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Volatile Siloxanes Emissions: Impact and Sustainable Abatement Perspectives

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Eliminating volatile siloxanes from gas emissions is increasingly important due to their persistent detrimental economic, societal, and environmental impacts. Although physicochemical technologies are currently the only commercially available abatement methods, recently developed biobased technologies are emerging as a more cost-effective and sustainable alternative to promote the removal of volatile siloxanes.

Sources, Fate, and Impact of Volatile Siloxanes

Siloxanes are organosilicone compounds that contain a silicon atom bonded to at least one carbon and one oxygen atom in their molecular structure. Methyl siloxanes with small and medium molecular weights (<500 g/mol) are volatile under normal conditions, and are usually classified into linear and cyclic volatile methyl siloxanes (VMSs) (see Figure I in Box 1) [1]. Siloxanes are extensively used in industrial applications (e.g., construction, electronics, automotive industry, textiles, medical equipment, food packaging, medicine, and cosmetics) due to their hydrophobicity and biocompatibility [1]. Thus, the manufacture of siloxanes has reached an annual production of millions of tons with an expected annual increase of ~6.5% in the next few years. In fact, the total worldwide production of silicones has increased from 2 million tons in 2002 to 8 million tons in 2020 (https://www.statista.com/statistics/573585/global-silicon-production/) [2].

More than 90% of all the VMSs entering the environment end up in the atmosphere. Their sources are either direct discharges (emissions from the silicone manufacturing industry or siloxanes accumulated in residential indoor air, and other microenvironments) or indirect discharges (volatile siloxanes transferred from water bodies to the atmosphere, and volatile siloxanes from sewage and solid waste which are emitted along with biogas and waste off-gases to the atmosphere) [3]. Recent research claims that VMSs should be classified as emerging environmental pollutants [2,3]. Furthermore, several studies have revealed that VMSs are potentially toxic to living organisms: at high doses they affect animals' reproductive systems, are carcinogenic, and harm the respiratory tract [4]. Additionally, the accumulation of silica particles derived from the oxidation of VMSs to SiO_2 has a negative economic impact in waste treatment facilities. Their deposition on equipment (engines, turbines, and boilers) causes clogging of pipes and valves and the abrasion of surfaces, reducing their lifespan and performance. For example, siloxane removal in a wastewater treatment plant facility can save an estimated 2.6–5.7 €/day per m^3 of treated wastewater [5].

Dealing with VMS-Loaded Gaseous Emissions: Current Treatment Methods

Commercially available technologies for siloxane abatement rely on the physical withdrawal of these contaminants from a gaseous stream via adsorption, absorption, or condensation. Activated carbon (AC) is the most common and least expensive adsorbent used in industrial applications, whose cost ranges from 1.5 to 4 €/$kg_{steam\text{-}AC}$ and from 4 to 8 €/$kg_{chemical\text{-}AC}$ (A. Cabrera-Codony, PhD thesis, Universitat de Girona, 2016). Molecular sieves, activated alumina, and silica gel are becoming more popular alternatives to overcome the main drawbacks associated with AC, such as its flammability and low adsorption capacity of 0.5–15 g siloxanes/(kg AC) versus 100 g siloxanes/(kg silica gel) [6]. Moderate removals have been obtained using absorption in water (due to the hydrophobicity of VMSs) and in organic solvents. However, chemical absorption in acidic solutions increases costs, and its improved effect on purification capacity is doubtful [7]. VMS volatility also hinders the implementation of cryogenic condensation processes: while −25°C is the typical operating temperature used in commercial applications, considerably lower temperatures are required for effective siloxane condensation [6].

Recent technological advances and patents intended for VMS removal are focused on improving the adsorption process, the existing adsorbents (including higher adsorption capacity, more effective regeneration, and resistance towards humidity), and on developing new tailor-made absorbents (such as Selexol, a dimethyl ether of polyethylene glycol with a high affinity for siloxanes, achieving removals up to 99%). However, research on physical technologies for VMS removal is currently focused on membranes for the selective separation of siloxanes. Regardless of the promising results (>80% removal of L2–L4 and D3–D5 in a PDMS membrane with ambient air as a sweep gas), there is still limited information on the process [7].

Despite the number of options available for cleaning siloxanes, none have proven ideal. Physicochemical technologies often entail detrimental environmental impacts and high investment and operating costs (Figure 1). The CO_2 footprint is a critical environmental indicator representing the

Box 1. Chemistry of Volatile Methyl Siloxanes

The volumetric mass transfer rate from the air to the microorganism-containing aqueous phase in conventional bioreactors is determined by $F_{G/A} = K_L a_{G/A}(\frac{C_G}{H} - C_L)$, where F is the overall mass transfer rate of contaminant ($g/m^3/s^1$), $k_L a$ (/s) is a volumetric coefficient that determine the mass transfer rate by factors independent of the concentration, C_G and C_L (g/m) are the concentrations of the pollutant in the gas and liquid phases, respectively, and H the Henry's law coefficient (dimensionless). Figure I shows the chemical formulas and Henry's law coefficients (www.henrys-law.org) for several volatile methyl siloxanes.

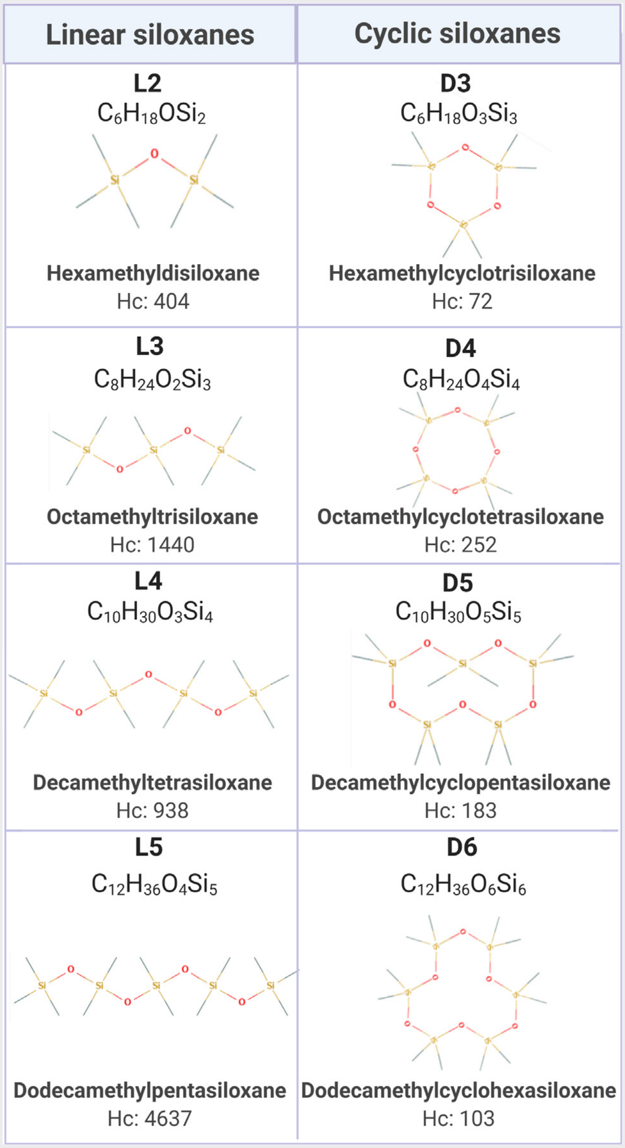

Figure I. Chemical Formulas and Henry's Law Coefficients for Several Volatile Methyl Siloxanes.

impact associated with a process, and physicochemical technologies have CO_2 footprints up to ten times higher than those of biotechnologies. In particular, process energy requirements, production and transportation of adsorbents or packing materials, and the use of chemicals such as acid or alkaline solutions used as absorbents, are the main contributors to climate change. Similarly, the high investment costs of these technologies are related to the regeneration or replacement of the adsorbent material, the use of organic solvents, the deactivation of the catalysts, the high energy consumption, and the extreme operating temperatures. Therefore, there is active interest in developing new, cost-efficient, and sustainable technologies for VMS removal.

Towards More Cost-efficient Removal of VMSs: the Promising Role of High Mass Transfer Bioreactors

The prospect of biologically removing siloxanes has been encouraged by recent investigations that confirm the capability of certain bacteria (such as *Phyllobacterium myrsinacearum*, *Pseudomonas* sp., and *Methylibium* sp.) to degrade these contaminants [1,8]. Nevertheless, the main limitation for biodegradation has less to do with microbiology than with the transfer of VMSs from the gaseous stream to the liquid phase that contains the microbial population. Indeed, the hydrophobicity and volatility of VMSs actually hinders the removal efficiency achieved in bioreactors devoted to VMS abatement, as denoted by their high Henry's law coefficient (Box 1) [9,10].

Biotrickling filters (BTFs) are the preferred bioreactor configuration for the implementation of this process, under both aerobic and anoxic conditions (e.g., siloxanes in raw biogas). With these systems, maximum removals of ~60% for D4 at initial concentrations ranging from 50 to 200 mg/m^3 have been reported at an optimum pH range of 4–6. However, BTFs require high gas residence times to promote mass transfer (12–30 min), ultimately leading to increased reactor volumes, and therefore higher investment costs [11].

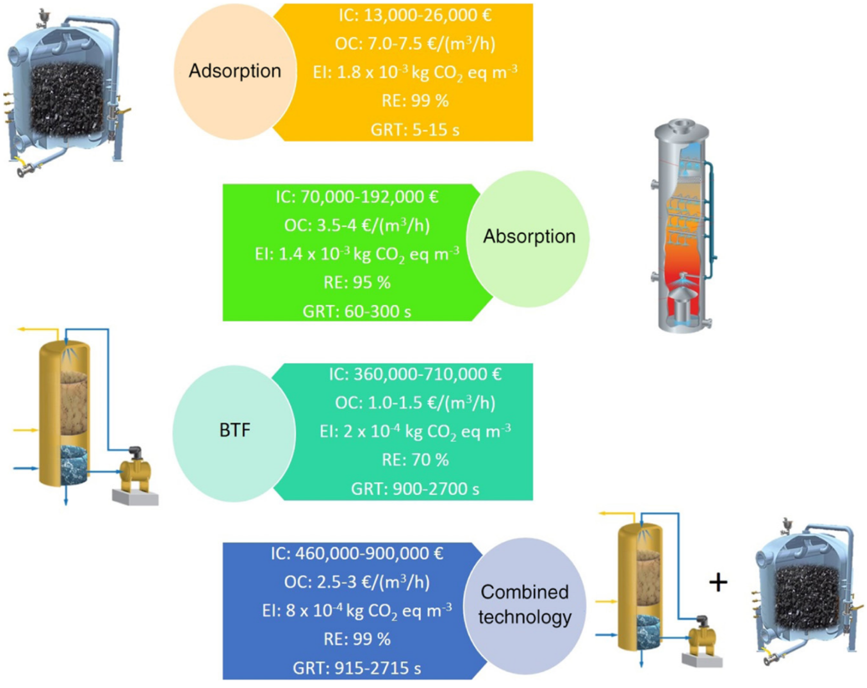

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Figure 1. Key Technoeconomic and Environmental Figures of the Main Siloxane Purification Technologies. Investment cost (IC, estimated for a treated gas flowrate of 1000 m^3/h), operating cost (OC), environmental impact (EI), siloxane removal efficiency (RE), and typical gas residence time (GRT). Climate change has been used as the environmental indicator for EI. Data from [13,14]. Abbreviation: BTF, biotrickling filters.

Thus, the biological removal of VMSs suggests that a feasible implementation relies on the optimization and scale-up of enhanced mass transfer bioreactors. For instance, the presence of rhamnolipids, organic biosurfactants produced by *Pseudomonas aeruginosa*, results in enhanced D4 removal in a BTF. In this context, novel technological solutions that overcome mass transfer limitations, such as two-phase partitioning bioreactors or membrane bioreactors, have been recently investigated. The addition of an organic, nonaqueous phase with a high affinity for the target pollutant is a feasible solution to boost the removal of hydrophobic volatile organic compounds in so-called two-phase partitioning bioreactors. This strategy was tested in a recent study for the aerobic removal of L2, L3, D4, and D5 in a two-phase BTF, and the total VMS removal increased from 30% to 70% at gas retention times of 60 min. However, despite the high removal performance obtained for D4 and D5 (80–90%), much lower efficiencies ranging from 20% to 60% were recorded for linear siloxanes [10]. Less encouraging results were achieved in a hollow fiber membrane bioreactor for the simultaneous removal of D4, D5, and trace compounds at considerably lower gas retention times: ~20% at 18–60 s [12]. Nevertheless, these are the first attempts to implement novel high mass transfer bioreactors for the abatement of siloxanes in gaseous streams, so many aspects of the process can still be improved.

The most appropriate purification technology must be selected on a case-by-case foundation based on the type of gaseous stream and its ultimate use (biogas upgrading, waste gas discharge, etc.). Thus, if the VMS concentration is too low, and provided the emission complies with the legal discharge limits, the costs of the gas purification system may exceed those associated with the presence of siloxanes. Under this scenario, not treating the siloxane-laden stream could be the preferred option, resulting in negative environmental and human impacts as previously discussed. There are three main factors that increase the costs of physicochemical technologies: the short lifespan of the packing material of the adsorption tower, the need for frequent regeneration and specific management of the spent adsorbent, and is the high consumption of chemical reagents in the absorption units. This might result in a more positive economic balance for biotechnological solutions. Although available data to perform a reliable cost–benefit analysis are still scarce or drawn from laboratory or pilot-scale units, and despite the higher investment expenditure, biotechnologies seem to offer up to seven times lower operating costs than physicochemical technologies, and have a lower carbon footprint (Figure 1). Moreover, biological technologies offer the possibility of simultaneously removing siloxanes together with H_2S or volatile organic compounds from waste gases, which entails another competitive advantage over more expensive conventional treatment technologies. Consequently, even though up-to-date biotechnologies are still characterized by lower VMS removal performance when compared to several physicochemical processes, their cost-effectiveness, sustainability, and promising results encourage further research on the optimization and scaling of these processes.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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