

REVIEW

From Biofilters to Biocatalysts: Advances in Biological Treatment of VOCs in Atmospheric Environments

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ABSTRACT

Volatile organic compounds (VOCs) have become a major concern that requires a viable and sustainable remedy as a substitute for conventional air pollution control technologies. This review follows the trend of biological VOC treatment, from the development of conventional biofilter systems to sophisticated biocatalytic systems. It also looks into the principles of VOC biodegradation and the importance of microbial communities, as well as the technology development of reactors such as biofilters, biotrickling filters, and hybrid biological systems. The efficiency and stability of biological treatment systems have been improved recently by material science, microbial resource engineering, and molecular biology, resolving the mass transfer limitation, microbial instability, and complexity of treating complex VOC mixtures. Nevertheless, technical bottlenecks, including fouling, clogging, and the formation of by-products, still hinder large-scale industrial use. The environmental trade-offs related to the treatment of biological VOCs mentioned in this article are the formation of toxic intermediates and the emission of greenhouse gases. However, with such challenges, process intensification, intelligent monitoring, and hybrid systems have been proposed to provide some promising directions toward limiting these constraints. The future of biological VOC treatment lies in its potential for combination with engineering innovations and biological processes, which will guarantee its scalability and long-term sustainability in atmospheric emissions management.

Keywords: Biological Treatment; Volatile Organic Compounds; Biofilters; Biocatalysis; Environmental Sustainability

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1. Introduction

Volatile organic compounds (VOCs) are some of the most widespread and difficult atmospheric pollutants emitted by industrial, agricultural, and urban activities^[1]. They consist of a wide category of carbon-based vapors with high pressure under ambient temperature, such as alkanes, aromatics, ketones, aldehydes, alcohols, esters, chlorinated hydrocarbons, and sulfur-based organics^[2]. The sources of these compounds are vast, including petrochemical processing, coating and painting processes, pharmaceutical production, printing, waste management, wastewater treatment plants, landfills, and interior building materials^[3]. When VOCs escape into the air, they are not passive: they are involved in complex photochemical reactions that lead to the production of troposphere ozone, secondary organic aerosols, and urban smog, and most individual VOCs are directly toxic, malodorous, mutagenic, or even carcinogenic^[4,5]. The growing strictness of air-quality standards, as well as the rising awareness of people about occupational exposures and environmental health, has thus made the search for effective, cost-effective, and sustainable technologies of VOC abatement increasingly strident.

Traditional solutions to gaseous VOC emissions, like thermal oxidation, catalytic incineration, adsorption, condensation, and plasma-based oxidation, have been extensively

implemented in industrial practice^[6]. Such technologies are very efficient, especially with a concentrated and comparatively uniform gas stream. Nonetheless, their general functionality is usually limited by high energy consumption, catalyst deactivation, secondary waste, and decreased economic feasibility of large volumes of air with low VOC levels. In practical atmospheric emission situations, VOCs are typically found as dilute, intermittent, and chemically complex mixtures, and expensive physicochemical treatments are not so appealing. This has spurred the invention of biological treatment systems, which take advantage of the metabolic power of microorganisms and enzymes to convert pollutants into less toxic products with relatively mild operating conditions^[7].

Biofiltration technologies have traditionally formed the basis of biological VOC treatment^[8]. Out of them, biofilters, biotrickling filters and bioscrubbers have become the predominant reactor design of relevance in the real-world air pollution abatement^[9]. These systems are based on the extraction of VOCs out of the gaseous phase into a wet bioactive phase, on which the compounds are oxidized by microorganisms using intracellular enzymatic routes. **Figure 1** depicts the overall mechanism of biological VOC treatment where the arrows reflect the steps of the processing of gas phase VOC to the biological degradation process and end treatment of the effluent.

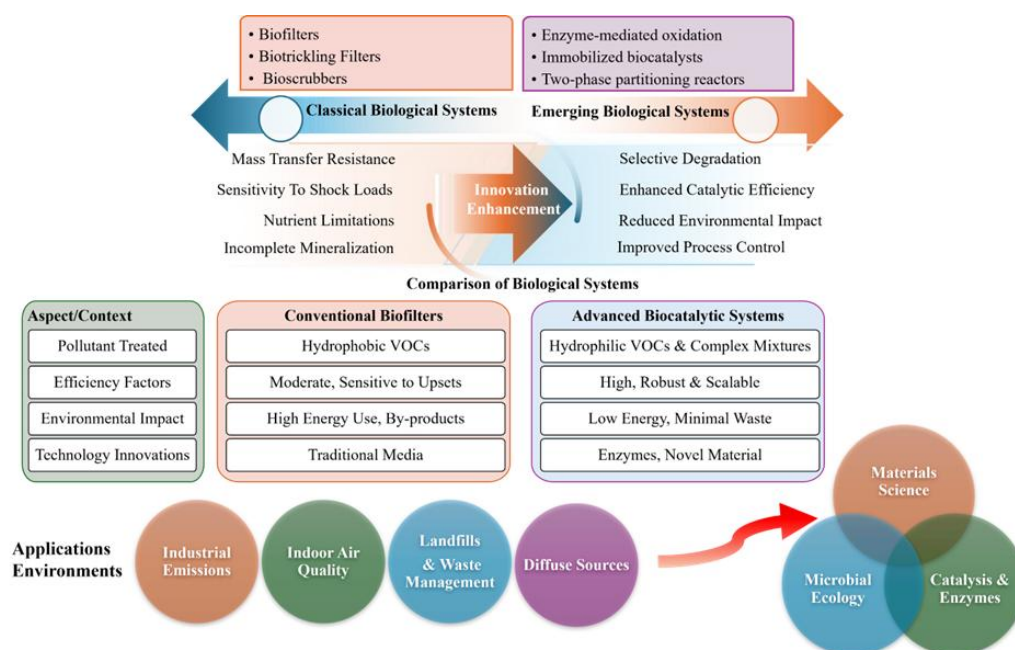


Figure 1. Schematic representation of the biological VOC treatment process, from pollutant entry to degradation by microbial communities.

They are attractive in their comparatively low operation expenses, small energy needs, simplicity in working, and their ability to continue treating large volumes of gases^[10]. Biofilters (especially biofilters) in particular have been viewed as a solid solution to biodegradable and soluble VOCs in water for several decades. However, besides their success, classical biological systems have serious constraints, such as resistance to mass transfer of hydrophobic VOCs, response to shock loading, biomass overgrowth, pressure gradient, pH shift, nutrient constraints, and partial mineralization of toxic/recalcitrant compounds^[11]. These have tended to limit their performance in efficiency, predictability, and scalability in the varied atmospheric conditions.

The past years have also seen an interesting technological and conceptual change in this sphere. Treatment of biological VOC is no longer limited to passive capture of pollutants in traditional filter beds^[12]. Rather, it is developing into more manageable, selective, and extreme systems that are more and more reminiscent of biocatalytic platforms. The factors that are leading to this transition are microbial ecology, enzyme engineering, reactor design, materials science, and molecular biotechnology. New support materials are being designed to enhance microbial attachment, moisture retention, pollutant sorption, and gas-biofilm mass transfer through novel support materials that include biochar-based media, synthetic composites, and functionalized carriers^[13]. Meanwhile, microbial resource engineering no longer depends on the natural acclimatization of communities but instead expressly enriches specialized degraders, fungal-bacterial consortia, bioaugmentation approaches, and even man-made microbial communities specific to mixed VOC streams. This is accompanied by the use of metagenomics, transcriptomics, proteomics, and metabolomics, which have started to demonstrate how microbial community structure, functional genes, and metabolic pathways are used to dictate the level of performance of treatment under realistic conditions of operational stress.

More to the point, the discipline is shifting away not only to whole-cell systems, but also to explicitly biocatalytic thought. The limits of the bio-physicochemical air treatment are being redefined by enzyme-based oxidation, immobilized biocatalysts, two-phase partitioning bioreactors, membrane-assisted contactors, and hybrid bio-physicochemical systems^[14]. In the newer designs, it is not just to offer a resi-

dence to pollutant-degrading biofilms, but rather to rationally increase the catalytic interface of the VOC molecules and the biological transformation pathways^[15]. This strategy leaves the possibility of breaking through some of the old bottlenecks of conventional biofiltration, particularly the hydrophobic, inhibitory, and structurally complex VOCs. It also adopts biological treatment in line with larger trends in green manufacturing and circular process engineering, where selective and low-temperature and low-carbon catalysis are being more prized.

Even with these developments, there is still a disjointed literature. The literature review usually talks about only one type of reactor, a group of VOCs, or an aspect in isolation, such as packing materials, microbial communities, or operating parameters. In most studies, biofilters and associated systems are still largely viewed as units in environmental engineering and not regarded as being integrated as a continuum with the perspective of active biocatalysis that is starting to be understood as an extension of passive biofiltration^[16]. Consequently, a single conceptualization about the relationship between classical gas-phase bioreactors, enhanced hybrid systems, and enzyme-assisted processes remains elusive and how these represent the next generation of VOC control technology.

This is the gap that is exactly covered in the novelty of this review. Instead of introducing biofilters, biotrickling filters, bioscrubbers, and advanced systems as distinct technical categories, this article looks at them as part of an innovation pathology as the term biofilters to biocatalysts suggests. This framing highlights the shift towards more engineered processes for the catalytic removal of microorganisms that are more specific and more resilient, as well as controlled. The review does not merely overview reactor configurations but it is a synthesis of the advances in the biological mechanisms, functional microbiology, catalytic enhancement plans, and intensifying the process^[9,11]. The article provides a more integrated view of how biological VOC treatment is changing to become more of an empirical practice toward a design-driven and more mechanistically informed field by connecting these dimensions.

The second new feature of this review is that it specifically addresses atmospheric environments. The concept of VOC control frequently appears to be limited to the case of industrial exhaust streams, but a large number of biologically

treatable emissions are found at more inclusive atmospheric interfaces, such as indoor environments, diffuse industrial sources, waste treatment infrastructure, and odor-generating facilities^[17]. The settings have specific demands of low levels of pollutants, varying humidity, mixed pollutants, and stability in operations over time. By placing the biological treatment in the broader context of the air, it is against this background that the review illustrates that technologies should not only be efficient in the laboratory environment but also be strong when subjected to real-world conditions of air treatment.

Moreover, this review anticipates the position of interdisciplinary convergence in the development of the field. Nowadays, biological air treatment is at the junction of environmental biotechnology, catalysis, materials engineering, systems biology, and digital process control^[18]. Omics-based diagnostics, predictive modeling, intelligent monitoring, and novel carrier design are creating the possibility to shift the operation of the black box reactor to data-driven performance optimization^[19]. This system-level view is necessary to determine the real constraints of existing technologies, as well as to develop the next-generation platforms that will be in a position to deal with the varied, multi-component VOC mixtures with fewer environmental trade-offs.

It is based on this that this article seeks to offer a holistic and critical summary of the fundamental principles, reactor technologies, recent advances, and long-standing obstacles in the process of treating biological VOCs. First, it revisits the basic principles of biodegradation and mass transfer between gases and biofilm, then it explores the development of treatment systems out of more traditional biofilter design towards more sophisticated and unequivocally biocatalytic designs^[7,20]. It also explains the existing mechanisms of performance improvement, such as new materials, microbial and enzyme development, and intelligent functionality^[21]. Lastly, it analyses technical bottlenecks, environmental trade-offs, scale-up problems, and prospects of future research. In that way, this review aims at illuminating the state of the art, as well as defining the new direction of the area: a shift in passive biological elimination towards precision-oriented, catalytically enhanced, and application-ready solutions to sustainability in mitigating atmospheric VOC levels.

2. Fundamentals of Biological VOC Treatment

Biological treatment of volatile organic compounds is governed by a sequence of tightly coupled physical, chemical, and biochemical processes rather than by biodegradation alone^[8,22]. In atmospheric applications, VOC removal efficiency depends first on the successful transfer of contaminants from a flowing gas stream into a biologically active phase, and only then on the capacity of microorganisms or their enzymes to transform absorbed compounds into less harmful intermediates and final products^[23]. This coupling explains why biological VOC control often performs well for some pollutants under stable operating conditions, yet deteriorates rapidly when pollutant hydrophobicity, toxicity, or loading fluctuations exceed the adaptive limits of the system. A fundamental understanding of these mechanisms is therefore essential for interpreting the strengths and weaknesses of biofilters, biotrickling filters, bioscrubbers, and emerging biocatalytic platforms.

2.1. Principles of VOC Biodegradation in Gas-Phase Biological Systems

Removal of VOC in biological air treatment systems, starting with partitioning into a gas phase/aqueous phase or a biomass-bound phase of the aqueous phase^[24]. This is a step determined by the forces of gas-liquid interface transfer, compound solubility, diffusivity, and physicochemical properties of support media and microbial matrix. In the case of hydrophilic VOCs, the aqueous phase rapidity of dissolution is commonly so high that biodegradation is the rate-limiting factor^[25]. In contrast, in the case of hydrophobic compounds, including most aromatics, terpenes, and chlorinated VOCs, the performance of the processes is often dominated by limited mass transfer^[26]. In this case, the observed biodegradation potential of the system can be less than the inherent metabolic capability of the microbial community due to the inability of the pollutant to reach the cells.

After becoming transferred into the bioactive phase, VOC molecules are sorbed by extracellular polymeric materials, carrier surfaces, or cell membranes and then enter microbial metabolism^[27]. Their further destiny is either total

mineralization or partial oxidation, co-metabolic transformation, or interim accumulation. The optimal end product would be the total mineralization, usually resulting in carbon dioxide, water, mineral salts, and biomass. Numerous VOCs, however, are not easily mineralized in just one pathway. Instead, they can be subjected to stepwise oxidation by alcohol, aldehyde, acid, or epoxide intermediates, some of which in their own right are also inhibitory or environmentally problematic. It is on this basis that high apparent removal efficiency should not necessarily be compared to detoxification. Biologically treated exhaust stream still can have transformation products, which need to be monitored and interpreted mechanistically^[18].

Reactor hydrodynamics and residence time of the pollutant also affect the biodegradation sequence. In continuous systems, contact efficiency and exposure of the microbes to the substrate in continuous systems are influenced by empty-bed residence time and gas distribution^[28]. In case of too short residence time, even an active microbial population will not be able to attain a significant level of removal because of a lack of transfer and reaction time. In case it is excessively long, the capacity to treat per unit reactor volume decreases, making the process less economical. The best biological systems are thus those that are a compromise between gaseous transport, diffusion in the liquid phase, and metabolic turnover as opposed to those that maximize a single factor. The same balance has been replicated in the evolution of the design of conventional biofilters to more intense biocatalytic systems.

2.2. Microorganisms and Functional Ecology of VOC Degradation

The biological process of removing VOCs depends on the presence of different communities of microbes, mostly bacteria and fungi, and sometimes yeasts and archaea, in particular environments^[8,29]. Bacteria have traditionally ruled engineered systems due to their rapid expansion, metabolic adaptability, and adaptation to a broad collection of oxygenated and aromatic substances^[30]. Some of the commonly used genera in VOC treatment systems tend to harbor metabolically flexible organisms that can use alcohols, ketones, aldehydes, and simple aromatic compounds as a source of carbon and energy. They have more advantages, especially in humid, nutrient-controlled systems that treat com-

paratively biodegradable and water-soluble contaminants.

Fungi are also equally significant, yet in some cases, undervalued, particularly in the elimination of hydrophobic VOCs^[31]. Their filamentous expansion increases the access to gas-biofilm interfaces, and interaction with poorly soluble substrates can be enhanced by their cell surface hydrophobicity. Most of the fungi are also resistant to acidic conditions, changes in moisture, and toxic substances compared to the bacteria. This renders them particularly useful in the treatment of compounds like styrene, toluene, xylene, and terpene-based emissions. However, fungal dominion is not always good. Uncontrolled mycelial proliferation can augment pressure decrease, obstruct pores, and create uneven flow trajectories, which can decrease long-term reactor steadiness. In this way, the higher degradation ability of fungi of a certain compound should be balanced with operational penalties.

It is usually observed that mixed microbial consortia are more resilient than pure cultures due to the ability of metabolic complementarity, sharing of substrates, removal of intermediates, and ecological stability to changing loadings^[32]. In natural VOC mixtures, a single species can catalyze the oxidation of a recalcitrant species, whereas another species catalyzes the oxidation of intermediate metabolites, which would otherwise build up. The division of labor, such as this, can be the difference between a system that can be removed at a steady rate and collapses when mixed pollutants take their toll. Meanwhile, there is uncertainty brought about by community complexity. Competitive exclusion, stratification of biofilms, and nutrient imbalances may cause a displacement of the most functionally desirable degraders. This means that microbial diversity is not to be considered as a free benefit; it is the functional organization of the community that is of greater significance than diversity itself.

More recent developments in the ecology of microorganisms have also demonstrated that VOC-degrading systems are dynamic adaptive ecosystems, and not fixed inoculated reactors^[33]. Succession of communities can be achieved as a response to the pollution composition, pH, nutrient addition, temperature, and temporal overloading. This is one of the reasons why inoculation is rarely an effective way of ensuring long-term performance. The problem with most successful systems is that they rely not on the starting strain composition but rather on the capacity of the microbial

assemblage to acclimate, reorganize, and tolerate functional redundancy. Critically speaking, this implies that the next generation of biological treatment of VOCs will not rely only on the search for the so-called best strains, but on the creation of ecological conditions that maintain the metabolic stability under conditions of real atmospheric variability.

2.3. Biochemical Pathways and Enzymatic Mechanisms

In the biochemical process, VOC is degraded by means of enzymes that trigger chemically stable organic molecules and direct these to central metabolism^[34]. Oxygenases are specifically significant under aerobic conditions, as this adds

oxygen to hydrocarbons and thus makes them more reactive so that they can undergo additional transformation. The oxidation of the first step of alkanes, aromatics, and other substituted organics is catalyzed by monooxygenases and dioxygenases, and is often what determines the overall degradability of a pollutant. These are followed by alcohol dehydrogenases, aldehyde dehydrogenases, hydrolyses and peroxidases, which then undergo later conversions to form intermediates that ultimately enter such pathways as the tricarboxylic acid cycle. **Table 1** gives an overview of the enzymes involved in the degradation of VOCs, with the focus being on the contribution of monooxygenases, dioxygenases, and dehydrogenases in the transformation of the enzyme.

Table 1. Enzyme systems involved in biological VOC degradation, including their function and typical VOC substrates.

Enzyme	VOC Class	Function	Typical Application
Monooxygenases	Alkanes, aromatics, terpenes	Introduce oxygen into non-polar substrates, initiating degradation	Degradation of aliphatic hydrocarbons and aromatic compounds
Dioxygenases	Aromatics, chlorinated VOCs	Incorporate two atoms of oxygen, facilitating further oxidation	Treatment of chlorinated VOCs and polyaromatic hydrocarbons
Alcohol Dehydrogenases	Alcohols, aldehydes	Convert alcohols to aldehydes or acids, initiating further degradation	Degradation of alcohols like ethanol and acetone
Peroxidases	Aromatics, phenols	Catalyze the oxidative transformation of aromatic compounds	Removal of phenolic compounds, especially in industrial effluents
Aldehyde Dehydrogenases	Aldehydes, organic acids	Convert aldehydes to acids, enabling further breakdown	Degradation of aldehyde intermediates in complex VOC mixtures

The first activation process is usually the critical point. Most VOCs are chemically inert and hydrophobic, which means that not only do they need physical access into the cell, but also special inducible enzymes^[8]. This is the reason why acclimation periods are typical of biological air treatment systems and why performance failure can occur due to a sudden alteration in influent composition. An ethanol or acetone removal reactor might not react well to a mixture of chlorinated aliphatics or aromatic mixtures since a completely different enzyme system is needed. In addition, the compounds are considered to be some enzyme inhibitors or membrane disrupters, which interfere with the metabolic machinery that they should be degraded by. These effects are particularly important at high inlet loadings or when mixtures consist of solvents of high cytotoxicity.

Another mechanism that is very critical but is poorly understood is co-metabolism^[35]. Incidentally, enzymes induced to degrade a major growth substrate transform some of the VOCs. This is able to widen the elimination range of a framework, particularly for compounds that do not individ-

ually promote the development of microbes. Nonetheless, co-metabolic transformation is invaluable since it requires the presence of a growth-promoting substrate and can produce unfinished products of degradation. Engineering-wise, co-metabolism can be both a threat and an opportunity: it can be used to get rid of otherwise recalcitrant pollutants, but it can also lead to loss of predictability in the reactor and to the likelihood of intermediate build-up^[7].

Caution should be taken, therefore, on the biochemical interpretation of performance data. Useful engineering metrics are elimination capacity and removal efficiency, which do not indicate the nature of degradation, i.e., whether growth-linked, co-metabolic, induction-limited, or toxicity-limited^[36]. In the absence of pathway-level understanding, it is hard to determine whether the observed improvement is biocatalytic or just temporary polluting of the medium or biomass. That is why, today, biological VOC studies tend to incorporate more and more reactor studies with enzymatic assays and molecular analyses in order to relate the removal of pollutants to the real catalytic activity.

2.4. Physicochemical and Operational Factors Controlling Treatment Performance

Biological VOC treatment systems are very sensitive to the environment and operating conditions since all factors of microbial activity, mass transfer, and biofilm organization are contingent on the environment^[7]. **Table 2** provides a summary of the major factors influencing the performance of biological VOC treatment systems, and the factor that

influences the system efficiency and stability. One of the most significant factors is moisture^[22]. Microbial viability requires adequate content of water to allow diffusion of substrates and transport of nutrients. However, overwatering may block the pathways of gases, raise pressure drop, and form anaerobic microzones that may change the pathways of degradation. The ideal moisture window is, hence, system-specific and is associated with packing structure, gaseous flow, and pollutant properties.

Table 2. Factors influencing the performance of biological VOC treatment systems include environmental and operational parameters such as moisture, temperature, pH, and nutrient availability.

Factor	Impact on Performance	Optimal Conditions
Moisture Content	Essential for microbial viability and VOC dissolution; excessive moisture can block airflow	40–70% moisture, depending on pollutant and reactor design
Temperature	Influences microbial activity and enzyme efficiency; extreme temperatures can inhibit microbial growth	20–30 °C for most systems, with adjustments for specific VOCs
pH	Affects microbial metabolism and VOC degradation; extreme pH can hinder microbial function	pH 6–8 for most VOCs, with specific adjustments for acidic or basic pollutants
Nutrient Availability	Microbial growth and enzymatic activity depend on balanced nutrients	Balanced nutrient supply, typically nitrogen, phosphorus, and trace elements
Gas Flow Rate	Affects contact time and the effectiveness of pollutant transfer to biofilm	Optimized based on pollutant concentration and reactor design
Inlet VOC Concentration	High concentrations may inhibit microbial activity and overwhelm system capacity	Gradual load increases to allow for microbial acclimatization and system adaptation

The effect of temperature is equally complicated. Over a biologically permissible range of temperature, temperature is expected to increase enzyme rates and mass transfer, although it can also decrease the solubility of gases and cause unstable microbial populations^[37]. Even the biodegradable pollutants might need preconditioning of the industrial emissions that are of high or varying temperatures. pH is also critical, especially in systems that treat sulfur- or chlorine-containing VOCs that produce acidic metabolites. The slow drop in pH can cause a change in the community structure, inhibit bacterial growth, and promote the growth of acid-resistant fungi. In others, this change enhances the degradation of hydrophobic products, but in most others, the change is an indicator of process imbalance and reduced control of reactor performance.

Another vital determinant is nutrient availability. Due to the fact that gaseous VOC streams usually supply carbon without adequate nitrogen, phosphorus, trace elements, and buffering capacity, nutrient supplementation is necessary to maintain biomass and enzyme generation^[38]. Excessive biomass growth, congestion, and diffusion inhibition can be induced by overfeeding, though. This demonstrates a more general fact of biological air treatment: microbial growth is required to be catalytic, but unregulated growth compro-

mises the performance of the reactor. The task is not merely to maximize biomass, but to have an active and spatially structured biofilm that has a low transport resistance.

The rate of loading inlets and the behavior of shock loading are of particular significance in the application of a real atmosphere where VOC concentrations are not always constant^[39,40]. Microbial systems can function effectively during extended durations under constant low-to-moderate loading. At transient peaks, toxicity of the pollutants and substrate overload may surpass the buffering capacity of the biofilm, leading to temporary breakthrough or long recovery periods. Problematic compounds are especially hydrophobic and inhibitory compounds that can build up in the biomass and have long-lasting toxic effects despite a reduction in inlet concentrations. This is among the primary causes why traditional biofilters, though quite simple, are not as dependable in the highly changing industrial environment as their stable-state laboratory behavior may indicate.

Lastly, the availability of oxygen and distribution of gases also have a significant influence on degradation efficiency^[41]. The majority of the biological VOC treatment systems are aerobic, and there may be local oxygen limitation in the thick biofilms or localized distribution of packing

zones. Skewed gas flow results in channeling, dead space, and uneven growth of biomass, all of which reduce effective utilization of the reactor. These physical heterogeneities are not generally considered when explaining the average performance of the reactor, but they lie at the heart of the scale-up failure. This is because a laboratory column that is uniformly packed and with controlled inflow might not be able to replicate the spatial complexity of full-scale systems, where local mass transfer constraints dominate. The critical observation made on the basis of fundamental research is therefore that the catalytic potential and transport architecture are what define biological VOC treatment, rather than merely microbial degradability.

2.5. Critical Perspective on the Fundamentals

Combined, the principles of biological VOC treatment can show the potential and intrinsic limitations of the technology. Its strongest advantage is the fact that living systems can modify, regenerate, and promote complex oxidation pathways at mild conditions^[7]. The main weakness of it is that this catalytic ability is built into a weak multiphase system that is vulnerable to transport constraints, ecological change, and variability in operation. A lot of the historic flaws in the application of the term poor biodegradability are not due to poor biodegradability, but to an inappropriate reactor design, lack of mass transfer, or failure of microbial functional balance.

Such a difference is crucial as it redefines innovation in the future. The following wave of biological VOC control does not need to aim at finding more degraders or more biomass, but to combine microbial activity with material design, interfacial engineering, and control of mechanistic processes^[42,43]. In that regard, the principles presented herein give the conceptual cover to the technological advances considered in the following section, in which traditional biofilters are reevaluated and enhanced with high performance as well as biocatalytically explicit systems.

3. Biological Treatment Technologies: From Biofilters to Biocatalysts

3.1. Conventional Biofilters

Traditional biofilters form the historical basis of the biological abatement of VOC and are the most well-known

technology in the field^[44]. In the classical form, dirty air is introduced to a porous packed bed that is colonized by microorganisms that are embedded within a thin aqueous biofilm. The first step involves a transfer of the pollutants between the gas phase and the wet surface of the packing medium, followed by absorption, adsorption, and biological oxidation. The packing medium, such as compost, peat, wood chips, bark, activated carbon-amended substrates, or synthetic structured media, is the material that retains moisture, attaches microorganisms, provides nutrients, and drops pressure not only physically but is also a determinant of each. This seemingly simple architecture is why biofilters are attractive, operationally simple, and efficient in treating large amounts of air with biodegradable VOCs at low to moderate concentrations, but they are also very sensitive to the stability of inherently heterogeneous biological and physicochemical reactions.

The main advantage of the traditional biofilters is their economic and ecological compliance with dilute gaseous emissions^[45]. They do not need high external energy input as compared to thermal or catalytic oxidation systems, can operate at ambient temperature and pressure, and do not need high temperatures. This renders them especially appealing to odor control and to hydrophilic or moderately biodegradable substances, including alcohols, ketones, aldehydes, and some sulfur-based VOCs. Besides that, their microbial communities tend to exhibit some levels of functional redundancy and resilience that allow them to adapt slowly to mixed streams of pollutants. This environmental strength has been one of the factors that have led to the continued use of biofilters in wastewater treatment plants, composting sites, food-processing processes, and in the isolated industry.

But what may seem to be the simplicity of biofilters sometimes masks considerable design and working vulnerability. They have limited treatment efficiency due to mass-transfer effects, particularly in the case of hydrophobic VOCs, whose low aqueous solubility restricts their ability to move to the biofilm where biodegradation can occur^[25]. This is to say that the working of a biofilter cannot be seen through the prism of microbial degradative potential; that is, even when the degraders are competent, the system may not be effective due to the inability to bring the pollutant to them at an appropriate rate. The conventional engineering solution has been to adjust the empty bed residence time, media com-

position, moisture content, or gas humidification. However, these trade-offs are usually introduced by such adjustments. Additional moisture can also increase dissolution, but can decrease bed porosity and augment pressure drop. Organic packing materials can enhance microbial colonization but are likely to be compact, degrade, and acidify with time. Therefore, classical biofilters are often excellent in predictable and favorable environments but are less predictable at times of changeable loads, peaks of toxicity, or prolonged industrial use.

The other significant constraint is that it is hard to have spatially uniform performance in the packed bed. The biofilters are naturally heterogeneous systems in which pollutant concentration, oxygen, moisture, pH, and biomass thickness gradients develop as the reactor length increases^[46,47]. These gradients may result in functional zonation, with the control of different populations of microbes in different parts of the bed. Such stratification may be beneficial to sequential degradation pathways, but most commonly, it increases the complexity of operation and scale-up, creating local channeling, biomass overgrowth, dry spots, or anaerobic microenvironments. In practice, the usefulness of a traditional biofilter is not only related to the activity of microorganisms but also to the overall ecology and hydrodynamics of the biofilter in the long run. It is one of the main lessons that led to the further development of more manageable biological systems.

3.2. Biotrickling Filters and Bioscrubbers

The biotrickling filters and bioscrubbers were developed mostly in reaction to the weaknesses of traditional biofilters, most especially the inability to regulate moisture, nutrients, and pH in organic packed-bed filters. Pollutants in biotrickling filters are treated in a packed column continuously or intermittently by recirculating the liquid phase^[48]. The microorganisms reproduce mostly in the form of biofilms on inert or semi-inert packing surfaces, and the trickling liquid provides nutrients, eliminates metabolic waste products, and assists in maintaining a constant water layer as a medium of mass exchange. This design provides a significant operational benefit in comparison with conventional biofilters in that the biological activity is decoupled, at least partially, from the structural instability of organic media. With bioscrubbers, on the other hand, the treatment is better separated into two phases: VOCs are initially captured in a liquid phase

in an absorption column and subsequently biodegraded in a separate suspended-growth bioreactor^[49]. This distinction of absorption and biodegradation gives even more control, but it is often accompanied by more complexity in the system.

The importance of these technologies is found in their higher tunability of operations. Due to the possibility of recirculation and replacement, and chemical manipulation of the liquid phase, biotrickling filters and bioscrubbers tend to be more appropriate for acidic or overloaded emissions, and are able to treat some inorganic or sulfurous gases more effectively than biofilters based on compost^[48,50]. They also prove to be beneficial in cases where VOC degradation produces acid metabolites or in cases of nutrient control of great importance. In terms of engineering, this is a radical change: where the biofilters rely on passive ecological equilibrium to a large extent, the biotrickling filters can offer a higher level of active control over the process. The rate of liquid flow, the dose of nutrients, pH control, and recirculation regime are some of the parameters that can be optimized in response to the variability of the influent composition, increasing reproducibility and simplifying the operation of the industries.

However, the increased controllability does not remove the essential constraints. The biotrickling filters rely on gas-liquid biofilm transfer, and the hydrophobic VOCs are still challenging due to their low dissolution in the liquid phase, hence decreasing the biodegradation of the liquid^[24]. In fact, in numerous aromatic hydrocarbons and chlorinated compounds, biotrickling filters enhance stability as compared to intrinsic treatability. In addition, it is possible that too much biomass may be deposited on inert packing to cause clogging, channeling, and higher-pressure drop, just as in biofilters, but the mechanisms and management techniques vary. New operational risks also arise as a result of the circulating liquid, which comprises foaming, nutrient imbalance, salt accumulation, and the necessity to control the waste trickling water. Whereas bioscrubbers can be more flexible in principle, they have the disadvantage of a lack of sufficient absorption of gases with low solubility, such that the biodegradation step is not fully utilized even with an active microbial population^[51].

Importantly, the decision between biofilter and biotrickling filter, and bioscrubber should not be interpreted as an incremental adjustment of the lack of sophistication to high

sophistication, but as the decision between various forms of tradeoffs between transfer efficiency, biological control, and operational burden^[52]. Traditional biofilters might be more effective than the newer system for treating low-cost, biodegradable emissions from the stables, but biotrickling filters are more robust to fluctuating or acidifying streams. Bioscrubbers are beneficial in cases where both the absorption and the biological conversion should be optimized separately. This implies that technological innovation in the biological control of VOCs was never a linear substitution of older systems by new ones, but rather an increase in the space of design due to variations like the emissions and the control interests.

3.3. Membrane-Based and Hybrid Biological Systems

The evolution of membrane-based and hybrid biological systems is more of an explicit effort to get around the structural constraints of classical gas-biofilm contact^[53]. The polluted air is isolated in membrane bioreactors in which the diffusible pollutant is transported to the microbial phase through a selectively permeable membrane that allows the passage of gas but inhibits the bubbles of gaseous contaminants and excessive shedding of biomass. This structure is capable of expanding the interfacial area of transfer significantly and stabilizing the contact of VOCs and biodegrading microorganisms. More to the point, it opens the potential of having independent control of the gas and liquid compartments and, in this way, curtailing some of the hydraulic and mechanical instabilities synonymous with packed-bed systems.

Systems based on membranes are especially important in compounds where the treatment is limited by the poor contact of gases and liquids or in compounds where the microbial community is sensitive to direct exposure^[53]. These systems can be used to maximize the delivery of target compounds to biodegrading populations by modulating membrane properties, surface area, and flow conditions, while keeping the environmental conditions more stable. But their pledge should be assessed rudely. Membranes increase the cost of materials and can be susceptible to fouling, wetting, loss of permeability, or selectivity issues when used over a prolonged period. The theoretical superiority of interfacial control is, in most instances, balanced off by practical maintenance

requirements, as well as by scale-up limitations. In this way, the idea of membrane bioreactor has a strong appeal; however, the question of their application in the industry lies in whether transfer efficiency and stability improvements can be considered worth the higher complexity.

Hybrid biological systems have also gained increased interest due to the lack of any biological system that can be effective in all VOC emission situations. Two-phase partitioning bioreactors are among the most significant as an organic phase with high affinity for hydrophobic VOCs (non-aqueous) is added to the aqueous microbial one^[54]. The non-aqueous phase is a reservoir and transfer vehicle that enhances the apparent pollutant availability and buffers the toxic shock loads. In the case of hydrophobic and inhibitory VOCs, this design is used to overcome one of the most enduring shortcomings of traditional biofiltration, namely, the incompatibility between low solubility and high levels of biodegradation. Here, the innovation in ideas is obvious. The reactor is reconfigured in such a way that the pollutant is exposed to a more advantageous thermodynamic pathway into the biological system instead of forcing the microorganism to adapt to the restrictions of aqueous-phase transfer.

Other hybrid systems are based on a biological reactor that is integrated with adsorption units, photocatalytic pretreatment, plasma oxidation, or catalytic oxidation^[9]. Such coupled systems are an extension of a wider appreciation that biological treatment is not necessarily the most effective solution to all VOCs, but rather a component of a treatment train in which various technologies are used to overcome various obstacles. Pretreatment can also transform recalcitrant VOCs to more biodegradable intermediates, adsorption can smear concentration peaks and shield biomass against shock loading, and biological polishing can lead to a lower energy requirement and secondary waste as compared to simply physicochemical systems^[8]. These combinations are particularly useful with mixed industrial emissions in which the composition may vary, and certain compounds may be biodegradable and others not.

The emergence of mixed systems demonstrates a significant change in thinking in the domain. The early biological VOC control tended to consider that microbial metabolism was the primary solution under advantageous operating conditions. The more recent designs propose a more nuanced perspective where biodegradation is incorporated within a

larger process architecture that is concerned with optimizing transfer, selectivity, and resilience. In this regard, hybridization is not a manifestation of biological inadequacy, but a biological maturity: the area is becoming more aware that high-performance treatment depends on intelligent non-biological and biological combinations^[9].

3.4. Biocatalytic and Enzyme-Assisted VOC Treatment

One of the most significant changes in the field in the recent past is the shift from whole-reactor biological treatment to specifically biocatalytic strategies. Biofilters and biotrickling filters, which have traditionally been used, rely on the overall metabolic activity of the microbial communities, although individual enzymes such as monooxygenases, dioxygenases, peroxidases, dehydrogenases, and hydrolases ultimately mediate the catalytic process of transforming VOC. More direct ways of exploiting this fact are biocatalytic treatment, which involves immobilized cells, enriched degradative consortia, isolated enzymes, or engineered catalytic assemblies to obtain more selective and controllable pollutant transformation^[55]. This change does not mean the abandonment of microbial systems, but a redirection of these systems from the viewpoint of catalytic functionality.

One intermediate stage in this transition is the system of immobilized cells. These systems aim to increase the density of active microorganisms on designed surfaces or in polymeric matrices by reducing environmental stress on degraders, increasing the reproducibility of catalytic activity, and increasing the density of active microorganisms^[56]. In comparison to loosely structured biofilms in conventional systems, immobilized cells provide easier control over the catalyst localization, and in certain instances, they are more tolerant to toxic substrates. Nevertheless, mass-transfer and deactivation issues are still transferred to them to a great extent, as with larger biofilm systems. The properties of support materials, resistance to diffusional processes in the immobilization matrix, and long-term viability and metabolic expression of the microorganisms are critically important to their performance.

Enzyme-based systems are further advanced by minimizing the use of the entire cell physiology. In isolated or semi-purified form, enzymes have the potential to enable

faster, more selective conversion of VOCs of interest without the overhead of maintaining whole-cell metabolism^[57]. This is especially desirable for compounds that are toxic to living cells or for applications that require transformation rather than complete mineralization. Oxidative enzymes, such as laccases and peroxidases, have also been of interest due to their capacity to attack aromatic or structurally complex compounds. However, the direct application of free enzymes in gaseous treatment is limited by the problems of stability, cofactor needs, vulnerability to inhibition, and expense. Fixation of enzymes on solids enhances reusability and stability, but in most cases reduces catalytic flexibility or creates diffusional limitations. Therefore, the VOC treatment based on enzymes is scientifically promising and technologically up-and-coming.

The biocatalytic paradigm is neither new in the use of enzymes nor a shift of design priorities. The performance of a reactor is commonly referred to as removal efficiency, elimination capacity, and microbial adaptation. With biocatalytic systems, more focus is made on catalytic specificity, control of reaction pathways, engineered surfaces, and focused catalytic rate-limiting steps^[58]. This gives the opportunity to build systems based on the chemistry of transformation and not on ecological acclimation. This strategy is particularly applicable to the case of complex VOC mixtures in which selective degradation of hazardous or vociferous constituents may be more important than total degradation.

Meanwhile, a critical point of view is required. It is not always practical and desirable to substitute robust mixed-culture systems with purified biocatalysts everywhere. Whole-cell communities are self-regulatory, co-metabolically flexible, and capable of adaptive capacity, which is frequently lacking in isolated enzymes. A closer-term path is more realistic, however, and will not be a replacement of biofilter by pure enzyme reactor, but rather a slow percolation of biocatalytic principles into biological reactor design. Cutting-edge support materials, biointerfaces that are enzyme-activated, biointerfaces engineered via genetic optimization, and catalytic hybrid reactors are likely to constitute the transition between the conventional biological treatment and the innovative engineered systems. **Table 3** is a comparative summary of the different types of biological VOC treatment technologies, their benefits, weaknesses, and common uses^[59].

Table 3. Comparison of the key features and limitations of different biological treatment technologies, emphasizing the trade-offs between biofilters, biotrickling filters, bioscrubbers, and hybrid systems.

Technology	Advantages	Limitations	Typical Applications
Biofilters	Low energy consumption, simple design, low operating costs	Limited for hydrophobic compounds, sensitive to shock loads	Odor control, wastewater treatment, food processing
Biotrickling Filters	Enhanced control over pH and nutrients, stable for acidic streams	May suffer from clogging, lower efficiency for hydrophobic VOCs	Industrial emissions, odor control, petrochemical facilities
Bioscrubbers	Effective for acidic VOCs, improved VOC absorption	Complexity in liquid-phase management, higher maintenance	Chemical manufacturing, agricultural VOCs
Hybrid Systems	Optimized VOC removal for complex mixtures, enhanced mass transfer	Increased system complexity, potential cost increase	Mixed VOC streams, high pollutant concentration industries
Biocatalytic Systems	High specificity, targeted removal of recalcitrant VOCs	Costly enzymes, potential loss of catalytic efficiency over time	Specialized VOC treatment, high-value applications

3.5. Technological Evolution and Comparative Perspective

Collectively, these technologies demonstrate that a consistent challenge, namely, how to transfer the pollutants to active catalysts, how to control the biological activity, how to respond to the variable emissions, and how to treat the hydrophobic or inhibitive compounds, has been a central focus of the development of biological VOC treatment. Traditional biofilters dealt with the removal of VOC using the simplicity of the ecology and the low cost of operation^[10]. Bioscrubbers and biotrickling filters came in with more active control in the liquid phase^[48]. Membrane and hybrid systems tried to create the interfacial and process environment more specifically^[60]. Biocatalytic methods, in their turn, have started to pay closer attention to the catalytic machinery on which pollutant conversion is based^[61].

This trend explains why this paper uses the framing of biofilters to biocatalysts. It is not simply a case of the field experiencing the accumulation of variants of reactors, but is increasingly moving beyond passive dependency on natural biodegradation to deliberate designing of biological transformation systems. The issue at hand is now to turn mechanistic sophistication into scalable, sustainable, and economically viable technologies. The further development will not rely on the production of totally new categories of reactors but on the amalgamation of material engineering, microbial resource development, and catalytic understanding of coherent platforms that would fit actual atmospheric emissions. That way, the future of biological VOC treatment might not lie in any single technology, but in the systems that are capable of integrating the strength of biofiltration with the accuracy of biocatalysis^[9].

4. Recent Advances and Performance Enhancement Strategies

The invention of new classes of reactors has not been the least important factor in the recent development of biological VOC treatment, but rather the continued improvement of the physical, biological, and informational layers according to which process performance is maintained^[9]. The classical methods, including biofilters and biotrickling filters, are no longer judged based on the inlet and outlet concentrations only or on mere elimination capacities. Rather, they are gaining more recognition as complex bioengineered systems whose performance relies on the architecture of support materials, microbial community structure and dynamics, catalytic structuring of degradation pathways, and real-time control and monitoring of such processes^[62]. The change toward the use of mechanisms as the basis of improvement over empirical maximization is among the key characteristics of the recent development of the field.

These advances can be helpfully understood as the fact that the majority of longstanding bottlenecks in biological VOC removal are due to incompatibilities between four coupled domains: pollutant transfer, microbial functioning, reactor stability, and process controllability^[9]. Hydrophobic substances are not able to reach active cells effectively; specialized degraders are frequently outcompeted or destabilized with mixed loading conditions; biomass filtration and metabolite synthesis slowly degrade hydrodynamics, and traditional methods of monitoring can only indicate degradation once treatment efficacy has been impaired. Recent improvement approaches are trying to respond to these shortcomings not individually but in a synchronized manner, by means of interventions in materials science, microbial ecology,

systems biology, and process engineering. In this, the discipline is headed to a more unified idea of biological air therapy, whereby performance is planned and not just monitored.

4.1. Novel Packing and Support Materials

Support materials have been central in biological VOC treatment; however, the role now has a more advanced interpretation than mere microbial adherence or retention of moisture^[7]. Traditional biofilters tended to use whatever was available and choose packing materials with the primary consideration being their porosity, the ability to hold water, and their cost. Organic matter compost, peat, bark, and wood chips had an inherent nutrient content and good colonization quality, but tended to compaction, degradation, acidification, and unstable long-term hydrodynamics. On the contrary, inert materials enhanced mechanical stability, but in many cases, did not have the interfacial properties to maintain high biological activity. Recent studies have hence been aimed at the design of support media that have active promotional functions on transferring pollutants, organizing microbes, and catalytic stability.

Biochar has become one of the most important materials in this regard. It is desirable as a sportive medium, as it has a high surface area, porosity, tunable surface chemistry, and relative chemical stability, and as a microbial carrier because it has a high surface area and is porous. Biochar can be used in biochemical VOCs to enhance transient adsorption of pollutants, particularly hydrophobic compounds, and hence reduce shock loading as well as contact time between contaminants and biodegrading populations^[63]. Simultaneously, its porous surface offers covered colonization sites, which might shield microorganisms against mechanical damage and toxicity. The benefits of biochar should not, however, be overrated. Its properties are diverse depending on feedstock and pyrolysis conditions, and it is very system-dependent. Sometimes, intense sorption can postpone biodegradation instead of accelerating it in the event of a limiting desorption to the bioactive phase. The usefulness of biochar is therefore not in its novelty, but in its capacity to achieve a balance in its sportive and biological properties in the reactor environment.

Functionalized and composite materials are another step in the rational carrier design. Researchers are building media that integrate structural polymers, mineral con-

stituents, activated carbon, metal oxides or surface-modified biogenic substrates in order to couple mechanical durability with customizable interfacial characteristics. These materials can enhance wettability, pollutant affinity, pH buffering, or anchoring of biofilms, and therefore multiple operational constraints can be mitigated at the same time^[9]. Of particular significance is the increasing amount of effort put into making carriers to be designed towards selective enhancement over general support. In the case of hydrophobic VOCs, the carriers can be designed to partition more into the biofilm interface, in acidifying systems, buffering capacity can be added, in enzyme-assisted processes, functional groups can be added to stabilize catalytic molecules or enable immobilization. This demonstrates a bigger trend: the support materials do not serve as the passive scaffolds any more but rather active elements of the treatment performance.

There has also been interest in nanostructured and advanced porous materials and how they might increase interfacial transport and change microbial activity at small scales^[64]. Substances with nanoscale structures have the potential to enhance the specific surface area and local adhesion behavior, moisture distribution and catalytic accessibility^[65]. However, their use in the biological air treatment is at an early stage. Although laboratory research frequently claims a higher removal performance, the understanding of the mechanism is not always conclusive, and issues of long-term stability, economic viability, and potential environmental hazards of the release of materials or deactivation are still of concern. Critical evaluation of this literature would indicate that material innovation can be most effectively useful when associated with clearly defined process requirements as opposed to being undertaken as a generic path towards high performance. The future significance of the advanced carriers will be based on the possibility of providing sustained benefits in mass transfer and biological stability at the scale of the real atmospheric treatment systems.

4.2. Microbial Resource Engineering

Microbial resource engineering defines the biological capability of a physical architecture of treatment as determined by support materials^[66]. Conventional systems tended to use natural communities that were mixed and were enriched with time, which adjusted to the incoming VOCs. This approach is still applicable, especially since the mixed

consortia are stronger and more likely to be representative of the industrial operating conditions than the isolates in the laboratory. Nonetheless, in recent years, it has been demonstrated that it is possible to boost biological performance by directing the composition, the structure, and the pattern of interaction of microbial communities in a more intentional manner.

Enhancing and bioaugmenting specialty degraders, which can degrade recalcitrant, toxic, or hydrophobic VOCs, has been one such strategy^[67,68]. Principally, the addition of strains whose degradation pathways are known to us should increase startup time, enhance elimination capacity, or increase substrate range. Practically, the results have been varied. Augmented strains often do well under artificial conditions but cannot take over and survive in established communities, where competition, predation, and environmental incompatibility constrain their long-term effect. This has resulted in a more critical view of bioaugmentation: success is not just determined by the degradative ability of the introduced organism, but ecological compatibility with the resident community and the environment of the reactor. The main problem, therefore, is not merely to introduce microbes, but to develop conditions that promote the expression of functions of interest in the long term.

This difficulty has triggered curiosity in synthetic consortia and functionally engineered microbial assemblages. Instead of having a single elite degrader, researchers are becoming more attracted to the significance of cooperative metabolism, niche partitioning, and the sharing of intermediates^[69]. Mixed VOC streams can be started with one population oxidizing a hydrophobic aromatic, another population oxidizing one of the toxic intermediates, and another population keeping the environmental conditions conducive to the catalytic core of the community. To design such consortia, it is necessary to know how the populations are interacting in their metabolic and spatial forms. Synthetic consortia have the potential to integrate specialization with resilience, and thus, that is the promise of synthetic consortia^[70]. Their weakness is that an engineered balance cannot be maintained easily in open, long-term, continuously running systems. Microbial resource engineering, therefore, is still primarily an ecological design issue rather than a microbiological issue.

A particular theme here has been the interactions between fungi and bacteria^[71]. Fungi have an advantage in

accessing hydrophobic pollutants by their filamentous morphology and surface characteristics, whereas bacteria may supplement fungal metabolism by taking downstream products or stabilizing biofilm activity. These collaborations are very applicable to VOC mixtures that are problematic for solely bacterial systems. However, they make reactor control more difficult as well because fungal overgrowth may increase pressure drop and change the distribution of gases. Whether fungi are helpful or not is not a critical question, but under what structural and operational conditions are their benefits more than their hydrodynamic cost. Recent evidence indicates that the most fruitful way would be controlled fungal participation, and not the uncontrolled fungal dominance.

In addition to the community composition, the molecular-level interventions are gaining importance. To enhance tolerance and substrate specificity, adaptive laboratory evolution, enrichment of metabolic pathways, and, in a few studies, genetically engineered degraders have been studied^[72]. These policies are closely connected with the overall transformation into biocatalytic thinking. Nevertheless, their conversion into biotreatment in the atmosphere is limited by the biosafety concerns, regulatory ambiguities, and the difficulty of maintaining engineered characteristics in the competitive reactor ecosystems. To date, it seems that guided ecological selection and community management based on functions are the most likely to provide realistic progress as opposed to the outright introduction of highly engineered microbes on a large scale.

4.3. Molecular and Omics-Based Insights

Although this is probably the most radical recent change in the bio-VCO treatment, the use of molecular and omics-based methods on processes that used to be treated as black boxes has been particularly transformative. The classical literature tended to deduce microbial functionality based on the performance metrics of a reactor, their enrichment behavior, or a few cultivated isolates. This method was helpful but blurred the inner structure of the microbial communities and could hardly tell why the systems worked, failed, or reacted in an unpredictable way to operational strains. This is starting to be changed with metagenomics, meta transcriptomics, proteomics, and metabolomics, which allow communities to be associated with real catalytic and

physiological processes based on their composition and gene content^[73].

Metagenomic studies have demonstrated that seemingly homogenous reactors can harbor functionally different microbial communities, and that the process of pollutant removal has been linked to a broader spectrum of metabolic potential than was previously considered^[74]. This has streamlined the idea of biodegradative potential: the distribution of the relevant functional genes in the community and their redundancy in changing conditions is a less informative measure than whether a pollutant-degrading taxon is present. That is, the resilience of biological VOC treatment is not necessarily determined by the dominance of one degrader, but distributed functional capacity of the ecosystem.

Transcriptomic and proteomic tools move a step further to show active expression of which pathways occur in the course of treatment^[75]. This especially comes in handy when it comes to the differentiation of latent capacity and operational function. A reactor community can have aromatic degradation genes, but in certain environmental circumstances, such genes can be silenced, and stress-response routes are preeminent. These differences can be used to understand why systems of related communities can exhibit entirely different performance in response to transient loading, pH changes, or even toxic loading. They also demonstrate that most of the operational failures are not caused by a lack of degraders but rather loss of catalytic expression caused by physiological stress.

Metabolomics can provide more information by monitoring the process of intermediate formation and pathway development^[76]. This is necessary since not all biological elimination of VOCs may be equated to full detoxification. These may be intermediate aldehydes, acids, epoxides, or even partially oxidized aromatics that develop temporarily or persistently, affecting system stability and the safety of the environment. The combination of metabolite data with transcriptomic and proteomic data can enable a more realistic determination of pathway completeness and bottlenecks. It also creates an opportunity to discover signature metabolites related to early reactor stress, incomplete mineralization, or changing degradation related to growth to co-metabolic transformation.

Omics approaches, although promising, are to be taken with a grain of salt^[77]. Their data sets are not easy to create,

are costly to create, and are not always related to engineering decisions. One pitfall is descriptive excess: listing the complexity of the community without deriving action-relevant process understanding. The real worth of omics is not the amount of information generated, but how it can be used to inform the design of reactors, their operation, and the management of microbes. When put into proper use, these tools can enable the field to shift away from correlation-based observation to the causal interpretation of performance.

4.4. Process Intensification, Modeling, and Intelligent Operation

Improvements in materials and microbiology are also changing how biological VOC treatment is being reshaped through process intensification and digital control strategies^[7]. In the past, most systems were operated on a semi-empirical basis where performance was evaluated by periodically monitoring influent and effluent levels. This paradigm is no longer sufficient to the current practice, where the emissions vary, treatment trains are combined and the performance is no longer limited to removal but it is also desired to be stable, selective and have a low environmental footprint. New strategies hence focus on real-time sensing, predictive modeling, and adaptive operation.

Intensification of processes in this area can take the form of the identification of the fact that the traditional systems are not efficient in terms of the use of reactor volume due to the lack of spatial optimization of catalytic activity and transfer conditions. To enhance contact efficiency and minimise the occurrence of dead spaces, excessive biomass layers or uneven pollution gradients, structured packings, staged reactors, segmented nutrient dosing, and controlled moisture regimes are under consideration. Multi-stage designs can be used in certain cases so that various parts of a system can favor different microbial populations or different stages of sequential degradation, which makes the treatment more robust when dealing with mixed VOC streams^[78]. These interventions are indicative of a wider rejection of the supposed assumption that a homogenous biofilm bed can be effective in dealing with the complexity of actual gaseous emissions.

There has also been an increase in mathematical modeling of simple empirical fits to more mechanistic formulations that include gas-liquid transfer, diffusion through biofilms,

microbial kinetics, and community adaptation^[79]. These types of models can be useful in performance prediction as well as finding the latent constraints. As an illustration, the loss of efficiency in removal can be related to transfer resistance and not to intrinsic biodegradative activity; a model can be used to differentiate between the two and implement relevant interventions. More and more hybrid models are found that integrate mechanistic structure with data-driven components in recognition that biological systems are too complex to be predicted by purely first-principles methods, but too structured to be treated by purely statistical methods.

These models are becoming actionable with real-time monitoring technologies. VC concentration, humidity, temperature, pressure drop, pH, oxidation-reduction conditions, and, in certain instances, dissolved oxygen or off-gas composition sensors give continuous information about a process, which can provide an early warning of instability. This becomes especially necessary since the biological systems tend to be degraded slowly and asymmetrically. An outlet VOC breakthrough can generate a lot of internal disruption before

it becomes evident. Smart monitoring enables control of the intervention at an earlier stage by changing irrigation rate, nutrient dosage, gas flow, residence time, or pretreatment. Process optimization and real-time monitoring are important functions to ensure the stability and efficiency of biological VOC treatment systems, as shown in **Figure 2**^[80]. The role of such systems in the future does not just entail automation, but rather renders the biological treatment more predictable and more responsive to the changing industrial conditions.

Another philosophy of control, which is promoted by digitalization, is another one. Rather than considering reactor biology to be opaque and self-regulating, intelligent operation considers reactor biology to be somewhat observable and controllable. This is an essential conceptual breakthrough. Biological VOC systems do not have to be empirically contained green boxes, and with proper sensing and interpretation, they can become actively regulated catalytic spaces^[81]. The difficulty is to make sure that data acquisition is converted into solid control logic as opposed to gathering as wasted complexity.

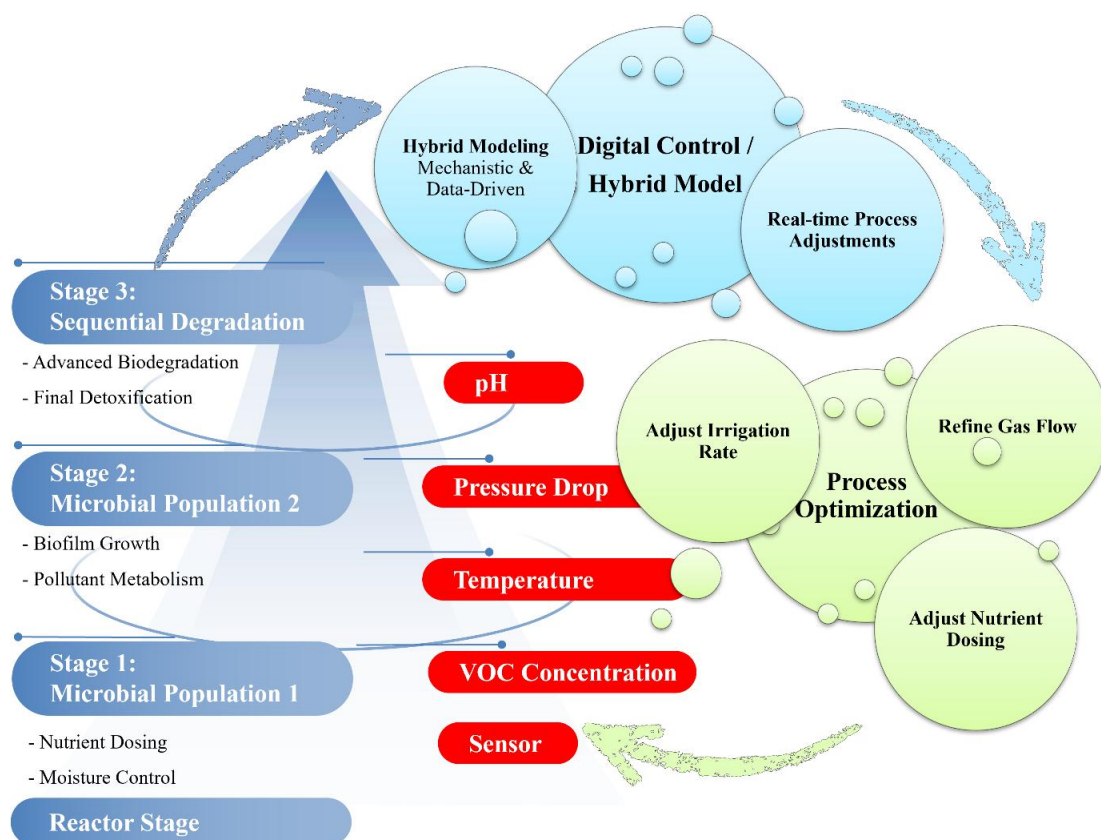


Figure 2. Illustration of process optimization and monitoring in biological VOC treatment systems, highlighting real-time sensor integration and intelligent operational control.

4.5. Integrative Perspective on Enhancement Strategies

The commonality of the current developments in the field is that there is a slow coming together of biological treatment with the concepts of engineered catalysis and systems design^[82]. New materials enhance the interfaces and structural environment of degradation. Microbial resource engineering tries to sculpt the catalytic community. Omics tools reveal the functional and failure molecular fundamentals. Intelligent control and process intensification are to ensure that the same function is maintained in a realistic loading condition. All these strategies are not enough. The lack of ecological stability in material innovation can be self-destructing; the lack of transfer optimization in advanced microbial communities can be underutilized; the lack of engineering application in omics can be descriptive; the lack of mechanistic interpretation in monitoring can give minimal control value.

The most significant lesson to learn thus is that performance improvement in biological VOC treatment is no longer an issue of incremental optimization of specific parameters^[7,83]. It is more and more relying on the coordinated integration at scales, both molecular pathways and reactor architecture and operation. It is also this system-level perspective that allows one to understand why certain seemingly promising laboratory discoveries fail to work at scale: they do a better job at one part of the system and ignore how that system interacts with other systems. The future problem is to transform these new developments into coherent, scalable treatment systems that can maintain the low-energy benefits of biological processing and surmount the instability and selectivity drawbacks that have historically limited the technology.

In that regard, the latest advances discussed in this section can be seen as a shift in the intellectual identity of the field. Biological VOC treatment is transforming into a less empirical but more multidisciplinary platform based on materials design, microbial ecology, catalytic science, and digital process engineering^[84]. The question, however, is whether these advances are enough to endure in real-life limitations, which have continued to hamper progress. The difficulties, trade-offs, and barriers to implementation are discussed in the next section as a direct result of that problem.

5. Challenges, Environmental Trade-Offs, and Practical Applications

Although the current developments in the field of biological VOC treatment are promising, there are still major challenges that prevent their implementation and sustainability. Although there have been tremendous gains in the area of improving performance by use of novel materials, engineered microbial systems, and improved process control, these have come with their fair share of trade-offs and operational challenges. The implementation of the treatment technologies for biological VOCs in practice, and especially in the real atmosphere, should take into account the significant importance of technical constraints, environmental effects, and economics. This section discusses these challenges in detail, with a look at the technical bottlenecks that keep on limiting system performance, the environmental hazards of using biological VOC treatment, and the practical challenges of scaling up these technologies to industrial and commercial applications^[17,85].

5.1. Technical Bottlenecks

The primary technical challenges associated with biological VOC treatment arise from several factors, including mass transfer limitations, microbial stability under fluctuating conditions, treatment of mixed VOCs, and the risk of system fouling and clogging^[7]. These factors impact both the efficiency and reliability of biological systems, often making them less predictable than their physicochemical counterparts.

5.1.1. Mass Transfer Limitations

The movement of pollutants from the gas phase into either the biofilm or aqueous phase, where microbial breakdown is possible, is one of the basic bottlenecks in the biological treatment of VOC^[12]. In the case of hydrophilic compounds, the issue of mass transfer is not severe, as such compounds dissolve easily in the aqueous phase. But in hydrophobic VOCs, like many aromatics, terpenes, and chlorinated compounds, their low solubility in water causes them to be unable to diffuse out of the gas phase into the biofilm, where microbial activity occurs. This leads to inefficient degradation rates, and the concentration of the pollutant in the biofilm is restricted.

In the traditional biofilter, the gas-biofilm contact is usually passive and is highly reliant on the physical characteristics of the support medium. In the case of hydrophobic VOCs, contact time can be increased by extending the bed height or by adding more moisture. This can be accompanied by operational complications, including an increase in pressure drop, an increase in maintenance costs, and a heightened risk of clogging^[24]. Although support materials have been improved and may result in increased solubility and surface interactions, high degradation rates of low-solubility compounds still remain a major challenge.

5.1.2. Microbial Community Instability

Although biological treatment systems in a natural state are inherently resilient and flexible, microbial communities may exhibit an unstable state due to varying environmental parameters^[86]. Numerous biological VOC systems have been developed to operate under constant, predictable conditions. Still, in practice, the true sources of emissions may be quite variable concerning pollutant concentration, composition, and variability of the load. Such variability may create disturbances in the activity of microbes, especially in more complicated mixed VOC streams.

Biological treatment systems contain microbial communities that are exposed to numerous stresses, including nutrient imbalances, pH changes, and changes in temperature and toxic metabolite buildup^[87]. Such stresses may lead to a change in the composition of the communities, with a number of strains dominating the others, which could decrease the overall efficiency of the system. When a dominant microbial strain is overwhelmed or outcompeted, the reactor can have a performance degradation or even reach the failure of the entire system. Moreover, the change of microbial communities towards novel or unfamiliar contaminants is not instant; that is, systems are likely to be inefficient or slow in starting when they are subjected to novel combinations of VOCs^[88]. This variability means that it is hard to design biological systems that can effectively treat complex, mixed, and changing VOC streams.

5.1.3. Treatment of Mixed VOCs

In the majority of real-life VOC emissions, these are complex mixtures of volatile organic compounds with unique physicochemical properties. This complicates the biological

treatment process since microbial communities tend to be adapted to degrade certain compounds. Some compounds in a mixed VOC stream can be degraded effectively, and others can be recalcitrant or toxic to the population^[89]. In addition, certain VOCs are also inhibitors to the enzymes involved in the degradation of them, which diminishes the total ability of the microbial system to treat the entire mixture.

To illustrate, certain VOCs have the capacity to inactivate the enzymes of microbes, hence making them ineffective in breaking down other pollutants in the stream. Co-metabolism, in which microbes break down one compound and at the same time convert another, can assist in increasing the list of compounds that can be treated in other instances^[35]. This, however, must be optimized for the microbial consortium and reactor conditions. The capability of a biological system to treat mixed VOCs and, more so, under high levels of some of the pollutants, is also a significant challenge to the successful application of biological VOC treatment systems in practice.

5.1.4. Fouling and Clogging

Another major technical problem is fouling and clogging of the reactor systems, especially in biofilters and biotrickling filters^[90]. With time microbial growth, buildup of organic material, and formation of extracellular polymeric substance (EPS) may result in thick biofilms that prevent the passage of air, limit contact of gases with biofilm, and raise pressure drop. This is especially common with systems that use organic packing materials, which may degrade and compress with time.

Although in biotrickling filters the recirculating liquid phase provides an advantage of greater pH and nutrient control, it may also contribute to the development of biofilm fouling and so cause operational problems of poor nutrient distribution, lack of mass transfer, and eventual clogging of reactor channels^[91]. Moreover, the salts and other by-products deposited in the liquid state can add to the clogging and the necessity to perform the frequent maintenance.

Fouling prevention needs constant monitoring and treatment, which may raise the operational costs and complexity^[92]. In other instances, there might be a need to use further pre-treatment methods like filtration, coagulants to minimize the accumulation of biomass and other substances that help clogging.

5.2. By-Products and Environmental Risks

Although biological VOC treatment is regarded as a green technology because it does not consume a lot of energy and it produces few secondary wastes, it is not risk-free to the environment. According to **Table 4**, the breakdown of VOCs

is usually accompanied by the production of by-products, some of which can be toxic, non-biodegradable, or even more toxic than the original contaminants^[93]. These by-products may either accumulate in the biofilm, recirculating liquid phase or the exhaust gas stream, which is hazardous to the environment and safety.

Table 4. Environmental risks and trade-offs in biological VOC treatment, including by-product formation, incomplete degradation, and greenhouse gas emissions.

Environmental Risk	Description	Potential Solutions
Incomplete Degradation	VOCs may undergo partial oxidation, producing toxic or persistent intermediates	Advanced monitoring, additional post-treatment steps, and pathway optimization
By-Product Formation	VOC degradation may lead to harmful by-products like aldehydes or acids	Reactor design adjustments to minimize by-product accumulation and enhance mineralization
Greenhouse Gas Emissions	Biological systems may produce methane, a potent greenhouse gas, during anaerobic degradation	Process optimization for aerobic conditions, methane capture for energy recovery
Toxic Intermediate Accumulation	Intermediate metabolites may accumulate, affecting reactor performance and safety	Implementation of real-time metabolite monitoring, adjustment of microbial consortia
Secondary Pollution	VOC degradation can lead to the formation of secondary pollutants like ozone and particulate matter	Control of exhaust air, integration with other emission control technologies

5.2.1. Incomplete Degradation and Toxic Intermediates

Most of the VOCs do not completely degrade in biological systems, leading to the occurrence of toxic intermediates that may either remain in the system or the effluent stream^[7]. As an example, some aromatics can be degraded by oxidation, but the intermediates (e.g., phenols or aldehydes) can be recalcitrant to further degradation by microorganisms^[94]. These intermediates may be deposited in the reactor and be poisonous to the microbial population, which further slows down the system's ability to break down the original VOCs. This is especially worrying in the context of industrial emissions, whereby complex VOC mixtures can have a large number of unknowns or poorly characterized compounds that can have special degradation requirements.

Although the ultimate objective is to completely convert it into carbon dioxide and water, this is not always the case. Biological systems can, in certain instances, lead to the generation of by-products that might need further treatment or disposal, which adds to the overall environmental impact of the treatment process. Also, the synthesis of by-products can cause the formation of secondary pollutants, including ozone or particulate matter, which also makes it difficult to assess the environmental impact^[8].

5.2.2. Greenhouse Gas Emissions

Even though biological VOC treatment systems are regarded as more sustainable than thermal or catalytic treat-

ment systems, they may also release greenhouse gases (GHG), particularly in the case of organic substrates and carbon-containing pollutants^[95]. To give an example, aerobic degradation can convert some VOCs into carbon dioxide, although the degradation of some pathways by some microbes can also lead to the generation of methane, an extremely powerful greenhouse gas. In environments where the treatment system is anaerobic or where there is low oxygen, like in low oxygen environments, there is the possibility that methane gases will become a major issue.

Moreover, when the VOCs have sulfur, chlorine, or other halogens, their breakdown can lead to the production of dangerous by-products like hydrogen sulfide, sulfuric acid, or hydrochloric acid^[96]. These substances might need further neutralizing or treatment in order to avoid contamination of the environment. Consequently, although biological systems have immense advantages over the conventional approaches in regard to energy use and cost, they are not completely devoid of the environmental hazards of transforming pollutants.

5.3. Scale-Up and Industrial Implementation

The major hindrance to the extensive use of biological VOC treatment technologies has been their scale-up between laboratory and industrial levels of utilization^[97]. Although these systems have performed well in small-scale and pilot-scale projects, the transfer of their performance to large-scale

industrial projects is a complicated and unpredictable process.

5.3.1. Laboratory-to-Pilot-to-Full-Scale Transition

Ensuring similar performance in the various scales is one of the most important problems in scaling up biological treatment systems. Whereas laboratory and pilot-scale reactors are often optimized based on a particular pollutant and operating conditions, full-scale systems are much more varied in the conditions under which they can operate, such as changing pollutant concentrations, complex mixtures, and varying environmental conditions, such as temperature and humidity^[7].

Laboratory-scale systems are often intended to be run under controlled conditions, with a given rate of gas flow, residence times, and concentrations of pollutants^[98]. Nevertheless, full-scale industrial emissions can differ greatly under such conditions, and it is necessary to make modifications to the reactor design, materials choice, and control process measures. Furthermore, the process such as scaling up predisposes more risks towards the operational problems of uneven flow distribution, pressure drop increase, and more complex maintenance procedures.

5.3.2. Process Optimization and Long-Term Stability

The optimization of the biological treatment processes to the actual real-world conditions is one of the major obstacles in the implementation of the biomedical industry. Complex mixtures of VOCs are common in industrial emissions that are not easily predictable or described; thus, it is hard to design systems that can be trusted to treat complex mixtures of VOCs^[99]. Additionally, the VOC levels might change with time, which creates further difficulties in keeping the microbial activity and performance constant.

Another consideration is stability in the long run. The many biological systems can operate effectively under constant operating conditions, yet fail to perform when subjected to extended periods of high pollutant loadings, temperature variations, or other environmental pressures^[100]. The survival and dependability of the biological systems are essential to their effective use in industries, particularly in the industrial processes that produce VOC that is consistent or widely fluctuating.

5.4. Economic and Regulatory Considerations

Besides the technical issues, the financial and regulatory environment also contributes to the viability of the biological VOC treatment technologies^[101]. Although biological systems tend to be relatively cheaper than conventional physicochemical systems with regard to both energy use and cost of operation, the initial cost, their maintenance needs, as well as the price of support materials and microbial systems may also be a great obstacle.

5.4.1. Cost-Effectiveness

The economics of biological VOC treatment systems are mostly influenced by the size of the system, reactor design, and stability of the system^[7]. Biological treatment can be a cost-effective solution to a variety of applications, especially those involving industries where VOCs are emitted constantly, since it does not require much energy or minimal chemistry or catalysts. Nonetheless, systems that need continuous maintenance, microbial inoculation, or a change in materials may soon become cost-prohibitive.

Additional pre-treatment steps (i.e., filtration or adsorption) to minimize the effects of toxic compounds or impurities might also raise costs^[17]. It is a question of striking a balance between the capital investment and the operating efficiency in the long term so that the biological systems should be economically viable compared to other treatment processes (particularly in the case of low-concentration or mixed-pollutant streams).

From an economic perspective, biological VOC treatment is most attractive for dilute, high-flow, and biodegradable emissions, where thermal oxidation or catalytic incineration may require excessive energy input. Full-scale biofilters and biotrickling filters can reduce operating costs because they function under ambient temperature and pressure and generally require limited chemical addition. However, the total cost depends strongly on reactor size, packing-media lifetime, humidification demand, pressure-drop-related energy consumption, nutrient supply, biomass control, pretreatment requirements, monitoring systems, and periodic media or catalyst replacement. Therefore, cost-effectiveness should be assessed not only by removal efficiency but also by long-term stability, maintenance frequency, downtime, and the ability to maintain performance under fluctuating industrial VOC loads.

5.4.2. Regulatory Compliance

VC regulations are getting stricter, especially in areas where the quality of air is very strict^[102]. Although it is almost a norm to prefer the use of biological treatment technologies due to their minimal environmental impact, they still should pass the strict regulatory standards regarding the level of emission, the formation of by-products, and the general characteristics of the functioning. Making sure that biological systems do not violate these regulations and, at the same time, keep operating in a stable manner, at the same time, cost-effectively is a crucial issue.

The air quality regulatory standards in certain instances might not reflect the peculiarities of the bio-treatment process, especially when it comes to the formation of by-products or incomplete mineralization of VOC^[96]. Consequently, the industries will have challenges proving compliance, particularly when it comes to complex or ill-defined emissions. This highlights the need to do further research to come up with standardized measures of assessing biological VOC treatment technologies so that clearer guidelines on how to be allowed into the law can be provided.

In practical implementation, biological VOC treatment has already shown relevance in odor and emission control at wastewater treatment plants, composting facilities, landfills, food-processing units, petrochemical operations, and coating- or solvent-related industrial exhausts. These examples indicate that the technology is especially suitable where emissions are continuous, relatively dilute, and biodegradable, although hybrid systems may be required for complex or hydrophobic VOC mixtures. From a regulatory viewpoint, full-scale systems must demonstrate stable outlet VOC compliance over long operating periods and under variable humidity, temperature, and pollutant loading. In addition, regulators and operators should consider not only parent VOC removal but also incomplete mineralization, formation of toxic intermediates, odor release, greenhouse gas emissions, liquid effluent management, and pressure-drop development. Including these parameters in monitoring protocols would improve confidence in the environmental safety and regulatory acceptance of biological VOC treatment.

Although the VOC treatment using biological methods has significant benefits compared to the conventional ones regarding sustainability, energy consumption, and minimal impact on the environment, there are still considerable issues

that have to be resolved before these technologies can be used on a large scale^[7]. Technical constraints in the mass transfer, microbial stability, and the processing of mixed VOCs necessitate further development in reactor construction, in microbial resource development, and in process management. On the same note, any environmental risks that are related to the unfinished degradation and generation of by-products should be taken into consideration to make sure that the bio-treatment is really a green solution. Lastly, the economic and regulatory factors that come with the process of scaling up biological systems for use in industries should be considered when developing cost-effective and regulatory treatment platforms.

There will be a need to pull together across disciplines to overcome these challenges by combining the efforts of material science, molecular biology, process engineering, and systems design. Biological VOC treatment can be one of the foundations of sustainable air pollution control in the future, providing a feasible and effective method of controlling VOC emissions into the atmosphere in the decades to come by removing these technical, environmental, and economic barriers.

6. Conclusions

Volatile organic compounds (VOCs) biological treatment has undergone considerable changes during the past decades, with substantial advances in the basic understanding of the principles, the optimization of the reactor design, and the improvement of the microbial and enzymatic potential. From conventional biofilters to advanced biocatalytic systems, the discipline has moved away from passive environmental processes to more regulated, efficient, and integrated biological systems. These technologies promise to provide a solution to one of the most urgent environmental problems of VOC emissions and provide alternative ways of sustainable treatment to the chemically demanding, energy-intensive physicochemical treatment processes.

Recent developments have drawn attention to the possibility of integrating engineered materials, management of microbial resources, and improved process control in order to overcome the shortcomings that have conventionally inhibited the ability of biological VOC treatment. Such materials as biochar, functionalized composites, and nanostructured

carriers have enhanced mass transfer, solubility of the pollutant, and microbial stability. In the meantime, the design of microbial consortia, synthetic communities, and enzyme-based systems has allowed more directed, robust, and effective treatment of even the most recalcitrant VOCs. Also, the incorporation of molecular biology techniques, including metagenomics, transcriptomics, and proteomics, has offered more information on the metabolic routes and functional diversity of VOC-degrading microorganisms, which can be used to design and operate the reactor more efficiently.

Though these breakthroughs have been made, the process of extensive industrial adoption of biological VOC treatment technologies is still a challenging one. Problems like the mass transfer constraint, microbial instability in changing conditions, the treatment of mixed VOCs, fouling and clogging, and the creation of harmful by-products still remain major obstacles. Moreover, the economic and regulatory challenges of implementing these technologies on a large scale are significant, particularly in terms of startup costs, maintenance, and regulatory compliance. The design of biological treatment systems should not be limited to high performance and efficiency, but also stability and scalability in real-life industrial situations where the concentration and composition of the VOC can vary.

However, the prospect of biological VOC treatment is bright. Further penetration of systems biology into material science, process engineering, and smart monitoring can provide the solution to most of the existing shortcomings. Mixed and complex VOC streams would be better solved with hybrid systems involving biological treatment in addition to other advanced technologies, including adsorption or catalytic processes. Moreover, novel digital tools, real-time control, and predictive modeling can improve the regulation, flexibility, and stability of biological treatment systems and make them stronger and more cost-effective when applied at a large scale.

Summing up, though the biological VOC treatment is still in its infancy, the treatment type promises great potential to serve as a sustainable and affordable way of dealing with atmospheric VOC emissions. The low energy use, little secondary pollution, and the flexibility to different pollutants make it a desirable alternative to the conventional practices. Interdisciplinary research and innovation to continue to tackle technical, environmental, and economic issues will

make biological VOC treatment a foundation of air pollution control technologies in the future, with the addition of cleaner air and a healthier environment.

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