4 increased from 18 to 58, 22 to 48 and 24 to 35 as the flowrate raised from 9 ml/min to 35 ml/min, respectively. Amo et al. (1998) reported a H_2S/CH_4 selectivity of about 70 in Pebax®4011 modules at pressure of 26.6 bar and 22 ^oC. Likewise, in the study of Chatterjee et al. (1997) on sour gas permeation through different rubbers materials a H_2S/CH_4 selectivity of 74 was reported for a poly (ether, urethane and urea) membrane at 10.1 bar and 35 ^oC. The H_2S/CH_4 selectivity factor determined in our study is not comparable with these values (Amo et al., 1998), because we run the membrane contactor at atmospheric pressure.

In general, the experimental results indicated that selectivity of PDMS membrane contactor followed the order $H_2S > CO_2 > CH_4$. This result was in agreement with a former study (Orme and Stewart, 2005) in which the same order of selectivity was determined using polyphosphazene membranes. On the contrary, with glassy membranes such as polyimides, the order of the selectivity of biogas components is $CO_2 > H_2S > CH_4$ (Stern, 1994).

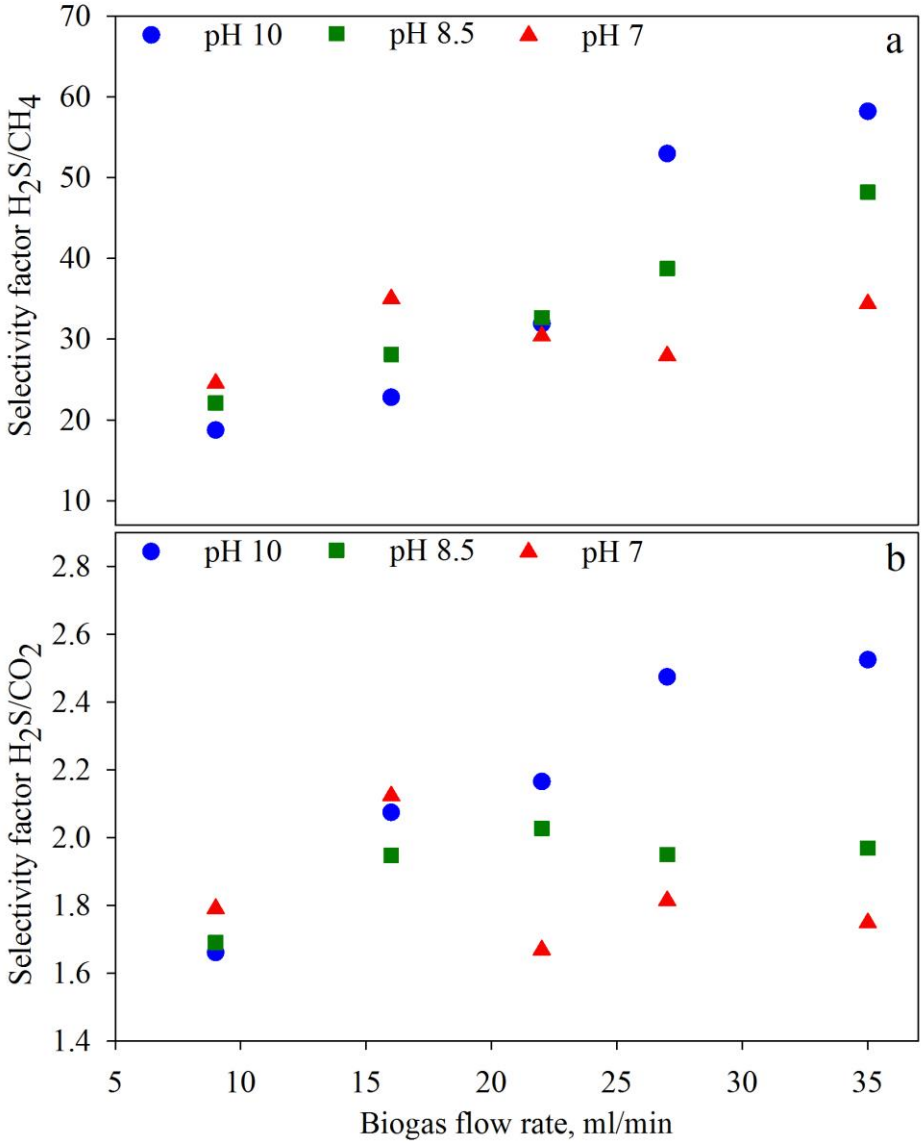


Figure 4.2 The Effect of pH and flow rate on, (a) selectivity of H_2S/CH_4 and (b) selectivity of H_2S/CO_2

4.1.3. The effect of temperature on CO_2 and H_2S removal efficiencies

The other parameter tested in this thesis was the effect of absorbing liquid temperature on CO_2 and H_2S removal efficiencies (Figure 4.3). The experiments were performed at pH10 with fixed biogas flowrate (9ml/min). Increasing the absorption liquid temperature from 10 to 45^oC, resulted in a gradual decline in H_2S absorption efficiency from 97.9±0.7 to 91.5±0.1%. Correspondingly, the effluent H_2S concentration significantly increased from 212 to 851 ppm. The mass transfer coefficient also shows

decreasing trend with increasing liquid temperature from 10 to 45 °C (Figure 4.3). Therefore, operation at lower temperature was more favorable for H_2S absorption. In another study (Mandal et al., 2004) similar observations were reported as at elevated temperature the rate of absorption was lower due to lower H_2S partial pressures. Its effect on CO_2 removal was negligible with average CO_2 removal of about 58 ± 0.4%. Similar trend was found by Xiao et al. (2014). As a general information, it is known that the absorption of H_2S and CO_2 are temperature dependent and decrease with increasing temperature (Dodds et al., 1956). When we increased the absorption liquid temperature, the H_2S/CO_2 selectivity factor decreased slightly from 1.7 to 1.6. The absorption of H_2S was more sensitive to increasing temperature than CO_2. Stern and Bhide (1989) found that, using silicone polymers H_2S was more permeable than CO_2 by approximately a factor of 1.8. However, the H_2S/CH_4 selectivity factor increased from 17 to 22 proportional with the increased temperature. The CH_4 loss declined from 5.5±0.2% to 4.04±0.02% as temperature increased. Likewise, the trend of CH_4 enrichment decreased from 80 to 77.5%. It confirms the findings of Atchariyawut et al. (2007). They reported that the solubility of CH_4 decreases with increasing liquid temperature. Consequently, working at low temperatures will be in favor of H_2S removal.

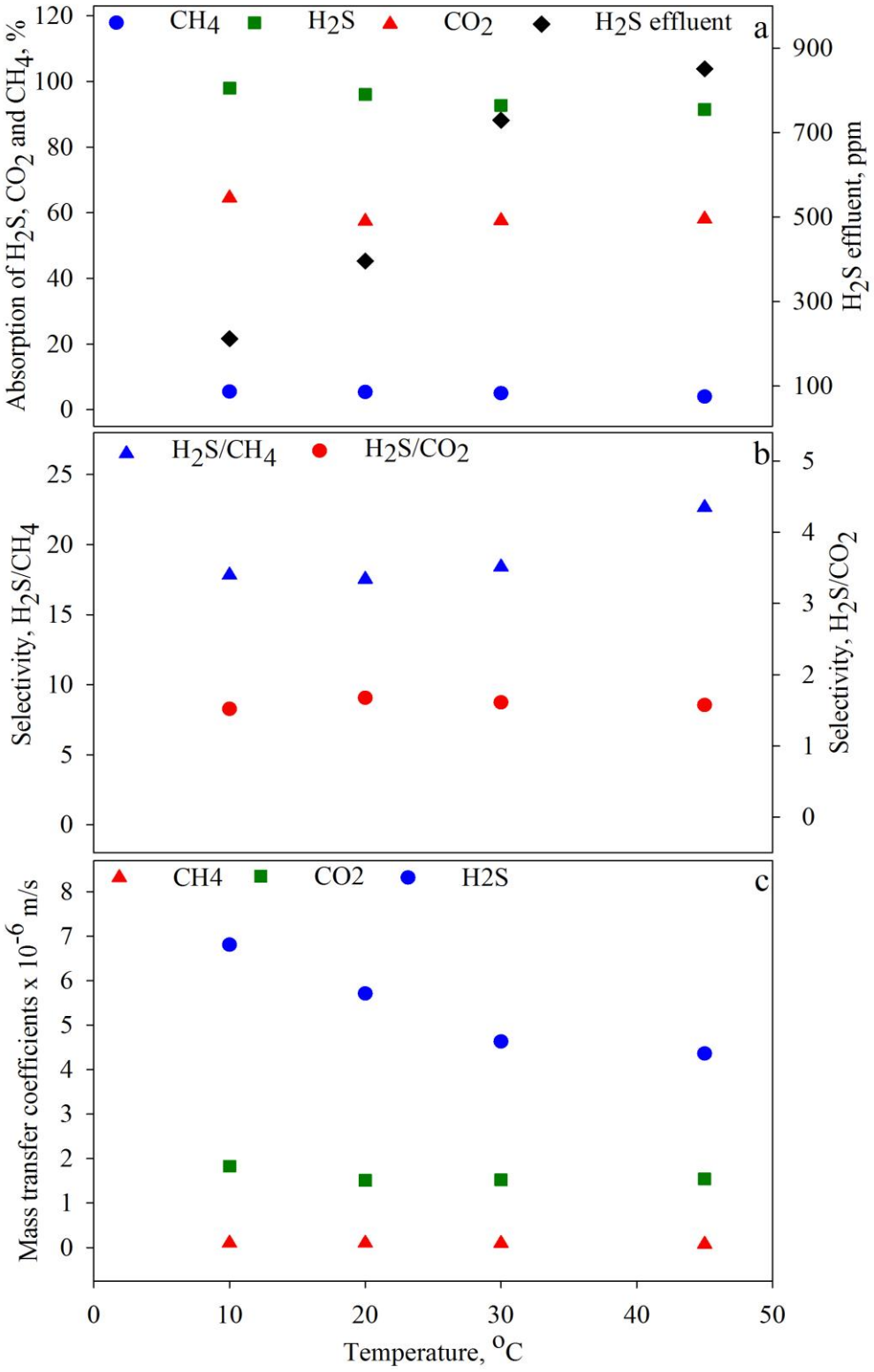


Figure 4.3 The effect of temperature on (a) H_2S, CO_2 and CH_4 absorption efficiency and H_2S effluent, (b) selectivity of H_2S/CH_4 and H_2S/CO_2, (c) mass transfer coefficients

4.1.4. The effect of pH on flux

Figure 4.4 illustrates the variation of H_2S, CO_2 and CH_4 absorption fluxes as a function of pH and biogas flowrates. The results showed that for pH10 and 8.5, the H_2S flux was 2.17±0.05 and 2.06±0.01 g/m^2.d at biogas flowrate of 9 ml/min. When the gas flowrate increased to 35 ml/min, H_2S flux increased to 3.4±0.05 and 2.5±0.1 g/m^2.d respectively. Although, the H_2S removal efficiency reduced considerably, the amount of H_2S absorbed and flux increased at higher feed biogas flowrates. It seems that increasing the biogas flowrate enhanced the mass transfer in the gas phase and through the membrane. On other hand, the absorption fluxes at pH 7 was lower compared to experiments performed at pH 8.5 and 10. The fluxes declined from 2.08±0.02 to 1.76±0.04 g/m^2.d, because at pH 7, the absorbent saturated rapidly due to the limited OH^- and the possibility of back diffusion of acid gases. At pH 7, nearly 50% of the dissolved H_2S exists in the original form, while the remaining half dissociates to HS^- ion, and around 20% of CO_2 exists in gaseous form (Esquiroz-Molina et al., 2013). In another study (Esquiroz-Molina et al., 2013), maximum flux of 32 g/m^2.d at pH 13 and lowest H_2S flux of 1.8 g/m^2.d were recorded at pH 7 with hydrophobic polypropylene hollow fiber membranes at different gas/liquid ratio. In another study (Mulder, 2012) the same trend was reported with varying monoethanolamine (MEA) concentrations on gas absorption efficiencies. Our results revealed that the H_2S fluxes at pH 10 and 8.5 were about 2 and 1.5 times higher than fluxes at pH 7, respectively. It indicates that higher NaOH concentrations enhanced H_2S mass transfer.

Referring to Figure 4.4, the flux values of CO_2 were consistently higher than H_2S due to its high inlet concentration (39% CO_2), i.e. higher driving force for the mass transfer. When gas flowrate increased, CO_2 absorption flux display a minor increase for pH 10 and 8.5, however CO_2 fluxes declined from 58.4±1.3 to 50±0.6 g/m^2.d at pH 7. It is in accordance with the results reported by Wang et al. (2005). Marzouk et al. (2012) also reported that at lower pH values the flux of H_2S and CO_2 decrease, when flowrate of the gas increased due to the reduction of its solubility. Yan et al. (2007) investigated the impact of gas flowrate on CO_2 flux using potassium glycinate and monoethanolamine as absorbents, and they described that increasing the gas velocity improves the CO_2 flux. Figure 4.4 also reveals that the CH_4 fluxes at all pH values declined approximately from

3 g/m^2.d to 1 g/m^2.d as the biogas flowrate increased.

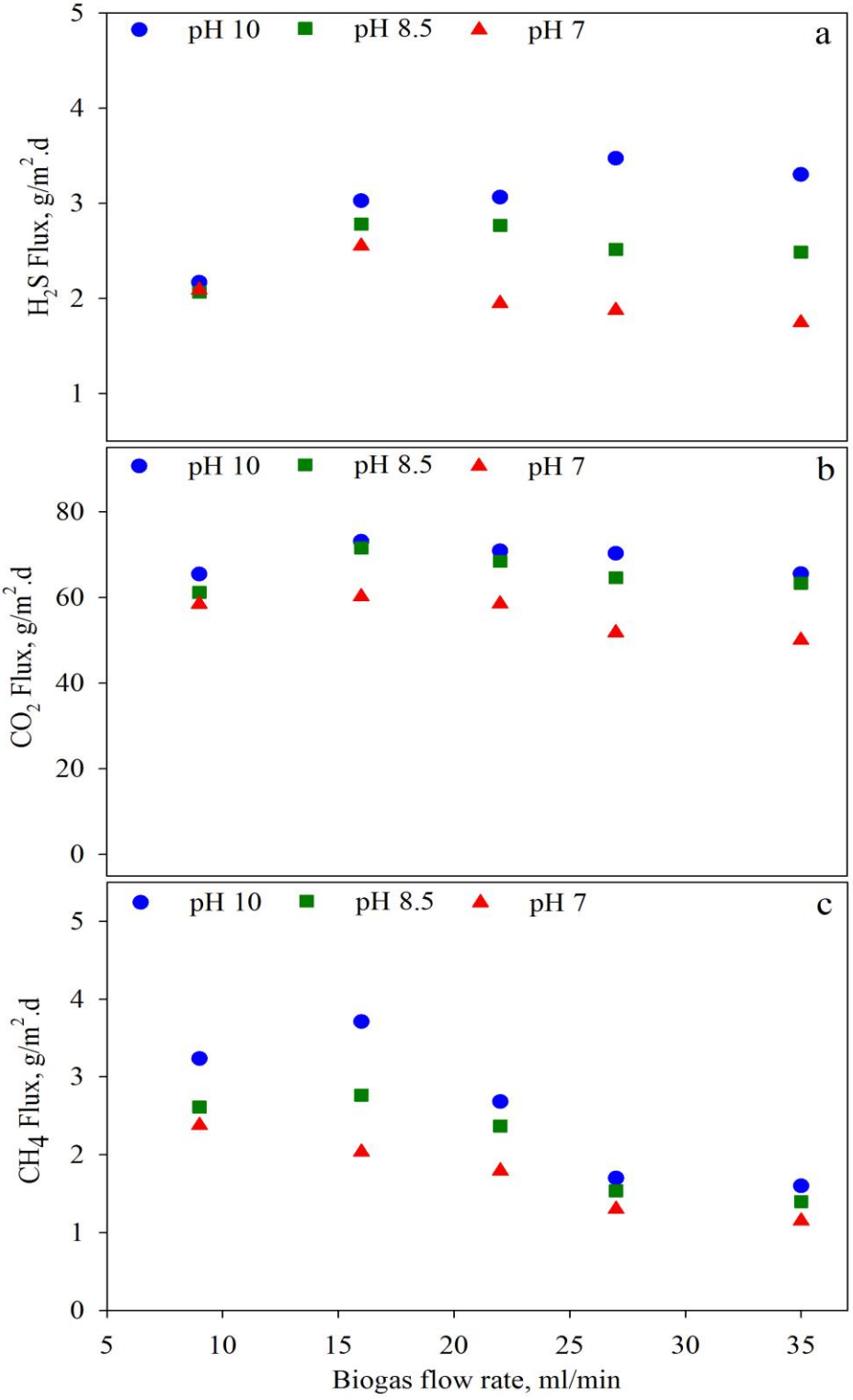


Figure 4.4 The effect of pH on flux of (a) H_2S, (b) CO_2 and (c) CH_4

4.1.5. The effect of pH on mass transfer coefficients

The effect of absorbing solution pH on mass transfer coefficients of each biogas components was shown in Table 4.1. It is clearly shown that the mass transfer coefficients generally increased as the absorbent pH elevated. When the absorbent pH increased from 7 to 10, the mass transfer coefficients increased on average by 226% for H_2S, 40% for CO_2 and 40% CH_4, at 35 ml/min of biogas flowrate. The overall mass transfer coefficient values of up to 6.91×10^{-6} m/s recorded for pH 10 (0.18M) much lower compared to earlier porous hollow fiber polypropylene membrane contactor, which was 2.5×10^{-3} m/s, as expected (Jefferson et al., 2005). Smet et al. (1998) also observed a sharp increase in hydrosulfide ion concentration when the pH was higher than 7.04. Similarly, González-Sánchez et al. (2008) reported that a slightly alkaline pH could improve the H_2S mass transfer from the gas phase to the liquid phase. Increasing the biogas flowrate from 9 to 35 ml/min resulted in decreased mass transfer coefficients. Similar trends were observed by Wang et al. (2002) using porous PVDF hollow fiber membrane. In other study, Hedayat et al. (2011) used a PVDF hollow fiber membrane contactor and found that increasing H_2S concentrations affected the performance of the system detrimentally and reduced the mass transfer coefficients. On the contrary, in another study increasing gas velocity has improved the mass transfer coefficient of H_2S from 2.38 to 3.43×10^{-6} m/s (Hedayat et al., 2011).

Table 4.1 Mass transfer coefficients of biogas components at different pH and flowrate

Flow rate (ml/min)	pH	Overall mass transfer coefficients (m/s) × 10^{-6}		
		H_2S	CO_2	CH_4
9	7	4.99	1.32	0.069
	8.5	5.86	1.49	0.079
	10	6.91	1.58	0.095
16	7	3.44	1.18	0.060
	8.5	3.99	1.45	0.082
	10	4.60	1.45	0.108
21	7	1.92	1.05	0.051
	8.5	3.14	1.27	0.069
	10	4.99	1.64	0.094
27	7	1.74	0.88	0.037
	8.5	2.60	1.17	0.045
	10	4.00	1.28	0.051
35	7	1.59	0.86	0.035
	8.5	2.59	1.19	0.041
	10	3.60	1.21	0.048

4.1.6. The effect of GRT and membrane thickness on desulfurization performance

The gas retention time (GRT) is one of the important parameters determining the biogas desulfurization efficiency. The effect of GRT on the removal efficiency (RE) of each gas component was displayed in Table 4.2. The pH of the liquid absorbent was constant (pH 10) in the experiments. The result shows that, the decrease in GRT reduces the membrane surface contact per unit volume of gas, which in turn reduces RE. The H_2S RE of the process was superior, especially when the GRT laid in the range of 19 – 10.4 min. The H_2S was completely removed at that GRT ranges. Moreover, at GRT of over 10 min, an effluent H_2S concentration below 300 ppmv was achieved, which is safe to use in cogeneration units (Ramos and Fdz-Polanco, 2014). However, lower GRT resulted in higher effluent H_2S concentrations which needs further treatment before using the gas for various applications. In the same way, CO_2 removal declined significantly with the decreased GRT. At all GRT tested, the RE of H_2S was much

higher than that of CO_2. Because H_2S has relatively high critical temperature or gas condensability and expected to permeate faster through the dense membrane than CO_2. Baker (Baker, 2004) stated that the permeation of gas components through rubbery polymers depends primarily on gas condensability. Over all, the RE of H_2S and CO_2 improved by more than 2.5 and 5.2 times, when the GRT was raised from 3.4 to 19 min, respectively (Table 4.2). This finding is in agreement with the results presented by (Wang et al., 2005). They reported that gas removal capacity decreased as the GRT declined owing to the shorter contact among the gas and liquid phases. Nevertheless, CH_4, having a low diffusivity through the PDMS membrane and low solubility in the liquid absorbent, could not permeate across the membrane. Figure 4.5 also illustrated that CH_4 content in the effluent stream increased along with the GRT and enriched from 60% to a maximum of 87% with only 4.68% loss. Heile et al. (2014) performed a similar study for upgrading of a biogas containing 20% of CO_2 and 80% of CH_4 using a PDMS membrane and they improved the CH_4 content up to 88% in the outlet.

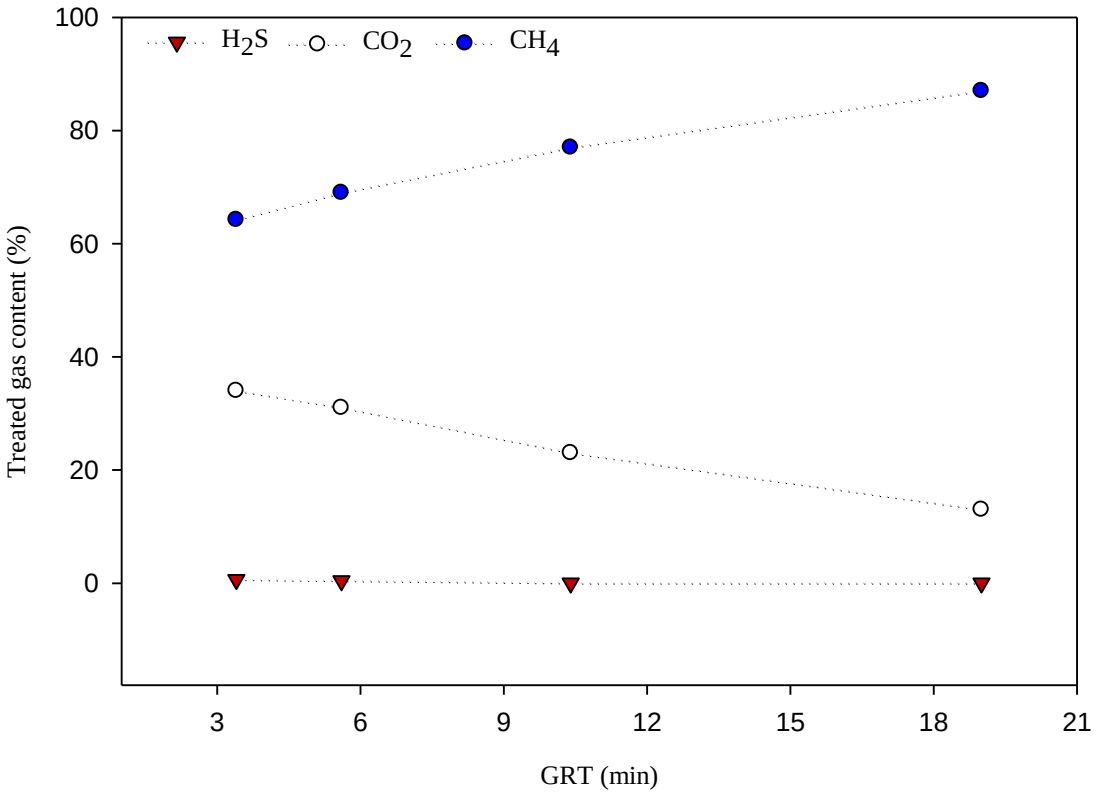


Figure 4.5 Impacts of GRT on the effluent gas contents at pH 10

In addition, experiments with varying membrane thicknesses of 1 mm, 1.5 mm and 2

mm were also performed. According to the results shown in Table 4.2, thicker membrane reduces the H_2S and CO_2 transfer rates across the membrane due to longer diffusion time. The negative impact of higher membrane (silicone) thickness on mass transfer of other permeates also described by (Raghunath and Hwang, 1992). They reported a significant mass transfer resistance when the thickness of a membrane was above 1.16 mm. In a similar manner, Brookes and Livingston (1995) used silicone based membranes and they reported a reduction in mass transfer coefficient of phenol by a factor of 1.5 when the thickness was increased from 0.3 mm to 0.5 mm. Therefore, with thinner membranes, higher loading rates could be attained. As a general trend, when the membrane thickness increases, the CO_2 removal efficiency decreases more significantly than that of H_2S even at high GRT. The reduction was much more pronounced for lower GRT. Nii et al. (1992) also used PDMS hollow fiber modules for the removal of CO_2 and achieved a higher performance with thinner membranes. It can be concluded that thicker membrane had introduced a considerable resistance to the gas diffusion, which decreased the absorption flux inevitably.

Table 4.2 The membrane contactor performance at different GRT and membrane thicknesses at liquid pH of 10

Thickness	GRT	Removal efficiency (RE) (%)			Selectivity	
(mm)	(min)	H_2S	CO_2	CH_4	H_2S/CH_4	H_2S/CO_2
1	19	100	79.3	4.68	21.4	1.26
	10.4	98.3	56.4	3.44	28.6	1.74
	5.6	63.6	34.9	1.84	34.6	1.82
	3.4	40.0	15.3	0.69	59	2.6
1.5	19	99.9	68.7	4.12	24.2	1.45
	10.4	97.8	43.0	2.86	34.2	2.27
	5.6	60.6	22.8	1.56	38.8	2.66
	3.4	38.2	12.1	0.63	60.6	3.06
2	19	99.7	60.5	3.58	27.8	1.65
	10.4	97.0	35.8	2.4	40.2	2.72
	5.6	56.9	18.0	1.23	46.3	3.16
	3.4	36.2	8.92	0.58	62.4	4.06

In the gas–liquid membrane contacting process used here H_2S of raw biogas diffused across the membrane and was absorbed in mildly alkaline absorbent. For that reason, permeate selectivity was used to describe the process performance. In order to examine the effect of different membrane thicknesses and GRT on the selectivity of membrane contactor, the overall mass transfer ratio of H_2S to CO_2 and CH_4 were calculated. During each experimental tests, pH of the liquid was adjusted to 10. As presented in Table 4.2, a higher selectivity of H_2S was observed at lower GRT. A change in membrane thickness from 1 mm to 2 mm had a positive influence on the selectivity due to the higher permeability of H_2S in thicker membrane compared to those of other gases. However, in that case a lower RE was observed as a result of additional resistance of the membrane. Consequently, for a gas liquid membrane contactor process used here, these two parameters can significantly influence the H_2S selectivity and RE. Specific to the experimental results of this work, the maximum separation factor for H_2S/CO_2 and H_2S/CH_4 were reached up to 4 and 62, respectively, in the case of using thicker membrane (2 mm). Stern and Bhide (1989) pointed out that H_2S is more permeable than CO_2 through PDMS by approximately a factor of 1.8. Chatterjee et al. (1997) also used cellulose acetate membrane to clean the biogas having 6% of H_2S, 29% of CO_2 and 65% of CH_4 at 10 bar, and they reported the H_2S/CH_4 separation factor as only 19. In another work on separation of gases using Poly (ether urethane) membrane, separation factor of H_2S/CO_2 and H_2S/CH_4 were reported as 3 and 21, respectively (Chatterjee et al., 1997).

4.1.7. The effect of absorbent pH and GRT on conductivity and ORP

As illustrated in Figure. 4.6, the conductivity of a solution depends on the concentration of all the ions existing, the higher the ions concentrations, the higher the conductivity. During operation of the system used here, the major cations are H^+, Na^+, Ca^{2+}, and Mg^{2+}. The major anions are, OH^-, HS^-, S^{2-}, HCO_3^- and CO_3^{2-}. Hence, acidic or basic solution resulted with high conductivity. Moreover, the conductivity is the sum of the contribution of all ions existing in the solution. For soft water samples, a pH of 7 will have the least conductivity. On other hand, samples with a pH above 7 are likely to be higher conductivity. Figure 4.6 also confirmed that when the pH of the liquid absorbent increased from 7 to 10, proportionally the conductivity raised up. This happened due to

higher dissociation of H_2S and CO_2 into sulfide and carbonate. Moreover, to kept constant pH sodium hydroxide has been supplied to the liquid phase. The turbulence in the liquid increases the diffusion of the molecules into the liquid phase due to reduction of boundary layer resistance between membrane and liquid interface. Our results were consistent with literature (Leveling, 2002).

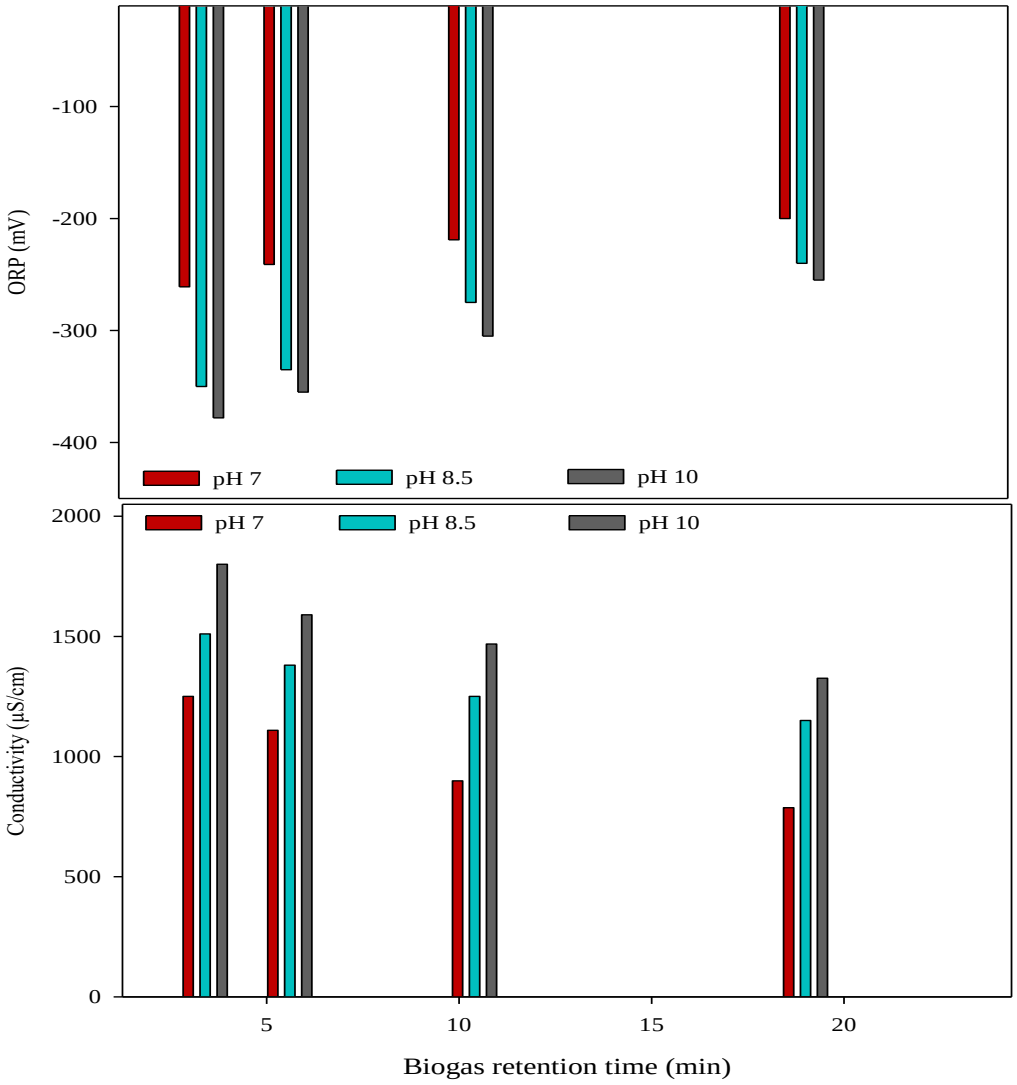


Figure 4.6 ORP and Conductivity observation at different pH and GRT

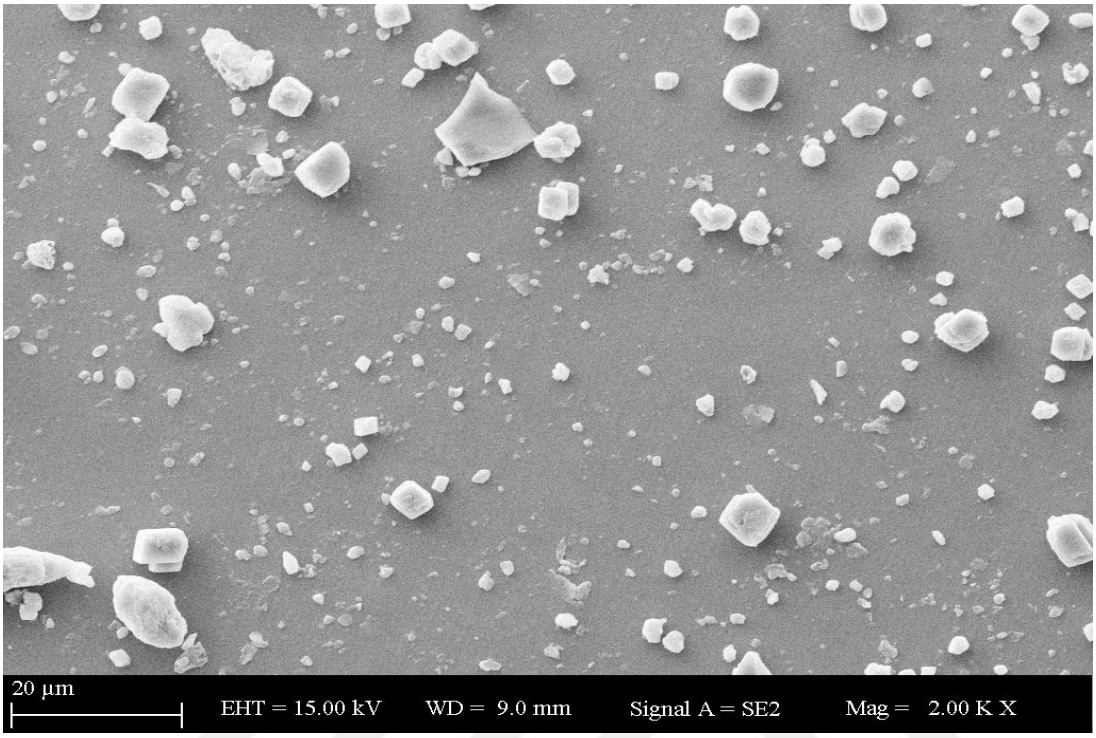
Figure 4.6 demonstrated that ORP decreased as the pH of the liquid absorbent increased, which was due to higher accumulation of sulfide. However, the pH of the liquid in this study was not increased above 10, to avoid much carbonate formation (CO_2 absorption) and CH_4 loss. ORP values was around –200 mV at low sulfide accumulation, whereas at higher loadings significant sulfide accumulation caused ORP

to drop below -380 mV. Besides, at pH 10, in particular with a GRT of 3.4 min, the ORP value decreased sharply as an indication of sulfide accumulation. This behavior proves a correlation between the ORP and H_2S absorption capacity of slightly alkaline liquid absorbent.

4.1.8. Membrane morphology and inorganics deposition

The surface morphology of PDMS membrane was examined using a scanning electron microscope (SEM). SEM images of virgin membrane and the used membrane are displayed in Figure 4.7 (a) and (b), respectively. The SEM images confirms there is no visible variation between the surface morphologies of the two membranes samples. However, when the surface of the membrane was magnified, the layer of deposits on the membrane surface could be clearly realized. As shown in Figure 4.7b, it is observed that after each experimental work a white crystal substances appeared on the surface of used membrane, which should be inorganic matters as confirmed by EDS analysis, whereas the virgin membrane surface viewed clean and smooth (Figure 4.7a). The SEM images also attributed to the fact that the pattern of inorganic matters is an unevenly distributed over the membrane surface. Despite minor deposition of inorganics on the membrane surface, the structure was not suffered after being exposed to sodium hydroxide aqueous solutions. In addition, the membrane used here was less sensitive to wetting since there is no pores that supports the liquid to penetrate through the membrane. Thus, membrane wetting was not observed in our PDMS membrane. However, other researchers attributed performance deterioration of the microporous membrane contactors due to wetting and blockage of the membrane pores. They reported significant drop in mass transfer capacity of the contactors owing to the developed membrane resistance (Atchariyawut et al., 2007; Attaway et al., 2002). Keshavarz et al. (2008) used a microporous hollow fiber membrane to investigate the simultaneous absorption of CO_2 and H_2S into the aqueous solution of diethanolamine and they found that the RE of both gases significantly decreased due to membrane wetting compared with the non-wetted mode. Wang et al. (2005) also studied on CO_2 absorption using a polypropylene microporous membrane contactor supported with diethanolamine absorbent solution. They reported that with only 5% membrane pores wetting the overall mass transfer coefficient of the contactor may reduce by 20%.

a



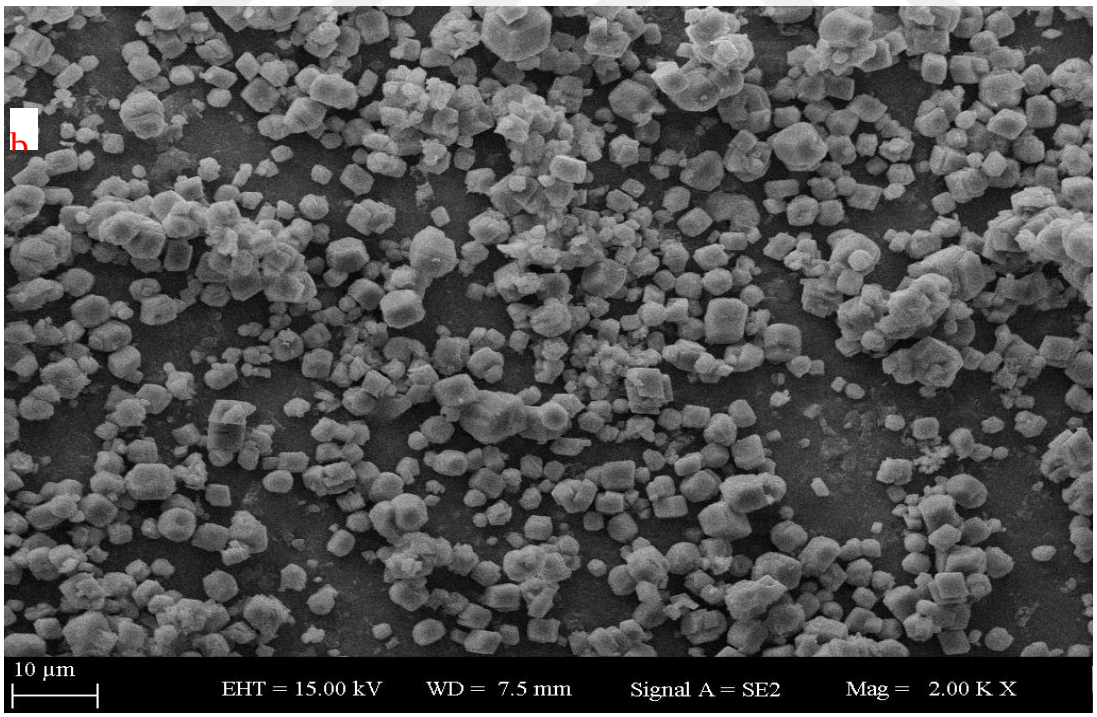


Figure 4.7 SEM image of the membrane surface (a) before (virgin) and (b) after the experiments (used)

b

With the use of scanning electron microscopy (SEM) associated with an energy

dispersive X-ray spectrometer (EDS) often focus on the top surface deposits as indicated in Figure 4.8 (a) and (b), and it is possible to detect the existence of metal sulfide and carbonate salts deposition. The semi-quantitative EDS composition analysis indicated certain amounts of inorganic elements were accumulated on the membrane surface. The presence of multivalent metal ions in the tap water, which used in the system as an absorbent liquid, was the origin of inorganics deposition. Thus, in the presence of ions such as Ca^{2+} and Mg^{2+} acting as cationic effects, there would be a strong interaction with anionic sulfide, and carbonate, which were generated during the dissociation of H_2S and CO_2, to form precipitates. Furthermore, Figure 4.6 also approves that when the pH of the liquid phase increased the conductivity of the liquid absorbent increased proportionally. The reason for this observation was the greater accumulation of sulfide and carbonate in the reactor as the pH of the liquid raised up (when the pH increased to 10). According to report of numerous researcher pH is considered as one of the dominating factor controlling calcium-carbonate binding strength during calcium carbonate precipitation conditions (Gebauer et al., 2008; Sheng Han et al., 2006). In other work by Hu et al. (2015) indicated the effect of solution pH on the equilibrium concentration of various carbon species such as bicarbonate and carbonate (Eqs.26 and 27). They adjusted the solution pH at 13.4 and 9 by adding NaOH, at pH 13.4 they observed almost all dissolved inorganic carbon existing in the form of carbonate, while at pH 9 only 10% of dissolved inorganic carbon is present as carbonate. Our result was also consistent with literatures, which indicated calcium precipitation at higher pH value. The average calcium concentration of tap water used in Istanbul is 45 mg/L and , it is possible to precipitate Ca in the tap water at pH above 9 (Hlavinek et al., 2009; Hu et al., 2015).

It can be observed that carbon (C) and oxygen (O) were the major elements present in the spot samples. The C and O peaks were likely due to the chemical structure of the membrane and entrapment of inorganic matters. As discussed above, the multivalent ions have been shown to form precipitates with sulfide and carbonates could contribute to the calcium (Ca), magnesium (Mg) peaks and their weight percent were about 36.1% and 0.5%, respectively. The sulfur (S) peaks possibly indicating that S containing compounds were able to penetrate through the membrane with some retained on the membrane surface. Silicon (Si) detected on the used membrane surface was mainly due

to its presence in the polydimethylsiloxane membrane layer. The EDS spectra of the virgin membrane has also strong Si and O peaks which originated from the membrane itself (data not shown). Gold (Au) and palladium (Pd) were used during coating procedures, due to its irrelevant to the elemental analysis of the membrane foulants their peaks were removed. In the present study regardless of inorganics deposition discussed above, the abiotic experiments show selective removal H_2S than CO_2 and CH_4. Besides, in this gas–liquid membrane contactor applications, membrane fouling and clogging were not observed, which resulted in almost stable flux during the operation of the membrane.

Previous studies also demonstrated nonporous membrane was more resistant to fouling (Côté et al., 1989). However, in the long run operation, an excess deposition may have reduced the mass transfer efficiency of the PDMS membrane. It was assumed that accumulation of inorganics on the membrane surface may decreased the cross sectional area, subsequently reduced the gas retention time and increased the pressure drop of the gas permeation. Moreover, it may create an additional film resistance for the gas to reach the liquid phase, which likely resulted in limitation of H_2S transfer. Chuichulcherm et al. (2001) used silicone membrane combined with biological sulfide production for the treatment of metal-containing wastewater. They reported that chemical reaction between sulfide and multivalent ions in the wastewater enhanced the sulfide mass transfer. However, accumulation of metal precipitates on the membrane surface limited sulfide transfer and the resistance due to the metal sulfide precipitates even exceeded the membrane resistance. Other studies also demonstrated the mass transfer reduction of membrane based reactors owing to the blockage of the membrane pores by the organic and inorganics accumulation (Alvarez-Hornos et al., 2011; Attaway et al., 2002; Yurtsever et al., 2016).

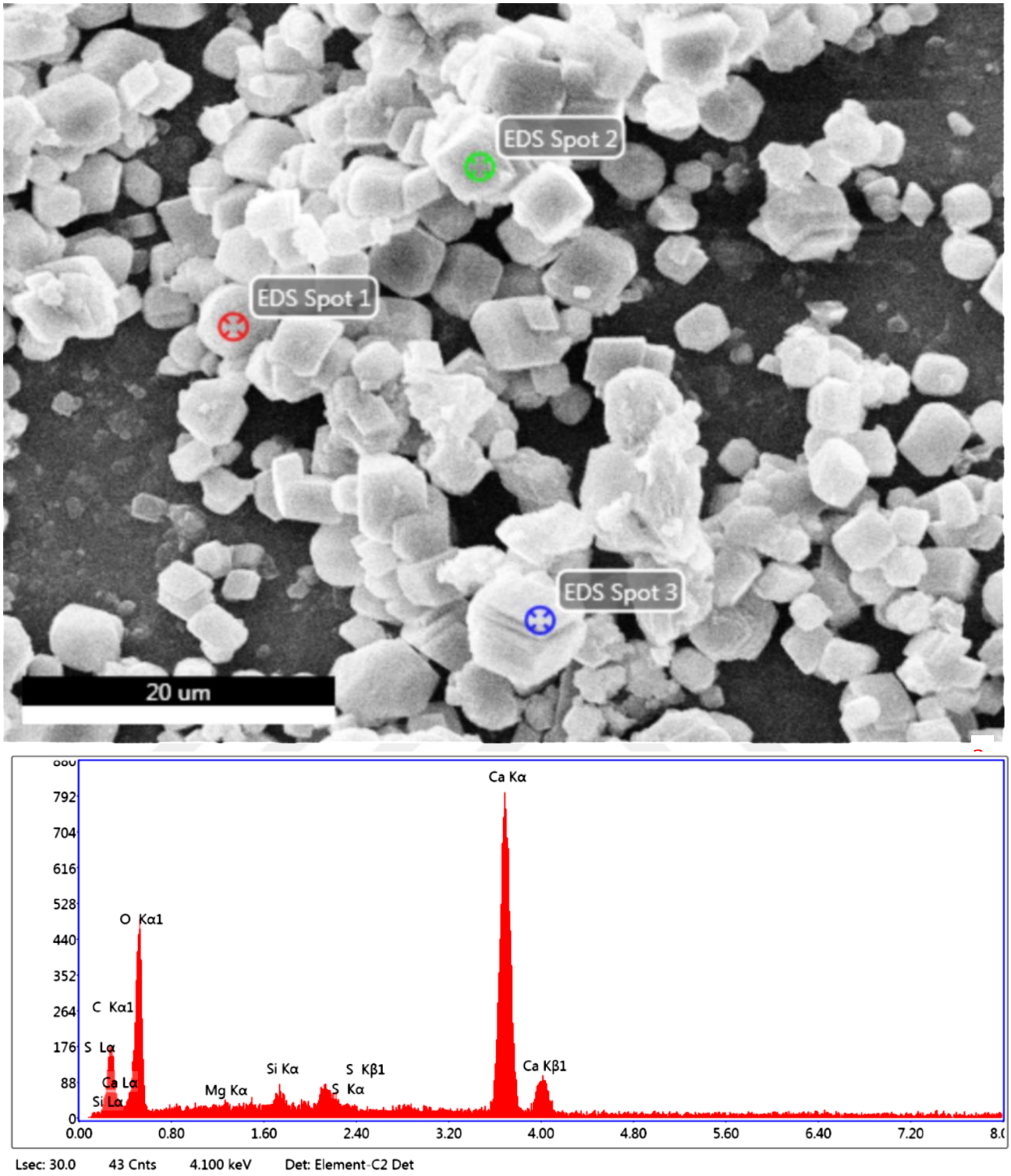


Figure 4.8 SEM-EDS image of the membrane surface after the experiment at pH 10 and 3.4 min GRT.

4.2. Biotic Gas-Liquid Membrane Contactor for H_2S Removal from Biogas

4.2.1. Desulfurization performance of MBS process

The impact of different operational parameters on the performance of MBS system was

b

investigated with long-term experiments. The desulfurization of biogas in the hybrid MBS occurred in two steps. Firstly, the H_2S diffused across the membrane and dissolved in the mildly alkaline absorption liquid. Secondly the dissolved sulfide was oxidized by SOB either on the membrane surface or in suspension. The DO concentration kept constant (about 4 mg/l) in the first operational period (Table 3.3). As a general trend the gas phase H_2S removal efficiency (RE) was enhanced when the gas flowrate decreased due to longer contact time between the gas and membrane (Table 4.3). Besides, altering the pH of the absorption liquid affect H_2S removal efficiency. Particularly at pH 7 with a gas flowrate of 8 l/d, a gas phase H_2S removal efficiency (RE) reached above 99.5±0.3%. This efficiency was higher compared to the results we achieved formerly at pH 7 (94%) using an abiotic membrane scrubber (AMS) see section 4.1. Moreover, when the gas flowrate was raised four fold (32 l/d), the biotic MBS removed H_2S more effectively than AMS by about 44%. In the former study, the maximum gas phase H_2S removal, at pH 7 with gas flowrate of 32 l/d, was only 36%. It is understood that in the abiotic process the diffused H_2S accumulated in the liquid phase, but not oxidized, therefore the liquid becomes saturated. However, in the biotic MBS the diffused H_2S immediately oxidized by SOB and kept greater H_2S driving force among the gas and liquid (biofilm) phase. Marzouk et al. (2010) studied on removal of H_2S using hollow fiber membrane contactor and they reported a drop in removal efficiency from 100 to 74%, when the gas flowrate increased from 0.576 to 1.44 m^3/d. As shown in Table 4.3, at about 15 l/d of gas flowrate, the effluent biogas contained less than 300 ppmv of H_2S gas. The achievement of such relatively low level of H_2S in the outlet proves adequacy and applicability of hybrid MBS process. In this way, a biogas desulfurized with the hybrid MBS can be directly used in a co-generation unit without any hesitation (Díaz et al., 2011b; Ramos and Fdz-Polanco, 2014). On other hand, increasing the gas flowrate by four times resulted in an increase in H_2S and CO_2 flux from 1.29±0.01 to 3.99 ±0.012 g/m^2.d and from 43±1 to 58±1 g/m^2.d, respectively (Table 4.3). This result revealed that high H_2S removal capacity was attained while CO_2 removal was kept low, because H_2S could easily diffused through the membrane and became available for SOB. With AMS we formerly (Tilahun et al., 2017) observed a maximum H_2S and CO_2 flux capacity of 1.9 g/m^2.d and 58 g/m^2.d. Hence, in the present study H_2S flux was significantly higher than that obtained in our earlier report. In

summary, the preliminary results indicated that the biotic MBS was more effective than abiotic membrane scrubber (AMS) for desulfurization of biogas and has a great potential for real scale applications.

In conventional biodesulfurization processes, especially the nitrogen in air which introduced into the reactor dilutes the biogas (Jenicek et al., 2008; P Jenicek et al., 2010; Krayzelova et al., 2015). However, in this study, the biogas stream was separated from aerated liquid by a membrane. As a result, dilution problem was not observed here, instead the CH_4 content in the outlet stream increased from 60% to 81±1% and from 60 to 67±0.5%, when the gas flowrate was 8 and 32 l/d, respectively. The CH_4 content of the biogas increased mainly due to the reduction in CO_2 concentration, because CO_2 has significantly higher permeability across the membrane and higher solubility in water compared to CH_4. The loss of CH_4 in this particular study was minimal (less than 3.4%) due to its lower transfer ability across the PDMS membrane (Table 4.3). In general, the results obtained here was able to conserve the energy content of the biogas. Charnnok et al. (2013) studied on biogas desulfurization using a biofilter process, and they stated rise in the CH_4 content of biogas from 80 to 83%. In the contrary, Chaiprapat et al. (2011) reported a decline of about 20% in total CH_4 content, due to the dilution of biogas with air. Thereby, the process used here could achieve a high biogas desulfurization performance with a considerable CH_4 enrichment at the outlet stream of the membrane contactor without any dilution problem. According to the result presented in Table 4.3, the greater the gas flowrate, the greater the selectivity of H_2S/CO_2 and H_2S/CH_4. This phenomenon could be explained by the differences between H_2S and other gas permeability and solubility in the membrane and mildly alkali absorption liquid, respectively (Baker, 2004; Kennedy et al., 2015; Tilahun et al., 2017). In addition, the biological oxidation of sulfide increases the driving force and allows gaseous H_2S to dissolve more in the aqueous phase. Thus desulfurization selectivity could be retained at high level compared to CO_2 and CH_4. In this study the highest H_2S/CO_2 and H_2S/CH_4 selectivity values were 3.5 and 63 at the highest gas flowrate (32 l/d) and pH 7, which was 2 times higher than those reported in our previous study where the H_2S was chemically absorbed by an alkaline solution after being diffused through the PDMS membrane (see section 4.1). Similar conclusions were also drawn by the others indicating that rising the gas flowrate improved the selective removal of H_2S gas

(Bontozoglou and Karabelas, 1993; Lu et al., 2006).

Table 4.3 The effects of different operational parameters on the performance efficiency of the biotic gas-liquid membrane contactor (DO concentration in the absorption liquid was 4 mg/l)

pH	Gas flowrate	Gas phase removal (RE) (%)			Selectivity		Gas flux ($g/m^2.d$)		
	(l/d)	H_2S	CO_2	CH_4	H_2S/CH_4	H_2S/CO_2	H_2S	CO_2	CH_4
7.0	8	99.5	67.2	2.80	36.0	1.48	1.29	43.6	1.00
	15	96.8	44.4	2.00	47.6	2.18	2.28	52.4	1.34
	23	84.6	33.2	1.53	55.3	2.55	3.02	59.4	1.53
	32	80.4	23.4	1.30	62.9	3.44	4.00	58.1	1.77
7.75	8	99.2	62.8	3.10	32.1	1.58	1.27	40.3	1.11
	15	96.2	42.6	2.40	40.5	2.26	2.24	49.8	1.55
	23	83.3	33.7	1.80	47.2	2.47	3.03	61.3	1.79
	32	79.0	25.4	1.60	50.4	3.11	3.85	61.9	2.13
8.5	8	99.8	65.9	3.38	29.5	1.51	1.30	42.9	1.23
	15	96.1	40.9	2.67	36.0	2.35	2.25	47.9	1.74
	23	82.5	35.9	2.13	38.8	2.29	2.97	64.9	2.14
	32	79.9	27.6	1.69	47.4	2.89	3.92	67.8	2.31

On the other hand, the selectivity was inversely proportional to gas phase H_2S removal efficiency. Therefore, the gas flowrate and pH should be optimized to achieve a selective biogas desulfurization and to maintain a high gas phase H_2S removal efficiency with minimal caustic consumption.

4.2.2. The effect of pH and Volumetric H_2S loading on sulfide oxidation

In this study, the first 23 days of operation were considered as adaptation period of the SOB. The rest of the period 1 was divided into three stages, i.e. stages I (pH 7), II (pH 7.75), III (pH 8.5), to assess the impact of operational pH on total system performance (Figure 4.9). During each of these stages the reactor was subjected to a range of loading conditions, A (79 g $H_2S/m^3.d$), B (148 g $H_2S/m^3.d$), C (227 g $H_2S/m^3.d$), D (316 g $H_2S/m^3.d$). The vertical dotted lines in Figure 4.9 indicate the days at which the H_2S loading rate increased. At this period the DO concentration inside the reactor was

maintained at about 4 mg/l by controlling the airflow rate.

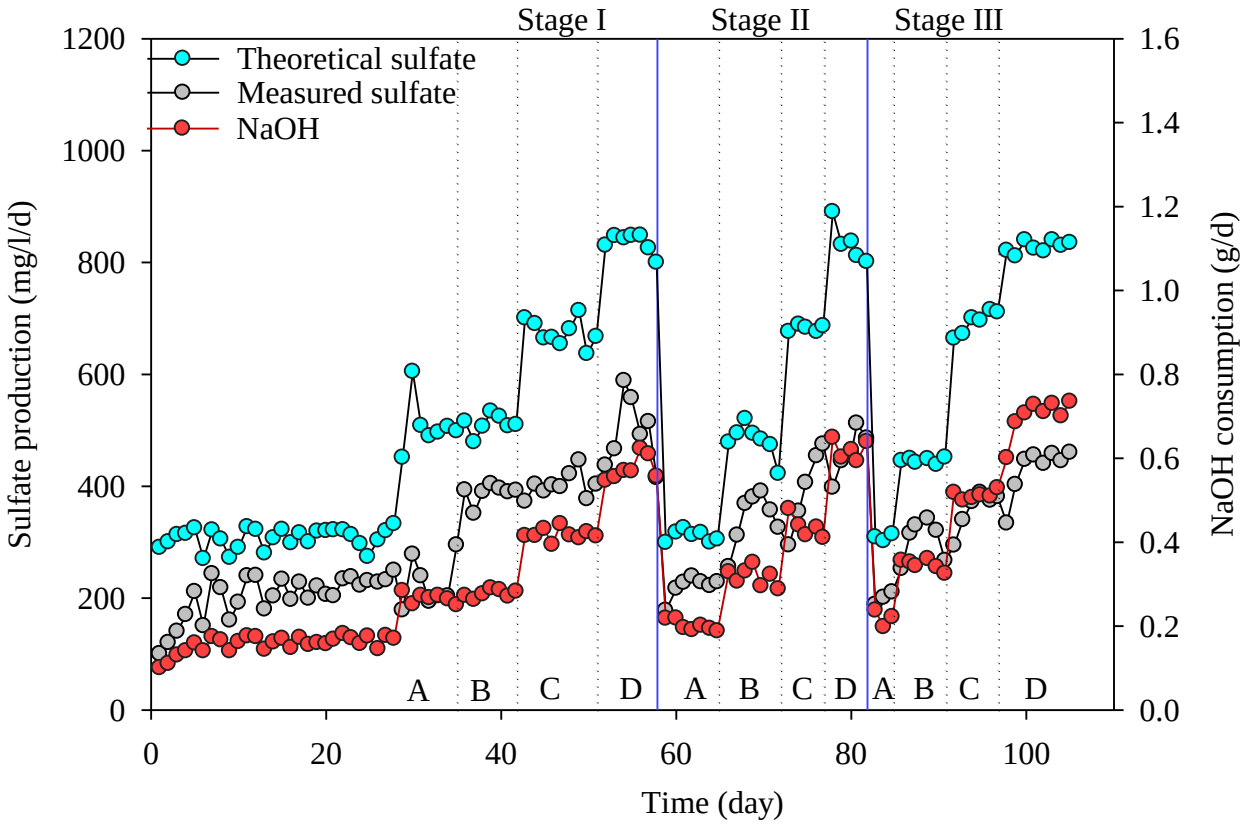


Figure 4.9 Sulfate production and NaOH consumption at different absorption liquid pH and volumetric sulfide loading

At all tested pH values, total H_2S removal (TSR) efficiency of 97.9±0.7% was observed at volumetric loading rate (VLR) of 79 g H_2S/m^3.d (8 L/d), while the TSR decreased to 78.2±1.2% when the VLR increased to 316 g H_2S/m^3.d (32 l/d). The TSR reduction at higher volumetric loading presumably due to the limitation of the membrane mass transfer capacity. Moreover, the maximum volumetric H_2S removal rate (VSRR) of the system reached up to 251 g H_2S/m^3.d, at the highest VLR (316 g H_2S/m^3.d) (Table 4.4). Kumar et al. (2010) used PDMS/polyacrylonitrile (PAN) composite membrane biofilm reactor for the reduction of dimethyl sulfide from waste air, and they observed removal rate of 258 g/m^3.h. De Bo et al. (2003) also studied on removal of dimethyl sulfide using PDMS/Polyvinylidene Fluoride (PVDF) composite membrane bioreactor, and they attained a maximum of 120 g/m^3.h dimethyl sulfide removal rate. It is clear that, a composite membrane bioreactor integrates the best characteristics of both porous (high

mass transfer rate) and dense nonporous materials (prevent wetting and biofouling problem). The removal rate reported here was similar to those found in biofilters or biotrickling filters (Bak et al., 2017; Ma et al., 2006; Ramírez et al., 2009; Sublette et al., 1994).

Table 4.4 The effects of absorption liquid pH and volumetric loading rate on sulfide oxidation

pH	Gas flowrate (l/d)	Total H_2S removal efficiency	Volumetric H_2S removal rate	Non-oxidized HS^- in liquid effluent (mg/l)
		TSR (%)	VSRR ($g/m^3.d$)	
7.0	8	98.62	77.91	0.7
	15	95.78	141.8	1.6
	23	83.37	189.3	2.9
	32	79.54	251.4	4.8
7.75	8	97.95	77.38	1.0
	15	94.92	140.5	2.0
	23	81.44	184.9	3.7
	32	77.67	245.4	6.2
8.5	8	97.20	76.79	2.1
	15	92.84	137.4	4.9
	23	78.97	179.3	8.1
	32	77.28	244.2	11

Figure 4.9 illustrated, under low volumetric H_2S loading rate (79 g $/m^3.d$) sulfate generation capacity was 233±8 g $SO_4/m^3.d$ and it accounts 75% of the theoretical sulfate generation. The theoretical sulfate concentrations were calculated based on the assumption of complete sulfide oxidation to sulfate. It was also displayed in the route of H_2S oxidation that at limited sulfide loading the biological sulfide oxidation is in favor of reaction 23. When the VLR elevated to 316 g $H_2S/m^3.d$, the sulfate generation gradually increased up to 524±49 g $SO_4/m^3.d$, (only 54% of the theoretical sulfate generation) (Figure 4.9). The reduction in the theoretical sulfate generation efficiency was associated with the incomplete oxidation of sulfide due to the lower level of oxygen in the biofilm or inside the flocs, particularly at higher loadings, and precipitation of sulfate ions particularly at higher pH, which was also verified by XRD analyses. As

seen in Figure 4.9, at higher pH value, the alkaline consumption was greater. In addition to this, when the pH raised to 8.5, the corresponding non-oxidized sulfide concentration in the liquid elevated up to 11 mg/l. This happened due to decreased biomass activity at higher pH values. Ramírez et al. (2009) studied on the elimination of H_2S using a biotrickling filter containing *Thiobacillus thioparus* species, and they described that the biological removal efficiency decreased from 88 to 72% when the pH of the liquid increased from 7.5 to 8.5. Specific to the desulfurization system of this work, optimal treatment performance was achieved at a loading rate of approximately 148 g H_2S/m^3.d and absorption liquid pH of 7 with TSR of above 97%.

4.2.3. Fate of sulfide oxidation at different DO concentrations

In period 2, the DO concentration decreased stepwise to investigate its effects on elemental sulfide (S^o) formation, sulfide removal efficiency and caustic consumption. Three stages were established, stage I_2 (DO 4±0.5 mg/l), II_2 (DO 2±0.3 mg/l) and III_2 (DO 0.9±0.15 mg/l) (Figure 4.10). Throughout the 75 days of operation, VLR, gas flowrate, gas retention time and reactor pH were maintained at 140 g H_2S/m^3.d, 14 l/d, 11 min and 7, respectively. From day 112 to day 126, due to failure of the temperature control unit the system run at room temperature. Accordingly, the lower temperature (12-18 ^oC) adversely affected the activity of SOB. Starting from day 127, the liquid temperature again increased to 30±1 ^oC and the ionic sulfur species in the liquid were monitored to evaluate the fate of sulfur in the MBS system.

In summary, the results revealed that S^o formation was significantly affected by DO concentrations. Even though the biologically produced S^o was not directly measured, the analyses of the solid deposits by SEM-EDS confirmed that the deposit was mainly composed of S^o and other inorganic components, such as C, N, O, P, Na, K, Si, Ca and Mg attached on the external surface of the membrane (Figure 4.11). Moreover, the results of XRD analysis showed the presence of S^o and other compounds which were suspended in the liquid side of the membrane. Although S^o and other inorganics were detected on the membrane surface and suspended in the liquid but not any fouling, clogging and wetting problems were observed in the long run experiments. This happened possibly because of two reasons; (i) the hydrophobic nature of the membrane resists the excess attachment of inorganics, (ii) in nonporous membrane there is no

liquid flow through the membrane.

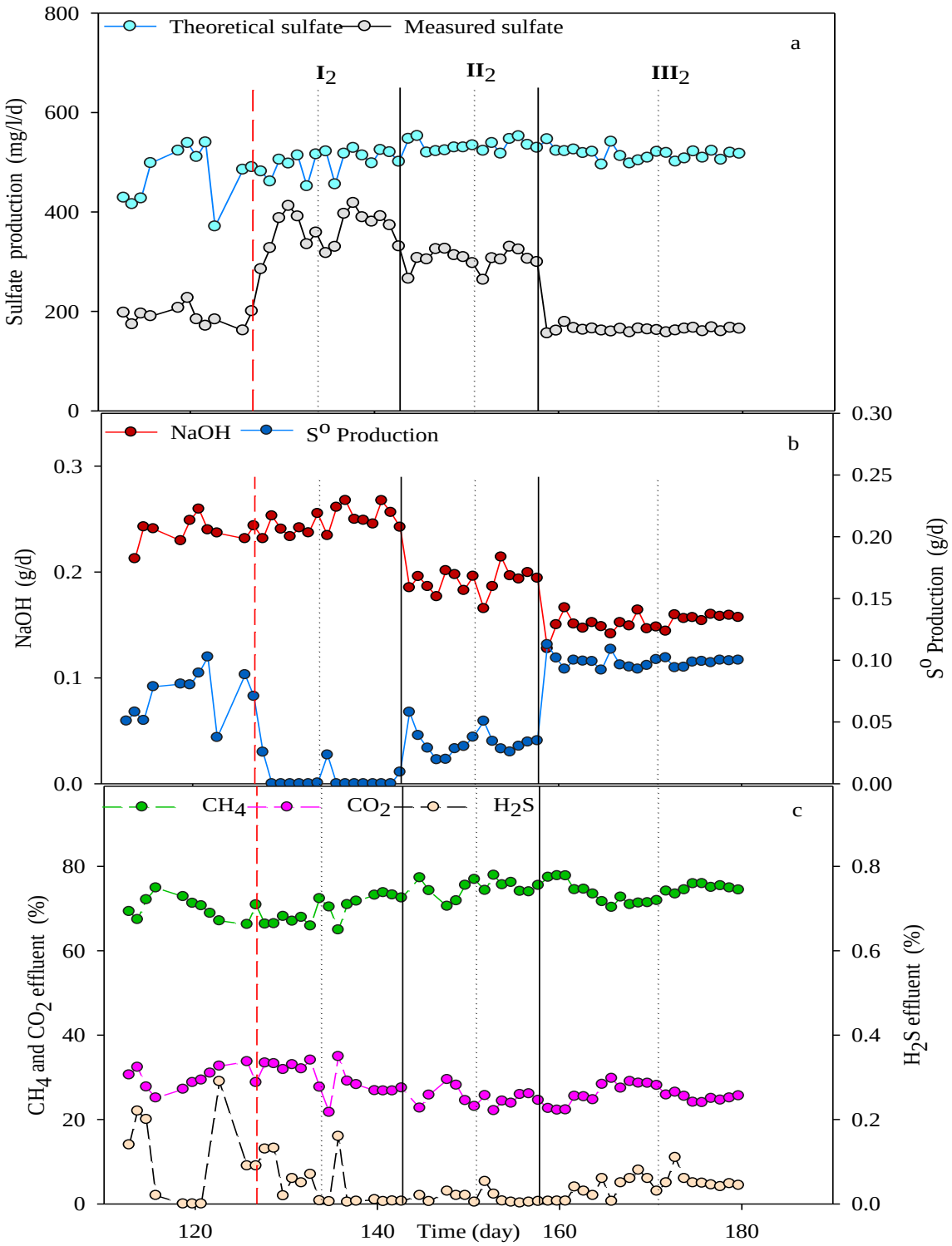


Figure 4.10 The effect of DO (DO 4 mg/L in I_2, 2 mg/L in II_2, and 1 mg/L in III_2) concentration on (a) sulfate production, (b) S^o production and NaOH consumption,

(c) effluent biogas components. The dotted lines in this figure indicates the days when 2/3 of the reactor medium was replaced by tap water due to salinity accumulation

However, in previous studies due to the blockage and conventional liquid flow through the membrane pores wetting and fouling were the reported as the main drawbacks of the process (Atchariyawut et al., 2007; Attaway et al., 2002; Wang et al., 2014).

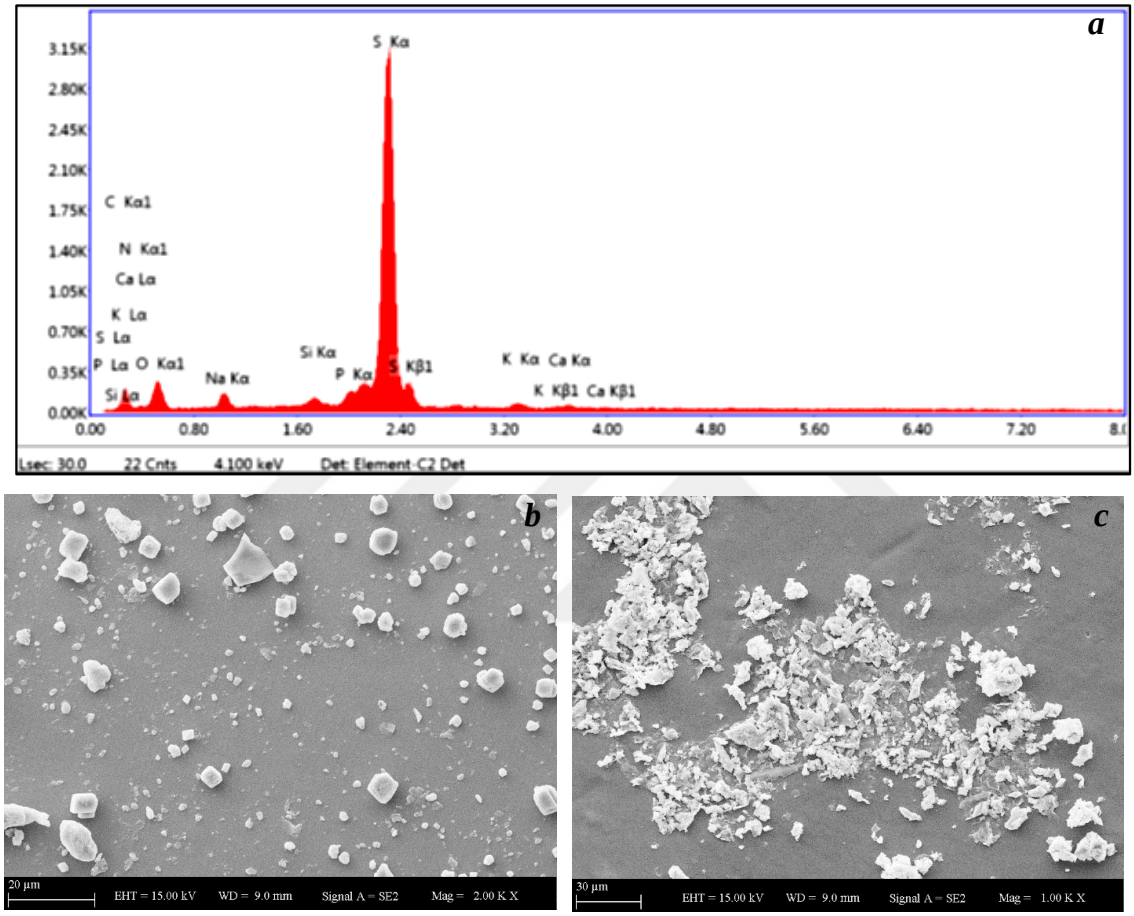


Figure 4.11 Membrane analyses results of (a) EDS, (b) SEM photographs before experiment and (c) SEM photographs after experiment

The major sulfur species detected in the absorption liquid were sulfate and S^o, and it accounts more than 97% of the diffused H_2S, while less than 3% of the diffused H_2S was found to be in dissolved form. Our results were agreed with the earlier study (Buisman et al., 1989). They observed comparable outcomes as a result of the oxidation of dissolved sulfide in a continuously stirred tank bioreactor. On other hand, the production of sulfate and S^o were varied significantly depending on the DO concentration in the membrane bio reactor (Figure 4.10a and b). The absorption liquid

was replaced (2/3 of the active volume) at days 134, 143, 151, 158 and 171 in order to remove the accumulated salts of sulfate and alkalinity, which could negatively affect the activity of SOB. As seen in Figure 4.10b, the S^o production increased significantly (100 mg/d) when the DO concentration decreased to approximately 1 mg/l. Reaction 22 also confirms, the higher the oxygen limitation the more the S^o and less sulfate formation, because S^o formation involves only one-fourth of oxygen required for the conversion to sulfate. In addition, a white to yellowish color was observed in the reactor indicating the accumulation of biologically produced S^o particles. This finding was in consistent with the observation of other studies (Bayrakdar et al., 2016; Cardoso et al., 2006). The S^o formation was also confirmed with the measured ORP values which fluctuated in range of -50 to -300 mV. Low ORP values are usually reported when S^o was the main end product of sulfide oxidation (Khanal and Huang, 2003; Kobayashi et al., 2012).

As illustrated in Figure 4.10b, at DO concentration of about 4 mg/l, the average caustic consumption was around 0.248 ± 0.012 g/d. Decreasing the DO concentration to 1 mg/l induced a saving of 0.1 g/d of NaOH, due to alkalinity generation during the oxidation of HS^- to S^o according to reaction 22. Former studies also investigated the advantage of operating the process with limited oxygen and decreased the ORP value to minimize the caustic consumption (Janssen et al., 1995; Kleinjan et al., 2006). A better control of DO concentration should be applied in order to have steady and cost effective operation. Operating the MBS at very low DO concentrations may lead to additional membrane resistance due to the attachment of excess biomass on the membrane surface as a result of limited oxygen. Whereas, supplying excess DO may lead to sulfate accumulation in the liquid which can negatively affect the activity of SOB and requires high alkaline consumption for neutralizing the absorption liquid (Eq. 23).

4.3. Conventional Bioscrubber (CBS) for H_2S Removal from Biogas

4.3.1. CBS process performance

CBS is a type of biological treatment in which H_2S is trapped into an alkaline solution. In another word, H_2S is solubilized in slightly alkaline solution inoculated with sulfide-oxidizing bacteria (SOB). The liquid medium in the bioscrubber contain suspended active microorganism whose function is to biochemically oxidize H_2S into either

elemental sulfur or sulfate depending on whether partial or complete oxidation is happening, while formation of sulfite and thiosulfate is not detected here.

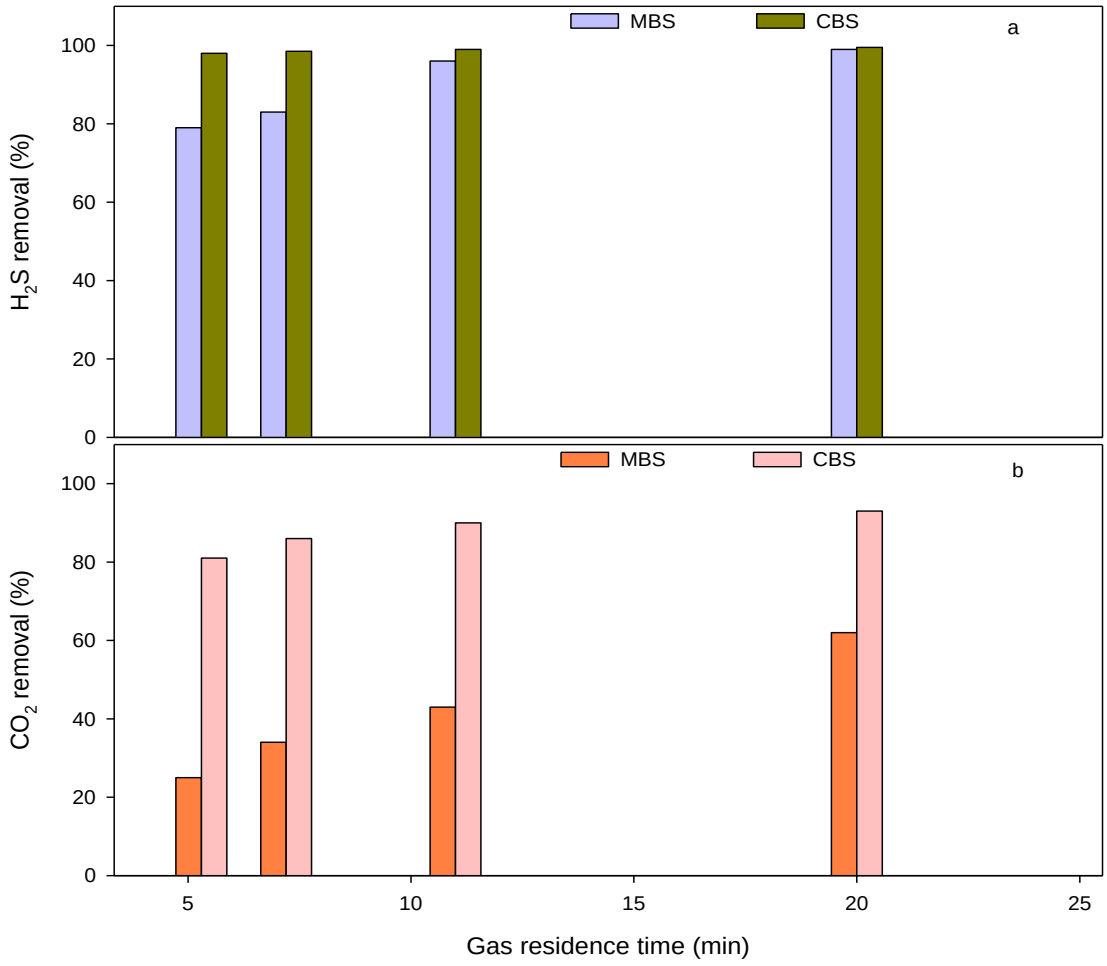


Figure 4.12 The H_2S and CO_2 removal efficiency in both bioscrubbers at pH 7.75

Figure 4.12a shows the comparative H_2S removal efficiencies of CBS with respect to the earlier MBS system. In addition, during the whole experimental time the pH was always kept above 7, in order to maintain high dissociation of H_2S in the liquid medium. For all the experimental work of CBS and MBS the H_2S removal efficiency increases almost linearly with the gas residence time and pH (Figure 4.12a). The results showed that the maximum removal efficiency of both bioscrubber was nearly 100% (at a gas residence time of 20 min). As shown in Figure 4.13a, in both bioscrubbers H_2S concentration of lower than 300 ppmv was recorded which is lower enough to avoid corrosion in the internal combustion engines, however compared to MBS, CBS

consumed two times more NaOH solution (Figure 4.14a).

However, in the CBS system the H_2S outlet concentration was constantly below the detection limits of the gas chromatograph used for H_2S measurement regardless of the gas residence time employed even at 5 min, and have H_2S RE ranged from 98% to nearly 100%, these RE were extremely exacerbated (Figure 4.12a). It happened due to the significant dilution of the biogas with nitrogen and oxygen, owing to dose of high DO concentration (4 mg/l), which is high enough for complete sulfide oxidation. Mixing of excess oxygen or air into biogas also undesirable owing to explosion risks of methane and oxygen mixtures. Likewise, Chaiprapat et al. (2015) also reported that the dissolved oxygen concentration highly controls the level of sulfide oxidation. At the lower gas residence time (5 min), in MBS around 460 mg SO_4/l.d while in CBS nearly 600 mg SO_4/l.d were generated and in both reactors the sulfate production was less than the expected theoretical sulfate generation (Figure 4.14b). One barrier which still limits the predicted sulfate generation is uneven distribution of both O_2 and H_2S within the bioscrubber. The other limiting factor were oxygen availability and mass transfer, this can be attributed to the low solubility of oxygen in water, i.e., 8.24 mg/l at 25 °C. Furthermore, the oxygen mass transfer capacity of the conventional gas diffusor used during operation of the reactors has resulted in lower oxygen transferred/oxygen supplied ratio. With respect to alkaline consumption, and selective H_2S removal the MBS is good enough compare to CBS process. However, at higher gas flowrate (lower contact time) the gas mass transfer efficiency of the MBS becomes limited because of the membrane resistant, thus leaving more H_2S unabsorbed.

Partial CO_2 absorption was also intended to clean and marginally enrich the calorific value of the biogas derived. The biogas was directly supplied into the liquid medium where it dissolved and reacted with sodium hydroxide solution for the removal of acid gases (CO_2 and H_2S). The alkali solution assured not only the absorption of H_2S but also the absorption of CO_2 owing to an acid-base neutralization reaction. Figure 4.12b and 4.13b represents the CO_2 removal efficiency and the variations of CO_2 contents at the outlet of CBS and MBS systems, respectively. After treatment the CO_2 content reduced steadily due to its direct contact with alkaline solution (NaOH) and very minor amount of CO_2 also used as carbon source for the growth of bacteria. In CBS, at higher contact

time (20 min) and 0.38 g NaOH addition (Figure 4.14a), the CO_2 content of the biogas was dropped from 39% to 3.4%. By contrast, in the MBS by adding half amount of NaOH (0.2 g) the CO_2 content was declined from 39% to 19.8%.

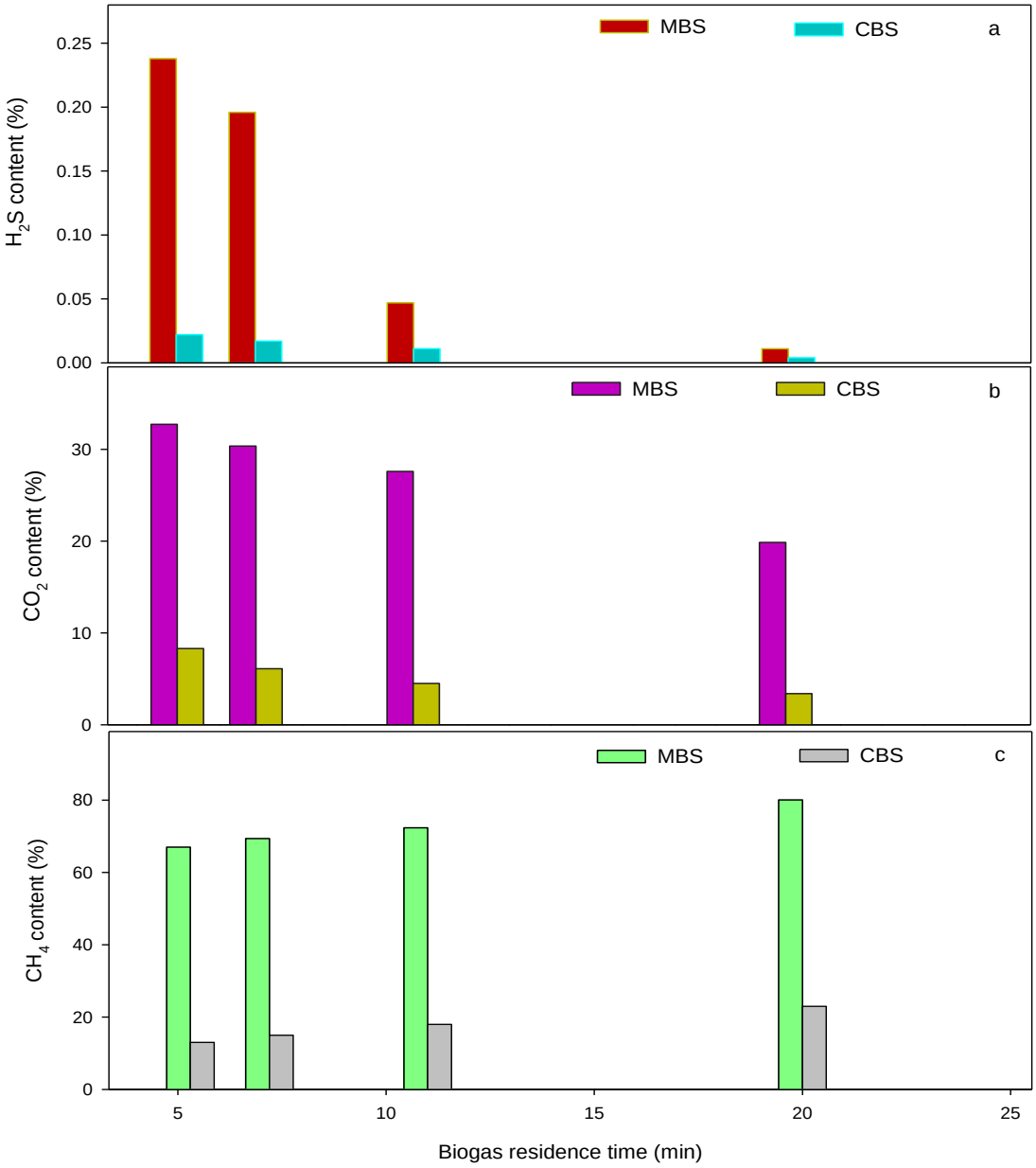


Figure 4.13 The H_2S, CO_2 and CH_4 content in the treated gas in both bioscrubbers at pH 7.75

It can be seen that the CO_2 content decreased sharply in CMS than MBS, this happened due to its direct contact between biogas and air in the absorbing liquid medium (i.e.

dilution of the biogas). But the contribution of diluion is more notheworty here. Besides, to avoid the accumulation of salt, while operating CBS, the liquid medium was frequently replaced with tap water, which favors more CO_2 absorption. As mentioned in earlier report in the section 4.1, lower gas residence time favors higher proportions of H_2S removal than CO_2. Also, high purity of CH_4 and efficient H_2S removal can be ensured at high gas residence time in MBS.

Figure 4.12c shows that the CH_4 content in the effluent biogas increased obviously with the increase of gas residence time in both bioscrubber. After treatment of the biogas with MBS system the CH_4 content increased from 60% to 80% at residence time 20 min and 0.2 g of NaOH, while CH_4 content dropped to 67% at 5 min retention time and 0.62 g of NaOH addition (Figure 4.14a).

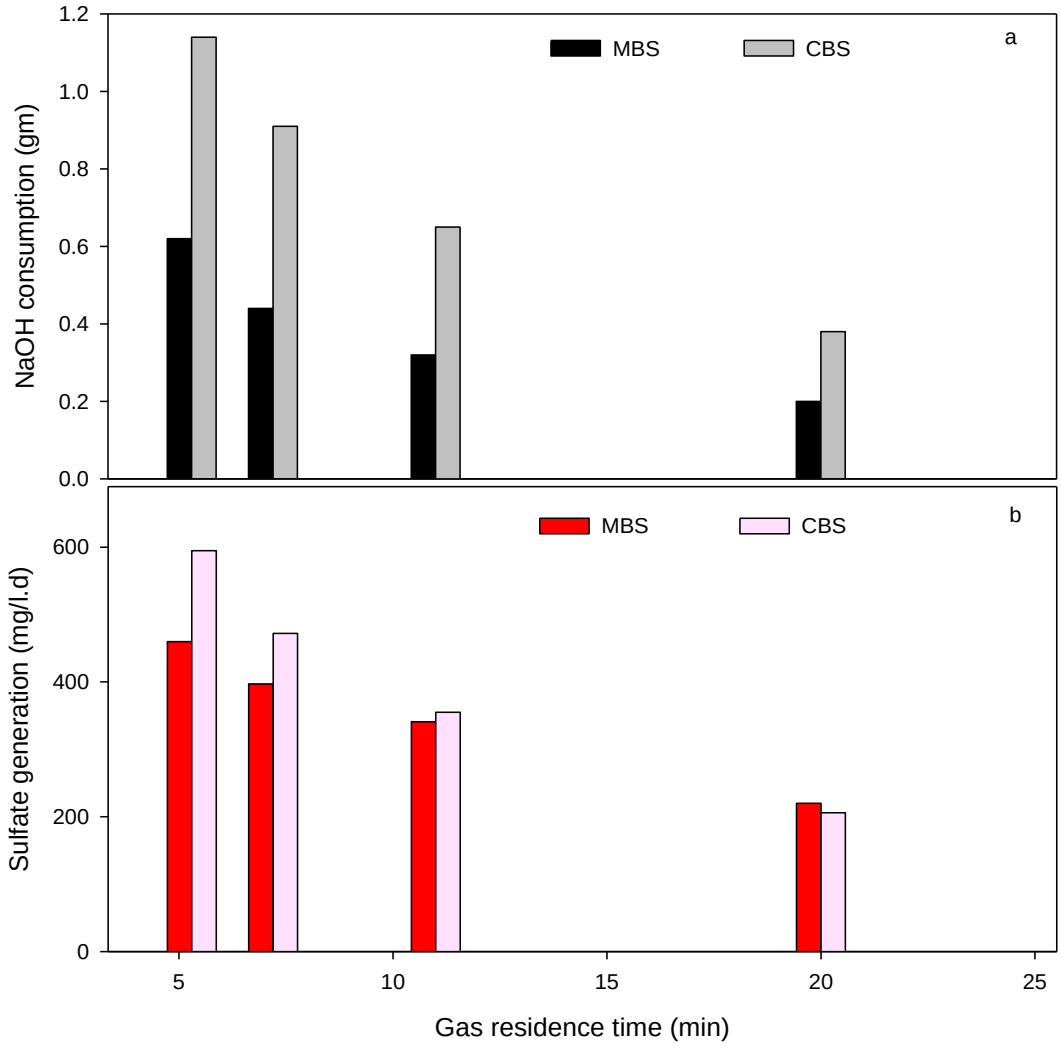


Figure 4.14 Operation of CBS and MBS systems at pH 7.75 (a) NaOH consumption (b) Sulfate generation

Thus in MBS the calorific value of the biogas enriched by 25% and 10% as gas retention time dropped from 20 min to 5 min. Whereas in CBS, the CH_4 content was dropped from 60% to 23% (0.38 g of NaOH) and 13% (1.14 g of NaOH) at gas residence time of 20 min and 5 min, respectively. Similarly, in CBS the calorific value of the treated gas declined by 2/3 and 3/4 as gas retention time fall down from 20 min to 5 min. This is particularly challenging when biogas has lower CH_4 content, because even a minor dilution of the biogas may complicate its further applications (Chandra et al., 2012). The maximum percentage of CH_4 (80%) was possibly avail by MBS, because almost complete H_2S and some CO_2 were selectively removed with the help of the PDMS membrane. The results also indicated that for $H_2S/CO_2/CH_4$ mixtures, the selective biogas desulfurization was achieved with MBS system. Comparing to MBS, the results of CBS show significant reduction in H_2S, CO_2 and CH_4 outlet concentration. The lower CH_4 content was probably caused by extreme dilution of biogas under the experimental conditions tested, since CH_4 is only sparingly soluble in water and not degraded in the bioscrubber (Nikiema et al., 2005; Sander, 1999).

5. CONCLUSION

The aim of this thesis is to evaluate the selective removal of H_2S and partial absorption of CO_2 from biogas with minimal methane loss. In this way, it will be possible to obtain a less corrosive and marginally methane enriched biogas. In the first part of the thesis study, the performance of abiotic PDMS gas-liquid membrane contactor was tested for the first time under varying operational conditions. At low biogas flowrates (9 ml/min) and thus at high contact times, almost all of the H_2S and more than half of the CO_2 were absorbed, while their absorption efficiency declined gradually as the flowrate increased. In addition, increasing membrane thickness reduced the rate of H_2S diffusion through the membrane. In comparison to H_2S and CO_2 absorption, the CH_4 loss remained quite low, thanks to its lower permeability through the membrane. On other hand, higher gas flowrates and membrane wall thicknesses significantly increased the mass transfer resistance against CO_2, but showed a marginal influence on H_2S removal; hence, it favors a higher selectivity for H_2S. Increasing temperature had no significant effect on CO_2 and methane passages through the membrane, but H_2S passages from gas to liquid side declined significantly. Except at pH 7, increasing gas flowrates resulted in improvements in both H_2S and CO_2 fluxes up to 3.4 $g/m^2.d$. and 70.2 $g/m^2.d$, respectively. The mass transfer coefficients increased when the pH raised up. However, to increase the mass transfer capacity, reduce the water consumption and volume of secondary waste, bioscrubber has become essential in the removal of H_2S from biogas.

According to the results shown in Section 4.3, nearly complete H_2S removal was achieved with conventional bio-scrubber (CBS). Even though CBS is considered as a solution to alleviate the corrosion risk of H_2S in the cogenerator, the system is not economically feasible due to excess dilution of biogas, explosive risk and higher operation costs.

Therefore, in the last part of the thesis study, the applicability of integrated system for selective removing of H_2S from the biogas was investigated. The hybrid membrane bio-scrubbing (MBS) process for H_2S removal was developed in this study and it is an easy-to-operate and cost-effective alternative than conventional desulfurization technologies and has a great potential for real scale applications.

Particularly at pH 7 with a gas flowrate of 32 l/d, 2.2 times more gas phase H_2S removal

was obtained with MBS than with abiotic membrane scrubbing (AMS) system. Moreover, H_2S removal using a gas diffusion PDMS membrane followed by partial oxidation of H_2S to elemental sulfur (DO at 1 mg/l) rather than sulfate (DO at 4 mg/l) decreased the operational cost of the system by reducing the caustic consumption and aeration requirement. The results of SEM-EDS analysis revealed that, even though sulfide and carbonate salts of Ca, Mg, and S deposits were detected on the membrane surface, no membrane clogging and fouling problems were observed. However, it is supposed that in long run, the excess precipitates on the outer surface of membrane may act as a secondary barrier and reduce the diffusion rates. The MBS used here was a simple and promising technology for selective desulfurization of biogas, without any dilution, explosion risk and secondary waste disposal problem. However, its low mass transfer capacity is the main drawback.

Concluding Remarks

The importance of this thesis and its contribution to the literature can be summarized as below:

1. A moderately high H_2S flux could be achieved with gas-liquid membrane contactor process.
2. The dense gas diffusion PDMS membrane ensured selective H_2S passage through the membrane from the biogas to the liquid side without reducing the heating value of methane. The treated biogas can be used in the cogenerator without any corrosion risk.
3. The methane content of the biogas increased slightly and therefore the economic (heating) value of biogas improved.
4. The MBS was more efficient than the AMS in H_2S removal from biogas without any dilution and explosive risks.
5. Partial sulfide oxidation significantly decreases oxygen consumption and favors elemental sulfur production. Hence, both alkaline consumption and air requirement are minimized. Elemental sulfur generation is one of the benefits of the system.
6. In spite of elemental sulfur and other inorganic deposition, the gas-liquid membrane contactor efficiently worked without membrane clogging and fouling

problems.

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3. The effects of trace element supplementation and ammonia removal on biogas production from nitrogen rich organic wastes. Scholar, 2013-2016, Scientific & Technological Research Council of Turkey, TUBITAK project No:113Y333.
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5. Desulfurization of Biogas Using A Membrane Bio-Scrubber. Researcher, 2017-2019, Marmara University Scientific Research Committee, BAPKO Project Project No: FEN-C-DRP-070317-0109

List of Publications:

Papers in SCI journals

1. Bayrakdar A., **Tilahun E**., Calli B. (2016). Biogas desulfurization using autotrophic denitrification process. Applied microbiology and biotechnology, 100(2), 939-948.

2. **Tilahun E**., Bayrakdar A., Sahinkaya E., Çalli B. (2017). Performance of polydimethylsiloxane membrane contactor process for selective hydrogen sulfide removal from biogas. Waste Management, 61, 250-257.

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1. Bayrakdar A., **Tilahun E**., Calli B. Hydrogen sulfide removal from biogas by autotrophic denitrificatıon. *5th International symposium on energy from biomass and waste*, November 17-20, 2014, Venice, Italy. (Oral Presentation)
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5. **Tilahun E**., Sahinkaya E., Çalli B. A Comparative Assessment of Membrane Bioscrubber and Classical Bioscrubber for Biogas Purification. *ICBST 2018: 20th International Conference on Biomass Science and Technology,* May, 21-22, 2018, Berlin, Germany. (Oral presentation)
6. Sahinkaya E., Tayran Z., Yurtsever A., **Tilahun E**. Performance and Fouling Propensities of Aerobic Sulfide-Oxidizing Membrane Bioreactor Treating Effluent of A Sulfate Reducing Bioreactor. *EuroAsia Waste Management Symposium*, May 2-4, 2018, Istanbul/Turkey. (Oral Presentation)

Presentations in National Conferences:

1. **Tilahun E**., Şahinkaya E., Çalli B. Biyogazdan H_2S giderimi için Geliştirilen Membran-Biyo-Kontaktör Prosesinin Farklı Koşullarda Test Edilmesi. *MEMTEK 2017 5. Ulusal Membran Teknolojileri Ve Uygulamaları Sempozyumu.* 21-23 Eylül 2017 Gebze Teknik Üniversitesi, Kocaeli, Türkiye. (Oral presentation)

Referee for international journals

1. Certificate of reviewing award in recognition of review made for the journal. October, 2017, The Editors of ***Waste Management,*** Elsevier, Amsterdam, The Netherlands
2. Certicate of reviewing award in recognition of reviewing made for the journal. April, 2018, The Editors of ***Bioresource Technology*** Elsevier, Amsterdam, The Netherlands
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