

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**TREATMENT OF VOLATILE ORGANIC SULFUR COMPOUNDS (VOSCs)
EMISSIONS USING BIOTRICKLING FILTER UNDER ANOXIC
CONDITIONS**



Ph.D. THESIS

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Department of Environmental Engineering

Environmental Science, Engineering and Management Programme

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Thesis Advisor: Prof. Dr. Kadir ALP

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**SÜLFÜR İÇEREN UÇUCU ORGANİK MADDE EMİSYONLARIN
ANOKSİK KOŞULLARDA BİYO DAMLATMALI FİLTRE SİSTEMİ İLE
GİDERİMİ**

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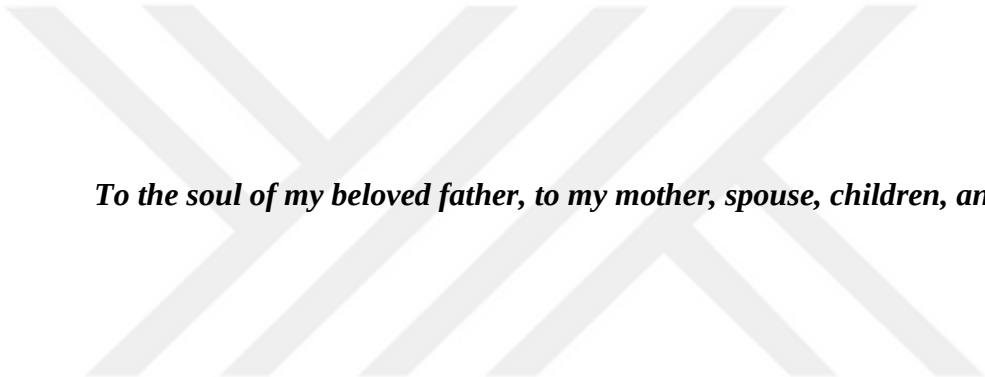
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To the soul of my beloved father, to my mother, spouse, children, and brothers.



FOREWORD

In the name of Allah, most Gracious, most Merciful. All praise is due to Allah, and may his peace and blessings be upon the Prophet (PBUH).

(وَمَا تَوْفِيقِي إِلَّا بِاللَّهِ ۖ عَلَيْهِ تَوَكَّلْتُ وَإِلَيْهِ أُنِيبُ)

(And my success is not but through Allah. Upon him I have relied, and to Him I return) (Hood- 88)

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ABBREVIATIONS

ABTF	: Anoxic Biotrickling Filer
COD	: Chemical Oxygen Demand
DMDS	: Dimethyl Disulfide
DMS	: Dimethyl Sulfide
DMSO	: Dimethyl Sulfoxide
DMSO₂	: Dimethyl Sulfone
EBRT	: Empty Bed Residence Time
EC	: Elimination Capacity
EM	: Ethyl Mercaptan
ET	: Ethanethiol
H₂S	: Hydrogen Sulfide
ILs	: Inlet Loadings
MM	: Methyl Mercaptan
MSM	: Mineral Salt Medium
NGS	: Next-Generation Sequence
RSC	: Reduced Sulfur Compounds
S.D.	: Standard Deviation
TRS	: Total Reduced Sulfur Compounds
TV	: Trickling Velocity
VOSCs	: Volatile Organic Sulfur Compounds



SYMBOLS

a	: Interfacial Area Per Volume Unit (m ² /m ³)
C_L	: Concentration in The Liquid Phase (mol/m ³)
C₀	: Concentration of Outlet Gas (g/m ³)
C_g	: Concentration in The Liquid Phase in Equilibrium with The Gas Phase (mol/m ³)
C_i	: Concentration of The Inlet Gas (g/m ³)
D_{AL}	: The Gaseous Pollutant Diffusivity in The Liquid (m ² / sec).
G_{eA}	: Gibbs Free Energy for Electron Acceptor (kJ/e -mole)
G_{eD}	: Gibbs Free Energy for Electron Donor (kJ/e -mole)
G_{eX}	: Gibbs Free Energy for Biomass (kJ/e -mole)
H	: Henry Coefficient (Dimensionless).
k	: The Pseudo-First-Order Substrate Removal Rate Constant (1/h)
K_i	: Inhibition Constant (mg/L)
k_L	: Overall Interfacial Mass Transfer Coefficient (m/sec)
K_m	: Half Velocity Constant (mg/L)
Q	: Gas Flow Rate (m ³ /sec)
R	: Mass Transfer Rate (g/ m ³ /sec)
R_a	: Half-Reaction for Electron Acceptor (Nitrate) (kJ/e -mole)
R_c	: Half-Reaction for Cell Synthesis (kJ/e -mole)
R_d	: Half-Reaction for Electron Donor (Sulfur/Sulfate) (kJ/e -mole)
S	: Substrate Concentration (mg/L).
SDR	: Specific Degradation Rate (mg S/ mg X. h)
V_{max}	: Maximum Degradation Rate Velocity (1/h)
X	: The Concentration of Microorganisms, (mg/L)
Y_{G/X}	: Gibbs Free Energy Released per C-mole of Biomass (kJ/e -mole)
Y_{X/D}	: Biomass Yield (C-mole of Biomass per C-mole of Electron Acceptor)
δ_{film}	: Liquid Film Thickness (m)
θ	: Porosity = Volume of Void Space / Volume of Filter Bed
τ	: True Residence Time (sec)
γ_X	: Degree of Reduction of Electron Biomass (e-mole/C - mole)

γ_D : Degree of Reduction of Electron Donor (e -mole/C - mole)
 Δp : Pressure drop a cross filter column (cm water)



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TREATMENT OF VOLATILE ORGANIC SULFUR COMPOUNDS (VOSCs) EMISSIONS USING BIOTRICKLING FILTER UNDER ANOXIC CONDITIONS

SUMMARY

Air pollution problems appear to be a modern social problem which is closely associated with urbanization, population density, and has increased exponentially with the industrial revolution. Undoubtedly, odor is the most complex of all the air pollution problems. Consequently, due to their public health affect and lifestyles, the environmental pollution control authorities have been concerned by odorous environment by implementing and developing a strict regulations.

Volatile organic sulfur compounds (VOSCs) contribute to odor problem as even when only, very small amounts are emitted i.e. parts per billion range (ppbv). The acute effects of (VOSCs) are directly related to its very low odor threshold values, high toxicity, flammability, and potential corrosive effect which caused an environmental annoyance towards human health and natural environment. Industrial sources represent the major concern in terms of (VOSCs) emission sources. Whereas, composting facilities, crude oil distillation, and chemical reactions in industrial activities i.e. petrochemical industry, rendering, animal processing, food industries, pulp and paper manufacturing, tanning, organic synthesis, textiles dyeing, paint remover, dyes, pharmaceuticals, insecticides, fungicides, surface active agents, fuel additives (LPG), and polymerization inhibitors. It has, also, an important function in the chemical reactions of atmospheric aerosol and cloud formation and is a significant natural compound in the regulation of climate and global sulfur circulation.

Ethanethiol (ET) and dimethyl sulphide (DMS) are considered a members of volatile organic sulfur compounds (VOSCs). Which also include hydrogen sulphide (H_2S), dimethyl disulphide (DMDS), and methyl mercaptan (MM); these compounds have an adverse health effects on people and environment and cause harmful reactions in human bodies.

ET is known as highly hazardous and it has potentially corrosive effect, low odour threshold value (0.35 ppb), vapour exposure limit 0.5 ppm, and considered as low soluble in water (ET solubility about 7.0 g/L). The odor threshold for DMS vapor is 9.75–20 ppb and the exposure limit is 10 ppm and considered as hydrophilic (DMS solubility 20 g/L). The foul smell and low odor threshold of ET and DMS are not just an environmental annoyance; they also cause public health problems like headaches, skin and respiratory irritation, and vomiting. Even though the US Environmental Protection Agency (EPA) says there is a lack of information on how the toxicity and carcinogenicity of DMS gas affect humans thus, their removal is of great concern. In this sense, development of effective ET and DMS removal technologies has considered as one of the primary issues.

Up to now many biological treatment alternatives, such as biofiltration, biotrickling filters, and bioscrubbers, are known to be well-suited waste gas control technologies to treat VOSCs, with a low maintenance cost and harmless by-product.

Hydrophobicity and water solubility of the organic odorous gas can be determined by dimensionless Henry constant (H). It has a crucial impact in selecting an appropriate biotechnology i.e. biotrickling filters and bioscrubbers are suitable for gases that having $H < 1$ and 0.01, respectively, while biofilters are preferred with more hydrophobic compounds $H < 10$.

However, biotrickling filters offer advantages over other biotechnologies, in special, in dealing with some of the following aspects, the successful removal of a wide range of pollutants with high concentrations, they have a free liquid phase and can treat the hot gases and/or acidic by-products and purge them out through the irrigation liquid. Moreover, the operational conditions as pH, can be controlled much easier via free liquid phase, hence the challenging applications can be implemented by a biotrickling filter.

Among the other biotechnological alternatives, anoxic biotrickling filters ABTFs as a new focus area in air emission controls is recently used especially with interstice local and global air quality laws and legalizations promotions that often require significant reductions of air pollutants emission to be permitted. It offers the ability to recover less harmful forms of sulfur, such as sulfate and thiosulfate or elemental sulfur in VOSCs abatement by exploitation of nitrate as oxidant.

In this sense, the study aimed to use a lab-scale anoxic biotrickling filter (ABTF) as an environmentally friendly alternative which results in the bio-conversion of malodorous ethanethiol (ET) and dimethyl sulfide (DMS) containing gas into less harmful by-products i.e. elemental sulfur and /or sulfate using nitrate as an electron acceptor under specific S^{2-}/NO_3^- molar ratio. Whereas the exploitation of nitrate as an electron acceptor in combination with other parameters: trickling velocity (TV) (0.12, 0.18, 0.24, 0.3, 0.45 m/h), empty bed residence time (EBRT) (10, 30, 60, 90, 120 sec), and inlet loadings (ILs) (9, 18, 48, 90 g/m³/h) were examined.

In batch test, the ET and DMS degradation patterns were simulated for five degradation cycles, this resulted in ~90% reduction in time (i.e from 85 to 9 hrs) when biomass concentration increased 10-fold (i.e. 300 to 3000 mg/L). The maximal desulfurization rates increased from 4.44 to 20.9 mg/m³/h and from 2.73 to 17.73 mg/m³/h for ET and DMS, respectively. The kinetic parameters of V_{max} , K_m , and pseudo-first order constant (k) were fitted to a Monod model using GraphPad Prism software 6.0. Over time, the ET degradation route showed better performance under anoxic conditions than DMS.

The thermodynamic analysis and half reactions showed that at a molar yield ratio of ET or DMS/ NO_3^- 0.75 and 0.34, elemental sulfur and sulfate were the main metabolic products, respectively. Hence, the mass balance of sulfurous compounds showed that 64% and 58% of the sulfur element in ET and DMS was biodegraded to elemental sulfur. Moreover, the mass balance calculations of NO_3^- revealed high denitrification efficiency i.e. 64.85% and 52.7% of the inlet NO_3^- that converted to N_2 in ET and DMS biodegradation process.

However, the evaluation performance of the ABTF showed that the effect of trickling velocity on removal efficiency depended on inlet concentrations; 0.24 m/h trickling velocity resulted in efficient ET removal (higher than 90.8% for 150 mg/m³ of inlet

concentration) while 0.45 m/h trickling velocity could only achieve a removal of 80.6% for 1500 mg/m³ of inlet concentration at fixed EBRT 60 sec. Increasing the EBRT up to 60 sec was adequate to achieve removal efficiency, i.e. 92 and 80% for ET inlet concentrations 150 and 1500 mg/m³ respectively, and the maximum elimination capacity was 75.18 g/m³/h at 0.45 m/h. Similarly, the best operation EBRT for DMS was found as 30 sec (corresponding to RE 89%), and 60 sec (corresponding to RE 78%) for inlet concentrations 150 and 1500 mg/m³, respectively. However, the maximum elimination capacity was 70.3 g/m³/h at EBRT 60 sec and trickling velocity 0.24 m/h. For the binary mixture of gases, the highest REs (i.e. 98.1 and 97.4%) for ET and DMS were obtained at ET: DMS 1:1.5.

The microbial composition and the relative abundance of the bacterial communities for *Proteobacteria* increased as the operation continued from 36.6% to 39.7% and 56.1% for inoculum, ET, and DMS, respectively. In class level, there were a noticeable increment in *Gammaproteobacteria* population i.e. from 16.3% to 35.1% and 21.4% for ET and DMS treatment, respectively. Interestingly, around 50% of the bacterial population was represented by *Firimcutes* phyla and *Bacilli* class throughout ET treatment period.

The study revealed that ABTF has a reliable biodegradation capacity in the oxidation of malodors ET and DMS gases under anoxic conditions while still process improvement on mass transfer enhancement for low waste gas concentrations be required.



SÜLFÜR İÇEREN UÇUCU ORGANİK MADDE EMİSYONLARIN ANOKSİK KOŞULLARDA BİYO DAMLATMALI FİLTRE SİSTEMİ İLE GİDERİMİ

ÖZET

Günümüzde hava kirliliği problemi, kentleşme ve buna paralel olarak kentlerde nüfus yoğunluğunun artması ve de endüstrileşme neticesinde modern bir sosyal problem olarak karşımıza çıkmaktadır. Kuşkusuz, koku emisyonları hava kirliliği sorunları içerisinde en yaygın olarak karşımıza çıkan ve kompleks yapıya sahip olan emisyonlardır. Bu etkiler neticesinde, koku emisyonlarının halk ve çevre sağlığı etkilerini önlemek amacıyla yetkili makamlar emisyonların kontrolüne yönelik yönetmelikleri yürürlüğe koymaktadır.

Uçucu organik sülfürlü bileşikler çok düşük konsantrasyonlarda dahi (ppbv) koku problemlerine sebep olan bileşiklerdendir. Bu bileşiklerin akut etkileri düşük koku emisyonlarında dahi yüksek zehirlilik, yanıcılık ve korozyon etki ile insan ve çevre sağlığına etki etmektedir. Endüstriyel kaynaklar ise uçucu organik sülfürlü bileşiklerin yaygın olarak ortaya çıktığı en büyük emisyon kaynaklarıdır. Bu kaynaklar arasında compost tesisleri, petrokimya endüstrisi, gıda endüstrisi, kağıt endüstrisi, hayvan kesim tesisleri en yaygın olarak uçucu organik sülfürlü bileşiklerin ortaya çıktığı tesislerdir. Kompost üretim tesisleri, ham petrol distilasyon tesisleri, petrokimya, gıda ve kağıt endüstrilerindeki çeşitli prosesler, tekstil boyama, tıbbi ilaç ve ürün sektörü, çeşitli organik sentezler, boyama işlemleri, yüzey aktif madde üretim prosesleri, LPG gibi yakıt türleri uçucu organik sülfürlü bileşenlerin yaygın olarak ortaya çıkmakta olduğu emisyon kaynaklarıdır. Ayrıca atmosferdeki aerosol ve bulut oluşumu reaksiyonlarında ve de iklim değişimlerinde de kayda değer etkilere sebebiyet vermektedir.

Hidrojen sülfür ve dimetilsülfid gibi etanetiol ve dimetilsülfür de önemli uçucu sülfürlü bileşikler arasında yer almakta ve insan ve çevre sağlığı üzerinde zararlı etkiler oluşturmaktadır.

ET düşük koku eşik seviyesine (0.35 ppb) sahip, suda düşük olarak çözünen (7.0 g/L) ve korozyon etki potansiyeli ile yüksek derecede tehlikeli bir kimyasal olarak tanımlanmaktadır. DMS ise 9.75-20 ppb arasında değişen koku eşik seviyesi ve 10 ppm maruziyet limitine sahip olan hidrofilik karakterde bir kimyasaldır (20 g/L). Her iki bileşiğinde sahip olduğu kötü koku karakteri ve düşük koku algı eşiği bireylerde yaratmış olduğu rahatsızlıkların yanı sıra baş ağrısı, solunum yolu problemleri, göz yaşarması gibi sağlık sıkıntılarına sebebiyet vermektedir. Ancak Amerika Çevre Ajansı verilerinde de bu iki kimyasal maddenin toksisitesi ve kanserojenik etkisi ile ilgili bilgi eksikliği göze çarpmış ve bu iki maddenin belirtilen bu özellikleri sebebiyle ET ve DMS arıtma teknolojilerinin geliştirilmesi sektörlerde en önemli konular arasında yer almaktadır.

Günümüze kadar biyolojik arıtma teknolojilerinden biofiltre, biyo damlatmalı filtre ve biyoyıkayıcı sistemler yaygın olarak uçucu sülfürlü organik bileşenlerin arıtımında

yaygın olarak kullanılmış ve düşük arıtma maliyeti ve de zararsız son ürün eldesi sağlanmıştır.

Organik maddelerin hidrofobisitesi ve suda çözünürlük derecesi boyutsuz Henry (H) sabiti ile tanımlanmaktadır. Henry sabiti uygun arıtma alternatiflerin seçilmesinde çok büyük öneme sahiptir. Atıkgazların arıtılmasında bio damlatmalı filtreler $H < 1$ ve bio yıkayıcı sistemler ise $H < 0.01$ sabit atıkgazların arıtılmasında daha yüksek verim elde etme alternatifi sunarken, biyofiltre sistemleri ile daha hidrofobik karakterde olan bileşiklerin ($H < 10$) giderimi söz konusu olmaktadır.

Ancak, bio damlatmalı filtre sistemleri diğer biyoteknolojilere göre bir çok farklı bileşiğin yüksek konsantrasyonlarda arıtılmasının sağlanması, sahip olduğu serbest sıvı faz ile yüksek sıcaklıkta ve/veya asidik karakterde oluşan yan ürünlerin tolere edilmesi ve bunların serbest sıvı faz ile ortamdan uzaklaştırılabilmesi gibi bir çok avantaj sunmaktadır. Bunun yanı sıra, sistem işletim parametrelerinin (pH gibi) sıvı faz ile kontrolünün kolaylığı biyo damlatmalı sistemlerin daha yaygın olarak kullanılmasına olanak sağlamaktadır.

Ortaya çıkan bu emisyonların arıtımında biyoteknolojik arıtma alternatifleri yaygınlıkla kullanılmaktadır. Biyolojik arıtma teknolojileri arasında anoksik biyo damlatmalı filtre sistemi atık gaz emisyonlarının arıtımında sağladıkları yüksek verim neticesinde yasal standartlara uyma bakımından kayda değer avantajlar sunmaktadır. Biyo damlatmalı filtre sistemleri ile sülfürlü bileşikler daha az zararlı sülfür formları olan sülfat, tiyosülfat ve elemental sülfüre nitratin oksidant olarak kullanıldığı sistemlerde okside edilmektedir.

Bu çalışma çerçevesinde çevre dostu arıtma alternatiflerinden biyo damlatmalı filtre sistemi laboratuvar ölçekli olarak anoksik koşullarda kötü koku karakterizasyonuna sahip olan etanetiol ve dimetilsülfür içeren atık gaz akımlarının elemental sülfür ve / veya sülfat gibi zararsız ürünlere nitratin elektron alıcı olarak kullanılması ile okside edilmesi amacıyla işletilmiştir. Sistem işletimi spesifik S^{2-}/NO_3^- molar oranında , farklı spreyleme hızlarında (0.12, 0.18, 0.24, 0.3, 0.45 m/sa), boş tank temas süresinde (10, 30, 60, 90, 120 saniye) ve farklı organik yüklemelerde (9, 18, 48, 90 g/m³/sa) gerçekleştirilmiştir.

Gerçekleştirilen kesikli deneysel çalışmalarda ET ve DMS degradasyon sistemi beş tam degradasyon döngüsünde simule edilmiş ve biyokütle konsantrasyonunun 10 kat artırılmasının (300 mg/L den 3000 mg/L) degradasyon süresini %90 oranında azalttığı belirlenmiştir. Maksimum desülfürizasyon hızı ET için 4.44 mg/m³/sa seviyesinden 20.9 mg/m³/sa seviyesine , DMS için 2.73 mg/m³/sa seviyesinden 17.73 mg/m³/sa seviyesine yükselmiştir. Gerçekleştirilen çalışma çerçevesinde GraphPad Prism software 6.0 yazılımı V_{max} , K_m , and birinci merteye sabiti (k) gibi Monod Model katsayıları belirlenmiştir. Zaman içerisinde ET degradasyonu anoksik koşullar altında DMS degradasyonuna göre daha iyi bir performans göstermiştir.

Termodinamik analizler ve yarı reaksiyonlar denklemleri, sırasıyla ET ya da DMS/ NO_3^- 0.75 ve 0.34 molar oranlarında yapılan organik yüklemelerde elemental sülfür ve sülfatın ana metabolik ürünler olduğu belirlenmiştir. Bu çerçevede yapılan çalışmalarda sülfür bileşiklerinin ET yüklemelerinde % 64'ünün, DMS yüklemelerinde % 58'inin elemental sülfüre biyolojik olarak parçalandığı tespit edilmiştir. Bunun yanı sıra nitratin N_2 gazına denitrifiye olması da yüksek verimle gerçekleşmiş ve ET yüklemelerinde nitratin % 64.85'i , DMS yüklemelerinde % 52.7 si denitrifiye olmuştur.

Bununla birlikte, ABDF'nin değerlendirme performansı, damlatma hızının, giderim verimliliği üzerindeki etkisinin, giriş konsantrasyonlarına bağlı olduğunu göstermiştir; 0.24 m / h spreyleme hızı, yüksek verimli ET giderimi (150 mg / m³ giriş konsantrasyonu için % 90.8'den daha yüksek) ile sonuçlanırken, 0.45 m / sa spreyleme hızı, 1500 mg / m³ 'lük giriş konsantrasyonu için % 80.6'lık bir giderim elde edilmiştir. Boş tank temas süresinin 60 saniyeye kadar çıkartılması ET arıtma verimini 150 mg/m³ için % 92'ye, 1500 mg/m³ konsantrasyon için % 80'e çıkartırken, maksimum eliminasyon kapasitesi 0.45 m/sa spreyleme hızında 75.18 g/m³/sa olarak belirlenmiştir. . Benzer şekilde, DMS için en iyi operasyon düşük konsantrasyon akımında(150 mg/ m³) için boş tank temas süresinin 30 sn (89% 'a tekabül eden giderim verimi) olduğu durum için % 89 arıtma verimi ile gerçekleşirken, 1500 mg/m³ giriş konsantrasyonları için 60 saniyelik temas süresi % 78'lik arıtma verimi sağlamaktadır. Bununla birlikte, maksimum eliminasyon kapasitesi, 60 saniyelik temas süresi ve 0.24 m/sa spreyleme hızı ile 70.3 g / m³ / saat olarak belirlenmiştir. İkili gaz karışımı için, ET ve DMS'nin en yüksek giderim (i.e. 98.1 and 97.4%) verimleri ET: DMS 1: 1.5'de elde edilmiştir.

Yapılan mikrobiyal analizler ışığında *Proteobacteria* popülasyonunun aşılama çamurunda % 36.6 olduğu belirlenirken, biyo damlatmalı filtre işletiminin ET organik yüklemeleri ile gerçekleştirildiğinde popülasyonun % 39.7'ye, DMS organik yüklemeleri ile %56.1' yükseldiği belirlenmiştir. ET ve DMS giderimi ile beraber *Gammaproteobacteria* popülasyonunda kayda değer artışlar tespit edilmiş olup, aşılama çamurunda % 16.3 olan oran ET ve DMS yüklemelerinde sırasıyla % 35.1 ve ,% 21.4'e yükselmiştir.. Şaşırtıcı olarak, ET arıtımı esnasında bakteri popülasyonunun yaklaşık% 50'si, *Firimcutes* phyla ve *Bacilli* türü bakterilere aittir.

Çalışma, ABDF'nin anoksik şartlar altında kokulu ET ve DMS gaz akımlarının biyolojik olarak okside edilmesinde etkin bir biçimde kullanılabileceğini ortaya koymakla beraber düşük konsantrasyondaki gaz akımlarında kütle transferinin arttırılmasına yönelik proses iyileştirilmesine ihtiyaç duyulmaktadır.



1. INTRODUCTION

1.1 Background

Air pollution issue has become a major concern topic since the twentieth century. It is reported as one of the most challenging and urgent environmental problems to be solved worldwide. Nowadays, anthropogenic sources like agricultural and industrial activities are considered primary air pollution sources and causing very serious environmental problems especially in many developing countries (Kanada et al., 2013). In this sense, the environmental pollution control strategies and regulations have forced towards the acute effects of air and water pollutants on human health and natural environment. Recently, as a result of the common market in the European Union, there is a movement to achieve a high degree of environmental protection. This progress has led to increasingly strict in respect of the permitted levels of gaseous emissions that specified in the Directive 2008/50/EC of the European Parliament of the Council of 21 (2008) and Directive 2010/75/EU of the European Parliament of the Council of 24 (2010). Which became an important driving force for the development and implementation of processes for reducing these emissions (Gómez & Cantero, 2007). Similarly, Turkey enacted in 2013 "Regulation on Control of Emissions that Contribute to Odor (KOEKHY)" to state the permissible level of odor emissions (Akmirza et al., 2018).

Odors emissions from industrial and urban areas have increased people's complaints towards air quality (Badach et al., 2018; Franssen et al., 2002; Pettarin et al., 2015). However, the developments in environmental and medical sciences have enhanced understanding of the toxic properties of these pollutants. Their association between the exposure to high concentrations of air pollutants and death's increment cases was investigated in many studies (Huang et al., 2018; Nobles et al., 2018). Depending on nature and composition of odorous gases, the long-term exposure can cause on people an emotional stresses symptoms prevalence in such states as a headache, anxiety, respiratory problems, eye irritation, nausea or vomiting (Wenjing et al., 2015).

The inappropriate disposal management, ineffective treatment processes, and leakage during transportation, are frequently introduce industrial air contaminants i.e. benzene, toluene, xylene, styrene, hydrogen sulfide (H_2S), ammonia (NH_3), dichloromethane (DCM), and hexane to atmosphere without any control mechanism. The potential health impact of the odor nuisance emissions can be related to the concentration level of the disposed chemical species and total time of exposure (Gómez, 2016).

Organo-sulfur off-gases are usually referred to as volatile organic sulfur compounds (VOSCs). They are frequently emitted by exhaust gashouse industries. Hence, they are reported as the most complex of all the air pollution problems, because of their contribution to ecological and hazardous effect on people well-being causing health problems (Nicell, 2009). Moreover, photochemical smog formation and particulate as secondary pollutants emissions, threatening human welfare and air quality when discharged into the atmosphere (Janssen et al., 2013; Li et al., 2015). The natural sources for emission of (VOSCs) are volcanoes, soil and plants, coastal wetlands, biomass burning and ocean. They have an important function in the chemical reactions of atmospheric aerosol and cloud formation and play an important role in global climate regulation and global sulfur circulation (Barona et al., 2004; Bentley & Chasteen, 2004; Bosch et al., 2008; Wu et al., 2010).

The most important characteristics of VOSCs compounds its very low odor threshold values (ppbv) range; as shown in Table 1.1, high toxicity, flammability, and potential corrosive effect which caused an environmental annoyance. In addition, public health problems like headaches, skin and respiratory irritation, and vomiting, thus, VOSCs control has been an area of concern and research for many years (Andersson, 2006; Arellano-García et al., 2018).

In order to develop effective odorous emission abatement, governmental authorities enacted strict legislation and have led industries to adopt proper air pollution treatment alternatives to comply with these legislations.

Up to date, many physical-chemical techniques, biological techniques, or a combination of these are used in the removal of VOSCs emissions from waste air streams. The most frequently traditional treatment technologies are thermal oxidation, condensation, incineration, chemical scrubber, and catalytic oxidation processes (Kennes & Thalasso, 1998). These technologies have confirmed their

efficiency and consistency and will continue to proof their role, but some disadvantages remain. First of all, they normally require higher investment and operation costs, because of high chemical, high technical complexity, and high energy and chemical reagent consumption compared with biological methods, furthermore, the possible formation of secondary waste streams (Kennes & Thalasso, 1998; Sercu, 2006). The inherent environmental problems of air streams containing VOSCs, and the drawbacks of physical and chemical treatment methods, have highly devoted to investigate and develop effective and new treatment techniques for odorous waste gas treatment depending on physical and chemical characteristics of the target compound such as polarity, solubility in water, vapor pressure and sorption define the compounds tendency to either volatilize into the air from the liquid phase or adsorb/absorb to the organic particulate material present in effluents (Giri et al., 2014; Lehtinen, 2012).

Table 1.1 : Physical and chemical properties of VOSCs (Janssen et al., 2013; Li et al., 2015; Roman, 2016; Smet et al., 1998; van Leerdam, 2007).

Sulfur compound	Odorant character	B.P. (°C)	M.P. (°C)	OT (ppbv)	H at 25°C	Solubility at 25°C (%)
H ₂ S	Rotten eggs	-60.7	-85.5	8.5–1000	0.41	0.334
CH ₃ SH	Decayed cabbage	6.2	-123.0	0.90–8.5	0.10	2.3
CH ₃ CH ₂ SH	Skunk	35.0	-147.9	0.01–350	0.15	0.676
CH ₃ (CH ₂) ₂ SH	Rotten cabbage, skunk	67.8	-113.1	3.1	0.17	—
(CH ₃) ₂ S	Decayed vegetables	37.3	-98	0.6–40	0.073	2.0
(CH ₃) ₂ S ₂	Irritating, putrefaction, foul	109.7	-85	0.1–3.6	0.045	—
(CH ₃ CH ₂) ₂ S	Garlic	92.1	-103.9	0.033	—	—
CS ₂	Sweet ether	46	-112.1	0.21	0.65	0.216
CSO	Pungent	-50	-138.8	—	1.94	0.125

B.P.: boiling point; M.P.: melting point; OT: odor threshold; H: dimensionless Henry coefficient.

As a result, biological treatment methods such as biofilters, biotrickling filters, and bioscrubbers has been known as well suited for waste gas control technology for treatment VOSCs at the low cost of maintenance and environmentally friendly by producing harmless by-products (Dumont, 2015; Sercu et al., 2005). Among these, biotrickling filters BTFs offer advantages over other biological air treatment alternatives. They have the ability to eliminate a wide range of pollutants with high

concentrations. Besides, they have a free liquid phase allowing them to treat the hot gases and/or acidic by-products and purge them through the irrigation liquid (Wu et al., 2018).

Nevertheless, it is necessary to investigate the appropriate techniques which can be used in VOSCs abatement to recover less harmful forms of sulfur, such as sulfate and thiosulfate or elemental sulfur.

Although, previous researchers were studied the simultaneous removal of sulfur compounds (as electron donor) with nitrate (as an electron acceptor) in industrial wastewater treatment systems (Cai et al., 2008; Turker et al., 2012). The process might be different in gases because the removal mechanism involves the mass transfer from the gas phase to the liquid phase, absorption/adsorption, and then biodegradation. The advantages of this method are that it combines sulfide removal with nitrogen removal in one process, in most industrial wastewater treatment systems.

Recently, the stoichiometric relations between sulfide and nitrate have been developed in few studies, wherein, nitrate has been used as electron acceptors in biogas desulfurization (H_2S) (Baspinar et al., 2011; Jaber et al., 2017; Li et al., 2016; López et al., 2018). However, the toxicity effect on human health of VOSCs is much higher than H_2S . The cost-effective treatment technologies had been used for a long time for the removal of both H_2S and VOSCs i.e. in natural sour gas treatment, but there is still lack in studies related the significance of biological desulfurization in VOSCs removal (Roman, 2016).

Up to our knowledge, there were no studies devoted to anoxic ET and DMS biodegradation in waste gas streams. In this sense, anoxic mineralization via NO_3^- denitrification represents a promising platform for the removal of VOSCs, particularly, ET and DMS from O_2 -deprived emissions, to produce less harmful by-products i.e. sulfate and/or elemental sulfur. Practically, the use of wastewater treatment plants effluents in full-scale application of biotrickling filters as an alternative and non-expensive nutrient sources were efficient in contaminants treatment. Although it may constitute of non-ideal composition (Cox & Deshusses, 2001). As a result, the use of wastewater from treatment plants, which represent a cheap source of NO_3^- , denote an interesting opportunity for the development of innovative bioprocesses enabling the simultaneous removal of VOSCs and NO_3^- .

Thus, the development of anoxic biotrickling filters ABTFs, as alternative biotechnology, able to use an electron acceptor other than O_2 during VOSCs oxidation will significantly improve the economic and environmental sustainability of VOSCs treatment in the various source of emissions. However, the scale-up of the laboratory process to a full-size plant remains a challenge.

1.2 Aims and Purpose

Priority in the research presented in this thesis is to focus on the biological desulfurization of odorous gases, specifically, ET and DMS. Considering the limited amount of work on bio-oxidation of VOSCs emissions utilizing nitrate as electron acceptor, further work is clearly required to explore the potential of nitrate-based sulfur removal from gas streams.

In this context, the conducted study has been emphasized using a unique biological system for treating and developing a low-cost high-performance generation and reduced footprint for odor abatement with a combination of heterotrophic denitrification process. The specific objectives of the study were listed as follows:

- To comprise a new biotechnological desulfurization technology as ABTFs, and improve the economic and environmental sustainability during VOSCs oxidation.
- To study the simultaneous removal of NO_3^- and ET, DMS individually and in the mixture by developing ABTFs, as alternative biotechnology, able to use an electron acceptor other than O_2 during ET and DMS treatment in the various sources of emissions.
- Consequently, deriving the S^{2-}/NO_3^- molar ratio which yields elemental sulfur and/or sulfate as harmless end products.
- To detect the best-operating conditions (i.e. empty bed residence time EBRT, trickling flow-rate, and inlet concentrations) for evaluating performance efficiency of the proposed biological treatment method i.e. ABTF.

1.3 Thesis Outline

This thesis presents the study of synthetic ET and DMS removal using a novel anoxic biotrickling filter (ABTF) application for odorous gases desulfurization. The simultaneous removal of NO_3^- and odorous gases under specific molar ratio of $\text{S}^{2-}/\text{NO}_3^-$ to produce less harmful by-products i.e. elemental sulfur and /or sulfate was the base of novelty that used in this application.

The thesis consists of five chapters. Chapter 1 is a general introduction, which presents some general background about air pollution and odors contaminants including volatile organic sulfur compounds and the necessity to develop new biological technology environmentally friendly, sustainable, and cost-effective such as ABTF. In addition to purpose and aims of this thesis. Chapter 2 elucidates the literature review which is focused on VOSCs categories, emissions sources, control systems, and biological process and their applications in VOSCs removal.

Chapter 3 identified the instruments and measurements that conducted throughout the experimental works. Batch test procedure in adaptation periods. The lab-scale model of the biotrickling filter installment and evaluation during the start-up period. Moreover, the microorganisms community analysis procedure using next-generation sequence protocol that presented by Zymo Inc., USA.

Part of chapter 4, was published in the Journal of Environmental Technology under-addressed article “Removal of Ethanethiol using a Biotrickling Filter with Nitrate as an Electron Acceptor”. This chapter addressed the kinetics studies of the ET and DMS under an anoxic condition in batch test and the evaluation performance of the ABTF in the removal of these gases using NO_3^- as an electron acceptor. The removal efficiency and elimination capacity of the ABTF were testified under different operational parameters including empty bed residence time, trickling flow rates, and inlet gaseous concentrations at a specific molar ratio of $\text{S}^{2-}/\text{NO}_3^-$.

Chapter 5 provides the reader with the overall conclusions of this thesis and recommendations for developments and forthcoming studies.

2. LITERATURE REVIEW

2.1 Volatile Organic Sulfur Compounds (VOSCs)

The volatile organic sulfur compounds (VOSCs) can be referred to the total reduced sulfur compounds TRS which are, mainly, contain sulfur and include organic reduced sulfur compounds i.e. hydrogen sulfide (H_2S), methyl mercaptan MM (CH_3SH), ethyl mercaptan EM ($\text{CH}_3\text{-CH}_2\text{-SH}$), dimethyl sulfide DMS ($\text{CH}_3\text{-S-CH}_3$), dimethyl disulfide DMDS ($\text{CH}_3\text{-S-S-CH}_3$), carbon disulfide (CS_2), and carbonyl sulfide (COS) (Ren, 2014). A volatile term defined as “any organic compound that has vapor pressure more than 0.1 mmHg at 25 °C”(Kennes, 2013). The human nose is particularly sensitive to VOSCs and is capable of detecting them at concentrations as less as 1 ppb of air. Thus, the annoying bad smell, toxicity, and corrosive properties of VOSCs emissions should be prohibited (Bajpai, 2014).

2.1.1 Hydrogen sulfide (H_2S)

It is a colorless, flammable, and weak acidic in aqueous solution with an extremely foul smelling rotten eggs. The distinctive odor of sulfur is characteristic of H_2S and to a lesser degree by other VOSCs. It is considered the main contributor to odors emission in wastewater treatment plants (WWTPs). Furthermore, it generally constitutes the major component of gaseous emissions in biogas (up to 4000 ppm) and landfill gas (up to 100 ppm), as shown in Table 2.1 (Moreno et al., 2013; Smet et al., 1998). Moreover, it is considered the primary odor emission source that originated from sodium sulfide breakdown in the Kraft cooking liquor (Bajpai, 2014).

2.1.2 Methyl mercaptan (CH_4S)

Methanethiol (MT) is a synonym for this compound. It is a gas at normal temperature and is extremely obnoxious odor similar to decayed cabbage even at very low concentrations. It is used as warranty odorant to detect natural gas and in methionine,

pesticides, jet fuels, and plastics synthesis. It is also emitted from pulp and kraft mill manufacturing plants (NRC, 2009).

Table 2.1 : Typical composition of biogas, landfill gas, and natural gas streams (Moreno et al., 2013).

Species	Biogas	Landfill gas	Natural gas
H ₂ S (ppm)	0–4000	0–100	0–5
NH ₃ (ppm)	~100	~5	0
CH ₄ (vol. %)	60–70	35–65	70–90
H ₂ (vol. %)	0	0–3	0
CO ₂ (vol. %)	30–40	15–50	0–8
N ₂ (vol. %)	~0.2	5–40	0–5
O ₂ (vol. %)	0	0–5	0–0.2
Aromatics (ppm)	0	0–200	0
Other hydrocarbons (vol. %)	0	0	0–20

2.1.3 Ethyl mercaptan (CH₃SCH₃)

Until 1930, VOSCs have named mercaptans, especially, ethyl mercaptan or ethanethiol (ET) due to their ability to crystalizes mercury solutions in a solid form (van Leerdam, 2007). It has a strong malodor that can be detected in a minute. The threshold for human detection is 0.36 ppb. Its distinct odor similar to cooked cabbage, leeks, and onions. ET is used as an intermediate and raw material in antioxidants, plastics, and insecticides industries (NRC, 2009). It is called "stench gas" and it was used in the mining industry as an alarm system to alert mine workers during an emergency. Whereas, the workers in the union oil company of California boosted a trace amount of ET in the natural gas to detect leaks easier. Since butane and propane in (LPG) fuels are normally odorless, flammable, explosive, and asphyxiation, ET is intentionally added as an odorant to LPG to impart an easily noticed smell to these odorless compounds (<https://en.wikipedia.org/wiki/Ethanethiol>). Interesting, (1- 6×10⁻⁹ g/L) of ET is detected in normal human breath (Janssen et al., 2013).

2.1.4 Dimethyl sulfide (CH₃)₂S

DMS is a neutral molecule, nonacidic liquid, highly volatile at normal temperature, doesn't react with proteins, and quite stable in numerous bio-systems. In mammals, free DMS is the only form known. While, two precursors i.e. S-methylmethionine and dimethylsulfoniopropionate (DMSP) belong to the sulfoniumions class have

been released by phytoplanktonic marine organisms. It has an important role in flavoring many cooked vegetables (Tangerman, 2009). Besides, it is formed during MT reaction with lignin component of the wood. There is a lack of information on how the toxicity and carcinogenicity of DMS gas affect humans according to the provisional peer-reviewed introduced by EPA/690/R-05/013F (2005).

2.1.5 Dimethyl disulfide (CH₃)₂S₂

Also known as methyl disulfide and methyl dithiomethane. It is a nonacidic liquid formed by the oxidation of MT throughout the recovery system in Kraft paper production.

2.2 Sources of VOSCs Emissions

A short overview of the natural and anthropogenic emission sources of VOSCs is presented in the following sections.

2.2.1 Natural sources

VOSCs have a significant role in the global interchange sulfur cycle between the ocean, estuarine, freshwater, and terrestrial and atmosphere. They have been identified as the main contributor to the atmosphere as organic sulfur compounds emissions, causing leaks and forests acidification and increasing sulfate deposition (Barona et al., 2004; Bentley & Chasteen, 2004; Bosch et al., 2008; Wu et al., 2010). In particular, DMS represents about 75% of the annual emissions of total sulfur flux which released to the atmosphere from ocean and sea causing local and global environmental problems. DMS considered the link between the ocean and atmosphere in global sulfur cycle as illustrated in Figure 2.1 It acts as cloud condensation nuclei that, subsequently formed dense clouds and reduced the global temperature as counteractive to the greenhouse gases behavior (Lomans et al., 2002).

However, about 90% of DMS can be degraded biologically by aerobic and anaerobic microorganisms before its releases to the atmosphere, thus, VOSCs flux from natural systems to the atmosphere can be controlled by biological conversion.

The annual emission rates of VOSCs which sinks into the atmosphere from different natural activities are presented in Table 2.2.

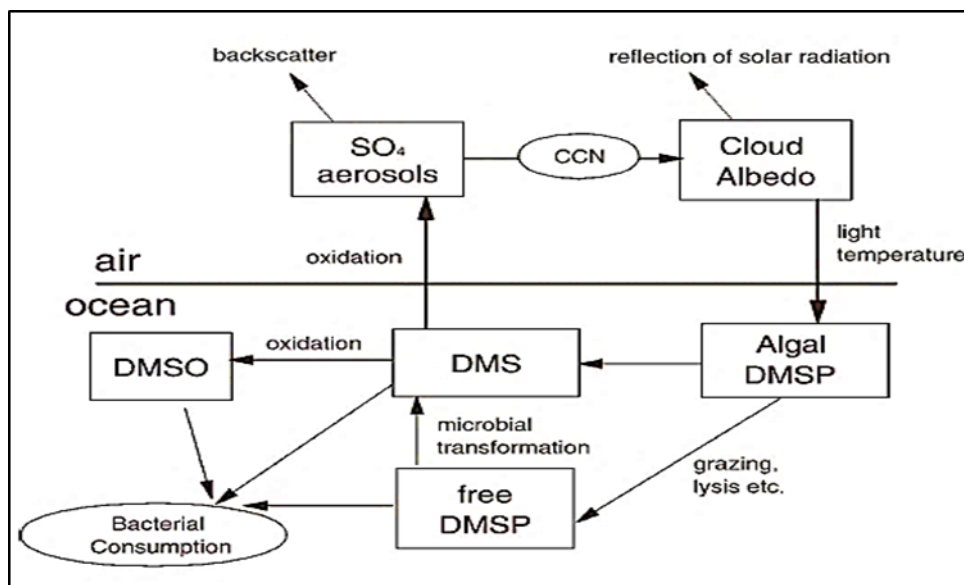


Figure 2.1 : Simplified diagram of DMS cycle (Lomans et al., 2002).

Table 2.2 : Natural sources of VOSCs emission rates to the atmosphere (Smet et al., 1998; van Leerdam, 2007).

Source	Sulfur compounds release (Tg S/year)						Total
	SO_2	H_2S	DMS	DMDS and MT	CS_2	COS	
Oceans	—	0-15	38-40	0.1	0.3	0.4	38.7-56.7
Salt marsh	—	0.8-0.9	0.58	0.13	0.07	0.12	1.7-1.8
Swamps	—	11.7	0.84	0.2	2.8	1.85	17.4
Soil and plants	—	3-41	0.2-4	1	0.6-1.5	0.2-1	5-48.5
Burning of biomass	7	0-1	—	0-1	—	0.11	7.1-9.1
Volcanoes	8	1	—	0-0.02	0.01	0.1	9.0
Total	15	16.5-70.6	39.6-45.4	1.3-3.4	3.8-4.7	2.7-3.5	78.9-142.6
Atmospheric concentration (ppb)	—	0.2	0.11	—	0.02	0.5	—
Atmospheric lifetime (days)	—	1	1	0.2 (MT)	12-40	730	—

2.2.2 Industrial sources

The contribution of anthropogenic emissions sources has a significant role in exceeding the odor threshold value to local concentrations, in contrast to natural emissions. The main emission sources of VOSCs is attributed to the composting and/or the anaerobic decay of protein's sulfur i.e. methionine and cysteine and

derivate. The anthropogenic sources, include a variety of industrial sources such as petroleum refineries, petrochemicals, production of viscose rayon, chemical reactions during manufacturing process in the Kraft paper pulping, food industry, pharmaceutical industries, thermal sludge-treatment plants, solid waste composting sites and the agriculture (e.g. animal breeding stations, swine and dairy manure wastewater) (Rappert & Müller, 2005; Smet et al., 1998). In such a composting plant, 8.3 mg of sulfur per kg of compost (fresh weight) are emitted during mushroom cultivation substrate production. The main odorous compounds emitted are H_2S , $(\text{CH}_3)_2\text{S}$, COS , CH_3SH , CS_2 , $(\text{CH}_3)_2\text{S}_3$, Me_2S , and $(\text{CH}_3)_2\text{S}_2$ with concentrations ranging between 24 and 840 ppbv. Also, over 65% of CS_2 production in worldwide is used in rayon manufacturing which requires 290 to 320 kg of CS_2 per ton viscose produced, of which 100 to 300 kg is lost to the atmosphere (Smet et al., 1998).

VOSCs are also present in the waste gases from municipal WWTPs, thermal sludge digestion processes, majorly DMS, as shown in Table 2.3. In brewery WWTP the measured waste gases consisted of 30 ppmv of DMS and 4 ppmv of H_2S . Moreover, facultative microorganisms formed VOSCs in oxygen-deficient parts of the plant. Also, in landfill gas, MT was found in concentrations of 44 ppm (van Leerdam, 2007).

Table 2.3 : VOSCs emissions from wastewater treatment plants (Sheng et al., 2008).

Source	Concentrations mg/m^3				
	DMS	DMDS	COS	CS_2	MT
Waste air	0.66-5.41	0.06-1.61	0.03-0.44	0.01-0.21	113-216.8
Wastewater	23.6-308.1	0.24-106.7	0.11-2.2	1.37-23.2	_____

Moreover, 2-3% of sulfur in the Kraft paper production process is transformed into MT, DMS, DMDS, and H_2S . The emitted concentrations for MT, DMS, and DMDS are 94.0, 16.6, and 21.7 ppmv, respectively. Also, MT is completely dissociated to methyl mercaptide ions in an aqueous solution of pH above 12 during the reaction of hydrosulfide ions and the methoxy lignin compounds of the wood, as in Simplified scheme for the formation and degradation of some VOSCs (Janssen et al., 2013). In addition, Ren (2014) detected the characteristics emission of VOSCs released from food waste processing plant. The results showed that the highest level of VOSCs was released from the hydrothermal reactor and the most abundant compound was ET

with an emission of 0.41mg/m^3 . While CS_2 , DMS and DMDS concentrations were 0.351 , 0.190 and 0.224 mg/m^3 , respectively.

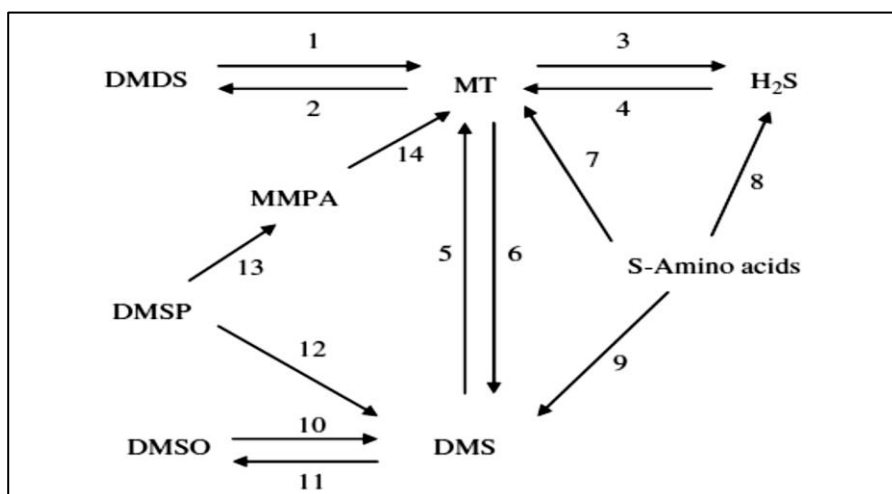


Figure 2.2 : Simplified scheme for the formation and degradation of some VOSCs (Janssen et al., 2013).

Odors in a petroleum refinery is another important source of VOSCs which involves hydrogen sulfide, mercaptans, sulfides, disulfides, and nitrogen compounds. Some typical refinery odorous compounds and their possible sources have been listed in Sources emissions of odors from refineries (Jafarinejad, 2016).(Jafarinejad, 2016). During crude oil distillation a low-boiling fraction like naphtha contains 2.5 up to 5 wt. % of sulfur. Accordingly, the US EPA regulations reduced the maximum allowable sulfur content for highway and non-road fuels from 500 to 15 ppm (w) per gallon in average (USEPA, 2016).

Table 2.4 : Sources emissions of odors from refineries (Jafarinejad, 2016).

Odor compounds	Sources
H_2S + trace of disulfides	Crude storage, distillation of gases, sulfur removal, flare stacks (cold flare)
DMS+ ET + MT	Effluent water, biological treatment plants, LPG odorizing spent caustic loading and transfer
Unsaturated hydrocarbons	Catalytic cracking unit, coking asphalt blowing, asphalt storage
Hydrocarbons	Product storage, American Petroleum Institute (API) and corrugated plate interceptor (CPI) separators
Benzene, toluene	Aromatic plants, Naphtha reformers
H_2S , mercaptans, hydrocarbons	Asphalt storage

Thus, in most of the petrochemical industries total sulfur content represent the key parameter in the quality control processes. Typically, in natural and synthesis, H₂S has to be below 4 ppm(v) to meet the sales specifications (Benschop et al., 2002). Based on the information in Table 2.5, it can be seen that H₂S and MT are the major sulfur compounds in various gas streams among the other species in sour gas streams.

2.3 Toxicological Effects of VOSCs on Humans and Animals

Primarily, H₂S can be absorbed by lungs easily and human exposures beyond 500 ppmv can cause nose, throat and lungs irritation, central nervous system paralysis, and loss of consciousness, also known as ‘knockdown’ (Chou et al., 2016; USEPA, 2003). While, H₂S concentration between 500-1000 ppmv can cause irregular heartbeat and immediate death according to (CCOHS, 2012; Smet et al., 1998; van Leerdam, 2007). As H₂S is readily detoxified in the body, the primary treatment of exposed persons consists of rapid removal from the contaminated environment (Smet et al., 1998). In addition, light sensitivity increments can be an indication of excessive exposure.

ET is more toxic than higher thiols and H₂S, even more toxic than DMS as reported in the inhalation studies with rats, as presented in Table 2.6.

The relatively low toxicity of DMS suggests that methylation of ET can be an effective detoxification method for rats (Janssen et al., 2013). The recent studies indicated that odorous sulfur compounds have an adverse effect on human health. Nevertheless, there is a lack of information about the health effects of ET and DMS even at low concentration exposure. Overall, the maximum concentration value (MAC) of VOSCs in the workplace must be less than or equal to 20 ppmv.

Table 2.5 : Sources emission and concentrations of some VOSCs (Roman, 2016).

Type of gas stream / source	Typical concentration									
	Unit	H ₂ S	MT	ET	PT	BT	DMS	DMDS	CS ₂	COS
Landfill gas	ppb(v)	540000	4000				1500	10	3300	
Landfill gas	ppb(v)	280000	1500				2600	210	240	
Landfill gas	ppb(v)	190	164000		2800	130	1700		60	710
Landfill gas	ppb(v)	110	4				7	20	2	
Landfill gas	ppb(v)	2200	14				77	4	125	
Synthetic natural gas	ppb(v)	150	130	400			220	230		
Liquefied petroleum gas	ppm(v)	2000	250					<10		50
Liquefied petroleum gas	ppm(v)	60	430	220						
Liquefied petroleum gas	ppm(v)		1500	5000						
Liquefied petroleum gas	ppm(v)	2000	1000	500						
Propane	ppm(v)	1000	600	10						500
n-butane	ppm(v)		1900	10000						
Gas samples from WWTP	ppb(v)						610	860	520	
Low pressure fuel gas	ppm(v)	12000	140	50						
Condensate from chiller separator	ppm(v)	90	151	139	159	10				
Anaerobic brewery WWTP	ppm(v)	4	30							
Rendering cookers	ppm(v)	<800	<200							
Kraft paper production	ppm(v)		100				20	20		

Table 2.6 : Toxicity limitation of VOSCs (Janssen et al., 2013; van Leerdam, 2007).

Sulfur compound	LC ₅₀ inhalation	LD ₅₀ oral	MAC (ppmv)
H ₂ S	444	-	1.6
CH ₃ SH	675-1664	-	0.5
CH ₃ CH ₂ SH	4970	1034	0.5
CH ₃ CH ₂ CH ₂ SH	7300	1730	-
CH ₃ (CH ₂) ₃ SH	4460	2575	-
CH ₃ SCH ₃	40,250	-	20
CH ₃ SSCH ₃	805	-	<20

LC₅₀: Concentration, which is lethal to 50% of the animals tested, LD₅₀: Dose, which is lethal to 50% of the animals tested, MAC: Maximum concentration value in workplace conditions

2.4 Technologies for VOSCs Abatements

The different technologies used for the treatment of gaseous emissions can be classified into physical, chemical and biological. For the selection of an appropriate treatment technique, a number of considerations must be taken into accounts, such as the composition and property of the waste stream, its quantity, and concentration, characteristics of the air or waste gas stream and the generation of by-products from the selected process.

2.4.1 Physical-chemical technologies

Physical-chemical technologies have been broadly implemented. The main merit of these technologies is low EBRT, rapid start-up, and high experience in design and operation (Ren et al., 2018). In this section, the different physical-chemical technologies used typically for waste gas treatment are briefly discussed.

2.4.1.1 Absorption

Usually, absorption techniques take place in packed scrubbers. It aims to transfer waste gases from air phase to the liquid phase, by contacting with a continuously trickling liquid. The mass transfer between gas-liquid phases depends on partitioning coefficient (Henry constant) and air/water concentrations gradient, temperature, and pH (Devinny et al., 1999; Kennes, 2013; Smet et al., 1998). There are different types of absorbents that used in the absorption process, i.e. water scrubbing, organic

physical scrubbing, and chemical scrubbing. Frequently, water is the most used scrubbing absorbent for hydrophilic waste gases while, silicone oil or polyethylene glycol is more adequate for hydrophobic waste gases (López et al., 2012; van Leerdam, 2007). However, high water flow rate to gas flow rate (L/G) is required for scrubbing VOSCs due to the high Henry constant of these compounds (Smet & Van Langenhove, 1998b). It is worth noting that light thiols MT, ET and PT can be scrubbed by an alkaline liquid with pH at least 11.0 (van Leerdam, 2007). Nevertheless, the most active and efficient oxidant for the chemical scrubbing of VOSCs is Hypochlorite (OCl^- , pH >6) (Smet & Van Langenhove, 1998b).

The main drawbacks of the chemical scrubbing are the relatively high energy input due to the regeneration of the solvent which involves the breaking of the bond between the pollutants and the solvent. Moreover, high investment and operating costs, since the pollution problem still remains as a new waste stream that generated from the transfer of pollutants from the gas phase to the liquid phase instead of being removed. Hence, a post-treatment step should be applied in order to treat emerged pollutants (Gómez, 2016; Kennes, 2013).

2.4.1.2 Adsorption

Adsorption systems consist of static beds of granular materials in vertical cylindrical columns. Accordingly, the gas phase contaminants are entering the column and retained in the surface of a solid phase adsorbent i.e. activated carbon AC, synthetic resins, clay minerals, zeolites, silica gel, and molecular sieves until contaminants “breakthrough” and clean air stream discharged out of the column (van Leerdam, 2007). The high moisture content, capacity, temperature etc. are crucial characteristics in system robustness (Devinny et al., 1999; Ren et al., 2018). Generally, the adsorption mechanism is efficient for abatement of VOCs with low vapor pressures and high molecular weights (Devinny et al., 1999; Kennes, 2013). Frequently, AC has high sorption capacity in VOSCs and H_2S removal based on physical adsorption mechanism, whereas DMS, DMDS, and CS_2 was removed very effectively (van Leerdam, 2007). Significantly, adding a few amounts of ozone (ppmv) to sulfurous gases prior to AC filter can extend filter bed life considerably (Smet & Van Langenhove, 1998b). Figure 2.3 highlighted the main differences between absorption and adsorption in a scrubber system.

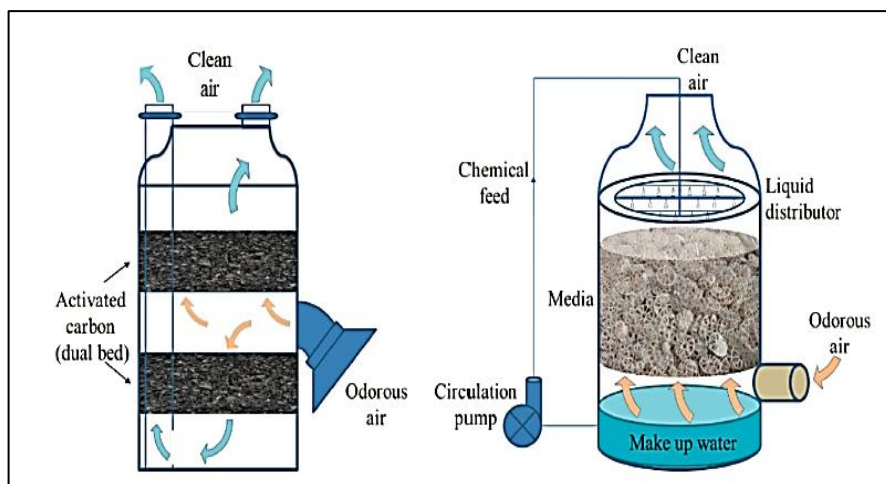


Figure 2.3 : Chemical absorption and adsorption scrubber systems (Ren et al., 2018).

2.4.1.3 Condensation

Condensation systems are based on the conversion of gases waste into a liquid by pressurization and/or by temperature reduction. These techniques have efficiently proved for VOCs controlling. Mainly, VOCs with a boiling point above 40°C, concentration more than 5000 ppmv, and relatively low mass flow rates (Gómez, 2016; Kennes, 2013; Rene et al., 2012). Typically, this technique can be applied to the applications in gasoline loading terminals and chemical reaction vessels. However, it is an economical method, particularly for concentrated waste air streams where there is recovery or recycles of some concentrated vapors (Devinny et al., 1999; Kennes, 2013).

2.4.1.4 Incineration

Incineration can be defined as complete combustion of the volatile compounds at a high temperature ranging between 300-1400 °C. Generally, it is broadly used as a secondary treatment for moderate gas flow, although, it is not economic for low concentration because of the high consumption of fuel amounts. Moreover, partial combustion generates more toxic compounds than the initial one i.e. NO_x, CO, and dioxins. Besides, an additional post-treatment may be required to deteriorate SO₂ emissions which results from the thermal oxidation of reduced sulfur compounds, posing ecosystem to global pollution i.e. acid rains (Smet & Van Langenhove, 1998b). Incineration does not allow the recovery of the contaminants, it requires a high operating and capital cost technique due to the high-temperature input that

necessary for complete combustion and oxidation (Devinny et al., 1999; Gómez, 2016; Kennes, 2013; Rene et al., 2012).

2.4.2 Biological technologies

In the last 25 years, full-scale applications of biological odor abatement technologies are becoming more popular, robust, and reliable alternative to conventional physical-chemical treatment systems (Barbusinski et al., 2017; van Leerdam, 2007). Besides, biological abatement methods do not require chemicals using and can be operated at normal temperatures (10-40 °C) and atmospheric pressure. Compared with the physicochemical treatments, biological methods such as bioscrubbing, biotrickling filtration, and biofiltration are less costly as illustrated in Table 2.7, simple to operate and benign to environment because the processes of microbial degradation are generally oxidative in nature and release ecologically harmless by-products such as carbon dioxide, water, sulfate, and nitrate (Barbusinski et al., 2017; Bindra et al., 2015; Estrada et al., 2010).

Because of the above mentioned reasons, they are considered intrinsically clean technologies and environment-friendly than physical and chemical technologies (Bajpai, 2014; Li et al., 2015).

Table 2.7 : Comparison of investment and operation costs for the main air pollution control technologies (Sercu, 2006).

Technology	Investment costs [EUR (m ³ /h) air]	Operating costs [EUR (m ³ /h) air]
Adsorption	13-103 7-28 12.7-98.5 *	9-30
Thermal oxidation	9-385 16.5-19.5 17-105	17-128
Catalytic oxidation		
Fixed catalyst	17-214	9-64
Fluidized catalyst	30-188	13-77
Absorption	13-60 11.2-14 12.7-57.7 7-140	21-103
Condensation	9-68	17-103
All biotechnologies	9-60	3-9
Biofiltration	4.2-13.9 5-150 5.9-13.7	

* For 50, 000 m³/h capacity.

However, bioprocesses used for the treatment of waste gases are mainly suitable for low to moderate pollutant concentrations (typically between 5-10 g/m³) and over a wide range of air flow rates, depending on its origin, the polluted gas flow can be as high as 100000 m³/h, as shown in Figure 2.4. Particularly, large gas flows are treated at municipal WWTPs (Janssen et al., 2013; Kennes, 2013). For compounds that are sufficiently water soluble and biodegradable, biological treatment methods can be considered as an attractive alternative to physical-chemical methods.

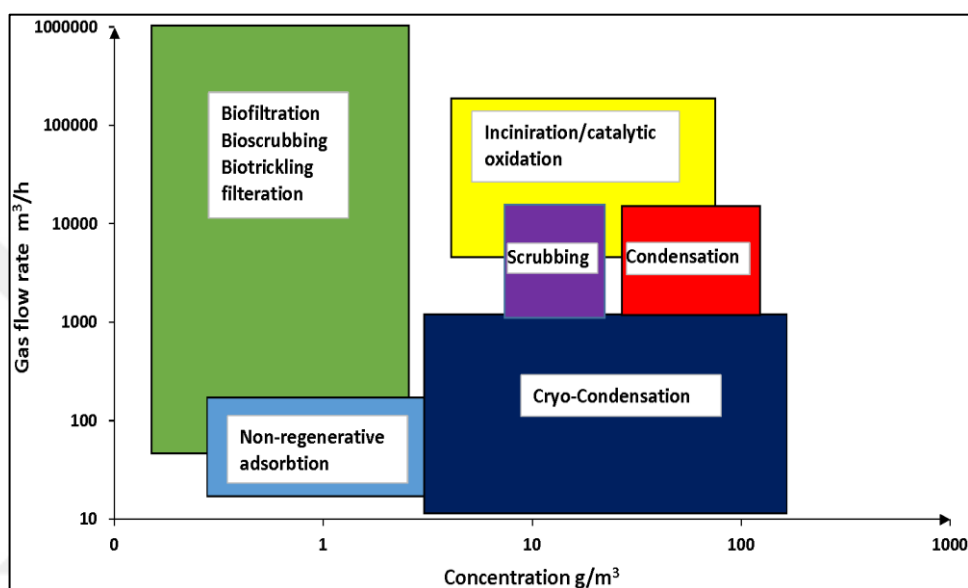


Figure 2.4 : Waste air streams treatment technologies as a function of air flow rate and concentration ranges (Li et al., 2015)

Traditionally, biofilters, bioscrubbers, and biotrickling filters are the main categories for air phase treatment technologies that based on absorbed volatile off-gases on aqueous, frequently, water followed by biodegradation (Smet et al., 1998). Recently, a combination of physical-chemical with biological techniques have been developed for hydrophobic and/or low biodegradable sulfur compounds (Li et al., 2015).

2.4.2.1 Biofiltration

The principle of the biofiltration is the oldest biotechnological method for removal of reduced sulfur compounds from the waste air streams since 1923 (van Groenestijn & Hesselink, 1993), as shown in Table 2.8. The pre-humidified gas is forced to flow through a bed packed with an organic or inorganic material and subsequently transferred and degraded at the attached biofilm, releasing clean air to the atmosphere (Kennes, 2010; Li et al., 2015).

Table 2.8 : Historical overview on biofiltration process (Bajpai, 2014).

Year	Events
1923	Biological methods proposed to treat odorous emissions.
1955	Biological methods applied to treat odorous emissions at low concentrations in Germany.
1960s	Biofiltration used for the treatment of gaseous pollutants both in Germany and the USA.
1970s	Biofiltration used with high success in Germany.
1980s	Biofiltration used for the treatment of toxic emissions and VOCs from industry.
1990s	More than 500 biofilters operating both in Germany and the Netherlands and biofiltration spreading widely in the USA.

The main advantage of the biofiltration system its low costs. Also, they are highly efficient with low molecular weight, high water solubility (hydrophilic gases), with simpler molecular bonds gases (Sercu et al., 2006). Besides, hydrophobic pollutants having $H < 10$ can be effectively treated due to the relatively high empty residence time (30-60 sec) and the high gas-liquid interfacial surface area ($300-1000 \text{ m}^2/\text{m}^3$) (van Groenestijn & Hesselink, 1993). The illustration of this process is depicted in Figure 2.5 A.

However, there are still major disadvantages behind, the limitation in controlling the operational conditions i.e. medium moisture and pH, temperature, and nutrient content, because of the intermittent feeding of the liquid phase (Devinny et al., 2017). Furthermore, large footprint requirements, since bed height is limited to 1–1.5 m (Sercu et al., 2006). And due to the absence in water recirculating continuation and the limited buffer capacity of common carrier materials, the acidic by-product will result from VOSCs breakdown causing an inhibition effect in the biofilter process (van Leerdam, 2007).

Typical applications of biofilters are used to treat malodorous gases i.e. NH_3 , VOCs, H_2S , DMS, DMDS, MT, etc. emitted from the processing of food wastes, wastewater treatment facilities, and composting and rendering plants. Bench and pilot scale studies using biofiltration techniques have shown that organic and inorganic sulfur compounds, such as H_2S , SO_2 , and VOSCs pollutants in industrial and municipal gaseous emissions can be successfully treated (Hort et al., 2009; Jaber et al., 2017; Luvsanjamba et al., 2008; Zhang et al., 2015).

2.4.2.2 Bioscrubbing

The first units of bioscrubbers were installed in the early 1980s to treat polishing ovens, smelting, and incinerators off-gases. Bioscrubbers was applied for handling high pollutant concentrations and large gas flows (Barbusinski et al., 2017). In the 1990s, the odors compounds i.e. H_2S , DMS, MM, NH_3 , and TMA that produced during sludge treatment process i.e. thickening, dewatering, or anaerobic digestion were treated by bioscrubbers (Nurul Islam et al., 1998). The bioscrubbing concept consists of absorption (physical separation) followed by the biological treatment in a liquid phase. Whereas, waste gas is contacted, hence, absorbed by the liquid phase, i.e. water in a spraying tower packed with inert materials as shown in Figure 2.5 B. The bioreactor effluent is recirculated to the top of the absorber unit, providing efficient gas cleaning of highly soluble pollutants (Barbusinski et al., 2017). Subsequently, the wastewater is treated in a bioreactor. Because of bioscrubbers is limited for the hydrophilic gaseous compounds treatment with $H < 0.01$, it is probably less popular than biofiltration (Kennes, 2010). This is of major drawbacks because most of the target air pollutants are volatile and poorly water soluble.

2.4.2.3 Biotrickling filtration

As the focus of this thesis is on the use of biotrickling filter, significant literature information in relation to their use in treating (VOSCs) has been provided.

Biotrickling filtrations have been developed to overcome the drawbacks of biofilters (Ren et al., 2018). Biotrickling filters can be categorized as an intermediate process between biofilters and bioscrubbers. The gaseous stream is forced through synthetic or natural inert packed medium covered with an active biomass as shown in Figure 2.5 C. The main feature of the biotrickling filter, is the continuous recirculation of the aqueous phase over the filter bed, allowing a better control of the reaction conditions (pH, temperature, nutrients addition, and intermediate removal). So that difficult applications are handled by a biotrickling filter more efficiently than by bioscrubbers and biofilters (Barbusinski et al., 2017).

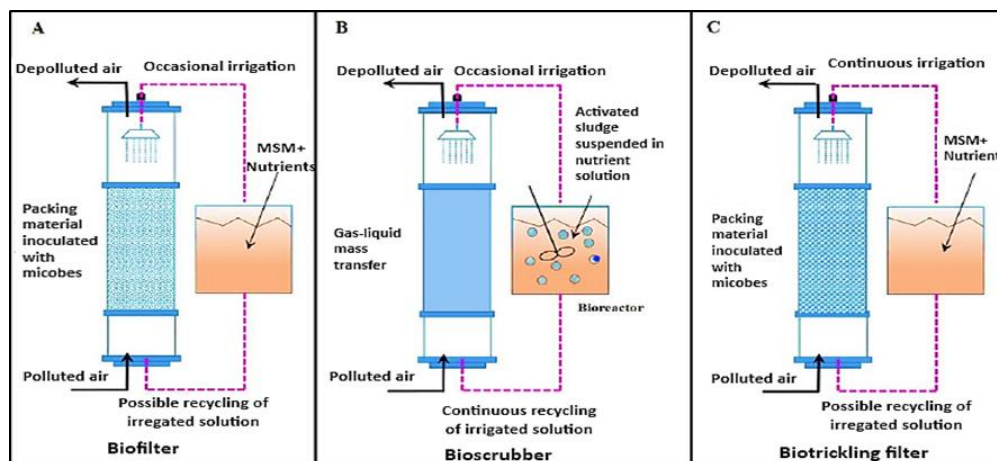


Figure 2.5 : Traditional biotechnological treatment. A: open biofilter; B: bioscrubber; C: biotrickling filter (Wu et al., 2010)

The advantages and disadvantages of bioscrubbing, biofiltration, and biotrickling filtration are summarized in Table 2.9.

Table 2.9 : Comparison of bioscrubbing, biofiltration, and biotrickling filtration (Cox & Deshusses, 2013; Groenestijn, 2013; Kennes & Thalasso, 1998).

	Advantages	Disadvantages
Biotrickling filtration	Simple and medium capital, low operating costs. Effective removal of pollutants including acid-producing ones. Low pressure drop. Good adaptation capacity of the active biomass.	Clogging by growing biomass if too much nutrient is added and high concentrations of VOCs are treated Gas transfer arising from the necessity of dissolving the gaseous pollutants in an aqueous phase.
Biofiltration	Simple and low capital and operating costs Effective removal of pollutants at low concentrations Low pressure drop No further waste streams produced Removal of reaction products by washing out, avoiding their possible inhibitory.	Filter bed replacement every 2-5 years Less suitable for high pollutant concentrations Moisture and pH sometimes difficult to control Particulate matter may clog the bed
Bioscrubbers	Easy control of the biological process, good adaptation capacity of the microbial biomass. Smaller volume of the equipment. Better pH control, and more reliable and predictable. No clogging problems of packing materials. Lower occurrence of toxic concentrations in the water phase	The gas transfer problems may arise due to the necessity to dissolve the gaseous pollutants in an aqueous phase. Only cost-effective for pollutants with a dimensionless Henry's coefficient below 0.01; More difficult to attain elimination efficiencies higher than 98%; Chance of the micro-organisms being washed out; and sludge disposal. Stagnation periods of some days are not permitted; More complicated start-up procedure; and higher operational costs.

2.5 Review Studies on VOSCs Removal by Biotechnologies

2.5.1 Anaerobic and aerobic systems

The technologies to remove VOSCs have received considerable attention in the last few decades. As aforementioned, the production and degradation of VOSCs have been studied intensively due to their impacts on global warming and on acid precipitation processes and because of their major role in the global sulfur cycle (Lomans et al., 1999). Furthermore, the anthropogenic activities, among which the combustion of fossil fuels is a major source. Consequently, a priority nowadays is to minimize emissions of these sulfurous compounds by, basically, biotechniques approach, to provide nuisance-free and healthy breathable air.

The bio-desulfurization processes mainly focus on the removal of H_2S but not on VOSCs, which also contribute to air pollution, notoriously difficult to biodegrade, and much more toxic to humans than H_2S (van Leerdam, 2007). The knowledge about the effects of biodesulfurization processes of VOSCs is relatively scarce. In the long term, cost-effective technologies are required to remove both H_2S and VOSCs to prevent air pollution and to meet the required product specifications, e.g. in the case of natural gas treatment (Roman, 2016).

In this context, Lomans et al. (1999) studied the aerobic and anaerobic degradation of DMS and MT in sediments slurries of minerotrophic peatland. The results pointed out that the maximum degradation capacity of DMS under aerobic conditions was 4.0 nmol/mL of sediment slurry/h. While under anaerobic conditions i.e. N_2 or H_2 shaken bottles, the maximum degrading capacities were 0.37 and 0.32 nmol/mL of sediment slurry/h, respectively. Kinetic analysis result in K_m values 6 to 8 mM and 3 to 8 mM for aerobic and anaerobic DMS degradation, respectively.

A two-stage biotrickling filter which inoculated with refinery sludge was developed for removing a mixture of H_2S , MT, and DMS. Where most of the H_2S was removed at pH 2 in the first stage- filter, while most of the MT and DMS were removed in the second- stage filter at pH 6.5. Higher removal efficiencies for gases mixture were tested i.e. 99% at inlet loadings 1150, 879 and 66 g $\text{S}/\text{m}^3/\text{day}$ for H_2S , DMS, and MT, respectively (Ruokojarvi et al., 2001).

In addition, a study was conducted by Zhang et al. (2006) to treat pulp and paper waste air pollutants, frequently DMS mixed with MeOH. The experimental results

obtained from three bench-scale biofilters packed with inorganic material showed that MeOH has a positive effect (11-fold increase) on the biofiltration of DMS. Furthermore, MeOH addition enhanced biomass viability by (3-fold) in the biofilters. However, the batch experiments suggest that MeOH addition has a competitive effect on DMS biodegradation. In the absence of MeOH, the metabolic by-products of DMS degradation was SO_4^{2-} , mainly, while the partial formation of S^0 was noticed when MeOH present. Hence, the study suggested an appropriate DMS/MeOH mixture should be provided.

van den Bosch et al. (2009) had developed a biotechnological process operated under natron-alkaline conditions (pH between 8.5–10) to overcome sulfidic by-products discharge when treating air streams containing H_2S and MT. In this process, the formation of the biosulfur particles consist of DMDS, dimethyl trisulfide (DMTS), and inorganic polysulfides in bioconversion process reacts with MT, hence the inhibitory effect of MT was diminished. Which emphasise the feasibility of biotechnological treatment at natron-alkaline conditions in H_2S and MT removal. The formation of these compounds has a negative effect on the biological oxidation rates of sulfide which were reduced by 50% at 0.05 1.5 and 1.0 mM for MT, DMDS, and DMTS, respectively.

An alternative process for the abatement and desulfurization of H_2S and VOSCs containing waste streams explored by Manconi and Lens (2009) which employs a silicon-based membrane to remove H_2S and VOSCs simultaneously. Sulfide and the VOSCs studied, i.e. MT, ET, and DMS were removed from the synthetic wastewater using a silicone rubber membrane. MT showed the highest mass transfer coefficient (k_{ov}) (8.72×10^{-6} m/s) and sulfide the lowest k_{ov} value (1.23×10^{-6} m/s). VOSCs adsorption had a passive effect on the overall (k_{ov}). When using Fe (III) EDTA as extractant k_{ov} for sulfide extraction was (5.81×10^{-7} m/s) i.e. one fold less than with anaerobic water (2.54×10^{-6} m/s). On the other hand, the removal efficiency of the sulfide increased from 60% up to 84%. Moreover, the formation of S^0 that attached on the membrane surface in anaerobic water limited mass transfer. Overall, membrane extraction process for sulfide and VOSCs from a synthetic wastewater solution showed a reliable alternative to treat VOSCs emissions efficiently.

An et al. (2010), have been compared in their study the ET biodegradation performance by two strain, namely RG-1 and B350 inoculated in two biotrickling filter. The results showed that RE for both RG-1 and B350 declined significantly from 100% to 70.90% and 47.20% when EBRT decreased from 332 to 66 sec, respectively. Corresponding to EC, the maximum EC was attained at EBRT 83 sec, i.e. EC was 38.36 g/m³/h for RG-1 strain (RE= 89.20%) and 25.82 g/m³/h for B350 strain (RE = 57.10%). As a result, RG-1 strain showed better performance than strain B350 in ET biodegradation.

Also, Ramírez et al. (2011) used two biotrickling filters in series for H₂S, MM, DMS and DMDS treatment. The first one was inoculated with *Acidithiobacillus thiooxidans* (BAT) and the second one with *Thiobacillus thioparus* (BTT). They highlighted the effect of H₂S on biodegradation of the VOSCs i.e. MM, DMS, and DMDS. H₂S concentration increment from 23 to 293 ppmv had an inhibitor effect on VOSCs degradation. Where the REs leveled off from 97 to 84%, 86 to 76%, and from 83 to 67% for DMS, DMDS, and MM, respectively. The sequence order of the ECs of these VOSCs was as following: H₂S > DMDS > DMS > MM. Hence, ECs of H₂S-S, DMDS-S, and MM-S were 57.5, 36, and 9.8 g/m³/h, respectively.

The removal performance of aerobic biotrickling filter seeded with *Lysinibacillus sphaericus* RG-1 was evaluated by Wan et al. (2011) for treating ET, DMDS, and thioanisole in single, binary and ternary gas mixture pattern. They reported that the sole ET, DMS, and thioanisole was completely removed (i.e RE 100%) when inlet concentration less than 1.05, 0.81 and 0.33 mg/L, respectively, and EBRT 110 sec. Also, in binary (ET:DMDS 1:1) and ternary (ET:DMDS:thioanisole 3:2:1), complete removal (i.e. RE100%) was achieved. The kinetic parameters were calculated for ET, DMDS, and thioanisole, where the maximum removal rate (*V_{max}*) was 56.18, 57.14 and 22.78 g/m³/h, respectively. Accordingly, RG-1 strain has a significant potential for degrading sole, even mixture of ET, DMDS and thioanisole.

2.5.2 Anoxic system

Surprisingly, there was a lack in studies related to optimize and detect the simultaneous removal of both organic sulfurous compounds and nitrate from gas waste streams although using nitrate as an electron acceptor instead of O₂ is more economic since the considerable cost of aeration process can be saved.

Lomans et al. (1997), were detect MT concentrations between 4 - 40 mM in 32 sample of sediment slurries that collected from different freshwater estuaries. The maximum production rates of MT was 1.44 $\mu\text{mol/L}$ of sediment slurry/day which attained after methanogenic and sulfate-reducing organisms were inhibited. Due to the high sulfide concentrations in the sediment slurries, MT production rates increased dramatically from 5 to 80 pmol of MT/mL of sediment slurry/h. Evidently, it was found that H_2S and DMS generated in methylation mechanism resulting in MT and DMS in freshwater sediments, respectively. The experiments supported that high concentration of H_2S (methyl acceptor) is the main factor which stimulates the methyl groups to follow MT or DMS route rather than other possible compounds.

Mahmood et al. (2007) used a lab scale anoxic-sulfide oxidizing bioreactor for treatment of synthetic wastewaters containing sulfide and nitrite. The maximal removal rates were 13.82 and 16.311 $\text{kg/m}^3/\text{day}$ for S^{2-} and NO_2^- , respectively, at HRT 2.4 hr. The results showed that under high sulfide concentrations i.e. 1920 mg/L, RE was equal to even more than 89%. At $\text{NO}_2^-/\text{S}^{2-}$ 0.93, there was partial oxidation of S^{2-} and higher concentrations of NO_2^- released in the bioreactor up to 2265 mg/L. When HRT decreased from 36 to 18 hr, NO_2^- was more critical than S^{2-} in bio-oxidation process. The results of the batch degradation and stoichiometric analyses showed that 89–90% of S^{2-} was reduced by NO_2^- . When NO_2^- concentrations were above 2265 mg/L, considerable amount of NH_3 i.e. 200–550 mg/L was accumulated in the bioreactor results process inhibition.

Cai et al. (2008), investigated the effect of $\text{S}^{2-}/\text{NO}_3^-$ molar ratio in the simultaneous removal of S^{2-} and NO_3^- . Where three $\text{S}^{2-}/\text{NO}_3^-$ molar ratios 2.5, 1.0, and 0.625 were selected. The maximum volumetric removal rates i.e. 4.86 $\text{kg/m}^3/\text{d}$ and 0.99 $\text{kg/m}^3/\text{d}$ for S^{2-} -S and NO_3^- -N, respectively, were achieved at S/N molar ratio 2.5. Moreover, S^0 and nitrogen were increased when the S/N molar ratio 2.5 rather than 1.0 or 0.625.

In another study, Campos et al. (2008) investigated the influence of S/N ratio in batch experiments on the autotrophic denitrification activity using thiosulfate as substrates and NO_3^- as oxidant. When S/N ratios were between 1.16 and 2.44 g/g, NO_2^- was the main end product. The inhibitory effects of NO_2^- and SO_4^{2-} were clearly noticed over the process while $\text{S}_2\text{O}_3^{2-}$, acetate, and NaCl have no significant effects at the concentrations tested. Similarly, under autotrophic denitrification experiments,

sulfur was not favorable for these microorganisms as electron donor, in contrary sulfide was oxidized successfully.

Soreanu et al. (2008) studied the removal of H_2S from anaerobic digester in real-time operating conditions using anoxic biotrickling filter fed with biogas flowrate ranged between 10 to 70 L/h and H_2S concentrations 1000 to 4000 ppmv. Nitrate was continuously fed in trickling liquid from batch reactor wastewater effluents as nutritive solution and electron acceptor. The study reported that better removal performance can be realized when NO_3^- concentration is about 200 mg $\text{NO}_3\text{-N/L}$. In another hand, increasing biogas flowrate from 40 L/h to 70 L/h and H_2S concentration from 1000 to 2000 ppmv results decreasing in RE from 99% to less than 80%. The observed results of this study showed that this unique biotechnology represents a platform for biogas removal in full-scale process.

The performance of the anoxic sulfide-oxidizing reactor under pH range of 4–11 was investigated by Mahmood et al. (2008). Sulfide was partially oxidized to SO_4^{2-} at influent pH of 7–7.5 during S^{2-} and NO_2^- loading. At acidic pH 3, S^{2-} and NO_2^- removal rates dropped significantly, where microorganisms under acidic condition were more sensitive compared with alkaline pH. Hence, anoxic sulfide-oxidizing reactor can be operated in a pH range 5–11.

Montebello et al. (2012), tested the aerobic and anoxic conditions in two biotrickling filters at neutral pH for H_2S and MT removal. Initially, MT concentration was gradually increased from 0 to 75–90 ppmv at constant H_2S loading rates of 53–63 g $\text{H}_2\text{S-S/m}^3\text{/h}$. Accordingly, ECs of around 1.8 g $\text{MT-S/m}^3\text{/h}$ were resulted. After that, the MT loading rates were increased by decreasing EBRTs from 180 to 30 sec. Maximum ECs of H_2S was found for both filters were between 100 and 140 g $\text{H}_2\text{S-S/m}^3\text{/h}$. High H_2S loading rates had a negative impact on MT's ECs in both filters. Sulfur mass balances showed that the impact of S^0 accumulation was reduced since MT and S^0 can react at neutral pH. Finally, the co-treatment of H_2S and MT as a feasible operation in biogas abatement under aerobic and anoxic conditions can be considered.

In a lab-scale continuous flow stirred tank reactor Doğan et al. (2012) studied sulfide bio-oxidation using NO_2^- as an electron acceptor. The removal efficiency of sulfide remained above 80% throughout the study period, although sulfide loading rates increased from 0.47 to 2.16 kg $\text{S}^{2-}\text{/m}^3\text{/day}$. The thermodynamic calculations of S^{2-}

/NO₂⁻ molar ratios suggesting main end-product S⁰ and SO₄²⁻ were 0.44 and 1.74, respectively. Hence, when S²⁻/NO₂⁻ molar ratio was above 1.48, the end product was mainly SO₄²⁻. Otherwise, a mixture of S⁰ and SO₄²⁻ can be distributed as end-products under the 1.48 ratio.

In real scale bioscrubber, Turker et al. (2012) carried out biogas desulfurization using aerobically treated wastewater containing a mixture of NO₃⁻ and NO₂⁻ from full-scale activated sludge treatment plant. When the volumetric sulfide loading rates ranged between 2 and 4 kg S²⁻/m³/d more than 95% of H₂S removed from biogas. The optimum wastewater/biogas ratio was 2-3 m³/m³ and minimum EBRT around 10 min for maximum removal rates of H₂S. The study work revealed that sulfide and nitrogen removal can be integrated efficiently with wastewater treatment plants.

Fernández et al. (2013a), conducted a study using anoxic biotrickling filter to remove H₂S. They studied the influence of the H₂S inlet concentration, nitrate feeding regime (manual and controlled) and liquid flow rate on the elimination capacity of the biotrickling filter. The results showed that RE decreased from 99% to 85% when the H₂S inlet loads increased from 120 to 180 g S/m³/h. The main by-product was S⁰ i.e. 68.4 ± 15.7% with an SO₄-S/S⁰ ratio of 0.46 since biotrickling filter was running at N/S molar ratio of 0.77 ± 0.32.

Cano-Santana (2015) also tested the effect of S/N molar ratios between 0.3-2.4 in a completely stirred tank reactor for sulfide removal using NO₃⁻. The denitrification efficiency of the *Thiobacillus* and *Thiomicrospira* reached up to 80% while sulfide was completely removed at S/N molar ratio 0.85, and the final metabolites product was SO₄²⁻. In contrast, nitrogen was reduced to ammonia at higher S/N molar ratio i.e. 1.3, hence accumulation in S⁰ occurred. The specific autotrophic denitrification rates increased from 5 to 26 mg N-NO₃/gVSS/h when S/N ratios increased from 0.8 to 1.2, respectively.

A review study prepared by Dumont (2015) aimed to summarize performance, description, and application area of aerobic and anoxic operating systems used for biogas cleaning from H₂S. The ability assay of aerobic and anoxic bioreactors (biotrickling filters, bioscrubbers, and a combination of chemical scrubbers and bioreactors) to degrade H₂S was presented. Using lab- scale biopresecees for biogas cleaning are feasible and provide the same performance regardless of their operating

mode. The major drawback of these bioprocesses is clogging due to S^0 deposition and biomass accumulation. In order to limit clogging effects, EC should not be higher than $90 \text{ g/m}^3/\text{h}$ at industrial-scale. For the development of aerobic processes at full-scale, the need to control the oxygen mass transfer accurately remains a key issue. As a result, the aerobic processes alone are probably not the most suitable bioprocesses for the treatment of biogas highly loaded with H_2S . For anoxic bioprocesses exploiting wastewater from treatment plants as a free source of nitrates represents an interesting opportunity for the development of innovative bioprocesses enabling the simultaneous removal of H_2S and NO_3^- . However, the scale-up of the laboratory process to a full-size plant remains a challenge.

Cano et al. (2016), stated that a lab-scale anoxic biotrickling filters model can be efficiently clean up biogas from H_2S . The effects of wide ranges of operational parameters were investigated, among these, N/S molar ratio (0.33- 0.4). The summarized results declared that optimum trickling liquid velocity was 10 m/h , the maximum EC $282 \text{ g S/ m}^3/\text{h}$ corresponding to RE 97.5% at EBRT 164 sec and H_2S concentrations $10,000 \text{ ppmv}$. In addition, increasing the height: diameter ratio has significant improvement in the anoxic biotrickling filters performance. For instance, at height: diameter ratio (9.8), the RE can be reached more than 99.55% at low EBRT 75 sec and for H_2S inlet concentration of 2000 ppmv . By increasing N/S molar ratio from 0.33 to 0.4, the maximum production of S^0 as metabolic products shifted from 91.5 to 98 %.

Another study conducted by Li et al. (2016) for simultaneous biogas desulfurization and wastewater denitrification. Two biological system i.e. biotrickling filter and a bio-bubble column were used in this study to investigate the effect of S/N on biogas desulfurization performance. The obtained results confirm that S/N molar ratio is inversely proportional with removal efficiency of H_2S . Where H_2S removal efficiency significantly raised from 66 up to 100 % when S/N molar ratio decreased from 3.6 to 0.7. In contrast, denitrification efficiency decreased from 100 to 70 % in both bioreactors. The intermitted feeding mode of nitrate increased sulfate production while H_2S removal efficiency did not affect evidentially. Due to the differences in gas-liquid modes, biotrickling filter performance surpassed bio-bubble column.

An evaluation study for H₂S removal from biogas using anoxic biofilter was introduced by Jaber et al. (2017). Whatever, N/S molar ratio was i.e. 0.4, 0.89 and 1.6, the resulted end-product of desulfurization process was a mixture of SO₄²⁻ (55%) and S⁰ (45%). However, the experimental results approved that H₂S concentrations up to 1100 ppmv are efficiently treated in anoxic biofilters at an EBRT of 300 sec, corresponding to RE 100% and maximum EC = 30.3 g/m³/h.

Finally, López et al. (2018) implemented the application of feedforward control strategy through nitrate addition in an aerobic and anoxic biotrickling filter. At the highest H₂S loading rate (141 g S-H₂S/m³/h), 68.4% and 62.6% of H₂S concentrations were removed in aerobic and anoxic biotrickling filters, respectively. In the anoxic biotrickling filters, the sulfate selectivity was kept constant at 32.8%±0.8% at loading rate above 49.2 g H₂S-S/m³/h and N/S_{in} molar ratio between 0.96 and 0.38, while it was 100% in aerobic one. However, in anoxic biotrickling filters, the feedforward strategy in nitrate addition was shown to be a robust strategy for reducing load fluctuations impact.

However, some extra research studies related to VOSCs treatment using traditional and non-conventional (combined) biotechnologies are presented in Table 2.10.

Table 2.10 : Survey of previous studies for biological removal of VOSCs emissions (Li et al., 2015; Mudliar et al., 2010; Ren et al., 2018; Wu et al., 2010).

Bioreactor type	Target pollutant	Source	Scale	C _{in} /loading	RE/EC	EBRT sec
Biofilter	H ₂ S	wastewater	Lab-scale	303–6071 mg/m ³	95 %	29–152
	H ₂ S		Lab-scale	227–1136 mg/m ³	99 %	60
	H ₂ S		Pilot-scale	3.2 g/m ³ /h	99 %	50
	H ₂ S	landfill gas	Lab-scale	3.8–7.6 mg/m ³	82 %	60
	H ₂ S				90–97 %	
	DMDS				90–97 %	
	ET	sewage sludge and yard waste composting	Pilot-scale	0.4–2.5 g/m ³ /h	100 %	60
	ET; DMS; DMDS					
	H ₂ S, MM		40,000 m ³ /h	10 mg/m ³	83 % (H ₂ S); 53 % (MM)	113
	DMS	rendering plant	Lab-scale	0.484 g/m ³ /h	62–74 %	384
	DMS		Lab-scale	9.4 g/m ³ /h	100 %	30

Table 2.10 (continued): Survey of previous studies for biological removal of VOSCs emissions (Li et al., 2015; Mudliar et al., 2010; Ren et al., 2018; Wu et al., 2010).

Bioreactor type	Target pollutant	Source	Scale	C _{in} /loading	RE/EC	EBRT sec
	DMS	pulp and paper industry	Bench-scale	4–28 g/m ³ /h	71 ± 11 %	360 ± 20
	H ₂ S		Lab-scale	3.8-7.6 mg/m ³	100	110
	DMDS				95	70
	ET				82	290
	H ₂ S	swine farm	On site	200 mg/m ³	100	
	DMS			8.8 mg/m ³	21	150
	MT			22 mg/m ³	66	
	H ₂ S			140 mg/m ³	99.5	
	DMDS	swine farm	On site	936 mg/m ³	97	115
	CS ₂			618 mg/m ³	82	
	MT			330 mg/m ³	100	
	H ₂ S	swine farm	On site	140 mg/m ³	100	130
	DMDS			625 mg/m ³	100	111
	CS ₂			448 mg/m ³	100	
Bioscrubber	H ₂ S		Lab-scale	303 mg/m ³	98 %	12.71
	H ₂ S		Lab-scale	32–326 g/m ³ /h	80 % at 37 g/m ³ /h	63
	H ₂ S		Pilot scale	83–916 g/m ³ /h	95 %	600

Table 2.10 (continued): Survey of previous studies for biological removal of VOSCs emissions (Li et al., 2015; Mudliar et al., 2010; Ren et al., 2018; Wu et al., 2010).

Bioreactor type	Target pollutant	Source	Scale	C _{in} /loading	RE/EC	EBRT sec
Biotrickling filter	H ₂ S		Lab-scale	3.8–27.3 mg/m ³	98 %	1–6
	H ₂ S		Lab-scale			
	MT	WWTP	Lab-scale	0.75-4.9 mg/m ³	90 %	4-84
	Toluene α -pinene,					
	H ₂ S	WWTP	Lab-scale	10-18 ppm	99%	13-19
	MT					
	DMS					
			Lab-scale	<25 mg/m ³	100%	123
	DMS		Lab-scale	300-650 mg/m ³	65-100%	53-79
	H ₂ S		Lab-scale	20-25 mg/m ³	47.8-100%	7-50
	MT					

Table 2.10 (continued): Survey of previous studies for biological removal of VOSCs emissions (Li et al., 2015; Mudliar et al., 2010; Ren et al., 2018; Wu et al., 2010).

Bioreactor type	Target pollutant	Source	Scale	C _{in} /loading	RE/EC	EBRT sec
Combined-bioreactor	H ₂ S	WWTP	Lab-scale	30–238 mg/m ³	98 %/22 g/m ³ /h	16
	H ₂ S		Pilot scale	84 g/m ³ /h	97.7 ± 0.3 %	120
	TAS		Lab-scale	0.59–5 g/m ³ /h	99 %	25
	ET		Lab-scale	1.2 × 10 ³ mg/m ³	100 %	66
	MM		Lab-scale	1.05 × 10 ³ mg/m ³	100 %	110
	DMS		Lab-scale	160–192 mg/m ³	1.8 g/m ³ /h	180
	SO ₂		Lab-scale	407 mg/m ³	90 % / 8.3 g/m ³ /h	120
	H ₂ S		Lab-scale	0.18 mg/m ³	1.49 × 10 ⁻² g/m ³ /h	60
	ET			0.85 mg/m ³	7.09 × 10 ⁻² g/m ³ /h	
	DMS			0.22 mg/m ³	1.85 × 10 ⁻² g/m ³ /h	
Bioreactors integrated with non-thermal plasma	DMS		Lab-scale	70–80 mg/m ³	96 %	10.3

Table 2.10 (continued): Survey of previous studies for biological removal of VOSCs emissions (Li et al., 2015; Mudliar et al., 2010; Ren et al., 2018; Wu et al., 2010).

Bioreactor type	Target pollutant	Source	Scale	C _{in} /loading	RE/EC	EBRT sec
Bioreactors integrated with an adsorption unit	H ₂ S, MM, DMS	night soil treatment plant	Lab-scale	303 mg/m ³ (H ₂ S)	100 % (H ₂ S) 93 % (MM) 97 % (DMS)	
Membrane bioreactor	DMS		Lab-scale	5–270 g/m ³ /h	5–200 g/m ³ /h	8–24
	DMS		Lab-scale	64 g/m ³ /h	54 g/m ³ /h	24
	DMS		Lab-scale	2.1 g/m ³	100 %/258 g/m ³ /h	32
	DMS		Lab-scale	5–270 g/m ³ /h	5–200 g/m ³ /h	8–24
	DMS		Lab-scale	64 g/m ³ /h	54 g/m ³ /h	24
	DMS, Toluene Hexane		Lab-scale	312 g/m ³ /h	77.6 ± 13.0 %	20–30
Fungal bioreactor	ET		Lab-scale	45 g/m ³ /h	98 %/26 g/m ³ /h	58
Thermophilic Bioreactor	SO ₂		Lab-scale	100–200 mg/m ³	93.10 %/50.67 g/m ³ /h (60 °C)	23
	H ₂ S		Lab-scale	0 –1.0 × 10 ⁵ mg/m ³	37.1 ± 1.7 g/m ³ /h	120

2.6 Biotrickling Filtration Removal Mechanism

In relevance to Table 2.8, biotrickling filters have higher performance in comparison to biofilter and bioscrubbers, especially in acidic and/or alkaline compounds. In addition, it exhibits defined control of pH, temperature, nutrient feeding, and toxic metabolic endure. However, some drawbacks in biotrickling filtration processes are exhibit i.e. clogging problems, mass transfer limitation, etc. Essentially, there are some critical parameters can limit the removal efficiency of the gaseous pollutants when using biotrickling filtration as treatment concept. Thus, investigation of these parameters is necessary to enhance and improve the removal efficiency of biotrickling filter as summarized inFigure 2.6.

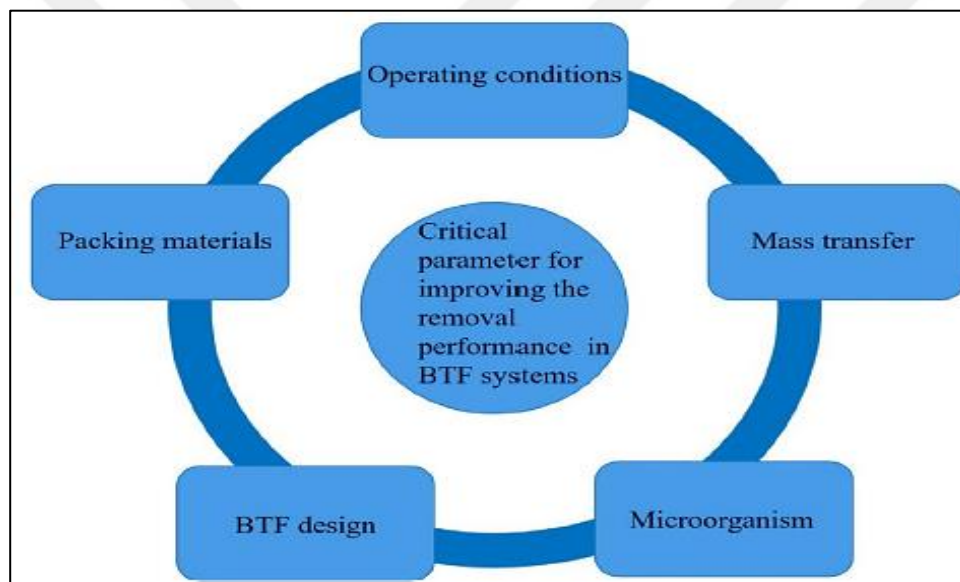


Figure 2.6 : Critical parameters of biotrickling filter systems for the removal of gaseous pollutants (Wu et al., 2010).

In biotrickling filter, the removal mechanism for waste air streams is a combination of various physical, chemical, and biological activities in one column. Where contaminated air stream forced co- or counter-current through packing bed, usually, inorganic material to be absorbed by the liquid layer (nutrients) which covers biofilm surface (Cox & Deshusses, 2001; Wu et al., 2018). Hence, the microorganisms break-down and utilize the nutrients and air contaminates simultaneously, as shown in Figure 2.7. Subsequently, the dissolved substances are metabolized to produce a new biofilm, secondary by-products, and CO₂ which release to the atmosphere and/or part of it dissolved in the aqueous phase to form carbonate.

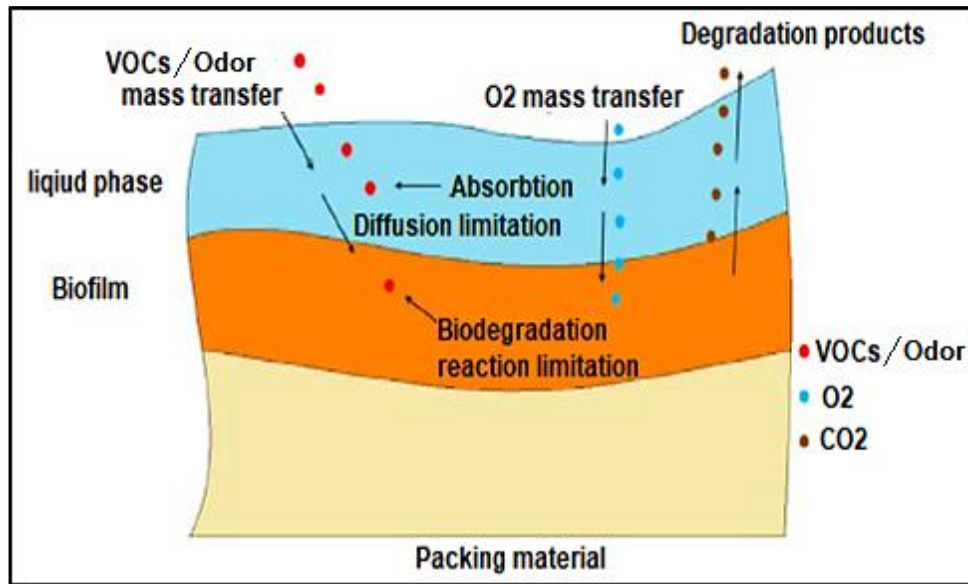


Figure 2.7 : Demonstration of consequent mechanisms within biotrickling filter (Wu et al., 2018).

In all biotechnologies, the removal mechanism consists of two combinations of processes mass transfer (diffusion limitation) and biodegradation (reaction limitation) (Kennes, 2010). Mass transfer or diffusion limitation can be defined as the transfer of the gaseous pollutants from the gas phase to the liquid phase that differs in concentration and not in balance at the two phase's interface according to Henry's constant as presented in Figure 2.8.

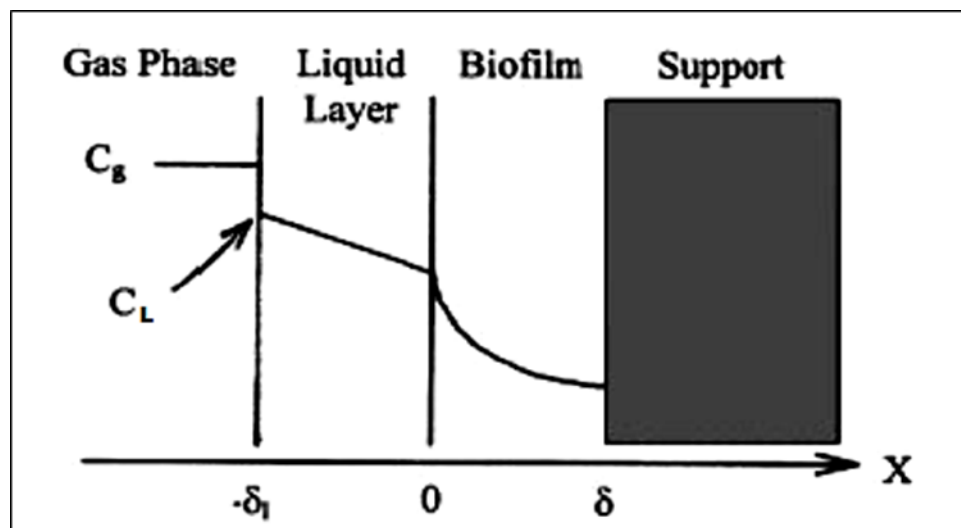


Figure 2.8 : Illustration of typical gas/liquid mass transfer for biological waste gas treatment (Kennes & Thalasso, 1998).

The mass transfer rate can be presented by the following equation (Kennes, 2010; Kraakman et al., 2011).

$$R = k_L a \left(\frac{C_g}{H} - C_L \right) \quad (2.1)$$

Where:

R = mass transfer rate (g/m³/sec)

k_L = overall interfacial mass transfer coefficient (m/sec)

a = interfacial area per volume unit (m²/m³)

C_g = concentration in the gas phase (g/m³)

C_L = concentration in the liquid phase in equilibrium with the gas phase (g/m³)

H = Henry coefficient (dimensionless).

Substances with ($H < 0.1$) are considered volatile with high toxicity risk (reaction limitation), and higher values ($H > 1$) are the less soluble (mass transfer limitation) as illustrated in the classification diagram in Figure 2.9 (Muñoz et al., 2012).

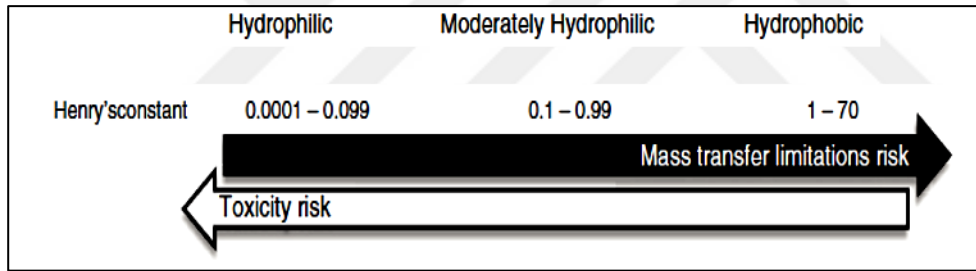


Figure 2.9 : Henry's coefficient classification in terms of mass transfer limitation and microorganism's toxicity risk.

Essentially, the mass transfer velocity (k_L) coefficient depends on the physical-chemical properties of the gas and liquid i.e. solubility, salt, organic content viscosity, pH, and temperature (Kraakman et al., 2011).

$$k_L = \frac{D_{AL}}{\delta_{film}} \quad (2.2)$$

Where

D_{AL} = the gaseous pollutant diffusivity in the liquid (m²/ sec).

δ_{film} = liquid film thickness (m).

The term volumetric coefficient denoted to $k_L a$ (per sec) since k_L and a cannot be obtained separately.

In order to differentiate between diffusion limitation and reaction limitation, Wu et al. (2016), had affixed inlet loading with high EBRT which means inlet concentration was high with low gaseous flow rate. Accordingly, the water covering the biomass surface was saturated with gaseous pollutants; thus, the degradation reaction was under reaction limitation control. In contrast, at low EBRT, the inlet concentration was low with a high gaseous flow rate. So, the contact time between the gaseous pollutants and the water was very short and most of the gaseous pollutants purge-out the biotrickling filter, hence, the diffusion limitation was the controlling process.





3. MATERIALS AND METHODS

The experimental work was subdivided to two main sections: the first one related with adaptation and acclimation of the microorganisms to anoxic conditions. After then the determination of the kinetic parameters in batch experiments. The second part was related to the start-up of a lab-scale biotrickling filter model for treating target pollutants (ET and DMS) separately and in combination.

3.1 Adaptation Procedure

Batch experiments were conducted for five cycles following the experimental procedure of Carvajal et al. (2018) using 100 mL of inoculum under anoxic denitrifying conditions; a 1200 mL sterile serum bottle in duplicate was sealed with Teflon-coated silicone septa and aluminum crimp caps (to avoid the volatilization of the odorous gas during the experiments) and stirred at 300 rpm, as shown in Figure 3.1. All experiments were conducted at room temperature ($25 \pm 2^\circ\text{C}$).

ET and DMS were injected in liquid form into the cultures through a Teflon-coated silicone septum using a 10 μL syringe (Hamilton, USA). Because of their readily volatile characteristics, they transferred to the gas phase in a few minutes. Biomass samples were taken at the end of the experiment for total and volatile suspended solids (TSS and VSS).

Two sets of batch experiments were conducted for biodegradability; 100 mL of inoculum with 300 mg/L and 3000 mg/L of (VSS) were used to establish the biodegradability and behavior of the microorganisms under anoxic conditions.

To create O_2 -free conditions, each bottle was flushed with N_2 gas, and NO_3^- was supplied as an anoxic electron acceptor according to the derived stoichiometric molar ratio.



Figure 3.1 : Adaptation experiments for ET and DMS in 1200 mL bottle inoculated with 100 mL inoculum at VSS = 300 and 3000 mg/L.

3.2 Inoculum

A granular biomass was collected from an anoxic bioreactor tank in Kemberburgaze treatment plant for landfill leachate (Istanbul, Turkey) in order to decrease the acclimation period of the microbial community to anoxic biodegradation. The particle size distribution PSD of the inoculum was $d_{(0.5)} \sim 33 \mu\text{m}$ and $d_{(0.9)} \sim 0.79 \mu\text{m}$ which estimated by Mastersizer Hydro 2000 MU (A) model in Memtek lab, as shown in the PSD hydrograph presented in Figure 3.2.

The inoculum was prepared by suspending one liter of bacterial cells in distilled water and centrifuging it for 10 minutes at 3000 rpm. The obtained cell pellet was re-suspended in 100 mL of MSM. The next generation sequence (NGS) processes and analyses for the inoculum were conducted following the protocol in ZymoBIOMICS[®] Service-Targeted Metagenomic Sequencing (Zymo Research, Irvine, CA). The microorganisms' diversity at the phylum level comprised the following relative abundance percentages: *Proteobacteria* 36.6%; *Bacteroidetes* 14.8%; *Actinobacteria* 8%. The predominance of these bacteria may be attributable to the potential for sulfur oxidation, sulfate-reduction, and degradation of the high molecular weight of hydrocarbons contained in leachate (Stevens et al., 2005; Thomas et al., 2011; Wei et al., 2013). The following sections explain the detailed information about the NGS test.

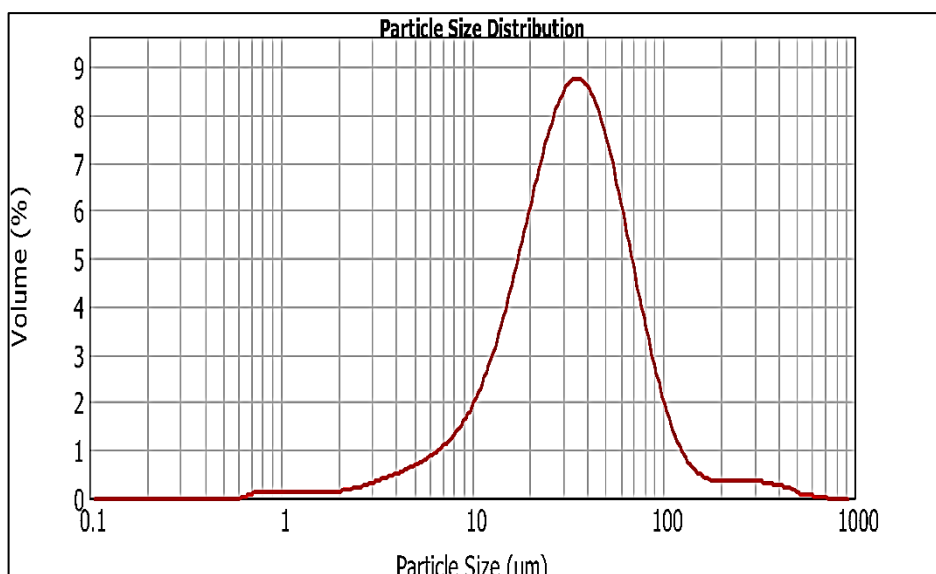


Figure 3.2 : Particle size distribution hydrograph of the sludge inoculum.

3.2.1 Microbial samples collection and preservation

The samples for NGS analysis were collected from the suspended sludge inoculum and the packing medium of the anoxic biotrickling filter by the end of the operation period and preserved at -4°C . It is worth noting that samples were collected from ABTF by scrubbing all polyethylene rings. Hence, the collected samples were representative of the whole media depth.

3.2.2 DNA Extraction

For each sample, 200 μl (~100mg) of the sludge solution was used for DNA extraction with the ZymoBIOMICS DNA Mini kit (Zymo Research, CA, US) according to the manufacturer's protocol. A negative control of DNA extraction process was performed together with the actual samples. Real-time PCR quantification showed that the negative control has a low Ct value (<37 cycles), indicating that the DNA extraction process carries low bioburden.

3.2.3 16S rRNA Sequencing

Bacterial 16S ribosomal RNA gene targeted sequencing was performed. The general bacterial 16S primers used were 341f (CCTACGGGNGGCWGCAG) and 805r (GACTACHVGGGTATCTAATCC), which amplified the theV3-V4 region of the 16S rRNA gene. The sequencing library was prepared by following a published protocol (Kozich et al., 2013) with some modifications to prevent PCR chimera

formation: the number of PCR cycles was carefully controlled for each sample so that each individual reaction did not overrun. The amplicon libraries were cleaned up with Zymo's Select-a-Size DNA Clean & Concentrator™ (>200 bp fragments were kept), quantified with TapeStation, normalized and pooled together. The final library was quantified with quantitative PCR and sequenced on Illumina MiSeq with V3 reagent kit (600 cycles). The sequencing was performed with >10% PhiX mix and in paired-end mode.

3.2.4 16SrRNA Taxonomic and Bioinformatic Analysis

Raw sequence reads were trimmed with Trimmomatic-0.33. (Bolger et al., 2014) The two paired-end reads in each pair were assembled to construct a complete amplicon sequence with SeqPrep (<https://github.com/jstjohn/SeqPrep>). Chimeric amplicon sequences were identified and removed with Usearch (v. 6.1) (Edgar et al., 2011) in ref mode against a curated database (http://drive5.com/uchime/rdp_gold.fa). Amplicon sequences smaller than 320 bp were removed. For each sample, up to 50,000 sequences were randomly sampled to reduce potential bias caused by uneven sampling. These amplicon sequences were compiled, clustered and analyzed with Qiime 1.9.1 (Caporaso et al., 2010). OTUs were picked by the workflow of pick_open_reference_otus.py using GreenGene database (gg_13_8) as a reference database. Singleton OTUs were removed. Composition bar charts were generated with the workflow of summarize_taxa_through_plots.py. Taxa that have an abundance significantly different among groups were identified by Segata et al. (2011) with default settings ($p > 0.05$ and LDA effect size > 2) if applicable.

3.3 Composition of Mineral Salt Medium and Trace Nutrients

All chemicals for mineral salt medium (MSM) preparation was with an analytical grade. MSM and nutrients solution of 10 mL/L was prepared in one liter of distilled water contained the following composition which detailed in Table 3.1 (Muñoz et al., 2013).

An NaNO_3 stock solution was composed of a 1000 mg/L supplemented as an electron acceptor for malodor gases oxidation and as a nitrogen source for microbial growth. The final pH of the liquid medium (MSM and NaNO_3) was about 7.2 ± 0.15 .

ET and DMS in the liquid phase with 99.9% purity, was obtained from Sigma-Aldrich, Germany.

Table 3.1 : Composition of MSM and trace nutrients.

Compound	Quantity (g)
MSM solution	
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	6.15
KH_2PO_4	1.52
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.2
CaCl_2	0.038
Trace nutrients solution	
EDTA	0.5
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.2
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.01
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.003
H_3BO_3	0.03
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.02
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.001
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.002
$\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$	0.003

3.4 Analytical Procedure

First of all, calibration curves have been set with high correlation coefficients (i.e. $R^2=0.99$) for ET, DMS, and CO_2 concentrations in the gas phase, as shown in Figure 3.3. After then, odorous gases were analyzed in an alignment gas chromatograph GC-7090A (USA) equipped with a mass detector MSD 5795C and HP-5MS 5% Phenyl Methyl Silox ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) capillary column, as depicted in Figure 3.4. Best alternatives for oven temperature was initially maintained at startup Temp: 40°C for 3 minutes, increased at $30^\circ\text{C}/\text{min}$ up to 50°C and then at $30^\circ \text{C}/\text{min}$ third step increase of temperature $30^\circ\text{C}/\text{min}$ to a final temperature of 110°C , total holding time was 5.33 minutes. Helium was used as a carrier gas at $0.97 \text{ mL}/\text{min}$. Nitrate and sulfate concentrations in the liquid phase were analyzed via ion chromatography (Dionex ICS-3000, USA). Samples were eluted into the column (Dionex IonPac AS9-HC) isocratically at $1 \text{ mL}/\text{min}$ at column temperature 30°C with a solution of $0.2\text{M Na}_2\text{CO}_3$ and injection volume $10 \text{ }\mu\text{l}$.

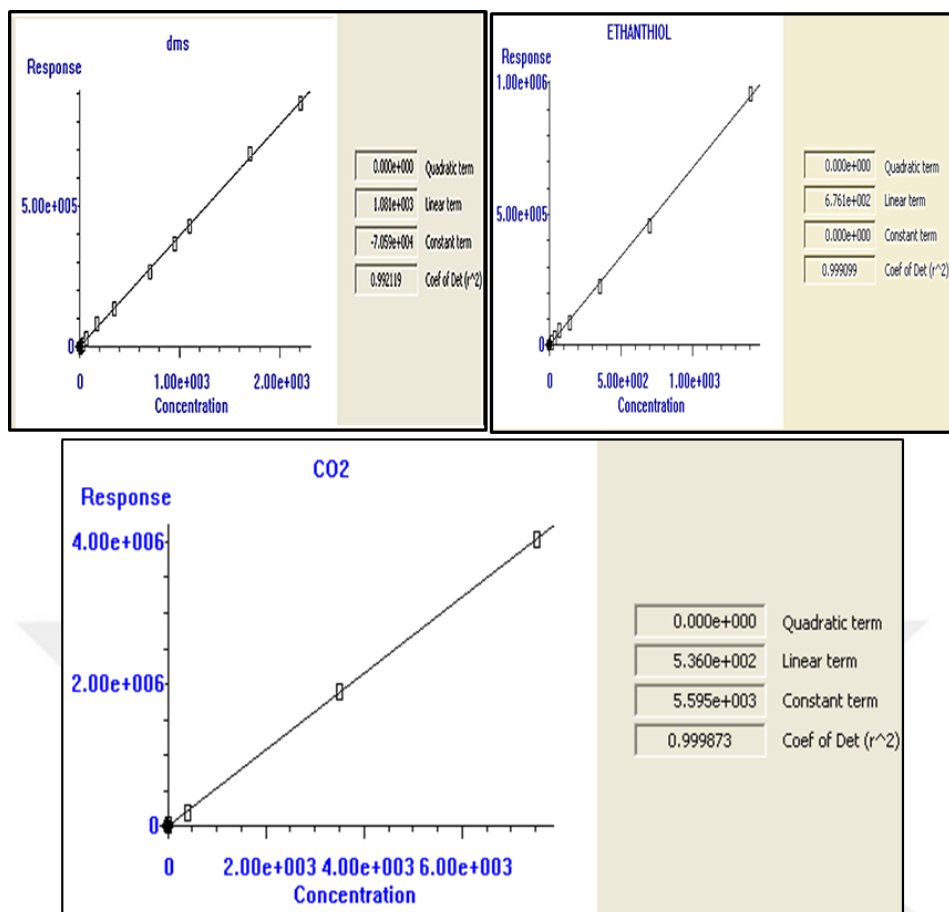


Figure 3.3 : Calibration curves for ET, DMS, and CO₂ gases.



Figure 3.4 : Alignment GC-7090A and MSD for odorous compounds measurements.

The pressure drop across the biotrickling filter's column was measured daily using a U-tube water manometer. The pH value was measured using the pH meter (HANNA HI 2211 model, USA). Biomass concentration was estimated as VSS, and chemical oxygen demand COD test was performed according to open reflex method section 5220 B in standard methods for the examination of water and wastewater APHA, AWWA (2005).

3.5 Kinetic Model

Among the various models which have been widely used for modeling the kinetics of VOSCs degradation, pseudo-first-order model was used to estimate the degradation rate constant of ET and DMS (Giri et al., 2015; Wan et al., 2010; Wang, X. et al., 2015).

In this sense, by integrating equation (3.1), the substrate removal rate constant (k) follows the pseudo-first-order kinetics presented in equation (3.2). Thus,

$$\frac{ds}{dt} = k S \quad (3.1)$$

Results in

$$\ln (S_t/S_0) = k.t + constant \quad (3.2)$$

The metabolism rate of the non-growth substrate in the presence of appropriate amounts of cells at low concentrations of substrate does not support cell division which in turn assimilate a first order simplest form of the Monod model (Criddle, 1993; Schmidt et al., 1985). Depending on the carbon and energy source the microorganism's growth may be limited. The ability of the microorganisms to utilize a non-growth substrate in the presence of growth substrates is the concept of co-metabolism (Chang & Criddle, 1997; Chen et al., 2008).

In this context, the maximum degradation rate velocity (V_{max}) and half velocity constant (K_m) as described by Monod expression for the biodegradation can be represented as follows (Sedighi et al., 2013; Wang, X. et al., 2015):

$$\frac{dS}{dt} = SDR X \quad (3.3)$$

Where:

X = the concentration of microorganisms, mg/L.

S = substrate concentration, mg/L.

SDR = specific degradation rate, mg S/ mg X. h

The SDR is related to maximum degradation rate velocity (V_{max}) and half velocity constant (K_m) as described in equation (3.4).

$$SDR = V \max \frac{S}{K_m + S} \quad (3.4)$$

In the modified Haldane-Andrews model an inhibition constant (K_i) was estimated to express the inhibitory effect of substrate concentration on bacterial growth, as follows:

$$SDR = V \max \frac{S}{K_m + S + \frac{S^2}{K_i}} \quad (3.5)$$

3.6 Experimental Set-up of Anoxic Biotrickling Filter

The second part of the study examined the biological treatment of ET and DMS compounds via a lab-scale anoxic biotrickling filter ABTF model. It covers a wide range of experimental conditions, as shown in Table 3.2. Since the target gaseous pollutants are categorized as hazardous and malodorous, the lab-scale model was installed in an air vacuum.

Table 3.2 : Operational parameters for evaluation performance of ABTF.

Target gas	Experiment	Time of operation (days)	ET concentration (mg/m ³)	Trickling velocity (m/h)	EBRT (sec)
ET	Adaptation	1-36	150-1500	0.12	60
		1-30		0.12	
	Stage 1	31-59		0.18	
		60-88		0.24	60
		89-120		0.30	
		121-147		0.45	
	Stage 2	148-154			30
		155-168			60
		169- 171		0.45	90
		172-180			120
DMS	Adaptation	1-26	150-1500	0.12	
		1-26		0.12	
	Stage 3	27-62		0.18	
		63-89		0.24	60
		91-116		0.30	
		120-140		0.45	
	Stage 4	141-154			10
		155-168		0.24	30
		169- 171			90
		172-185			120
ET:DMS mixture (1:1)	Stage 5	1-30	150-1500	0.24	60

The laboratory scale of the ABTF consisted of a 50 cm transparent Plexiglas column with internal diameter of 9.4 cm and a working volume of about 2 L, supported by a perforated plate at the bottom and top. The liquid medium (MSM and NaNO_3) was recycled at variable flow rates, counter-current to the gas stream from the feeding tank (diameter 15 cm, height 20 cm) located at the bottom of the biotrickling filter, using a peristaltic pump (type PR1 Seko, Italy). ET and DMS in the gaseous phase were prepared by injecting liquid phase using a dual channel syringe pump (LSP02-1B model, USA) into a mixing chamber that was connected to an N_2 gas stream. The gas flow rate was controlled by a rotameter (Aalborg Instrument Inc., USA) to satisfy the required empty bed residence time (EBRT), the experimental and schematic of lab- scale ABTF model are presented in Figure 3.5 and Figure 3.6, respectively.



Figure 3.5 : Real photos of the laboratory-scale of ABTF model and packing medium.

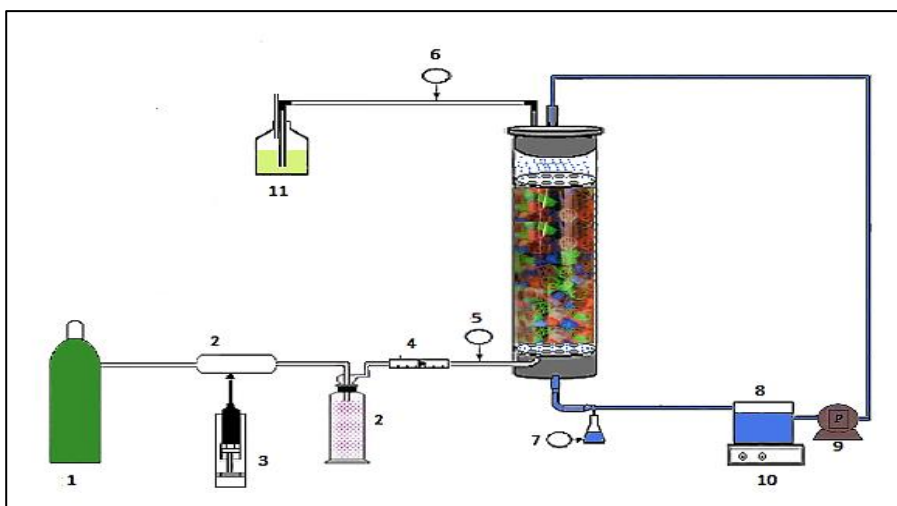


Figure 3.6 : Scheme of experimental ABTF (1) N₂ gas bottle (2) mixing chambers (3) syringe pump (4) gas flow controller (5&6) inlet and outlet gas sampling ports (7) liquid sampling port (8) mineral medium and NO₃⁻ feeding tank (9) recirculation pump (10) magnetic stirrer (11) NaOH solution.

Inert inorganic packing materials with BIOfix polyethylene rings type (Fix06) were supplied by TKN FILTER Ltd. Company, Turkey. The Fix06 ring (diameter× height 14.5×9.8 mm) had 6 holes with initial porosity >85 %, efficient surface area >800 m²/m³, and average density 0.95 g/cm³. It was randomly packed into the biotrickling filter column as supporting media for biomass growth. The detail information about packing material and initial conditions are presented in Table 3.3.

Table 3.3 : Specification of ABTF model and initial conditions.

Parameter	Value
Total height of the column (cm)	50
Height of the packed bed (cm)	30
Inner diameter of the column (cm)	9.4
Total volume (L)	3.46
Effective volume (L)	2.08
Flow rate of waste gas (L/h)	62, 82, 124, 248
Empty bed residence time (sec)	120, 90, 60, 30
Superficial gas velocity (m/h)	9, 12, 18, 36
Substrate loading rate (gr/m ³ /h)	9, 18, 48, 90
Trickling velocity (m/h)	0.12, 0.18, 0.24, 0.35, 0.45
Inlet ET concentration (mg/m ³)	150, 300, 800, 1500
Moisture content of packing medium (%)	75–80
Bed porosity (%)	90
Pressure drop across packing (cm water)	3 -14
Initial biomass (g sludge/g packing media)	0.24

3.7 Assessment of the ABTF Performance

The performance of the ABTF for the treatment of ET and DMS has evaluated hereunder the following process parameters (Devinny et al., 1999):

3.7.1 Empty bed residence time (EBRT)

The term EBRT relates the flow rate to the size of the filter column. It is defined as the empty bed filter volume divided by the gas flow rate:

$$EBRT = \frac{V_f}{Q} \quad (3.6)$$

$EBRT$ = Empty bed residence time (sec)

V_f = Filter bed volume (m^3)

Q = gas flow rate (m^3/sec)

EBRT is also given in terms of true residence time, which is defined as the total filter bed volume multiplied by the porosity of the filter medium divided by the air flowrate.

$$\tau = \frac{V_f \cdot \theta}{Q} \quad (3.7)$$

τ = True residence time (sec)

θ = Porosity = volume of void space / volume of filter bed

EBRT of the biotrickling filter was varied with changing the gas flow rate through the rotameter. The results in terms of removal efficiency and elimination capacity were obtained at different EBRT of the biotrickling filter.

3.7.2 Inlet loading (IL)

Inlet concentration of compounds was varied at an optimal EBRT and thus load was varied. Load at which removal efficiency of the compound was maximum, that load was considered to be optimal for the system.

Loading rates are defined in terms of volumetric loading as the volume of gas per unit volume of filter material per unit time. In the present study, volumetric mass loading was calculated in terms of:

$$IL = \frac{C_0 \cdot Q}{V_f} \quad (3.8)$$

3.7.3 Removal efficiency (RE)

The effectiveness of the reactor system depends on the removal of the pollutant from the system. The removal efficiency of the system is generally expressed in percentage and is denoted as follows:

$$\%RE = \frac{(C_0 - C_i)}{C_0} \times 100 \quad (3.9)$$

Where,

C_0 = Concentration of the gas in the inlet of the biotrickling filter (mg/m^3)

C_i = Concentration of the gas in the outlet of the bio biotrickling filter (mg/m^3)

3.7.4 Elimination capacity (EC)

The elimination capacity is generally defined as the mass of contaminant (grams) degraded per unit volume (m^3) of filter material per unit time (h).

$$EC = \frac{(C_0 - C_i) \cdot V_f}{Q} \quad (3.10)$$

Where:

C_0 = Concentration of inlet gas (g/m^3)

C_i = Concentration of the outlet gas (g/m^3)

V_f = Volume of the packing material (m^3)

Q = Flow of waste-gas (m^3/h)

Removal efficiency is an insufficient descriptor for biotrickling filter performance because it only reflects the specific conditions under which it is measured. The elimination capacity allows for a direct comparison of the results of two different biotrickling systems because the volume and flow are normalized by definition; however, elimination capacity is also a function of inlet load.

$$EC = IL \times RE \quad (3.11)$$

Under low load conditions, the system is calculated to be at RE 100% and EC essentially equals the inlet load. By increasing the load on a system, the REs will be less than 100%, hence, the critical load or critical elimination capacity will be generated where the overall mass loading rate will exceed the overall elimination capacity as presented in Figure 3.7. This maximum overall elimination capacity is independent of contaminant concentration and residence time within a reasonable range of operating conditions.

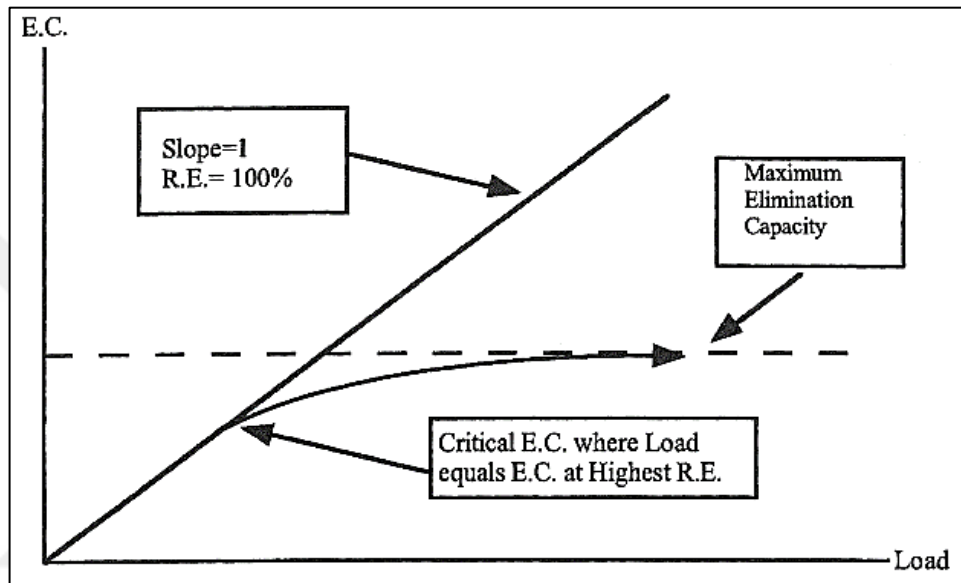


Figure 3.7 : Typical elimination capacity vs. inlet load curve (Devinny et al., 1999).



4. RESULTS AND DISCUSSIONS

4.1 Adaptation and Kinetics Assays

In the adaptation period the desulfurization capacity of the two malodorous gases ET and DMS was evaluated under different conditions for five cycles. Each cycle lasted ~85 and ~ 9 hrs for initial VSS 300 and 3000 mg/L, respectively, as depicted in Figure 4.1. Clearly, DMS has lower biodegradability than ET, although both completed five cycles. Nevertheless, the desulfurization capacity for DMS-S increased from 0.87 in the first cycle to 2.73 mg/m³.h in the fifth cycle. ET showed better performance in biodegradation; ET-S desulfurization capacity increased from 1.65 to 4.44 mg/m³.h, for the same initial conditions, i.e. VSS 300 mg/L and initial gas concentration ~385±31 mg/m³. However, there were no significant increments in desulfurization rates in either gas between the first and the fourth cycle. This may be explained by the high mass loading of the substrate compared to the low microorganism concentration, i.e. VSS 300 mg/L; hence, removal capacity was limited by reaction limitation (Wan et al., 2010).

The behavior was entirely different when VSS concentration increased 10-fold, i.e. to 3000 mg/L; in this case, complete degradation of both gases occurred in ~9 hrs. Moreover, the desulfurization capacity was almost doubled in both gases by the end of the fifth cycle; DMS-S increased from 8.53 to 17.73 mg/m³ h while ET-S increased from 11.77 to 20.9 mg/m³.h. Obviously, the trend in the ET biodegradation rates surpassed DMS, even though ET had lower water solubility than DMS. The difference in their biodegradation rates can be attributed to the C-S bond and chemical structure. Visscher and Taylor (1993), declared that the monooxygenase enzyme which attacks the methyl group in DMS is responsible for degradation in the presence of oxygen, while under anoxic conditions, DMS is catabolized by the methyltransferase enzyme instead of monooxygenase, as indicated in the inhibitor studies.

Increasing the biomass concentration had a significant and positive effect on decreasing the biodegradation time; more than ~90% reduction was achieved in the degradation time for both gases. Hence, increasing the biomass may enhance the biodegradation capacity of the gases and increase the competition between the microorganisms for the substrate, as both gases are considered the only source for carbon. Accordingly, for these odorous pollutants, high biomass concentration with an acclimation period of not less than five cycles is necessary for effective treatment.

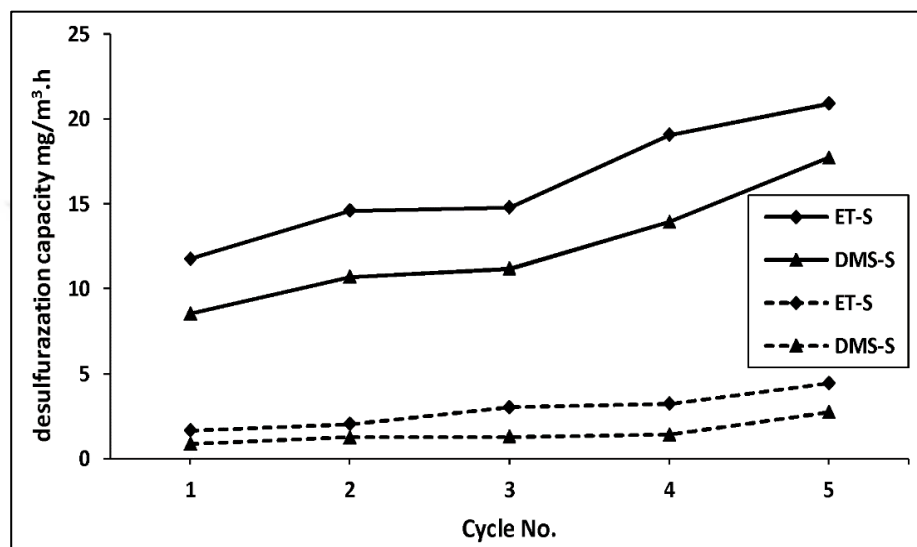


Figure 4.1 : Time course of ET and DMS during adaptation period (for solid lines VSS conc. = 3000 mg/L and for dashed lines VSS conc. = 300 mg/L).

Several studies have used batch reactors for treating VOSCs as the sole carbon and energy source. Sedighi et al. (2013) found that 115~320 mg/m³ of gaseous ET was completely degraded by *R. eutropha* within 120~168 h. Wan et al. (2010) noted that complete biodegradation of 2-4 mg/L ET in an aqueous medium was achieved within 96 h by a new *Lysinibacillus sphaericus* strain RG-1. In another study, ET was oxidized by methyl mercaptanoxidase, purified from *Thiobacillusthioparus* TK-m grown on DMS (Gould & Kanagawa, 1992). Lomans et al. (1999), showed the maximal anaerobic DMS degrading capacities obtained from bottles shaken under N₂ were 0.37 nmol /ml of sediment slurry/ h, and maximal degrading capacities under aerobic conditions were 4.95 nmol /ml of sediment slurry/h, i.e. 10-fold higher. Finally, Cha et al. (1999) showed that *Thiobacillus novellus* SRM removed 30 ppm of DMS in 7 h and 50 ppm of MM in 2.6 h; optimal pH and temperature for DMS removal were 7.0 and 30°C, respectively.

4.2 Kinetics Analysis

After an adaptation period, the time course of both gases individually and in the mixture (ET: DMS 1:1) were simulated in batch bottles in order to derive the pseudo-first order constant (k) at the following initial conditions: $S_0 = 375 \text{ mg/m}^3$, $VSS = 3000 \text{ mg/L}$, Temp. 25°C , pH 7.5, as shown in Figure 4.2 a, b, and c.

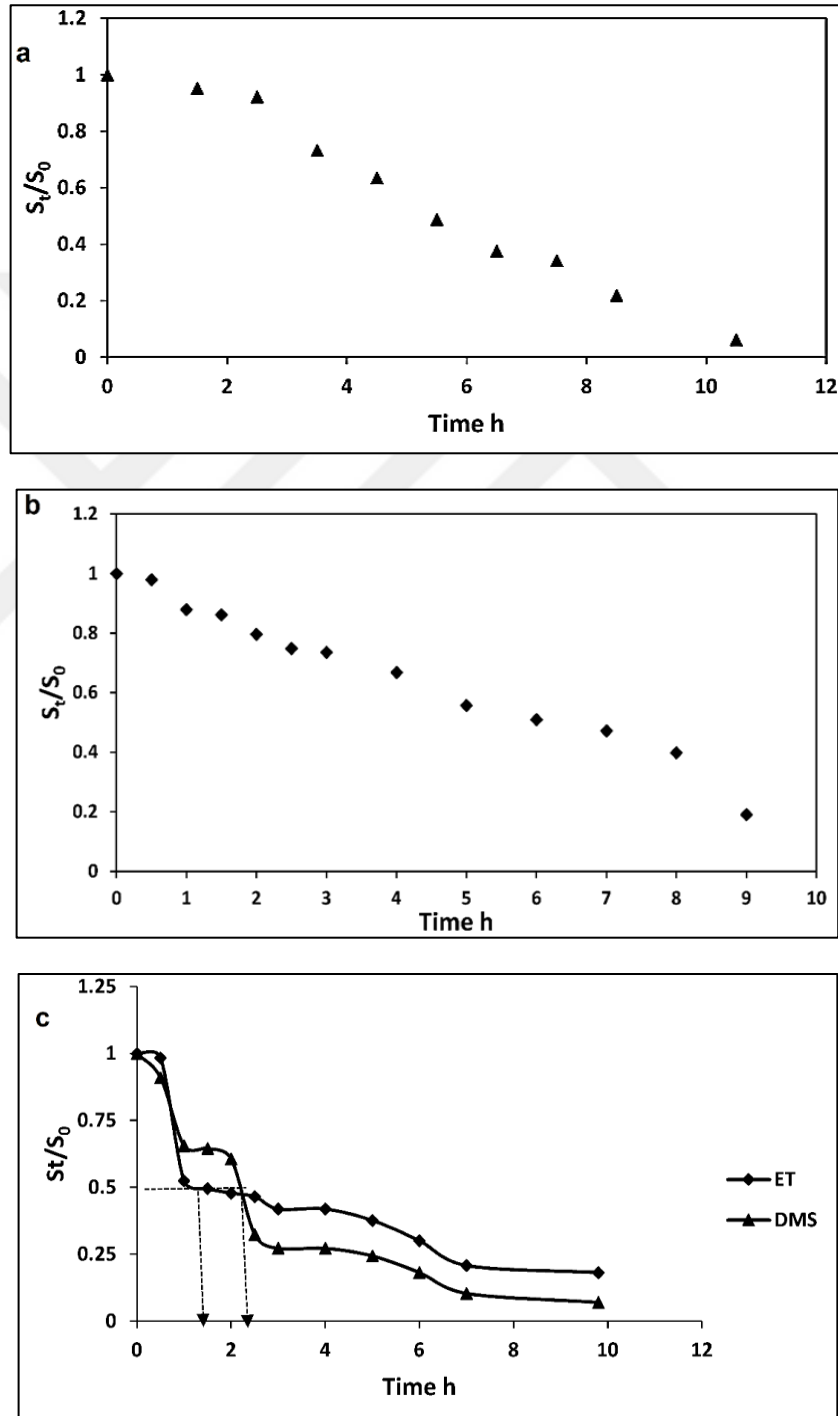


Figure 4.2 : Time course of a) ET, b) DMS, and c) ET: DMS 1:1 mixture during kinetic assays.

In order to understand the interface concept of these gases, ET: DMS mixture in (1:1) ratio was established in these batch tests. As depicted in Figure 4.2 c, gases mixture has a different pattern from individual gas. Furthermore, a positive effect was noticed in the degradation time of 50% of ET and DMS was decreased from 5.5 to 1.5 and from 7 to 2.3 h. However, gases mixture have a lesser effect regarding biodegradation time pattern, comparing to increasing biomass concentration from VSS 300 to 3000 mg/l.

Refereeing to equation (3.2), the extracted values of pseudo-first order constant k were 0.113 and 0.14 /h, for DMS and ET, respectively, as shown in Figure 4.3 a and b.

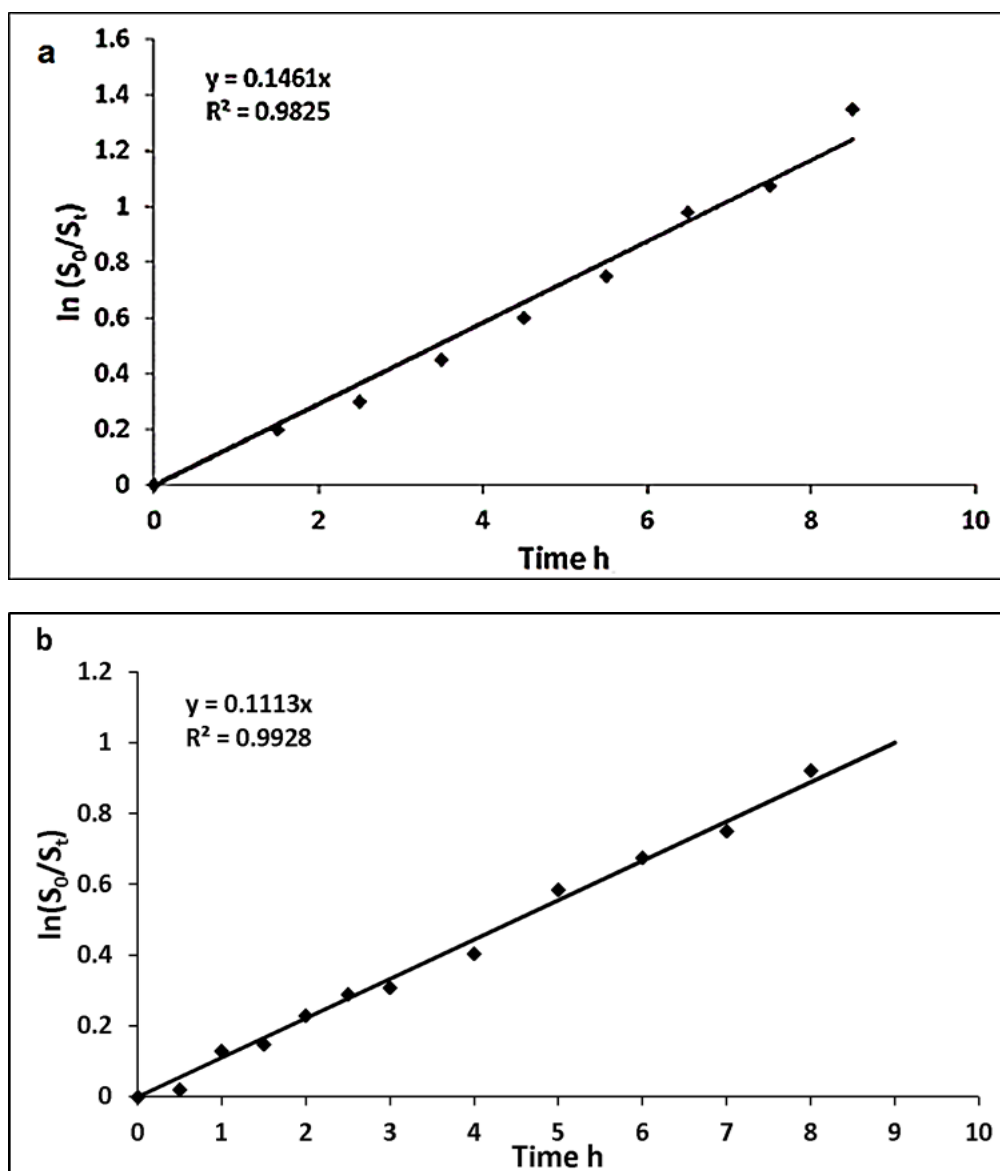


Figure 4.3 : Pseudo-first order constants representation of a) ET and b) DMS.

The experimental data were fitted to a Monod model using GraphPad prism .6 software to describe the specific degradation rate's relationship with substrate concentrations in the liquid phase as presented by the program output shown in Figure 4.4. The saturation kinetics, well described by the Michaelis-Menten equation, were determined by considering the catalytic (enzymatic) degradation of the microbial cells for a particular single substrate, following the Monod equation for simulations.

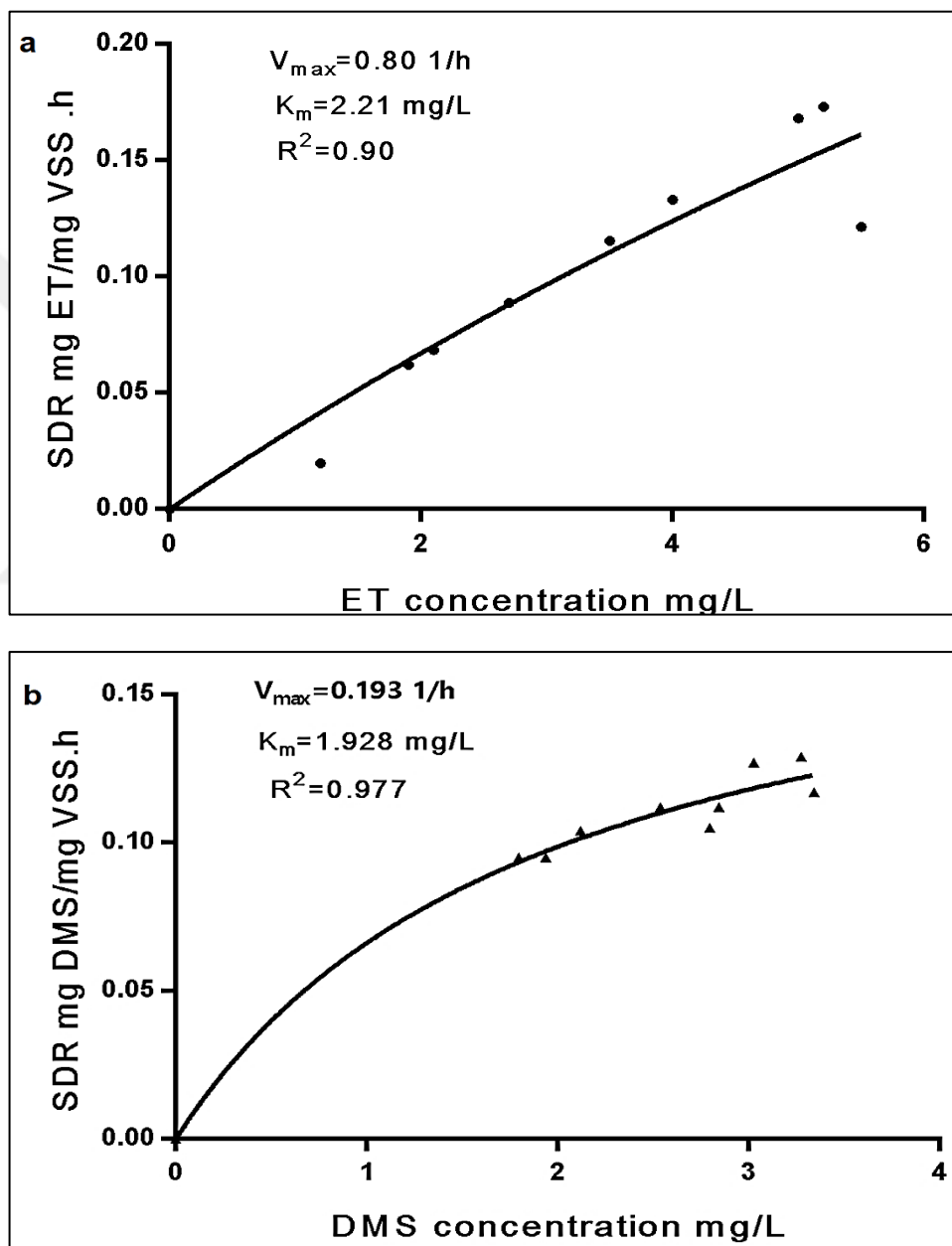


Figure 4.4 : Fitted model of the specific degradation rate of a) ET and b) DMS.

The extracted kinetic values for DMS and ET are summarized in Table 4.1; as the table shows, the non-linear regression analysis found a high correlation factor. The

inhibition constants K_i in the Haldane-Andrews model were very high (data are not shown); accordingly, the inhibition effect of substrates on bacterial activity within the ranges in Figure 4.4 was not considered.

Table 4.1 : Summary of kinetic parameters of ET and DMS.

Parameter	DMS	ET
k (1/h)	0.11	0.14
K_m (mg/L)	1.92	2.21
V_{max} (1/h)	0.193	0.809
$R^2(k)$	0.99	0.98
$R^2(K_m \text{ and } V_{max})$	0.97	0.90

Kong et al. (2002) suggested the DMS bio-kinetic parameters depend on fractional-order diffusion limitation and proposed an average fractional kinetic coefficient of $0.0879 \pm 0.0178 \text{ ppm}^{1/2}/\text{sec}$. Sun et al. (2016) evaluated the DMS degradation kinetics and found the maximum specific growth rate and degradation rate of *Alcaligenes* sp. SY1 was 0.17 1/h and 0.63 g S /g VSS. h. respectively, using the Haldane–Andrews model and the pseudo-first-order model. The parameters of the growth kinetics for the biodegradation of DMS through flask culture experiments were obtained by Giri et al. (2015) as 0.022 mg/L, 0.0057 1/h and 0.013 1/h for K_m , μ_{max} , and k , respectively. Wang, X. et al. (2015) reported that maximum specific growth rates of *Pseudomonas* sp. were 0.166 and 0.12 /h, and maximum specific degradation rates were estimated as 1.46 and 0.50 mg S/g X. h for ET and DEDS degradation, respectively. The pseudo-first-order (k) reached a maximum value of 0.175 /h at DEDS concentration of 24.6 mg/L and 0.52 /h at ET concentration 41.8 mg/L. Using nitrate as an electron acceptor, Visscher and Taylor (1993) found the growth rates for thiosulfate and DMS were 0.09 and 0.08 /h, respectively. Sedighi et al. (2013) fitted the kinetic parameters using the Monod model and obtained the maximum specific degradation rate of 0.23 mg S/g X. h and K_m of 1.379 mg/L at initial ET concentrations of 1~4 mg/L by *R. eutropha*.

These values were much lower than those found in our study. The ET degradation rate was 3.47×10^3 times higher than that of *R. eutropha*. Furthermore, the pseudo-first-order constant (i.e. 0.14 /h) was 4.5 times higher than that reported in a previous

study on ET degradation by *L. sphaericus* (i.e. 0.0308 /h) (Wan et al., 2010). In similar trend, DMS kinetic parameters in this study were 10 fold higher than Giri et al. (2015) results.

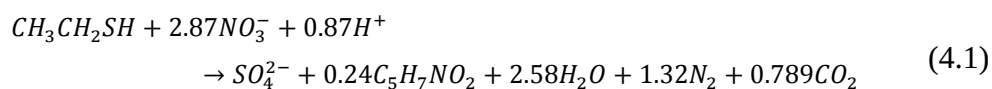
Although, it is difficult to compare our observed results to those in the literature, as different forms of the seeded microbial culture were used. Nevertheless, the obtained results indicate biodegradation of ET and DMS under anoxic conditions was effective.

4.3 Stoichiometric and Thermodynamic Reactions

The required energy for microorganisms' growth and maintenance can be determined from a combined oxidation and reduction reaction using an electron donor (the food substrate for microorganisms) and an electron acceptor (Rittmann & McCarty, 2012). In energy metabolism, for all non-photosynthetic microorganisms, the most common donor is organic matter, and under anaerobic conditions (anoxic conditions), nitrate, sulfate and carbon dioxide are used as electron acceptors. The half-reaction approach is the simplest way to form energetic reactions, particularly for complex reactions, such as those involving ET and DMS. Although many studies have investigated the simultaneous removal of sulfide and nitrate in wastewater where the end products of desulfurization greatly depended on the S/N molar ratios similar studies related to gaseous pollutants remain scarce. To the best of our knowledge, no studies have considered the influence of an anoxic process on the removal of the odorous ET and DMS gas under a specific S^{2-}/NO_3^- ratio. Mass transfer and biodegradation limitations are considered the core of the gas phase removal mechanism, and this differs entirely from the wastewater treatment process.

By following the thermodynamic and half reactions approach, (Heijnen, 2002; Rittmann & McCarty, 2012; Sawyer, 2003) the study derived the following stoichiometric equations using thermodynamic analysis (details appear in the appendix).

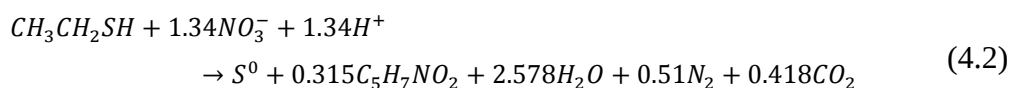
1. The stoichiometric reaction of ET where sulfate is the main product can be expressed as:



$$\therefore Ratio = \frac{CH_3CH_2SH}{NO_3^-} = \frac{1}{2.87} = 0.34$$

$$\Delta G = -1389.26 \text{ kJ/e-mole}$$

2. The stoichiometric reaction of ET where elemental sulfur is the main product can be expressed as:



$$\therefore Ratio = \frac{CH_3CH_2SH}{NO_3^-} = \frac{1}{1.34} = 0.74$$

$$\Delta G = -674.61 \text{ kJ/e-mole}$$

Accordingly, the study thermodynamically calculated and experimentally compared two different ratios for two final products, i.e., sulfate and elemental sulfur, as shown in Table 4.2. The average experimental molar ratios of Y_{ET/NO_3^-} and Y_{DMS/NO_3^-} values were scattered between $(0.43 \pm 0.1 - 0.6 \pm 0.06)$ and $(0.52 \pm 0.19 - 0.75 \pm 0.11)$, respectively, i.e. within the estimated theoretical range limits (0.34-0.75 mole/mole). So, the expected end products of both gases were a mixture of sulfate and to a larger extent elemental sulfur.

Table 4.2 : Summary of experimentally and thermodynamically calculated yield of ET and DMS oxidation as a function of the end product.

Trickling velocity m/h	Inlet gas conc. mg/m ³	Average ET removal g/day	Average ET-NO ₃ ⁻ Consumption g/day	Average DMS removal g/day	Average DMS- NO ₃ ⁻ Consumption g/day	Y ET/ NO ₃ ⁻ mole/mole	Y DMS/NO ₃ ⁻ mole/mole	Thermodynamically calculated yield (mole/mole)	
								Main product	
								S ⁰	SO ₄ ²⁻
0.12	150	0.36	0.49	0.35	0.68	0.73	0.52	0.74	0.34
	300	1.2	2.13	0.77	1.27	0.56	0.60		
	800	1.98	3.39	1.78	3.87	0.58	0.46		
	1500	2.72	4.14	3.02	3.54	0.6	0.88		
					Average ±S.D.	0.62±0.06	0.61 ±0.16		
0.18	150	0.41	0.8	0.27	0.73	0.51	0.59	0.74	0.34
	300	0.91	2.45	0.35	0.48	0.37	0.37		
	800	2.14	3.54	0.61	0.98	0.66	0.31		
	1500	2.34	5.56	3.02	3.54	0.42	0.80		
					Average ±S.D.	0.49±0.10	0.52 ±0.19		
0.24	150	0.38	0.76	0.49	0.57	0.5	0.85	0.74	0.34
	300	0.93	3.2	0.84	1.25	0.29	0.68		
	800	2.02	2.91	1.94	2.22	0.69	0.87		
	1500	3.2	6.37	3.64	5.99	0.5	0.61		
					Average ±S.D.	0.50±0.14	0.75 ±0.11		
0.3	150	0.31	0.61	0.29	0.64	0.51	0.47	0.74	0.34
	300	0.87	2.57	0.75	1.26	0.34	0.59		
	800	1.85	3.07	1.70	3.80	0.6	0.45		
	1500	3.61	6.13	3.02	3.54	0.58	0.88		
					Average ±S.D.	0.51±0.10	0.60±0.17		
0.45	150	0.37	0.71	0.35	0.52	0.52	0.68	0.74	0.34
	300	0.79	2.85	0.81	1.30	0.28	0.62		
	800	2	4.7	1.98	2.88	0.42	0.69		
	1500	4.14	7.74	3.77	4.78	0.53	0.79		
					Average ±S.D.	0.43±0.10	0.70±0.05		

S.D. =standard deviation.

The results in Figure 4.5 a and b show that both biodegradation capacity (EC) and NO_3^- consumption rate were directly proportional to inlet loading, $R^2 = 0.99$ and 0.94 , respectively, suggesting denitrification efficiency. However, there was stability, even a slight decrease in NO_3^- consumption, when ET and DMS loading ranged between 80 and 100 $\text{g/m}^3/\text{h}$. This suggests an excess level of NO_3^- . Hence, more electron acceptor was provided and the remaining NO_3^- was purged from the system. Moreover, the high level of NO_3^- may have an inhibition effect on some denitrifiers (Zhu et al., 2004).

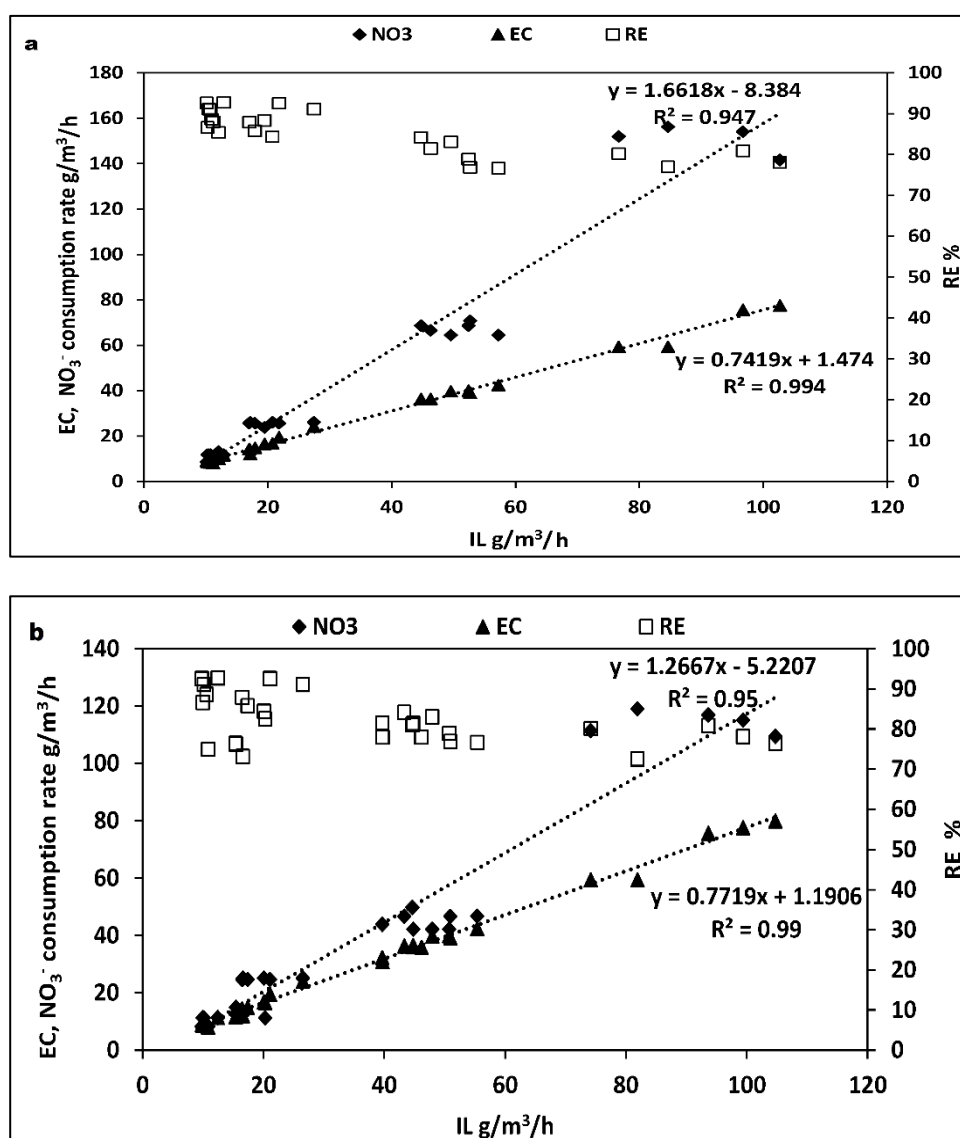


Figure 4.5 : Trend of the experimental yield of a) ET/ NO_3^- b) DMS/ NO_3^- molar ratio.

Few studies report on gas phase denitrification in trickled biofilters, even though there are many studies on wastewater treatment (Zhu et al., 2004). The present study

demonstrates that in a gas-phase O_2 -free biotrickling filter, NO_3^- can serve as a major electron acceptor responsible for the degradation of a significant portion of a treated VOSC, in this case, ET and DMS. This can be affirmed by following the NO_3^- mass balance approach depicted in Figure 4.6 a and b. The data suggest that 64.8% and 52.7% of the averaged inlet NO_3^- was consumed in the denitrification process of ET and DMS, i.e. converted to N_2 , with enhanced biomass playing a catalytic role. N_2 estimation was based on the stoichiometric Eq. A.4 (see appendix). With this estimation procedure, the study found that nitrogen molecules used in biomass assimilation were 23.5% of the averaged inlet NO_3^- -N, suggesting that most of the NO_3^- i.e. 86.3% and 76.2%, was used as an electron acceptor for ET and DMS, while the remaining part, i.e. 11.6 and 14.5% was removed from the system within the liquid medium.

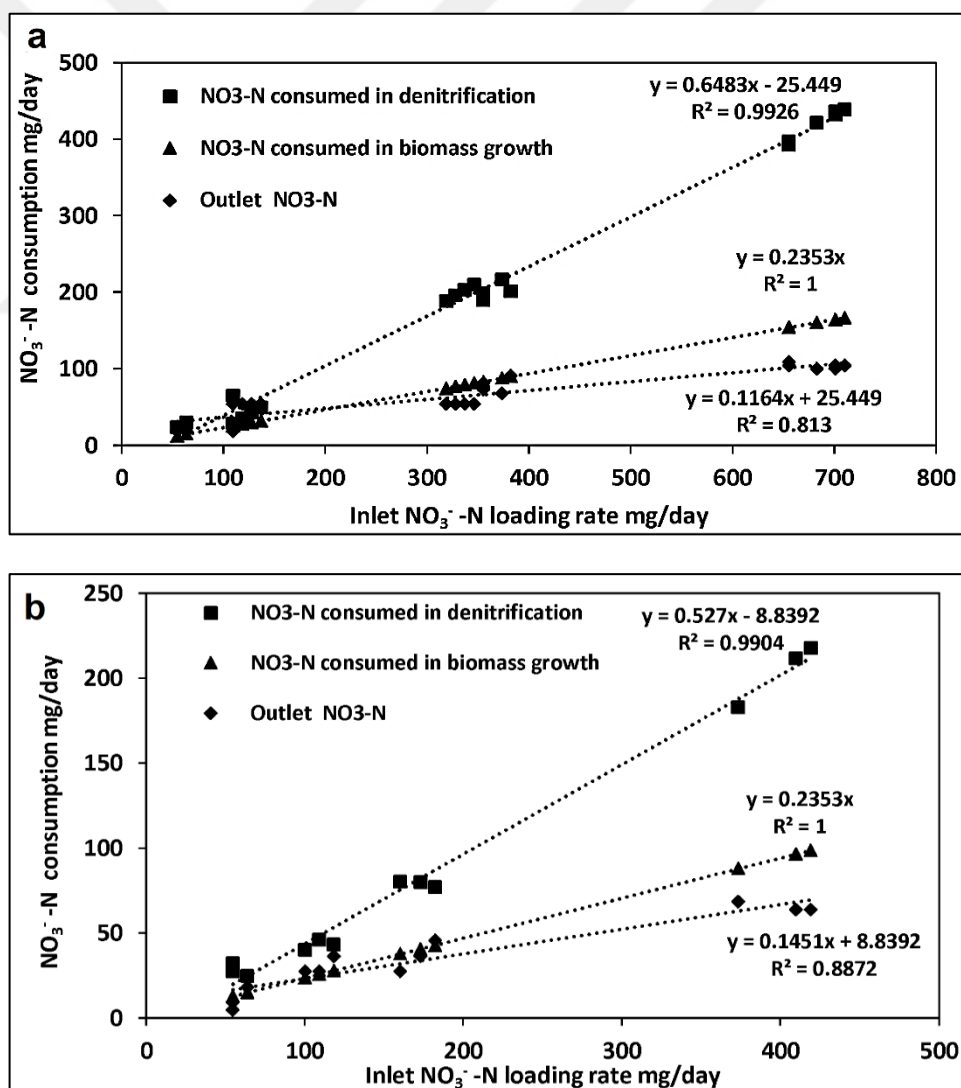


Figure 4.6 : Mass balance approach of NO_3^- consumption rate a) ET and b) DMS.

The biological utilization and aerobic degradation routes of ET and DMS can produce sulfate, according to the pathways which have been fully elucidated by (Barreiros et al., 2008; Kennes et al., 2013; Wang, X. et al., 2015; Wei et al., 2015) as depicted in Figure 4.7. For the calculation and analysis of sulfur mass balance, the study assumed that the only final products were elemental sulfur and sulfate. Elemental sulfur was estimated by subtraction, because of the difficulty measuring and scrubbing elemental sulfur S^0 from the biofilm (Montebello et al., 2012).

Thus, sulfate is a major concern of research on enzymatic reactions involved in energy production. When electrons transfer from sulfur to NO_3^- , sulfite is produced as a first step in the sulfate assimilation pathway throughout the cell membrane (the electron transport system). This requires a reduction in the power of ATP and NADPH (Sedighi et al., 2013). The study's results agree with the literature; the presence of sulfate was associated with the formation of ATP (a dissimilar pathway).

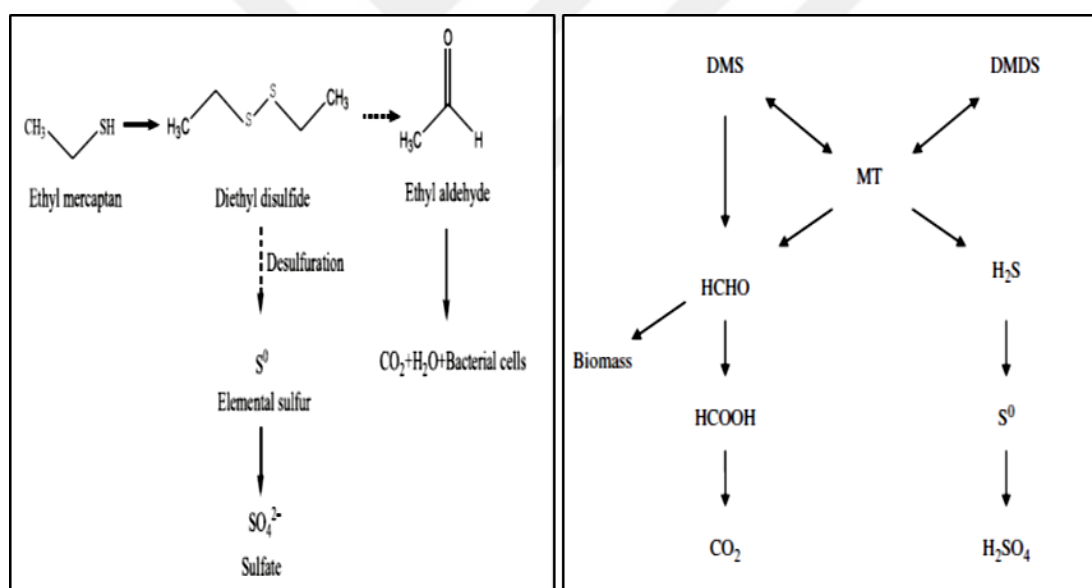


Figure 4.7 : Illustration of aerobic degradation pathways of ET (left) and DMS (right).

As shown in Figure 4.8, the sulfur mass balance (i.e., the balance of sulfate and ET) was calculated according to the amount of ET consumed and the amount of sulfate produced. Obviously, the (ET-S) consumption rate was directly proportional to (SO₄²⁻-S) production, with the latter dramatically increased from 200 to 800 mg/day, although that the initial Y_{ET/NO_3^-} was equal to 0.74 mole/mole, elemental sulfur should be the main by-product. Similarly, An et al. (An et al., 2010) found when the S-C bonds were broken, sulfate production increased steadily from 0 to 3378.82 and

2442.02 mg/L, and ET oxidation took place following an H_2S oxidative pathway. According to the stoichiometric equation (Equation 1), 1 mg of ET-S should be converted to 1 mg of $\text{SO}_4^{2-}\text{-S}$, but the experimental results showed only 36% of ET-S was bio-converted to $\text{SO}_4^{2-}\text{-S}$; this suggests the remaining (ET-S) was produced as elemental sulfur (i.e. 64%) in the desulfurization process. This study determined the sulfur mass balance using subtraction (Li et al., 2016; Turker et al., 2012; Wang, P. et al., 2015). Other studies observed similar levels of elemental sulfur production (65-68%) at N/S molar ratio of 0.7 ± 0.32 in H_2S degradation (Fernández et al., 2013a; Fortuny et al., 2008; Soreanu et al., 2008).

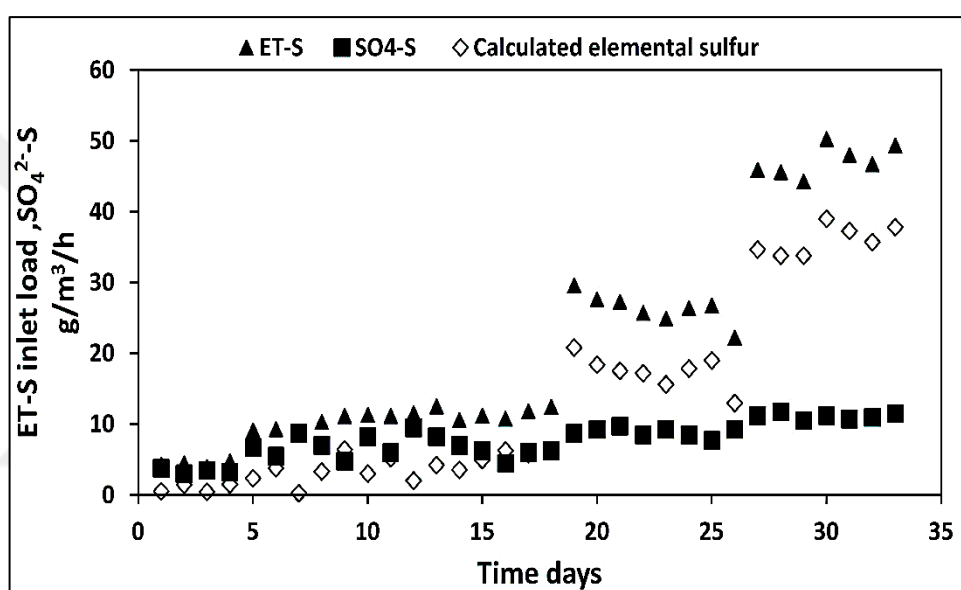


Figure 4.8 : Sulfur mass balance demonstration for ET at $Y_{\text{ET}/\text{NO}_3^-} 0.75$.

A similar trend was noticed for sulfate production in DMS degradation. As the results presented in Figure 4.9 show, sulfate production increased slightly to approximately 50% of the inlet DMS-S loading rate, i.e. $9.8 \text{ g/m}^3/\text{h}$, by day 19, while the elemental sulfur produced in ABTF was $11.44 \text{ g/m}^3/\text{h}$. Contrary to expectations, after day 23, the amount of sulfate produced stabilized at about $16.17 \text{ g/m}^3/\text{h}$ and even slightly decreased by day 26, even though DMS-S loading rates abruptly increased to about $42.65 \text{ g/m}^3/\text{h}$. Janssen et al. (1997) declared that at a constant yield ratio of the supplied oxygen over sulfide, sulfate production should increase proportionally with the imposed sulfur loading rate. Their explanation for this observation was that oxygen penetration supplied as NO_3^- becomes limited to the deeply attached biofilm near a packing ring's surface (mass transfer limitation), forcing it to form elemental sulfur. The outer surface of the biofilm, which is not

oxygen limited, will produce sulfate. Accordingly, with a high DMS-S loading rate ($42.65 \text{ g/m}^3/\text{h}$), it was found that the cumulative production of elemental sulfur and sulfate under nitrate-limited conditions was about 58% and 42% respectively.

Similar results were observed by Fernández *et al.* (Fernández *et al.*, 2014). In their study, 70% of the H_2S working at a high inlet loading ($>164 \text{ g S/m}^3/\text{h}$) was oxidized to elemental sulfur under nitrate-limiting conditions (N/S ratio of $0.7 \pm 0.32 \text{ mol/mol}$). The partial oxidation of DMS-S for S^0 production has interesting environmental aspects, as it suggests S^0 can easily be removed by sedimentation. Moreover, lower energy consumption, i.e. Gibbs energy -598.8 kJ/e-mole , was required for the elemental sulfur reduction, two times less than the energy required for sulfate conversion, i.e. $-1335.48 \text{ kJ/e-mole}$ (see appendix equations A.4 and A.6).

As mentioned, by the end of the experiment, about 42% of the sulfur element in DMS was biologically converted to SO_4^{2-} ; this is relatively high. However, the subsequent reduction of S^0 to S^{2-} (under anaerobic conditions) and to SO_4^{2-} (under aerobic conditions) after DMS demethylation can be the reason for the relatively high SO_4^{2-} concentrations (Kennedy *et al.*, 2013; Wei *et al.*, 2015). These results strongly suggest that DMS gas can be stabilized by biomass assimilation under anoxic conditions.

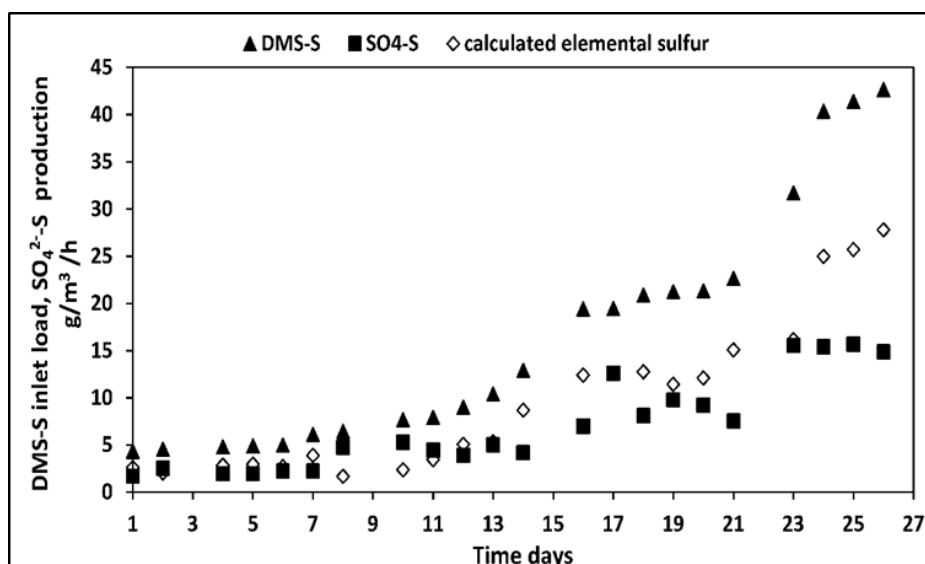


Figure 4.9 : Sulfur mass balance demonstration for ET at $Y_{\text{DMS}/\text{NO}_3^-} 0.75$.

Because of the difficulty analyzing and separating elemental sulfur from biomass, this study created an optical micrograph of immobilized biomass, depicted in Figure 4.10. The pale yellow substances produced in the irrigation liquid may affirm

elemental sulfur production (Doğan et al., 2012). Moreover, the pale yellow substances produced in the irrigation liquid may affirm elemental sulfur production.

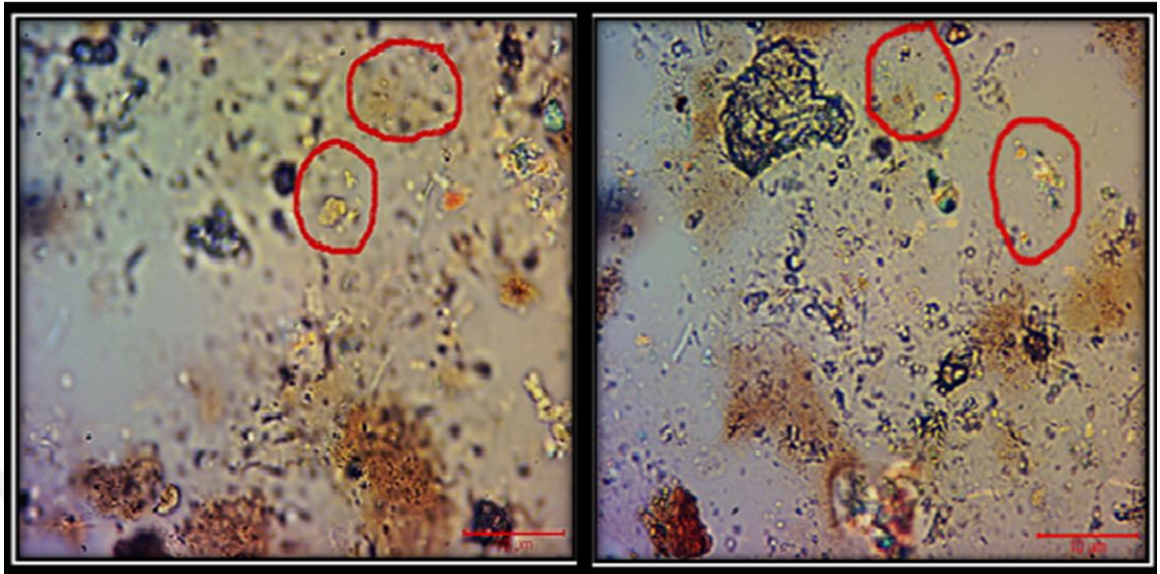


Figure 4.10 : Optical micrograph of immobilized biomass (1000x).

4.4 Assesment of ABTF Performance

The robustness of the ABTF was tested by changing various operational parameters, i.e., trickling velocity (TV), empty bed residence time (EBRT), and inlet loading IL, for determining the maximum elimination capacity (MEC) and removal efficiency (RE).

4.4.1 Start-up operation

To obtain proper results, it was essential to adapt the microorganism to the odorous waste gas streams until steady-state conditions were attained; i.e. inlet and outlet gas concentrations were in a regular pattern.

The lab-scale biotrickling filter was operated for 36 days using an ET inlet concentration ranging from $136 \pm 18 \text{ mg/m}^3$ to $1531 \pm 150 \text{ mg/m}^3$, trickling velocity 0.12 m/h, and EBRT 60 sec. The study followed the procedure depicted in Figure 4.11. For the first five days (1-5), a relatively low concentration of the odorous ET gas, i.e. $136 \pm 18 \text{ mg/m}^3$, was introduced into the biotrickling column. The resulting competition between microorganisms for organic substrate (ET) as the only carbon source was evident in the high RE of 88%. Consequently, as the microorganisms adapted to the treated gas, there was a gradual increase in inlet gas concentration, up

to a maximum value $1531 \pm 150 \text{ mg/m}^3$. When stability was reached in the outlet concentrations, i.e. on day 36 of operation, the initial pressure drop across packing was measured at about 6 cm water/m of column height.

In the acclimation period, the inlet and outlet gas concentrations were dissimilar and varied from day 1 to day 36.

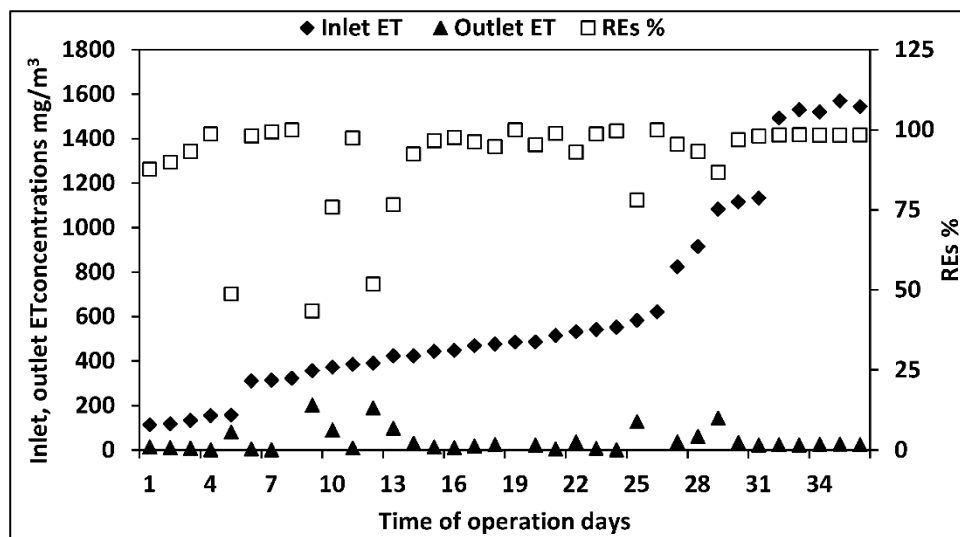


Figure 4.11 : Time course of ET throughout adaptation period.

The steady-state conditions of DMS were achieved in 24 days as a start-up period to get steady-state conditions as shown in Figure 4.12. Until the 24th day of operation, the liquid medium (MSM and NaNO_3) was replaced daily with a new one; the pH was fixed at approximately 7.2 ± 0.15 .

Initially, the microbial population within filter's column was fed with a low range of DMS concentration ($169 - 442 \text{ mg/m}^3$) for 12 days with continuous feeding of NO_3^- , nutrients, and MSM solution. The REs fluctuated between 73 and 91% for output concentrations ranging from 15 to 39 mg.m^{-3} respectively. From the 13th to the 21st day of operation, there was a progressive increment in DMS inlet concentration ($800 - 1560 \text{ mg/m}^3$), while REs slightly decreased (83–72%). Symbiotically, inlet, outlet, and removal efficiency of DMS were attained during the last 4 days of the adaptation process (21- 24th day). Up to the 24th day, the inlet DMS concentrations were 1548 mg/m^3 , on average, with no significant variations in REs or outlet of DMS concentration, indicating that steady-state conditions were attained.

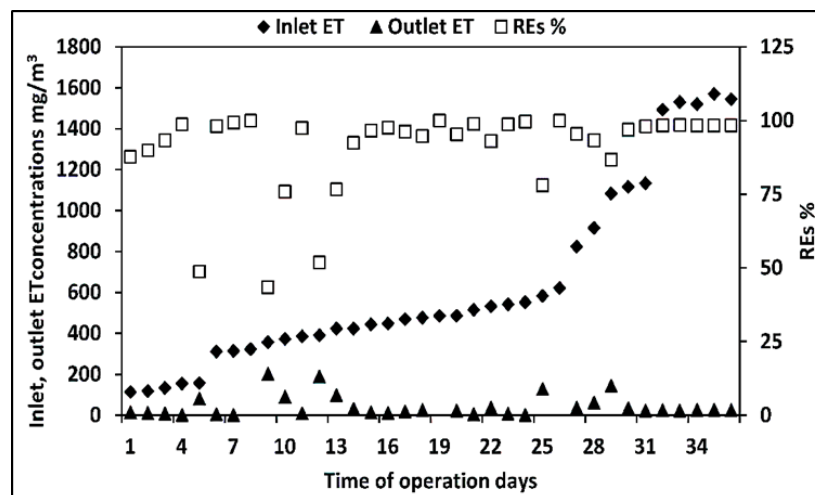


Figure 4.12 : Time course of DMS throughout adaptation period.

4.4.2 Effect of trickling velocity on removal efficiency

The biodegradation process for ET and DMS in anoxic conditions (O_2 limitation) depends on Henry's constant, as a determining factor. ET gas is considered moderately hydrophilic, while DMS gas is more hydrophilic i.e. dimensionless Henry's constant as 0.15-0.21 and 0.073, respectively (Roman, 2016; Wang, P. et al., 2015; Zhu et al., 2004). Since the liquid recycling rate is a crucial parameter in mass transfer in biotrickling filter operations, the optimum values have to be set experimentally (Mudliar et al., 2010). In the study, the effect of the trickling velocity (TV) of MSM and $NaNO_3$ volumes was tested for five values (0.12, 0.18, 0.24, 0.3, and 0.45 m/h). These values in most, have been cited in the literature (Sedighi et al., 2016; Wan et al., 2011; Wang, P. et al., 2015). RE and EC of the target gases (ET and DMS) were estimated for different inlet concentrations (150, 300, 800, 1500 mg/m^3) at fixed EBRT 60 sec.

Generally, as shown in Figure 4.13, ET RE increased gradually from 63.5 to 80.6% and EC increased from 58.3 to 75.18 $g/m^3/h$ at highest ET concentration (1500 mg/m^3) when TV increased from 0.12 to 0.45 m/h. This trend in the ET degradation process can be credited to the reduction in the diffusion limitation because of the increase in the gas-liquid concentration gradient, despite the poor solubility of ET.

It is estimated that extreme water supplementary may limits the rate of oxygen diffusion hence, the availability of hydrophobic pollutants to the biofilms restricted (Bak et al., 2017). The abundance or lack of nutrients in the liquid medium can a possible limiting factor in regulating a microorganism's metabolic speed of ET

biodegradation and maintaining a normal metabolism for biofilm growth (An et al., 2010; Jaber et al., 2014; Wang, P. et al., 2015). More specifically, increasing the trickling velocity may enhance the metabolic activity of the microorganism by increasing the amount of necessary nutrients, thus degrading ET. However, there was no significant effect on REs in this study when TV was increased at low ET concentrations, i.e. 150 and 300 mg/m^3 . When it increased from 0.24 to 0.45 m/h , RE remain constant around 92.4% at ET concentration 150 mg/m^3 ; there was a similarly negligible increase, from 88.4 to 89.2%, at ET concentration 300 mg/m^3 .

These findings suggest that increasing the liquid flow rate at high ET concentrations (i.e. 1500 mg/m^3) will increase the substrate concentration on the surface of the cells and the biodegradation rate while reducing the diffusion limitation. They also suggest that because of the porous structure of the packing media, the formation of a dense biomass enhances the ability to reduce the mass transfer limitation and diffusion (Sedighi et al., 2016).

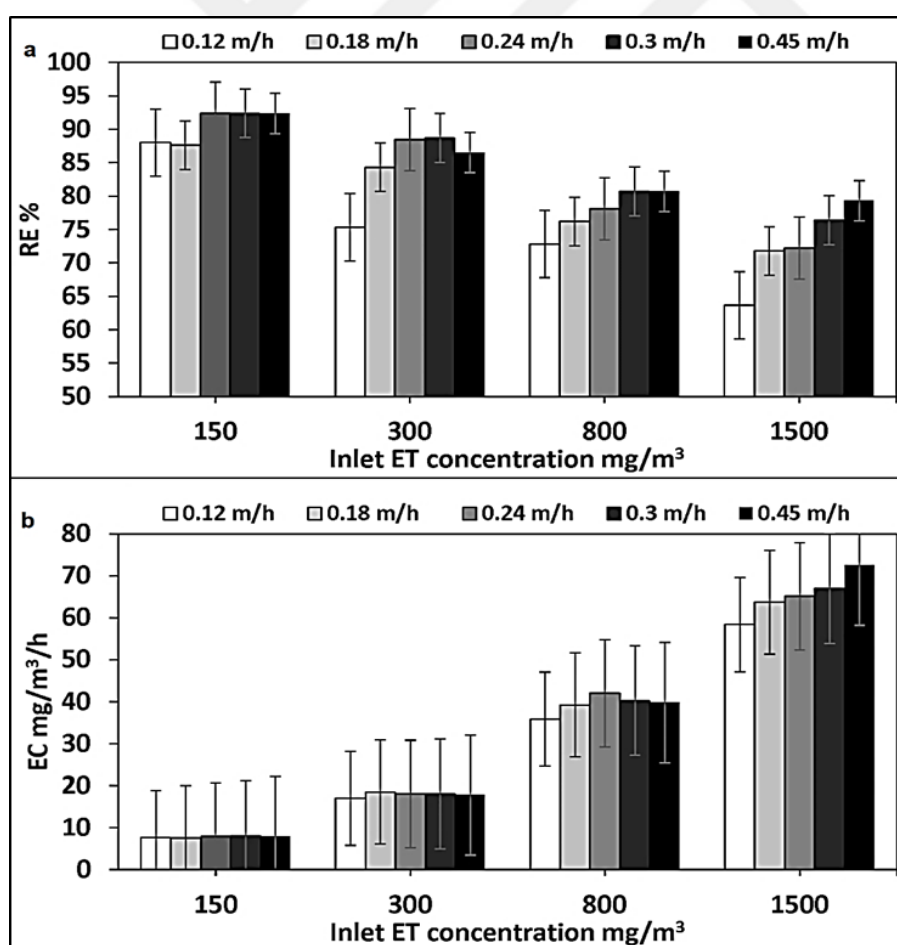


Figure 4.13 : Effect of TV on ET a) Removal efficiency and b) Elimination capacity under various inlet concentrations.

Briefly stated, by increasing the trickling velocity to 0.24 m/h, RE of 92.4% and 72.2% can be reached at low and high inlet concentration of ET (i.e. 150 and 1500 mg/m³ respectively). At a higher ET inlet concentration (i.e. 1500 mg/m³), the trickling velocity must be increased to 0.45 m/h to have a significant effect on RE (about 80.6 %).

Wang, P. et al. (2015), examined the effect of spray density on the ability of biotrickling filter systems to remove ET. In this study, the REs of three levels of ET concentration (i.e. 110, 200, and 300 mg/m³) greatly improved when spray density was increased to 0.24 m³/m².h. When spray density was greater than 0.24 m³/m².h, a stable RE trend was achieved in the three groups, with RE values about 60%. Chou and Huang (1997) found that the RE for Methylethylketone increased from 90 to 100% in a biotrickling filter when trickling velocity increased from 0.5 to 2.0 m/h at C₀ = 1800 mg/m³. At lower concentrations, i.e. C₀ = 700 mg/m³, the increment of liquid recycling velocity had a marginal effect on RE.

Chen et al. (2006), showed that when the liquid to gas ratio (L/G) was increased from 0.001 to 0.005 corresponding to irrigation velocity 0.22–1.13 m/h, the RE of H₂S increased from 88.5% to 99.7%. A study by Abdehagh et al. (2011) found that when the liquid recycling rate increased from 0.46 m/h to 0.92 m/h, the RE of H₂S increased from 85 to 100% respectively, at inlet H₂S concentration 40 ppm and EBRT 45 sec.

The biodegradation process for DMS in anoxic conditions is presented in Figure 4.14. There was a stable tendency in DMS removal efficiency at low liquid recycling rate i.e. TV 0.12 and 0.18 m/h. REs fluctuated between 70.5 and 79.6% corresponding to inlet DMS concentration 1500 and 150 mg/m³ respectively, with MEC 62.1 ± 2.8 g DMS/m³/h. When the TV was increased to 0.24 m/h, REs abruptly increased to 79 and 92.6 %, corresponding to inlet DMS concentration 1500 and 150 mg/m³, respectively, and MEC climbed to 70.3 g/m³/h. It is worth noting that the further increment of TV to 0.3 and 0.45 m/h had no significant effect on REs at constant inlet DMS concentrations. The trend reveals that with excessive amounts of minerals and nutrients in solutions, i.e. increasing the liquid recycling rate may not lead to more DMS absorption; hence, the availability of DMS to the biofilms may be restrained, causing the water scrubbing effect to play a limited role in DMS removal (Bak et al., 2017; Wei et al., 2013). Moreover, a higher trickling rate in the biofilter

may result in the DMS gas being purged, along with the leachate medium (NO_3^- and MSM) (Giri et al., 2010). However, Arellano-García et al. (2009) found that when the trickling velocity was increased from 2.75 to 7.85 m/h, the performance of BTF in DMS removal was enhanced, suggesting mass transfer limitations can be diminished with liquid turbulence and increments in absorption capacity.

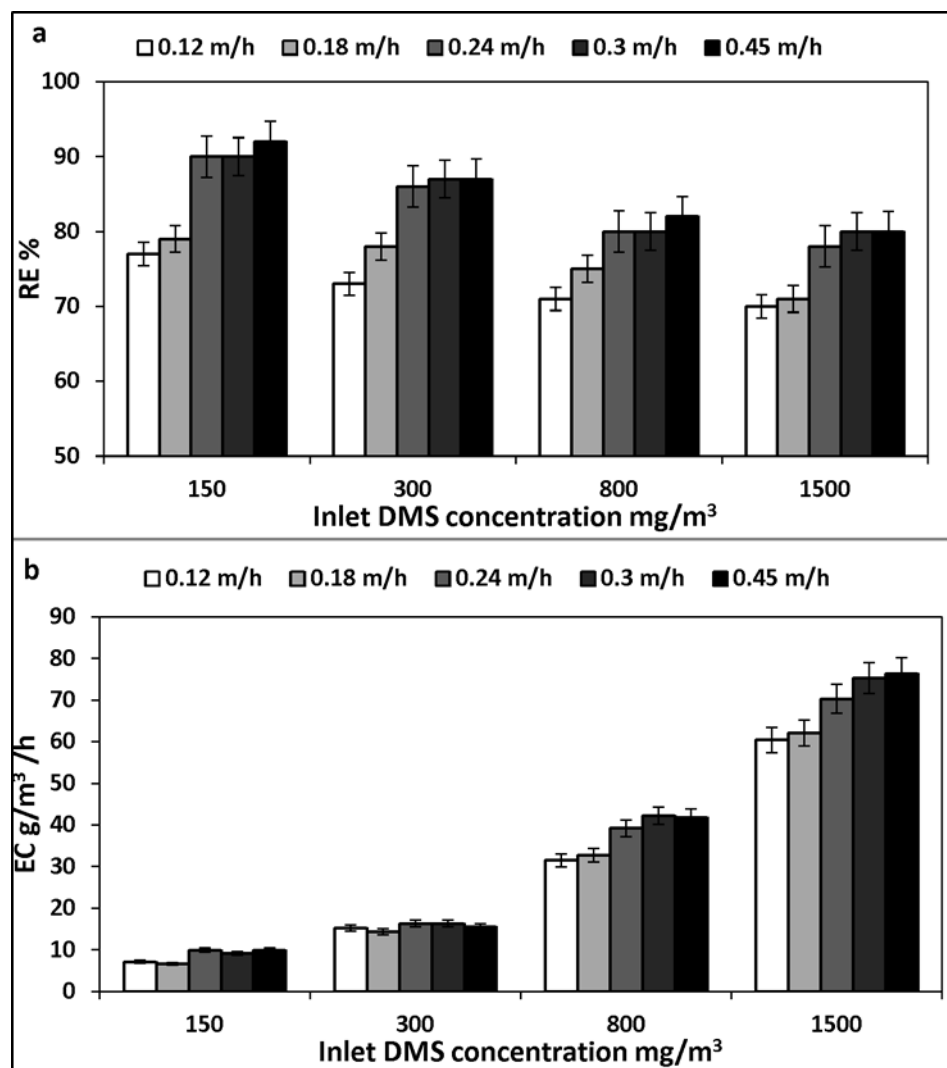


Figure 4.14 : Effect of TV on DMS a) Removal efficiency and b) Elimination capacity under various inlet concentrations.

The effect of TV on EC was noticeable, especially at higher inlet concentrations, i.e. 1500 mg/m^3 . Interestingly, ECs remarkably increased from 70.3 to 76.4 $\text{g/m}^3/\text{h}$ when the TV increased from 0.24 to 0.45 m/h, respectively. However, RE remained stable; hence, the intermediate metabolic had no inhibition effect on microorganism bioactivity, and mass transfer limitation was the controlling process. The results showed that the TV effect depended on DMS inlet concentrations since there was a

significant decrease in REs when inlet concentrations increased 10-fold, i.e. from 150 to 1500 mg/m³, for different TV values. The suggested critical limit for TV is 0.24 m/h, as the further increment in trickling flow may cause biomass detachment and flush it out of the system.

Two different behaviors were noted for inlet concentrations:

- At low gas concentrations, i.e. 150 and 300 mg/m³, diffusion limitation was the main controlling process.
- At high gas concentrations, i.e. 800 and 1500 mg/m³, diffusion limitation was reduced because of increases in the gas concentration differences. Hence, the gas-liquid mass transfer flux which is proportional to the gas concentration's gradient can abate the poor solubility effect. This approach can be improved by increasing nutrient irrigation flow and, consequently, increasing the biomass levels and providing extracellular metabolites, such as biosurfactants (Kraakman et al., 2011).

4.4.3 Effect of EBRT on removal efficiency

Depending on various features, such as the liquid recycling rate, the packing material surface area and structure, and liquid distribution within the biotrickling filter column, the optimum EBRT can be set between 20 and 120 sec for DMS waste gas, particularly in simulated biofiltration systems (Giri et al., 2015). EBRT has a considerable impact on biotrickling filtration processes. Therefore, the study investigated four intervals of EBRT (30, 60, 90, and 120 sec) to evaluate the performance of the biotrickling filter for ET removal at four inlet concentrations (150, 300, 800, 1500 mg/m³). The TV was set at 0.45 m/h, as shown in Figure 4.15. RE steadily increased with increasing EBRT, but there was a remarkable increase in RE when EBRT increased from 30 to 60 sec (i.e. RE increased from 70.4 and 61.4% to 92.3 and 80.6% at ET inlet concentrations of 150 and 1500 mg/m³, respectively). These increments in RE can be attributed to the extension in contact time between gas molecules and liquid, as more gaseous molecules were diffused into the bulk surface of the biofilm (An et al., 2010). However, no significant effect was observed when EBRT increased from 60 to 120 sec. RE barely increased, going from 80% to 86% at high ET inlet concentrations of 1500 mg/m³ for 60 and 120 sec, respectively. At low ET inlet concentrations, RE was approximately constant, remaining at about

92% for concentrations of 150 mg/m^3 when EBRT increased from 60 to 120 sec. The results indicate that increasing EBRT up to 60 sec was sufficient to improve the removal efficiency of the biotrickling filter. In a related study, An et al. (2010) showed that at fixed recycling flow 7.5 L/h and inlet ET concentration 1.05 mg/L , RE for RG-1 and B350 strains increased from 70.9% and 47.2%, respectively, to 100% when EBRT increased from 66 to 332 sec.

In this study, the best conditions were determined as the following: trickling velocity 0.24 and 0.45 m/h for 150 and 1500 mg/m^3 inlet ET concentrations, respectively, and EBRT 60 sec .

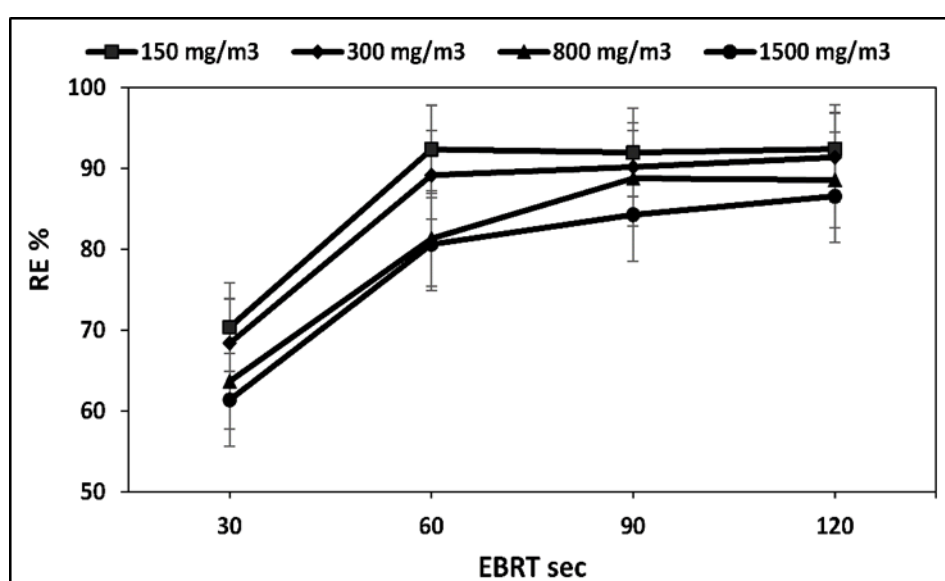


Figure 4.15 : Effect of EBRT on removal efficiency at different inlet ET concentrations.

From another hand, a wide range of EBRT (10-120 sec) was selected to detect the optimal EBRT value for DMS gas removal at constant TV of 0.24 m/h .

As presented in Figure 4.16, RE is an increasing function of EBRT at fixed inlet concentration. The lowest REs, i.e. 72% (inlet concentration 150 mg/m^3) and 58% (inlet concentration 1500 mg/m^3), were attained for shorter EBRT 10 sec , when fewer gaseous molecules diffused in the bulk surface of the biofilm because of the short contact time between gas molecules and liquid; this likely increased mass transfer limitations (An et al., 2010; Shu & Chen, 2009). The finding suggests that higher values of EBRT must be maintained for proper DMS removal. Shu and Chen (2009), found that removal efficiency decreases by at least 10% when EBRT is shorter than 20 sec .

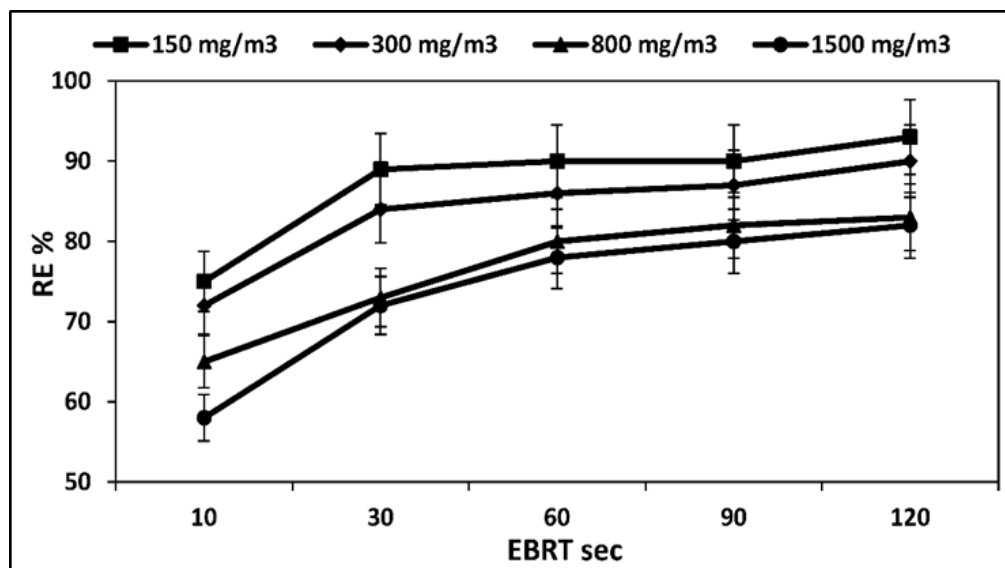


Figure 4.16 : Effect of EBRT on removal efficiency at different inlet DMS concentrations.

RE gradually increased, from 89 to 93 (inlet concentration 150 mg/m³) and from 72% to 82% (inlet concentration 1500 mg/m³) when EBRT increased from 30 to 120 sec in the system. The slight increment in RE for both low and high DMS concentrations may be attributed to the inhibition effect of the metabolic intermediates produced through the DMS oxidation pathway, basically H₂S (Shu & Chen, 2009). In this study, the effect of acidification was excluded since the pH values fluctuated between 7.2±0.15 and 7.5±0.4 along the experiment's period.

It is worth noting that increasing the inlet concentration of DMS gas can enhance the gas flux transferal to the biofilm, causing RE to decline at fixed EBRT, as such mass transfer limitation can be controlled by EBRT. Thus, it can be stated that the optimum EBRT was 30 sec; about 90% of DMS gas was bio-converted at 150 mg/m³. More time was needed for the microorganisms to degrade gaseous DMS at higher concentrations, i.e. 1500 mg/m³ when EBRT 60 sec (at least) was required to attain an RE of about 78%. However, the results differ from those of other studies; for example, Giri et al. (2013) reported that a biotrickling filter could remove 40.9 % of DMS at an average loading rate of 0.56 mg/m³ /h at EBRT 84 sec. In a similar study, Giri et al. (2010) found that 62–74% of inlet DMS concentration 510 mg/m³ was removed with an optimum EBRT of 384 sec and an average moisture range of 65–70%. They attributed the higher EBRT to the microbial culture differences and the limitations of a mass transfer which eventually increased the contact time between the gaseous phase and the thin biofilm (liquid phase) in the biofilter.

4.4.4 Effect of IL on removal efficiency

To determine the impact of IL on RE and EC, the study used fixed EBRT 60 sec and TV 0.45 m/h, as the best operational conditions leading to higher RE for both ET concentrations (150 and 1500 mg/m³). Generally, as depicted in Figure 4.17, RE decreased gradually with increasing ET inlet loading (IL) (8.5±1.2 to 90±2.6 g/m³/h). When the IL increased from 8.5±1.2 to 96±8.0 g/m³/h, RE decreased from 92.3% to 80.6%, indicating RE is a decreasing function dependent on inlet concentration. In fact, increasing IL of ET has two effects, one related to constraints on the biodegradation of the substances or diffusion limitation, and the other to the metabolic activity inhibition of the microbial population because of the substrate concentration in the biofilm (Jin et al., 2005; Wan et al., 2011b; Wang, X. et al., 2015). However, increasing the inlet gaseous compound of ET from 150 to 1500 mg/m³ may result in enhanced biomass, and this may allow the thickness of the biofilm to increase synchronously (Wang, X. et al., 2015). Accordingly, in this study, the biomass was increased about four times, i.e. from 240 mg to 1.08 g per 1g of packing media in 147 days.

EC is another important factor in the evaluation of biotrickling performance. This study attained EC 6.54 g/m³/h at ET load 8.5±1.2 g/m³/h to 75.18 g/m³/h with a relatively high loading 96±8.0 g/m³/h, as shown in Figure 4.17. Interestingly, at high inlet concentrations of 800 and 1500 mg/m³, REs for both concentrations was the same, about 80% (as shown in Figure 4.15) while EC increased significantly from 47 to 75.18 g/m³/h. This suggests that increased inlet concentration of ET at fixed EBRT may enhance mass transfer from gas to liquid phase; hence, more biomass takes part in biological degradation (Wan et al., 2011a). The increment in EC suggests there was no inhibition effect when inlet concentration of ET was increased to the maximum level, i.e. 1500 mg/m³. The results were better than those of An et al. (2010) in their work on aerobic biotrickling filters; inlet concentration of ET increased from 0.42 to 1.05 mg/L, and total EC scaled from 13.64 to 34.23 g/m³/h.

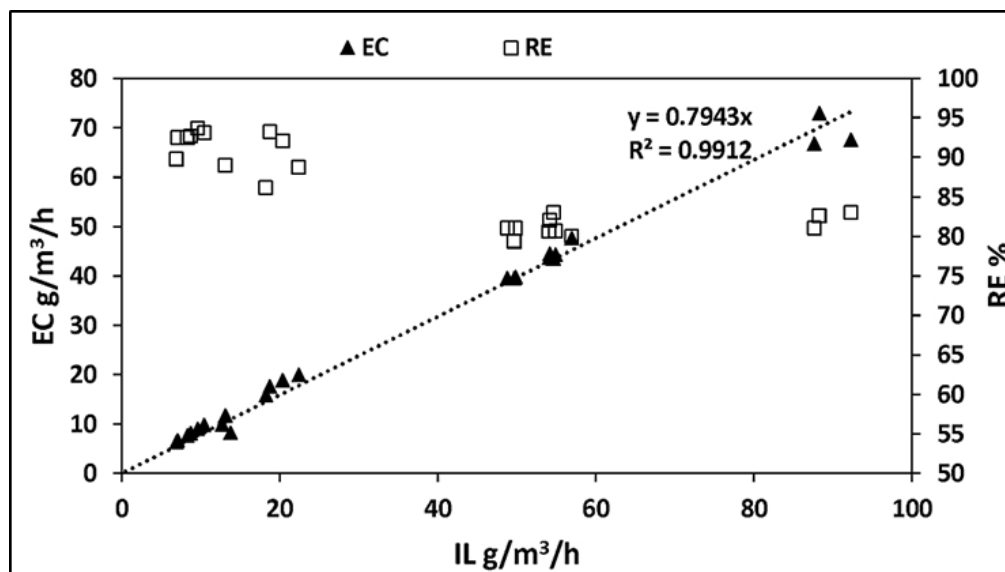


Figure 4.17 : Effects of inlet loadings of ET on elimination capacity and removal efficiency.

The ILs of DMS were ranged between 9.48 ± 1.7 - 85.8 ± 8.5 g/m³/h that fed into the ABTF. The results revealed a good adaptation of microorganisms to degrade DMS gas under varying loading rates, with optimum EBRT 60 sec and TV of 0.24 m/h, as demonstrated in Figure 4.18.

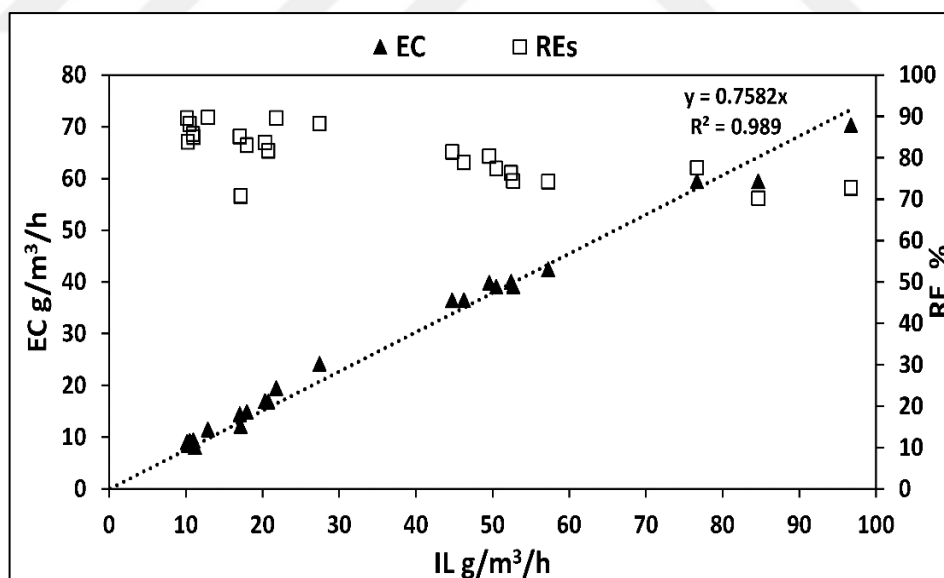


Figure 4.18 : Effects of inlet loadings of DMS on elimination capacity and removal efficiency.

The mass transfer flux from the gas phase to the liquid phase is generally proportional to the gas concentration differences at fixed EBRT. When the gas phase concentration is low, mass transfer is usually the limiting step; otherwise,

biodegradation would be reaction-limiting (Jin et al., 2005). Accordingly, the removal efficiency decreased and EC increased with increased inlet loading. As described above, at low ILs of DMS, i.e., 10.1 g/m³/h, MEC was about 9.0 g/m³/h (corresponding to RE 89.6%). When ILs increased ~10-fold, i.e. to 96.6 g/m³/h, the RE gradually decreased to 72.6%, while MEC increased abruptly to 70.3 g/m³/h. The continuation in EC increment indicates that DMS has relatively high biodegradation capacity. Moreover, there was no inhibition in microbiological activities at high inlet loading; the decline in ABTF performance (i.e. RE) was limited by the transport of DMS from the gas phase to the biofilm (mass transfer limitations) (Akmirza et al., 2017; Giri et al., 2010; Wan et al., 2011). In this sense, inlet loading rates can be considered a significantly limiting parameter in biotrickling filters' performance.

However, the results were comparable or even better than those reported in previous studies for DMS degradation during aerobic biofiltration. Lower EBRTs can be applied when oxygen is used as an electron acceptor because biodegradation rates are commonly faster. In the biofilter inoculated with *Hyphomicrobium* VS, DMS elimination capacities were observed as 8.2 g DMS/m³/h (RE = 90%) after two days of operation, and maximum observed ECs were 57 g/m³/h (RE = 92%) and 58 g/m³/h (RE = 89%) at EBRT 120 and 60 sec, respectively (Sercu et al., 2005).

4.4.5 Treatment of the binary gas mixture

Previously, most studies for the control of various odorous compounds by biotrickling filter have been limited to a sole contaminant. Generally, in practical odorous gaseous pollutants are a mixture of various species rather than a single one. To our date, there were a few publications have reported on VOSCs biofiltration in the presence of mixture composition using biotrickling filters.

The binary mixture of with different combinations was selected as target compounds to be treated. Best operational conditions that influence the biodegradation of the ET and DMS mixture, i.e. EBRT=60 sec and TV 0.24 m/h have been selected.

In this context, the REs and ECs for different ratios of ET to DMS at fixed EBRT 60 sec and TV 0.24 m/h were illustrated in Figure 4.19 and Figure 4.20, respectively, and Table 4.3.

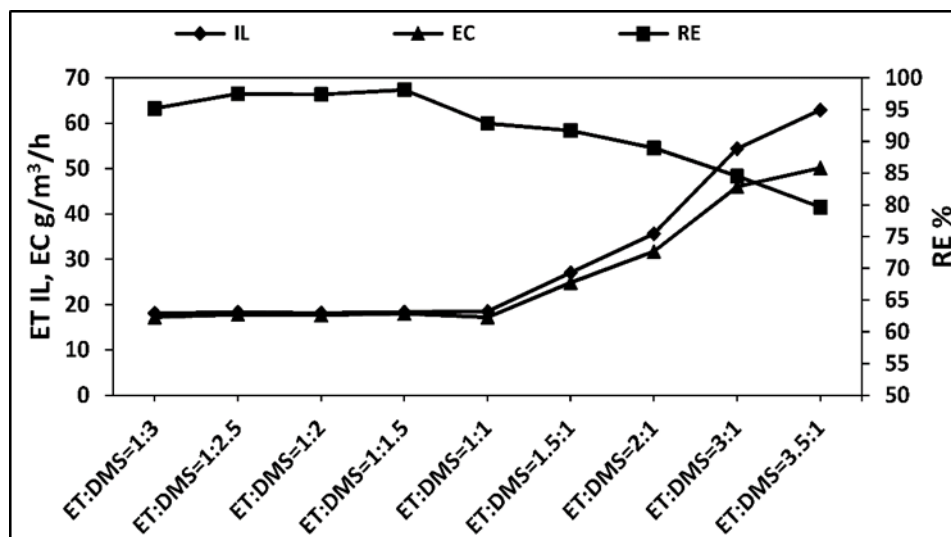


Figure 4.19 : The effect of mixing ratio of binary gas mixture on RE and EC of ET.

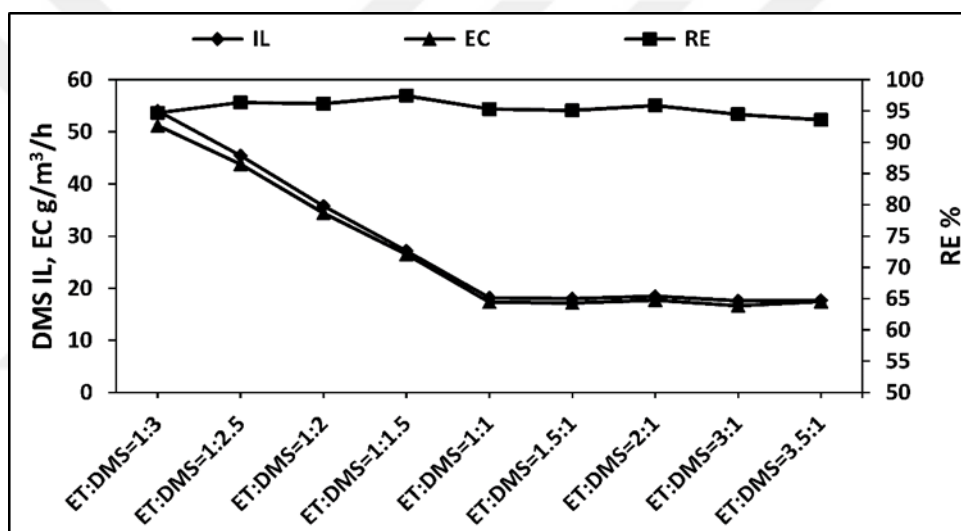


Figure 4.20 : The effect of mixing ratio of binary gas mixture on RE and EC of DMS.

To investigate the effect of a co-substrate with DMS on the performance of the biotrickling filter, initially, the inlet concentration 300 mg/m^3 of both ET and DMS was maintained constant throughout a test with step-increases of both gases to the specified mixture ratios.

Obviously, as shown in Table 4.3, that increasing DMS ratio (inlet loading rate) by 1.5 times, has significant pros effect on DMS and ET removal efficiency. Clearly, RE increased from 92.9% at ET: DMS 1:1 to about 98.1% (corresponding EC $18.07 \text{ g/m}^3/\text{h}$) at ET: DMS 1:1.5. In contrary, although IL increased from 18.21 to $27.22 \text{ g/m}^3/\text{h}$, the removal efficiency of DMS has marginal increment from 95.3 up to 97.4% (EC $26.52 \text{ g/m}^3/\text{h}$). Interestingly, the corresponding EC of DMS has been

increased significantly from 17.36 to 51.21 g/m³/h, while REs were constant or slightly decreased. This trend can be attributed to the diffusion limited regime, in which, the transfer rate of substrates from gas to biofilm was enhanced by increase of inlet concentration so that more microorganisms participate in the biodegradation activity. Thus, REs remain constant and ECs are increased with increase of inlet concentration at fixed EBRT (Wan et al., 2011b). In another view, the increment in ET inlet concentration i.e. ET: DMS ratio from 1:1 up to 3.5:1 has a passive effect on ET and in less on DMS. Eventually, RE decreased to 93.6% (EC 16.56 g/m³/h) for DMS and to 79.9% (EC 51.12 g/m³/h) for ET.

Overall, higher ET and DMS removal efficiencies were obtained at ET:DMS (1:1.5), whereas ET and DMS RE was 98.1% and 97.4%. While at higher concentrations of ET (i.e. ET:DMS 3.5:1) led to abrupt drop in ET removal efficiency to 79.9% and slight drop in DMS RE to 93.6%.

These results indicate that DMS REs can be affected by ET presence and vice versa. Accordingly, the optimal ratio of ET: DMS was 1:1.5, in which the changes obtained for the REs of DMS in the presence of ET were much less significant than those of ET.

Table 4.3 : Total EC and REs of the binary mixture of ET and DMS at fixed EBRT 60 sec.

Mixing ratio	IL g/m ³ /h		EC g/m ³ /h		RE%	
	DMS	ET	DMS	ET	DMS	ET
ET:DMS=1:3	54.06	18.10	51.21	17.23	94.7	95.2
ET:DMS=1:2.5	45.46	18.34	43.82	17.88	96.1	97.5
ET:DMS=1:2	35.76	18.18	34.40	17.71	96.2	97.4
ET:DMS=1:1.5	27.22	18.41	26.52	18.07	97.4	98.1
ET:DMS=1:1	18.21	18.56	17.36	17.23	95.3	92.9
ET:DMS=1.5:1	18.04	27.09	17.16	24.84	95.1	91.7
ET:DMS=2:1	18.49	35.66	17.73	31.72	95.9	89.0
ET:DMS=3:1	17.62	54.40	16.64	45.98	94.5	84.5
ET:DMS=3.5:1	17.7	62.92	16.56	50.12	93.6	79.7

Finally, Table 4.4 summarizes the results of previous studies. As the table shows, the biotrickling filter was comparatively more reliable when NO_3^- was used as an electron acceptor instead of oxygen for ET and DMS biodegradation. The results suggest anoxic biotrickling filters are economically viable and environmentally sustainable in the treatment of O_2 -deprived VOSC.



Table 4.4 : Comparison of ABTF performance for ET and DMS degradation with conventional BTF and BF.

Bioreactor type	Packing media	Inoculum strain	Electron acceptor	EBRT sec	$C_{in} / IL \text{ mg/m}^3 \text{ g/m}^3/\text{h}$	RE%	References
Lab-scale BTF	polyethylene rings	anoxic activated sludge	NO_3^-	60	150-1500	92-80	This study
Lab-scale BTF	ceramic particles	RG-1 and B-350	O_2	110	640-1050	100	(An et al., 2010)
Pilot-scale BTF	polyurethane foam	alkaliphilic sulfo-oxidizing	O_2	40	25-380	50	(Arellano-García et al., 2010)
Lab-scale BTF	poplar wood chips	mixed culture	O_2	32	100-300	95	(Hernández Sicilia et al., 2012)
Lab-scale BF	polyurethane foam	activated sludge supernatant	O_2	60	20	98	(Liu et al., 2008)
Lab-scale trickled bed bioreactor	kissiris particles	<i>Ralstonia eutropha</i>	O_2	92	1600-36900	100-95	(Sedighi et al., 2016)
Lab-scale BF	composted wood mulch + pine bark	activated sludge	O_2	60	3.8-7.6	97-90	(Jaber et al., 2014)
Lab-scale BTF	ceramic particles	B350 group microorganisms	O_2	110	600	100	(Wan et al., 2011a)
Lab-scale BTF	ceramic particles	<i>Lysinibacillus sphaericus</i> RG-1	O_2	110	420-1210	100-93	(Wan et al., 2011b)
Lab-scale BTF	iron oxide porous ceramsite	activated sludge	O_2	60	200-400	60	(Wang, X. et al., 2015)
Lab-scale BF	-----	fungi	O_2	58	725	98	(Zhu & Liu, 2004a)
Lab-scale BTF	polyurethane foam	garden soil	O_2	84	9.7-65.12 $\text{mg/m}^3/\text{h}$	13-100	(Giri et al., 2013)
Trickle-bed bioreactor	polyethylene ralu rings	rod of <i>Cedecea davisae</i> and <i>Pseudomonas</i> species	O_2	19.2-57.6	27-61	9.4-100	(Bak et al., 2017)
BTF	ceramsite	<i>Bacillus</i> species <i>Rhodobacteraceae</i> bacterium	O_2	19-114	5.5-249	54-100	(Wei et al., 2013)

4.5 Metabolic By-product and Pressure Drop

The ET and DMS were eventually converted to CO₂ and other intermediates and used by the cells to produce biomass. Thus, as shown in Figure 4.21 a and b, there was a dramatic increase in CO₂ production related to inlet concentration increments at optimum trickling velocities. At ET trickling velocity of 0.45 m/h, there was an abrupt increment in CO₂ concentration, from 200 to 857 ppm (91.8 g/m³/h), with inlet concentrations increasing from 150 to 1500 mg/m³. While maximum CO₂ production in DMS gas mineralization was about 537 ppm (59 g/m³/h), at a trickling velocity of 0.24 m/h. Which emphasized that ET and DMS have been effectively assimilated in ABTF column.

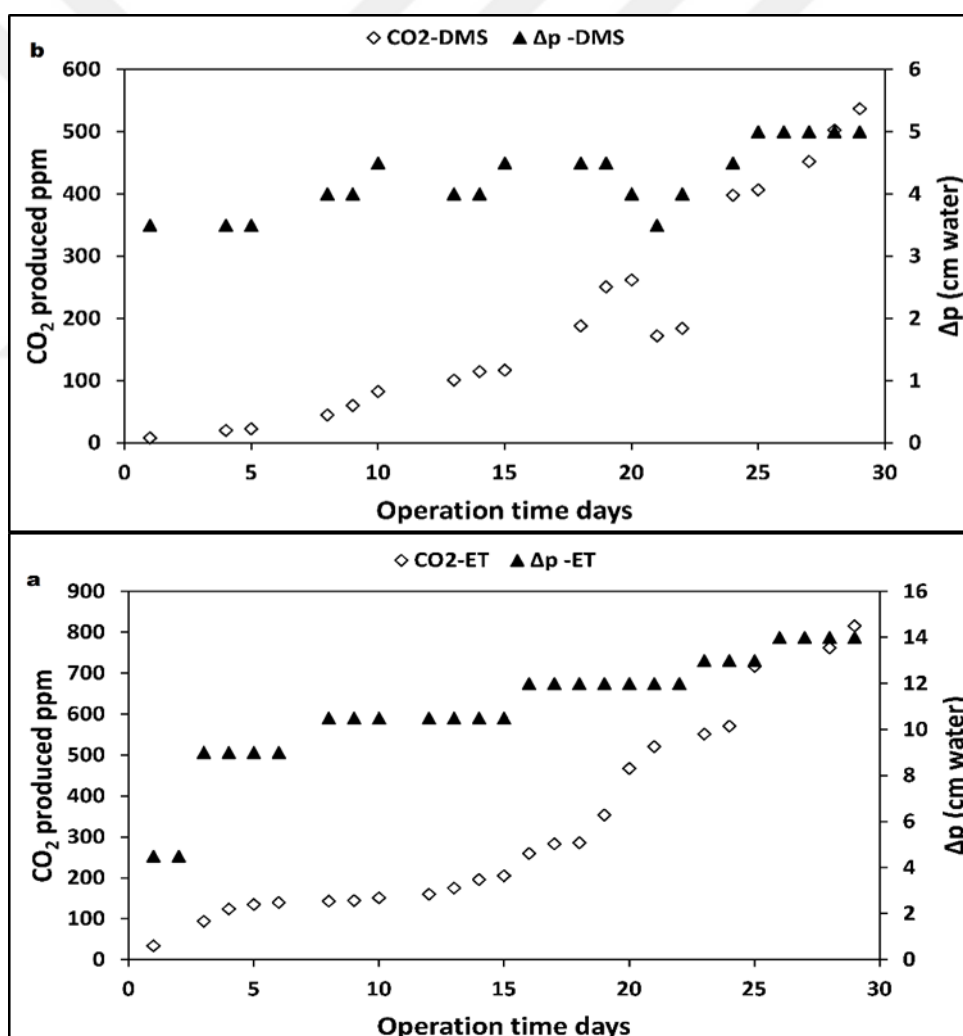


Figure 4.21 : CO₂ production and pressure drop development during the operation period of a) ET and b) DMS.

The control of biomass accumulation is the focus of many biotrickling filter investigations. Biomass accumulation can be linked to pressure drops that result in short-circuits in the bed. An increase in pressure drop can also increase the operating cost of the biotrickling filters leading to possible system failure (De Vela & Gostomski, 2018; McNevin & Barford, 2000). The total pressure drop in the biotrickling filter developed linearly, from 4.5 to 14 cm of water, through out of ET operation periods whilst the inlet concentration increased from 150 to 1500 mg/m³. This indicates clogging and blocking problems may occur with biomass accumulation, something also noted by Yang and Allen (Yang & Allen, 1994). This deduction was affirmed by measuring biomass density; in fact, it increased significantly from 0.24 at the start to 1.08 g sludge/g packing media at the end of the operation period. At this point, the filter's column was cleaned and backwashed. In contrary, during DMS operation the pressure drops fluctuated between 3.5-5 cm, hence neglable increments in biomass accumulation were noticed in filter coloumn.

In addition, the study investigated the fate and degree of mineralization of ET and DMS as a sole carbon source, by collecting samples and measuring COD in the recirculating liquid solution. The COD of the samples taken at the end of each experiment ranged between 14-56 mg/L and 33-173 mg/L, indicating well mineralization of ET and DMS in the metabolic activity of anoxic microorganisms, respectively.

The pH values of the re-circulated liquid in the biotrickling filter were regularly determined. Although sulfate SO_4^{2-} was produced in the biofiltration, thus emphasizing the desulphurization process, pH values ranged between 7.1 ± 0.06 and 7.5 ± 0.17 ; this can be attributed to the proton consumption (H^+) caused by the denitrification process in the oxidization of sulfur compounds. The daily use of a fresh inflow medium of the irrigation liquid prevented further acidification, and the formation of neutral elemental sulfur, as a major metabolic, stabilized the system's buffer capacity (Ho et al., 2008; Kim & Deshusses, 2005).

4.6 Composition of Microbial Communities

In this study, the bacterial community of ABTF treating ET and DMS gas was investigated using Illumina Miseq next-generation sequencing (NGS) analysis with a V3 reagent kit. The biomass samples were taken from the suspended growth in

inoculum tank on day 0 and from the scrubbed polyethylene rings on the end of the experimental operation. At the end of the operation period, the Shannon diversity index had abruptly decreased from 7.07 to 4.49 for ET, in contract, it was slightly increased from 7.07 to 7.24 for DMS at 20000 sequences per sample for inoculum and attached biomass, respectively, as shown in Figure 4.22.

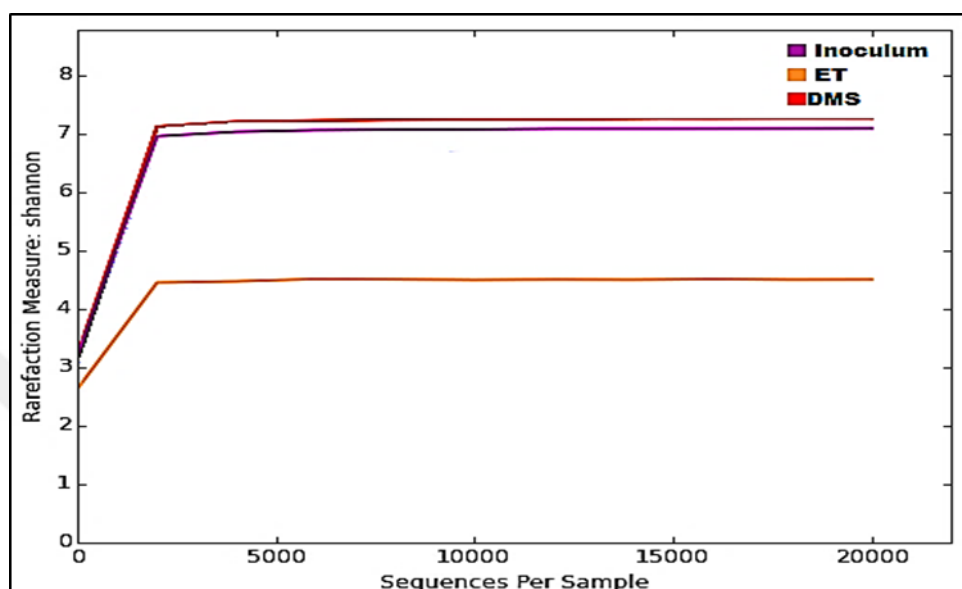


Figure 4.22 : Average Shannon diversity index.

The diversity in the bacterial community in the phylum and class level for ET and DMS gas is demonstrated in Figure 4.23 and Figure 4.24, respectively. The particular conditions applied in ABTF seemed to promote the development of a marginal percentage of the microbial communities able to grow in limited oxygen environments. The microorganisms' diversity was evaluated by the relative abundance percentages at the phylum level; this was dominated by *Proteobacteria* (36.6%), followed by *Bacteroidetes* (14.8%), *Actinobacteria* (8%), and *Chlorobi* (7%). The results showed that *Proteobacteria* was at the highest level in ABTF, and its relative abundance significantly increased as the operation continued from 36.6% to 39.7% and 56.1% for inoculum, ET, and DMS, respectively. Since DMS can be metabolized to DMSO, MM, H₂S, and SO₄²⁻ (Wei et al., 2013), the predominance of this bacteria may be attributable to the simultaneous oxidation-reduction processes under anoxic conditions for sulfur, sulfate, and carbon in the BTF. In a related study, Wei et al. (2013) showed that *Proteobacterium* bacteria is a potential candidate for purifying waste gas containing DMS.

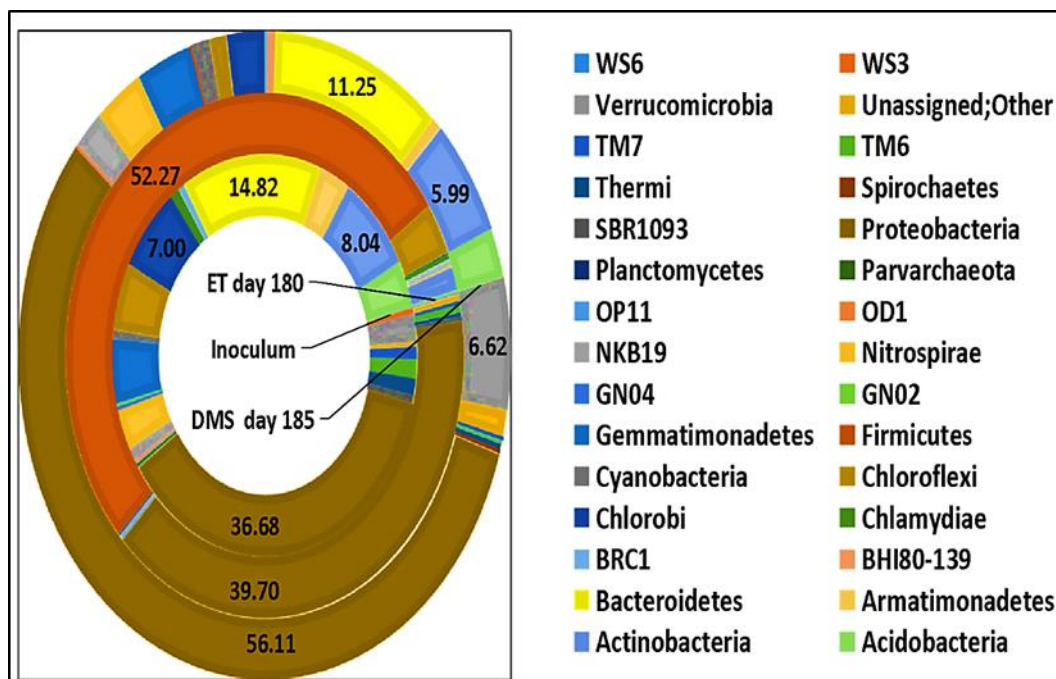


Figure 4.23 : The relative abundance of bacterial communities at phylum level.

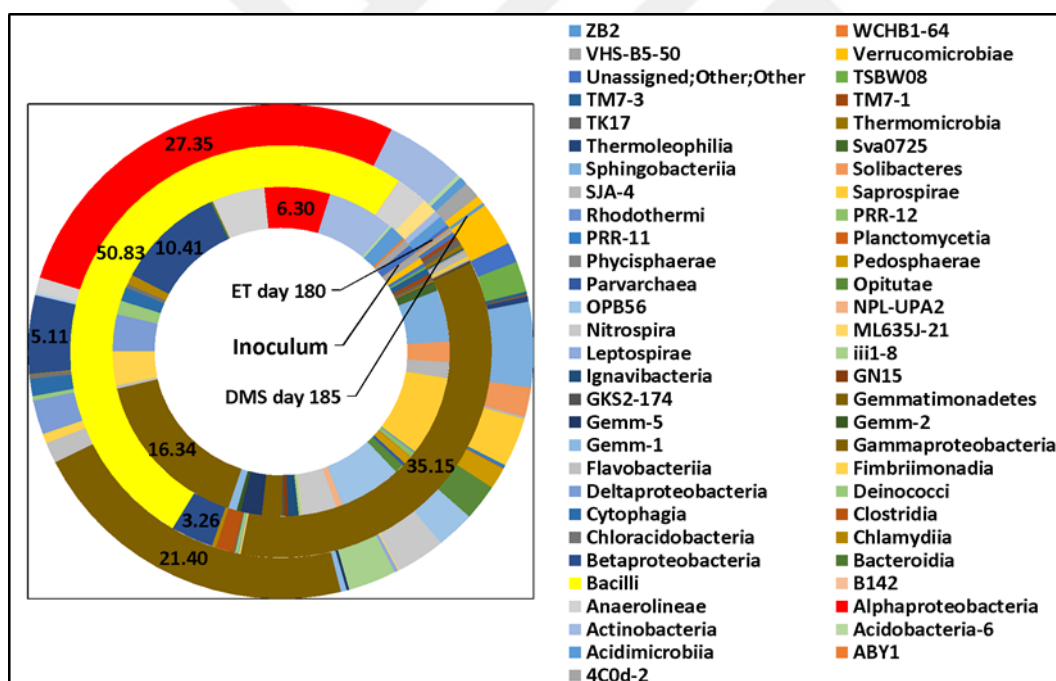


Figure 4.24 : The relative abundance of bacterial communities at class level.

Noticeably, 52.2% of *Firmicutes* of bacterium phylum with *Bacillales* order appeared in ET biofilm which has an important role in the mineralization of various nitrogen sources such as denitrification and nitrogen fixation soil in nitrogen-cycling processes (Mandic-Mulec et al., 2016). Seong et al. (2018) isolated 173 of *Firmicutes* species from natural environments in Korean territory, fermented foods,

and solar salterns. The most abundant species were belong to the class *Bacilli*, of which 151 species were affiliated with the order *Bacillales*. In another study by In a study on the anaerobic treatment of diluted chicken manure using anaerobic ammonium oxidizing (Anammox), Yangin-Gomec et al. (2017) reported that the relative abundance of the predominant phylum *Proteobacteria* increased from 20 at day 0 to 25% at day 120. *Bacteroidetes*, the second most abundant class in the ABTF, generally identified as Gram-negative, obligates in anaerobic environments and has a high degradation capacity for high molecular weight compounds, i.e. proteins (Fernández et al., 2014). This bacterium and *Actinobacteria* was completely disappeared (0%) throughout ET treatment, while slightly decreased towards the end of the operation period from 14.8% and 8% to 11.2 % and 5.9% after 185 day of operation for DMS treatment. The analysis revealed that *Chloroflexi*, which is related to the granular structure sustaining (Fernandez-Gomez et al., 2013), *Cyanobacteria*, and *Verrucomicrobia* were also present in ABTF at the phylum level. In another study, Cao et al. (2016) highlighted the similar abundance of bacterial phyla, i.e., *Proteobacteria*, and *Bacteroidetes* in the partial denitrification process throughout the anaerobic oxidization of ammonium.

The most abundant classes in the inoculum were *Gammaproteobacteria*, *Betaproteobacteria*, and *Alphaproteobacteria* at about 16.3%, 10.4%, and 6.3%, respectively. There was a noticeable increment in *Gammaproteobacteria* population i.e. from 16.3% to 35.1% and 21.4% for ET and DMS treatment, respectively. Interestingly, around 50% of the class level was represented by *Bacilli* class in ET treatment period. A study by Arellano-García et al. (2009) reported that *Thiobacillus thioparus* which accumulated in the packing medium was responsible for gaseous DMS elimination in a BTF. In a similar study, they evaluated the removal of H₂S and DMDS in an alkaline BTF at pH 10. Their results showed that the use of a DMDS and H₂S mixture was related to *Proteobacteria* (64.6%) in the phylum level with *Gammaproteobacteria* (47.4%) and *Alphaproteobacteria* (8.5%) in the class level (Arellano-García et al., 2018).

Distinct groups within order level (data not shown) were *Pseudomonadales* (7%), *Burkholderia* (1.5%), and *Nitrospirales* (3%); these are all well-characterized as ubiquitous bacteria capable of performing complete nitrification and playing a role in nitrogen fixation (Arellano-García et al., 2018; Zhu et al., 2004).



5. CONCLUSIONS AND FUTURE PERSPECTIVES

5.1 Conclusions

To the best of our knowledge, this is the first study of the biodegradation of ET and DMS under anoxic denitrifying conditions in a biotrickling filter. In this study, the results suggest ABTF is a promising biotreatment alternative which surpassed other biological treatments in the abatement of odorous ET and DMS gases.

Considering the experimental results obtained during this study, the major conclusions are presented below:

- Basically, the results can refer that the biotrickling filter operation has reliable treatment efficiency and a greater impact under anoxic conditions when nitrate was used as an electron acceptor.
- The chemotrophic biodegradation of DMS and ET in batch processes showed that ET desulfurization route was better than that for DMS under anoxic conditions using NO_3^- as an electron acceptor. Furthermore, complete degradation of both gases at fixed inlet concentrations $\sim 385 \pm 31$ mg/m was achieved in ~ 9 hrs at VSS concentration 3000 mg/L for five degradation cycles.
- The kinetic parameters of the maximum degradation rate velocity (V_{max}), half velocity constant (K_m), and pseudo-first order constant (k) for both gases was fitted to a Monod model using GraphPad Prism software 6.0. Where k , K_m , and V_{max} values were 0.14/h, 2.21 mg/L, and 0.809/h for ET and 0.11/h, 1.92 mg/L, and 0.193/h for DMS.
- In the long term evaluation performance of ABTF, the results suggest that the best operational conditions for ET were obtained when MEC was 75.18 g/m³/h (RE 80%) at EBRT 60 sec, TV 0.45 m/h, at an average IL 90 ± 2.6 g/m³/h.

- While for DMS, MEC was 70.3 g/m³/h (RE 78%) at EBRT 60 sec, TV 0.24 m/h, at an average IL 96.7 g/m³/h.
- The experimental results of ET and DMS to nitrate molar ratio were compatible with the derived stoichiometric equations and thermodynamic estimations i.e., between 0.34 and 0.74 mole/mole.
- The sulfur bioconversion and mass balance estimation showed that 64% and 58% of the cumulative inlet loading rate of the ET-S and DMS-S was biologically converted to elemental sulfur.
- The denitrification efficiency calculations revealed that 64% and 52.7% of the inlet NO₃⁻-N was converted to N₂ in ET and DMS biodegradation, respectively.
- The results of the binary mixture of ET: DMS indicated that REs of DMS were much less affected than those of ET. Where the optimal ratio of ET: DMS was 1:1.5, in which RE was 98.1% and 97.4% for ET and DMS, respectively.
- Finally, the consequent confirmation of the findings using sequencing analysis distinguished the dominant abundance routes for ET and DMS removal as bacterial communities *Firmicutes* (52.2%) and *Proteobacteria* (56.1%) in phylum level, *Bacilli* (50.8%) and *Alphaproteobacteria* (27.3%) in class level, respectively.

5.2 Future Perspectives

Based on the conducted study which discussed in this thesis, several aspects need to be covered in the future. These aspects are presented below:

- Different inorganic synthetic or inert packing materials, such as open-pore foam, lava rock, ceramic or plastic structures, or mixtures are needed to be investigated for obtaining long-term operation performance of ABTF.
- Studying the effect of the non-aqueous phase liquid (NAPL) addition i.e. silicone oil, large branched alkane, and a plastic polymer to the aqueous phase to improve the mass transfer process especially for poorly soluble (hydrophobic) gaseous pollutants.

- Using specific and pure inoculum rather than mixed culture are required to be examined deeply.





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APPENDIX A

The half reactions of ET for different products were derived according to the steps presented by (Rittmann & McCarty, 2012). The same procedure can be followed for DMS half reactions derivation. Free Gibbs energy for this reactions was calculated depending on Table A.1, as shown below:

Table A.1 : Free Gibbs energy of compounds at 25° C and pH=7 (Heijnen, 2002; Rittmann & McCarty, 2012; Sawyer, 2003).

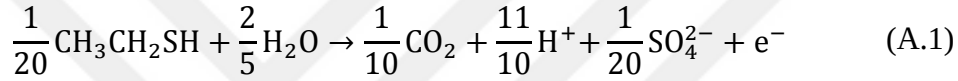
Compound	Gibbs energy kJ/e-mole
CH ₃ CH ₂ SH	-4.8
CH ₃ SCH ₃	+7
H ₂ O	-237.2
CO ₂	-394.35
H ⁺	-39.87
SO ₄ ²⁻	-744.63
N ₂	Zero
NO ₃ ⁻	-111.34
Biomass (C ₅ H ₇ NO ₂)	-340.28

While the total energetic stoichiometric equations were derived as shown in Table A.2.

Table A.2 : Half-reactions of ET derived for different sulfur products.

Reduced/oxidized Compounds	Half-reaction	ΔG^0 kJ/ e. mole
$\text{SO}_4^{2-}/\text{CH}_3\text{CH}_2\text{SH}$	$\frac{1}{10}\text{CO}_2 + \frac{11}{10}\text{H}^+ + \frac{1}{20}\text{SO}_4^{2-} + \text{e}^- \rightarrow \frac{1}{20}\text{CH}_3\text{CH}_2\text{SH} + \frac{2}{5}\text{H}_2\text{O}$	+25.4
$\text{S}^0/\text{CH}_3\text{CH}_2\text{SH}$	$\frac{1}{7}\text{CO}_2 + \text{H}^+ + \frac{1}{14}\text{S}^0 + \text{e}^- \rightarrow \frac{1}{14}\text{CH}_3\text{CH}_2\text{SH} + \frac{2}{7}\text{H}_2\text{O}$	+28.07
NO_3^-/N_2	$\frac{1}{5}\text{NO}_3^- + \frac{6}{5}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{10}\text{N}_2 + \frac{3}{5}\text{H}_2\text{O}$	-72.2
$\text{NO}_3^-/\text{BIOMASS}$	$\frac{5}{28}\text{CO}_2 + \frac{1}{28}\text{NO}_3^- + \frac{29}{28}\text{H}^+ + \text{e}^- \rightarrow \frac{1}{28}\text{C}_5\text{H}_7\text{NO}_2 + \frac{11}{28}\text{H}_2\text{O}$	+10.36

(1) Stoichiometric reaction of ET when SO_4^{2-} is the main product:



$$\Delta G_{\text{free}} = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}}$$

$$\Delta G_{\text{free}} = +25.4 \text{ kJ/e-mole}$$

Accordingly, the total energetic stoichiometric equation was derived as shown in the Table (A.2). Corresponding to Heijnen (2002) approach, the value of $Y_{G/X}$ for electron donors is $\approx 1157 \text{ kJ/C-mole}$. When the biomass yield is known, the reaction stoichiometry can be estimated (Yavuz et al., 2007):

$$Y_{X/D} = \frac{\gamma_D}{\gamma_X} = \frac{\Delta G_{eD} - \Delta G_{eA}}{(\Delta G_{eD} - \Delta G_{eA}) + \left[\frac{Y_{G/X}}{\gamma_X} + (\Delta G_{eX} - \Delta G_{eD}) \right]} \quad (\text{A.2})$$

Where:

$Y_{X/D}$: biomass yield (C-mole of biomass per C-mole of electron acceptor)

G_{eD} , G_{eA} : Gibbs free energy for electron donor and acceptor respectively (kJ/e.mole),

G_{eX} : Gibbs free energy for biomass (kJ/e - mole),

γ_D , γ_X : Degree of reduction of electron donor and biomass (e -mole/C - mole),

$Y_{G/X}$: Gibbs free energy released per C-mole of biomass (kJ/C -mole).

The degree of reduction of sulfate to ET, $\gamma_D = 6.66$

The degree of reduction of biomass, $\gamma_X = 28/5 = 5.6$

So, according to Eq. A2.

$$\begin{aligned}
 Y_{X/D} &= 0.40 \frac{\text{C_mole biomass}}{\text{mole ET}} \cdot \frac{1 \text{ mole ET}}{6.66 \text{ e - mole}} \cdot \frac{5.6 \text{ e - mole biomass}}{1 \text{C_mole biomass}} \\
 &= 0.34 \frac{\text{e - mole biomass}}{1 \text{C_mole biomass}} \quad (A.3)
 \end{aligned}$$

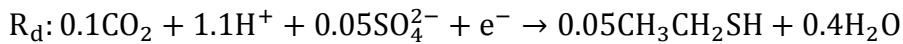
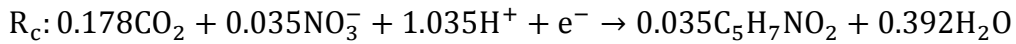
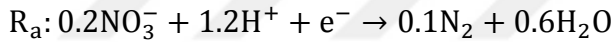
$$R = R_d - Y_{X/D} R_C - R_a(1 - Y_{X/D})$$

Where:

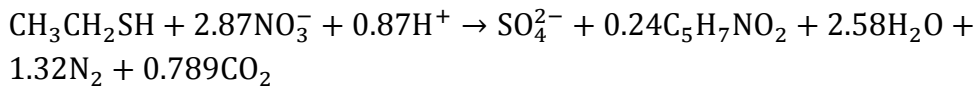
R : Overall reaction for cell synthesis and energy generation.

R_d , R_c , and R_a are denoted to half-reaction for electron donor (sulfur/sulfate), cell synthesis, and an electron acceptor (nitrate) respectively.

$Y_{X/D}$ and $(1 - Y_{X/D})$ refers to the percentile of electron equivalent in the donor for synthesis and energy respectively.



Based on equation (A.3):

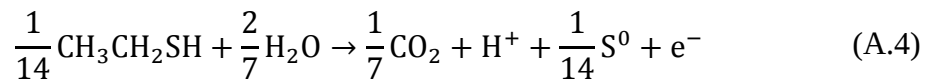


$$\therefore \text{Ratio} = \frac{\text{CH}_3\text{CH}_2\text{SH}}{\text{NO}_3^-} = \frac{1}{2.87} = 0.34$$

The total energy of the reaction:

$$\Delta G = -1389.26 \text{ kJ/e-mole}$$

(2) Stoichiometric reaction of ET when S^0 is the main product:



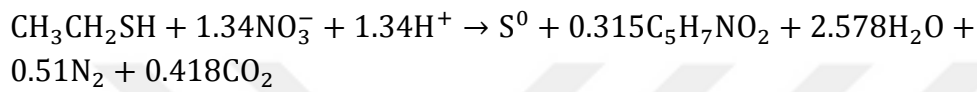
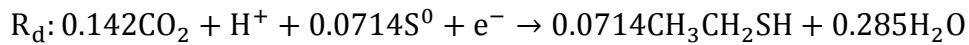
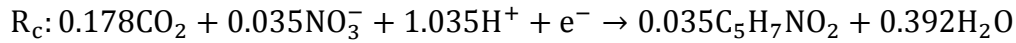
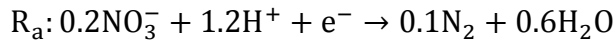
Free Gibbs energy of this reaction was calculated depending on the Table (A-1).

$$\Delta G_{free} = \sum \Delta G_{product} - \sum \Delta G_{reactants}$$

$$\Delta G_{free} = +28.07 \text{ kJ/e-mole}$$

Similarly, $Y_{G/X} = 427 \text{ kJ/C-mole}$, $\gamma_D = 4.66$ and $\gamma_X = 28/5 = 5.6$

$$Y_{X/D} = 0.63 \frac{\text{e - mole biomass}}{1 \text{C - mole biomass}}$$



$$\therefore \text{Ratio} = \frac{\text{CH}_3\text{CH}_2\text{SH}}{\text{NO}_3^-} = \frac{1}{1.34} = 0.74$$

The total energy of the reaction

$$\Delta G = -674.6 \text{ kJ/e-mole}$$

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- 2006-2011 worked as teaching assistant at Civil Engineering Department, University of Mosul.
- 2011-2014 worked as Lecturer at Environmental Engineering Department, University of Mosul.
- In 2014, he got a granted scholarship from the Iraqi Ministry of Higher Education and Scientific Research to accomplish Ph.D. degree from Istanbul Technical University.

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

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