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Biomass for Sustainable Applications

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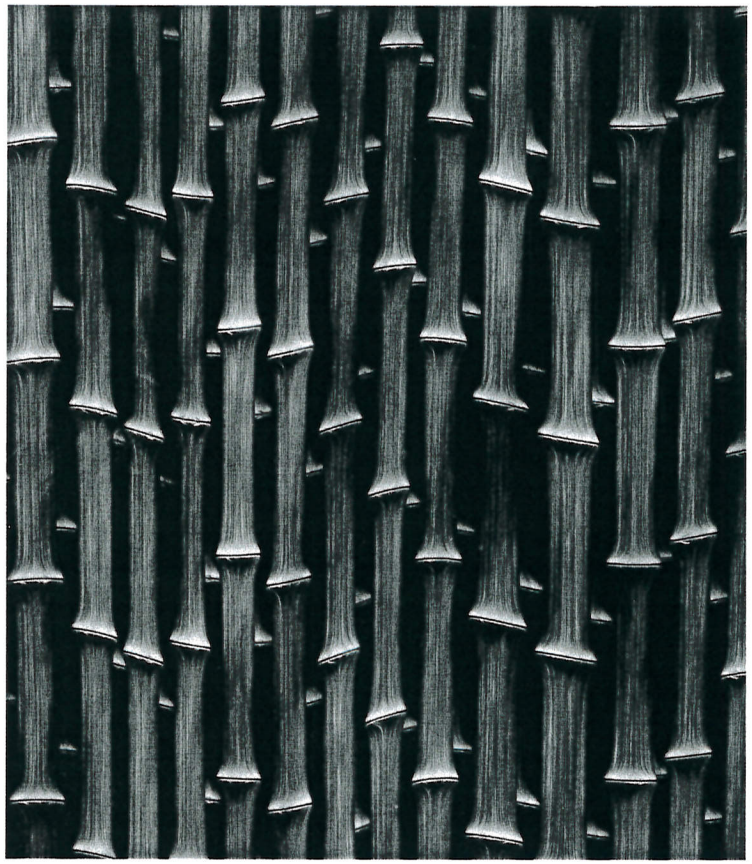

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CHAPTER 5

Biological Waste Gas Treatments

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5.1 Introduction

Human health and welfare (the population in general and plant operators) and environmental protection (domestic and wild animals, plants, paintwork or damage to buildings) are strong arguments for the development and use of new and original processes to control waste gas emissions from agricultural, industrial or domestic activities. International treaties for environmental protection (Rio, Kyoto) have been transcribed and applied in many countries. From these ratifications of international agreements, local legislation has been written, particularly for solid waste management, water and wastewater treatment, and air quality. Air pollution control regulations reflect the concern of governments for the protection of people and the environment. Bravo-Alvarez[1] mentioned two fundamental reasons for cleaning up the waste gas stream: profit and protection. This is the case, for example, for the upgrading of biogas, the cleaning of waste incinerator flue gas[2] or the treatment of industrial process emissions.

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According to the nature of the contaminants and/or the complex mixture of pollutants in the gaseous phase, their concentrations and the flow to be cleaned, removing non-particulate pollutants from a gas stream is achieved by different processes involving different mechanisms.[3–6] These processes can be classified into three categories:

- Thermal and/or catalytic oxidation, biological transformation
- Transfer into a liquid phase (absorption) or onto a solid phase (adsorption) with or without chemical reactions such as acid–base interaction, oxidation, complexation, physisorption or chemisorption
- Phase change (condensation).

Depending on the emission characteristics in terms of concentrations and flow, one of these technologies will be chosen with the aim of achieving the required performance for the lowest investment and operating costs.

These processes are widely used in industrial applications to remove single toxins or a mixture of contaminants. Many activities are concerned such as chemistry, petrochemistry, pharmacy, cosmetics, surface cleaning, polymer production, printing, painting, mechanical and car manufacture, waste and wastewater treatments.

Biological treatments of gas streams are relatively recent technologies compared with thermal destruction or mass transfer systems. However, researchers have been paying attention to these promising and interesting processes for several years and indeed bioprocesses appear to be a very competitive way to treat the waste gas stream before its discharge into the atmosphere. The removal of a large number of soluble and biodegradable volatile organic compounds (VOCs) or odorous molecules has been the subject of many previous studies and industrial applications.[7,8] The optimal range of pollutant concentration goes from a very diluted pollutant present in the gas stream (from some $\mu g\ m^{-3}$ to $mg\ m^{-3}$) to above $1\ g\ m^{-3}$. The installation designs cater for an air flow from a few $m^3\ h^{-1}$ to 100 000 $m^3\ h^{-1}$, or even more in some systems.

This chapter presents general approaches to the bioreactors used in waste gas stream treatments and describes more specifically the different biosystems such as biofilters, biological trickling beds and bioscrubbers. The general presentation, operating conditions, yields and industrial applications of these bioprocesses are discussed.

5.2 General Approaches to Biological Treatment of Waste Gases

Clearly, the final objective of a biological treatment is to transform the contaminants present in the gaseous phase and used as substrates by microorganisms (bacteria, fungi and yeast) into innocuous compounds. A very simplified reaction pathway expressing the principle of biodegradation is given in Table 5.1. According to the oxygen level provided by the air to be treated, the

Table 5.1 Simplified reaction system of the degradation of contaminants by enzyme (E) of aerobic bacteria (X).

Contaminants (substrates) + O_2, N, P, trace elements H_2O	E, X →	$CO_2 + H_2O + X$ Metabolites Internal energy

Table 5.2 Examples of particular bacterial families degrading specific contaminants present in air.

Contaminants	*Microorganisms*	*References*
Ethanol	*Pseudomonas* sp. *Pseudomonas putida*	68
Phenol, benzene, toluene, xylene, ethylbenzene, isopropylbenzene	*Pseudomonas putida*	69, 70
Toluene	*Pseudomonas putida* To11A	71, 72
Styrene	*Exophilia jeanselmei, Tsukamurella, Pseudomonas, Sphigomonas, Xanthomonas*	73, 74, 75
Styrene and Xylene	*Nocardia*	76
1-Chlorobutane	*Rhodococcus*	77
Butanal	*Pseudomonas fluorescens*	78
Hydrogen Sulfide	*Pseudomonas putida* CH11	79, 80
Methyl sulfide	*Hydromicrobium* sp.	81
Dimethyl sulfur	*Pseudomonas acidovorans*	82, 83
Dichloromethane	*Hydromicrobium* sp.	84, 85
Dichloroethane	*Xanthobacter*	86
Trichloroethylene	*Methylosinus*	87
Ammonia	*Actinomadura nitrigens* sp.	88, 89

biomass used is mainly composed of aerobic species. Nevertheless, some anaerobic microorganisms are suspected to be present in potentially anoxic zones caused by a non-ideal gas or liquid flow through the reactor, which leads to the occurrence of plug flow with a non-active zone, favouring the creation of channels and by-passing others.[9] To maintain biological activity, the addition of water is required. The equilibrium of substrates is necessary to stimulate biomass activity and thus nitrogen compounds, phosphate and trace elements are often added through incorporation or solution injection into the biosystem. The degradation of organic contaminants gives mostly carbon dioxide (CO_2) and water (H_2O). Anionic metabolites, such as nitrates, sulfates and chlorides, accompanied by oxonium cations (H_3O^+), are frequently produced. Microorganism growth (X) is controlled by the substrate load applied to the bioreactor and by operating parameters such as pH, temperature and moisture content. Internal energy is also produced by the bacteria.

A large number of previous publications have mentioned the degradation of specific contaminants by a particular microorganism family. Table 5.2 presents examples of pollutant-degrading biomass for some organic or inorganic volatile compounds. Although some researchers advise the utilization of such pure strains, it is difficult to avoid a possible external bio-contamination. In other

words, the reactor is not under sterile conditions and can be naturally colonized by a large number of bacteria. As a consequence, a consortium of microorganisms generally grows in the biological reactor depending on the nature of the available biodegradable substrates. These microorganisms, responsible for this bio-contamination, can be initially present on the packing materials, induced by polluted gas or provided by water or the initial inoculation step. For industrial applications, diluted activated sludge coming from a wastewater treatment plant is inoculated in the early days of bioreactor implementation or when restart is required. During the acclimatization period, when the performance increases gradually, a microbial selection occurs. The most adapted microorganisms grow to the detriment of other species.

In terms of the process, an important initial question is how to put microorganisms in contact with water and substrates present in the gas phase. Taking into account the mobility of the aqueous phase and the microorganisms, three processes are generated as shown in a conventional matrix: biofilters, trickling beds and bioscrubbers (Table 5.3).

As degradation of the compound is carried out by microorganisms present in the aqueous phase or structured as a biofilm rich in water, the water solubility of the pollutants appears to be a major factor in choosing a technology. A diagram of decision support, based on the pollutant concentration and its air–water partition coefficient, has been proposed.[10] As a result, biofilters are recommended for the treatment of pollutants having an air–water partition coefficient <1. Bioscrubbing is useful for gaseous pollutants with a Henry's constant or partition coefficient of <0.01, while trickling filters can be used efficiently for the treatment of compounds characterized by an air/water partition coefficient <0.1.[11]

More recently, other types of more complex bioreactor have been studied in the laboratory or at pilot unit scale: membrane bioreactors or multiphase bioscrubbers. The schematic presentations of the main different biological processes are given in Figure 5.1. Biomass is attached to the packing material of

Table 5.3 Biological treatment processes: classification according to the mobility of the liquid phase and biomass.

		Liquid phase: Mobile	Liquid phase: Immobile	Reactor
Biomass	Free	Bioscrubber		Scrubber + treatment tank
	Fixed	Biotrickling	Biofilter	Packed column
Nutrient supply		Nutrient solution	Nutrient solution, packing assimilation	

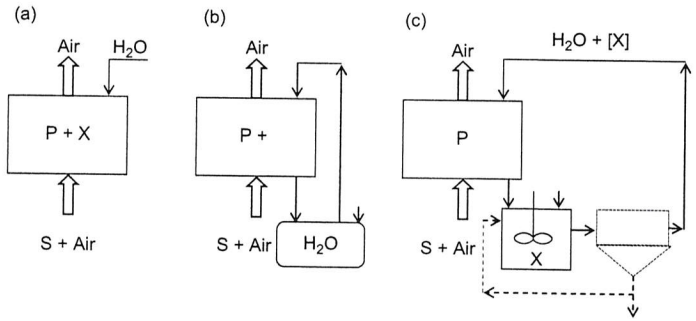

Figure 5.1 Schematic presentations of the different biological processes used in gas stream treatment: (a) biofilter; (b) trickling bed; and (c) bioscrubber (S = substrate; X = biomass; P = packing materials).

the bioreactor or in the form of an activated sludge. Water moistens the media in a biofilter and is recycled for the other two processes. In these cases, absorption of the pollutant into water or an organic solution is required before degradation by microorganisms.

5.3 Biofilters

In recent decades, biofiltration has shown interesting development prospects in the field of VOC and odour treatment.[12] It is particularly suitable for the treatment of high air-flow rates at low concentrations of a large number of pollutants. This, along with its low implementation and maintenance costs, has made biofiltration one of the most used methods for the treatment of industrial gaseous emissions. Many successful industrial applications include the treatment of gaseous emissions from water treatment plants, composting platforms, rendering plants and printing factories.[13,14]

5.3.1 Process Description and Mechanism

5.3.1.1 Process Description

In its implementation, a biofilter consists of a porous organic or inorganic bed through which a moist polluted gaseous stream passes (Figure 5.2). A complex microbial consortium of pollutant-degrading microorganisms is immobilized at the material surface and carries out the degradation of VOCs and odours under given operational parameters (moisture content, pH, nutrient availability, temperature).[11,15]

To maintain the packing material humidity and avoid biofilter drying, the air flow is generally moistened to bring the relative humidity above 98%.

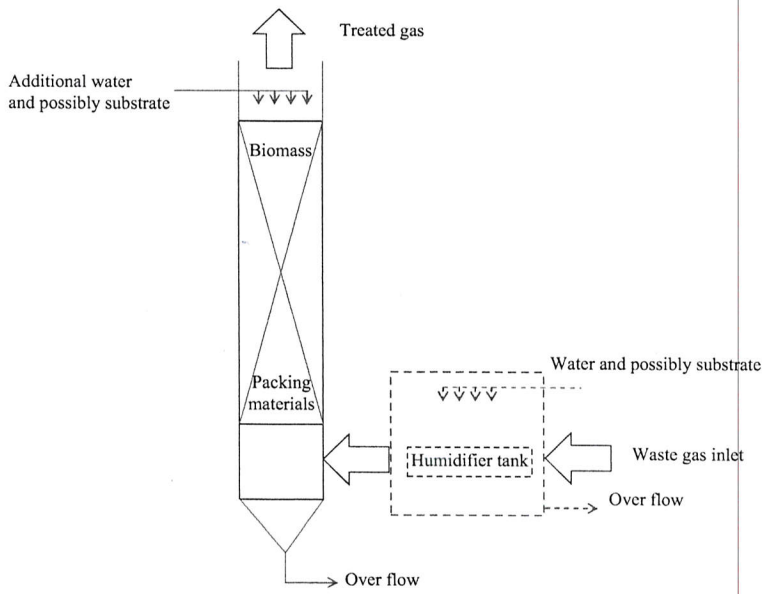

Figure 5.2 Diagram of a biofilter for waste gas stream treatment.

Humidification has various positive impacts since it reduces the temperature by energy consumption through water evaporation, promoting the development of mesophilic microorganisms at the packing material surface. It also removes particles (dust, fat vesicles), thus limiting the clogging of the reactor, the packing material and the air distribution system.[16] This step can be carried out by a cyclone, a wet electrofilter or a venturi scrubber.[17] In addition to the air stream humidification, a superficial watering is generally performed to control the moisture content.

As far as the microorganisms are concerned, they are mainly mesophilic, with an optimum development temperature close to 37 °C, even though some applications have been carried out in psychrophilic and thermophilic conditions. Considering their carbon sources, autotrophic and heterotrophic species related to the pollutants to be removed are observed. Their development depends on the nutrient availability. For instance, odorous sulfur compounds are treated by autotrophic microorganisms on inert inorganic material which require two main nutrients for microbial growth such as carbon (HCO_3^- or the carbon dioxide contained in the air) and nitrogen (use of NH_4^+).

An example of a biofilter treating an odorous gas is presented in Figure 5.3. The flow is 50 000 $m^3\ h^{-1}$. The filter surface is 2 × 50 m^2 and the depth is close to 2 m. The packing material was initially an inorganic solid waste reacting with

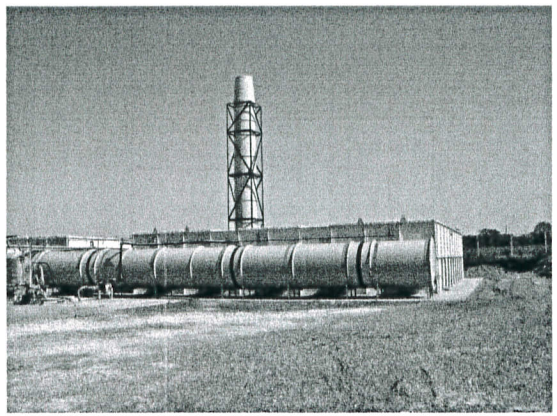

Figure 5.3 Example of a biofilter used to treat odorous molecules: treated air is emitted into the atmosphere through a stack.

acidic compounds such as H_2S and mercaptans, inducing clogging. Because of this problem, the biofilter was refilled with peat. The purified air is evacuated into the atmosphere by a chimney.

5.3.1.2 Specific Mechanisms

The elimination of pollutants in a biofilter involves several successive steps, which are briefly schematized in Figure 5.4:

- Pollutant transfer from the gaseous phase to the gas-liquid interface
- Diffusion of pollutants within the liquid phase and the biofilm
- Biodegradation of the pollutants by the microbial population of the biofilm; they are used as carbon and energy sources by the microorganisms (Figure 5.4)
- Diffusion of the metabolites produced into the liquid phase and then into the gas phase.

The diffusion of the pollutants, as well as their microbiological degradation, is a complex phenomenon. The sorption process of contaminants at the material surface is frequently observed at the startup of a biofilter, namely when biofilm formation is still weak. During this acclimation phase of the microorganisms, the packing material acts as a conventional adsorbent and a significant decrease in the pollution load can be observed. However, biofilm development induces a decrease in the available adsorption sites, leading to a decrease in the adsorption capacity.

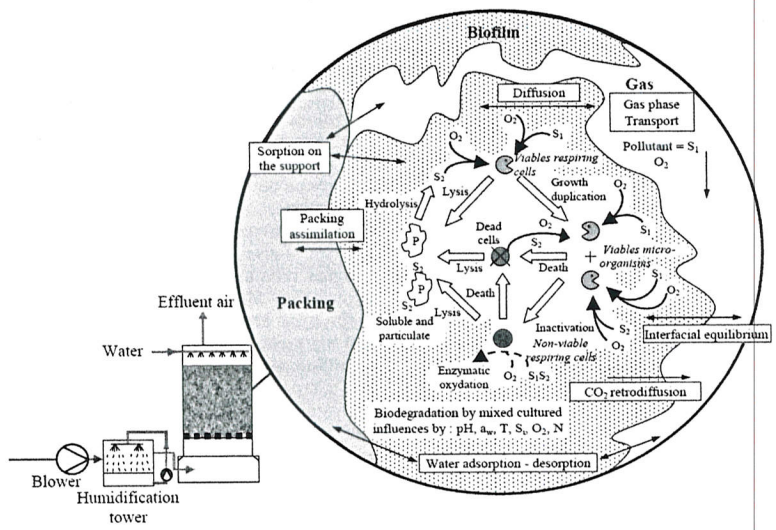

Figure 5.4 Representation of the biological and physical mechanisms involved in the biofiltration process (adapted from ref. 37).

5.3.2 Operating Conditions and Performance

5.3.2.1 Operating Conditions

General operating conditions are given in Table 5.4. The performances of a biofilter are dependent not only on its design (gas residence time as a function of bed surface, depth and void fraction) but also on the operating conditions such as watering, pH and especially waste gas velocity, which is low (100–500 m h^{-1}) due to the slow biodegradation kinetics.

5.3.2.2 Factors Affecting Biofilter Performance

The performance of a biofilter depends on many parameters such as pH, humidity, nutrient supply and concentrations, and the structural properties of the packing material.[18]

5.3.2.2.1 Packing Material. Although the effectiveness of a biofilter is associated with the microbial activity, it should be emphasized that the material is at the heart of the process because it is where the purifying biomass develops.[16,19] The intrinsic properties of the packing material induce the establishment of a more or less conducive environment for the development of an effective microbial consortium and a homogeneous gas distribution

Table 5.4 General operating conditions for waste gas stream treatment in biofilters (adapted and updated from ref. 4).

Parameter	*Value*	*Comments*
Gas phase velocity (U_G)/m. h^{-1}	50–500	Low values due to low kinetics of degradation
Air residence time/s	15–90	Depending on the molecule degradation kinetics alcohols > ketones > *n*-alkanes > aromatics
Bed porosity/-	0.4–0.95	High values avoid clogging
Specific surface area (S)/ m^2 m^{-3}	100–400	High values give a better mass transfer and a higher biomass concentration (biotrickling filter)
Filter depth (H)/m	0.5–2.5	Compromise between the residence time and the pressure drop
Pressure drop/m H_2O	0.1–0.5	Depending on packing material, clogging and compaction
Air humidity/%	60–100	High values are advised to maintain biofilter humidity
Water pH	5–9	Depending on the pollutant solubility
Temperature (T)/°C	10–40	Mesophilic microorganisms Thermophilic microorganisms at temperature ranging from 50 to 70 °C
Acclimation time/day	8–30	Function of the biodegradability of pollutants Utilization of an inoculum (diluted activated sludge)
Pollutant concentration/ mg m^{-3}	1–1000	Possible inhibition at higher concentration by molecules or degradation by-products
Efficiencies/%	90–99	Depending on molecules
Lifetime/year	2–5	Structured and inorganic materials increase lifetime

throughout the bed. For these reasons, numerous laboratory and industrial studies have focused on the influence of the packing material on biofilter performances[20–23] or on the improvement of hydrodynamic properties.[24,25] Several authors have highlighted the following characteristics as suitable for biofilter material:[17,19,26,27]

- A large porosity and a high void fraction for promoting the development of microorganisms and gas flow distribution
- A large surface area to improve the transfer of pollutants, nutrients and oxygen, and to promote water retention—the accumulation of microorganisms is optimal in the presence of pores with sizes ranging between one and five times that of the microorganisms (1–10 μm)[28]
- A dense and diverse microbial population and chemical characteristics favouring the development of microorganisms (pH, buffering capacity and nutrients)
- A good mechanical stability to avoid bed compaction
- Low investment costs and a long life.

The most commonly used organic packing materials are peat, compost, bark and wood chips. Peat and compost are good supports for bacterial development in terms of nutritive supplement, but their mechanical resistance is insufficient and their hydrodynamic properties vary with time. This dysfunction can be avoided by the use of more structured packing, such as bark and wood chips which remain, like peat and compost, biodegradable but which have to be replaced more often than inorganic ones. Inorganic supports such as activated carbon, which is expensive for this application, or pozzolan have better mechanical properties enabling bed depths above 2 m and providing a longer life time. Nevertheless, their implementation necessarily requires a nutrient supply.[29]

There is no universal material that meets all these criteria, whether organic, inorganic or synthetic. It is often necessary to achieve a compromise between these different properties, or to consider a mixture of different materials, which may be in the form of layers or mixtures, to benefit from the advantages of each.

5.3.2.2.2 Biofilter Design. Filter depth is in the range of 0.5 to 2.5 m with a usual value of 1 m for organic packing materials, giving a significant residence time to treat pollutants while minimizing footprint and pressure drop. Greater filter depths can result in support compaction, thus increasing pressure drop and energy consumption as well as favouring the formation of preferential paths. These can induce a rise in local flow rates, leading to a lower residence time and consequently lower treatment efficiency.

In terms of design, and especially for the direction of gas and liquid flow, two modes are observed. The open counter-current configuration allows easy access for maintenance but the effectiveness of these units is affected by heavy rainfall, sometimes justifying coverage. Although it enables better management of moisture and nutrient dispersion, the co-current mode is less employed due to the seal required at the top of the biofilter. Configurations in parallel or in series are also possible in order to isolate units during maintenance operations or to remove compounds in specific biofilters combining special operating conditions (pH, material and humidity).

5.3.2.2.3 Water Requirements and Air Moisture. Among the major operating parameters, biofilter moisture is considered the most important for biofilter management.[30] The presence of water is essential for microorganisms. Humidity evaporation by the unsaturated air flow through the packing material can result in localized bed drying, leading to a negative impact on the microbial community and density, and also on gas distribution. With high evaporation rates, cracks can appear leading to the creation of preferential paths resulting in a lower removal capacity.[31] It should be noted that water reclamation can increase for the treatment of high loads of components because of the exothermicity of the biological reactions involved.

Conversely, excessive wetting of packing material can induce oxygen transfer limitations and hydrophobic volatile compounds at the packing material and

biofilm surface. It can also promote the appearance of anaerobic zones in the biofilter, decreasing the reaction kinetics and transfer rates, and hence the removal efficiency.[32] Furthermore, over-watering can lead to compaction of the bed and opposition to the flow of gas, increasing the pressure drop.[33]

The optimal moisture of a biofilter varies with the type of packing material implemented, and especially with characteristics like porosity and specific surface area; the amount of water in packing materials is generally in the range of 30% to 60%. To optimize the material moisture, air to be treated can be humidified before the biofilter to maintain a relative humidity in the range of 95% to 99%. A periodic spraying of the material can also be carried out; the spraying solution can also contain nutrients to supply microorganism growth or can be alkaline to increase its buffer capacity.

5.3.2.2.4 Oxygen and Nutrient Supply. Microorganisms found on the material are mainly aerobic and hence require oxygen for their metabolism. For instance, heterotrophic aerobic bacteria found on biofilter material require between 5 and 15% oxygen.[34] In the case of flow gases heavily loaded with organic compounds, biofiltration performance can be negatively impacted by the amount of oxygen in the gas to be treated.[35] However, in most biofiltration processes, the oxygen content does not constitute a real problem owing to its abundance in the gaseous effluent and the low biofilm thickness, which avoids diffusional limitations.

Microorganisms require various resources to cover their energy and nutritional needs. In situations of nutrient deficiency, microorganisms reduce their metabolic activity[36] while an excessive dose, from a continuous supply, induces uncontrolled development of the biofilm leading to clogging.[37,38] Some authors suggest that the metabolic activity of microorganisms is stimulated in the presence of key elements in certain proportions, *i.e.* in a C : N : P ratio of 100 : 15 : 3 or 100 : 5 : 1.[39–41] In general, whatever the material used, a nutritional supplement is often required to maintain a satisfactory treatment efficiency. It has been observed that an extended use of compost leads to a gradual depletion of nutrient resources,[42,43] which can become a limiting factor in the long term.[44]

5.3.2.2.5 Temperature. Accurate control of gas temperature is required to optimize pollutant transfer from the gaseous phase to the biofilm and to promote microbial growth. Mass transfer is favoured by low temperatures while degradation kinetics are favoured by high temperatures.[32] Based on growth temperature, three groups of microorganisms can be found in biofiltration: psychrophilic, mesophilic and thermophilic, growing below 20 °C, between 20 and 40 °C and above 45 °C, respectively. The temperatures observed in biofiltration are generally in the range of 20 to 40 °C,[16,32] showing that the microbial population is mainly mesophilic. Even though the biological activity within the packing material can induce an increase in temperature, in the range of 2 to 10 °C,[16] the temperature is generally set by the gas to be treated[32] and hence upstream gases may need to be cooled or heated to avoid temperature shocks which can be harmful to cells. Consequently, in the case of cold or hot air treatment, the costs associated with temperature control can be a major drawback to the use of biofiltration.

5.3.2.2.6 pH. Not only does pH have a major impact on microbial metabolism it also seems to play a role in microbial attachment to the packing material.[32] Generally, biofiltration is implemented in a pH range of 5 to 9, and microorganisms do not easily support more than 2–3 units of pH variation.[16] Drastic changes in pH can damage the plasma membrane and also inhibit enzymatic activity and transmembrane proteins. They can also limit the bioavailability of certain nutrients. For example, the bioavailability of ammonia, which is an excellent source of nitrogen, is increased in its protonated form (NH_4^+; p*K*a $NH_4^+/NH_3 = 9.2$). As a consequence, mass transfer and hence pollutant absorption can lead to improved performance, for example, due to biofilter acidification during ammonia treatment.[45]

The pH of the filter medium depends on several factors, primarily the nature of the pollutants and their ability to generate acidic by-products.[16] Microbial degradation of pollutants can affect the pH by an acidification due to CO_2 production or the formation of acidic metabolites.[16,17] For example, the treatment of H_2S concentrations above 15 ppm leads to a rapid acidification by sulfuric acid formation.[46]

To maintain appropriate values, the pH in the packing material can be adjusted by the addition of an alkaline solution sprayed above the material, or the material itself can have a buffer capacity, for example, through addition of lime[47] or crushed oyster shell.[48]

5.3.2.3 *Advantages, Drawbacks and Limitations of the Process*

Biofilters show clear advantages for the treatment of gaseous effluents due to their simplicity of implementation, their rusticity and their efficiency for low pollutant concentrations. In addition, they are characterized by low operating costs and, unlike biotrickling filters, do not generate large amounts of effluent, liquid or sludge. However, the residence times needed for efficient degradation require large-size facilities, leading to high civil engineering costs. Moreover, the packing material needs to be replaced periodically (after 2–5 years of use). In addition, biofilters show decreasing efficiency in the case of high pollutant concentrations or recalcitrant compounds. Finally, and despite biofilter rusticity, special attention should be paid to process optimization.[16]

5.3.2.4 *Fate of By-products Generated during Biofiltration*

Biofilter use leads to the production of liquid and solid wastes, which should be treated or exploited. The liquid effluents are mainly leachates and water run-off due to rainfall for non-covered biofilters. These effluents, which contain large amounts of organic matter, salts from microbial metabolism (sulfates, chlorides, carbonates), acids (HCl, H_2SO_4) and microorganisms are sent to the wastewater treatment plant of the industrial site.[16] The solid wastes are mainly

components from the packing material. Since these materials can be organic, mineral or inert, various waste treatments can be implemented. Energy recovery from organic material (peat, pine bark) can be considered through incineration, pyrolysis or methanogenesis/biogas, or can be sent to compost units. Non-biodegradable inorganic materials (*e.g.* pozzolan) are generally recovered and sent to landfill sites.

5.3.3 Modelling a Biofilter

The model generally applied to simulate the different steps of diffusion and biodegradation was proposed by Ottengraf.[49] Presented succinctly, this model is based on the following assumptions:

- Biodegradation occurs in the biofilm liquid phase.
- The liquid phase in the biofilm is assimilated to water.
- The biofilm thickness is small compared with the packing material dimension, so that the surface of the biofilm is considered flat.
- The biomass concentration is assumed to be homogeneous in the reactor volume and constant as a function of time.
- The gas flow is a plug flow.
- The gas phase is considered ideal and there are no reactions between the chemical species.
- The mass transfer resistance in the gas phase is negligible.
- The regime is steady-state, thus there is no variation in operating conditions or in the biofilm (concentration of microorganisms, depth).
- Equilibrium occurs at the gas–biofilm interface.

Three cases can be considered for the mechanisms of biodegradation (Figure 5.5):

- First-order kinetics: the substrate concentration is a limiting factor. The reaction rate is controlled by the pollutant diffusion inside the biofilm.
- Zero-order kinetics—biological regime: the substrate concentration in the biofilm is high ($S_L \gg K_s$) but the diffusion into the biofilm is not a limiting factor.

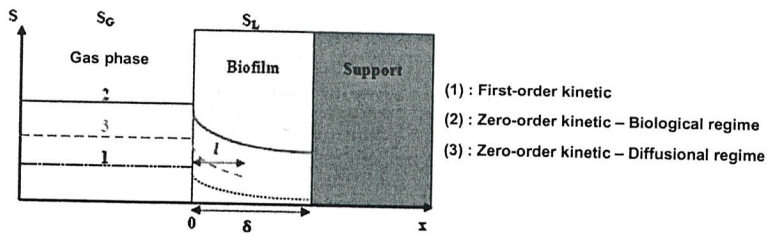

Figure 5.5 Substrate concentration profile in the biofilm as a function of the kinetic order.[38]

Table 5.5 Overview of kinetic constants and biodegradation yield as a function of the kinetic order.[38]

	Kinetic constant (K_i)	*Biodegradation yield* (BY)	*Total biodegradation condition*
First-order kinetics	$K_1 = \frac{a.D}{\delta}\phi_1 \tanh\phi_1$ (s^{-1})	$BY = 1 - \exp\left(\frac{-K_1 Z}{m.U_G}\right)$	$-\frac{K_1 Z}{m.U_G} \rightarrow \infty$
Zero-order kinetics: biological regime ($\phi_{cr} < \sqrt{2}$)	$K_0 = R_0.a.\delta$ (g m^{-3} s^{-1})	$BY = \frac{K_0 Z}{U_G.S^e_G}$	$\frac{K_0 Z}{U_G.S^e_G} \geq 1$
Zero-order kinetics: diffusional regime ($\phi_{cr} > \sqrt{2}$)	$K_0 = R_0.a.\delta$ (g m^{-3} s^{-1})	$BY = 1 - \left(1 - \frac{Z}{U_G}\sqrt{\frac{K_0.D.a}{2S^e_G.m.\delta}}\right)^2$	$\frac{K_0 Z}{U_G.S^e_G} \geq 2$

a specific surface area (m^2 m^{-3})
BY biodegradation yield
D diffusivity in the liquid phase (m^2 s^{-1})
K_i kinetic constant
m partition coefficient (Henry's law) (dimensionless; g m^{-3} gas and g m^{-3} water)
R_0 maximal biodegradation rate (g m^{-3} s^{-1})
SG substrate concentration in the gas phase (g m^{-3})
U_0 empty bed velocity (m s^{-1})
U_G gas velocity (m s^{-1})
Z biofilter length (m)
δ biofilm thickness (m)
ϕ_i Thiele number for an *i*-th order reaction (dimensionless)

- Zero-order kinetics—diffusional regime: the substrate concentration in the biofilm is high ($S_L \gg K_s$) and the diffusion into the biofilm is a limiting factor.

The substrate concentration evolution in the biofilm is S_L(g m^{-3}). K_s (g m^{-3}) is the Monod affinity constant. For carbon substrates, K_s is low and ranges from 10^{-3} to 10^{-2} g m^{-3}. Table 5.5 gives an overview of the biofiltration yields for the three cases.

5.4 Biotrickling Filters

5.4.1 Process Description and Mechanism

As shown in Figures 5.6 and 5.7, a biotrickling filter is a column packed with solid materials (inorganic grains, Rashig rings, Berl saddles) which is covered by a biofilm formed by predominantly aerobic microorganisms. The waste gas stream is introduced at the bottom of the system and flows through the packed bed; treated gas is vented to the atmosphere. Counter-current recycled water trickles over the packing and is recovered in a buffer tank. Fresh water and possibly

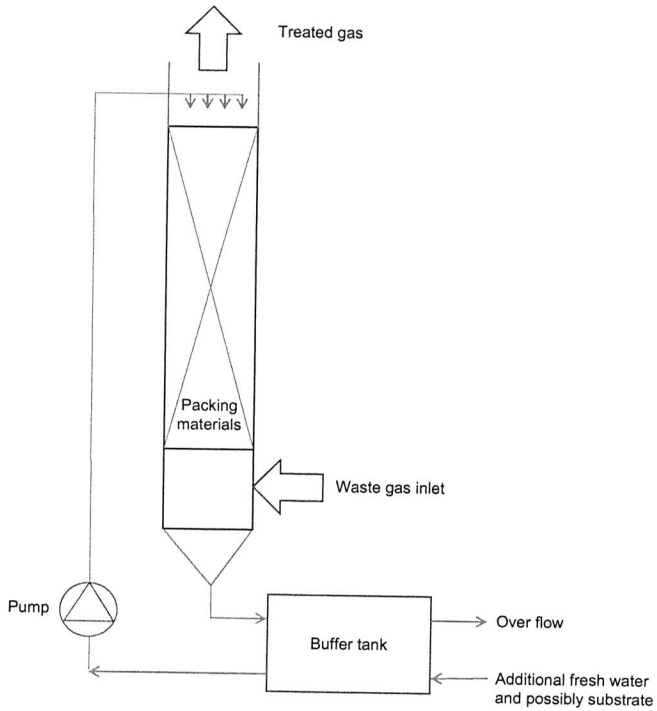

Figure 5.6 Diagram of a biotrickling filter for waste gas stream treatment.

substrates are added to this tank. These operations are required because of water evaporation by the gas stream and an increase in inorganic ions and/or metabolites in the aqueous solution. The water pH is also controlled by the addition of base or acid to the fresh solution to obtain appropriate bacterial growth.

The contaminants present in the gaseous phase are first transferred into the aqueous phase and then degraded in the biofilm present at the surface of the packing. Metabolites are removed by the solution flowing in the column. Some bacteria are also detached and are carried away by water. Washing the packing materials is sometimes necessary, due to clogging of the column by uncontrolled biofilm growth.

5.4.2 Operating Conditions and Performance

An adapted and updated summary of previously published information[4,50] on the operating conditions and performance of biotrickling filters is given in Table 5.6. To obtain optimal performance, a column design taking into account

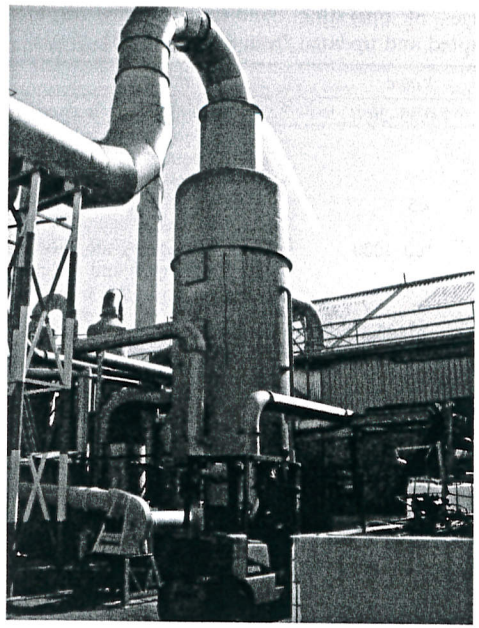

Figure 5.7 Example of a biotrickling filter used to remove ammonia present in air extracted from a waste storage room.

the residence time and the liquid to gas (L/G) mass ratio has to be optimized according to the properties of the contaminants, especially their solubility and biodegradability. L/G is a value adjusted to minimize the pressure drop and to optimize the mass transfer and thus the removal efficiency. Temperature in the column ranges from 10 to 40 °C and is similar to the temperature of the inlet gas. pH has to be close to neutral for good microorganism growth. Acid or base is added to the solution to control the mass transfer (slightly basic for acid pollutants such as H_2S and mercaptans or slightly acidic for basic molecules like ammonia and amines). A pH value ranging from 5 to 9 is also required for biofilm stability.

Table 5.7 presents data on the performance of a biotrickling filter in removing various pollutants. The majority of compounds are carbon and energy sources for heterotrophic microorganisms in aerobic conditions. The removal rates are correlated to the properties of the molecules such as solubility, given by the Henry's law coefficient (m), and biodegradability. For soluble compounds (weak m), mass transfer is easier and for biodegradable molecules, the removal rate is significant. This step of gas–liquid transfer is essential to obtain good performance from a biotrickling filter.

Table 5.6 Ranges of operating conditions applied in biotrickling filters (adapted and updated from ref. 4 and 33).

Parameter	*Value*	*Remarks*
Liquid velocity (U_L)/m h^{-1}	0.05–20	Compromise between the solubility of contaminants in water, the flooding point and the biomass loss due to significant flow of the solution
Liquid hold-up/%	<5	Value to be optimized for a better mass transfer
Air velocity (U_G)/ m h^{-1}	100–1000	Limited by the flooding point (*cf.* liquid velocity) and the clogging of the column due to microorganism growth by a supply of substrate
Air residence time/s	<60	Residence time lower than for biofilters depending on the biodegradation kinetics of pollutants
Bed porosity/ dimensionless	0.5–0.95	High value decreases clogging and head loss
Pressure drop/m H_2O or bar	0.005–0.5 0.0005–0.05	Depending on mass flow ratio of air and solution, bed porosity and concentration of biofilm
Specific surface area (S)/m^2 m^{-3}	100–400	Lower value compared with biofilters Better mass transfer due to an increase in external surface area.
Filter depth (H)/m	2–15	Light packing materials allow taller columns.
Solution pH	5–9	Relatively easy to control by addition of acid or base to the liquid phase
Temperature/°C	10–40	Mesophilic microorganisms. Treatments with temperatures ranging from 50 to 70°C could be efficient with thermophilic populations
Lag time/days	5–210	Function of the biodegradability of the molecule
Optimal performances/% removal	90–99	Depending on solubility and biodegradability of contaminants

5.4.3 Modelling a Biotrickling Filter

A multiscale approach integrating different mechanisms is required to model biological treatments and especially biotrickling filters. The hydrodynamic approaches such as holdup, head loss and residence time distribution are performed using classical equations used in multiphase reactors.[51–53] In terms of mass transfer and biodegradation, the assumptions are as follows:

- The column is working in a counter-current gas–liquid.
- For the gas phase, the column is considered as a plug flow reactor.
- The system is steady-state in terms of pollution loads, operating conditions (L/G), biofilm depth and bacteria concentrations.
- The double-film theory is applied in the contaminant transfer from the gas to liquid. In this case the transfer resistance in the gas phase is negligible.

Table 5.7 Removal rate of different contaminants in a biotrickling filter (adapted from ref. 7, 90 and 91).

Pollutant	*Biodegradability*	*Henry's law coefficient* (m)	*Removal rate*/g m^{-3} h^{-1})	*Ref.*
Alkanes				
n-Hexane	++	74.0	7.5	52, 92
n-Heptane	++	83.2	24	7
Aromatics				
Styrene	++	0.11	32	93
Toluene	+++	0.28	80	7, 94
Oxygenated compounds				
Methanol	+++	0.00019	100	95
n-Butanol	+++	0.00035	100	96
Propionaldehyde	+++	0.0025-4	300	97
Acetone	+++	0.0016	500	57
Methyl ethyl ketone	+++	0.0024	40	98
Diethylether	+	0.028	60	99
Methylterbutylether	+	0.023	45	100
Chlorinated compounds				
Dichloromethane	+++	0.093	150–200	101, 102
Chlorobenzene	++	0.18	60–300	103–105
Nitrogenous compounds				
Ammonia	+++	0.0007	4.9–22.6	106, 107
Trimethylamine	+++	6.6	13.3	108
Nitrobenzene	+	0.00098	50	61
Nitrogen oxides (NOx)	+		25	109, 110
Sulfur compounds				
Hydrogen sulfide	+++	0.94	100	111, 112
Carbon disulfide	++	0.39	220	113
Dimethyldisulfide	+	0.054	22.1	114

- The transfer resistance at the liquid-biofilm interface is not taken into account. Biodegradation in the biofilm is processed *via* a Monod kinetic equation.

Three phases are present: (i) the biofilm coating an inert packing material; (ii) the aqueous solution absorbing the contaminants; and (iii) the gas stream to be treated. The multiphase mechanisms of transfer and biodegradation and the concentration evolution profile are presented in Figure 5.8.

The equation system of the engineering model is as follows:[54,55]

- Global transfer coefficient for the absorption of contaminants into the aqueous solution:

$$\frac{1}{K_L} = \frac{1}{mk_G} + \frac{1}{k_L} \quad (5.1)$$

where K_L (m s^{-1}) is the global transfer coefficient, m (dimensionless g m^{-3} gas/g m^{-3} water) is the partition coefficient between the gas and the liquid

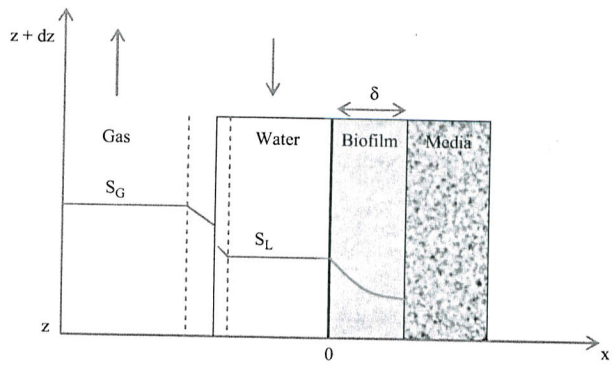

Figure 5.8 Schematic representation of the gas-water-biofilm-media system: evolution of substrate concentrations.

(Henry's law), k_L and k_G are the transfer coefficients (m s^{-1}) in the liquid and gas phase, respectively.

- Substrate mass flow (J) into the biofilm with Monod kinetics (first-order):

$$J = \sqrt{2DK_sR_0\left[\frac{S_L}{K_s} - \ln\left(1 + \frac{S_L}{K_s}\right)\right]} \qquad (5.2)$$

In the previous equation, D (m^2 s^{-1}) is the diffusion coefficient of the substrate into the biofilm. S_L is the substrate concentration at the liquid-biofilm interface (g m^{-3}), K_s is the Monod constant (g m^{-3}) and R_0 (g substrate s^{-1}) is the maximum substrate consumption rate.

In cases where all the depth of the biofilm is used and the concentration is high, compared with the Monod constant K_S, the biodegradation kinetics are zero-order. The maximal transfer flux (J_{max}) is then:

$$J_{max} = R_0\delta \qquad (5.3)$$

where δ (m) is the biofilm thickness.

- Mass balance in the gas phase

$$U_0\frac{dS_G}{dz} = \pm K_La\left(\frac{S_G}{m} - S_L\right) \qquad (5.4)$$

where a is the packing material specific surface area, S_G (g m^{-3}) is the substrate concentration in the gaseous phase and z (m) the height of the packing.

- Mass balance in the liquid phase (transfer and biodegradation) Ja : mass flow of substrate transferred in the biofilm (g/s)

$$U_L\frac{dS_L}{dz} = -K_La\left(\frac{S_G}{m} - S_L\right) - Ja \qquad (5.5)$$

The initial conditions are the inlet pollutant concentration in the gas phase and the recirculation of the liquid phase, which has the same substrate concentration in the inlet and outlet of the column. These conditions are written:

$$S_G^{z=0} = S_{Ge} \quad S_L^{z=0} = S_L^{z=Z} \qquad (5.6)$$

where Z (m) is the total height of the packing. The differential equation system is solved using a numerical method (the Runge–Kutta method, for example).

The model has been used for parametric studies. It was shown that performance is limited not by the gas–liquid transfer but by the compound's Henry's law coefficient and the substrate biodegradation step. However, this model has some limitations. The substrate consumption in the biofilm is overestimated due to a negligible transfer resistance between the liquid and the biofilm, and thus performance is overestimated. A variation in the biodegradation kinetics, due to inhibition by some substrate or metabolite concentrations, is not integrated into the model's equations.[56]

5.5 Bioscrubbers

5.5.1 Process Description and Mechanism

A schematic presentation of a bioscrubber is given in Figure 5.9. The removal of contaminants present in the gas stream is performed by an association of two steps:

- Mass transfer in a gas–liquid column. An empty column with a spray injector, a packed column or a venturi scrubber are the principal types of gas–liquid contactor.[14] Water is generally used but an organic solution can be used for hydrophobic molecules.[57–59]
- An activated sludge basin, possibly with a settling tank. The pollutant, transferred previously into the solution, is degraded in the bioreactor. The microbial suspension may settle in a sedimentation basin. The water is recycled at the top of the gas–liquid column.

Consequently, the mechanisms are similar to absorption and to biodegradation in an activated sludge reactor. To avoid clogging of the gas–liquid contactor, a settling tank separates the solid and liquid phases.

This system is particularly useful for hydrophilic molecules. In the case of hydrophobic compounds, an organic solution (silicone oil, for example) is used as the absorption solution in the transfer column.[60,61] The bioreactor is a multiphase system comprising organic and aqueous solutions, air injected into the solutions and a bacterial suspension.[62,63]

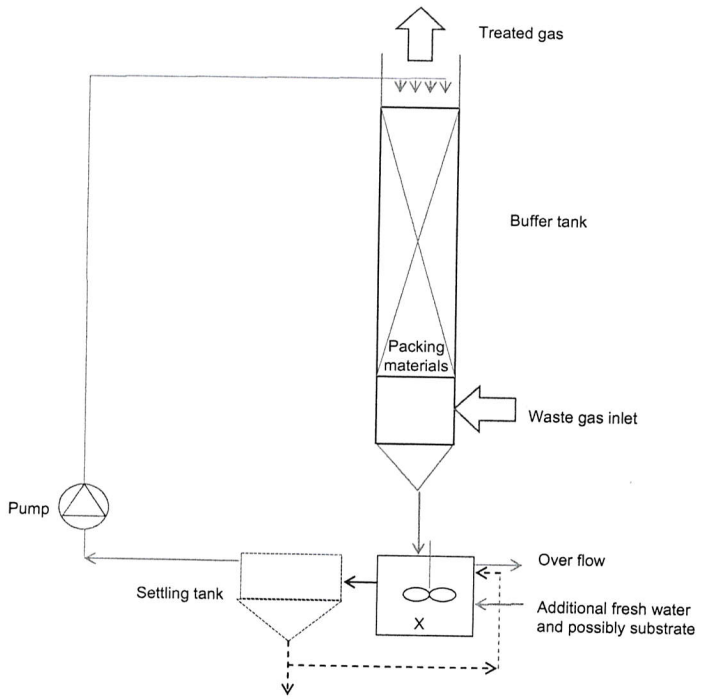

Figure 5.9 Diagram of a bioscrubber for waste gas stream treatment. X : activated sludge – biomass.

5.5.2 Operating Conditions and Performance

The operating conditions in a bioscrubber are similar to these in a biotrickling filter.[64] Table 5.6 gives some data for the absorber column. The activated sludge basins are managed as classical bioreactors found in wastewater treatment plants. The residence time ranges from 30 min to 2 h depending on the mass load of pollutants in the solution coming from the absorber.[65] Generally, the mass load is small and the activated sludge concentration is also at a low level (from 0.1 to 1 g L^{-1}).[66]

An example is given in Figure 5.10. Air extracted from a unit used to prepare food has to be treated to remove odorous emissions. A column (2.5 m in diameter and 4 m in length) is packed with Berl saddles. Waste gas flow is 7500 m^3 h^{-1} and is loaded with odorous molecules (aldehydes, ketones, organic acids) at low concentrations (between 1 and 10 mg m^{-3}) and fat aerosols. To remove fat particles, a cyclone is positioned just before the absorber. This system, which has been working for three years, gives good results with a removal percentage close to 90–95% in terms of pollutant concentrations and standard odour units.

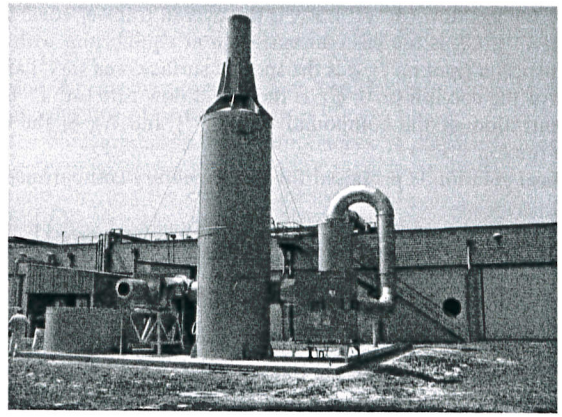

Figure 5.10 Example of a bioscrubber used to remove odorous molecules present in air extracted from a semi-prepared food factory.

5.5.3 Modelling a Bioscrubber

To describe the bioscrubber behaviour and especially the mass transfer column numerically, a set of transfer equations with hydrodynamic parameters is required.[67] An extensive description has already been published.[50] A succinct presentation is given here. The assumptions retained are as follows:

- The regime is assumed to be steady-state.
- Biodegradation of transferred pollutant is negligible in the gas–liquid column.
- There is no change in concentration with time in the liquid phase.
- A plug flow model, with and without axial dispersion, is used to represent the gas flow in the column.
- The tanks-in-series with a mass exchange model is used to represent the washing solution flow.

The model is based on the partial mass balance in the gas phase and liquid phase and is written as:

$$-Q_G \cdot \frac{dC_G^i}{dz} + D_a \cdot S \cdot \frac{d^2C_G^i}{d^2z} - K_G \cdot (C_{Gz}^i - C_G^{iE}) \cdot a \cdot S \cdot dz = 0 \qquad (5.7)$$

$$Q_L(C_L^{i+1} - C_L^i) + \int_0^{\Delta h} N_A^i \cdot a \cdot S \cdot dz = 0 \qquad (5.8)$$

with dz the height of a compartment i, Q_G is the gas flow rate (m^3 s^{-1}), C_G is the volatile compound concentration in the gas phase (mol m^{-3}), D_a is the axial

dispersion of the gas flow ($m^2\ s^{-1}$), K_G is the overall transfer coefficient in the gas phase ($m\ s^{-1}$), C_G^E is the gas concentration at equilibrium with the liquid phase concentration ($mol\ m^{-3}$), a is the specific surface area (m^{-1}) and S is the surface area of the column (m^2), Q_L is the liquid flow rate ($m^3\ s^{-1}$), C_L is the liquid concentration of the compound ($mol.m^{-3}$) and N_A is the density of transfer flux ($mol.m^{-2}.s^{-1}$).

An analytical solution is proposed for an elementary compartment i:

$$\text{Gas}: C_G^i - C_G^{i-1} = (H' \cdot C_L^i - C_G^i) \cdot \left[1 - \exp\left(\alpha \cdot \frac{Z}{J}\right)\right] \tag{5.9}$$

$$\text{Liquid}: C_L^{i+1} - C_L^i = \gamma \cdot (C_G^i - C_G^{i-1}) \tag{5.10}$$

where H' is the Henry's law coefficient (dimensionless), Z the height of the transfer column (m), and J the number of tanks-in-series. α and γ are coefficients whose expressions vary according to the type of transfer and reaction:

- For a plug flow of the gas phase:

$$\alpha = \frac{-K_G.a.S}{Q_G} \tag{5.11}$$

- For a plug flow with axial dispersion of the gas phase:

$$\alpha = \frac{U_G}{2 \cdot D_a} \cdot \left(-1 + \sqrt{1 + 4 \cdot \frac{K_G \cdot a \cdot D_a}{U_G^2}}\right) \tag{5.12}$$

- For a transfer without reaction in the liquid phase:

$$\gamma = \frac{-K_G \cdot a \cdot S}{\alpha \cdot Q_L} \tag{5.13}$$

- For a transfer with reaction in the liquid phase:

$$\gamma = \frac{K_G \cdot a \cdot S}{\alpha \cdot Q_L} \cdot \left(1 + \frac{K_2}{[H_3O^+]} + \frac{K_1 \cdot K_2}{[H_3O^+]^2}\right)^{-1} \tag{5.14}$$

This model has been applied to a bioscrubber used to remove ethanol (a very biodegradable molecule) and hydrogen sulfide. A statistical approach shows that the prediction of the transfer efficiency has a 95% confidence interval.

5.6 Conclusions and Trends

Different bioprocesses used to remove contaminants found in waste gas have been presented: biofilters, biotrickling filters and bioscrubbers. The technologies have been described according to their principles, operating conditions and performances. Although numerous publications have appeared in recent decades, more research into these complex systems is still required to:

- determine the mechanisms of mass transfer into aqueous solution for complex mixtures of contaminants in the gas phase;
- study the biodegradation in the biofilters or in activated sludge basins;
- examine the engineering and design of these bioprocesses;
- model and simulate the multireactor systems.

Some laboratory studies have been published on multiphase reactors using organic/aqueous solutions to capture hydrophilic and hydrophobic contaminants before biodegradation. However, more work is still necessary to scale up the pilot unit to an industrial process.

Strong collaborations and research programmes between researchers in microbiology, biochemistry, chemistry and chemical or environmental engineering are required to obtain realistic mechanisms and performances. A good design of processes and simulation of these systems will then be achieved.

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