

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**REMOVAL OF SILOXANES FROM BIOGAS USING UV
IRRADIATION**



ÜMMÜ GÜLSÜM KIRAL

A THESIS OF MASTER OF SCIENCE
DEPARTMENT OF ENVIRONMENTAL ENGINEERING

ADVISOR: ASSIST. PROF. DR. İLKER AKMIRZA

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GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

BİYOGAZDAN UV IŞINIMI İLE SİLOKSAN GİDERİMİ

ÜMMÜ GÜLSÜM KIRAL

YÜKSEK LİSANS TEZİ
ÇEVRE MÜHENDİSLİĞİ ANABİLİM DALI

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ŞUBAT 2025

MASTER of SCIENCE JURY APPROVAL FORM

A thesis submitted by Ümmü Gülsüm KIRAL, defended on 24/02/2025 before the jury formed with the 03/02/2025 date and 2025/08 numbered decision of the GTU Graduate Administration Board, has been accepted as a MASTER of SCIENCE thesis in the Department of Environmental Engineering.

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To my Family

ABSTRACT

The problems caused by global warming are increasing day by day and people all over the world face these problems, albeit in different ways. Preventing global warming and climate crisis is basically possible by replacing the energy resources used with renewable resources. The depletion of fossil fuels day by day and the environmental problems they cause have increased the demand for renewable energy sources and made them important.

Agreements and protocols between countries offer highly innovative and environmentally friendly solutions, with all parties accepting the targets set by the agreements and acting.

With the agreements, not only the positive effects of replacing fossil fuel-based resources with renewable energy sources, but also the harmful emissions released into the atmosphere such as greenhouse gas emissions that cause global warming are reduced through innovative and sustainable changes in areas such as waste management and water management. Although many renewable energy sources have gained popularity from the past to the present according to the conditions of the day, what is important today is the use of energy sources that are innovative and compatible with green cycles.

Biogas is seen as one of the most effective technologies for meeting energy needs. In order for this gas to have high energy efficiency, impurities such as CO₂, H₂S and siloxane must be removed. The removal of siloxane compounds in the biogas stream has become a priority due to the damage caused to engine components during power generation.

This study focused on biogas upgrading through siloxane removal by UV irradiation. L2 and D4, the most common species in biogas, were studied. During the study, various siloxane concentrations (70, 140, 280, 560, 1120 mg/m³) and different residence times (42 s, 84 s, 168 s) with constant UV radiation were studied. Although no significant siloxane removal efficiency was observed in this study (less than 20%), the results obtained can be a preliminary for future studies and aim to highlight the limitations in siloxane removal by UV.

Keywords: Biogas upgrading, Siloxane, UV irradiation.

ÖZET

Küresel ısınmanın yol açtığı sorunlar her geçen gün artmakta ve dünyanın her yerinde insanlar farklı şekillerde de olsa bu sorunlarla karşı karşıya kalmaktadır. Küresel ısınma ve iklim krizinin önlenmesi temelde kullanılan enerji kaynaklarının yenilenebilir kaynaklarla değiştirilmesi ile mümkündür. Fosil yakıtların gün geçtikçe tükenmesi ve yol açtığı çevre sorunları yenilenebilir enerji kaynaklarına olan talebi artırmış ve önemli hale getirmiştir.

Ülkeler arasında yapılan anlaşmalar ve protokoller son derece yenilikçi ve çevre dostu çözümler sunmakta, tüm taraflar anlaşmalarla belirlenen hedefleri kabul ederek hareket etmektedir.

Anlaşmalar ile sadece fosil yakıt temelli kaynakların yenilenebilir enerji kaynakları ile değiştirilmesinin olumlu etkileri değil, aynı zamanda atık yönetimi, su yönetimi gibi alanlarda yenilikçi ve sürdürülebilir değişiklikler ile küresel ısınmaya neden olan sera gazı emisyonları gibi atmosfere salınan zararlı emisyonlar da azaltılmaktadır. Geçmişten günümüze birçok yenilenebilir enerji kaynağı günün koşullarına göre popülerlik kazanmış olsa da günümüzde önemli olan yenilikçi ve yeşil döngülerle uyumlu enerji kaynaklarının kullanılmasıdır.

Biyogaz, enerji ihtiyacının karşılanmasında en etkili teknolojilerden biri olarak görülmektedir. Bu gazın yüksek enerji verimliliğine sahip olabilmesi için CO₂, H₂S ve siloksan gibi safsızlıkların giderilmesi gerekmektedir. Biyogaz akışındaki siloksan bileşiklerinin giderilmesi, enerji üretimi sırasında motor bileşenlerine verdiği zarar nedeniyle bir öncelik haline gelmiştir.

Bu çalışma, UV ışınlama ile siloksan giderimi yoluyla biyogazın iyileştirilmesine odaklanmıştır. Biyogazda en yaygın türler olan L2 ve D4 üzerinde çalışılmıştır. Çalışma sırasında, sabit UV radyasyonu ile çeşitli siloksan konsantrasyonları (70, 140, 280, 560, 1120 mg/m³) ve farklı bekleme süreleri (42 s, 84 s, 168 s) çalışılmıştır. Bu çalışmada önemli bir siloksan giderim verimi gözlenmemiş olsa da (%20'den az), elde edilen sonuçlar gelecekteki çalışmalar için bir ön hazırlık olabilir ve UV ile siloksan giderimindeki sınırlamaları vurgulamayı amaçlamaktadır.

Anahtar Kelimeler: Biyogaz iyileştirme, Siloksan, UV son arıtımı.

ACKNOWLEDGEMENTS

I would like to thank and express my gratitude to my advisor, Assistant Professor İlker Akmirza for his invaluable guidance, experience, suggestions, patience and endless support throughout my research.

Special thanks to my colleagues and fellow researchers at Universidad de Valladolid / Instituto de Procesos Sostenibles (ISP) / VOC and Microalgae Research Group, especially Prof. Dr. Raúl Muñoz for the opportunities, supports, and collaboration throughout this journey. Their feedback and motivation have played a crucial role in my academic development.

I am also extremely grateful to my family for their support and understanding during this challenging yet rewarding period. Their encouragement and patience have given me the strength to persevere.

I would also like to express my deepest gratitude to Anıl Akbulut for his endless encouragement and for always reminding me of my abilities when I needed it most.

Finally, I extend my gratitude to myself for my own hard work, perseverance and dedication, perseverance in the face of adversity and determination to see this journey through to the end. This thesis is a testament to my efforts, and I am proud of this achievement.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	vi
ÖZET	vii
ACKNOWLEDGEMENTS	viii
TABLE OF CONTENTS	ix
LIST OF SYMBOLS AND ABBREVIATIONS	x
LIST OF FIGURES	xi
LIST OF TABLES	xii
1. INTRODUCTION	1
1.1. Literature Review	1
1.1.1. Biogas	4
1.1.2. Biogas Production	5
1.1.3. Biogas Production Systems	6
1.1.4. Siloxanes	9
1.1.5. Siloxane Removal Methods	11
1.1.5.1 Conventional Siloxane Removal Methods	12
1.1.5.2 Emerging Siloxane Removal Methods	13
1.1.5.2.1 Biological Siloxane Removal	13
1.1.5.2.2 Hybrid Technologies	14
1.1.5.2.3 Recent Methods	15
1.1.5.2.4 Ultraviolet (UV) Photodecomposition For Siloxane Removal	17
2. PURPOSE OF THE STUDY	19
2.1. Selection of Siloxane Removal Techniques	19
2.2. Selected Siloxane Compounds	20
3. EXPERIMENTAL PROCEDURE	22
4. RESULTS AND DISCUSSION	28
4.1. Results	28
4.2. Discussion	32
5. CONCLUSION	35
REFERENCES	36
BIOGRAPHY	40
PUBLICATIONS AND PRESENTATIONS FROM THE THESIS	41

LIST OF SYMBOLS AND ABBREVIATIONS

CFCs	: Chlorofluorocarbons
CH ₄	: Methane
CO ₂	: Carbon Dioxide
D4	: Octamethylcyclotetrasiloxane
H ₂	: Hydrogen
H ₂ S	: Hydrogen Sulfide
HFCs	: Hydrofluorocarbons
L2	: Hexamethyldisiloxane
N ₂	: Nitrogen
N ₂ O	: Nitrous Oxide
PFCs	: Perfluorocarbons
SF ₆	: Sulfur Hexafluoride
AD	: Anaerobic Digestion
C/N ratio	: Carbon to Nitrogen Ratio
COP26	: 26th Conference of the Parties to the UNFCCC
COP27	: 27th Conference of the Parties to the UNFCCC
EC	: Elimination Capacity
GC-FID	: Gas Chromatography-Flame Ionization Detector
MSW	: Municipal Solid Waste
NDCs	: Nationally Determined Contributions
NH ₄ -N	: Ammonium Nitrogen
UASB	: Up-flow Anaerobic Sludge Blanket
UNEP	: United Nations Environment Programme
UV	: Ultraviolet

LIST OF FIGURES

	<u>Page</u>
Figure 1.1: Anaerobic Digestion Process Diagram.	6
Figure 1.2: Structure of Siloxane Compounds.	9
Figure 3.1: Experimental Set-up.	22
Figure 3.2: Experimental Set-up Illustration.	23
Figure 3.3: Experimental Set-up / UV lamp.	24
Figure 4.1: Siloxane Concentration Results Under Constant Biogas Flow, Constant Siloxane Concentration and Constant Residence Time Depending on Operating Time.	29
Figure 4.2: L2 Siloxane Concentration Results Under Air Flow With Different Residence Times.	30
Figure 4.3: D4 Siloxane Concentration Results Under Air Flow With Different Residence Times.	31

LIST OF TABLES

	<u>Page</u>
Table 1.1: Sources for Biogas Production.	4
Table 1.2: Biogas Composition.	8
Table 1.3: Siloxane Removal Methods.	17
Table 3.1: First Stage of the Experiment.	27



1. INTRODUCTION

Climate change is one of the most crucial and impactful global challenges in the 21st century and currently it is becoming one of most challenged problems in environmental sciences. Within the development of cities and increasing human-activity induced a major problem primarily by emitting greenhouse gas emissions to the atmosphere without any control mechanism.

From that start-up of industrial revolution over the centuries using fossil fuels as energy sources increased the greenhouse gas emissions in the atmosphere and resulted in an accumulation of greenhouse gases in the atmosphere. As a result of the accumulation of these emissions many serious environmental problems come into prominent and it effects all of the communities in worldwide. One of the major effects of global warming is obvious via temperatures increase, and it results in melting glaciers, rising sea levels, and extreme weather conditions that are impressive on a global scale and whose effects are becoming more visible day by day.

In order to reduce its adverse effect on the environment proper management of energy sources is compulsory. At this point of concept, using renewable energy alternatives is becoming prominent and nowadays the tendency towards renewable energy sources instead of fossil fuel sources has increased compared to the last decades. In other word renewable energy sources have become today's rising trend due to their unlimited source presence and, emit low or zero greenhouse gas emissions and the targets and incentives set for the use of renewable energy sources. On a contrast, many pipe end technologies should be implemented to renewable energy sources before they used as an pure alternative to the fossil fuels.

1.1. Literature Review

Global acknowledged to environmental concerns become prominent with the United Nations Conference on the Human Environment (Stockholm Conference) in 1972. With this conference, the United Nations Environment Programme (UNEP), which played an important role in global environmental management, was established in

1972, United Nations Environment Programme (UNEP). With the help of Montreal Protocol that established in 1987, it is aimed to reduced greenhouse gas emissions by the agreement , which targets substances that deplete the ozone layer, such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF₆), nitrogen trifluoride (NF₃). Although various targets were set with the Copenhagen Agreement of 2009 and the Cancun Agreement of 2010, the real breakthrough was made with the Paris Agreement in 2015. European Union countries, the United States of America, the United Kingdom, China, Canada, as well as major countries in the field of economy and industry such as Turkey are among the countries that have signed the agreement.

With the signing of the Paris Climate Agreement, all signatory countries committed to submitting Nationally Determined Contributions (NDCs) to mitigate climate change, aiming to keep global warming below 2°C and continue efforts to limit it to 1.5°C **[Falkner et al., 2016]**. The Glasgow Climate Pact (2021), which emerged from the COP26 conference in 2021, emphasized the urgency of reducing emissions by 2030 and called for a phase-out of coal and fossil fuel subsidies. Similarly, the Sharm el-Sheikh Implementation Plan (2022), adopted at COP27 in 2022, emphasized the equity dimensions of climate action by establishing a ‘Loss and Damage’ fund to support vulnerable countries disproportionately affected by climate change. As a result, international protocols and agreements have laid the groundwork for addressing climate change and promoting renewable energy.

Renewable energy sources have become globally indispensable in combating climate change and transition to sustainable energy systems. Solar, wind, hydroelectric, geothermal, and biomass energy now account for major renewable energy sources. Though their dissemination is uneven, with solar and wind energy dominating, and biomass being predominantly untapped, worldwide, solar and wind power grew rapidly with technological innovation, cost reductions, and supportive policies, contributing enormously towards the production of electricity **[REN21, 2023]**. Hydroelectric power is a prevalent renewable source, especially in water-endowed nations **[International Energy Agency, 2022]**. Geothermal power, while limited by areas with high geothermal activity, has been successfully utilized wherever conditions allow. Biomass energy, with immense potential as a perennial, sustainable energy

source, is, however, far from being fully utilized due to feedstock availability, technological, policy, and economic viability reasons **[Scarlat et al., 2018]**. Biomass possesses the unique advantage of supplying thermal energy as well as biofuels, but in the global renewable mix, it is still limited. This is particularly so in advanced economies, with land use issues, emissions, and competition with food production having retarded its dissemination **[International Energy Agency, 2022]**. Technological innovation, better policies, and sustainable feedstock management can bridge these gaps, unlocking the full potential of biomass energy, which can play a critical role in the shift towards a low-carbon future. The fact that the resources used are unlimited, keep up with the changing trends of the world, and are promising resources has increased the tendency towards renewable energy resources day by day.

Biomass energy is derived from various organic materials and can be categorized into various types depending on its source and conversion process **[Mignogna et al., 2024]**. Biomass energy can basically be divided into five categories. These are solid biomass, biofuels including biogas, ethanol and biodiesel, organic fraction of MSWs and aquatic biomass **[Reid et al., 2020]**. Solid biomass is generally used for combustion to generate heat and electricity. Biogas is produced through anaerobic digestion of sources such as animal manure, food scraps and waste sludge and is a form of methane-rich gas that can be used as a source of power, heat or fuel **[Oladoye et al., 2024]**. Biofuels are liquid fuels derived from crops such as sugar cane, corn, soya beans and are renewable alternatives to fossil fuels. MSW and aquatic biomass are new sources of biomass energy that contribute to sustainable waste management and clean energy production **[International Energy Agency, 2022]**. In summary, biomass energy is characterized by its ability to transform organic waste into a versatile energy source while contributing to waste management.

1.1.1. Biogas

Biogas is recognized as a versatile renewable energy source due to its potential to address both waste management and energy generation challenges. Biogas is basically obtained from the digestion of organic matter in the absence of oxygen. As a result of this process, a gas with high calorific content consisting mainly of methane (CH₄) and carbon dioxide (CO₂) is produced by microorganisms digesting organic wastes. Biogas production can be done by using many different resources. The waste sources generally used in biogas production and common examples are given in **Table 1.1**.

Table 1.1. Sources for Biogas Production.

Sources	Category	Examples	References
Agricultural Wastes	Animal Manure	Cattle manure, pig manure, chicken feces	[Weiland, 2010]
	Crop Residues	Corn husks, wheat straw, rice straw	
Food and Kitchen Waste	Municipal Organic Waste	Banana peels, apple cores, vegetable scraps	[Bond and Templeton, 2011]
	Industrial Food Waste	Whey, spent grain, molasses	
Sewage and Wastewater	Sewage Sludge	Sludge from urban sewage systems	[IEA Bioenergy, 2020]
	Industrial Wastewater	Wastewater from breweries, paper mills, ethanol plants	
Landfill Organic Waste	Landfill Gas	Methane from decomposing food and yard wastes	[Scarlat et al., 2018]
Dedicated Energy Crops	Silage Crops	Silaged corn, sorghum straw, soybean straw	[Weiland, 2010]
	Grasses and Legumes	Red clover, lucerne	
Fats, Oils and Grease	Waste Cooking Oils, Animal Fats	Waste frying oil, tallow, lard	[IEA Bioenergy, 2020]
Aquatic Biomass	Algae, Aquatic Plants	Spirulina Algae, Water Lettuce	[IEA Bioenergy, 2020]
Co-digestion of Mixed Feedstocks	Combination of different materials	Cow manure + kitchen scraps, pig slurry + brewery waste	[Weiland, 2010]

1.1.2. Biogas Production

Biogas production takes place through anaerobic digestion (AD), a biological process involving the breakdown of organic matter in the absence of oxygen [IEA Bioenergy, 2020]. Anaerobic digestion takes place in four main stages, resulting in a calorific-rich gas containing 45-70% CH₄ by volume, 20-55%CO₂, N₂ (0-3%), O₂ (0-1%), water vapor (1-10%), hydrogen sulfide (0-10,000 ppm), siloxane (0-200 ppm), ammonia (0-100 ppm), and trace amounts of hydrocarbons and chlorinated compounds [Li et al., 2019]. The anaerobic digestion stages are hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

First, hydrolysis involves the separation of complex organic substances such as carbohydrates, proteins and lipids into soluble derivatives with the aid of extracellular enzymes secret by various bacteria in acidogenesis and acetogenesis processes, molecules containing sugar and amino acids are converted into CO₂, H₂, NH₄-N and organic acids [Ermiş, 2020]. Next, organic acids are converted to acetic acid. In the final part, methanogenic bacteria convert the formed products into CH₄, CO₂ and water. During the digestion process, about 20-95% of the raw material organic matter is degraded [Ermiş, 2020]. The process of anaerobic digestion shows in a diagram in **Figure 1.1**.

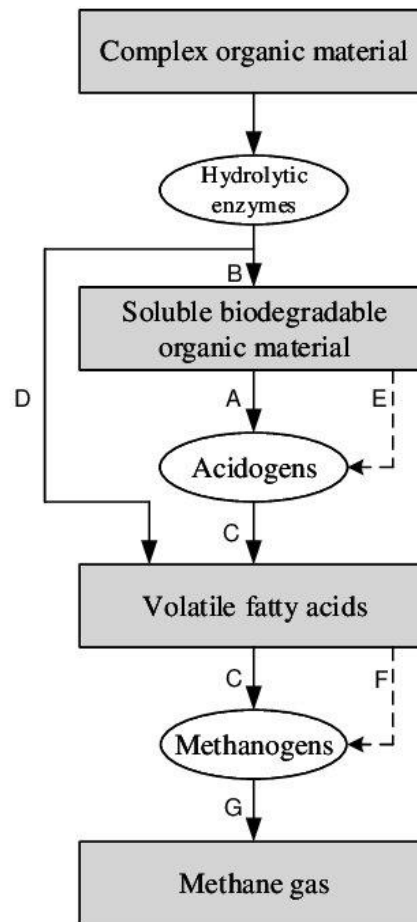


Figure 1.1: Anaerobic Digestion Process Diagram [Haugen et al., 2013].

1.1.3. Biogas Production Systems

The main biogas production systems are batch and continuous digesters, plug-flow digesters, covered lagoon digesters, dry fermentation digesters, Up flow Anaerobic Sludge Blanket (UASB) Reactors, Two-Stage Anaerobic Digesters [Shen et al., 2021]. Biogas production varies according to raw material characteristics, climatic conditions and energy demand.

Batch and continuous digesters are reactor types that are generally operated with agricultural residues, animal manure, food waste and sewage sludge by loading the raw material into the reactor, closing it and subjecting it to anaerobic digestion for a certain period of time. In these systems, raw materials with high C/N ratio are used [Ammerberg et al., 2017].

Plug-flow digesters are systems that operate with a continuous and linear flow principle throughout the system with raw materials such as animal manure, energy crops, and organic industrial waste. These systems require the use of feedstock with medium to high solid content (10-15%) [Kulichkova et al., 2020].

Covered lagoon digesters are systems designed for highly diluted organic wastes with low solid content (1-5%) such as liquid animal waste, agricultural wastewater, wood processing wastewater, municipal wastewater. They are large pond systems covered with membrane to capture the biogas produced. Systems with low biogas yields due to the high-water content of the feedstock [Piechota et al., 2024].

Dry fermentation digesters are designed for feedstocks with high solids content (>20%) and minimum water input such as MSW, agricultural residues, garden and yard waste, organic industrial waste. They are more advantageous systems for large-scale solid waste management applications [Abubakar, 2022].

Up Flow Anaerobic Sludge Blanket (UASB) Reactors are systems specialized in the treatment of highly concentrated liquid waste such as industrial wastewater, pulp and paper industry effluents, domestic sewage. They are widely used in industries with high methane production rates.

Two-Stage Anaerobic Digesters are systems commonly operated with raw materials such as high-fat and protein waste, energy crops, organic kitchen waste, algae and aquatic biomass. By separating the acidogenesis and methanogenesis steps into different reactors, the digestion efficiency of complex substrates such as fats and proteins is increased [Klang et al., 2020].

Biogas is a gas mixture containing CH₄, CO₂, N₂, O₂, water vapor, hydrogen sulphide, siloxane, ammonia and trace amounts of hydrocarbons and chlorinated compounds [Scarlat et al., 2018]. The content of biogas may vary depending on the type of feed stock used and anaerobic digestion conditions. The composition of biogas from different sources is given in **Table 1.2**. Methane is the primary energy content of biogas and accounts for 50-70% of the total gas. The energy efficiency of biogas is directly proportional to the methane content. Carbon dioxide is present in 30-50% biogas and does not contribute to the calorific value. The presence of CO₂ in biogas is inversely proportional to the energy efficiency of biogas and the treatment process is needed to reach the desired purity according to the intended use of biogas. Hydrogen sulfide

(H₂S) is a toxic and corrosive gas, its concentration in biogas varies between 50-10,000 ppm [Chen et al., 2015]. Removal of H₂S before the use of biogas is very important for the equipment used. Water vapor is an inevitable component due to the biogas formation process. Its concentration varies depending on factors such as temperature and system design. In cases where water vapor is not removed, problems such as condensation, clogging and corrosion may occur, which reduce system efficiency. Even in trace amounts, the presence of siloxane in biogas causes serious problems in the systems and equipment used.

Table 1.2. Biogas composition [Kajolinna et al., 2015].

Component	Unit	Landfill Gas	Waste Water Treatment Digester	Household Waste Digester	Industrial Waste/Animal Manure Digester
Methane	vol. %	36–52	65	65	60–80/50–70
Carbon Dioxide	vol. %	30–41	33.5	29	20–40/30–50
Water Vapour	vol. %	0.1–3.3	2	0.5	1–4
Nitrogen	vol. %	<10	<5	-	n.d./<5
Oxygen	vol. %	<3	<1	-	n.d./<1
Siloxanes ^(a)	mg/m ³	1.4–9.8	1.3	1.35	n.d.
Sulphur	mg/m ³	29–900	<25	30	-
Hydrogen Sulfide	ppm	10–1000	150–300	-	<30000/<5000
Ammonia	ppm	<5	<5	<5	<5
Halogenated Compounds ^(b)	mg/m ³	0–7	n.d.	n.d.	<0.1
Benzene	mg/m ³	<36	<0.3	-	-
Toluene	mg/m ³	<287	<12	-	-

^(a) L2–L4, D2–D4, TMS.

^(b) Quantified as toluene equivalent; n.d. = not detected.

1.1.4. Siloxanes

Siloxanes are relatively non-toxic compounds, originating from the breakdown of silicone-based products that are usually present as inert additives to pharmaceutical products, cosmetic and personal care products, cleaning products, sealants [Soreanu et al., 2011]. Under environmental conditions there are no greenhouse effects from siloxanes [Soreanu et al., 2011]. The term siloxane refers to a subgroup attached to the silicon atom containing organic chain Si - O bonds. The structure of siloxane compounds can be linear or cyclic, as shown in **Figure 1.2**.

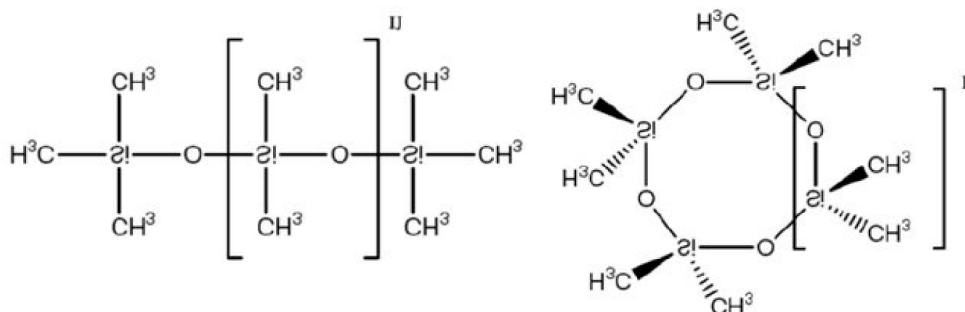


Figure 1.2: Structure of siloxane compounds [Nyamukamba et al., 2020].

Siloxanes accumulate in biogas due to the widespread use of silicone-containing substances (e.g. shampoos, cleaning products, pharmaceutical products, cosmetics) and their incorporation into biogas production processes such as municipal wastewater systems and landfills. Siloxanes found in volatile forms in biogas are mainly found as cyclic (D3, D4, D5) or linear (L2, L3, L4) type siloxanes [Appels et al., 2008].

Biogas contains siloxanes, including cyclic (D3, D4, D5) and linear (L2, L3, L4) structures, that are oxidized through several methods: thermal, catalytic, and advanced oxidation processes (AOPs). These methods drive the siloxanes to higher oxidation states, resulting in the production of silica (SiO_2) and other silicon-based materials that can make runs through equipment problematic, cause run time extension penalty fees, or create the conditions for penalties due to emissions that are possible when violating the Clean Air Act (CAA). The Clean Air Act is an Act of the Congress of the United States, started in 1963, that regulates air emissions from stationary and mobile sources.

Common oxidants used to eliminate siloxane include molecular oxygen (O_2), ozone (O_3), and hydroxyl radicals ($OH\bullet$). Of these oxidants, advanced oxidation processes (AOPs) like UV/ H_2O_2 and Fenton reactions are particularly effective at siloxane removal [Schweigkofler and Niessner, 2001].

Thermal oxidation can also be effective at removing siloxanes—provided the temperature is high enough. Mineralization is complete when the temperature reaches above 800°C . However, even lower temperatures ($400\text{--}600^\circ\text{C}$) can work, especially in the presence of catalysts like platinum (Pt) and palladium (Pd) [Alves et al., 2023].

Biological oxidation using specialized microbial consortia has shown potential for the removal of volatile methylsiloxanes (VMS) under aerobic conditions. However, this method is far less effective than the two methods above.

The volatile nature of siloxanes causes them to be transported with the biogas stream and to be involved in combustion and energy conversion systems, leading to contamination of the systems.

Siloxanes in biogas cause serious problems in the utilization processes and systems, and as a result, they are undesired substances in biogas.

The main problem originates from the combustion of biogas with siloxanes; this process generates silicon dioxide (SiO_2) and other silicon-based materials. These volatile methylsiloxanes (VMS) are oxidized during combustion and transformed into hard deposits of solid silica, which build up on engine surfaces, the hot section turbine blades, and heat exchangers [Ajhar et al., 2010]. Such deposits create abrasion, clogging, and erosion, resulting in reduced equipment efficiency, increased maintenance costs, and recurring downtimes [Schweigkofler and Niessner, 1999]. Siloxanes also have an impact on the longevity of catalysts in energy conversion processes, primarily because silica sedimentation poisons catalysts by blocking active sites [Shen et al., 2018].

In addition, siloxanes can create fine particulate material within the exhaust gas, adding further risks to both the environment and human health. Particulate silica released into the air can cause air quality problems and possibly lead to noncompliance with regulatory standards [Alves et al., 2023]. Moreover, siloxanes pose issues for gas processing systems, including biogas upgrading to biomethane, through contaminating

adsorbent materials and membranes. Consequently, removal of impurities becomes less effective, resulting in increased operating costs because of more regular replacement of filtering materials [Ajhar et al., 2010].

Siloxane contamination has important economic implications. Siloxanes lower the calorific value of biogas and compound removal is expensive, which creates a need for complex treatment processes prior to biogas utilization [Schweigkofler and Niessner, 2001]. Thus, successful removal of siloxanes is essential for the sustainable running of biogas energy systems in the long term, giving assurance for keeping equipment operational for the required period of time and in compliance with environmental standards. An advantage of these references is that they build awareness of the limitations of traditional siloxane removal technologies and their inability to control the problems they cause in biogas streams.

When biogas containing siloxanes is combusted, these compounds turn into silica deposits and cause serious operational difficulties such as wear, reduced engine efficiency and premature equipment failure [Jameel et al., 2024]. Therefore, the removal of siloxanes from biogas is a crucial step in biogas upgrading and efficient utilization.

1.1.5. Siloxane Removal Methods

Siloxane resulted in many serious problems when it presented in a gas stream. Many applications / technologies have been used worldwide to overcome limitations due to the siloxane presence. Up to date these mechanisms were subcategorized under conventional siloxane methods, emerging siloxane removal methods and hybrid siloxane removal mechanisms. Below detailed information has been presented for these mechanisms.

1.1.5.1. Conventional Siloxane Removal Methods

Adsorption-Based Methods

It is one of the most common methods used for siloxane removal. Materials with high surface area and affinity for siloxanes such as activated carbon, silica gel, and zeolites are used.

Activated Carbon: It is a widely used adsorbent due to its high porosity and ability to trap volatile organic compounds. The adsorption capacity of siloxanes on activated carbon is generally 50 to 250 mg of siloxane per gram, depending on the carbon type, relative humidity, and competing contaminants [Ajhar et al., 2010]. Nonetheless, hydrogen sulfide (H₂S), volatile organic compounds (VOCs), and moisture also compete for adsorption sites and cumulatively reduce the life of the carbon [Nyamukamba et al., 2020]. Activated carbon treatment is relatively expensive (between \$1–5 kg⁻¹) and also entails additional costs for the replacement and disposal of spent carbon, which may require controlled incineration or regeneration [Shen et al., 2018]. These challenges aside, activated carbon continues to be a cost-effective and scalable siloxane removal method, particularly when appropriately coupled with pre-treatment methods so as to maximize performance and media lifespan [Alves et al., 2023]. Due to its non-selective nature, it quickly becomes saturated. For this reason, it requires frequent regeneration and replacement, which results in high operating costs [Weiland, 2010].

Silica Gel: Although widely used in many different areas, they are also very successful products in siloxane retention. Although it is known that it can absorb 0.1 g siloxane per gram, its performance decreases significantly in the presence of moisture in the environment and its efficiency decreases [Bayram et al., 2022].

Zeolites: With their uniform pore structure, they allow effective retention of siloxane. Although they are resistant to moisture, they are expensive and have low adsorption capacity, which is one of the reasons why they are not preferred for large-scale applications [Angelidaki and Sanders, 2004].

Cryogenic Condensation

It is a method of removing siloxanes by condensation and separation from the gas phase by cooling the biogas to low temperatures (-70°C to -100°C). It is very effective

at high siloxane concentrations, especially in landfill gas applications. High energy and equipment costs are among the important reasons for not being preferred. Efficiency is low at low siloxane concentrations [Bond and Templeton, 2011].

Absorption Methods

It is a method of passing biogas through a liquid medium that selectively dissolves siloxanes. It is effective for continuous operation but is characterised by high operating cost, solvent degradation and challenges such as spent solvent disposal [Ammenberg et al., 2017].

Membrane Separation

It is a method that works on the principle of retaining siloxanes by passing the biogas stream through the membrane. Although it offers a compact and scalable solution, it has significant challenges such as membrane fouling, decreasing efficiency over time and membrane replacement cost [Kabeyi et al., 2022].

1.1.5.2. Emerging Siloxane Removal Technologies

1.1.5.2.1. Biological Siloxane Removal

Biological removal of siloxanes is an innovative and sustainable strategy which utilizes microbial compounds to mineralize volatile methylsiloxanes (VMS) into non-toxic by-products such as silicic acid ($\text{Si}(\text{OH})_4$), carbon dioxide (CO_2) and water. This approach builds on the ability of certain microbial consortia to use siloxanes as a carbon and energy source, cleaving its Si–O bonds through enzymatic oxidation and hydrolysis [Lamaa et al., 2014]. Biological removal of siloxanes is advantageous because it requires less energy than traditional adsorption or oxidation methods and could potentially be employed on a large scale. Yet the biological siloxanes degradation is still limited to research and pilot scales, owing to problems including microbial acclimatization, low degradation rates, pronounced deflation of the process under fluctuated conditions typical to biogas [Rivera-Montenegro et al., 2023].

This process usually takes place in biofiltration systems, in which siloxane degrading bacteria. The function of these systems creates appropriate conditions for microbial growth, allowing for the adsorption and biodegradation of siloxanes [Shen et al.,

2018]. In biofilters, biogas flows through a moist biofilm rich in specialized microorganisms, including *Pseudomonas*, *Methylobacterium*, and *Rhodococcus* species, which produce oxidative enzymes capable of degrading siloxanes into intermediate metabolites **[Xiang et al., 2021]**. Pre-cursors such as silanols and silanediols, which undergo further hydrolyzation yield silicic acid, the final product, it's a non-toxic water-soluble and bioactive compound. A robust removal efficiency can be ensured by optimizing factors such as microbial acclimatization, nutrient supply, gas retention time and biofilm stability. Moreover, biogas contains a variety of inhibitory compounds (e.g., H_2S , and volatile organic compounds (VOCs)), which inhibit microbial activity; hence, pre-treatment steps or adaptive microbial selection are required to improve system resilience. However, since siloxane removal can also occur through biological processes, this can be a more sustainable option than traditional methods, and there are plenty of studies currently looking into the optimization of the microbial efficiency and robustness of the process.

1.1.5.2.2. Hybrid Technologies

Hybrid technologies for siloxane removal combine different treatment methods to improve efficiency, lower operational costs, and reduce the need for material replacement. These systems benefit from the strengths of the various removal mechanisms, while the limiting factors of each process are overcome by the use of a complementary mechanism for siloxane capture. One of the most promising hybrid ones is the adsorption + biological degradation method, in which activated carbon or other adsorbents are used as a primary siloxane trapping medium **[Haldar et al., 2023]** with subsequent microbial degradation which would be used to regenerate the adsorbent material and extend its life-time. As a result, this will not require to act often with matter replacement, making it an environmental and economic solution. Siloxanes adsorb onto porous media in this system, and specialized microorganisms that can degrade siloxane compounds are added to metabolize or convert the adsorbed pollutants into benign byproducts like silicic acid ($Si(OH)_4$) and carbon dioxide (CO_2) **[Ajhar et al., 2010]**. Nonetheless, the real incentive of optimizing system performance stems from additional challenges including biofilm stability, as well as compatibility between microbial activity and the adsorbent material.

A sophisticated hybrid process integrates membrane separation with chemical absorption to enhance siloxane selectivity and alleviate OPEX. In this method, a gas separation membrane selectively removes siloxanes from the biogas stream and a chemical absorption stage follows for enhanced removal efficiency [Schweigkofler and Niessner, 2001]. Membranes serve as a pre-filtration operation to concentrate the siloxanes and these allow for targeted chemical treatment which limits the volume of chemicals required and reduces maintenance costs [Alves et al., 2023]. In this hybrid system, common absorbents comprise organic solvents or liquid scrubbing agents that target siloxanes to react and produce a non-volatile compound allowing them to be removed further down after the process to avoid clogging the equipment. One important benefit of this technology is that it can run continuously with minimal fouling, since the membranes prevent excess loading onto the absorption unit. Still, long-term viability depends on addressing membrane fouling and chemical regeneration expenses. First, hybrid siloxane removal technologies are developed for better/energy-efficient sustainable biogas purification by avoiding traditional single-stage processes, and second, they are designed to treat complex matrices comprising multiple siloxane species.

1.1.5.2.3. Recent Methods

The research on siloxane removal from biogas has been progressed recently to improve efficiency and sustainability by employing innovative techniques. Conventional techniques such as adsorption with activated carbon, absorption with liquid solvents, and condensation via refrigeration have been commonly employed; however, these approaches frequently encounter issues such as elevated operational expenses, rapid material turnover, and restricted efficacy across various siloxane types [Ajhar et al., 2010]. In order to overcome these disadvantages, researchers have focused on alternative methods like advanced oxidation process (AOPs), membrane separation technologies, and biological treatments. They are designed to enhance siloxane selectivity, maximize removal efficiency, and minimize operational costs [Alves et al., 2023].

Ultraviolet (UV) photodecomposition is certainly one of the most promising new methods so far, which consists of exposing biogas to UV radiation to start photochemical reactions that break siloxane molecules into smaller, less toxic parts

[Divsalar et al., 2018]. Research has shown that siloxanes can be captured or destroyed by ultraviolet treatment, making it a potential alternative to traditional removal methods. Its practical application is influenced by the reactor design, energy needs and interactions with other biogas components, which could modify its efficiency [Schweigkofler and Niessner, 2001]. Similarly, membrane separation technologies have attracted interest as a means of siloxane removal, using selective membranes to remove siloxanes from the biogas stream based on differences in molecular size and solubility [Alves et al., 2023]. Although polymeric membranes allow for continuous operation and very little chemical use, membrane fouling, as well as the long-term effect of acidic gases on membranes, are critical aspects of their long-term industrial viability that must be carefully managed [Kulichkova et al., 2020].

Another developing strategy is biological siloxane removal, a method in which microbial consortia bio transform siloxanes to innocuous by-products (e.g., silicic acid (Si(OH)_4) and carbon dioxide (CO_2)). This technology is very appealing in terms of energy efficiency and environmental advantages; however, up to now, the research has been confined to pilot-scale work to tackle some challenges associated with the acclimatization of organisms, the slow rate of degradation, and difficulties in sustaining stable operating conditions under variable biogas composition [Ajhar et al., 2010], [Haldar et al., 2023]. Hybrid systems integrating different treatment technologies (e.g., adsorption together with biological degradation to improve adsorbent lifetime or membrane separation and chemical absorption to improve siloxane selectivity and reduce operational costs) are emerging as the way forward for siloxane removal technologies [Schweigkofler and Niessner, 2001]. This knowledge contributes to the developing of improved material efficiency, better optimization of these hybrid strategies and up-scaling aspects to be integrated in terms of industrial applications, which ultimately leads to more cost-effective and sustainable biogas purification processes.

Various methods are available for the removal of siloxanes from biogas, some of which are presented in **Table 1.3**.

Table 1.3. Siloxane removal methods [Nyamukamba et al., 2020].

Method	Removal Efficiency (%)
Adsorption e.g., silica-gel, activated carbon, zeolites	90–99
Degradation (using 97% sulfuric acid).	95–99 (60 °C) 56–70 (at RT)
Liquid Absorption	97-99
Membrane	-
Refrigeration/Condensation	95 (–28.89 °C)
Biotrickling filtration	10–43

1.1.5.2.4. Ultraviolet (UV) Photodecomposition for Siloxane Removal

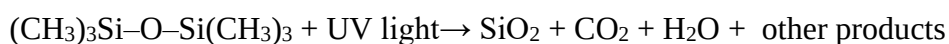
Ultraviolet (UV) photodecomposition has become one of the most promising methods for the elimination of siloxane pollutants in biogas streams. In this method, the siloxane compounds in biowaste is dissolved under the UV radiation and converted into less harmful materials, which improves the biogas properties and protects the downstream devices from damage caused by siloxane deposits [Divsalar et al., 2018], [Haldar et al., 2023].

Process Overview

The biogas with VMS is passed through a reactor in a UV photodecomposition system where UV lamps emitting at 185 nm and 254 nm (typically) irradiate the system. The aforementioned wavelengths are effective for starting photochemical reactions which lead to the breakdown of siloxane molecules [Schweigkofler and Niessner, 2001], [Ajhar et al., 2010]. The photolysis occurs as the biogas proceeds through the reactor; the siloxane compounds absorb UV light and are decomposed. With downstream filtration systems extracting the resulting byproducts, like silicon dioxide (SiO₂) particulates, from the gas stream. Not only does this decrease the concentration of siloxanes, but its classification also as class 1 biosolid prevents the build-up of deposits that corrode equipment [Alves et al., 2023].

Mechanism of UV-Induced Decomposition

The decomposition of silicon-carbon (Si–C) bonds is the main pathway in the UV-induced decomposition of siloxanes. When a DNA strand absorbs UV photons, the energy breaks these bonds leading to the formation of reactive intermediates [Divsalar et al., 2018]. These intermediates may also react with oxygen available in the system to yield silicon dioxide plus a range of other organic fragments [Divsalar et al., 2018]. The overall reaction can be simplified as follows:



The reaction occurs when a linear siloxane compound is degraded to silicon dioxide (SiO_2), carbon dioxide (CO_2), water (H_2O) and some other minor products [Alves et al., 2023]. Efficiency of this process is highly dependent on UV light intensity and wavelengths, gas residence time in the reactor, and oxygen presence facilitating oxidation of intermediates [Ajhar et al., 2010].

Changes in Siloxane Compounds

UV radiation alters the siloxane molecular structure substantially. This results in a cleavage of the Si–C bonds and produces smaller Si-containing species and thus, organic fragments [Divsalar et al., 2019], [Shen et al., 2018]. Studies have concluded that linear siloxanes (such as hexamethyldisiloxane (L2)) are degraded more easily under UV compared with cyclic siloxanes (D3, D4, D5) that are more stable in view of their ring structures [Lamaa et al., 2014]. The pathway of degradation commonly includes a stepwise demethylation pathway yielding intermediates such as silanols and silanones prior to full mineralization of siloxane to SiO_2 and gaseous substrates [Ajhar et al., 2010], [Haldar et al., 2023].

2. PURPOSE OF THE STUDY

Biogas is an important renewable energy source alternative and the demand for biogas is increasing day by day. The wide usage area of biogas and the ease of use of biogas bring biogas to the forefront. Although the biogas major content is mainly composed of CH_4 and CO_2 , other trace gases such as siloxanes in its content are harmful to biogas systems. Siloxanes are compounds that pass into biogas from sources such as cleaning materials, pharmaceuticals, personal care products, etc. and reduce the efficiency of biogas, even in small amounts. Therefore, siloxane removal from biogas is an important issue. Commonly used methods for siloxane removal have disadvantages such as energy cost and operational difficulties.

2.1. Selection of Siloxane Removal Techniques

In biogas streams, the presence of siloxane represents serious operating and environmental problems, especially in energy conversion technology because SiO_2 deposited on the surface equipment causes physical wear of equipment, raising maintenance costs, and efficiency loss [Ajhar et al., 2010], [Alves et al., 2023]. Conventional approaches for removal such as adsorption on activated carbon, absorption employing liquid solvents, and catalytic oxidation have garnered much implementation, albeit with high operational costs, a considerable need for material replacement, and limited long-term viability [Schweigkofler and Niessner, 2001], [Haldar et al., 2023]. To address these issues, UV photodecomposition has recently been proposed as a new solution that uses high-energy UV radiation to cleave the siloxane molecule into less toxic byproducts, including silicon dioxide (SiO_2), carbon dioxide (CO_2), and water (H_2O) [Divsalar et al., 2018]. Indeed, whilst UV treatment has many possible advantages, it is still underexplored and relatively new technology [Lamaa et al., 2014], [Shen et al., 2018], and there are only few studies that focus on UV treatment in terms of effectiveness, scalability and feasibility for industrial application. With siloxanes presenting a unique challenge to alternative removal methodologies, this study aims to assess the purchase of ultraviolet (UV) photodecomposition as a treatment option, exploring efficiencies, reaction pathways, and system limitations. Overall, the findings of this study provide valuable insights

for industry practitioners, policymakers, and researchers working towards the development of more sustainable and cost-effective biogas purification technologies as there are still some gaps in knowledge when it comes to UV treatment for siloxane degradation that need to be addressed in order to ensure its optimal applicability under real-world conditions. In the scope of this study, we synthesized and applied a UV-post treatment for sample which is aimed at removal of siloxane compounds from biogas.

2.2. Selected Siloxane Compounds

Some of the most prominent VMS detected in biogas and waste gas streams, especially those from landfills and wastewater treatment plants, include hexamethyldisiloxane (L2) and octamethylcyclotetrasiloxane (D4) [Ajhar et al., 2010], [Reddy and Rao, 2020]. D4 is established as the most ubiquitous siloxane in landfill gas, with a relative share of around 60% of the total siloxane content, alongside L2, D5, and L3 [Alves et al., 2023], [Papurello et al., 2019]. These compounds are prevalent in other matrices, including biogas and various industrial emissions, making it imperative to focus targeted research on their removal mechanisms, particularly because their presence is known to lead to equipment degradation and persistence in the environment [Schweigkofler and Niessner, 2001], [Rücker and Kümmerer, 2015].

Chemical Structure of L2 and D4

The chemistry of L2 is a linear siloxane, $[(CH_3)_3Si]_2O$, with two silicon atoms linked by an oxygen atom, each bonded to three methyl groups [Varaprath et al., 1999], [Shen et al., 2018]. Whereas, D4 is a cyclic tetrameric compound $[(CH_3)_2SiO]_4$ which forms a structure that is a V-shape, in which a silicon atom and an oxygen atom alternate, and a methyl group bonded to each silicon [Steinfink et al., 1955], [Rojas Devia et al., 2014]. These structural distinctions impact their physical properties, reactivity, and removal efficiency in oxidation processes.

Oxidation Stability and UV Testing Feasibility

The silicon-oxygen (Si–O) and silicon-carbon (Si–C) linkages in L2 and D4's are quite stable which makes those compounds resistant to mild oxidative conditions [Lamaa et al., 2014], [Ajhar et al., 2010]. Given that they possess stable bonds, effective degradation usually relies on powerful oxidants or high-energy mechanisms

able to rupture these stable connections [Alves et al., 2023]. Studies have also shown that under certain conditions UV photodecomposition is able to catalyze such bonds [Divsalar et al., 2018], [Papurello et al., 2019]. UV irradiation of L2 for example causes Si–C bonds cleavage, generating intermediates like silanols and further oxidation products [Varaprath et al., 1999], [Rücker and Kümmerer, 2015]. Likewise, the photocatalytic oxidation of D4 generates several degradation products, resulting from the cleavage of its cyclic structure [Shen et al., 2018], [Lamaa et al., 2014].

Due to the high resistance of L2 and D4 to traditional oxidation techniques [Divsalar et al., 2019], [Haldar et al., 2023], UV treatment is considered as a potential method for their degradation. The high-energy area of UV radiation is able to break stable Si–O and Si–C bonds, assisting to the fragmentation of these siloxanes into lower toxic products [Ajhar et al., 2010], [Schweigkofler and Niessner, 1999]. This reduces the negative impacts associated with siloxanes in biogas applications and gives a chemical-free alternative to conventional removal methods.

Literature review collected average concentrations of L2 and D4 compounds in biogas, which can vary with the origin. L2 is usually present in ranges from 0 to 10 mg/m³ while D4 occurs at higher concentrations (1 to 50 mg/m³) in biogas from landfills and wastewater treatment plants [Nyamukamba et al., 2020], [Schweigkofler and Niessner, 1999]. Biogas from municipal wastewater treatment has relatively higher D4 than agricultural or landfill [Ajhar et al., 2010]. However, actual plume concentrations can vary substantially and are site specific [Rasi et al., 2011].

Literature research showed that there is a relative new method to remove siloxane using UV treatment. The siloxane concentration of 70 mg/m³ was selected to simulate a worst case scenario. So, in this study, the removal of the most common biogas siloxanes (L2 and D4) from biogas by post-treatment using UV was studied.

3. EXPERIMENTAL PROCEDURE

The schematic diagram of the experimental setup is shown in **Figure 3.1**, in the diagram there are gas line, rotameter, mixing chamber, closed quartz gas photoreactor, syringe pump, UV lamp. The actual experimental set-up is shown in **Figure 3.2**. A siloxane laden inlet air stream was created through the injection of a liquid mixture of siloxane species L2 (purity $\geq 98.5\%$ (GC), Hexamethyldisiloxane) and D4 (purity 98%, Octamethylcyclotetrasiloxane) using a syringe pump (Fisher Scientific Single Infusion Pump 100 Model 9034914) that was dispersed into the air and synthetic biogas stream governed through rotameter and held constant. The siloxane injected air stream then flowed through a continuous 1.2 L mixing chamber to ensure complete mixing of the siloxane in the air stream. The mixed air stream was conveyed through a quartz photoreactor for the exposure of UV radiation, which wrapped there is a UV lamp (254 nm Pen-Ray® 90-0012-01 (11SC-1)) inside.

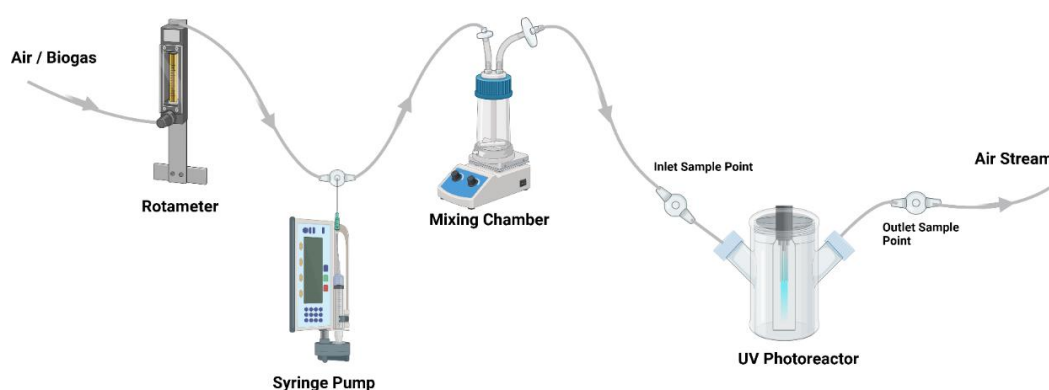


Figure 3.1: Experimental Set-up Illustrations.

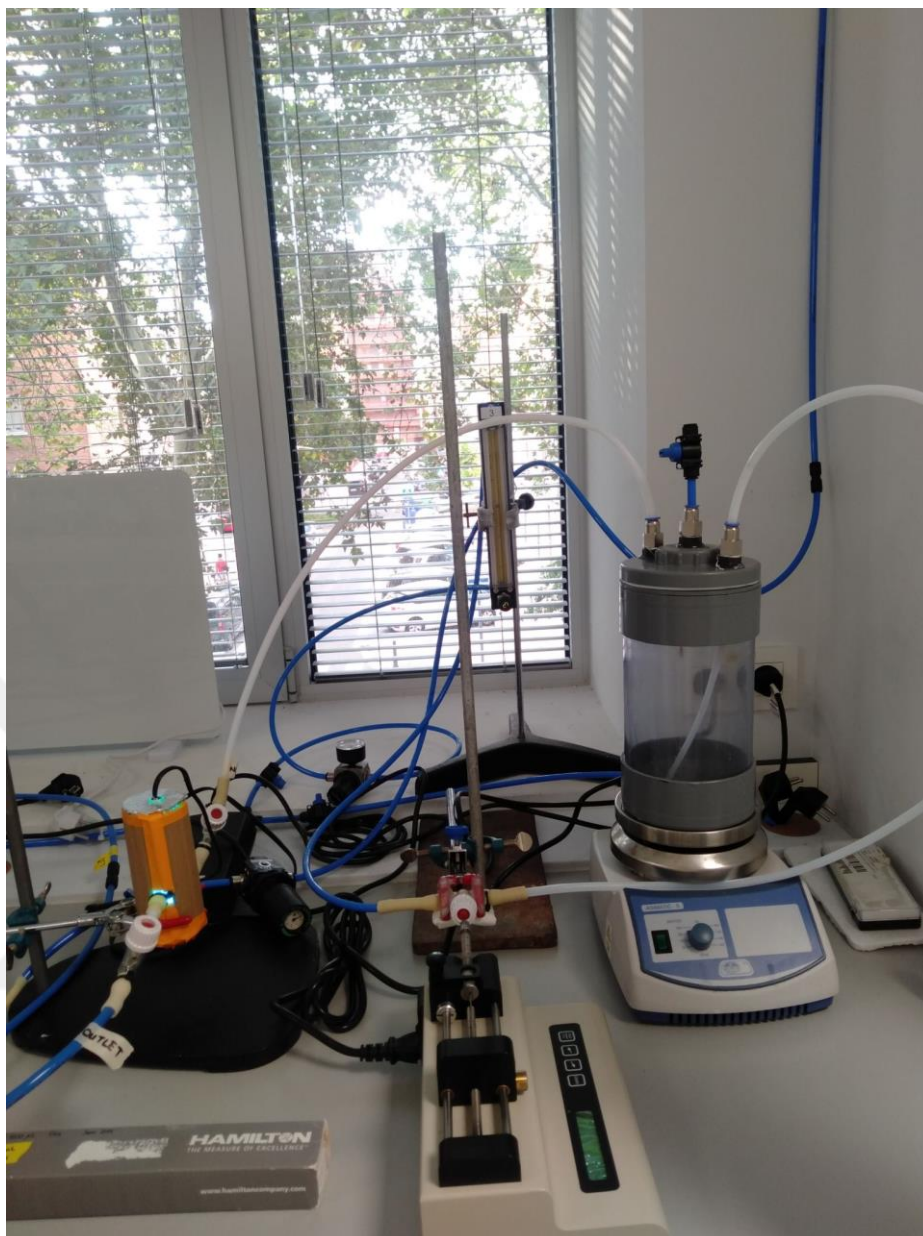


Figure 3.2: Experimental Set-up.

Figure 3.3 shows the photoreactor and sample points. The analytical measurements were performed using samples collected from gas sampling ports at the inlet and outlet of the photoreactor.

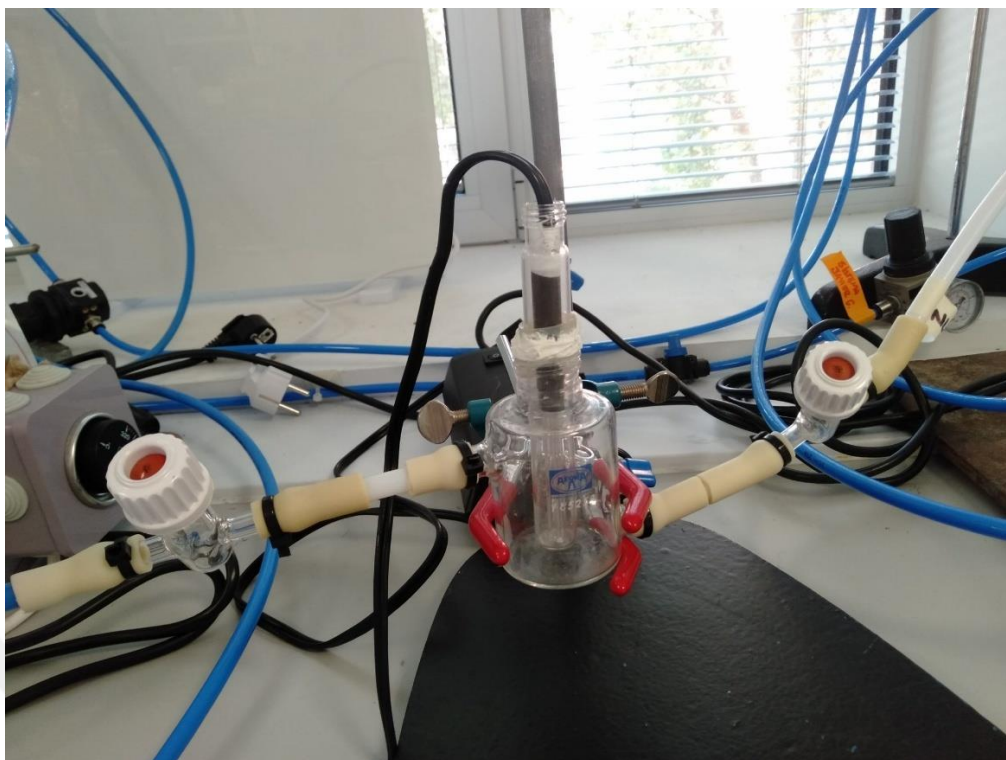


Figure 3.3: Experimental Set-up / UV lamp.

2 mL stock solution of siloxane mix was prepared (56% L2 and 44% D4) as the siloxane mixture for this experiment. The tests were performed in multiple stages at different siloxane concentrations and flow rates. However, air flow is used for the first two phases of the experiment instead of biogas, mainly to ensure safety. In the final phase of the study, the flow of synthetic biogas (70% CH₄, 30% CO₂) was investigated. Using air as the carrier gas eliminated the detriments associated with handling biogas which includes flammable and dangerously toxic species like CH₄ and CO. Combustible gases which might have obscured the degradation behavior of siloxanes, resulting significance from prolonged exposure to UV radiation were ruled out as controlled conditions in the pristine stages of the study. The last part of the study took place using synthetic biogas flow, where it was found to better simulate the conditions of a real biogas. Air is initially used however it does not affect the reliability of the found results for multiple reasons.

L2 (Hexamethyldisiloxane, $C_6H_{18}OSi_2$) and D4 (Octamethylcyclotetrasiloxane, $C_8H_{24}O_4Si_4$) are first of all chemically stable with experimental conditions. Both compounds will not spontaneously react with air components (as O_2 , N_2) or main (major) biogas components (as CH_4 , CO_2) without an important catalyst or important activation energy. Second, in standard conditions, methane and carbon dioxide, which are the main constituents of biogas, do not react with L2 or D4. Although biogas typically has traces of hydrogen sulfide, which can affect the chemical stability of L2 and D4 in the gas phase at the tested concentrations and temperatures due to its propensity to react with metal-based catalysts and some organic compounds, such traces do not significantly result in effects. Similarly, air's oxygen and nitrogen also do not react with siloxanes at the given experimental conditions.

Additionally, the breakdown of this study siloxanes is promoted by UV irradiation, leading to the cleavage of Si–O and Si–C bonds. As long as there are sufficient amounts of oxygen to take part in oxidation reactions when necessary, this photolytic process does not depend on the use of air or biogas as carrier gas. However, because air already acts as a controlled oxidizing environment, the photochemical degradation pathways of L2 and D4 remain unchanged moving from air into biogas. Also, carry out the first stages in air will reduce the risk of dealing with flammable gases and ensure a better controllability in experimental conditions. Experiments in air provided insight into siloxane degradation efficiency without the need of implementing enhanced safety protocols when handling biogas. The switch to synthetic biogas in the final step was essential to verify whether the degradation trends seen in air were maintained under biogas conditions. Thus, the air used in the first two stages does not change the final goal of the study, which is improved safety and reproducibility of experiments. Since L2 and D4 show the same photodegradation behaviors in air and biogas, the results from air-based experiments can be directly applied to real biogas conditions.

Siloxane compounds were injected into air or biogas stream with a Fisher Scientific Single Infusion Pump 100 Model 9034914 syringe pump, which was then passed through a mixing chamber, and subsequently exposed to UV photolysis in the quartz photoreactor that was installed in the inlet gas line the gas stream in a closed area at all stages. UV light is incident behind the glass, and the volume of the reactor through

which the gas stream passes is 70 mL. During the experiment, residence times calculated for each different flow rate.

The residence time is calculated as follows:

$$t = \frac{V}{Q} \quad (3.1)$$

Where;

t = residence time

V = volume of photoreactor

Q = flowrate of feed stream

For the first experimental condition, 70, 140, 280, 560 mg/m³ siloxane concentrations were applied. This concentration was achieved by injecting the stock siloxane mixture into a 100 mL/min air stream at 1, 2, 4 and 8 µL/hr (using a syringe pump). The generated gas stream with siloxane compounds was transferred into a mixing chamber to mix well and passed through a sealed quartz reactor, where it was exposed to UV light.

In the second experimental condition with 560 mg/m³ siloxane concentration was performed under two different residence times, these are 84 sec and 168 sec. For simulate the 84 sec residence time, stock mixture of 4 µL/hr siloxane injected into 50 mL/min air stream. The gas mixture passed through the mixing chamber before it was radiated with the UV radiation inside the quartz reactor.

Table 3.1 shows additional concentrations and flow rates tested in this study. Given that siloxanes are dissolved in hydrocarbon solvents, a UV-irradiated beaker (at 264 nm for siloxane degradation) was prepared for each of the experimental conditions.

In the last step, synthetic biogas flow (70% CH₄, 30% CO₂) was applied together with siloxane concentration of 1120 mg/m³ which is the highest siloxane concentration used, with maximum residence time of 168 sec.

At the inlet and outlet, samples were periodically taken to observe the effect of UV on the siloxane removal. Sample points are shown in **Figure 3.3**. Samples analyzed at both the inlet and outlet of the UV photolysis as shown to see the effect of UV photolysis, with the gas-phase concentrations of L2 and D4 siloxanes then determined by gas chromatography (GC) using an Agilent 8860 gas chromatograph (Santa Clara,

California, USA) with a flame ionization detector (FID) and HP-5 capillary column (15 m $\times$ 0.25 mm $\times$ 0.25 μ m). Both the injector and detector temperatures were set at 250 °C, the oven temperature program started with 2 minutes at 40 °C, then increased at a rate of 30 °C/min to 180 °C for 1 minute, and then raised at the same rate to a final temperature of 200 °C; helium was used as carrier gas at a flow rate of 3.5 mL/min.

Table 3.1. Stages of the experiment.

Stage	Feed Stream	Siloxane Concentration	Residence Time
1	100 mL/min air stream	70 mg/m ³	42 sec
	100 mL/min air stream	140 mg/m ³	42 sec
	100 mL/min air stream	280 mg/m ³	42 sec
	100 mL/min air stream	560 mg/m ³	42 sec
2	50 mL/min air stream	560 mg/m ³	84 sec
	25 mL/min air stream	560 mg/m ³	168 sec
3	25 mL/min Synthetic biogas stream	1120 mg/m ³	168 sec

4. RESULTS AND DISCUSSION

4.1. Results

Two siloxanes selected, L2 (Hexamethyldisiloxane) and D4 (Octamethylcyclotetrasiloxane), that were found in both air and biogas streams, and evaluated the feasibility of removing siloxanes from these two streams by UV treatment. The focus of the study was to ascertain whether UV exposure can degrade or reduce the levels of these siloxanes, and the different conditions under which this can be accomplished.

The experiment performed at atmospheric pressure in the controlled laboratory environment at average temperature of 25 °C to maintain uniformity in experimental conditions. To evaluate the effect of siloxane concentration and residence time on removal efficiency, a variety of initial siloxane concentrations and residence times were tested. With the exception of these discrepancies, results showed that UV treatment alone does not significantly decompose or remove siloxanes from the gas phase.

In other words, even in the case of L2 and D4, UV removal efficiency remained at approximately 20%, implying that siloxanes appear to be resistant to UV degradation under the tested conditions. Moreover, there was no significant decrease in the siloxane concentrations upon UV exposure; the concentrations were similar before and after the UV exposure. These results illustrated the inadequacy of UV treatment as a sole method for siloxane removal from air and biogas flows and proposed that alternative, oxidating treatments, combined with adsorption methods, could be used to reach further removal efficiencies.

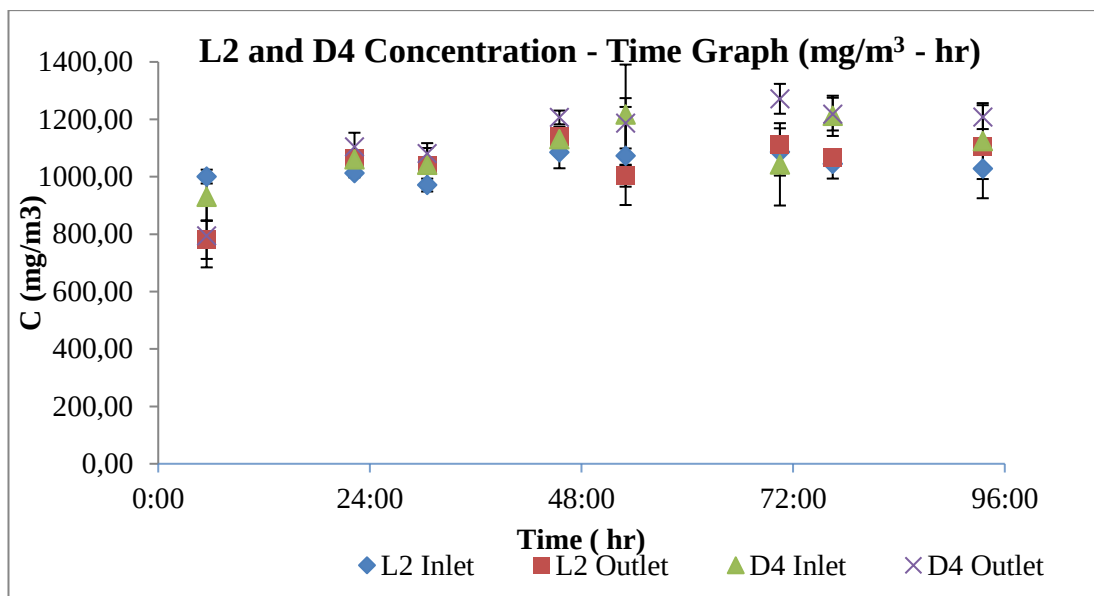


Figure 4.1: Siloxane Concentration Results Under Constant Biogas Flow, Constant Siloxane Soncentration and Constant Residence Time Depending on Operating Time.

The results depicted in **Figure 4.1** were obtained with the system running on synthetic biogas flow with the highest siloxane concentration and the highest residence time tested in the study. The experiment was performed in controlled environment at 25 mL/min synthetic biogas flow rate, siloxane injection rate of 4 $\mu\text{L/hr}$, siloxane concentration at 1120 mg/m^3 , residence time of 168 seconds. Siloxane concentrations are on the y-axis of the following graph, and operating time on the x-axis. Data points denoted as inlet are from samples collected prior to UV exposure, while data points labeled outlet are from measurements taken post-UV treatment.

From the graph, it shows that both L2 and D4 inlet and outlet siloxane concentrations are quite low, suggesting the little impact from UV treatment. The maximum calculated removal efficiency for L2 was 22% and the maximum calculated elimination capacity was 4.73 $\text{g/m}^3\cdot\text{h}$, indicating an insignificant or possibly even upward trend due to measurement uncertainties. Likewise, the removal efficiencies for D4 were 14.6% and the maximum calculated elimination capacity was 2.91 $\text{g/m}^3\cdot\text{h}$, with little difference. However, when it comes to overall siloxane elimination performance, the total estimated elimination efficiency of the system was only 18%, this is a low value that validates that UV treatment is unable to oxidate siloxanes under these conditions.

The ultimate results confirm the earlier ones as it can be concluded that UV exposure doesn't seem to have a meaningful impact on the silica concentrations in the biogas stream, even when maximized in concentration and residence time. The low efficiencies indicate resistance of siloxanes to photodegradation, hence, other treatment options such as adsorption, catalytic oxidation or advanced oxidation should be investigated to improve siloxane removal from biogas.

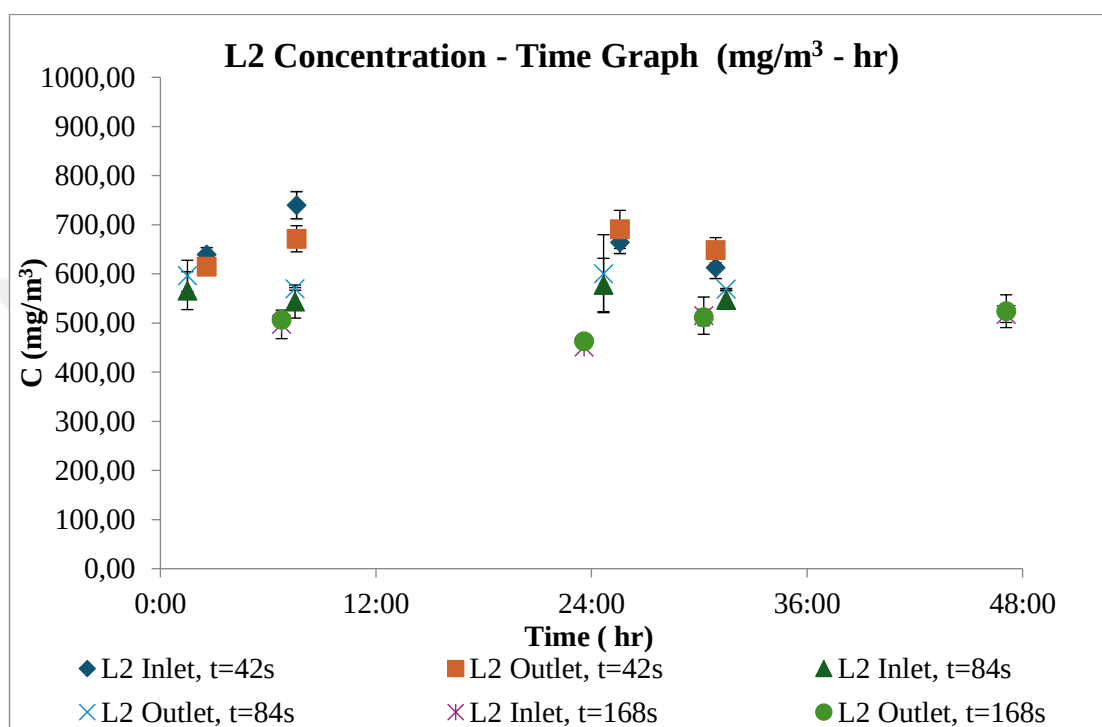


Figure 4.2: L2 Siloxane Concentration Results Under Air Flow With Different Residence Times.

As seen in **Figure 4.2**, the concentration values obtained as a result of the phase studied with constant air flow and different residence times are given in the graph depending on time. As can be seen from the graph, although different residence times were used, the inlet and outlet concentration values are close to each other. According to the results obtained from the data, the maximum siloxane removal efficiency for type L2 is 10.5% and the elimination capacity (EC) is 2.76 (g/m³·h).

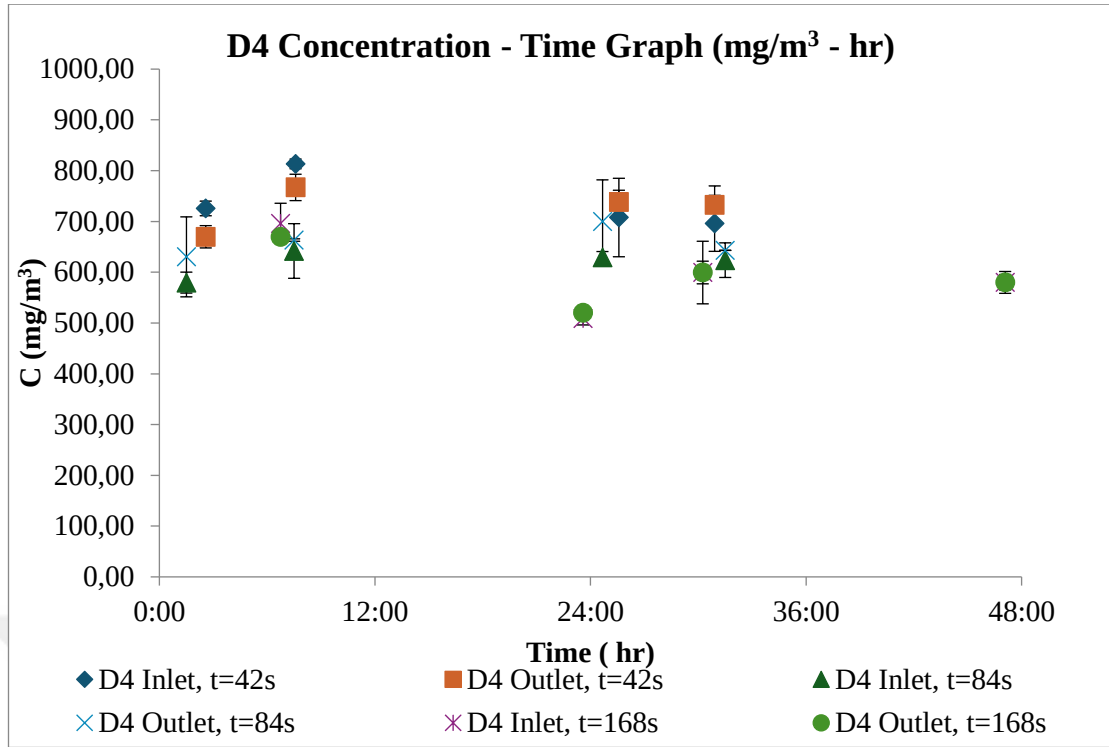


Figure 4.3: D4 Siloxane Concentration Results Under Air Flow With Different Residence Times.

Figure 4.3 shows the time-dependent concentration graph of D4 siloxane type under constant air flow and different residence times. When we look at the values represented in the graph, it can be seen that the input and output concentration values are quite close. According to the results obtained from the data, the maximum removal efficiency of the D4 siloxane type was calculated as 9.4% and the elimination capacity (EC) is 2.28 (g/m³·h).

The elimination capacity (EC) calculated as follows:

$$EC = \frac{(C_{in} - C_{out}) \cdot Q}{V} \quad (4.1)$$

Where;

EC = Elimination Capacity (g/m³·h or mg/m³·h)

C_{in} = Inlet concentration of the pollutant (g/m³ or mg/m³)

C_{out} = Outlet concentration of the pollutant (g/m³ or mg/m³)

Q = Volumetric gas flow rate (m³/h)

V = Volume of the packed bed or bioreactor (m^3)

The maximum removal efficiency of L2 and D4 siloxane types is 9.9% and the elimination capacity (EC) is $2.52 \text{ (g/m}^3\cdot\text{h)}$, in the case shown in **Figures 4.2 and 4.3**, working with constant air flow and different residence times. Although the removal efficiency is low, it can be said that the study is promising because it is one of the new siloxane removal methods and the study was carried out in a limited time.

4.2. Discussion

There are several factors contributing to the low siloxane removal efficiency observed in this study. Primarily, the application of UV treatment for siloxane removal remains a relatively novel approach and has not yet been extensively investigated in the literature. Furthermore, the total study duration of 30 days may have been insufficient to fully optimise experimental conditions. The short testing periods are likely to be the cause of this limitation, as each concentration and residence time was only tested for two days, with the maximum values tested for four days. The exposure durations used in this study may have been too short to result in significant degradation. Additionally, the UV radiation intensity used in this study was relatively low and may not have been sufficient to break the stable chemical bonds present in siloxane molecules.

For UV, the removal of siloxane also initially has an effective action via first contact, but its efficiency decreases and stabilizes after a certain time. This is indicative of initial degradation of siloxane molecules by UV oxidation, but resistance of residual siloxane fractions means that the reaction decays as fewer more resistant fractions remain to oxidise. However, the treatment efficiency gradually decreases, which may be caused by the formation of intermediate molecules that are more stable and less reactive with UV radiation.

The crucial point for the UV oxidation resistance is the chemical structure of L2 (Hexamethyldisiloxane) or D4 (Octamethylcyclotetrasiloxane). Notably, L2 is a linear siloxane while D4 is a cyclic siloxane, and both of them contain strongly stable Si–O–Si bonds that need strong oxidative conditions to facilitate degradation. Even better, the alkyl (methyl, $-\text{CH}_3$) groups (green clusters) bonded to silicon atoms (light blue) increase their stability making them not prone to straightforward photodegradation. Dissociation of these frameworks needs energy-demanding

oxidation processes that can corrupt the si–o–si chain, generating smaller and more homey compounds that can be additionally decomposed.

A limitation observed in this study is that the measurement system can accumulate Siloxane. The residues of siloxanes might have remained in the syringe of the sampler such that the measurement appeared with increasingly lower concentrations over time. Moreover, the accumulation of siloxane in the column of the gas chromatograph with a flame ionization detector (GC-FID) could further have affected the analytical results, possibly resulting in retention time shifts, peak broadening, or incomplete elution, complicating the quantification even more.

The other thing that makes siloxane degradation complex is its volatility, which is not perfectly constant. Variable concentrations in the gas phase due to fluctuations in volatilities pose additional difficulties in consistently achieving attractive removal efficiencies. Although the absolute values of siloxane removal efficiency can only be compared qualitatively between different studies, this variability could account for some of the differences in removal performance, because under non-ideal conditions, actual siloxane exposure to UV treatment is likely to be influenced by changes in phase distribution.

The low UV wavelength and intensity applied in this study might be a reasonable explanation for the moderate UV efficacy documented in this study. Although there were slight variabilities with increased residence time, removal efficiency was less than 20%, indicating that more intense UV light or a different range of wavelengths may have been needed to facilitate breakdown. Indeed, studies indicate that the breakdown of siloxanes can be improved by using shorter wavelengths of UV (e.g. 185 nm as opposed to 254 nm) or the addition of other oxidative agents like ozone (O_3) or hydrogen peroxide (H_2O_2).

An alternative strategy to improve the efficiency of siloxane removal can therefore be envisaged. One such modification is providing higher UV light intensity which may enhance irradiation energy available for photodegradation and possibly improve siloxane removal. On top of that, different UV wavelength optimization might be important, since 254 nm UV light, the most popular, could be insufficient for breaking siloxane bonds. A shorter wavelength UV (185 nm) may work better, because it has

shown to yield hydroxyl radicals that complement oxidation and may help disintegrate stable molecular structures.

Another promising technique using titanium dioxide (TiO_2) as a photocatalyst followed by UV oxidation. Under UV light, TiO_2 can produce highly reactive hydroxyl radicals ($\bullet\text{OH}$) that are proved more effective in degrading siloxanes. The enhanced oxidative degradation on a TiO_2 -coated surface inserted in the reactor would contribute to a better removal efficiency of the siloxane-based compounds. Ultraviolet (UV) treatment is another factor that can improve siloxane degradation when combined with ozone (O_3) or hydrogen peroxide (H_2O_2) oxidation. Considering the real-time generation of extra reactive oxygen species by these AOPs, the strong oxidation capability of reactive oxygen can cleave the inert Si–O–Si backbone of siloxanes, and thus enhances their decomposition and detoxification.

Alternatively, increasing the residence time may also improve efficiency, since leaving siloxanes for a longer period under UV treatment may help to degrade them more thoroughly. Although only minimal enhancements were shown based on increased residence time in this study, increased exposure time, paired with more robust oxidation techniques, may prove to be more effective. Additionally, alternative oxidation processes (e.g., plasma oxidation or non-thermal plasma (NTP) treatment) have been explored for removal of volatile organic compounds (VOCs) and their application for siloxane removal would need to be investigated. On the other hand, catalytic oxidation could involve paper-based catalysts like MnO_2 or Fe_2O_3 that might break down the siloxane structures and further improve degradation efficiency.

In conclusion, UV-initiated siloxane removal is proposed as a viable method, as indicated by these preliminary results. Further researches should emphasize the optimization of UV wavelength and intensity, the examination of advanced oxidation processes (AOPs), and the use of photocatalytic materials like TiO_2 to improve the efficiency of siloxane degradation. Furthermore, integrating adsorption, plasma oxidation and catalytic processes as a pre-treatment stage, followed by UV treatment could lead to more comprehensive removal of siloxanes in biogas applications.

5. CONCLUSION

Although major content of biogas stream consist of CH_4 and CO_2 some trace components such as siloxane is present in the gas streams. Removal of toxic compounds from biogas is very important for its effective utilization. The presence of siloxane in biogas, even in trace amounts, can lead to critical and costly problems over time. Siloxanes should be removed from biogas streams like other toxic compounds in order to extend the life of the equipment used, reduce operating costs and have a better quality gas content. Presence of siloxane limits usage/application areas of biogas and results operational problems and additional costs. To overcome these limitations many siloxane removal systems based on adsorption processes were used worldwide. High operational and equipment cost and non-environmentally nature of processes prompted to search new opportunities.

It is very important to find innovative siloxane removal methods and make them widely used in order to keep up with the high costs, operational difficulties and global innovations that occur during the installation and operation stages of traditional removal methods and to extend the life of the resources.

Within the content of thesis UV oxidation to air and biogas streams for siloxane removal L2 D4 were used. Results highlights although UV oxidation have a limited success to breakdown siloxane L2 and D4 into their metabolites and that resulted low efficiency to removal of siloxane from gas streams. That findings match within the persistent character of siloxane. The removal efficiencies of 22% and 14.6% for L2 and D4 respectively, which translate to elimination capacities of $4.73 \text{ g/m}^3\cdot\text{h}$ and $2.91 \text{ g/m}^3\cdot\text{h}$, show that photolysis alone is not enough to degrade L2 and D4 into their metabolites. However, integrating the UV photolysis system with advanced oxidation mechanisms (such as ozone or H_2O_2) alongside UV exposure can facilitate the formation of smaller siloxanes, potentially leading to their conversion into siloxane metabolites. Further studies on this topic should be planned for future research.

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