

Chapter 1

Introduction

1.1 Backgrounds

Industrial plants and processes use and emit many types of volatile organic compounds (VOCs) that rapidly become atmospheric pollutants. VOCs are widely used in many industries, such as printing, coating, plastics, refrigerant, electronics and paint manufacturing. Most VOCs, such as benzene, toluene, methanol, chloroform, trichloroethylene, and isoprene, are toxic and carcinogenic substances even at very low exposure levels. The presence of VOCs in air emissions has been the subject of recent environmental regulations and the industry is required to apply an appropriate technology to reduce its emissions. The current control technologies for VOCs (e.g. thermal incineration, wet scrubbing, and adsorption onto activated carbon) are often cost intensive, especially in cases where there are low concentrations of the pollutants

Biofiltration is a new technology to treat low concentration of VOCs. This technology is very cost-effective. In addition, it is environmentally friendly because the contaminants are completely converted to non-hazardous final products at low temperature. Generally, a biofilter is a column filled with a porous and humid packing material inoculated with microorganisms able to degrade pollutants. The air pollutants are transferred from the gas phase to the liquid phase and diffuse through the biofilm fixed on the surface of the packing material. The pollutants are subsequently biodegraded in the biofilm to water and CO₂ and used as the essential carbon source for the microbial growth.

Any porous material capable of adsorbing gaseous compounds and supporting biological growth can possibly be used as a packing material. The packing materials commonly used are natural materials such as peat, compost, soil, and sludge from sewage treatment plants and synthetic materials such as vermiculite, granular activated carbon, and extruded diatomaceous earth pellets (Aizpuru *et al.*, 2003).

The degradation of VOCs by microorganisms is affected by various environmental factors such as moisture content, temperature, pH, VOC input rate, the kind of contaminant, and accessibility to the target substances (Yoon and Park, 2002). The effectiveness of the biofilter largely depends upon the solubility of the compounds in the liquid layer of the biofilm (Shareefdeen and Baltzis, 1994). The hydrophilic and hydrophobic characteristics of the pollutants discharged in air emissions may significantly influence their removal capacities in biofilters.

In this work, the effects of operating conditions such as VOC input concentration, empty bed gas residence time, the height of the column, temperature, pH, and pressure drop on the treatment

of air polluted with methanol, air polluted with toluene, and air polluted with toluene and methanol were studied. After 122 d of operation, the optimal operating conditions were determined.

1.2 Theory

1.2.1 VOCs

The VOCs to be investigated in this research were toluene and methanol because these VOCs are usually used in chemical industries, furniture industries, etc. Toluene is hydrophobic substance which is less dissolve in water (with a water solubility of 0.53 g/l at 25°C); on the other hand, methanol is a hydrophilic substance which can easily dissolve in water (with a water solubility of 1,000 g/l at 25°C). They both are the hazardous air pollutants (HAPs) listed in Title III of the 1990 Clean Air Act Amendments (CAAA90) proposed by the US Environmental Protection Agency (EPA). The physical properties of toluene and methanol are presented in Table 1.1.

Table 1.1 Physical properties of studied VOCs (Spicer *et al.*, 2002).

Properties	Toluene	Methanol
Vapor pressure (mmHg, 25°C)	28.6	118
Polarizability (cm ³ /mole)	31	8.2
Water solubility (g/l, 25°C)	0.53	1000
Chemical formula/structure	C ₇ H ₈	CH ₃ OH
Molecular weight	92.1	32
Boiling point	111	65

Toluene is an aromatic hydrocarbon (C₇H₈) and identified as CAS#108-88-3 (Spicer *et al.*, 2002). Toluene was commonly used as an industrial solvent such as gasoline, acrylic paints, varnishes, lacquers, paint thinners, adhesives, glues, rubber cement, airplane glue, and shoe polish in the manufacturing of paints, chemicals, pharmaceuticals and rubber. At room temperature, toluene is colorless, sweet smelling, and volatile liquid. Toxicity can occur from accidental or deliberate inhalation of fumes, ingestion, or adsorption through the skin. The Occupational Safety and Health Administration (OSHA) has determined the acceptable level of occupational exposure to toluene for people in the workplace. Toluene levels of 100 ppm are considered safe for workers. Levels of 150 ppm are acceptable for short periods (<8 h). Toluene levels of 2000 ppm are considered dangerous to life and health. The duration of the exposure, not just the level, may be significant as well. Recent animal studies have suggested that exposure to subtoxic toluene levels, as low as 40 ppm, for prolonged periods, 104 hours per week for 16 weeks, may cause neurotoxicity (Martin, 2004).

Methanol is a clear, colorless and volatile liquid at ambient temperatures and identified as CAS#67-56-1 (Spicer *et al.*, 2002). Methanol is found commonly in antifreeze, perfumes, paint solvents, beverages, photocopying fluid, and windshield washing fluid. In addition, shellac is a common source of methanol toxicity (Likosky, 2005). Methanol is also used as a solvent in the production of single-cell protein, which is used as animal feed additives replacing such supplements as powdered milk, soybean meal, and fishmeal. Methanol can cause permanent blindness when breathed, ingested, or passed through the skin. Exposure to high concentrations can cause death. A coma resulting from massive exposures may last as long as two to four days. Because of the slowness with which it is eliminated by the human body, methanol should be regarded as a cumulative poison. Exposure can damage the liver and cause headaches, cardiac depression, nausea, vomiting, blurred vision, dizziness, a feeling of intoxication, and irritations of the eyes, nose, mouth, and throat. Repeated or prolonged contact can cause dryness and cracking of the skin.

1.2.2 Biofiltration

Biofiltration is relatively new application of bioprocess engineering in waste management. The process is inexpensive compared with the conventional techniques and very effective for treating large volumes of moist air streams with low concentrations of the biodegradable pollutants. In addition, the treatment is environmental friendly, treatment is performed at ambient temperatures, and it does not generate nitrogen oxides or secondary waste streams.

Biofiltration is a general term applied to the conversion of gas-phase chemical compounds to the common biological degradation products of carbon dioxide, water, and inorganic salts. Technologies considered to be forms of biofiltration include biofilters, bioscrubbers, and biotrickling filters. While all of these operate based on the same fundamental mechanisms of contaminant sorption and biodegradation, they have different design and control parameters, operational flexibility, and performance characteristics. In bioscrubbers the microbes are suspended in water, which is generally contacted with the polluted stream in a tower containing packing, such as pall rings. In biofilters, the microbes are located permanently in the path of the polluted stream, fixed and growing on some form of biological attachment media. Biotrickling filters work in a similar manner to biofilters, except that an aqueous phase is trickled over the packed bed, and that the packing is usually made of some synthetic or inert material, like plastic rings, open pore foam, lava rock, etc. Note that the conventional trickling filter used for wastewater treatment is sometimes referred to as a biofilter, but it is a completely different technology.

A typical biofilter configuration is shown in Figure 1.1. The contaminated off-gas is passed through a preconditioner for particulate removal and humidification (if necessary). The conditioned gas stream is then sent to the filter media (packing material). The off-gas stream is typically either forced or induced through the system with a blower. A vent stack is employed when necessary to meet monitoring or discharge requirements.

Any porous material capable of adsorbing gaseous compounds and supporting biological growth can possibly be used as a filter media. The packing materials commonly used include natural materials such as peat, compost, soil, and sludge from sewage treatment plants and synthetic materials such as vermiculite, granular activated carbon, and extruded diatomaceous earth pellets. The filter media provides a surface for microorganism attachment and growth. Mixtures of media types are sometimes used to provide operational advantages. In a soil, peat, or compost bed, the media itself may provide some or all of the essential nutrients required for microbial growth. Bulking agents and/or minerals can be incorporated into the media, depending on pH control requirements.

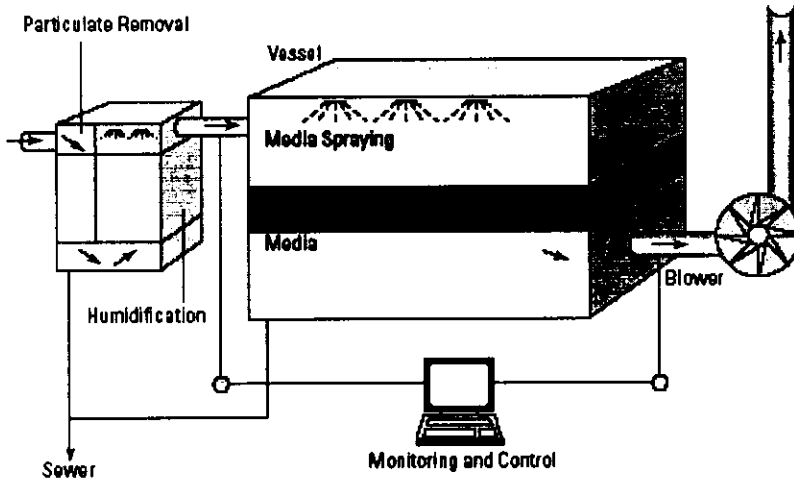


Figure 1.1 Typical biofilter configuration (Adler, 2001).

As the contaminated gas stream passes through the bed, contaminants are transferred from the gaseous phase to the media. Three primary mechanisms are responsible for this transfer and the subsequent biodegradation in organic media biofilters:

1. Gas stream \rightarrow adsorption on organic media \rightarrow desorption/dissolution in aqueous phase \rightarrow biodegradation.
2. Gas stream \rightarrow direct adsorption in biofilm \rightarrow biodegradation.
3. Gas stream \rightarrow dissolution in aqueous phase \rightarrow biodegradation.

Once adsorbed in the biofilm layer or dissolved in the water layer surrounding the biofilm, the contaminants are available to the microorganisms as a food source to support microbial life and growth. Air that is free, or nearly free, of contaminants is then exhausted from the biofilter. There are many variations to this basic approach. Biological activity in a filter will eventually lead to degradation of a soil or compost media as organic matter is mineralized and the media particles are compacted. Degradable filter materials typically require replacement every three to five years. Proper media selection affects biofilter performance with respect to its compaction and useful life. In addition, the media largely determines environmental conditions for the resident microorganisms. These

microorganisms are the most critical component of the biofilter, since they produce the actual transformation or destruction of contaminants. Microorganisms can vary significantly in metabolic capabilities and preferences. Naturally occurring microbes are usually suitable and most desirable for treating most gas-phase contaminants. However, some of the more unusual anthropogenic chemicals may require specialized microorganisms. Sometimes these organisms can simply be taken from sewage sludge and acclimated to the specific contaminants that are present; in a few cases, specially grown pure, mixed, or genetically engineered cultures may be preferred. Microbial cultures require a carefully controlled environment for optimal contaminant degradation.

The microorganisms grow in a biofilm on the surface of a medium or are suspended in the water phase surrounding the medium particles (Figure 1.2).

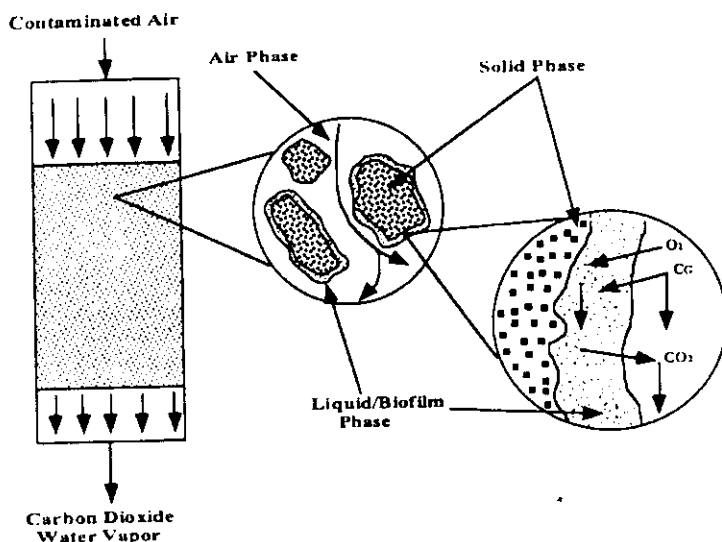


Figure 1.2 Internal mechanisms of a biofilter. Contaminated air (C_c) passes through the filter bed medium with oxygen and sorbs into a microbial biofilm/liquid phase attached to the filter medium. Microbes convert the contaminant to carbon dioxide and water (Deviny *et al.*, 1999).

Biofilters are not filtration units as strictly defined. Instead, they are systems that use a combination of basic processes: absorption, adsorption, degradation, and desorption of gas phase contaminants. Biofilters usually incorporate some form of water addition to control moisture content and add nutrients. 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 inoculum, medium pH, temperature, and the medium moisture and nutrient content.

The most important environmental factor for microbial function is the moisture in the contaminated air stream entering the biofilter. Most industrial or remediation off-gases have less than 100% relative humidity, so supplemental humidification is often needed to minimize bed drying. This can be achieved with an upstream humidifier (commonly a spray tower), spray nozzle humidifiers mounted within the biofilter, or steam injection built into the biofilter.

To describe the mechanisms of biofiltration clearly, general terminology pertinent to the field should be well defined.

Empty Bed Residence Time

The term "empty bed residence time" (also "empty bed contact time" or "empty bed detention time") relates the flow rate to the size of the biofilter. It is defined as the empty bed filter volume divided by the air flow rate (Equation 1.1):

$$EBRT = \frac{V_f}{Q} \quad \text{(Equation 1.1)}$$

where EBRT = empty bed residence time (seconds, minutes); V_f = filter bed volume (m^3 , ft^3 , etc.); and Q = air flow rate (m^3/h , scfm, etc.).

The empty bed residence time overestimates the actual treatment time. The medium occupies a substantial fraction of the biofilter, reducing the volume within which the flows and shortening the contact time. Even so, it is a commonly used parameter because it is easily calculated. The true residence time, which is the actual time a parcel of air will remain in the biofilter, is defined as the total filter bed volume multiplied by the bed porosity of the filter medium, divided by the air flow rate (Equation 1.2):

$$\tau = \frac{V_f \times \theta}{Q} \quad \text{(Equation 1.2)}$$

where τ = true residence time (seconds, minutes); θ = porosity = volume of void space / volume of filter material.

In literature, the terms "empty bed residence time" (EBRT) and "true residence time" (τ) are both commonly used. The difference between these two terms is the porosity factor (θ) and can be quite substantial. The effects of the empty bed residence time or true residence time on the performance of a biofilter are parallel. Generally, as either EBRT or τ increases, either by reducing the volumetric flow rate or by increasing the volume of medium, the system performance will improve. For many particular biofilter sites, the flow rate is fixed and a function of the contaminant producing process. Hence, reactor volume is often the only variable that can be increased. Increasing the porosity or size of the filter bed can increase this volume. However, biofilters with larger volumes and longer gas residence times are more expensive. Typical vapor residence times for commercial and

industrial applications range from 25 seconds for the treatment of odor and low VOC concentrations to over a minute for high concentrations of VOCs (Leson and Winer, 1991).

Surface (or Volumetric) and Mass Loading Rate

Surface (or volumetric) and mass loading rate are terms used to define the amount of air or contaminant that is being treated. Both terms are normalized, allowing for comparison between reactors of different sizes. Surface loading rate is defined as the volume of gas per unit area of filter material per unit time (in metric units as m^3 of gas per m^2 of bed surface per hour) as shown in Equation 1.3. Similarly, the volumetric loading rate is defined as the volume of gas per unit volume of filter material per unit time (in metric units as m^3 of gas per m^3 of filter material per hour).

$$\text{Surface loading} = \frac{Q}{A} \quad (\text{Equation 1.3})$$

where A = filter area (m^2 , ft^2).

$$\text{Volumetric loading} = \frac{Q}{V_f} \quad (\text{Equation 1.4})$$

The mass loading rate (either surface or volumetric) is the mass of the contaminant entering the biofilter per unit area or volume of filter material per unit time, often expressed as grams per m^2 or m^3 of filter material per hour. Because flow remains constant through a filter bed, the mass loading along the length of the bed will decline as contaminant is removed. However, generally an overall mass loading rate for a system is defined:

$$\text{Mass loading(surface)} = \frac{Q \times C_{Gi}}{A} \quad (\text{Equation 1.5})$$

where C_{Gi} = inlet concentration (g/m^3).

$$\text{Mass loading(volumetric)} = \frac{Q \times C_{Gi}}{V_f} \quad (\text{Equation 1.6})$$

Removal Efficiency and Elimination Capacity

Removal efficiency and elimination capacity are used to describe the performance of a biofilter. Removal efficiency (RE) is the fraction of the contaminant removed by the biofilter, expressed as a percentage:

$$\text{Removal efficiency} = \left(\frac{C_{Gi} - C_{Go}}{C_{Gi}} \right) \times 100 \quad (\text{Equation 1.7})$$

where C_{Gi} = inlet concentration (ppmv, g/m^3); C_{Go} = outlet concentration (ppmv, g/m^3).

Elimination capacity (EC) is the mass of contaminant degraded per unit volume of filter material per unit time. Typical units for elimination capacity are grams of pollutant per m^3 of filter material per hour. An overall elimination capacity is generally defined:

$$\text{Elimination capacity} = \frac{(C_{Gi} - C_{Go}) \times Q}{V_f} \quad (\text{Equation 1.8})$$

$$\text{Elimination capacity} = \text{Volumetric mass loading} \times \text{RE} \quad (\text{Equation 1.9})$$

Removal efficiency is an incomplete descriptor of biofilter performance because it varies with contaminant concentration, airflow, and biofilter size and only reflects the specific conditions under which it is measured. The elimination capacity allows for direct comparison of the results of two different biofilter systems because the volume and flow are normalized by definition; however, elimination capacity is also a function of input concentrations. Effluent concentration (or percent removed) is still commonly used as the goal of regulatory compliance. Elimination capacity can only be equal to or less than the mass loading rate. Under low load conditions, the elimination capacity essentially equals the load, and the system is calculated to be at 100% removal efficiency. By increasing the load on a system, a point will be reached where the overall mass loading rate will exceed the overall elimination capacity, generating removal efficiencies less than 100%. This point is typically called the critical load or critical elimination capacity. The decline in removal efficiency may be explained differently depending on which parameter is increased to increase the overall mass loading rate. If the flow rate is increased or the volume decreased, the residence time is reduced, and the contaminant may not have sufficient time to diffuse into the biofilm and be readily oxidized. Conversely, if the concentration is increased and the flow rate and volume remain the same, the biofilm may not be able to absorb the increase in concentration, with some of the contaminant simply passing through the system untreated. As the loading rate continues to increase, a maximum overall elimination capacity (EC_{max}) will eventually be reached. This maximum overall elimination capacity is independent of contaminant concentration and residence time within a reasonable range of operating conditions. Elimination capacities for conventional biofilters treating common pollutants typically range from 10 to 300 g/m³h.

The mechanisms of biofilters are complex. The biofilter contains a porous medium whose surface is covered with water and microorganisms. Treatment begins with transfer of the contaminant from the air stream to the water phase. The dissolved contaminant is moved by diffusion and by advection in the air (biofilters are presumed to see little water flow in comparison to biotrickling filters, but some percolation may occur). The contaminant may form complexes with organic compounds in the water. It may adsorb to the exopolysaccharides released by the biofilm-forming cells or to the cells themselves. It may also be adsorbed by the support medium. Ultimately, biotransformation converts the contaminant to biomass, metabolic by-products, or carbon dioxide and water. If the contaminant contains chlorine or sulfur, these will appear as chloride and sulfate. The biodegradation is carried out by a complex ecosystem of degraders, competitors, and predators that are at least partially organized into a biofilm.