

**ASSESSMENT OF LOW-COST ADSORBENTS FOR SILOXANES REMOVAL FROM
LANDFILL GAS**

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Report #

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List of Abbreviations & Acronyms

Landfill Gas.	LFG
Environmental Protection Agency	EPA
Life Cycle Assessment.	LCA
Siloxane Removal Unit	SREU
Waste to Energy	WTE
Municipal Solid Waste	MSW
Landfill Gas to Energy	LFGTE
Technoeconomic Analysis	TEA
Hexamethyldisiloxane	L2
Octamethylcyclotetrasiloxane	D4
Total Capital Investment	TCI
Total Annual Cost	TAC
Internal Combustion Engine	ICE

ABSTRACT

Landfill gas (LFG) is increasingly used and researched as a feedstock for a variety of traditional and proposed Waste-to-Energy (WTE) technologies, which includes electricity generation, compressed natural gas, or liquid hydrocarbon fuels. In these various scenarios, contaminants in the LFG can have substantial economic and environmental consequences in the WTE processes. Specifically, siloxanes are an emerging component in many consumer products that are landfilled and have a high enough vapor pressure such that a substantial amount is contained in the LFG. Siloxanes decompose to silica causing equipment damage that results in process downtime and reoccurring maintenance costs. The current purification techniques available are too expensive, in that it costs less to repair damaged engine parts than to adopt the current gaseous siloxane scrubbing technology. In order to accelerate adoption of waste to energy processes, a desire for more economical ways for removing siloxanes from LFG exists.

In the work reported here, a natural zeolite (clinoptilolite), which costs as low as ~\$100/ton, as compared to activated carbon that is factors of 3+ more expensive, and four other low-cost materials (diatomaceous earth, crushed glass, biochar and hydrochar), were characterized and tested for siloxane adsorption. Characterization techniques adopted includes N₂ physisorption, x-ray diffraction, CO₂ adsorption and water vapor sorption analysis. Clinoptilolite showed the best result for siloxane adsorption among all samples tested and hence was used in further analysis.

Technoeconomic analysis (TEA) and life cycle assessment was conducted for siloxane removal units with clinoptilolite as an adsorbent and then compared with the current state of technology, activated carbon and a material tested in literature, 13X zeolite. The TEA results revealed that clinoptilolite as an adsorbent for siloxane removal is too expensive as compared to activated carbon and 13X zeolite. Sensitivity analysis was conducted to study the effect of the adsorption capacity of activated carbon on the total annual cost. The result from the sensitivity analysis revealed that 13X zeolite becomes a more cost-effective adsorbent for siloxane removal from LFG when compared with activated carbon that possesses an adsorption capacity less than 500 mg D4/g media. The result from the life cycle assessment revealed that the CO₂ emissions from all siloxane removal units analyzed are approximately equal and therefore, only the cost of systems can be used in making decisions on adoption.

1. INTRODUCTION

1.1. Motivation

Municipal and agricultural solid waste (MSW) biomass offers tremendous opportunity as a major, near-term, energy resource. In 2015, U.S. generated a total of 262.4 million tons of MSW (4.8 lb/person/day) of which about half (52.5%) was landfilled (EPA 2018). With Florida's population continually increasing (now the third most populous state) and being the leading agricultural state (thus generating significant agricultural/organic resources), there is tremendous potential for Florida to be a leader in the conversion of MSW/agricultural residue to energy. The biodegradable component of these wastes/residues produces an estimated 215 billion cu.ft. of LFG from landfills (EPA 2012). Concerns about the contribution of methane in LFG to global warming led EPA to regulate these emissions. LFG has the potential to be converted to useful energy by a variety of techniques as compared to flaring the gas in Table 1. However, regardless of the LFG-to-energy options, contaminants in the LFG cause equipment damage, increase processing costs, and lead to harmful emissions (Ajhar *et al* 2010, Kuhn *et al* 2017, Tansel and Surita 2013). Specifically, siloxanes are an emerging source of problematic contaminants in LFG. Siloxanes are the name of a class of C, Si, O, and H containing compounds (Dewil *et al* 2006, Surita and Tansel 2015) incorporated into a variety of personal care products over the last couple of decades and have high enough vapor pressures to be in measurable and significant concentrations (Figure 1 for nomenclature and general properties) in LFG and are still emerging in use (Ajhar *et al* 2010, Dewil *et al* 2006). This trend is evident in the fact that the first siloxane removal patent was issued in 1999 (Ajhar *et al* 2010) and in regards to the exponential increase in articles and citations on siloxanes and LFG (Figure 2). According to a recent review (Rucker and Kummerer 2015), the worldwide annual capacity of siloxanes is estimated to be several million tons (~5 as gathered from several sources, with ~ 20% produced each in China and EU) with a previous growth rate of 2% from 1998 to 2002 and a predicted growth rate 6.5% from 2012 to 2017. Also, siloxanes are a common classroom VOC (Tang *et al* 2015).

Since anaerobic conditions are reached within one to three years, with peak LFG production being reached within five to seven years, there is a significant delay between landfilling and changes in LFG composition. LFG is produced for 20 to 30 years following MSW being landfilled. With this

substantial lag time between landfilling and contaminant evolution, changes in LFG handling and addition of conditioning steps may be necessary in response to future changes in LFG composition.

Table 1: Comparison of WTE technologies (Kent 2016)

	Flaring	Electricity	Liquid Fuel
Product Rate (per year)		49.36 Million kWh	2,021,760 gal diesel 758,160 gal gasoline
FCI (MM \$)	2.8	9.4	12.5
OP-EX (MM \$/yr)	0.5	0.8	4.9
Revenue (MM \$/yr)	-	3.2	6.4
NPW (MM \$)	-4.8	-2.0	2.9

Despite the increasing use of siloxanes in products that are landfilled, there is no economic solution available. Current state-of-technology solutions are water scrubbing and adsorption. While water scrubbing can be efficient, the capital and operating costs for compressors and moisture removal, which may be required twice (before and after the scrubber) as well as water treatment can be cost prohibitive. Adsorption can also be efficient; however, frequent replacement of moderately expensive adsorbents can be cost prohibitive. This situation leaves LFG WTE operators with the challenge of make a bet to either focus on gas cleanup or equipment maintenance. Our calculations, assuming 5 mg/m³ of siloxanes in the feed, indicate that the cost of siloxanes removal (just siloxanes, not all contaminants) is ~ 30% of revenue from electricity generation in an LFG WTE process (Elwell *et al* 2018).

Compound	Molar mass (g/mol)	Typical Concentration (mg/m ³)	Allowed Concentration (mg/m ³)
Siloxanes (L2-D5)	162-371	0.005-15	Engine: 5 – 28 Turbine: 0.03 – 0.1
Sulfides: (H ₂ S-CH ₄ S)	34.1-48	0.56-280	60-120
Chlorides (CCl ₄ -C ₂ HCl ₃)	112-166	0.14-452	ND
VOCs (Benzenes, isopropyl benzene, halogenated compounds)	78-120	0.85-5.6	ND
Alkanes/ alkenes (C ₇ H ₈ -C ₁₆ H ₃₄)	92-226.4	0.1-85.3	ND
Mercury compounds (CH ₃ Hg-(CH ₃) ₂ Hg)	216-231	1-91e ⁻³	ND

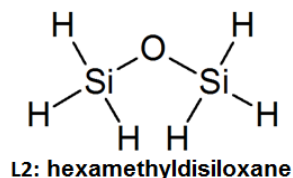
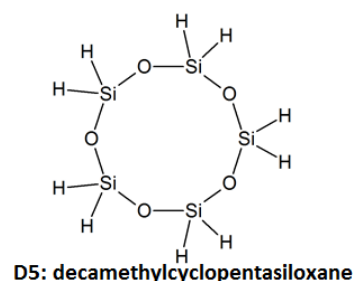


Figure 1: Details on siloxane contaminants and their structure.

1.2. Goals and Objectives

The overall goal of this project is to evaluate technologies that have potential for low-cost removal of siloxanes.

Specific objectives for this project are:

1. Characterize and test natural zeolites and low-cost/waste inorganic materials for adsorption capacity and regeneration ability of adsorbents for selected siloxanes in inert and surrogate LFG.
2. Design a process flowsheet and conduct techno-economic analyses of the adsorbents evaluated in this project (as part of objective 1).
3. Conduct lifecycle analysis for facilities with siloxane removal units installed and compare with facilities without siloxane removal units installed.

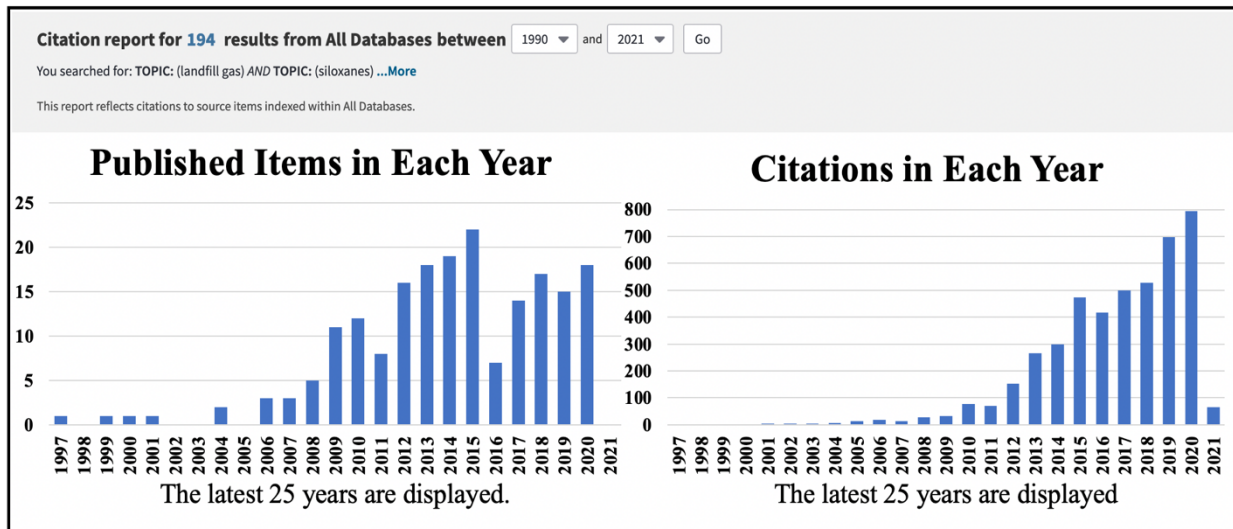


Figure 2: Web of Science search and citation report for “landfill gas” and “siloxane” conducted on 02/25/21

1.3. Scope of Work

This work will procure inexpensive natural zeolite (clinoptilolite) from a supplier and also low-cost inorganic/waste materials such as diatomaceous earth, crushed glass, biochar and hydrochar will be obtained. Chosen materials will be characterized before and after siloxanes adsorption. Conventional characterization techniques will be employed to thoroughly evaluate the structure-function relationships. Static isotherms will be obtained to estimate performance. These results are often important as technology is considered to scaleup. The siloxanes selected as the representative species are octamethylcyclotetrasiloxane (D4) and hexamethyldisiloxane (L2), based on previous research efforts (Elsayed *et al* 2017, Elwell *et al* 2018, Kuhn *et al* 2017). The materials will then be tested in demonstration scale separation/regeneration in a fixed bed configuration over a range feed composition typical of LFG.

The results will be used to feed the techno-economic and environmental analyses. These simulations of these processes will be conducted using Excel and SimaPro. We will create two scenarios: one in which the purified gas is sent to an engine to produce power and look at the total capital and operating expenses associated with the process setup scaled up for a typical landfill producing about 1000 SCFM of landfill gas. The second in which the siloxane removal system is not in place in which case we will simulate the cost of added equipment shutdown and maintenance

resulting from the engine fouling caused by the siloxanes. We will also compare costs using conventional adsorbents.

1.4. Significance of work

This project's success would provide a technology to lower the cost of siloxanes removal from LFG. If achieved, this would allow LFG WTE operators to invest into purification processes rather than to gamble on low maintenance costs. The long-term outcome from this research could be a highly efficient, low-cost purification process for siloxanes removal from LFG. This achievement would provide MSW facilities avenues to have more efficient WTE processes using LFG as a feed. Specifically, it will provide an avenue to limit maintenance costs and process downtime in LFG WTE facilities.

2. BACKGROUND

LFG is a mixture of gases produced from the anaerobic decomposition of municipal solid waste. It is comprised mainly of methane gas, but also contains carbon dioxide, water vapor and contaminants such as hydrogen sulphide and siloxanes. Methane is a very potent greenhouse gas which poses a global warming threat. Due to this concern, the EPA regulated the emissions of methane. With methane being a major constituent of LFG, LFG serves as a feedstock to various waste to energy technologies. However, contaminants present in the LFG can have substantial economic and environmental consequences in the waste to energy process.

There are several classes of contaminants contained in varied quantities in LFG such as siloxanes, sulfur compounds, chlorides, halogenated volatile organic compounds (VOCs), nitrogen, oxygen, carbon monoxide, alkanes/alkenes and mercury compounds (Andriani *et al* 2013). However, the two most important classes of contaminants requiring further treatment are the sulfur species and siloxanes, as these contaminants lead to substantial processing challenges and irreversible damage even at low concentrations and require removal technologies. Damages caused by hydrogen sulphide (which is the major sulfur specie present in LFG) includes corrosion of equipment such as pipelines, compressors, engines and storage tanks; poisoning of fuel cells and catalysts; conversion to harmful sulfur dioxide during combustion of LFG composed of H₂S, thereby raising environmental concerns (Andriani *et al* 2013). Siloxanes decompose into silica at high temperatures causing damage to engine parts (see Figure 3) during electricity production and catalyst poisoning (see Figure 4) during thermocatalytic conversion of LFG into liquid fuels.

A wide variety of the concentrations of these contaminants (siloxanes and hydrogen sulphide) in LFG has been reported in literature. The concentrations of siloxanes can be much higher in biogas from WWTPs than in LFG. Wheless and Pierce (2004) reported the highest value of siloxane concentration in LFG as 136 mg/Nm³ and Hill (2014) reported the highest value of siloxane concentration in WWTP biogas as ~ 417 mg/Nm³. In biogas derived at WWTPs in Europe, total siloxane concentrations as high as 127.4 mg/Nm³ have been reported (Raich-Montiu *et al* 2014). These high values for WWTP biogas are factors of ~ 5 to 20 than those on the high end of LFG (see Table 2).



Figure 3: Examples of Equipment Damage caused by Siloxanes (a) Spark plugs, (b) engine head, (c) cylinder head.

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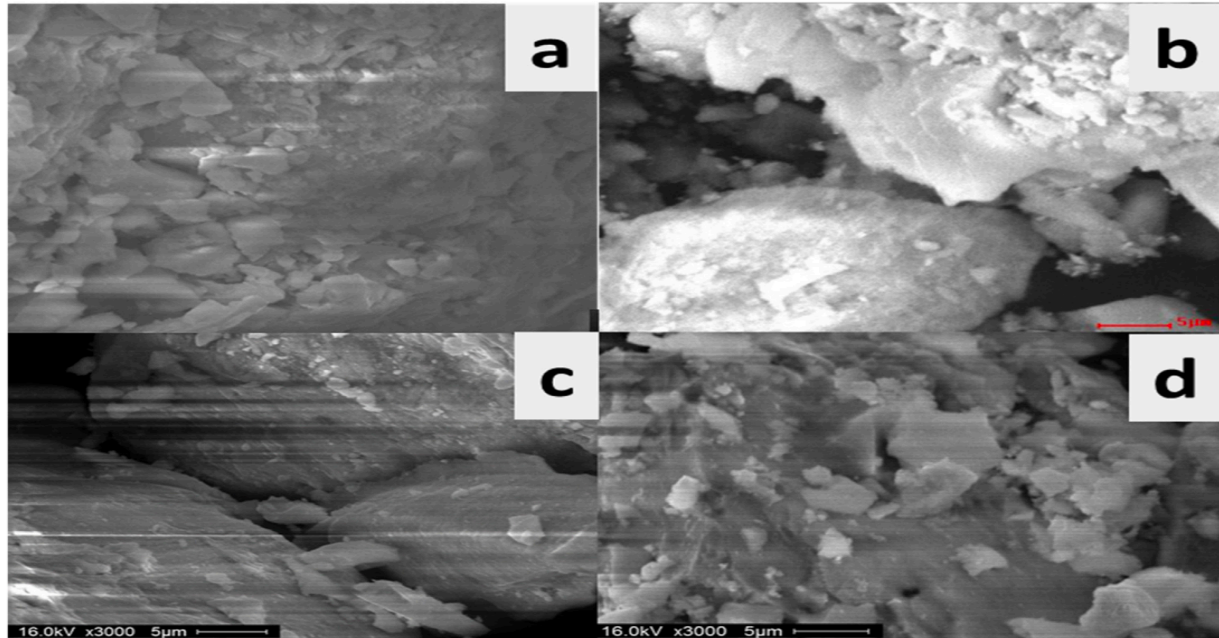


Figure 4: (a) SEM image of fresh 0.16Pt catalyst (b) SEM image of 6M-Pt catalyst (c) SEM image of fresh NiMg catalyst (d) SEM image of 6M-NiMg catalyst.

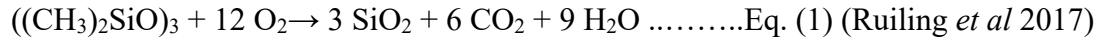
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Table 2: Comparison of highest reported and typical values for key contaminants

Biogas	Contaminant	Concentration		References
		Highest	Typical	
LFG	H ₂ S	5400 ppmv	63 ppmv	(Papadias <i>et al</i> 2012)
	Siloxanes	136 mg/Nm ³	16.8 mg/Nm ³	(Dewil <i>et al</i> 2006, Schweigkofler and Niessner 2001, Tansel and Surita 2013, Wheless and Pierce 2004)
WWTP	H ₂ S	3 %	400 ppmv	(de Arespacochaga <i>et al</i> 2014, Papadias <i>et al</i> 2012)
	Siloxanes	400 mg/Nm ³	46 mg/Nm ³	(Dewil <i>et al</i> 2006, Raich-Montiu <i>et al</i> 2014)

Table 3 shows reported values on the concentration of siloxanes in LFG. The varied siloxane concentration values depend on several factors such as location, age and contents of the landfills. Data obtained from landfills in manatee county showed that siloxane concentration as of 2016 was about 25 mg/m³ (see Table 4), and as of 2019, it had doubled to about 45 mg/m³ (see Table 5). This shows that the age of the landfill is a very important factor affecting the siloxane concentration.

Contaminant tolerance limit has been imposed on several WTE technologies. Table 6 shows the tolerance limits of various LFGTE technologies to key contaminants. Comparing the tolerance limit on Table 6 to the highest and typical concentrations shown on Table 2, it becomes evident that siloxanes are the key contaminant requiring removal as there is a stricter requirement for siloxanes than for hydrogen sulphide. This is because the harm caused by silicon is fatal to engines. Silicon exists in the form of siloxanes in biogas. “In the process of combustion, silicon transforms into SiO₂, which is referred to as quartz (Ruiling *et al* 2017).” The reaction process is shown in Eq. (1):



“This quartz can form a layer of covering film within a few hours, wear down the cylinder surface, and cover the spark plugs (see Figure 3a), valves and the turbo compressor (Ruiling *et al* 2017).”

Table 3: Reported Values for Siloxane Concentration in LFG

Siloxane Type	Siloxane concentration (mg/m ³)	Reference
L2 – D5	1 - 17	(Kuhn <i>et al</i> 2017)
Total Siloxanes (L2, L3, L4, L5, D3, D4, D5, D6, Trimethylsilanol)	1 - 136	(Wheless and Pierce 2004)
“	7.48 - 19.18	(Schweigkofler and Niessner 1999)
“	28.21 - 36.24	(Urban <i>et al</i> 2009)
“	3.31	(Läntelä <i>et al</i> 2012)
“	1.84 – 7.37	(McBean 2008)
“	3 - 24	(Ajhar <i>et al</i> 2010)
Sum of VMSs (Germany)	3 - 25	(Arnold 2009, Gaj 2020)
L2 – L4 + D3 – D6 (Finland)	2 - 8	(Arnold 2009, Gaj 2020)
Sum of VMSs (Poland)	18 – 39	(Gaj 2020, Piechota <i>et al</i> 2012)
L2 – L4 + D3 – D6 (Germany)	Up to 50	(Gaj 2020, Schweigkofler and Niessner 2001)
L2 – L5 + D3 – D6 (Europe, Canada)	2 - 24	(Gaj 2020, Wang <i>et al</i> 2019)

Table 4: Siloxane Analysis result from Lena Road Landfill, Manatee County (samples submitted 12/05/2016)

Siloxane type	g/mol	ppbv	mg/m ³
L2	162	295	1.96
D4	297	927	11.25
D3	222	126	1.15
D6	445	2.53	0.05
D5	371	69.1	1.05
L3	237	12.6	0.12
Trimethylsilane	74	2530	7.67
		Total	23.25

Table 5: Siloxane Analysis result from Lena Road Landfill, Manatee County (sample received 11/04/19)

Siloxane type	g/mol	ppbv	mg/m ³
L2	162	360	2
D4	297	2400	29
D3	222	700	6
L5	385	480	8
		Total	45

Table 6: Tolerance of LFGTE processes to key contaminants

LFGTE process ^a	Manufacturer / Type	Contaminant Tolerance				Reference
		H ₂ S (mg/Nm ³ CH ₄)	Siloxanes (mg/Nm ³ CH ₄)	Halides (mg/Nm ³ CH ₄)	Ammonia (mg/Nm ³ CH ₄)	
Internal Combustion Engine	Caterpillar		28 ^b			(De Arespacochaga <i>et al</i> 2015, Wheless and Pierce 2004)
		2140	21	713	105	(SEPA 2004)
	Jenbacher		10 ^b / 12 ^b			(De Arespacochaga <i>et al</i> 2015, Wheless and Pierce 2004)
		1150	20	100	55	(SEPA 2004)
	Waukesha		25 ^b / 30 ^b			(De Arespacochaga <i>et al</i> 2015, Wheless and Pierce 2004)
		715	50	300		(SEPA 2004)

	Deutz		5 ^b			(Wheless and Pierce 2004)
		2200	10	100		(SEPA 2004)
	Tech3solution		5 ^b			(De Arespacochaga <i>et al</i> 2015, Wheless and Pierce 2004)
Turbine	Solar Turbines		0.1 ^b			(Wheless and Pierce 2004)
	IR Microturbines		0.06 ^b			(Wheless and Pierce 2004)
	Capstone Microturbines		0.03 ^b			(De Arespacochaga <i>et al</i> 2015, Wheless and Pierce 2004)
Stirling Engine	n/a		No limit			(De Arespacochaga <i>et al</i> 2015)
Fuel Cells	MCFC	1-5 ^c		Few ppm		(Sun <i>et al</i> 2015)
	PAFC		0.05-0.1 ^b			
	SOFC	1 ^c		Few ppm		(Sun <i>et al</i> 2015)

Natural Gas Grid ^c	(varies by country)		0.5-10 ^b			(De Arespacochaga <i>et al</i> 2015)
Vehicle Fuel ^b	n/a	5 ^b				(Sun <i>et al</i> 2015)

^a All LFGTE technologies require some degree of water removal

^b mg/Nm³ (i.e., per total LFG volume, not per CH₄ partial volume as stated)

^c ppm (not per CH₄ partial volume as stated)

^d requires substantial CO₂ and air removal

Certain factors affect the economics of siloxane removal from LFG. As identified by Kuhn *et al* (2017), these factors include (i) amount of contaminant in LFG, (b) LFG flowrates, (c) tolerance limit of LFGTE processes to contaminant and (d) contaminant removal cost associated to various technologies. Table 3 already highlighted the reported siloxane concentrations found in LFG, and Table 6 reported the allowable tolerance of LFGTE processes to siloxanes. According to data collected from EPA Landfill Methane Outreach Program, LFG flowrates range from a minimum of 35 scfm to a maximum of 31,300 scfm with an average of about 2420 scfm (Kuhn *et al* 2017).

There are several technologies used for siloxane removal from LFG. These technologies include: Adsorption, Absorption, Cryogenic condensation, Catalytic process, Biological removal and membrane separation (Ruiling *et al* 2017). The technologies that currently have commercial application are adsorption, absorption and cryogenic condensation (gas chilling) (Ajhar *et al* 2010, Ruiling *et al* 2017). Among these technologies, adsorption has been identified to be the most cost effective at small scale, of which developments are of utmost need.

The most widely used adsorbent for siloxane removal is activated carbon. Other commonly tested adsorbents for siloxane removal includes silica and zeolites. Studies up to this point have concluded that activated carbon has the highest siloxane adsorption capacity. Finocchio *et al* (2009) determined activated carbon (570 mg/g media) to have higher capacity than inorganic

materials (silica gel, 230 mg/g media; Faujasite zeolite, 276 mg/g media). In a follow up study, a higher regeneration ability for Faujasite zeolite (16 to 23%, depending on temperature) than activated carbon (4 to 8%) was reported, with no regeneration possible for silica gel (Montanari *et al* 2010). Ortega and Subrenat measured from 300 to 400 mg siloxanes/g media, depending on the specific conditions for different types of activated carbon, and lower values for zeolite and silica gel adsorbents (Ricaure-Ortega and Subrenat 2009).

Some studies have demonstrated silica gel to be better than activated carbon. Sigot *et al* demonstrated silica gel (216 to 260 mg D4/g media) to have the highest adsorption capacity while activated carbon (52 to 53 mg D4/g media) had minimal uptake when tested at 30 ppm_v D4 (Sigot *et al* 2014, Sigot *et al* 2016). The lowest report of adsorption capacity of siloxanes on carbon was 4 mg siloxanes / g media (Wheless and Pierce 2004). The activated carbon that Sigot *et al* (2014), Sigot *et al* (2016) and Wheless and Pierce (2004) describe is coconut-based, so perhaps there is some unique feature of this material that limits siloxane adsorption. A very wide range for siloxane adsorption capacity on activated carbon has been reported in literature. Table 7 shows the reported adsorption capacity of activated carbon from various authors.

Table 7: Adsorption Capacity of siloxanes on various kinds of carbon-based adsorbents.

Adsorbent material	Adsorption Capacity (mg/g)	References
AC	155 – 307 (Total VMS)	(Gaj 2020)
AC	36 – 404 (D4)	(Gaj 2020)
Chezacarb	63 (D5)	(Vagenknechtova <i>et al</i> 2017, Wang <i>et al</i> 2019)
AC	16 (D5)	(Jung <i>et al</i> 2017, Wang <i>et al</i> 2019)
AC	334 (D4)	(Gong <i>et al</i> 2015, Wang <i>et al</i> 2019)
AC	52 (D4)	(Sigot <i>et al</i> 2014, Wang <i>et al</i> 2019)
ACF	365 (D4)	(Giraudet <i>et al</i> 2014, Wang <i>et al</i> 2019)
MWV-2	1732 (D4)	(Cabrera-Codony <i>et al</i> 2014, Wang <i>et al</i> 2019)
AC	100 (L2)	(Gislon <i>et al</i> 2013, Wang <i>et al</i> 2019)
AC1	123 (L2)	(Wang <i>et al</i> 2019)

AC	225 (D4)	(Wang <i>et al</i> 2019, Yu <i>et al</i> 2013)
AC 6	404 (D4)	(Oshita <i>et al</i> 2010, Wang <i>et al</i> 2019)
AC 6	531 (D5)	(Oshita <i>et al</i> 2010, Wang <i>et al</i> 2019)
AC-9	192 (D4)	(Matsui and Imamura 2010, Wang <i>et al</i> 2019)
FM 30K	320 (L2)	(Ortega and Subrenat 2009, Wang <i>et al</i> 2019)
NC-60	350 (L2)	“
FM 30K	410 (D4)	“
AC	4	(Wheless and Pierce 2004)

Apart from the type of raw material used for activated carbon production, other factors that may affect the adsorption capacity include feed composition (including siloxane concentration), temperature, pressure and relative humidity which are rarely reported. Activated carbon has been reported to possess poor regeneration ability of siloxanes due to the polymerization (Ajhar *et al* 2010). Thus, adsorbent beds have to be replaced regularly, thereby increasing operating cost. In costing an adsorption system, two costs must be considered: the initial capital cost and the annual cost. The annual cost includes the ongoing replacement of the adsorbent. The frequency of replacement depends on the adsorption capacity of the adsorbent and the siloxane mass loading rate which is a function of the siloxane concentration in the LFG and the LFG flowrates. LFG with very high siloxane concentration will need frequent replacement of adsorbent material thereby increasing replacement cost, for example, the biogas of Trecatti (UK) had siloxane concentration of up to 400 mg/m³ which led to a major engine failure within 200 h of operation (Dewil *et al* 2006). For this reason, a weekly change of the activated carbon was necessary, with a one-day downtime at the adsorber and a cost of nearly €2000 per change (Dewil *et al* 2006).

Activated carbon costs ~ \$1/lb and based on the siloxane concentration and delivery flowrate of LFG, replacement cost for activated carbon can go as high as \$2400 per weekly change as seen for the biogas of Trecatti (UK) which cumulates to over \$100,000 per year, or ~\$20,000 / year as reported by Elwell *et al* (2018). Natural zeolites can be purchased for as little as ~\$100/metric ton. If similar performance can be obtained for other materials, this cost could be substantially lowered

or even removed if waste materials can be used. Figure 5 shows the cost comparison between clinoptilolite (a natural zeolite) and activated carbon.

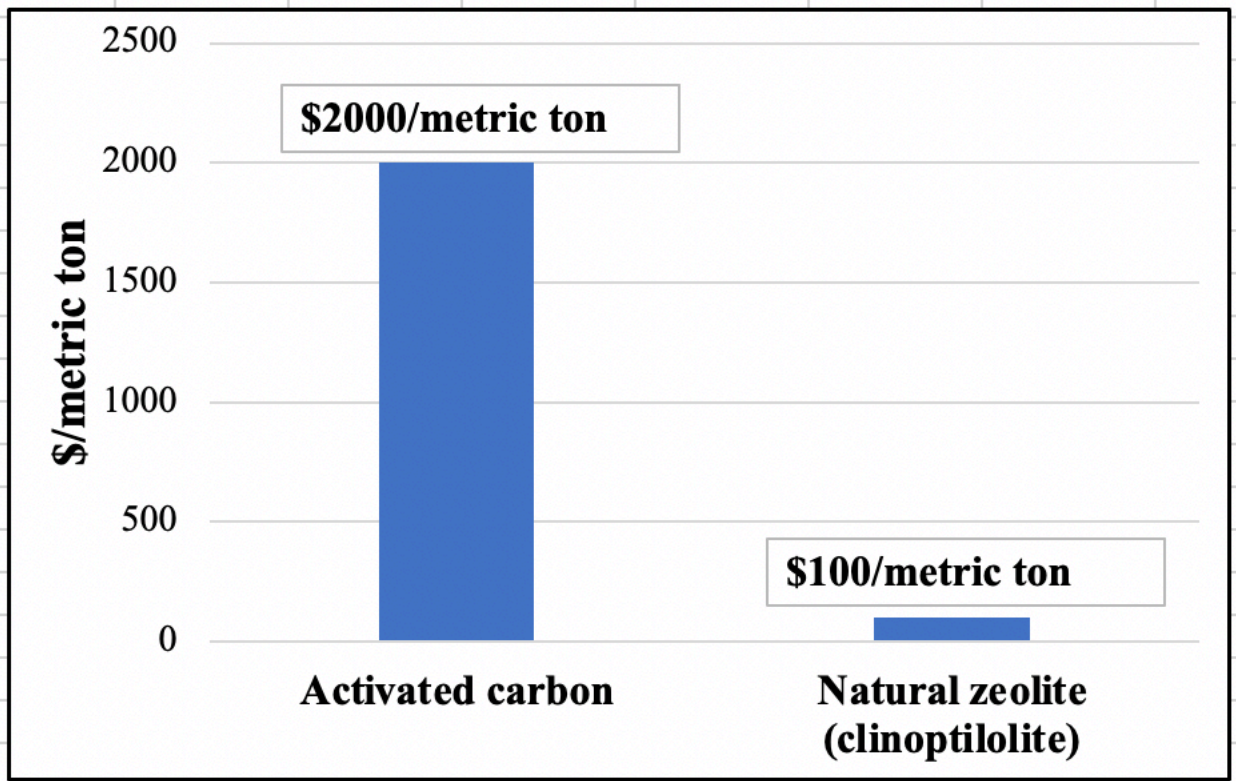


Figure 5: Cost comparison between state of technology (SOT) and proposed technology.

3. METHODS

3.1. Materials used

Five adsorbent materials were analyzed in this study: Clinoptilolite, diatomaceous earth, crushed glass, biochar and hydrochar.

3.1.1 Clinoptilolite

Clinoptilolite is a natural zeolite with complex chemical formula: $(\text{Na}, \text{K}, \text{Ca})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$. KMI clinoptilolite with a 97% minimum purity was purchased.



Figure 6: Clinoptilolite sample

3.1.2. Diatomaceous Earth

Diatomaceous Earth (DE) is a naturally occurring fossilized remains of diatoms—single-celled aquatic algae. It contains 90% silica, 4% Alumina, 2% iron oxide with chemical formula: SiO_2 . It is commonly used as swimming pool filters, hence will be readily available. For this research, Dicalite natural diatomaceous earth (DE) was purchased.



Figure 7: Diatomaceous earth sample.

3.1.3. Crushed Glass

Crushed glass samples were obtained from the “Rosebud Continuum Sustainability Education Center.” The crushed glass was made from waste bottles by crushing into smaller bits and grinding into pellets/powder using a garbage disposal unit (InSinkErator garbage disposal). The crushed glass samples obtained are displayed in Figure 8 below:

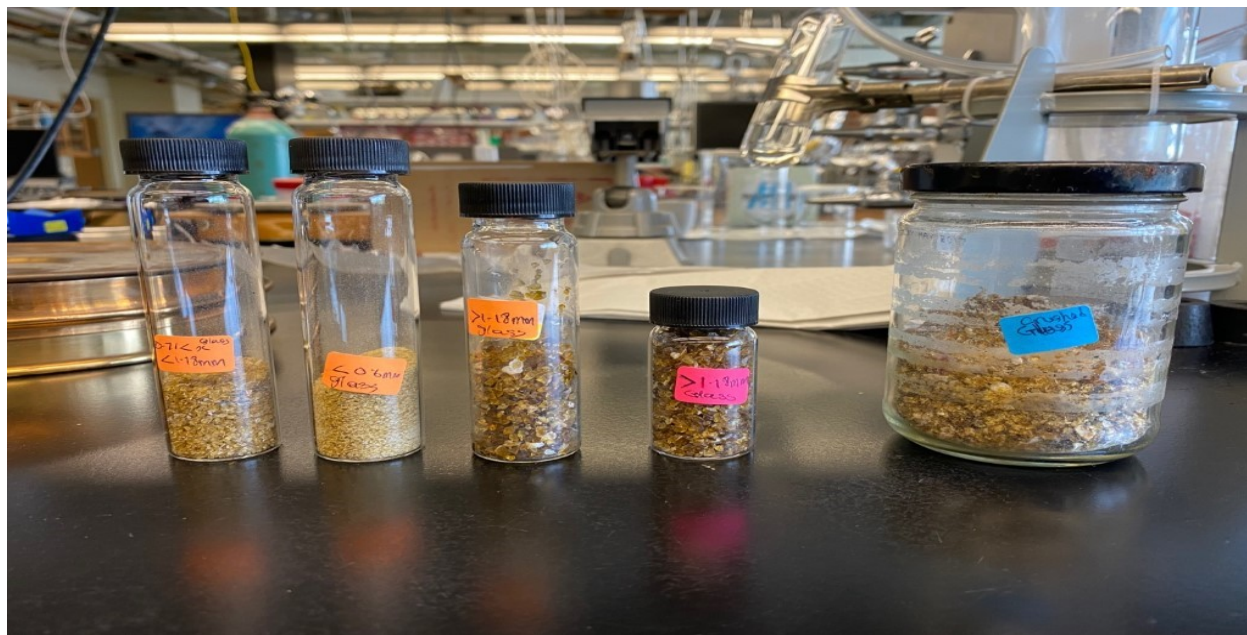


Figure 8: Crushed glass samples

3.1.4. Biochar

Biochar samples were obtained from the Department of Civil and Environmental Engineering at the University of South Florida. The biochar samples obtained are displayed in Figure 9 below.



Figure 9: Biochar samples.

3.1.5. Hydrochar

Hydrochar samples were obtained from Professor George Philippidis' research group. These samples were produced using hydrothermal carbonization of lipid extracted algae (LEA). Dried LEA of *Picochlorum oculatum* and distilled water are used. The feedstocks are transferred into a lab-scale high temperature and pressure Parr reactor (Model 4564, Parr Instruments, Moline, IL, USA) with a capacity of 160 mL. The reactor (batch type) consists of a stainless-steel vessel, a heater, and a manometer. Nitrogen gas is used to achieve anaerobic conditions during the reaction. The operating temperature ranged between 175 and 220 °C with the reaction run for 1 to 3h. The solids loading (concentration) varies between 8% to 15%. The contents of the reactor are mixed vigorously at 200 rpm. After the reaction, the vessel is cooled down to 30 °C and then the reaction products are collected as a mixture of solid and liquid phases. Vacuum filtration is used to separate the char product (hydrochar) from the liquid phase, which contains water and solubilized products. The filtered solid is washed with water and oven dried overnight under vacuum at 110 °C while

the aqueous phase is stored at -20 °C until further characterization. Hydrochar sample analyzed is displayed below:



Figure 10: Hydrochar samples

3.2 Characterization Methods

N₂ physisorption analysis, x-ray diffraction analysis, CO₂ adsorption and water vapor sorption analysis were used for the characterization of chosen adsorbents.

N₂ physisorption analysis was conducted to determine the surface area and pore size distribution of the adsorbent materials at 77K. A static adsorption instrument (Autosorb; Quantachrome), was used in conducting this analysis. The samples used for the N₂ physisorption were outgassed using a soak time of 300 min at 300 °C. Brunauer –Emmett-Teller (BET) method was used to calculate the surface area inside the range of relative pressure from 0.05 to 0.3 and Barrett-Joyner-Halenda (BJH) method was used to find the pore size distribution of the samples by determining the volume of N₂ adsorbed at a set interval of relative pressures (P/P₀).

X-ray diffraction analysis was conducted to obtain information on the chemical structure of the adsorbent materials. An X-ray diffractometer (Bruker D8 Advance Diffractometer) was used in conducting this analysis. Cu K α radiation (0.154 nm) was used to get the XRD diffraction patterns. A Bragg angle ($2\theta^\circ$) in the range of 10-90⁰, with a step size of 0.02 was used with a dwell time of 1.5 sec for each step.

CO₂ and water vapor sorption experiments were conducted on chosen adsorbent materials to examine the competition of adsorption sites by these compounds. The vapor sorption experiments were conducted using a static adsorption instrument (Autosorb; Quantachrome) and adsorption isotherms were generated. From these adsorption isotherms generated, the adsorption capacity of CO₂ and water vapor on the chosen adsorbents were calculated.

4. RESULTS & DISCUSSION

4.1. Characterization results

The chosen adsorbent materials were characterized using N₂ physisorption, XRD, CO₂ adsorption and water vapor sorption analysis. The BET surface area and the pore size distribution gotten from the N₂ physisorption analysis is displayed on Table 8 below. According to Cabrera-Codony *et al* (2018), “the porous features of adsorbent media are responsible for siloxanes uptake in competitive adsorption” (p. 572). Given that the critical diameter of bulky siloxanes like octamethylcyclotetrasiloxane (D4) is 1.08 nm (Cabrera-Codony *et al* 2018), the pore diameter of these adsorbent materials as displayed on Table 8 shows they are capable of adsorbing siloxanes.

Table 8: N₂ physisorption analysis of Selected Adsorbent Materials

Sample	Specific Surface Area [m²/g]	Pore Volume [cc/g]	Average Pore Diameter [nm]
	S_{BET}	V_{BJH}	D_{BJH}
Clinoptilolite	17	0.020	4.3
Diatomaceous Earth	1.04	0.001	5.2
Crushed Glass	0.08	0.000	3.4
Biochar	467	0.029	3.1
Hydrochar	1.15	0.003	4.3

XRD analysis was conducted on the chosen adsorbent samples to obtain information on its chemical structure. The XRD analysis profiles of the chosen adsorbent materials are displayed in Figure 11 and they all match the structures found in literature.

CO₂ adsorption and water vapor sorption experiments were conducted on chosen adsorbent materials to examine the competition of adsorption sites by these compounds. The results from

these analyses are displayed on Table 9. The results shows that it is necessary to remove carbon dioxide and water vapor from LFG before the siloxane removal step.

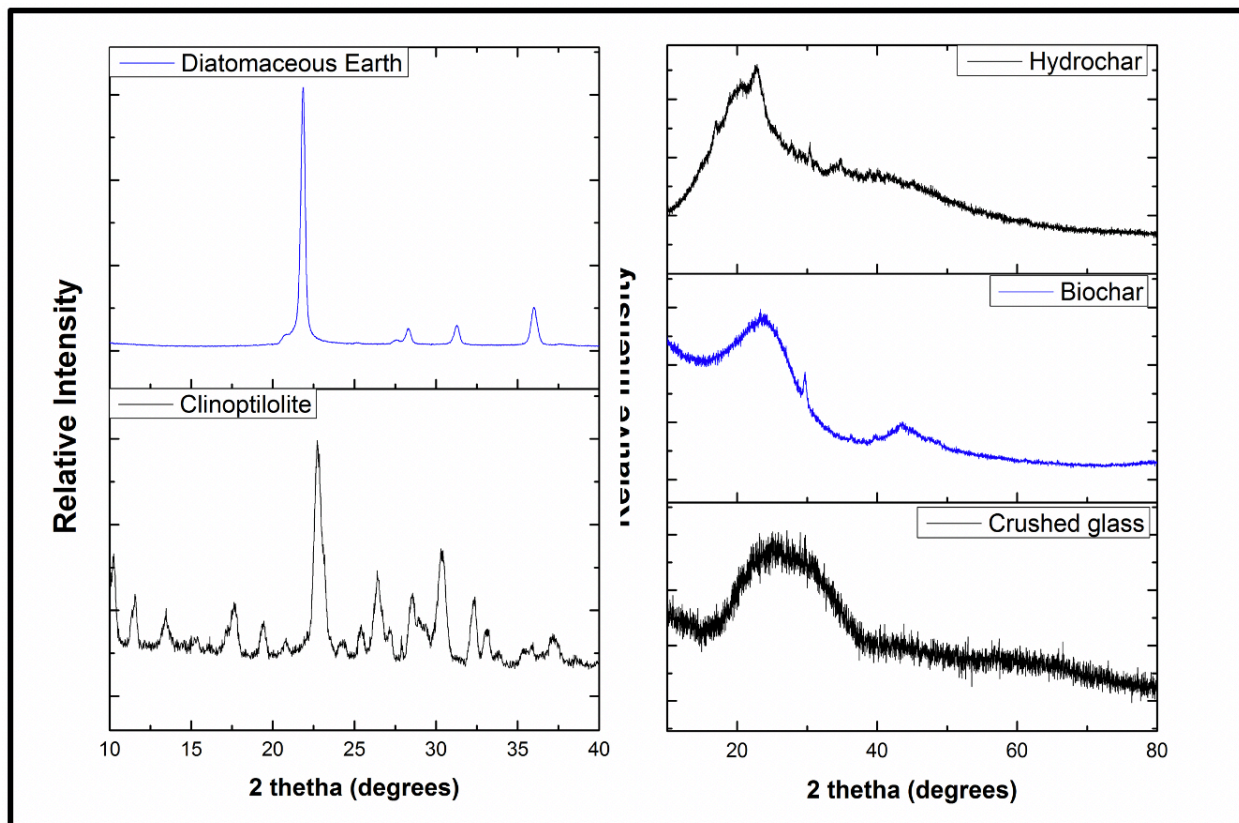


Figure 11: XRD Profile for Diatomaceous Earth, Clinoptilolite, Biochar, Hydrochar and Crushed glass.

Table 9: CO₂ and water vapor adsorption experiments on selected adsorbents.

Adsorbents	CO ₂ Adsorption capacity (mg CO ₂ / g Adsorbent)	H ₂ O Adsorption capacity (mg H ₂ O/ g Adsorbent)
Clinoptilolite	98	111
Diatomaceous Earth (DE)	0.284	0.278
Crushed glass	0.06	0.146
Biochar	22.5	-
Hydrochar	1.01	9.63

5. TECHNO-ECONOMIC ANALYSIS OF SILOXANE REMOVAL UNITS USING ACTIVATED CARBON, CLINOPTILOLITE AND 13X ZEOLITE.

5.1. Design and Modelling Approach of Siloxane Removal Units

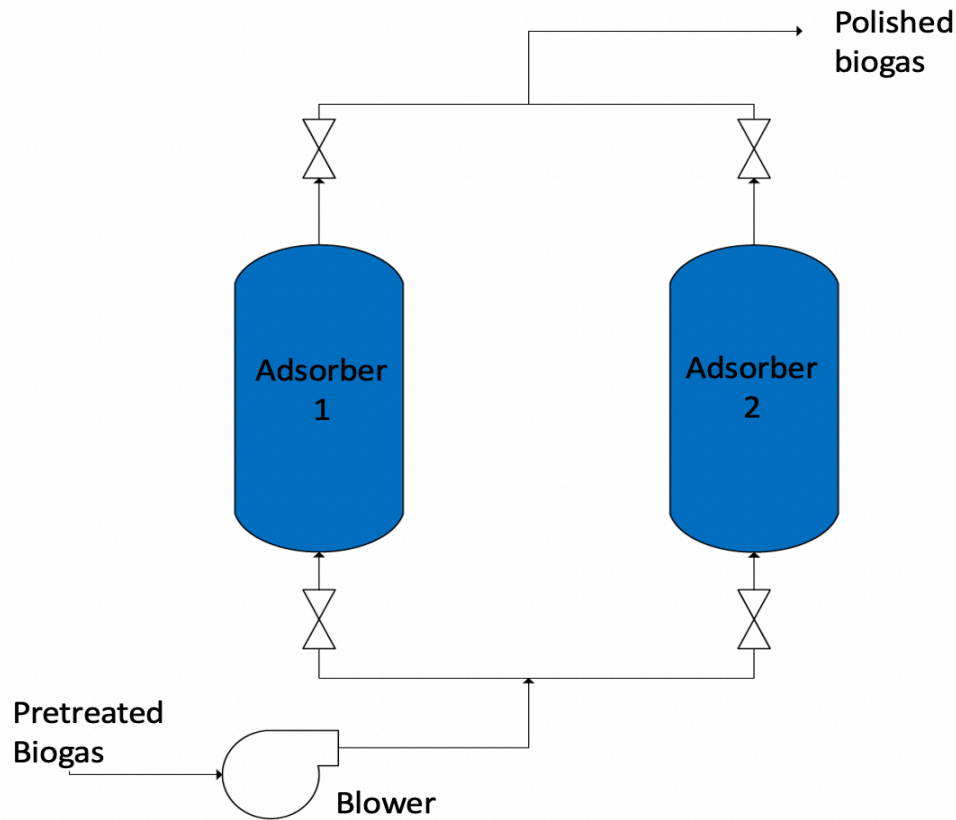


Figure 12: Siloxane Removal Unit.

A techno-economic analysis was conducted for a siloxane removal process utilizing a consumable media as an adsorbent which is replaced once saturated with siloxane. To ensure a continuous process, two adsorption chambers are used in this system as shown on Figure 12. LFG flows through the adsorbing packed bed till it is saturated with siloxane after which the operation of the two packed beds between saturated/fresh media is switched by a valve. Siloxanes removal units using activated carbon, clinoptilolite and 13X zeolite media as adsorbents were compared. TEA was conducted based on the literature values of the adsorption capacity of octamethylcyclotetrasiloxane (D4) on activated carbon, clinoptilolite and zeolite. D4 was chosen as the target siloxane as it is the most occurring siloxane type in biogas (Tran *et al* 2019).

Table 10 shows the equipment required for the siloxane removal units.

Table 10: Equipment Needed for Siloxane Removal Unit.

Equipment	Quantity
Process Vessel	2
Blower	1

5.2. Siloxane removal unit design conditions.

The adsorbent materials used in this analysis include: Activated carbon, clinoptilolite, and 13X zeolite. Activated carbon and 13X zeolites were used in this TEA to compare the cost of clinoptilolite with that of commonly used adsorbents for siloxane removal from LFG. A wide range for adsorption capacity of D4 on activated carbon has been reported in literature from as low as 4 mg D4/ media to as high as 1732 mg D4/ g media (Cabrera-Codony *et al* 2014, Matsui and Imamura 2010, Oshita *et al* 2010, Sigot *et al* 2014, Sigot *et al* 2016). Removing outliers, an average value of the siloxane adsorption capacity of activated carbon between 50 mg/g to 1000 mg/g was used. Table 11 shows the adsorption capacity of the selected adsorbents used in this analysis.

Table 11: Adsorption capacity of selected adsorbents

Adsorbents	Adsorption Capacity (mg D4/g media)	References
Activated Carbon	340	Average
Clinoptilolite	11.2	(Cabrera-Codony <i>et al</i> 2017)
13X Zeolite	276	(Finocchio <i>et al</i> 2009)

The process design conditions used are displayed on Table 12.

Table 12: Process design conditions.

Biogas flowrate (scfm)	500 to 3500
D4 concentration (mg/m³)	50
Molecular weight of D4 (g/mol)	296.4
Adsorption time (hrs)	4200
Activated carbon density (kg/m³)	450 (Target Products 2019)
Clinoptilolite density (kg/m³)	2150 (Mineral News n.d.)
13X zeolite density (kg/m³)	640
Bed void fraction	0.5
Operating pressure (barg)	1
Adsorption temperature (°C)	25

In sizing the process vessel, the following were required:

- M_{D4} = Maximum D4 inlet loading (kg/hr) = (siloxane concentration (mg/m³) * biogas flowrate (m³/hr))/10⁶ (Sorrels *et al* 2018)
- M_m = Mass of media needed (kg) = ($M_{D4}/(w_c/1000)$) * θ_A
- w_c = Adsorption capacity (mg D4/ g media)
- θ_A = Adsorption time (hrs) = 4200 hrs.
- ϵ = bed void fraction = 0.5
- ρ_b = bulk density of media (kg/m³)
- V_m = Volume of media required (m³) = M_m/ρ_b
- V_b = bed volume (m³) = $(1+\epsilon)* V_m$
- H/D = Bed height to diameter ratio = 5

- $D = \text{Process vessel diameter} = ((4 \cdot V_b) / (\pi \cdot 5))^{1/3}$
- $H_b = \text{Height of bed} = D \cdot (H/D)$
- $H_s = \text{Head space for distribution of gas} = 2 \text{ in} = 0.05 \text{ m}$
- $H = \text{Height of process vessel} = H_b + H_s$
- $V_p = \text{Volume of process} = (\pi \cdot D^2 / 4) \cdot H$

In this study, a desired lifetime of the adsorbent beds was assumed to be 6 months. The costing of the overall process includes a gas blower, and two adsorption beds operating for 8400 h per year to provide scheduled downtime. It is assumed that H₂S and moisture has already been removed in previous purification steps.

Table 13 shows the volume of process vessel as the biogas flowrate is varied from 500 to 3500 scfm in siloxane removal units using activated carbon, clinoptilolite and 13X zeolite adsorbent media.

Table 13: Siloxane Removal Unit with Activated Carbon Media

Biogas Flowrate (scfm)	Process Vessel Volume (m³) (Activated carbon)	Process Vessel Volume (m³) (Clinoptilolite)	Process Vessel Volume (m³) (13X zeolite)
500	2.9	17.9	2.5
1000	5.8	36	4.9
1500	8.7	54	7.3
2000	12	71	9.8
2500	14	89	12
3000	17	107	15
3500	20	126	17

5.3. Economic Model

5.3.1. Estimation of Total Capital Investments

The capital investment includes the cost of the process vessels, LFG blower, siloxane monitor and initial media cost.

The Purchased Equipment Cost is estimated using the Eq. 2 below:

$$C_p^\circ = \text{Antilog}_{10}(K_1 + K_2 \log A + K_3 (\log_{10} A)^2) \dots \text{Eq. 2. (Turton et al., 2012)}$$

The Material Factor and Bare module cost is estimated using Eq. 3 & 4 below:

$$C_{BM} = C_p^\circ F_{BM} = C_p^\circ (B_1 + B_2 F_M F_p) \dots \text{Eq. 3.}$$

$$F_{p,vessel} = \text{Pressure factor} = \frac{\frac{(P + 1)D}{2(850 - 0.6(P + 1))} + 0.00315}{0.0063} \dots \text{Eq. 4.}$$

Where D= diameter of the vessel in meters, and P= Operating pressure (barg)

Operating pressure = 1 barg

Table 14 shows the equipment cost data for the process vessel and fan.

Table 14: Equipment Cost Data (Turton *et al* 2012)

Equipment Type	Equipment Description	K1	K2	K3	Capacity A, units	Min	Max
Process Vessel	Vertical	3.4947	0.4485	0.1074	Volume, m ³	0.3	520
Fan	Centrifugal radial	3.5391	- 0.3533	0.4477	Gas flowrate (m ³ /s)	1	100

The cost of fan for biogas flowrate at 1 m³/s was calculated and the equipment cost attribute was used to correct the cost as shown in eq. 5 and Table 15 (Turton et al., 2018) below:

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b} \right)^n \dots \text{Eq. 5.}$$

Table 15: Typical Values of Cost Exponents for a Selection of Process Equipment

Range of Equipment Type	Correlation	Units of capacity	Cost Exp (n)
Centrifugal blower	0.24 to 71	std m ³ /s	0.6

Table 16: Chemical Engineering Plant Cost Index (CEPCI)

Index	2001	2020
CEPCI	394	596.2

The CEPCI for year 2020 as shown on Table 16 above was used to correct the bare modulus cost from 2001 to 2020 using Eq. 6 below:

$$C_2 = C_1 \left(\frac{I_2}{I_1} \right) \dots\dots\dots \text{Eq. 6}$$

Where:

C = Purchased Cost, I = Cost Index. (Turton *et al* 2012)

Table 17: Price of selected adsorbents

<u>Adsorbents</u>	<u>Price (\$/kg)</u>	<u>References</u>
<u>Activated Carbon</u>	<u>1.49</u>	<u>(Alibaba, n.d,-a)</u>
<u>Clinoptilolite</u>	<u>0.12</u>	<u>(Alibaba, n.d,-b)</u>
<u>13X Zeolite</u>	<u>0.4</u>	<u>(Alibaba, n.d,-c)</u>

Table 18: Estimation of Total Capital Investment (TCI)

C_{BM} (2001)	C _{BM} (Process vessels) + C _{BM} (Fan)
C_{BM} (2020)	C _{BM} (2001) *(Index (2020)/Index (2001))
Contingency cost (C_{cont})	15% of C _{BM}

Engineering Fee (C_{fee})	10% of C_{BM}
Total Module Cost C_{TM}	$C_{BM} (2020) + C_{cont} + C_{fee}$
Initial Media cost	Raw material Cost (\$/kg) * Mass of media required (kg)
Siloxane Monitor (Engineering Estimate)	\$50,000
TCI (Total Capital Investment)	$C_{TM} + (\text{Initial Media Cost}) + \text{Siloxane Monitor Cost}$

5.3.2. Estimation of Total Annual Cost

The total annual cost consists of the following components:

- Operating labor cost
- Siloxane removal system media replacement cost.
- Cost of electricity required for blower.
- Capital recovery cost and
- Indirect operating cost.

5.3.2.1. Operating labor cost

A single operator works on the average 49 wks./yr., five 8-hour shifts a week, 245 shifts/operator/year. A chemical plant normally operates 24 hrs/day. The required number of shifts needed in a year is 1095 operating shifts/year (Turton *et al* 2012).

Assuming that half of a single operator's time is needed to effectively run the siloxane removal step. The pay rate was assumed to be \$40 per hour.

$$\text{Annual labor cost (\$/yr)} = 40 (\$/\text{hr}) * 4 (\text{hr}/\text{shift}) * 1095 (\text{operating shifts}/\text{year}) = \$175,200/\text{year}$$

5.3.2.2. Siloxane removal system media replacement cost

This was calculated based on initial media cost, annual operating time (8400 hrs) and adsorption time (4200 hrs).

Siloxane removal system media replacement cost (\$/yr) = Initial media cost (\$) * (8400 hrs/yr)/Adsorption time (hr)

Initial media cost (\$) = cost of raw material (\$/kg) *mass of media required (kg)

5.3.2.3. Cost of electricity required for blower

The power output for the blower based on the biogas flowrate was found using an online calculator (Díez n.d.). The electricity consumed by blower was calculated using the average electricity cost per kWh (13.19 cents/kWh) (Electric Choice 2020). Table 19 shows the cost of electricity consumed by the blower based on biogas flowrate.

Table 19: Electricity Consumed by Blower based on biogas flowrate

Biogas Flowrate (scfm)	Electricity Cost (\$/yr)
500	26000
1000	53000
1500	79000
2000	106000
2500	130000
3000	159000
3500	185000

Table 20: Assumptions used for estimation of indirect operating costs for siloxane removal system (Tansel and Surita 2019) .

Item	Value
Overhead (for labor + maintenance)	60%
Property tax	1% of total capital investment
Insurance	1% of total capital investment
Administration	2% of total capital investment
Interest rate	7%
Annualization years	10

The TCI was annualized over a lifetime period of 10 years with an interest rate of 7%. This annualized value was incorporated into the TAC calculations as the capital recovery cost.

5.3.3. Cost associated with manual removal of decomposed siloxane (Silica) on engine parts for facilities without siloxane removal system.

According to Dewil *et al* (2006) and Griffin (2004); “the biogas of Trecatti (UK), possessed volatile siloxane concentration of up to 400 mg/m³ which led to a major engine failure within 200 hrs. of operation.”

As a result of decomposed siloxanes

- Engines are stripped down, and the deposited silica is manually scraped off the piston, cylinder head and valves.
- Through the combustion process, some silicon compounds are partitioned to the engine oil which needs to be changed more frequently at sites with high siloxane levels in the inlet gas fuel.

Using Trecatti plant in Great Britain as a case study:

Assumptions made:

- Biogas of Trecatti (UK) was supplied at 1000 scfm (1700 m³/hr)
- Biogas of Trecatti (UK) contained 400 mg/m³ of D4 siloxane only.

Based on the above assumption, the maximum D4 inlet loading is calculated to be 0.68 kg/hr.

Trecatti plant is shut down for maintenance after 200 hours.

- Inlet loading of siloxanes for 200 hours = 136 kg siloxanes.
- Based on the above assumptions, it can be concluded that maintenance is needed after accumulation of approximately 136 kg siloxanes.
- Assuming 2 days (48 hours) is required to tear down and rebuild of engines due to silica accumulation

Man-hours required for manual removal of siloxane per year (hr/yr.) = (Maximum D4 inlet loading (kg/yr.)/ 136 kg) * 48 hrs.

Assuming:

labor cost (\$/hr) = 40

Supervisor's cost = 200% of operating labor

Management and overhead cost = 100%

Total Annual Labor cost for manual removal of siloxanes (\$/yr) = Labor cost (\$/hr) * man-hours (hr/yr)

The conversion factors below were used in calculating the amount of revenue lost from electricity generation during downtime related to manual removal of decomposed siloxanes (silica particle):

CONVERSION FACTORS (IRENA 2016)

- 1 m³ of biogas = 0.65 m³ of methane
- 1 m³ of methane = 34 MJ of energy
- 1 m³ of biogas = 22 MJ of energy
- 1 m³/day of biogas = 8,060 MJ/year

MJ/3.6 = kWh (Saqlain 2014)

The cost of average electricity = 6.60 cents per kilowatt hour (kWh) (Electric Choice 2020)

Annual Revenue lost from electricity sales due to downtime (\$/yr) = Annual Electrical energy lost due to downtime (kWh/yr) * average electricity rate per kWh (\$/kWh)

Electrical energy generated from biogas was considered to be 35% of the total energy generated from the biogas.

5.4. Excel Economic Model Outlook

	Values
Biogas flowrate (scfm)	500
Biogas flowrate (m3/hr)	850
MW of D4 (g/mol)	296
D4 concentration (mg/m3)	80
D4 massflowrate (kg/hr)	0.068
Adsorption time (hr)	4200
Mass of D4 (kg)	286
Adsorption capacity of D4 on Activated Carbon @ R.T (mg/g)	340
Mass of Activated Carbon required (kg)	840
Activated carbon density (kg/m3)	440
Volume of Activated Carbon required (m3)	1.91
bed void fraction	0.5
bed volume (m3)	2.86
bed length to diameter ratio	5
bed diameter (m)	0.90
bed height (m)	4.50
Head space (m)	0.05
Process Vessel height (m)	4.55
Process Vessel volume (m3)	2.90
Operating pressure (barg)	1
Adsorption Temperature (degree celsius)	25

DIRECT OPERATING COSTS (DOC):				
Cost Items	Cost Factors	Factor	Removal System Cost (\$)	Default Factor
(1) Operating Labor			201000	
(a) Operator			175000	
hr/shift		4		4
Pay Rate (\$/hr)		\$40		40
Operating Shifts per year (shifts/year)		1095		1095
(b) Supervisor	15% of operating cost	15%	26000	15%
(2) Maintenance (labor and material)	1.5% of TCI	1.5%	1900	1.5%
(3) Siloxane Removal System Media Replacement Cost	Calculated by program		2500	
(4) Blower Electricity Requirement	Calculated by program based on flowrate		185000	24000
TOTAL DOC:	(a)+(b)+(2)+(3)+(4)		391000	
INDIRECT OPERATING COSTS (IOC):				
(1) Overhead	60% of (operator labor (1)+maintenance (2))	60%	122000	60%
(2) Property Taxes	1% of total capital investment	1%	1200	1%
(3) Insurance	1% of total capital investment	1%	1200	1%
(4) Administration	2% of total capital investment	2%	2500	2%
(5) Capital recovery costs (CRC)	CRF x TCI		18000	
Capital recovery factor (CRF)	0.1424			
Interest rate		7%		7%
Annualization years		10		10
TOTAL IOC:	(1)+(2)+(3)+(4)+(5)		145000	
Recovery Credits (RC)	Engineering Estimate	\$0	0	\$0
TOTAL ANNUAL COST (TAC):	DOC+IOC+RC		536000	

5.5. TEA Results and Discussion

5.5.1. Total Capital Investment and Total Annual Cost

The total capital investment (TCI) and the total annual cost (TAC) for siloxane removal units utilizing activated carbon, clinoptilolite and 13X zeolite as adsorbent materials were estimated for biogas flowrates between 500 scfm to 3500 scfm. As displayed on Figures 13 and 14, the cost of siloxane removal units utilizing clinoptilolite as an adsorbent material is more expensive as compared to siloxane removal units that utilizes activated carbon and 13X zeolite as adsorbents. Siloxane removal unit that utilizes 13X zeolite is slightly cheaper than siloxane removal units that utilizes activated carbon, but this is based on the adsorption capacity of activated carbon being 340 mg/g media.

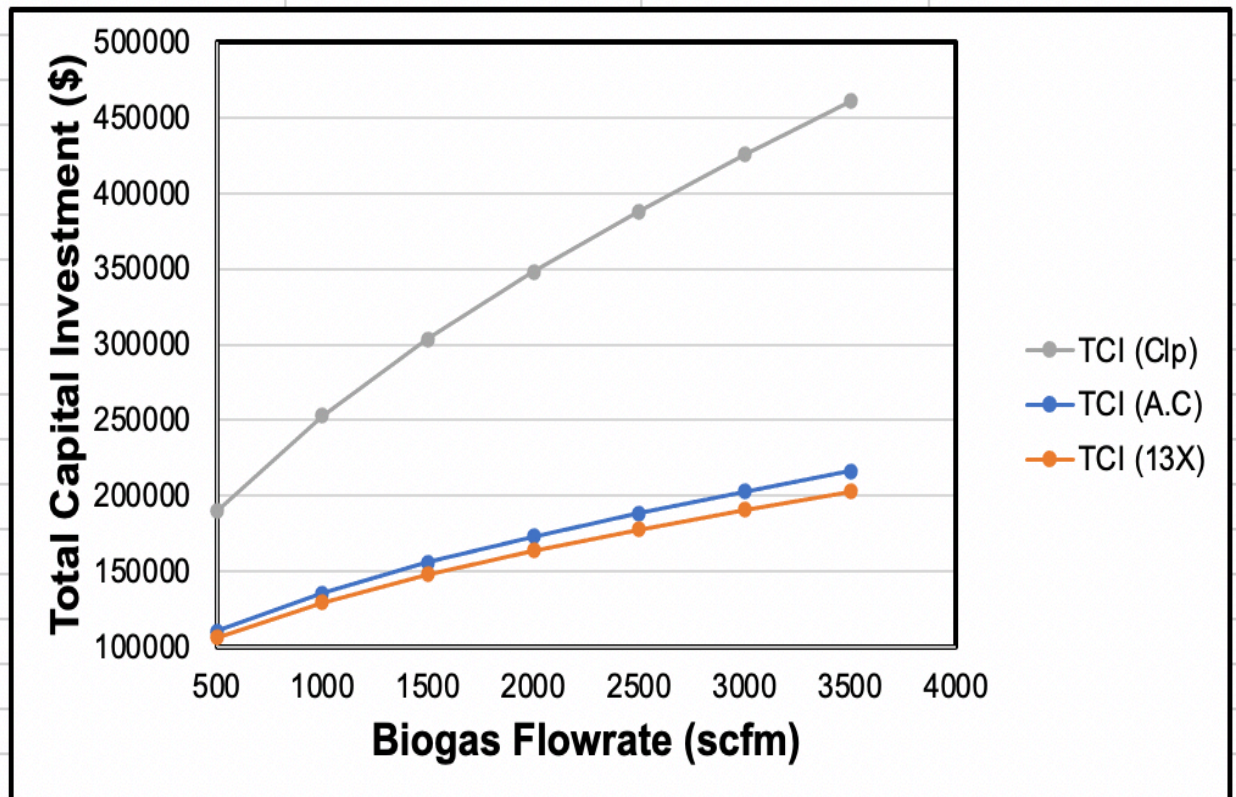


Figure 13: TCI comparisons for siloxane removal units using activated carbon, clinoptilolite and 13X zeolite as adsorbents.

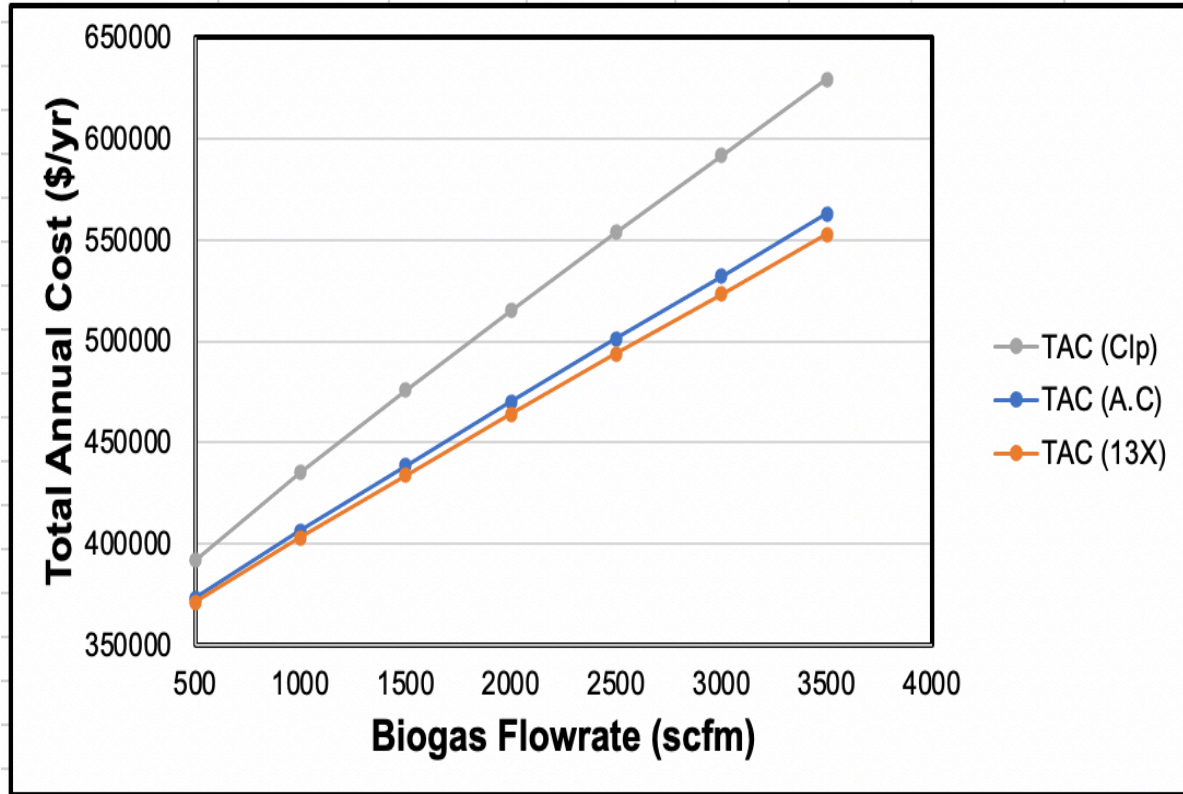


Figure 14: TAC comparisons for siloxane removal units using activated carbon, clinoptilolite and 13X zeolite as adsorbents.

The process vessel cost is the major cost component of the TCI as displayed on Figure 15. Siloxane removal systems utilizing clinoptilolite as an adsorbent media requires much more clinoptilolite media than systems using activated carbon and 13X zeolite media due to the very low adsorption capacity of clinoptilolite for siloxanes as compared to the adsorption capacity of activated carbon and 13X zeolite for siloxanes. A greater mass of adsorbent media needed leads to a greater volume of process vessel required thereby increasing the capital cost. The indirect operating cost which is a function of the TCI as shown on Table 20, and the media replacement cost are the major source of TAC cost difference between the adsorbents studied as displayed on Figure 16.

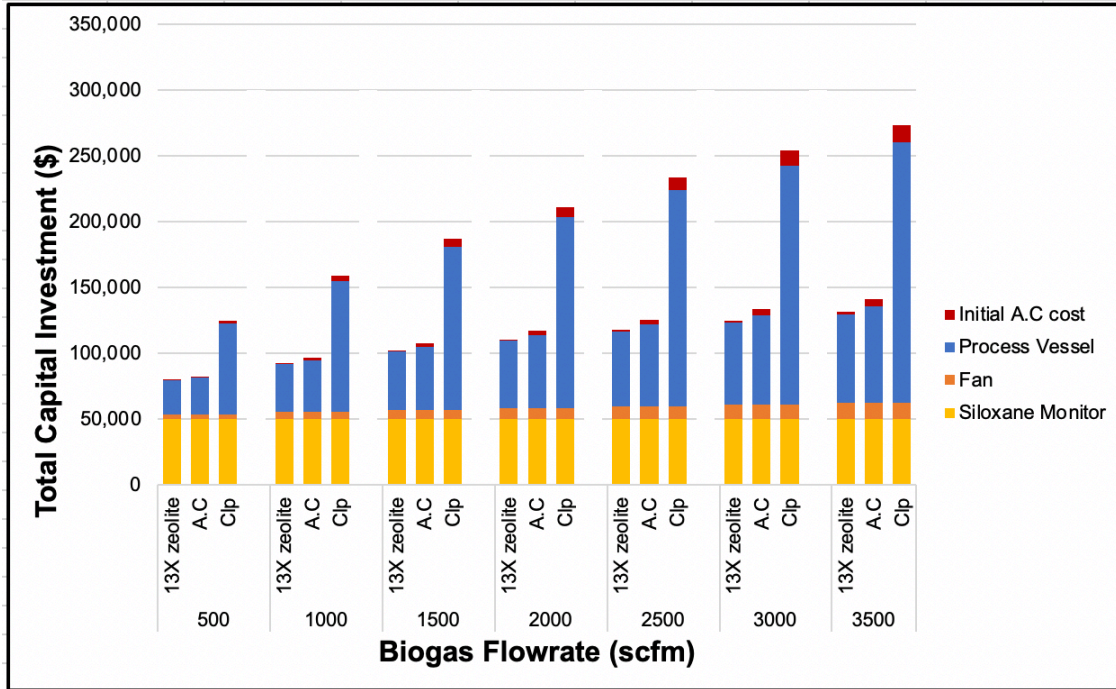


Figure 15: TCI components for siloxane removal units using activated carbon, clinoptilolite and 13X zeolite as adsorbents.

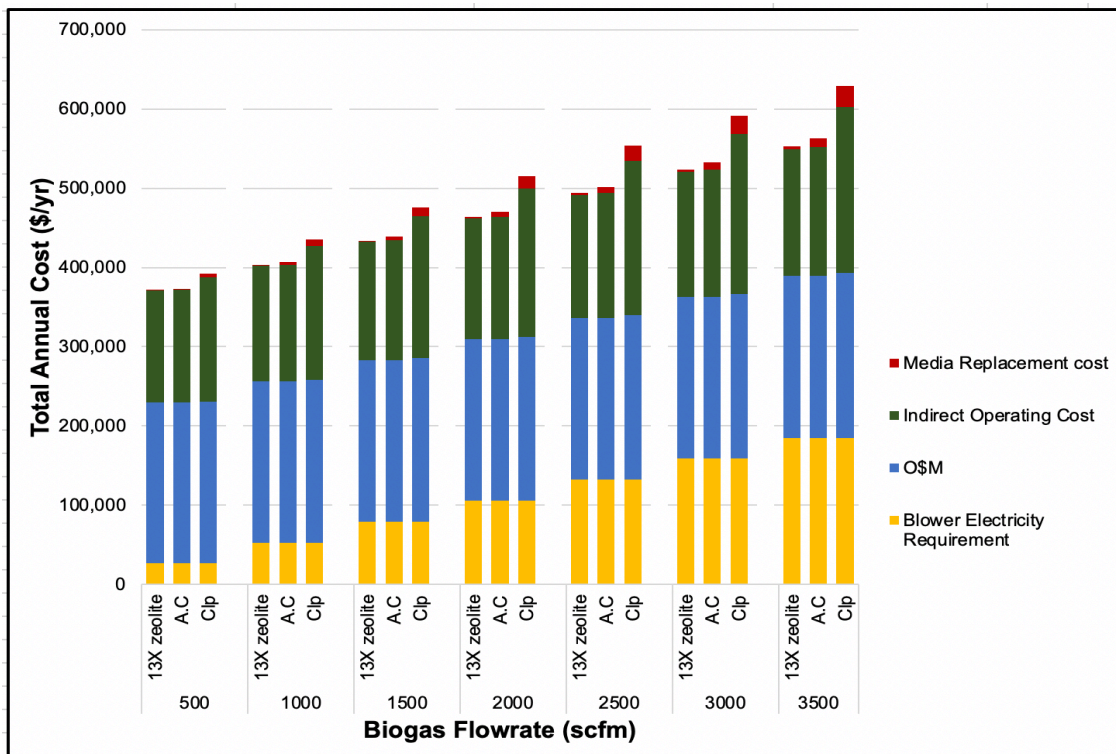


Figure 16: TAC components for siloxane removal units using activated carbon, clinoptilolite and 13X zeolite as adsorbents.

5.5.2. Sensitivity Analysis

Since a wide range of values for siloxane adsorption capacity on activated carbon had been reported in literature, a sensitivity analysis was conducted to study the effect of adsorption capacity of the activated carbon on the total annual cost (TAC). As expected, the TAC reduced as the adsorption capacity increased as shown on Figure 17. It was observed that for activated carbon with adsorption capacity less than 500 mg/g activated carbon, it becomes cheaper to use 13X zeolite as adsorbent for siloxane removal from LFG.

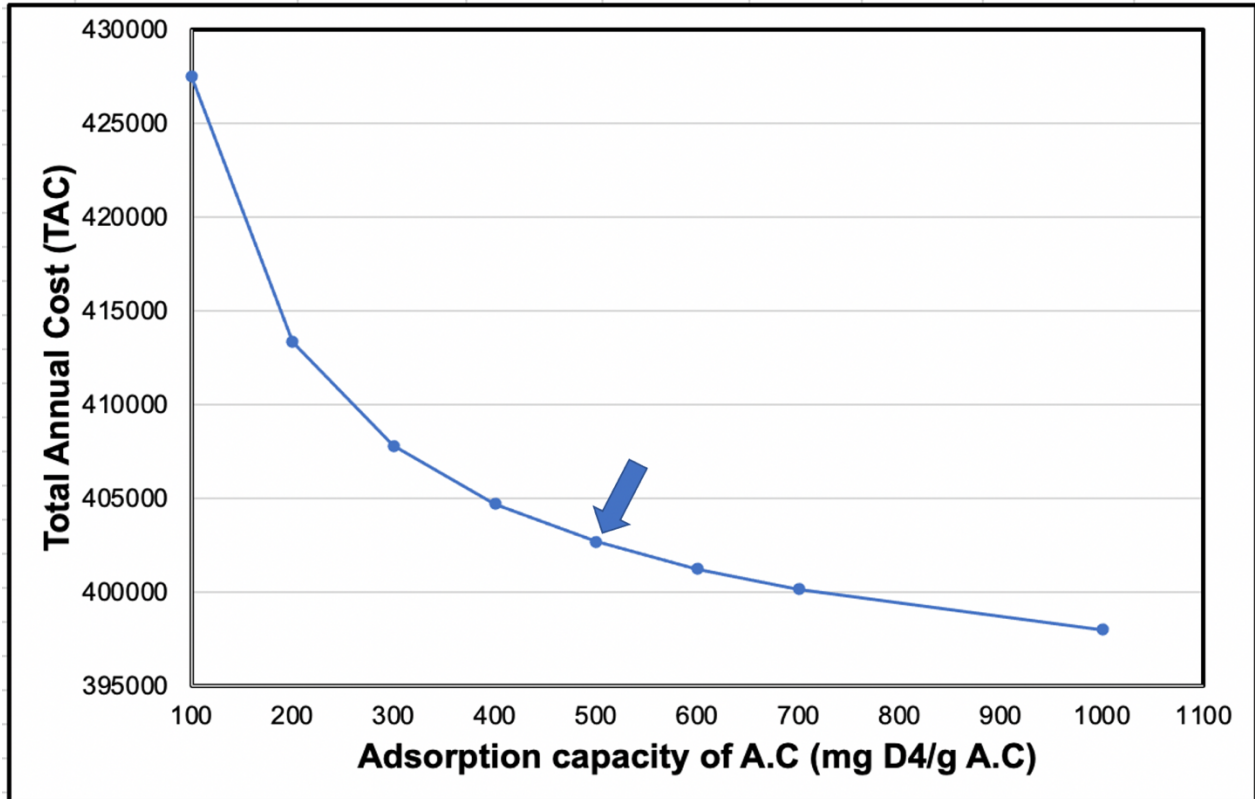


Figure 17: Sensitivity analysis of adsorption capacity on the TAC in siloxane removal units using A.C.

An important question had to be answered: “If a LFG facility with siloxane removal unit designed to use activated carbon adsorbent decides to switch to another adsorbent, how is the TAC affected?”

In such situation, only the media replacement cost will be affected. Using the adsorption capacity for selected adsorbents for this study as stated on Table 11, the media replacement cost was

calculated, and results displayed on Figure 18. It can be seen that 13X zeolite has the lowest media replacement cost.

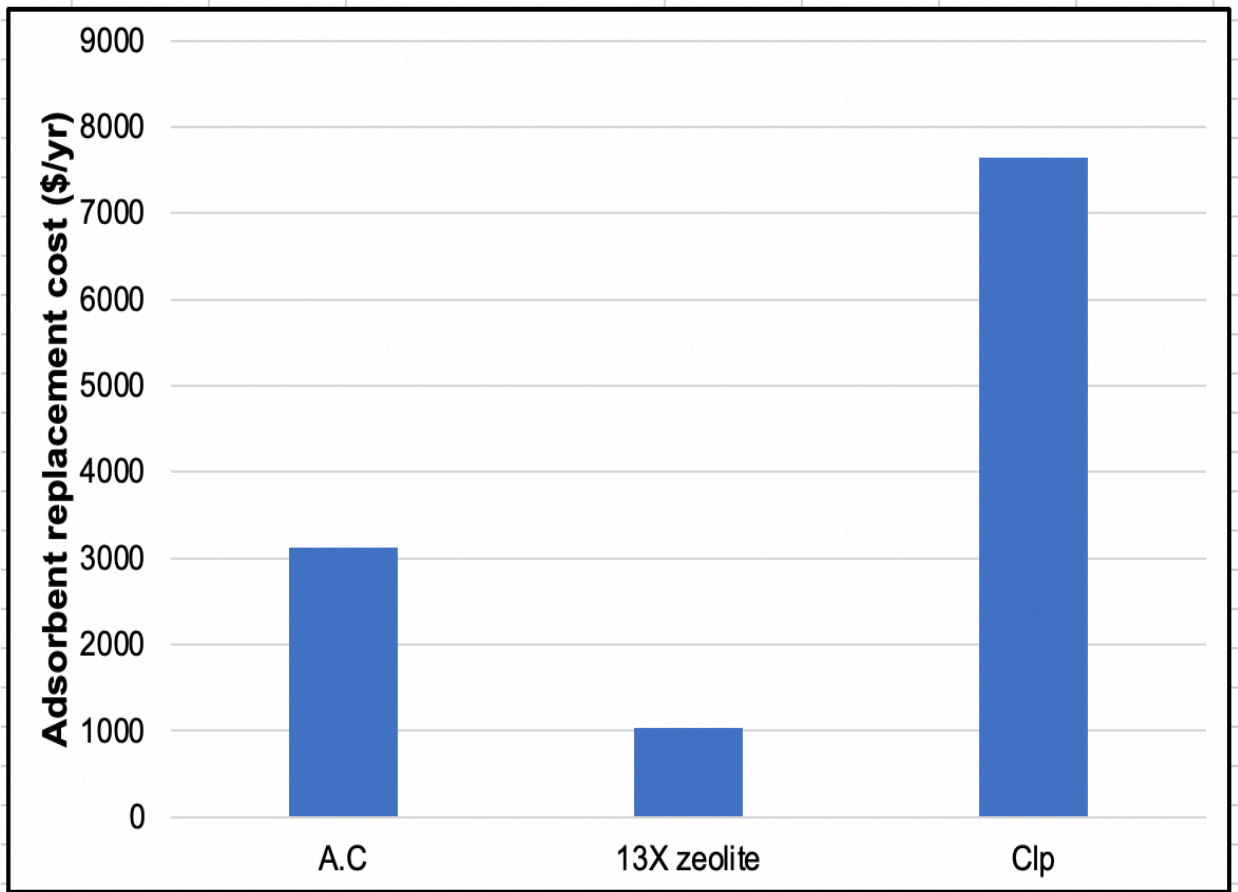


Figure 18: Adsorbent replacement cost for siloxane removal units using A.C, clinoptilolite and 13X zeolite.

5.5.3. Comparison of Siloxane Removal Unit TAC with Maintenance Cost Associated with Manual Removal of Silica Deposits

Figure 19 below shows the comparison of TAC between facilities with siloxane removal systems installed (using activated carbon and clinoptilolite as adsorbent media) and facilities without siloxane removal systems installed. It also shows the effect of siloxane concentration on break-even biogas flowrate. The term “break-even biogas flowrate” refers to the biogas flowrate above which it becomes economically sensible to install a siloxane removal system in a facility. With a siloxane concentration of 15 mg/m³, it can be seen on Figure 19 (a) that it becomes economically

sensible to install a siloxane removal system in facilities having biogas flowrate greater than 1300 scfm. Figure 19 shows that increase in siloxane concentration reduces the break-even biogas flowrate.

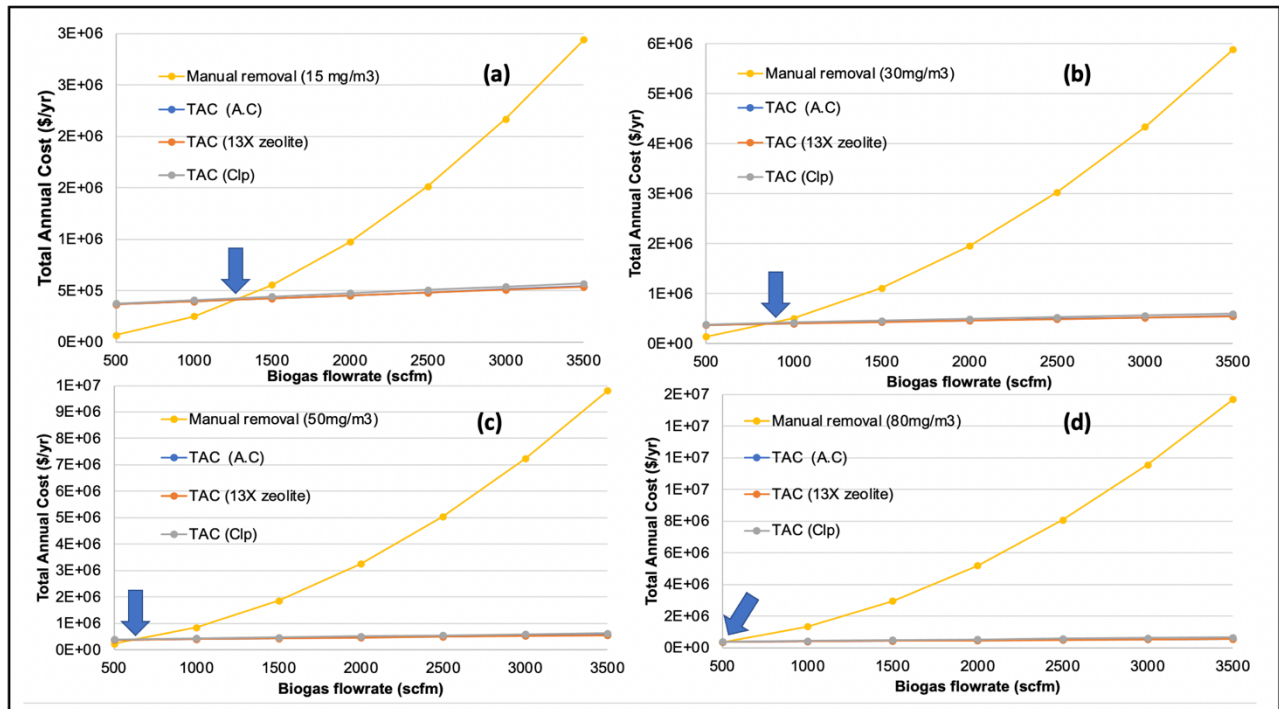


Figure 19: Effect of siloxane concentration on break even biogas flowrate: (a) 15 mg/m³, (b) 30 mg/m³, (c) 50 mg/m³ (d) 80 mg/m³

These cost values are closely related to results previously reported in literature. Tansel and Surita (2019) conducted a study that provided economic comparison between facilities with siloxane removal systems using activated carbon and facilities without siloxane removal system. Tansel and Surita (2019) concluded that “Installation of a carbon adsorption system to remove siloxanes prior to the combustion chamber becomes feasible especially for facilities with biogas flows over 1700 m³/h (1000 scfm). For facilities with biogas flows less than smaller than about 1300 m³/h (750 scfm), the added capital and operational costs of carbon adsorption systems may not be feasible.”

6. Life Cycle Assessment

6.1. Goal: To determine the environmental impact associated with installing siloxane removal units using various adsorbent materials in LFG facilities.

6.2. Scope:

- A full scale LCA comparing siloxane removal system using clinoptilolite, activated carbon and 13X zeolite as consumable media.
- LCA for a facility that produces electricity with no siloxane removal system installed.
- LCA for a facility that does not produce electricity with no siloxane removal system installed.

6.3. Functional Unit:

The amount of electricity generated in a year from biogas delivered at a flowrate of 1000 scfm, with D4 concentration of 50 mg/m³.

6.4. Boundary Conditions

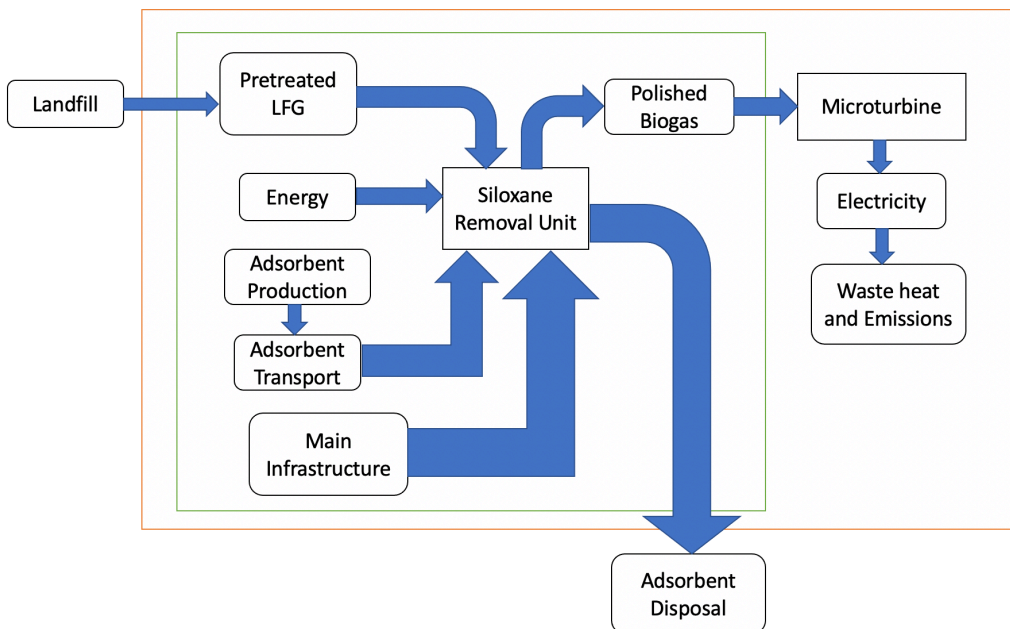


Figure 20: System boundary for facilities with siloxane removal unit installed.

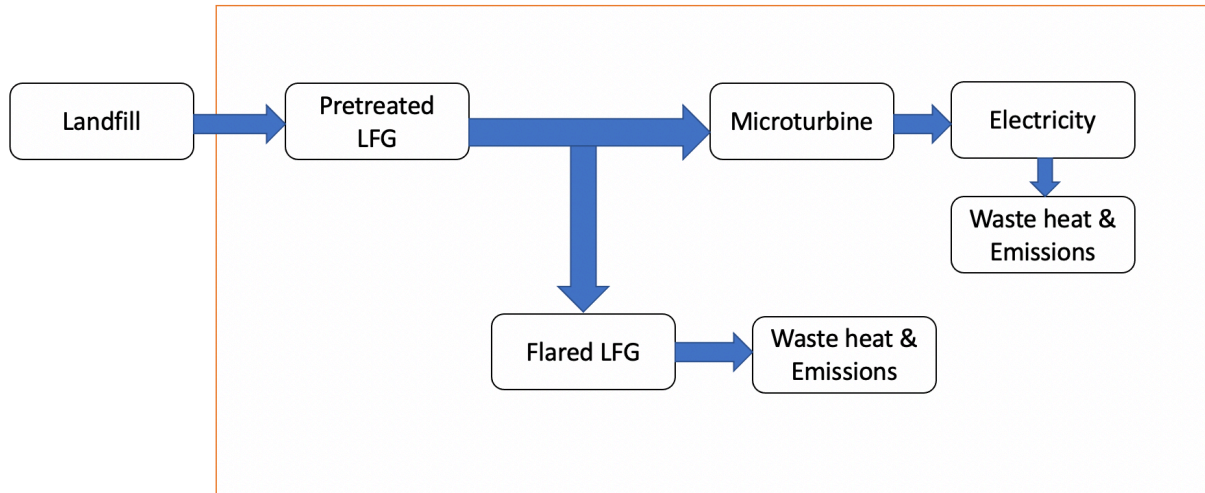


Figure 21: System boundary for facilities without siloxane removal unit (SREU) and with electricity production.

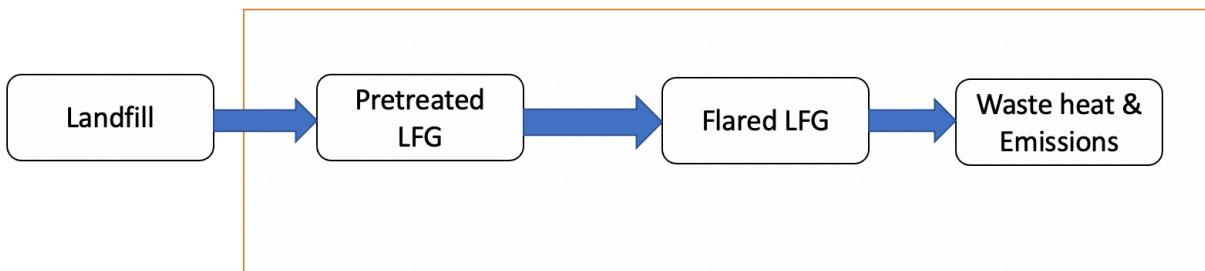


Figure 22: Boundary conditions for facilities without siloxane removal unit (SREU) and without electricity production.

6.5. Inventory Analysis

Values for inventory analysis was gotten based on the functional unit stated for this study. With a biogas flowrate of 1000 scfm and 8400 operational hours, the amount of biogas processed for electricity generation in a year is approximately $1.43E7 \text{ m}^3$ of biogas.

SimaPro 7.3 software was used in this study.

Table 21: Inventory Analysis per 1.43E7 m³ of biogas processed for Electricity generation

	SREU (Clinoptilolite)	SREU (Activated Carbon)	SREU (13X zeolite)
Inputs			
Pretreated Biogas (m³)	1.43E7	1.43E7	1.43E7
Pumps and Compressor (USD)	5.74E3	5.74E3	5.74E3
Tank and Tank components (USD)	9.95E4	4.51E4	3.61E4
Electricity consumed (MJ)	1.64E5	1.64E5	1.64E5
Clinoptilolite (clay) (kg)	6.38E4	-	-
Activated carbon (charcoal) (kg)	-	2.86E3	-
13X zeolite (clay) (kg)	-	-	2.59E3
Lorry Transport; Euro 0, 1, 2, 3, 4 mix; 22 t total weight, 17,3 t max payload RER (kg)	6.38E4	2.86E3	2.59E3
Internal Combustion Engine (USD)	7.46E6	7.46E6	7.46E6
Output			
Polished biogas (m³)	1.43E7	1.43E7	1.43E7

Electricity generated (MJ)	1.10E8	1.43E8	1.43E8
Electricity generated (kWh)	3.06E7	3.06E7	3.06E7

Most values used in inventory were gotten from TEA study.

Assumptions made:

- Blower has a power rating of 7Hp.
- Clay was used in place of clinoptilolite in SimaPro software.

Activated carbon material was created in SimaPro 7.3 using inventory analysis provided by Hjaila *et al* (2013) for production of 1 kg of activated carbon. I used waste wood chips as the starting point. Wood chips with a density of 380 kg/m³ (n.d.) was used as the starting raw material for the activated carbon created.

Electrical energy generated from biogas was considered to be 35% of the total energy generated from the biogas.

“LFG Energy Project Development Handbook” (2020) stated: “Internal combustion engines have generally been used at landfills where gas quantity is capable of producing 800 kW to 3 MW, or where sustainable LFG flow rates to the engines are approximately 300 to 1,100 cfm at 50 percent methane.” Since the base study was set to 1000 scfm of biogas, internal combustion engine was more suitable than microturbines.

The typical capital and annual operating cost per kW for internal combustion engines = \$1800 + \$250 = \$2050/kW (“LFG Energy Project Development Handbook,” 2020). This was used in costing the internal combustion engine (ICE).

Total electricity generated = 3.06E7 kWh (in 8400 hrs)

Generator power rating = (3.06E7)/8400 = 3641 kW

Cost of ICE (\$2050/kW) = \$7.46E6

Table 22: Inventory Analysis for Facilities without Siloxane Removal Units

Base siloxane inlet concentration (mg/m³)	50
Base biogas flowrate (scfm)	1000
Base biogas flowrate (m³/hr)	1700
Downtime due to siloxane buildup in one year (hrs)	252
Volume of biogas to be flared during downtime (m³)	428400
Total annual operating time (hrs)	8400
Total volume of biogas to be processed in a year (m³)	1.43E7
Volume of biogas to be converted into electricity (m³)	1.39E7
Electricity generated (kWh)	2.97E7
Pumps and Compressors (USD)	5735
Internal Combustion Engine (USD)	7.46E6
Electricity consumed by compressor (MJ)	1.64E5

To account for CO₂ emissions from the combustion of LFG in internal combustion engines and flares, the equation below was used to determine the CO₂ emission rate:



16 g of CH₄ + 44g CO₂ of produces 88g of CO₂

CO₂ emission rate per mass of LFG = 88/60 = 1.46 g CO₂/g LFG (Bradbury *et al* 2015)

Density of biogas = 1150 g/m³

CO₂ emission rate per volume of LFG processed = 1.46*1150 = 1679 g CO₂ /m³ LFG

Total volume of LFG processed = 1.43E7 m³ of LFG

Total mass of CO₂ emitted = 2.4E10 g CO₂

The landfill gas energy benefits calculator (EPA n.d.) was used to estimate the direct GHG emissions reductions for LFG.

Avoided emissions reduction was accounted for as credit for generating electricity from LFG as against electricity generation from natural gas power plant.

6.6. Impact Assessment

CML 2 baseline 2000 was adopted for the impact assessment. Ten impact categories were analyzed as shown on Table 23, however, this study was most interested in the global warming potential (GWP 100) which shows the amount of CO₂ emissions into the atmosphere. Figure 23 shows the comparison of the GWP 100 for the five different facilities analyzed in this study.

Table 23: Impact Categories for Landfill Gas Facilities.

Impact category	Unit	Facility with SREU (13X Zeolite) & Electricity Production.	Facility with SREU (Activated Carbon) & Electricity Production.	Facility with SREU (Clinoptilolite) and Electricity Production.	Facility without SREU & with Electricity Production.	Facility without SREU & no Electricity Production.
Abiotic depletion	kg Sb eq	-538.7E+3	-538.1E+3	-538.1E+3	-534.5E+3	7.1E+3
Acidification	kg SO ₂ eq	-727.7E+3	-727.2E+3	-727.3E+3	-723.2E+3	21.8E+3
Eutrophication	kg PO ₄ -- eq	-23.4E+3	-23.4E+3	-23.4E+3	-22.7E+3	5.2E+3
Global warming (GWP100)	kg CO ₂ eq	-54.3E+6	-54.2E+6	-54.2E+6	-52.7E+6	10.5E+6
Ozone layer depletion (ODP)	kg CFC-11 eq	46.7E+0	46.8E+0	47.1E+0	48.0E+0	141.8E-3
Human toxicity	kg 1,4-DB eq	-29.6E+6	-29.6E+6	-29.6E+6	-29.3E+6	523.6E+3

Fresh water aquatic ecotox.	kg 1,4-DB eq	-6.0E+6	-6.1E+6	-6.0E+6	-5.9E+6	936.6E+3
Marine aquatic ecotoxicity	kg 1,4-DB eq	-32.0E+9	-32.0E+9	-32.0E+9	-31.9E+9	614.9E+6
Terrestrial ecotoxicity	kg 1,4-DB eq	2.0E+6	2.0E+6	2.0E+6	2.1E+6	6.4E+3
Photochemical oxidation	kg C2H4	-19.3E+3	-19.3E+3	-19.2E+3	-18.5E+3	2.6E+3

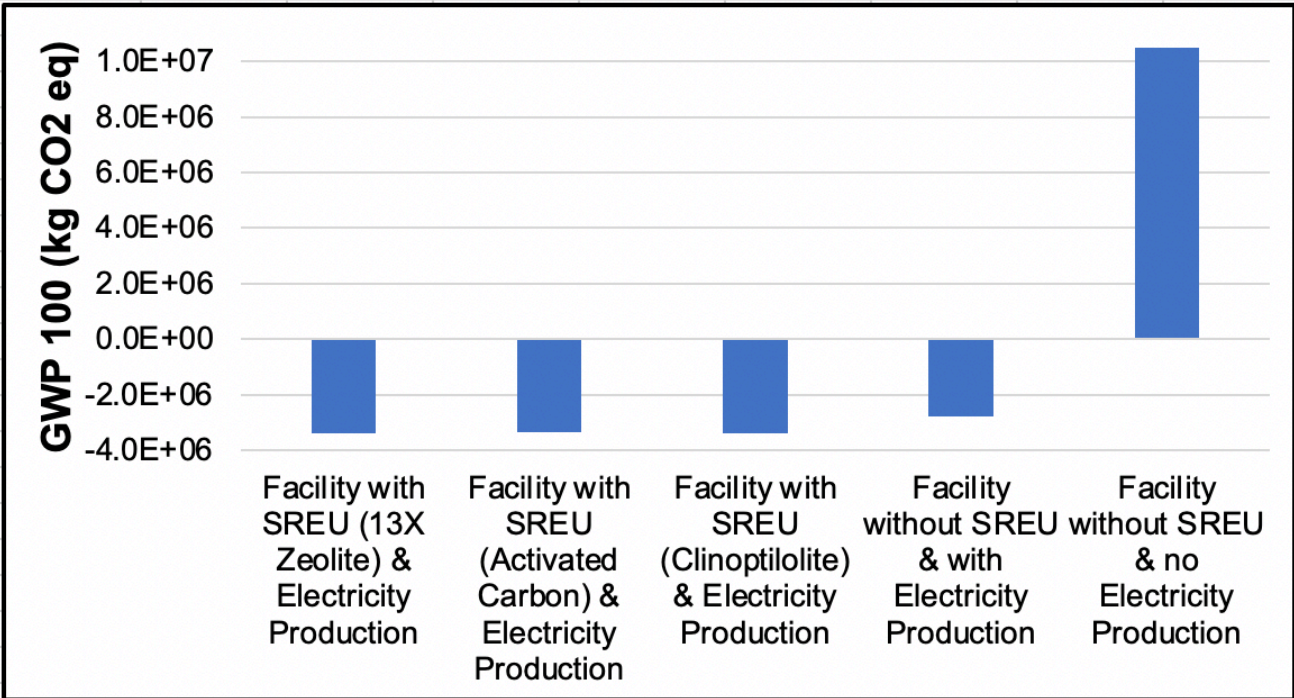


Figure 23: GWP 100 for Landfill Gas Facilities.

As shown on the Figure 23, all facilities with siloxane removal units have approximately equal environmental impact in terms of CO₂ emissions and this can be attributed to the fact that the CO₂ emissions related to the adsorbent media is minimal when compared to the emission from the entire facility. All facilities with electricity production are actually saving CO₂ emissions and this is because avoided emissions reduction was accounted for as credit for generating electricity from LFG as against electricity generated from natural gas power plant. The facility without siloxane removal unit, but with electricity generation saved lesser CO₂ than facility with siloxane removal unit due to flaring of LFG during engine downtime associated with siloxane build up. However, the CO₂ savings is only slightly lesser because the amount of LFG flared is very small compared to the amount that was converted into electricity. The facility that does not produce any electricity emits CO₂ contributing to global warming as it does not replace electricity generated from fossil fuel.

7. CONCLUSIONS AND FUTURE WORK

The environmental impact for all siloxane removal units analyzed are approximately the same, therefore, the cost of systems can be used for making decisions on adoption. Using clinoptilolite as an adsorbent for siloxane removal is too expensive as compared to activated carbon and 13X zeolite. When compared with activated carbon that possesses an adsorption capacity less than 500 mg/m³, 13X zeolite becomes more cost-effective as a siloxane adsorbent.

Some limitations faced during this research project includes scarcity of literature on breakthrough experiments for siloxane removal on clinoptilolite, siloxane adsorption experiments on several adsorbent materials found in literature were conducted at siloxane's concentrations far higher than that found in real LFG. Due to these limitations faced, future research should investigate conducting breakthrough experiments for siloxane removal from LFG using natural zeolites like clinoptilolite and chabasite at siloxane concentrations closer to what is found in real LFG.

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