



Review Paper

Biofiltration of Volatile Organic Compounds (VOCs) – An Overview

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Abstract

Volatile organic compounds excreted to the environment are highly susceptible to ecological and health hazards. Many conventional methods have been developed for the waste air treatment in the recent past but biological waste air treatment processes have acquired high approval due to its cost effectiveness and environment friendly technologies. This review presents an overview of biofiltration technologies for the control of VOCs and odours, functioning mechanism and its operational parameters.

Key words: VOCs, Gas biofiltration, Biofilter, Biodegradation.

Introduction

Over the past few decades enormous quantities of industrial pollutants have been released into the environment. Due to high releases of wide variety of pollutants there has been increase in number of environment related problems¹. These xenobiotic compounds are usually removed slowly and tend to accumulate in the environment. Due to the high degree of toxicity, their accumulation can cause severe environmental problems². With increasing public concern about deteriorating environment air quality, stringent regulations are being enforced to control air pollutants.

In spite of the fact there are numerous technologies for control of volatile organic compounds (VOCs) emission, all are not applicable everywhere. Table 1 compares the various available VOC control technologies. All technologies have its own applicability depending upon the source, type and concentration of the VOC³. The conventional methods such as thermal incineration, adsorption, absorption, condensation and some recent techniques such as membrane separation, electronic coagulation are very effective at reducing emission of VOCs from various industrial operations^{4, 5, 6}. But they generate undesirable byproducts⁷. These are energy intensive and may not be cost-effective for treating high flow air streams contaminated with low concentrations of pollutants. Biological treatment is an attractive alternative for low concentration gas streams because of its low energy consumption, relatively moderate operating costs and minimal by-products generation.

The most successful removal in gas-phase bioreactors occurs for low molecular weight and highly soluble organic compounds with simple bond structures. Compounds with complex bond structures generally require more energy to degrade which is not always available to the microbes.

Hence, little or no biodegradation of these types of compounds occurs, as microorganisms degrade those compounds that are readily available and easier to degrade. Organic compounds such as alcohols, aldehydes, ketones, and some simple aromatics demonstrate excellent biodegradability table-2. Some compounds that show moderate to slow degradation include phenols, chlorinated hydrocarbons, polyaromatic hydrocarbons, and highly halogenated hydrocarbons. Rate of biodegradation for inorganic compounds such as hydrogen sulphide and ammonia is also good. Certain anthropogenic compounds may not be biodegradable at all because microorganisms do not possess the necessary enzymes to break the bond structure of the compound effectively^{8,9}.

In biodegradation, the contaminants are sorbed from a gas to an aqueous phase where microbial attack occurs^{10, 11, 12}. Through oxidative and occasionally reductive reactions, the contaminants are converted to carbon dioxide, water vapour, and organic biomass^{13, 14}. These air pollutants may be either organic or inorganic vapours and are used as energy and sometimes as a carbon source for maintenance and growth by the microorganism populations. In general, natural occurring microbes are used for biological treatment. These microbial populations may be dominated by one particular microbial species or may interact with numerous species to attack a particular type of contaminant synergistically. Microbes within these biological treatment systems are also engaged in many of the same ecological relationships that are typical of macro organisms. Such relationships are necessary to provide an important balance within the system. In this study, an attempt has been made to provide an overview of biofiltration technologies used for the control of VOCs and odours, functioning mechanism and its important operational parameters.

Table-1
Current technologies for air pollution control

Methods (Conventional and upcoming)	Technology involved	Operational characteristics			Advantages	Limitations
		Gas flow (m ³ h ⁻¹)	Temperature °C	VOC (gm ⁻³)		
Adsorption	Activated carbons, zeolites	5-50000	<55	< 10	Proven and efficient	Adsorbant is too specific and can saturate fast; Risk of pollutant reemission
Incineration	Thermal oxidation	>10000	371	2- 90	Efficient	Not cost effective, incomplete mineralization and release of secondary pollutants.
Catalytic oxidation	Thermal catalysts (Pt, Al, ceramics)	>10000	149	2-90	Efficient, conserves energy	Catalyst deactivation and its disposal, formation of by- product
Absorption	Washing gas with contaminated water	100- 60000	Normal	8-50	Possible recovery of VOC	Not suitable for low concentrations, generates wastewater
Condensation	Liquefaction by cooling or compression	100- 10000	Ambient	>60	Possible recovery of VOC	Further treatment is required, Applicable in high concentrations only
Filtration	Air passed through fibrous material coated with viscous materials	100- 10000	10-41	>60	Efficient for particle removal, compact and commonly used	Unable to remove gases, fouling, particle reemission can occur due to microbial growth.
Electrostatic precipitator with Ionization	Electric field is generated to trap charged particles	-	-	-	Efficiently removes particles and are compact	Generates hazardous by- products
Ozonation	Strong oxidizing agent	-	-	-	Removes fumes and gaseous pollutants	Generates unhealthy ozone and degradation products.
Photolysis	UV radiations to oxidize air pollutants and kill pathogens	-	Normal	-	Removes fumes and gaseous pollutants	Release of toxic photoproducts, UV exposure may be hazardous and energy consuming.
Photo catalysis	High energy UV radiation used along with a photocatalyst	-	-	-	Energy intensive popular method suitable for broad range of organic pollutants	Exposure to UV radiation may be harmful
Membrane separation	Separation through semi permeable membranes	5-100	Ambient	>50	Recommended for highly loaded streams	Membrane fouling and high pressure is needed
Enzymatic oxidation	Use of enzymes for treatment of air pollutants	-	35-55	-	Promising	Requirement of new enzymes periodically
Phytoremediation	Use of plants and microbes for the removal of contaminants	-	-	-	Cost effective, pollution free and complete mineralization occurs	Large as compared to other technologies
Microbial abatement	Air passed through a packed bed colonized by attached microbes as biotrickling filters or microbial cultures in bioscrubbers,	200-1500	-	<5	Cost effective, more efficient, eco-friendly,	Need for control of biological parameters

Table-2
Biodegradability of typical indoor VOCs

Substance	Biodegradability	Henry's law constants H^b ($\text{atm m}^3 \text{mol}^{-1}$)	References
Acetaldehyde (Ethanal; CH_3CHO)	Good	5.88×10^{-5} 7.69×10^{-5} 5.88×10^{-5}	Zhou and Mopper(1990) Sander (1999) US EPA (1982)
Benzene (C_6H_6)	Moderate	6.25×10^{-3} 5.55×10^{-3} 4.76×10^{-3}	Staudinger and oberts(1996) US EPA(1982) Sander (1999)
Formaldehyde (Methanal; HCHO)	Good	3.33×10^{-7} 3.23×10^{-7} 3.13×10^{-7}	Sander (1999) Zhou and Mopper(1990) Staudinger and Roberts(1996)
Naphthalene (C_{10}H_8)	Low	4.76×10^{-4} 4.76×10^{-4}	Sander (1999) US EPA (1982)
Tetrachlorethylene (Tetrachloroethene; C_2Cl_4)	Low	2.78×10^{-2} 1.69×10^{-2} 1.56×10^{-2}	US EPA (1982) Staudinger and Roberts(1996) Sander (1999)
Toluene (Methylbenzene; $\text{C}_6\text{H}_5\text{CH}_3$)	Moderate	6.67×10^{-3} 6.67×10^{-3}	US EPA (1982) Staudinger and Roberts(1996)
Trichlorethylene (Trichloroethene; C_2HCl_3)	Low	9.09×10^{-3} 1.12×10^{-2} 1.00×10^{-2}	Sander (1999) US EPA (1982) Staudinger and Roberts(1996)

Table-3
Comparison of bioreactors for VOC and odour control

Bioreactor	Application	Advantages	Disadvantages
Biofilter	<ul style="list-style-type: none"> Removal of odour and low VOCs concentrations Target VOC concentration is less than 1 g m^{-3} 	<ul style="list-style-type: none"> Low initial investment and subsequently operating cost is minimized Degrades a wide range of components Easy to operate and maintain No unnecessary waste streams are produced Low pressure drop 	<ul style="list-style-type: none"> Less treatment efficiency at high concentrations of pollutants Extremely large size of bioreactor challenges space constraints Close control of operating conditions is required Packing has a limited life Clogging of the medium due to particulate medium
Biotrickling filter	<ul style="list-style-type: none"> Low / medium VOC concentrations Target VOC concentration is less than 0.5 g m^{-3} 	<ul style="list-style-type: none"> Less operating and capital constraints Less relation time / high volume through put Capability to treat acid degradation product of VOCs 	<ul style="list-style-type: none"> Accumulation of excess biomass in the filter bed Requirement of design for fluctuating concentration Complexity in construct and operation Secondary waste stream
Membrane bioreactor	<ul style="list-style-type: none"> Medium/High VOC concentrations Target VOC concentration is less than 10 g m^{-3} 	<ul style="list-style-type: none"> No moving parts Process easy to scale up Flow of gas and liquid can be varied independently, without the problems of flooding, loading, or foaming 	<ul style="list-style-type: none"> High construction costs Long-term operational stability (needs investigation) Possible clogging of the liquid channels due the formation of excess biomass
Bioscrubber	<ul style="list-style-type: none"> Low/medium VOC concentrations Target VOC concentration less than 5 g m^{-3} 	<ul style="list-style-type: none"> Able to deal with high flow rates and severe fluctuations Operational stability and better control of operating parameters Relatively low pressure drop Relatively smaller space requirements 	<ul style="list-style-type: none"> Treats only water soluble compounds Can be complicated to operate and maintain Extra air supply may be needed Excess sludge will require to disposal Generation of liquid waste

Material and Methods

Increasing stringent environmental legislation is generating great interest in industry towards the biological waste air treatment technique^{15,16}. All biological technologies rely on two primary fundamental mechanisms-sorption and biodegradation. The biodegradation is done by microorganisms, which are either supported on media or maintained in suspension. Supported microorganisms are immobilized on organic media or inorganic structures, while suspended microorganisms are maintained in a liquid phase such as activated sludge. In all instances, VOCs and odour are biodegraded by microorganisms into carbon dioxide and water. Organic compounds serve as the substrate or source of carbon and energy. These compounds provide the food supply, which allows the microorganism to function and multiply¹⁷.

Biological waste air treatment technology makes use of several types of bioreactors. There are mainly four types of related biological treatment units: biofilter, biotrickling filter, membrane bioreactor and bioscrubber. A comparison of bioreactors for removal of VOCs and odour has been done table-3. These systems have differences in their complexity, process design, equipment dimensions and working parameters, but all of these operated based on the same principle of biological removal^{18, 19, 20}.

Results and Discussion

Biofilters (BFs) are reactor in which polluted air stream is passed through a porous packed bed on which a mixed culture of pollutant-degrading organisms is immobilized. Biofiltration uses microorganisms fixed to a porous medium to break down pollutants present in an air stream. The microorganisms grow in a biofilm on the surface of a medium or are suspended in the water phase surrounding the medium particles. The filter-bed medium consists of relatively inert substances like compost, peat, etc. which

ensure large surface attachment areas and additional nutrient supply. As air passes through the bed, the contaminants in the air phase sorb into the bio film and onto the filter medium. The contaminants are biodegraded on biofilm²¹. Biofilters usually incorporate some form of water addition for control of moisture content and addition of nutrients. In general, the gas stream is humidified before entering the bio filter reactor.

The overall effectiveness of a biofilter is largely governed by the properties and characteristics of the support medium, which include porosity, degree of compaction, water retention capabilities, and the ability to host microbial populations. Critical biofilter operational and performance parameters include the microbial inoculums, pH, temperature, moisture and nutrient content.

Biofiltration is a general term applied to the biodegradation of chemical compounds in gas phase to the carbon dioxide, water and inorganic salts. Biofiltration is the oldest and the simplest method of the four biological technologies for the removal of contaminated components from waste gases^{19, 20, 22}. A typical biofilter configuration is shown in figure-1. The contaminated off-gas is passed through a preconditioner for particulate removal and humidification (if necessary). The conditioned gas stream is then passed from the bottom of a filter bed of soil, peat, composted organic material (such as wood or lawn waste), activated carbon, ceramic or plastic packing or other inert or semi-inert media. The media provides a surface for microorganism's attachment and growth. The bed and air stream are kept moist to encourage microbial activity. Humidification is generally the most influential parameter affecting the sorptive capacity of a biofilter, especially at lower inlet concentration, where Henry's Law controls mass-transfer rates within the biofilter. Nutrient could be mixed with the packing material either before biofilter installation or after construction^{18, 19, 20, 22}.

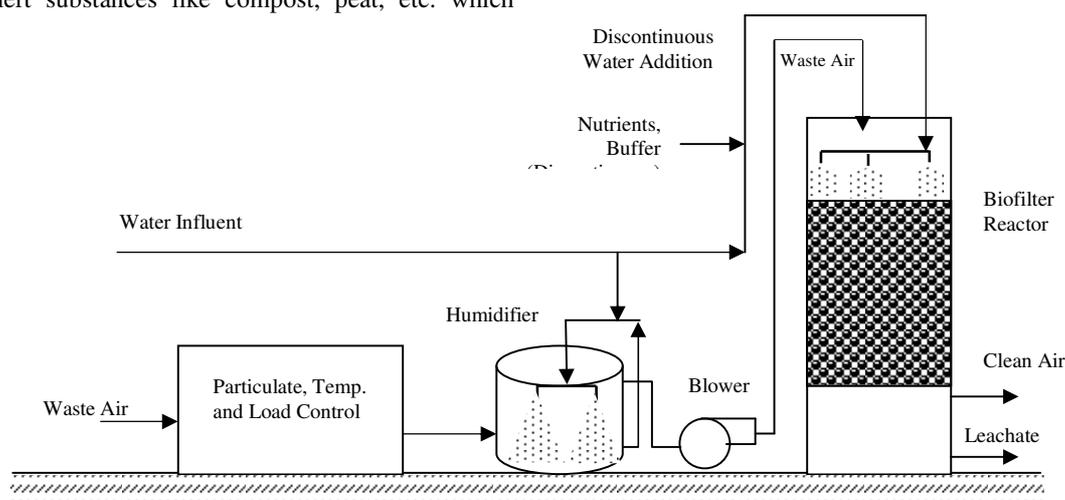


Figure-1
Schematic diagram of a biofilter unit

Biofilter Operations: The operations of biofilters involve a series of steps beginning with the transfer of the pollutant air to the aqueous phase.

Transfer of pollutant from air to aqueous phase.

Adsorption onto the medium or absorption into the biofilm

Biodegradation of VOCs within the biofilm

The most important physical, chemical and biological parameters affecting the biofiltration process are described below:

Biofilm: In the biofiltration system, the pollutants are removed due to the biological degradation rather than physical straining as in the case of normal filters. Biofilm is a group of microorganisms (aerobic, anaerobic, and facultative type bacteria, fungi, algae and protozoa) which attach themselves on the surface of the packing media and forms a biological film or slim layer of a viscous, jelly like structure²³. The development of biofilm may take few days or months depending on the microorganisms' concentration. There are three main biological processes that occur in the biofiltration systems - Attachment of microorganisms, Growth of microorganisms and Decay and detachment of microorganisms.

Since the microorganisms are attached to the surface, the supply of organics or substrate (food) to the microorganisms in a biofilm is mainly controlled by the bulk and substrate transport phenomena. The substrate must be transported from the bulk fluid to the biofilm's outer surface where it is metabolised after diffusion. The factors which influence the rate of substrate utilization within a biofilm are (i) substrate mass transport to the biofilm, (ii) diffusion of the substrate into the biofilm, and (iii) utilization kinetics of the biofilm.

Biomass detachment is one of the most important mechanisms that can affect the maintenance of biomass in the biofilter²⁴. Several forces (i.e. electrostatic interaction, covalent bond formation and hydrophobic interactions) are involved in microbial attachment to a surface. The strength of the attachment and the composition of forces are dependent on various environmental conditions viz gas flow rate, pollutant concentration, oxygen supply, nutrient availability, type of microbial species and their surface properties^{23, 25}.

Generally a rapid flow rate through the biofilter will hinder the growth of bacterial film resulting in thin film formation. Microorganisms form thinner layers upon smooth surfaces in comparison to those upon porous materials and each treatment system has a typical biofilm thickness. The biofilm thickness usually varies from 10 micro meters to 10,000 micro meters, although an average of 1,000 micro meters or less is usually observed. However, whole of the biofilm is not active. The activity increases with the

thickness of the biofilm up to a level termed the 'active thicknesses'. Above this level, diffusion of nutrients becomes a limiting factor, thus differentiating an 'active' biofilm from an 'inactive' biofilm²⁵.

Biofilter bed: Biofilter bed is the vital part of the biofiltration process as it provides the main support for microbial growth. A list of characteristics that are necessarily needed for an ideal biofilter reactor is established by Bohn. The most anticipated characteristics of the BF bed comprise:

Optimum specific surface area for development of microbial biofilm and gas-biofilm mass transfer. High porosity to expedite homogenous distribution of gases. High-quality water retention capacity to preclude bed drying. Manifestation and availability of intrinsic nutrients and Presence of a dense and diverse indigenous microflora.

The most habitually used materials in BF beds are peat, soil, compost and wood chips. These materials are generally abundant and economical as well. They satisfy most of the desirable criteria and has their own merits and demerits²⁶. The main advantage of soil is that it has a rich and varied microflora. But it contains restricted amount of intrinsic nutrients, gives low specific area and spawn high-pressure drops²⁷. Peat contains high amount of organic matter, has high specific area, good water retaining capacity and good permeability. But peat comprises neither high levels of mineral nutrients nor a dense indigenous microflora as that of soil or compost. Compost employs a dense and varied microbial system, good water holding capacity, good air permeability and contains large amounts of intrinsic nutrients. That's why composts are most widely employed in biofiltration.

Furthermore, the consumption of compost in BFs represents an effective way of recycling and utilizing waste residual organic matter, specifically activated sludge from waste water treatment plants, forest products (branches, leaves, barks), domestic residues, etc.^{28,29,30}. Moreover, composts are frequently less stable than that of soil or peat and have the propensity to collapse and become compact, prominent to increase in pressure drop in BF beds. This among other reasons is ascribed to their high water holding capacity. The study of biofiltration using wood chips or barks as packing material has already been carried out by some authors^{31,32,33}.

Certainly, to preclude bed pulverization and compression, most authors proposed materials that furnish the bed with good structure, easy maintenance and rigidity, thereby hindering the clogging phenomena ultimately enhancing the bed lifespan. For example wood chips or barks³⁴, perlite³⁵, vermiculite³⁶, glass beads³⁷, polyurethane foam³⁸, polystyrene³⁹, lava rock⁴⁰, etc. Ibrahim et al. prepared a filter bed composed of activated sludge immobilized on gel

beads⁴¹. Christen et al. and Sene et al. used technologically advanced sugarcane-baggase based bed, for the treatment of ethanol and benzene^{42, 43}. Some bed structuring agents also hold interesting chemical characteristics as they contribute to bed properties such as pH-buffering capacity (limestone), or general adsorbing capacity (activated carbon)⁴⁴. The efficiency of a BF material with respect to the pollutant for treatment is a function of its adsorption coefficient or partition coefficient. The partition coefficients of toluene are 1.43 mg g⁻¹ with compost, 2.0 mg g⁻¹ with diatomaceous earth and 0.89 mg g⁻¹ with chaff⁴⁵. The adsorption coefficients for toluene were calculated to be approximately 10–20 times greater than that of granulated activated carbon^{45, 46}.

Nutrients: The pollutants brought into the biofilters form the major carbon and energy source for microbes. The presence of macronutrients (N, P, K and S) and the micronutrients (vitamin and metals) is partly delivered by the filtering materials used in BF. Compost is considered to be a suitable material since it contains various nutrients. From the literature it has been confirmed that irrespective of the filtering material used, steady addition of nutrients is essential to withstand microbial degradation activity⁴⁷. Progressive exhaustion of the intrinsic nutritive resources occurs when there is long-term utilization of compost based beds⁴⁸. This eventually leads to nutrient deficiency which ultimately becomes a limiting factor for the long-term biofiltration performance^{49, 50}. Nutrients for microbial growth are supplied either in the solid form which is directly inserted into the filter bed⁵¹ or as aqueous solutions, which is the most frequently used method. Compounds such as KH₂PO₄, KNO₃, (NH₄)₂SO₄, NH₄Cl, NH₄HCO₃, CaCl₂, MgSO₄, MnSO₄, FeSO₄, Na₂MoO₄ and vitamins are the most commonly used nutrient solutions in BFs⁵². Models of biofiltration performance as a function of nutrient supply, of nitrogen in particular have been developed and experimentally validated^{49, 50, 53}.

pH: For several biological processes, pH has a significant impact on biofiltration efficiency. Microbial activity is severely disturbed by any deviation from an optimum pH range. Due to neutrophilic (optimum pH is 7) behavior of the microorganism, maximum degradation observed for BTEX between pH values of 7.5 and 8.0⁵⁴. Veiga et al. studied the effect of pH on alkyl benzene degradation (between pH 3.5 and 7.0) and found that alkyl benzene degradation increased with pH⁵⁵.

Microorganisms: Microorganisms are considered as the catalysts for the biodegradation of VOCs. Heterotrophic microorganisms such as bacteria and fungi are used for the degradation of VOCs. The bed vaccination is completely influenced by the nature of the filtering material and the

biodegradability level of the VOC to be treated. By taking the ecological advantages, the most defiant population to the toxic VOC is naturally selected and a microbial hierarchy is formed in the bed^{49, 50, 56, 57}. The inoculation of BF beds with consortia extracted from sewage sludge or strains derived or isolated from previously operated BF are done for the intractable VOCs. Within BFs, the degrading species comprises between 1 and 15% of the total microbial population^{50, 58, 59}. The biomass density of BF should contain 10⁶ and 10¹⁰ cfu of bacteria and actinomycetes, respectively per gram of bed⁶⁰.

Oxygen levels: Oxygen level is one of the most important parameter which governs the performance of BFs. The oxygen dependency on biofiltration has been studied by various researchers. Oxygen was found to be a limiting factor even at low inlet VOC concentration for hydrophilic solvents⁶¹. The concurrent removal of a mixture of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) did not have any significant improvement with the increase in oxygen content in air. Deshusses et al¹⁷. suggested that the cross –inhibition of MEK and MIBK biodegradation occurred. They also found that the kinetic effects were more important than diffusion effects. In transient experiments it has been verified that when either of the compounds were inoculated into BFs, both cross and self-inhibition was observed.

Moisture Contents: The moisture content of the filter bed plays an important role in biofilter performance because microorganisms need water to carry out their metabolic activity. Deficiency of water in microorganisms leads to substantial reduction in the biodegradation rate. On the other hand, availability of excess of water to the microorganisms hinders the transfer of oxygen and hydrophobic pollutants to the biofilm, leading to the development of anaerobic zones within the bed. This leads to reduction in reaction rates, foul smell, increased back pressure due to reduced void volume and channelling of the gas within the bed. Partial optimization of moisture levels leads to drying of bed and growth of fissures which eventually cause channelling and short-circuiting⁶². Moisture content for optimal operation of the biological filter should be within 30–60% by weight, depending on the filtering medium used. Depending on medium, surface area and porosity, optimal water levels vary with different filtering material. Moisture levels are maintained by the pre-humidification of the inlet gas stream which is also necessary to provide direct water to the bed through nozzle system at the top of the bed. Sakuma et al. stated that biofilters tend to experience drying at the air inlet port, which causes decrease in pollutant removal over time⁶³. Drying of the packing material can lead to localized dry spots, non uniformed gas distribution and reduction in the activity of microorganisms⁶².

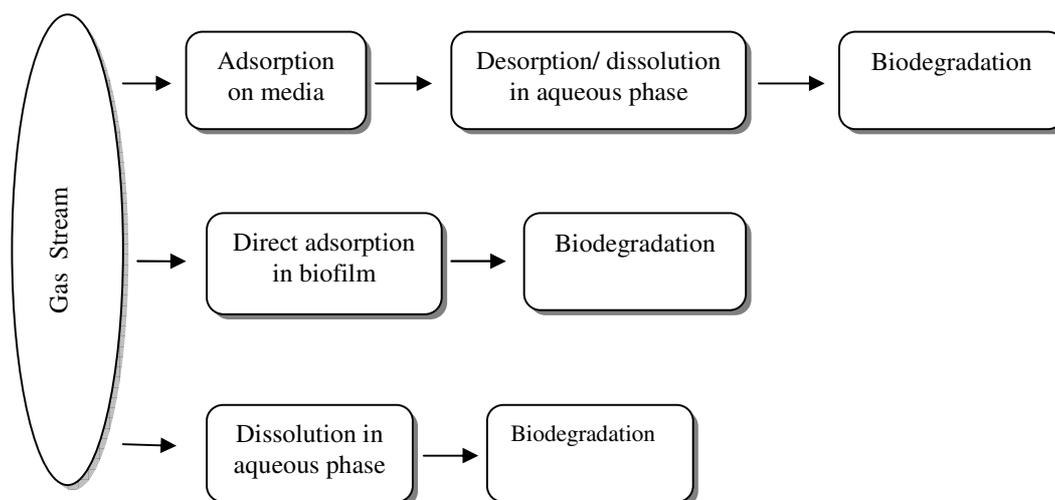


Figure-2
Mechanism of biofiltration

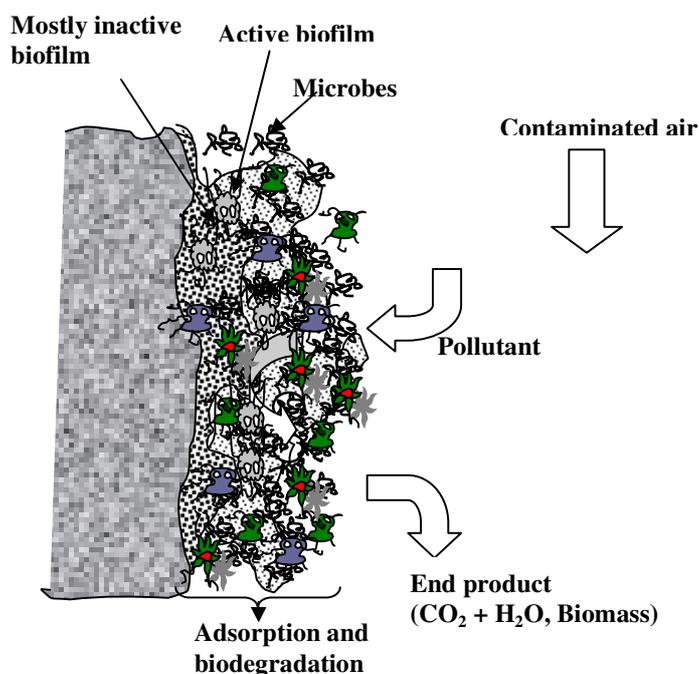


Figure-3
Phenomena involved in the operation of biofilters (Devinny and Ramesh,2005)

Mechanisms: The biodegradation of pollutants in the biofilm of a biofiltration system is a combination of physico-chemical and biological phenomena. Basically following three mechanisms are responsible for the transfer and subsequent biodegradation within the bed^{20, 27, 64} figure-2.

Once the pollutants are adsorbed on the biofilm or dissolved in the water layer surrounding the biofilm, the contaminants are available to the microorganisms as a food source to support the microbial life and growth. Air that is free, or nearly free, of contaminants is then exhausted from the

biofilter. Figure-3 shows the mechanism of mass transfer occurring during biofilter process. As the gas stream passes through the packing, contaminants are transferred from the gas stream to the water in the biofilm. A number of researchers have worked on the measurement of concentration of contaminants by GC-FID⁶⁵. The contaminants diffuse into the depth of the biofilm, where they are adsorbed by the microorganisms in the biofilm and biodegraded. Contaminants may also be adsorbed at the surface of the packing. The greater majority of reactors utilize aerobic respiration, so that oxygen and nutrients must

also be dissolved in the water or biofilm and degraded by the microorganisms. During operation at moderate-to-high concentration of contaminant, the biofilm will gradually grow thicker. At some point, diffusion will no longer provide all the needed compounds to the deeper portions of the biofilm, and microorganisms will become inactive. Because the pores within the packing are highly irregular in shape, the growing biofilm will change the pore size distribution.

Conclusions

This review postulates a brief outline of the biofilter used for waste gas treatment, drawbacks of current bioreactors and attention required in development and design aspects. There is a need to work on innovative strategies such as pre-treatment of VOCs to remove particulates to enhance biodegradability and improve techniques to treat more complicated polluted airstreams especially multiple pollutant mixtures. Due to failure in large scale BFs, understanding of the fundamental principles underlying the biofiltration process, scope exists for designing better bioreactors with optimization in operating conditions. The flow parameters such as gas flow, liquid flow and gas velocity has an influence on gas diffusion in the reactor and gas residence time and pressure drop over the system. These parameters are needed for optimization of bioreactor. The development of bioreactor should be also engrossed on problems like heftiness i.e. amenable to process fluctuations per failures, large pollutant loadings, high temperatures, halogenated compounds and poorly water soluble compounds.

Moreover, modernization of bioreactor remains in high priority because single bioreactor alignment never stipulates a universal solution to existing VOCs treatments methods. Advancement of reactor design will oblige similar progress in understanding the fundamentals of the bioprocess, so that a more logistic, innovative and focused approach in bioreactor design can be employed and its performance. For the treatment of VOCs there is a necessity of continuous innovation in bioreactor arrangement.

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