

Review

Combined Biological Method for Simultaneous Removal of Hydrogen Sulphide and Volatile Methylsiloxanes from Biogas

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Abstract: Hydrogen sulphide (H_2S) and volatile methylsiloxanes (VMSs) are key pollutants from the point of view of the operators of biogas plants. H_2S poses corrosive hazards, while VMSs transform into difficult-to-remove deposits, reducing the availability and yield of biogas combustion equipment. This study provides a critical overview and evaluation (so-called SWOT analysis) of implemented and promising methods to reduce the content of the above pollutants in biogas, with particular emphasis on biological techniques. The aim of the analyses was to develop an innovative concept for a hybrid biological method for the combined removal of H_2S and VMSs using the same device, i.e., a two-phase biotrickling filter (BTF), in which the organic phase that intensifies the mass transfer of VMSs is in the form of a low-viscosity methyl silicone oil. The finally developed technological schematic diagram includes the basic devices and media streams. The concept is characterized by closed media circuits and comprehensively solves the problem of purifying biogas from sewage sludge. In conclusion, key issues requiring further research are identified.

Keywords: biogas treatment; biological desulphurization; biological removal of volatile organic silicon compounds; two-phase biotrickling filter; circular economy



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1. Introduction

In times of global climate change, political and economic crises, the depletion of fossil fuel resources and the search for new ways to ensure energy security, the rapid development of biogas plants is desirable and inevitable. The more so that they fit very well into the circular economy and the global pathway to net-zero CO_2 emissions by 2050 [1]. The controlled production of biogas, in addition to being a source of renewable energy, ensures a reduction in greenhouse gas emissions and the disposal of problematic waste.

Biogas, in the sense of an anaerobic digestion gas, consists mainly of methane (40–75%_v), carbon dioxide (25–50%_v) and water vapour (2–7%_v). In its raw form, apart from these basic components, it also contains substances harmful in terms of biogas energetic use, such as organic and inorganic sulphur compounds (including hydrogen sulphide and mercaptans), volatile organosilicon compounds (including methylsiloxanes), halides and ammonia. They require removal to an extent that depends on the technology and devices that use biogas. The injection of biogas into the natural gas grid and its use for vehicle propulsion, especially fuel cells, requires particularly deep cleaning. Such biomethane, in addition to the elimination of the above-mentioned impurities, should be treated to reach the quality of natural gas (>90%_v CH_4 , free of moisture and CO_2). The quality requirements of biogas/biomethane vary depending on the country or the manufacturer of the equipment for its use [2–4].

Particularly troublesome pollutants in technical terms are hydrogen sulphide (H_2S) and volatile methylsiloxanes (VMSs). H_2S is a decomposition product of sulphur-containing organic substances, mainly proteins. It may also be the result of the biological reduction of sulphates contained in substrates. Its share in biogas, depending on the raw materials used, can reach several percent (e.g., in the case of fermentation of molasses, pig manure and rape).

It can cause the corrosion of biogas plant components and acidification of lubricating oil in biogas-burning engines. After combustion, it pollutes the atmosphere with sulphur oxides, which, in turn, leads to acid precipitation. Even more technically problematic pollutants are VMSs, especially in biogas from landfill and wastewater-treatment plants (WWTPs). They are the substrates (or hydrolytic depolymerization products) of silicones, the production of which has increased rapidly in recent years. Due to their unique properties [5], they are commonly used in cosmetics, paints, adhesives, solvents, lubricants, impregnates, detergents and many other everyday products, ending their life in sewage-treatment plants and landfills, and consequently entering biogas. From a chemical point of view, they are linear or cyclic alternating connections of silicon atoms with oxygen atoms and methyl functional groups (Table 1). Their concentration in biogas may reach several dozen mg/m³ [6–8]. As a result of combustion, they transform into hard-to-remove silica and silicate deposits on the surfaces of boilers, combustion engine chambers, heat exchangers, exhaust gas catalysts, cylinder heads, valves, spark plugs and others [9], reducing the efficiency and availability of the devices, increasing servicing costs and potentially causing increased air pollutant emissions.

Table 1. Main VMSs identified in biogas from sewage sludge and landfills.

Compound	Abbreviation	Chemical Formula	Structure
Octamethylcyclotetrasiloxane	D4	Si ₄ -O ₄ -(CH ₃) ₈	cyclic
Decamethylcyclopentasiloxane	D5	Si ₅ -O ₅ -(CH ₃) ₁₀	
Dodecamethylcyclohexasiloxane	D6	Si ₆ -O ₆ -(CH ₃) ₁₂	
Hexamethyldisiloxane	L2	Si ₂ -O-(CH ₃) ₆	linear
Octamethyltrisiloxane	L3	Si ₃ -O ₂ -(CH ₃) ₈	
Dekamethyltetrasiloxane	L4	Si ₄ -O ₃ -(CH ₃) ₁₀	

Both H₂S and VMSs could be removed from biogas by physical, physicochemical and biological methods. The choice of the process depends mainly on their concentrations and the purpose of the biogas, i.e., the required degree of purification. Biological methods, due to low energy consumption and low demand for chemicals, are considered relatively cheap and environmentally friendly. They have been tested and implemented many times in the case of H₂S, but in the case of VMSs, they face many barriers and are still in the research stage. Very few of these studies have explored the combined, integrated biological removal of both of the above pollutants.

This study examines the available and potential methods for purifying biogas from H₂S and VMSs (with particular emphasis on biological techniques) and aims to propose a hybrid, regenerative and low-waste technology concept using microorganisms for their simultaneous removal, which should contribute to reducing costs in relation to standard sorption methods. The proposed concept of the integrated, biological removal of H₂S and VMSs includes methods for intensifying the mass transfer from the gas phase to the liquid phase and shortening the biodegradation time of VMSs. An innovative method of regenerating the two-phase BTF wetting liquid (with the addition of specific methyl silicone oil), parameters for the selected processes and devices for their implementation have also been proposed. An important advantage of the proposed technology is the closed material cycles, which fits well with the development of the circular economy.

2. Physical and Chemical Methods of Biogas Desulphurization

2.1. Physical Methods

The physical methods are dominated by absorption processes in polar solvents, such as water (especially at WWTPs, where the process water can be used) and some organic solvents. In both cases, the solubility of H₂S may be intensified by increasing the pressure (up to 1 MPa) or reducing the process temperature [10]. The most common organic ab-

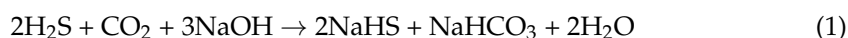
sorbents are “Selexol” (made on the basis of dimethyl ether of polyethylene glycol) and “Genosorb” (with polyglycol dibutyl ether as the main ingredient), to which methanol is sometimes added. They exhibit an affinity for H_2S several times greater than that of water [2], which allows the use of a lower liquid-to-biogas ratio. Methanol itself is also used (“Rectisol”, “IFPEX-2” and “IFPEXOL” processes); however, due to the necessary cooling (down to approx. $-40\text{ }^\circ\text{C}$), the process is more expensive. The advantages of physical absorption processes are the possibility of the effective regeneration of the sorption liquid at elevated temperatures (up to $80\text{ }^\circ\text{C}$), with the possible use of steam or inert gas, and the possibility of the simultaneous removal of CO_2 . Popular physical methods also include adsorption with the use of activated carbon or zeolites (especially hydrophilic ones [11]) based on the mechanisms of the reversible bonding of molecules with physical forces and condensation in micro- and mesopores of a porous solid. Activated carbon (AC) does not work selectively; therefore, in order to avoid the frequent replacement/regeneration of the bed, it is mainly used at a low H_2S concentration. Contrary to the absorption in aqueous solutions, the treated gas should be dried prior to the process. Zeolites have a higher affinity for H_2S (they are alkaline by nature— $\text{pH} \sim 10$). In their case, adsorption is additionally catalysed by the oxides contained in them— Al_2O_3 and Na_2O [12].

Future-proof physical methods for removing H_2S from biogas include gas–gas membrane separation, absorption in ionic liquids, absorption in deep eutectic solvents and adsorption using biochar. The gas–gas membrane separation method employs the selective diffusion permeation of a component or components of the mixture (in this case, H_2S) through a thin-film porous barrier, usually in the form of interconnected hollow plastic fibres (e.g., silicone polymers) due to the difference in concentration and/or pressure on both sides of the membrane. It is an interesting method, especially in the case of a high concentration of H_2S (in the order of several %_v) and in the aspect of the simultaneous enrichment of biogas, i.e., removal of CO_2 . Currently, intensive research is being carried out on new membranes to reduce their cost, increase their efficiency and improve their chemical resistance to biogas components while minimizing CH_4 losses [13]. The potential for the desulphurization of biogas also seems to lie in absorption with the use of ionic liquids (molten salts with a melting point below $100\text{ }^\circ\text{C}$). They are absorbents with high sorption capacity, low volatility and high thermal and chemical resistance [14]. The same applies to deep eutectic solvents. They are mixtures with a significantly lower melting point compared with the ingredients (e.g., choline chloride with urea [15]). Both of the above absorbents are in the preliminary research phase. Prospective methods, especially in the context of biogas enrichment, also include adsorption using biochar (obtained by the pyrolysis of organic matter, preferably from waste, e.g., from sewage sludge [16,17]). Moreover, physical methods of gas purification include cryogenic separation processes; however, due to the energy consumption and relatively low concentrations of H_2S , they are not used for exclusively biogas desulphurization.

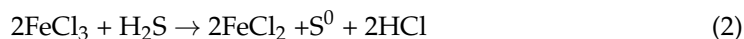
2.2. Absorptive Physicochemical Methods

In chemical absorption processes, in addition to physical dissolution, the removal of H_2S is additionally intensified by a chemical reaction, minimizing the mass transfer resistance in the liquid phase. They include, among others, the absorption of H_2S in solutions containing alkalis (e.g., NaOH and KOH), iron compounds (FeCl_2 , FeCl_3 and $\text{Fe}(\text{OH})_3$), strong oxidants (both liquid (e.g., H_2O_2) and solid (e.g., MgO_2)) and in alkanolamines. An example of chemical absorption is the process known under the trade name Sulfurex[®]CR [18], in which an aqueous solution of NaOH is used as the absorbent. The method is not selective. Apart from H_2S , other acid compounds are removed, including CO_2 (reaction 1), which may result in the high consumption of expensive hydroxide, especially because it is not regenerable (the exception is the CBS method—see Section 3.2.2).

The primary products of the process are sodium bisulphide and sodium bicarbonate, which are environmentally problematic and require oxidation prior to deposition.



In the case of using solutions of iron (III) compounds, including chlorides (e.g., reaction 2), the H_2S binding reaction may be accompanied by its oxidation to elemental sulphur:



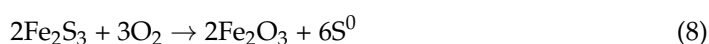
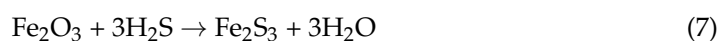
This mechanism is also used in “in situ” pretreatment methods, consisting of the precipitation of water-insoluble sulphur compounds (e.g., FeS) already in the fermentation chamber by dosing iron (II) or (III) salts, usually in the form of chlorides [2,19]. Iron-chelated Fe (III)/EDTA solutions are also used as chemical absorbents of H_2S , with the simultaneous oxidation of H_2S to elemental sulphur and regeneration of the absorbent with oxygen. An example is the Biosulfex process [20] used in some WWTPs in Poland. Proven processes, such as Sulferox [21] and LO-CAT [22], are also available. In the case of alkanolamines, the most popular H_2S absorbents include monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and N-methyldiethanolamine (MDEA). Their advantages are relatively low prices, good thermal regenerability, low affinity for CH_4 and the possibility of simultaneous CO_2 removal. They are especially used for the final treatment of biogas, especially for grid injection.

2.3. Adsorptive Physicochemical Methods

In chemical adsorption processes, in addition to the physical binding of the adsorbate with relatively weak physical forces (e.g., van der Waals surface forces), the removal of H_2S is additionally intensified by a specific (reversible or irreversible) chemical reaction on beds containing substances chemically active towards H_2S . In this case, AC is also used most often, but it is subject to some modifications. They can consist of admixing alkaline additives or zeolites and/or impregnating AC granules with potassium iodide (KI), hydroxides (e.g., NaOH and KOH), Na_2CO_3 , metal oxides (e.g., MgO and ZnO) or potassium permanganate (KMnO_4). An example is the Bicarbox process [23] used in Poland by some WWTPs, in which the AC is impregnated with KI. It is constantly regenerated by dosing a small amount of oxygen (reactions 3–6):

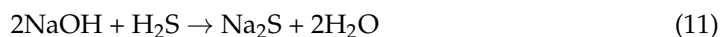
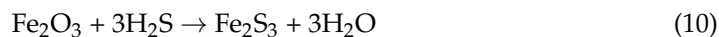
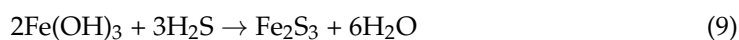


This method is risky due to the heat release and the possibility of self-ignition of the bed. Moreover, the use of AC requires drying the biogas to a relative humidity (RH) of < 50%. It is also possible to use adsorptive, catalytic oxidation of H_2S during the flow of biogas through a bed containing iron (III) compounds, e.g., based on bog ore, or through a bed intentionally prepared from crystalline Fe (III) oxide hydrates ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) deposited onto wood chips [24]. The main product of the process is iron (III) sulphide (reaction 7), which can be regenerated by the action of oxygen, releasing elemental sulphur and heat (reaction 8):



In Poland, at WWTPs, due to its availability and low price, bog ore is often used [25]. It is a shallow mineral consisting mainly of limonite ($\text{Fe}_2\text{O}_3 \cdot \text{nH}_2\text{O}$) formed as a result of biochemical processes and the chemical oxidation of iron compounds found in wetlands

and peat bogs. In neutral and alkaline environments, when the sorbent activator is sodium hydroxide, the H₂S binding reactions are as follows:

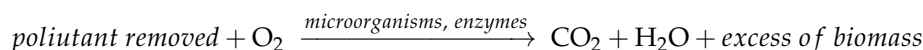


The disadvantage of the method is the necessity to replace the bed after a few/several months and the limited possibilities for process control. The management of the used sorbent is also problematic. Instead of bog ore, a bed of granulated iron (III) oxide can be used, with the possibility of regeneration during the process by the small addition of oxygen/air to the treated biogas.

Adsorption–catalytic processes (e.g., the Selox method [26]), using a selective catalyst for the oxidation of H₂S to elemental sulphur in the presence of water vapour and a small amount of added oxygen, are also known. After filling the pores of the catalyst with the reaction product (S⁰), the process of regeneration takes place by evaporating elemental sulphur at elevated temperatures with the use of an inert gas. Pure sulphur is condensed and discharged from the regeneration system, with the possibility of its further use (e.g., in the chemical industry).

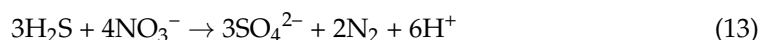
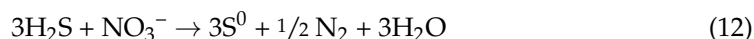
3. Biological Methods of Removing Hydrogen Sulphide from Biogas

In general, the idea of biological gas purification can be defined as a process based on two—simultaneous or separate—mechanisms: physical sorption in water and/or on the active surfaces of moist solids inhabited by microorganisms and biodegradation, usually under aerobic conditions:



The conditions for effective courses of the process are: (i) at least partial solubility of a pollutant in water; (ii) temperature in the range of 5–50 °C (preferably ~30 °C); (iii) pH ~5–9 (although, in the case of some sulphuric bacteria, the process may take place at pH = 2–4); (iv) the availability of macro- and micronutrients in the appropriate proportions and (v) the lack of inhibitors. Therefore, in the case of aerobic biogas desulphurization, the following are necessary: (i) the stoichiometric addition of O₂ as an electron acceptor from H₂S, (ii) the presence of chemoautotrophic sulphuric bacteria that derive energy from the oxidation of H₂S and (iii) the supply of carbon necessary for the growth of microorganisms, preferably from CO₂ contained in biogas. Depending on the excess oxygen, the products of the process may be elemental sulphur (when the O₂/H₂S mole ratio <0.5) or sulphuric acid (VI) (when the oxidation is complete, i.e., when the O₂/H₂S molar ratio is >2). In the former case, the clogging of the installation with precipitating sulphur may occur, and in the latter, a decrease in the pH, corrosion and inhibition of microorganisms may occur. For these reasons, the former seems to be more advantageous.

The biological oxidation of H₂S under anoxic conditions is also possible. Then, nitrates (NO₃[−]) can be used as electron acceptors [27,28], which are reduced to N₂ (reactions 12 and 13), e.g., by bacteria *Thiobacillus denitrificans*:



The advantage of this process, apart from the lack of dilution of biogas with nitrogen and the reduction in the explosion risk, is a lower biomass increase than that in the case of the aerobic process, which minimizes the risk of clogging [29]. Unfortunately, the anoxic process is still in the research stage (e.g., [29–31]).

H₂S and other reduced sulphur compounds can be oxidized by widely distributed autotrophic gram-negative bacteria that use these compounds as electron donors. They can be divided into two groups: photoautotrophs and chemolithoautotrophs. The former, however, does not play a significant role in biogas purification due to the light deficit in this type of installation. Among the chemolithoautotrophs, which can be both aerobic and anaerobic, the former are of greater importance. The conversion of H₂S is their source of energy, while the carbon source is CO₂; therefore, there is no need to dose it from the outside. Strains from the *Thiobacillus* family, especially *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, recently reclassified into *Acidithiobacillus*, preferring neutral or acidic conditions (pH = 2–6) are of particular importance in the oxidation of H₂S. On the other hand, under anoxic conditions, a special role is played by *Thiobacillus denitrificans* (facultative anaerobic), which uses nitrates as electron acceptors.

Promising from the point of view of the combined removal of CO₂ and H₂S are processes using microalgal cultures (e.g., prokaryotic cyanobacteria) that live in symbiosis with sulphur-oxidizing bacteria [19]. The idea of the method is the simultaneous absorption of both pollutants, followed by their treatment in a bioreactor with the availability of light, inhabited by algae and sulphuric bacteria. CO₂ is taken up by algae and the O₂ produced in the photosynthesis process oxidizes H₂S.

The biological processes limiting the content of H₂S in biogas can be carried out “in situ” in a fermentation chamber and “ex situ” by the treatment of biogas outside the fermenter.

3.1. “In Situ” Method

This method consists of precipitating sulphur in the fermenter by supplying a small amount of air (2–6%_v of the volume of biogas [2]) or an appropriate amount of O₂, preferably to its headspace [19,32]. The desulphurization process is carried out by the aforementioned aerobic and chemolithotrophic sulphuric bacteria present in the substrates and in the biofilm covering the walls of the fermenter in the space above the liquid surface (according to reaction 6) [28]. In the scientific literature, this process is most often referred to as “microaeration”, “microoxygenation” or “microaerobic digestion”. The products are elemental sulphur and/or sulphates, depending on the oxygen dose. With the small amounts of air mentioned above, the major product is S⁰. The effectiveness of the process, in addition to the appropriate dose of O₂, is determined by the biogas residence time in the space above the liquid. Sulphur remains in the fermented mass, which can be used as a fertilizer. It is one of the simplest and cheapest methods that can support further stages of biogas purification. However, when air is used as a source of supplemental oxygen, it adversely affects the quality of the biogas due to its dilution with nitrogen and the inhibition of anaerobic microorganisms. Additionally, the resulting sulphur and/or sulphates can block the inside of the reactor, pipes and instrumentation (stirrers, sensors of oxygen and pH, etc.). The method also poses an explosive risk. The relative air/oxygen dose must, therefore, be strictly controlled.

Another future-proof “in situ” method includes the use of biochar in digesters—mainly in the context of biogas enrichment, but also desulphurization [16,33].

3.2. “Ex Situ” Methods

3.2.1. Biofilters

Biofilters (BFs) are boxes or containers filled with an organic, porous bed (e.g., bark, peat, sawdust, coconut fibres and compost with additives for loosening and improving the structure of the bed) that is periodically moistened with the simultaneous dosing of mineral nutrients. The bed should be pre-inoculated with appropriate microorganisms and adapted. As gases flow through the bed, pollutants are absorbed and then assimilated by microorganisms. BFs can be used to remove impurities that are poorly soluble in water (due to the relatively long retention time) and have low concentrations, which allows for a relatively long period of operation without the cumbersome replacement of the

bed. Their most important advantages are: (i) low costs (cheap bed material and low energy consumption), (ii) simple, modular structure and (iii) uncomplicated operation. The disadvantages include: (i) large dimensions, (ii) difficult process control and automation, (iii) potential rotting of the organic bed material and generation of secondary pollutants, (iv) the risk of clogging and acidification of the bed with the products of H_2S oxidation and (v) the difficult to maintain a large area of the bed with uniform composition and humidity. These are devices dedicated mainly to air deodorization in aerobic conditions (e.g., BIOMIXTM technology [20]). Due to the above-mentioned disadvantages, lack of oxygen and relatively high concentrations of H_2S in biogas, BFs do not seem to be suitable devices for biogas desulphurization.

3.2.2. Bioscrubbers

In standard installations with bioscrubbers (BSs), absorption takes place in a packed bed column sprayed with an activated sludge suspension and biodegradation in a separate, aerated reactor where nutrients are introduced and metabolic products with excess biomass are discharged. The advantages of BSs are: (i) high throughput, associated with a relatively high gas velocity (which results in relatively small dimensions of the absorber); (ii) high turbulence in the flow of media, which may result in high mass transfer coefficients and (iii) the possibility of the self-cleaning of the bed. Moreover, in the case of biogas desulphurization, owing to the separation of sorption and biodegradation processes, there is no need to dose air/oxygen to the biogas (eliminating the risk of an explosion or reducing the calorific value of biogas). However, the high investment and operating costs of these complex installations, as well as the relatively short phase contact time, make their use for biogas desulphurization questionable. Furthermore, feeding the absorber with active sludge suspension is often associated with the clogging of the packed column and blocking of grates, nozzles and drip separators. These problems can be avoided by using chemical absorption involving an aqueous solution of an alkaline liquid (reaction 1) and a separate bioreactor, i.e., a combined chemical scrubber with a bioreactor (CBS). This solution additionally minimizes the mass transfer resistance in the liquid phase, which allows the use of a smaller absorber. Examples of the implementation of this type of method include the processes known under the trade names: Thiopaq[®] [34], Sulfurex[®]BR [35] and Sulfothane [36]. These methods use an aqueous NaOH solution as an H_2S absorbent in combination with its biological regeneration in a separate, oxygenated bioreactor, where the NaHS formed in the scrubber, is microbiologically converted into elemental sulphur. However, also in their case, the absorber may be clogged by the precipitating sodium carbonates in the reaction of the hydroxide with CO_2 . In this context, a similar, two-stage process (Bio-SR, [28]) using a solution of iron sulphate ($Fe_2(SO_4)_3$) as both the H_2S absorbent and oxidant under acidic conditions ($pH < 2$) seems to be more advantageous.

3.2.3. Biotrickling Filters

Biotrickling filters (BTFs), unlike BFs, are continuously sprinkled columns filled with non-biodegradable material (mineral or plastic), on which, after inoculation—usually with active sludge—and after an appropriate adaptation period, an active biological film is formed. The spraying medium is water, possibly with the addition of a mineral nutrient solution. The liquid circulates in a closed system until the pH drops below the assumed limit level, after which it is replaced or regenerated. The absorption and microbial decomposition of the removed pollutants, unlike BSs, take place in one apparatus. Standard BTFs for biogas desulphurization usually work in an aerobic system, i.e., with the addition of a small amount of O_2 (close to stoichiometric) or, more often, an appropriate amount of air. In order to avoid biogas dilution and creating an explosion risk, it is also possible to oxygenate the circulating liquid [28]. The process can also be operated under anoxic conditions with the use of nitrates, as mentioned earlier. In the case of the aerobic process, it is advantageous for efficient H_2S oxidation to provide a neutral or slightly acidic environment favoured by some of the aforementioned autotrophic sulphuric bacteria. The products are elemental

sulphur (S^0) (reaction 6) or sulphuric acid (VI) (reaction 14) and sulphates (e.g., calcium sulphates—by the reaction of SO_4^{2-} ions with Ca^{2+} ions present in water), depending on the molar ratio of O_2/H_2S :



Increasing biomass is also an undesirable product. As a consequence, the clogging of the column may occur. An effective counteraction in this case may be the use of an automatic washing system based on the control of the gas pressure drop. Compared with BFs, BTFs are characterized by more stable operation, better possibilities of process automation, higher durability and strength of the bed (which allows the possibility of extending the contact time by building tall towers) and lower terrain demand. Technologies using BFs are undoubtedly cheaper and easier to use than those using BSs, in which the sorption and biodegradation processes are separated and the entire installation is more complicated and less available. They are particularly suitable for applications in WWTPs, where the process water can be used as a spraying liquid, then recycled in the wastewater treatment process. Examples of commercial technologies using BTF for biogas desulphurization include Biogasclean[®]QSR [37] and Sulfurex[®]BF [38]. In Poland, the CES system [39] is very popular.

A comparative summary of the potential methods and devices that can be used for biological biogas desulphurization is presented in Table 2.

Table 2. Comparison of the potential biological methods and devices for biogas desulphurization.

Method/Device	Advantages	Disadvantages
“In situ” microaeration	1. Low capital and operational costs (use of a fermenter space instead of building an end-of-pipe installation). 2. Simple construction and uncomplicated operation. 3. Possibility of low-cost support of subsequent stages of biogas purification at high concentrations of H_2S. 4. Intensification of the hydrolysis process in the fermenter. 5. Enrichment of the digestate with precipitating sulphur, increasing its usefulness as a fertilizer.	1. Reducing the calorific value of biogas by diluting it with N_2, when air is used as an O_2 carrier. 2. Necessity of precise air/oxygen dose control in order to avoid the explosion hazard. 3. Toxic effect of O_2 on anaerobic microorganisms and potential decrease in the efficiency of the fermentation process. 4. Risk of clogging of the fermenter space with precipitating sulphur.
Traditional biofilter with an organic bed (BF)	1. Simple, modular design. 2. Low energy consumption due to the low gas flow velocity. 3. Simple operation (except for the cumbersome replacement of the bed). 4. Cheap and available materials for the bed. 5. Suitable for impurities with limited water solubility (long contact time).	1. Large dimensions. 2. Limited possibilities of process automation. 3. Unstable operation (difficulty in ensuring uniform physicochemical conditions across the entire cross-section of the apparatus). 4. Risk of rot of the organic matter and generation of secondary pollutants. 5. Risk of deactivation of the bed due to acidification with process products.
Traditional bioscrubber sprayed with activated sludge (BS)	1. Moderate investment costs of the absorber (relatively small dimensions due to the high gas flow velocity, especially in the case of a column with a fluidized bed). 2. Easier automation compared with other biological methods, especially BFs. 3. Turbulence of media flow affecting the intensification of the mass exchange process. 4. No air/oxygen dosing to the biogas, no sulphur precipitation in the scrubber. 5. Absorption can be intensified by using an alkaline absorbent (see below—CBS).	1. Capital and operating costs of the entire installation are the highest among the methods compared (separate sorption and biodegradation devices, additional devices for sludge management and high energy consumption by fans and pumps). 2. Risk of clogging of the absorber, demister, nozzles, sprinklers and grates by growing biomass. 3. Short retention time in the absorber—not suitable for impurities with poor solubility in water.

Table 2. Cont.

Method/Device	Advantages	Disadvantages
Combined chemical scrubber with bioreactor (CBS)	1. The use of an alkaline aqueous solution as an absorbent allows the minimization of the mass transfer resistance in the liquid phase, which contributes to the reduction in the absorber size. 2. The elimination of a suspension improves the availability of the absorption system. 3. It is possible to regenerate the absorbent. 4. The technology has been implemented under industrial conditions.	1. Relatively high cost (reasons as above plus an extra cost of alkali—usually NaOH). 2. Two-step process, unlike BTF. 3. Possibility of carbonate precipitation in the absorber.
Biotrickling filter (BTF)	1. The sorption and biodegradation processes take place in one apparatus. 2. The higher retention time than that in BS allows the possibility of obtaining high mass transfer coefficients. 3. Compared with BF, the packed mineral bed is more durable, mechanically stronger (high towers can be built) and is easily cleaned of growing biomass. 4. Easy process automation. 5. The process is proven and commercially available. 6. BTFs are especially useful in biogas plants at WWTPs (free spray liquid, combined wastewater and biogas treatment can be considered). 7. The method is cheaper in terms of investment and operation than BS and CBS.	1. The dilution of biogas with nitrogen when using air for H₂S bio-oxidation. 2. The need for precise control of the O₂ concentration in biogas due to the lower explosion limit of the CH₄/O₂ mixture. 3. The potential risk of BTF clogging by precipitating sulphur (sludge flushing system required).

The above analysis clearly shows the advantages of BTFs over BFs and BSs, especially in the case of low concentrations of H₂S. In the case of high concentrations, they may additionally cooperate with the biological “in situ” methods, described in Section 3.1.

In general, biological methods of biogas desulphurization, compared with physicochemical methods, are characterized by relatively low operating costs and less environmentally harmful waste products, with a similar H₂S removal efficiency ($RE = (C_{in} - C_{out})/C_{in}$, where C_{in} is the inlet concentration and C_{out} is the outlet concentration)). CBS and BTF technologies are proven and available on an industrial scale, but the latter, mainly for economic reasons, seem to be more attractive.

4. Physical and Chemical Methods of Removing Volatile Methyl Siloxanes from Biogas

Due to the previously mentioned technological limitations related to the energy use of biogas containing VMSs, their content should be limited in accordance with the technical requirements of the devices’ manufacturers. This particularly applies to the use of biogas in fuel cells, microturbines and Stirling engines, as well as plants with a selective catalytic reduction afterburner. In other cases, e.g., gas piston engines, economic analysis should decide on whether it is more profitable to pay for more frequent engine maintenance (including oil change) or for biogas treatment. Upgrading biogas to biomethane before it is fed into the natural gas grid or applied to vehicle engines also requires a reduction in the VMSs content, in line with the applicable national standards.

Among the methods of biogas purification from VMSs, physical processes dominate, which is a consequence of the low chemical reactivity of these compounds. Nevertheless, there are known “in situ” attempts to chemically oxidize VMSs, usually carried out at the WWTP biological stage, i.e., in the aeration chamber or directly in front of the fermentation chamber. An example may be the use of peroxydisulphate or dimethyldioxirane, as a result of which complex VMS molecules decompose into simpler compounds that are more susceptible to hydrolytic degradation, and the precipitated solid products, in the form of silicates and/or silica, are easy to separate [6]. There are also known attempts to remove VMSs from the wastewater of cosmetics production using electrochemical oxidation with hydroxyl radicals [40]. Liquid-phase oxidation also has the advantage of breaking down the extracellular polymeric substances (EPSs) that make up the biofilm on the wetted surfaces of the tanks at WWTPs, releasing the VMSs adsorbed on them.

Among the “ex situ” methods, there are known attempts to use strong acids as VMS absorbents (concentrated H_2SO_4 and HNO_3 at a temperature above $60\text{ }^\circ\text{C}$) to break Si–O bonds and form nonvolatile PDMS polymers [41]. However, their practical usefulness is controversial as they are corrosive and pose environmental hazards. Attempts to use strong bases (NaOH) to absorb VMSs by the same authors have also been abandoned because of carbonates precipitating in the reaction with CO_2 clogging the installation. The other known methods of reducing the VMSs content in biogas are based on physical processes. In the case of “in situ” methods, they rely on the desorption of VMSs from the sewage or sludge subjected to fermentation by their more intensive aeration in the biological stage of WWTPs or their thermal treatment prior to the fermentation process. The thermal disintegration of sludge can additionally increase the efficiency of biogas production by shortening the hydrolysis step and stripping off some inhibitors (e.g., NH_3). This method may be particularly advantageous when the fermentation process is carried out under thermophilic conditions. The thermal disintegration of microorganism cells also facilitates sludge dewatering. In contrast to H_2S , the biodegradation of VMSs, in the processes of both wastewater treatment and sludge digestion, practically does not take place.

Three standard technologies are commercially available for the purification of biogas from VMSs—adsorption (using AC), absorption (using organic absorbents, most often based on glycols) and condensation/freezing. The most common is adsorption on AC, removing VMSs simultaneously with H_2S and other undesirable components (e.g., halides). It is a non-selective method, and the large number and variety of adsorbed impurities result in high consumption of the adsorbent. Furthermore, its effective regeneration, due to the polymerization of VMSs in AC pores, is problematic. Another disadvantage of AC is competing adsorption, i.e., the ability to displace the previously adsorbed VMSs by high-molecular-weight aromatic VOCs and water vapour, and, especially, lighter linear VMSs by heavier cyclic ones. For this reason, biogas needs to be dried below 50% RH. The use of silica gel also does not seem to be rational in the case of biogas purification due to its high affinity for water vapour and the resulting need for deep drying (<10% RH). More advantageous in this regard is the use of hydrophobic zeolites. They can act selectively, both in relation to H_2S and VMSs, and are more susceptible to regeneration than AC. It is also possible to use adsorbents based on alumina, polymer resins [42] and, according to recent reports, raw and expanded perlite [43] and biochar [44]. However, their full industrial use requires further research.

The simplest and cheapest method of physical absorption is absorption in water. It can be used for the pretreatment of biogas (for dust and foam removal, cooling and pre-absorption of H_2S , NH_3 and water-soluble volatile organosilicon compounds, including TMS-OH (trimethylsilanol), TMS (tetramethylsilane) and, partially, L2). More thorough purification of biogas with this method is possible at increased pressures (2–2.5 MPa) [45]. In industrial practice, organic liquids are used for the absorption of VMSs, and the most commonly used absorbent is Selexol, produced on the basis of polyethylene glycol dimethyl ether. However, like AC, it is not selective. It absorbs, among others, CO_2 , H_2S , VOCs and VMSs; therefore, it can be used in processes upgrading biogas to biomethane. Its advantages include: (i) low vapour pressure (no risk of vapour emission), (ii) low viscosity (positively influencing the intensity of mass transfer), (iii) low affinity for CH_4 , (iv) chemical stability, (v) non-toxicity and (vi) easy regeneration. On the other hand, it is relatively expensive and poses a risk of the desorption of the absorbed VMSs as a result of increasing the biogas temperature and flow rate. Attempts have also been made to use methanol (Kryosol process [46]) and oils, e.g., silicone oil [47]. The latter, due to its high thermo-oxidative resistance, low surface tension, low vapour pressure and physiological indifference, seems to be more promising. Furthermore, methanol requires cooling and poses a fire hazard.

Condensation methods for biogas purification are commonly used for drying it before adsorption on AC and silica gel. Additionally, as a result of cooling the biogas to $\sim 5\text{ }^\circ\text{C}$ under atmospheric pressure, part of the H_2S and VMSs is removed along with the condensate. On the other hand, freezing, i.e., cooling below $0\text{ }^\circ\text{C}$, may be more efficient,

but it is too energy-consuming and requires periodic defrosting. This method can only be considered for high concentrations of VMSs, in the order of several hundred mg/m³, or for the simultaneous removal of CO₂ by this method.

Membrane techniques and biological methods for removing VMSs from biogas are in the preliminary research stage. The use of the former has already been implemented in biogas-enrichment installations, i.e., the separation of CO₂ and H₂O from CH₄. However, their suitability for removing VMSs seems to be questionable due to the large differences in the molecular sizes of the individual VMSs and their high adsorption potential (risk of membrane blockage). Biological methods, which are the main focus of this study, are still in the stage of laboratory research, mainly with the use of artificial biogas.

5. Possibilities of Biological Purification of Biogas from Volatile Methylsiloxanes

The idea of the microbiological removal of VMSs from biogas, i.e., their use by microorganisms as a source of carbon and/or energy, due to their potentially low cost, environmental friendliness and the possibility of integrating the removal of VMSs and H₂S in the same route, has been the subject of many studies published in the last twelve years. They focused mainly on the intensification of the mass transfer of VMSs from gas to the liquid phase and biodegradation processes, which significantly limit their removal in this way. In the 1970s, these unnatural compounds were considered as non-biodegradable. So far, no biological mechanisms leading to the formation of bonds between silicon atoms and methyl or other organic groups have been identified. On the other hand, biochemical processes have been identified, the result of which is the breakage of such bonds [48]. The poor susceptibility to anaerobic biodegradation of D4 and D5 and its lack in the case of D3 and D6 were reported by Xu et al. [49]. In turn, Accettola et al. [50] showed that the decomposition of VMSs under aerobic conditions by the bacteria *Pseudomonas aeruginosa* was possible, but its intensity, tested under various gas flows, was small (RE ≤ 20%). This was also confirmed by Li et al. [51]. Wang et al. [52] investigated the aerobic degradation of D4 using the isolated bacterial strain *Phyllobacterium myrsinacearum* from silicone factory wastewater (which was inoculated on the BTF filling) and artificial biogas, with air as a D4 carrier. The authors reported a higher biodegradation efficiency of D4 using the above-mentioned strain compared with bacterial strains derived from municipal WWTPs. However, a very long empty bed resident time (EBRT) of 24 min was required to reach 60% RE of D4. On the other hand, the possibilities of D4 biodegradation in anaerobic, laboratory BTF, using the bacteria *Methylibium* sp. were reported by Boada et al. [53,54]. The authors proposed a hybrid biogas purification technology [54] based on the combination of adsorption on AC with biodegradation on a biofilm formed on its surface in anoxic BTF. In addition to VMSs, VOCs in the form of toluene, limonene and hexane (compounds often detected in biogas from landfills) were additionally dosed to the artificial biogas. Such a system, when compared with BTF with a lava rock filling (inert mineral packing material shredded to a size of ~10 mm), turned out to be more effective in the biodegradation of VMSs. An interesting study on H₂S and D5 removal in an acidic, aerobic BTF was conducted by Zhang et al. [55,56]. They confirmed earlier reports that acidic conditions increase the intensity of VMSs hydrolysis. According to the authors, the main mechanism of D5 removal was chemical absorption in the presence of SO₄²⁻ ions (a product of the biological oxidation of H₂S) under acidic conditions (pH < 2), which resulted in ring-opening hydrolysis, leading to the formation of DMDS and L2, i.e., compounds that are less hydrophobic and, therefore, easier to remove by physical absorption in aqueous solutions. They hypothesized that, under these conditions, nitrogen was transformed into nitrates, which mainly oxidized D5 into silanols. Undoubtedly, this mechanism was also supported by adsorption on the biomass deposited in BTF and contained in the flocs in the circulating liquid. From a practical point of view, the relatively short EBRT used in research (0.6–2.2 min) requires emphasis. It can be expected that, for real biogas containing other carbon sources besides VMSs (e.g., VOCs), this “co-degradation” will be more efficient.

The mechanism of VMSs biodegradation was investigated by Accettola and Haberbauer [57] using the example of D4, which is usually dominant in biogas from sewage sludge and landfills. As a result, they proposed an interesting, multi-stage flow diagram of its decomposition, leading to the formation of silanols (mainly dimethyl dihydroxy silane—DMDS), i.e., compounds with much higher water solubility and better biodegradability. According to Sabourin et al. [58], DMDS is biodegradable in soil under anaerobic conditions by the bacteria *Arthrobacter* and fungi *Fusarium oxysporum Schlechtendahl*. Other indirect decomposition products include silicic acids, formaldehyde, methanol and, finally, CO₂ and H₂O [51,59]. The main degradation mechanism is the hydroxylation of the methyl group to the hydroxymethyl group, followed by oxidation to the formyl group. Similar end products, including DMDS, can also be obtained chemically by oxidizing VMSs with hydroxyl radicals (OH^{*}). The obstacle in biological biogas purification from VMSs, apart from their poor biodegradability, is the high vapour pressure and low water solubility of VMSs, many orders lower than that of H₂S. This is especially true for D4, D5 and D6, which are most often found in biogas. In the practice of gas purification, owing to the need to overcome large mass transfer resistances in the liquid phase, there is a need to ensure a long phase contact time in the absorber, i.e., the construction of devices with a large diameter and height that are, therefore, expensive. For example, a study [60] using an aerobic BTF showed that, with an EBRT of 19.5 min, the RE of D4 was only 43%. It can be easily calculated that, for a typical biogas flow of 1000 m³/h and the assumed flow velocity of 0.0074 m/s (value converted to the empty cross-section of the apparatus; tested gas stream: 0.5 dm³/min and column diameter: 0.038 m), the diameter of such apparatus (Ø) should be:

$$\varnothing = \sqrt{\frac{4 \cdot 1000 \frac{\text{m}^3}{\text{h}}}{\pi \cdot 3600 \frac{\text{s}}{\text{h}} \cdot 0.0074 \frac{\text{m}}{\text{s}}}} \approx 7 \text{ m}$$

And its minimum height (h) should be:

$$h = 0.0074 \frac{\text{m}}{\text{s}} \cdot 19.5 \text{ min} \cdot 60 \frac{\text{s}}{\text{min}} \approx 9 \text{ m}.$$

This means that the dimensions are completely unrealistic, both from an economic and process point of view. It is worth adding here that the EBRT in the case of biogas desulphurization with BTF is usually below 3 min. Nevertheless, the authors' undoubted merit is the confirmation that the biodegradation of VMSs under aerobic conditions is possible and that they can be the only source of carbon and energy for microorganisms. However, for this process to be implemented, the retention time must be significantly reduced by intensifying both absorption and biodegradation. In order to increase mass transfer from gas to the liquid phase, the authors proposed the use of an additional, non-miscible-with-water and hardly biodegradable organic absorbent, oleyl alcohol, a compound with good partitioning for VMSs. A similar idea was used by Pascual et al. [61–63] in laboratory studies on artificial biogas containing D4. To sprinkle BTF, they used an additional organic phase in the form of a more durable silicone oil (the authors did not specify the type and origin of the oil). Its addition in the amount of 30% caused a significant (from approx. 20% to 70%) increase in the RE in relation to the sum of VMSs at EBRT = 11 min. The only carbon sources were: TMS-OH, L2, L3, L4, L5, D4 and D5. Biodegradation, as the basic mechanism for the removal of VMSs, was confirmed by the additional CO₂ production reported by the authors [61]. It is also possible to intensify mass transfer by adding surfactants, i.e., compounds lowering the liquid surface tension [50], or, even better, biosurfactants. A positive effect of biosurfactants (rhamnolipids) produced by the strain of *Pseudomonas aeruginosa* S240 on the efficiency of D4 removal in aerobic BTF was found by Li et al. [51]. The authors also proposed a metabolic pathway for D4 degradation by the above-mentioned strain. However, even with the participation of biosurfactants, the obtained mass transfer coefficients were many times lower than those in the case of H₂S, and the EBRT required to achieve 74% RE of

D4 was over 13 min. On the other hand, studies [64] have shown that the use of specific enzymes may have great potential to intensify the biodegradation of VMS.

In conclusion, apart from the above-mentioned studies by Zhang et al. [55,56], who examined the ability of BTF to simultaneously remove H_2S and D5 under aerobic conditions (stating that the latter was mainly removed by abiotic chemical absorption), no research has been conducted to develop a technology for the biological, integrated removal of H_2S and VMSs from biogas. The only attempts were made to combine biological processes with the use of BTF and separate adsorption on AC for both impurities [65]. As demonstrated by the authors, such a solution is economically justified, as it significantly reduces the operating costs, mainly due to the longer lifetime of AC.

Due to the numerous implementations in the case of H_2S , it seems that the greater potential of the combined biological removal of H_2S and VMSs lies in the aerobic mechanisms of their decomposition with the use of BTF. This is based on simultaneous absorption (intensified in the case of VMSs with an additional, non-biodegradable organic phase), adsorption on the bed surface and biomass flocs and biodegradation, assisted by possible additions of bio/surfactants and enzymes. The concept of such technology is presented in the next section.

6. Technological Concept of a Combined Biological Method for the Removal of Hydrogen Sulphide and Volatile Methylsiloxanes from Biogas

A schematic diagram of the proposed idea is presented in Figure 1. The sewage sludge fermentation process in a typical municipal WWTP (1) was adopted as a source of biogas. The thickened mixture of primary and secondary sludge is introduced into a closed, mesophilic fermentation chamber (2). The resulting biogas is optionally pre-desulphurized by the “in situ” method by supplying air to the fermentation chamber head in an amount of up to 5%_v. As a result, elemental sulphur precipitates in the chamber, and the digestate enriched with it can be used as a fertilizer. Raw biogas is subject to the dedusting and removal of any foam in a preliminary water scrubber (3), and then directed to an aerobic BTF (4) with filling prepared based on halloysite [3]. In the BTF, the simultaneous sorption and biodegradation of H_2S and VMSs take place, with the EBRT not exceeding 5 min. The aerobic conditions are ensured by dosing O_2 (or air) to the BTF in a stoichiometric ratio to the H_2S contained in the biogas. The initial biofilm on the BTF filling, containing chemoautotrophic sulphuric bacteria (which draw energy from the oxidation of H_2S), is created by sprinkling the bed with an activated sludge suspension from the WWTP biological stage. It is then inoculated with a bacterial strain grown in site (6) capable of degrading VMSs, e.g., with *Pseudomonas aeruginosa* S240 strain. An additional advantage of this strain is the production of biosurfactants (rhamnolipids) that intensify the processes of mass exchange and the biodegradation of VMSs. The process of VMSs absorption is intensified by the addition of a low-viscosity silicone oil to the circulating process water (in the amount of ~20–40%), in which they dissolve much better than in water. The silicone oil was chosen due to its high resistance to chemical and biological oxidation, thermal stability, low surface tension, low volatility, non-toxicity and insolubility in water [66]. It is proposed to use the POLSIL OM-10 methyl silicone oil [67] with a kinematic viscosity of 10^{-5} m²/s, density of 930 kg/m³ (298 K) and flash point 423 K, or another with similar properties. The circulating liquid tank (5) is also supplied with a mineral nutrient solution and pH correctors. The biogas purified in the BTF is pumped to the tank (8) with a drainage system (the leachate, together with excess biomass from the BTF, is directed to the WWTP inflow); then, it is dried using the condensation method (9) (cooling to ~5 °C and reheating to ensure RH < 50%). The biogas treated this way, after possible final cleaning in an adsorber with AC (10), feeds the CHP unit (11), the heat from which is used for heating the fermentation chamber and for other local purposes. The electricity will supply the receivers at WWTP and/or be sold. The combustion gases from the CHP engine will undergo optional NO_x treatment with the use of a reduction catalytic afterburner (12). In the event of a CHP failure, the biogas will be burned in a

high-temperature ($\sim 1000^\circ\text{C}$) closed-type flare (13). The BTF spraying liquid undergoes periodic regeneration in a system consisting of a gravitational separator (14), a desorber (15), a cooler (16), a reactor (17) and a sludge-dewatering system (18,19). In the separator (14), the oil is separated from the heavier water phase and directed to thermal regeneration in the desorber (15), then cooled (16) and returned to the tank (5). The regeneration of the water phase take place in the reactor (17), into which the following are introduced: (i) the water phase containing S^0 and any biomass flocs from the separator (14), (ii) an oxidant (e.g., CaO_2 or MgO_2 [68]) for the oxidation of S^0 and residual sulphur compounds and VMSs, (iii) an alkaline agent (e.g., CaO) to neutralize acid oxidation products and (iv) residual VMSs with air from the desorber (15) (by bubbling, intensifying the mixing of reactants and additionally oxygenates the circulating liquid). As a result, in the reactor (17), easy-to-separate solid products will precipitate in the form of, among others, sulphates and silicates, which will be separated in a clarifier (18) and a drum filter (19) for further use, e.g., for the production of building materials. The mixture of water phase and oil circulate in closed cycles, supplemented periodically.

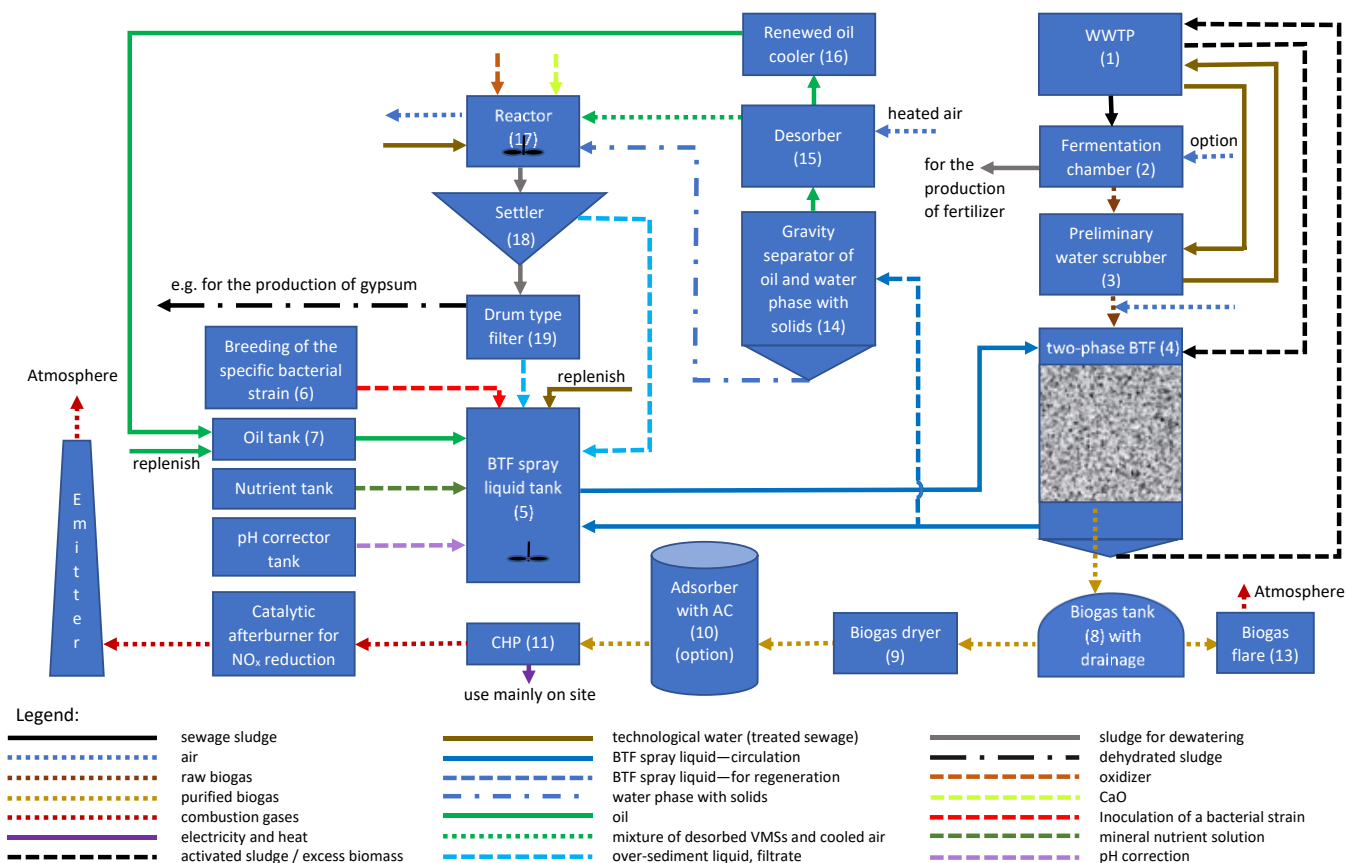


Figure 1. Schematic diagram of the concept of the regenerative biological method for the integrated removal of H₂S and VMSs from biogas generated from sewage sludge, along with the management of biogas and by-products of the process.

7. Summary and Conclusions

In times of efforts to eliminate fossil fuels and the intensive development of renewable energy sources and a low-emission circular economy, there is an urgent need to intensify the production of biofuels, including biogas. In this context, the implementation of new, environmentally friendly and waste-free methods of biogas cleaning from two technologically key pollutants—hydrogen sulphide and volatile methylsiloxanes—has gained particular importance. Such methods undoubtedly include biological techniques. So far, they have been successfully implemented to remove H_2S ; however, the biological removal of VMSs is

difficult due to their poor water solubility and biodegradability. The review of the current research on biologically cleaning VMSs from biogas has shown that, to the knowledge of the authors, it was solely based on laboratory tests with the use of artificial biogas. Nevertheless, many studies have confirmed that microorganisms, such as *Pseudomonas* bacteria (*P. aeruginosa*, *P. fluorescens*, *P. putida* and *P. citronellosis*), *Agrobacterium* (*A. radiobacter*), *Arthrobacter* and *Fusarium oxysporium* fungi, are able to use VMSs (especially D4, which is dominant in the biogas from sewage sludge) as the only carbon source (*Pseudomonas* was identified as the predominant genus in the mixed population). However, the results of testing the effectiveness of this process to date have been unsatisfactory. Therefore, it is necessary to search for further methods of intensifying both the sorption process and the biodegradation of VMSs.

The economics of biological biogas treatment can be significantly improved by the implementation of integrated methods for the combined removal of various pollutants, as proposed in this study. Furthermore, according to the authors' knowledge, apart from one preliminary study by Zhang et al. [55], which showed a chemical, rather than biological, mechanism for the removal of VMSs, there have been no such studies. The proposed technological concept meets this demand. Its main advantages, in addition to using the same two-phase BTF to remove H₂S and VMSs simultaneously, include closed material loops, process operation under ambient conditions and potentially low operating costs. Like any idea, it requires practical confirmation. More research is needed, including the selection of (i) more efficient bacterial strains capable of simultaneous, effective biodegradation of VMSs and H₂S; (ii) types and concentrations of synthetic surfactants, biocatalysts and organic phase additives for the spray liquid; (iii) types and doses of mineral nutrients and oxidants; (iv) the optimal oxygen concentration in the biogas; (v) BTF performance parameters (apparent gas flow velocity, spray density, EBRT, temperature and pH) and (vi) BTF packing materials with the possible lowest clogging potential and possible largest contact surface of the phases. It is also worth undertaking research on poorly understood biological oxidation processes under anoxic conditions, e.g., with the use of nitrates (NO₃[−]) as electron acceptors. The use of such processes avoids the dilution of the biogas and the risk of explosion, and also reduces the risk of clogging due to the lower biomass increase.

In conclusion, due to the importance and topicality of the discussed issues, their interdisciplinarity and the identified gaps in knowledge, a wide field for research, both basic and applied, has opened.

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