

Biofilms in the Removal of VOCs and Foul Odors

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1. Introduction

Volatile Organic Compounds (VOCs) are widely used in many industries such as printing, petrochemicals, plastics, refrigerant, electronics, and paint manufacturing. (Babu and Raghuvanshi, 2004). However, large quantities of VOCs are released into the air, soil and groundwater because of occasional accidents and the absence of proper treatment technologies. Most VOCs are toxic and carcinogenic substances. Loss of these substances to the ambient air may have an adverse impact on air quality and thus endanger public health. Therefore, it is very important to develop effective means of removing these compounds to preserve human health and the environment.

There are various methods which are available for the removal of VOCs and odors. Physical and chemical methods such as incineration, ozonation, combustion, and adsorption, are expensive and require elaborate equipment and /or fuel. These processes also generate secondary pollutants that require further treatment because they simply convert target material into another phase. Compared to above conventional processes, biological treatment is effective and economical for low concentrations of contaminants in large quantities of air. The contaminants are sorbed from the gas to an aqueous phase where microbial attack occurs. In this process contaminants are converted to carbon dioxide and water vapor and organic biomass. Some of the industrial processes where biological air pollution control may be effectively utilized are such as adhesive production, chemical manufacturing, chemical storage, coating industry, composting, food processing, fragrance industry, iron foundries, landfill gas extraction, petrochemical manufacturing, petroleum industry, printing industry, pulp and paper industry, sewage treatment plant and wood products production etc. (Devinny *et al.*, 1999).

2. What is a Biofilm?

A biofilm is a complex aggregation of microorganisms marked by the excretion of a protective and adhesion matrix. Biofilms are also often characterized by surface attachment, structural heterogeneity, genetic diversity, complex community interactions and an extra cellular matrix of polymeric substances.

Single-celled organisms generally exhibit two distinct modes of behavior. The first is the familiar free floating or planktonic form in which single cells float or swim independently in some liquid medium. The second is an attached state in which cells are closely packed and firmly attached to each other and usually a solid surface.

Biofilms are the collection of microorganisms surrounded by the slime they secrete, attached to either an inert or living surface. Biofilm exists wherever surfaces contact water. More than 99 percent of all bacteria live in biofilm communities and out of this some are beneficial. Sewage treatment plants, for instance, rely on biofilms to remove contaminants from water. But biofilms can also cause problems by corroding pipes, clogging water filters, causing rejection of medical implants, and harboring bacteria that contaminate drinking water.

3. Why learn about biofilms?

"Microbiologists have traditionally focused on free-floating bacteria growing in laboratory cultures; yet they have recently come to realize that in the natural world most bacteria aggregate as biofilms, a form in which they behave very differently. As a result, biofilms are now one of the hottest topics in microbiology" (Potera, 1996).

As in any water system, 99 percent of the bacteria in an automated watering system is likely to be in biofilms attached to internal surfaces. Biofilms are the source of much of the free-floating bacteria in drinking water, some of which can cause infection and disease in laboratory animals. One common biofilm bacteria, *Pseudomonas aeruginosa*, is a secondary pathogen which can infect animals with suppressed immune systems. Besides being a reservoir of bacteria which can affect animal health, biofilms can also cause corrosion in stainless steel piping systems. In order to design and operate automated watering systems that deliver the bacterial quality required by the customers, understanding of how biofilms develop is important, some of the problems they can cause, and how they can be controlled.

4. Steps in Biofilm Development

4.1 Surface conditioning

The first substances associated with the surface are not bacteria but trace organics. Almost immediately after the clean pipe surface comes into contact with water, an organic layer deposits on the water/solid interface (Mittelman, 1985). These organics are said to form a "conditioning layer" as shown in Fig. 1 which neutralizes excessive surface charge and surface free energy which may prevent a bacteria cell from approaching near enough to initiate attachment. In addition, the adsorbed organic molecules often serve as a nutrient source for bacteria.

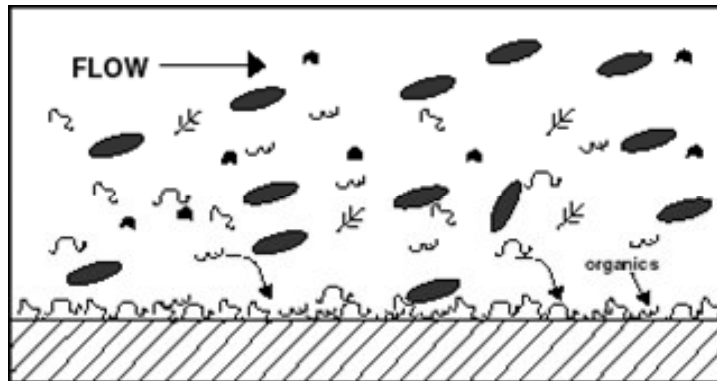


Fig. 1. Adsorption of organic molecules on a clean surface forms a conditioning film. (Characklis, 1990)

4.2 Adhesion of 'pioneer' bacteria

In a pipe of flowing water, some of the planktonic (free-floating) bacteria will approach the pipe wall and become entrained within the boundary layer, the quiescent zone at the pipe wall where flow velocity falls to zero. The Fig. 2 shows the transport of bacteria to the conditioned surface. Some of these cells will strike and adsorb to the surface for some finite time, and then desorb. This is called reversible adsorption. This initial attachment is based on electrostatic attraction and physical forces, not any chemical attachments. Some of the reversibly adsorbed cells begin to make preparations for a lengthy stay by forming structures which may permanently adhere the cell to the surface. These cells become irreversibly adsorbed.

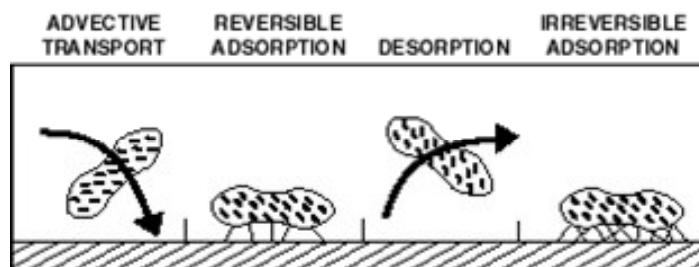


Fig. 2. Transport of bacteria cells to the conditioned surface, adsorption, desorption, and irreversible adsorption. (Characklis, 1990)

4.3 Glycocalyx or 'slime' formation

Biofilm bacteria excrete extracellular polymeric substances, or sticky polymers, which hold the biofilm together and cement it to the pipe wall as shown in Fig. 3. In addition, these polymer strands trap scarce nutrients and protect bacteria from biocides. According to Mittelman "Attachment is mediated by extracellular polymers that extend outward from the bacterial cell wall much like the structure of a spider's web as shown in Fig. 4. This polymeric material, or glycocalyx, consists of charged and neutral polysaccharides groups that not only facilitate attachment but also act as an ion-exchange system for trapping and concentrating trace nutrients from the overlying water (Mittelman, 1985).

The glycocalyx also acts as a protective coating for the attached cells which mitigates the effects of biocides and other toxic substances". As nutrients accumulate, the pioneer cells proceed to reproduce. The daughter cells then produce their own glycocalyx, greatly increasing the volume of ion exchange surface and a thriving colony of bacteria is established. (Mayette,1992). In a mature biofilm, more of the volume is occupied by the loosely organized glycocalyx matrix (75-95%) than by bacterial cells (5-25%) (Geesey, 1994). Because the glycocalyx matrix holds a lot of water, a biofilm-covered surface is gelatinous and slippery.

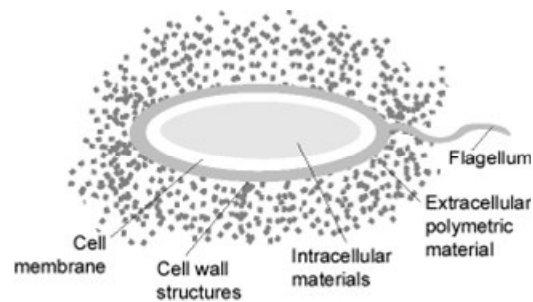


Fig. 3. Wild bacteria are "hairy" cells with extracellular polymers which stick to surfaces. (Mittelman, 1985)

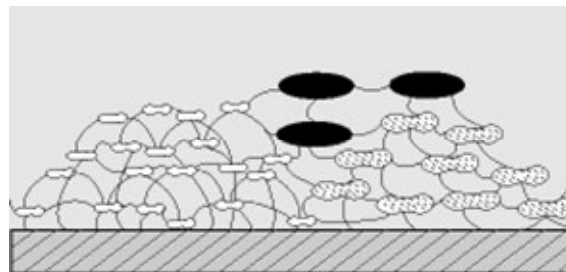


Fig. 4. Biofilm is made up microbes and a "spiders web" of extra cellular polymers, (Borenstein, 1994)

4.4 Secondary Colonizers

As well as trapping nutrient molecules, the glycocalyx net also snares other types of microbial cells through physical restraint and electrostatic interaction. These secondary colonizers metabolize wastes from the primary colonizers as well as produce their own waste which other cells then use in turn. According to Borenstein (1994), these "other bacteria and fungi become associated with the surface following colonization by the pioneering species over a matter of days."

4.5 Fully Functioning Biofilm: A cooperative "consortia" of species

The mature, fully functioning biofilm is like a living tissue on the pipe surface. It is a complex, metabolically cooperative community made up of different species each living

in a customized microniche. Biofilms are even considered to have primitive circulatory systems.

4.6 Biofilms grow and spread

A biofilm can spread at its own rate by ordinary cell division and it will also periodically release new 'pioneer' cells to colonize downstream sections of piping. As the film grows to a thickness that allows it to extend through the boundary layer into zones of greater velocity and more turbulent flow, some cells will be sloughed off as shown in Fig. 5. According to Mayette, "These later pioneer cells have a somewhat easier time of it than their upstream predecessors since the parent film will release wastes into the stream which may serve as either the initial organic coating for un colonized pipe sections down stream or as nutrient substances for other cell types" (Mayette, 1992).

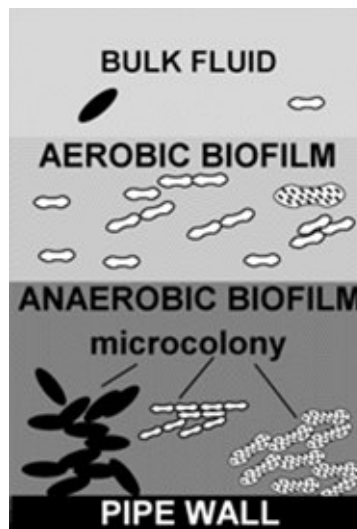


Fig.5. Bacteria and other microorganisms develop cooperative colonies or "consortia" within the biofilm, (Mayette,1992)

5. How fast does biofilm develop?

According to (Mittelman, 1985), the development of a mature biofilm may take several hours to several weeks, depending on the system. *Pseudomonas aeruginosa* is a common 'pioneer' bacteria and is used in a lot of biofilm research. In one experiment researchers found that *Pseudomonas* cells adhere to stainless steel, even to electropolished surfaces, within 30 seconds of exposure.

6. Advantages of Biofilm

- Nutrients tend to concentrate at surfaces
- Protection against predation and external environment
- Waste can accumulate to toxic levels inside biofilm
- Access to oxygen and water can become limited

7. Industrial Applications of Biofilms

The ubiquity and significance of the biofilm phenomenon is confirmed by wide range of applications in industries, including petroleum, specialty chemicals, health, household products, drinking water, mining, and utilities. Some of the industrial applications are given as following.

7.1 Bioremediation

Biological remediation is the use of cultured bacteria to remove harmful contaminants from soil and wastewater. Biological agents are also used to control fats and grease and sulfides in wastewater systems. Biological remediation programs also include the use of certain chemicals that select for a specific type of bacteria known to metabolize certain environmentally objectionable materials. The process also takes place in the biofilm as formed by the microbial degradation.

7.2 Odor Control

A variety of odors are created or liberated in waste treatment applications. Odor causing compounds include inorganic and organic gases and vapors generated as a result of biological activity. Odors are due to multiple compound mixtures consisting of many volatile organic compounds (VOCs, i.e. aldehydes), reduced sulfur compounds (i.e. dimethyl disulfide, mercaptans), nitrogen based compounds (i.e. amines). Organic vapors may also originate from the direct discharge of industrial chemical wastes. Identification of the odor-producing compounds in the wastewater provides an important step in selecting the appropriate control strategy (or strategies). A complete survey and characterization of the odors is the first step of any cost-effective control program. Odors can be a problem for many industries including municipal wastewater, industrial, food and beverage processing, pulp and paper plants and during environmental remediation projects.

7.3 Bioreactors

Bioreactors are vessels in which a chemical process occurs by means of bio chemically active substances or organisms. The chemical process can be either aerobic or anaerobic. The process is done under a particular temperature, residence time and pH value. The different applications of bioreactors are as follows:

- Widely used for cell culture and fermentation.
- In pharmaceutical drug production.
- For VOC and head-space analysis.
- For municipal wastewater treatment.
- Tissue or cell growth.

- Chemical reactions.

7.4 Biofiltration

Biofiltration is a viable and potentially cost-effective alternative for the treatment of airstreams with low concentrations of pollutants. It utilizes a microbial population immobilized in the biofilm grown on a solid support to degrade organic pollutants in waste gas streams (Raghuvanshi and Babu, 2006). The pollutants diffuse from the gas phase into the biofilm where they are metabolically consumed by the microorganisms and degraded to carbon dioxide and water. Under proper conditions biofilters can offer high removal efficiency through a process that is environmentally friendly.

7.4.1 Mechanism of Biofiltration

7.4.1.1 Biofilter and Bio trickling filter mechanics

Among modelers there is general agreement on the mechanisms of biofilters and bio trickling filters as shown in Fig. 6. Contaminants are carried into the biofilter by the air at such rates that the flow is presumed to be laminar, although dispersion occurs because of the tortuosity of the pores in the porous packing. As the air passes through the packing, contaminants are transferred from the air to the water in the biofilm. The contaminants diffuse into the depths of the biofilm and microorganisms in the biofilm absorb the contaminants and biodegrade them. Contaminants may also be adsorbed at the surface of the packing. The great majority of reactors utilize aerobic respiration, so that oxygen and nutrients must also dissolve in the water or biofilm and diffuse to the microorganisms.

During operation at moderate-to-high concentrations 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 they will become inactive. Because the pores within the packing are highly irregular in shape, the growing biofilm will change the pore size distribution. The moving layer of water in bio trickling filters provides operators with a greater degree of control. It ensures high water content in the biofilm. It is generally recirculated from a storage tank, where pH and nutrient concentration can be monitored and controlled. It may also encourage some sloughing of biofilm, reducing clogging. Some modelers have presumed that the water layer in bio trickling filters represent a negligible barrier to contaminant transfer, and so have ignored it. Others have included the layer of moving water explicitly. Typically, the layer is presumed to be well mixed because of its rapid flow. Mass transfer occurs from the air, and again at the interface between the water layer and the biofilm (Barton *et al.*, 1998). Other phenomena, however, may be significant: the water carries contaminant downward (which may be either co-current or counter-current to air flow) and if the water is recirculated, any contaminant remaining in the water as it exits the bottom of the biofilter may be returned to the system at the top. In a system in which the air is flowing upwards, contaminant may be transferred from the recirculating water to the outgoing air, causing some reduction in removal efficiency. The thickness of the flowing water layer has been approximated by Alonso *et al.* (2001) as:

$$L_{bf} = \left(\frac{Q_w 3\mu_w}{a_0 H_T \rho_w g} \right) \quad (1)$$

where Q_w is the water flow rate, μ_w the viscosity, a_0 the surface area of the packing, H_T the height of the tower, ρ_w the density, and g is the acceleration of gravity.

It is commonly observed, however, that in biotrickling filters the flowing water does not produce a uniform layer, but wets some of the packing surface while leaving other parts exposed to the gas phase. Kim and Deshusses (2003) modeled this effect, using a previously developed empirical relationship to predict the fraction of packing surface wetted.

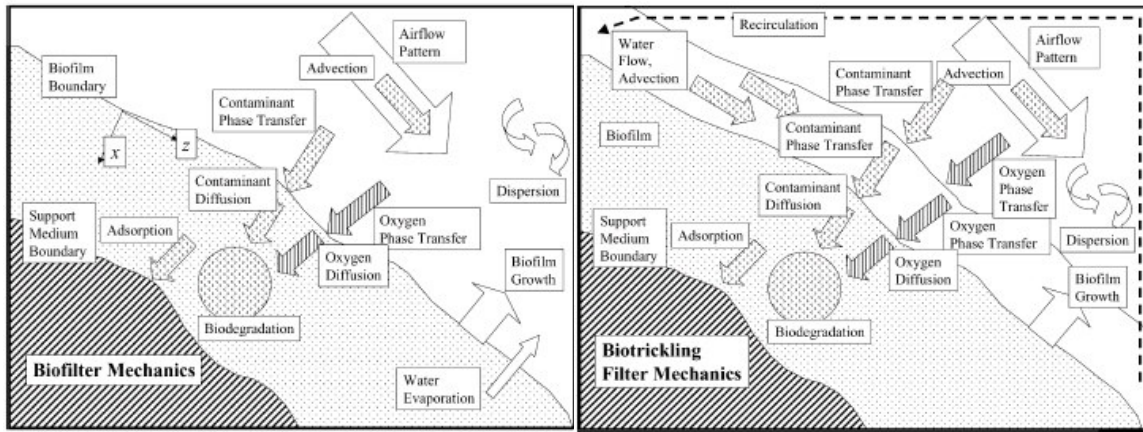


Fig.6. Phenomena involved in the operation of biofilters and biotrickling filters, (Devinnny, 2005).

7.4.2 Air flow

7.4.2.1. Advective transport in plug flow

Most biofilter or biotrickling filter models assume that air flow within the reactor can be adequately modeled as “plug flow”. Under these conditions, the effects of advection can be modeled in one dimension as:

$$\left[\frac{dC_{air}}{dt} \right]_{adv} = -V \frac{\partial C_{air}}{\partial z} \quad (2)$$

Where t is time, C_{air} the concentration of the contaminant in the air, V the interstitial flow velocity, and z is the axial dimension of the biofilter. Interstitial flow rates are higher than approach velocities:

$$V = \frac{V_A}{\theta} \quad (3)$$

Where V_A is the approach velocity and θ is the porosity of the medium.

7.4.2.2 Longitudinal dispersion

Because there are typically no radial gradients in concentration, radial dispersion has no effect and is neglected. Axial gradients may be substantial, however so, a few models have considered the possibility of axial dispersion. Hodge and Devinny (1995) produced such a model that modeled dispersion in the form:

$$\left[\frac{dC_{\text{air}}}{dz} \right]_{\text{disp}} = D_{\text{flow}} \frac{\partial^2 C_{\text{air}}}{\partial z^2} \quad (4)$$

where D_{flow} is the dispersion coefficient. However, both calculations and experiment indicated that axial dispersion was negligible except for biofilters operating at high flow rates - with empty bed detention times of a few seconds (Hodge and Devinny, 1997). While dispersion occurs as a result of molecular diffusion, in biofilters and biotrickling filters the dominant process is dispersion resulting from the tortuosity of flow.

7.4.2.3 Detailed models of air flow

Only a few models have attempted to depict the flow field in greater detail, including pore-level variations in flow speed and direction. (Nukunya *et al.*, 2004) produced a pore-network biofilter model in which the pore space was modeled as a cubic lattice of tubes, with various tube diameters chosen according to a realistic pore size distribution and placed randomly within the lattice. At each step in the calculation, the air flow field was recalculated to reflect the effects of the decrease in pore diameters as the biofilm grew. Flows perpendicular to the biofilter axis varied on a tube-by-tube basis and possible wall effects were implicitly included because the network was of limited extent.

(Ozis *et al.*, 2002) used a model based on percolation theory that specified the statistical characteristics of packing porosity without specifying a geometry. However, it implicitly recognized that some portions of the pore network in the biofilter could be blocked, producing reduced and irregular air flow.

7.4.3 Phase transfer

Transfer of a contaminant from a gas to a stagnant liquid or a biofilm can be viewed as limited by diffusion resistance within a laminar layer of gas near the interface and by resistance within the liquid or biofilm. Water within the biofilm is presumed to be stagnant, so that molecular diffusion is the only transport mechanism. It has been generally accepted that phase transfer is limited by diffusion in the water phase: the pores are relatively small, dispersion caused by advection tends to mix the gas phase, and molecular diffusion constants in water are on the order of 10⁴ times lower than those in air (concentrations, and therefore concentration gradients, are generally higher in the biofilm, but usually only by one order of magnitude). Typically, modelers presume that the concentration at the surface of the biofilm is determined by Henry's Law equilibrium with the concentration of contaminant in the bulk air phase, and that the flux of contaminant into the biofilm is controlled by diffusion resistance in the biofilm at the surface:

$$J_{bf} = D_w \left[\frac{\partial C_{bf}}{\partial x} \right]_{x=0} \quad (5)$$

Where J_{bf} is the flux of contaminant per unit of surface area, C_{bf} the concentration of contaminant in the biofilm, and x is the coordinate perpendicular to the biofilm surface, which is zero at the air–biofilm interface. In a biotrickling filter, it is typical that transfer in the flowing water layer is slower than transport in the air and faster than in the biofilm. The same formulation is used for transfer from water to the biofilm, and a parallel form is used for transfer from the air to the water. However, some investigators have observed mass transfer resistance at the interface. This is most likely to occur where contaminant solubility is high and biodegradation is rapid. It is less likely in a biofilter treating volatile organic compounds, but Kim and Deshusses (2003) observed strong external mass transfer limitation in laboratory and full-scale biotrickling filters treating hydrogen sulfide. In such cases, models presume that transfer is limited by diffusion resistance in a laminar layer of gas at the surface, and transfer occurs at a rate determined by the degree to which the gas–liquid interface of the biofilm is below saturation:

$$J_{bf} = k_{air-bf} \left[\frac{C_{air}}{H} - C_{bf} \right] \quad (6)$$

Where k_{air-bf} is the gas transfer coefficient and H is the Henry's law constant for the contaminant. Li *et al.* (2003) further approximated the gas transfer coefficient for spherical packing particles as:

$$k_{air-bf} = \frac{D_{air}}{2R_p} [2 + 1.1 Re^{0.6} Sc^{0.33}] \quad (7)$$

Where D_{air} is the gas-phase diffusion constant, R_p the particle radius, Re the Reynolds number, and Sc is the Schmidt number. Either of the flux terms must be multiplied by the surface area of the biofilm to determine total flux, and divided by the volume of the phase in order to determine changes in concentrations.

7.4.4 Diffusion within the biofilm

Diffusion of the contaminant into the biofilm is presumed to follow Fick's Law:

$$\left[\frac{\partial C_{air}}{\partial t} \right]_{diff} = D_{bf} \frac{\partial^2 C_{bf}}{\partial x^2} \quad (8)$$

where D_w is the molecular diffusion constant of the contaminant in water. While there is general agreement on this form of the equation, there is less certainty about the appropriate values for the diffusion constant. Molecular diffusion constants have been measured in pure water for most compounds, but diffusion within biofilms may be different. The abundance of cells and exuded polysaccharides reduces the cross-section of water actually available for diffusion and restricts the contaminant to diffusion along

tortuous pathways. Some investigators have used the empirical equation developed by Fan *et al.* (1990) that relates the diffusion coefficient in the biofilm to the diffusion coefficient measured in water and the total biomass density in the film (in g/L):

$$D_{bf} = D_w \left[1 - \frac{0.43X^{0.92}}{11.19 + 0.27X^{0.99}} \right] \quad (9)$$

Miller and Allen (2004) noted that additional complications are possible. In biofiltration of α -pinene, they showed that biological materials in the biofilm would adsorb the contaminant, causing an initial delay in transport but not affecting the steady-state rates of transport. They also found that in biological films, but not in abiotic films, enzymatic reactions rapidly convert α -pinene to a secondary product that is far more soluble, greatly increasing the effective solubility and degradation rates over those predicted for the parent compound.

7.4.5 Adsorption on the solid phase

Contaminants that diffuse to the bottom of the biofilm, particularly during the early stages of treatment when the biofilm is thin, may be adsorbed on the surface of the packing. Adsorption capacities vary widely with packing material. For biofilters using activated carbon packing, for example, modeling adsorption is necessary for accurate description of treatment of waste streams in which the concentration varies with time. Some modelers have also assumed that the particles are porous and contain significant amounts of water that can absorb contaminant (Deshusses *et al.*, 1995, Zarook *et al.*, 1997, Jorio *et al.*, 2003). For biofilters using lava rock, at the other extreme, adsorption of contaminant is negligible. For all of the packing materials, biofilm exopolysaccharides and other biofilm compounds may compete for adsorption sites, reducing adsorption of the contaminant. Finally, adsorption has no effect on steady-state conditions: the adsorbed material is simply an inactive reservoir that has no influence on treatment efficiency.

Adsorption and desorption have been included in unsteady-state models, where it is generally presumed that the mass of material adsorbed per unit surface area at equilibrium is linearly proportional the concentration of the contaminant in the biomass at the bottom of the biofilm, C_{bfbot} .

$$C_{adseq} = K_{ads} C_{bfbot} \quad (10)$$

Where K_{ads} is an empirically determined constant. (Ranasinghe *et al.*, 2002) took this approach but further modeled the adsorption constant as having Arrhenius-type dependence on temperature:

$$K_{ads} = K_0 \exp \left[\frac{-\Delta H}{RT} \right] \quad (11)$$

Where ΔH is the heat of adsorption, R the gas constant, T the temperature, and K_0 is a constant.

Zarook et al. (1997) and Ranasinghe et al. (2002) also considered non-equilibrium adsorption, assuming the flux from the biofilm to the surface occurred at a rate proportional to the degree to which it was below equilibrium. Their formulations were equivalent to:

$$J_{ads} = k_{ads} (C_{adseq} - C_{ads}) \quad (12)$$

Where J_{ads} is the flux per unit surface area, k_{ads} the rate constant, and C_{ads} is the concentration adsorbed.

7.4.6 Biomass growth and biodegradation

Biodegradation rates are a fundamental controlling factor for the effectiveness of biofilters. Most commonly, Monod Kinetics are assumed for growth as a function of existing concentrations of biomass and the concentrations of contaminant:

$$\frac{dX_{act}}{dt} = \mu X_{act} \quad (13)$$

$$\mu = \frac{\mu_{max} C_{bf}}{K_s + C_{bf}} \quad (14)$$

$$\frac{dX_{act}}{dt} = Y \frac{dC_{bf}}{dt} \quad (15)$$

For low values of C , growth is linear with contaminant concentration, and some modelers have presumed first-order kinetics. However, when the model includes sufficient detail to show biodegradation rates as a function of depth within the biofilm, concentrations will range from the Henry's equilibrium value at the surface of the biofilm to zero at the maximum depth of penetration, so it is likely that both regimes will be encountered and the full form of the Monod equation will be needed. Often the appropriate values for K_s and μ_{max} are uncertain. Both values are strongly dependent on the conditions under which they are determined and most data in the literature are from experiments performed on microorganisms in stirred, well-aerated suspensions, rather than in biofilms (and are highly variable even so). Thus, these parameters are often fitted to the biofilter data developed in the experiment being modeled.

7.4.7 Effect of biofilm thickness in biofiltration

Several studies have shown that the biofilm thickness is a crucial parameter for the removal. It is clear from these results that the biofilm thickness is one of the most crucial parameters that affect the removal. Increasing removal with increasing biofilm thickness is observed for low values of biofilm thickness (5-20 μm). This is indicative of a reaction-controlled process. A further increase in the biofilm thickness (30-100 μm) does not

affect the removal anymore, suggesting that the system is now diffusion-controlled. In diffusion limitation, the contaminant or oxygen fails to reach the depths of the biofilm. Therefore, an additional thickness is not beneficial. A wide variation in the biofilm thickness used by different investigators has been reported in the literature as shown in Table 2. However, none of the investigators have measured it directly from experiment. For example, Shareefdeen et al.11 reported effective biofilm thickness values ranging from 27 to 110 μm . These thickness values were theoretically calculated using an iterative procedure based on the assumption that all substrate/oxygen gets consumed within a fraction of biofilm.

8. Biofilm growth

Biomass growth produces a corresponding thickening of the biofilm. This thickening means that deeper portions of the biofilm receive less contaminant and oxygen, and become less efficient. In one case, it was shown that biofilm farther than 75–100 m from the surface was no longer active (Ozis *et al.*, 2002) The thickening biofilm reduces pore sizes, and beginning with the smallest pores, plugs them. The surface area available for mass transfer from the air phase declines. Pressure drops will increase. Thus, long-term biofilter models must recognize the phenomenon of biofilm growth. Biofilm growth is frequently ignored in modeling for moderate or short duration, as this is adequate for understanding phenomena not related to clogging, and greatly simplifies the models. Growth of the biofilm as a whole is equal to net growth of the film throughout its depth:

$$\frac{dX_{\text{act}}}{dt} = \int_0^{L_{\text{bf}}} \left(\frac{Y\mu_{\text{max}} C_{\text{bf}}}{K_s + C_{\text{bf}}} - b + \beta b \right) X_{\text{act}} dx \quad (16)$$

Song and Kinney (2002) approximated this integral by dividing the biofilm into layers and treating each layer as a cell in a cellular automaton model. Biomass grew in each cell according to Monod kinetics, died at a rate proportional to the amount of biomass present, and contributed a constant fraction of the dying cells to the store of dead biomass. When the total biomass present exceeded a preset value, the excess was pushed into the next outward cell.

9. Mathematical Models of Biofiltration

The model of biofiltration is being explained with respect to the case study for modeling and simulation of trickle bed air biofilter for removal of VOCs.

Case Study 1: Modeling and Simulation of Trickle Bed Air Biofilter for Removal of VOCs_(Raghuvanshi and Babu, 2005)

Theory

The stream containing VOCs is moving through a column filled with coal particles. The coal particles are covered with the biofilm. VOCs are transported to the air / biofilm interface where they are absorbed into the biofilm and then these are degraded by the

microbes as shown in Fig. 7. The microbes utilize these VOCs as the carbon and energy source.

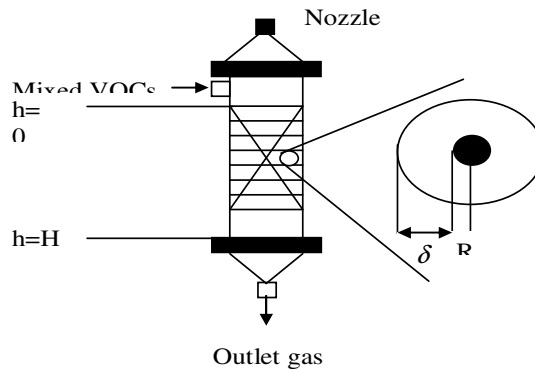


Fig. 7: Schematic diagram of trickle bed air biofilter for treating mixed IPA and ACE vapor

Limitations of Mathematical Model

1. The system is in a pseudo-steady state operating conditions.
2. The gas flow is in the axial direction alone and the flow velocity remains constant.
3. Since the biofilm thickness is very small compared to the inner radius of coal particle, the convective transport within the biofilm is neglected.
4. There is no boundary layer at the air / biofilm interface and the concentration of compound within the biofilm is a function of the concentration of that compound in the gas phase in contact with the biofilm.
5. The sum of all microorganisms is regarded as one kind of biomass within the biofilm.
6. The metabolic reactions occur within the biofilm.
7. The mass diffusivity (D), biofilm density (X_v) and biofilm thickness (δ) are constant through the TBAB.
8. In the gas phase, there are no concentration variations in the radial direction of the biofilter column and the axial diffusion of each compound can be neglected as compared to the axial convection.

Mathematical Model

On the basis of above assumptions, the governing equations that describe the transport of isopropyl alcohol (IPA) is given as following:

$$f(X_v)D_I \frac{d^2 S_I}{dr^2} = -f(X_v)D_I \frac{2}{r} \frac{dS_I}{dr} + \frac{X_v}{Y_I} \mu_I \quad (17)$$

$$f(X_v)D_A \frac{d^2 S_A}{dr^2} = -f(X_v)D_A \frac{2}{r} \frac{dS_A}{dr} + \frac{X_v}{Y_I} \mu_A \quad (18)$$

$$f(X_v)D_O \frac{d^2 S_O}{dr^2} = -f(X_v)D_O \frac{2}{r} \frac{dS_O}{dr} + X_v \left(\frac{\mu_I}{Y_{OI}} + \frac{\mu_A}{Y_{OA}} \right) \quad (19)$$

The specific growth rate of microorganisms is given by Dual Haldane type dependence as following:

$$\mu_I = \frac{\mu_{mI} S_I}{K_{SI} + S_I + S_I^2/K_{iI} + K_{IA} S_A} \frac{S_O}{K_{OI} + S_O} \quad (20)$$

$$\mu_A = \frac{\mu_{mA} S_A}{K_{SA} + S_A + S_A^2/K_{iA} + K_{AI} S_I} \frac{S_O}{K_{OA} + S_O} \quad (21)$$

$$\text{at, } r = R + \delta, \quad S_I = \frac{C_I}{m_I}, \quad S_A = \frac{C_A}{m_A}, \quad S_O = \frac{C_O}{m_O} \quad (22)$$

$$\text{at, } r = R, \quad \frac{dS_I}{dr} = \frac{dS_A}{dr} = \frac{dS_O}{dr} = 0 \quad (23)$$

The governing equations for IPA and ACE with trickle bed column height is given as following along with its initial conditions

$$u_g \frac{dC_I}{dh} = A_s f(X_v) D_I \left(\frac{dS_I}{dr} \right)_{r=R+\delta} \quad (24)$$

$$u_g \frac{dC_A}{dh} = A_s f(X_v) D_A \left(\frac{dS_A}{dr} \right)_{r=R+\delta} \quad (25)$$

$$u_g \frac{dC_O}{dh} = A_s f(X_v) D_O \left(\frac{dS_O}{dr} \right)_{r=R+\delta} \quad (26)$$

With initial conditions

$$\text{at } h = 0, \quad C_I = C_{Ii}, \quad C_A = C_{Ai}, \quad C_O = C_{Oi}, \quad (27)$$

Solution Algorithm

Eqs. (24-26) along with boundary conditions constitute a set of coupled boundary value problem (BVPs) that describe the simultaneous mass transfer and metabolic reactions of VOCs. The set of ordinary differential equations are converted in non-dimensionalised

form and then these equations are reduced to set of non-linear algebraic equations by using orthogonal collocation technique. Orthogonal collocation technique has successfully been applied to solve such type of ordinary differential equations in other studies by Babu and Sastry (1999). These non linear equations are then solved by Newton-Raphson method to obtain the substrate concentration inside the biofilm. A mathematical algorithm to solve these coupled equations is developed and implemented into a computer program using MATLAB (v.6.1) software. The same parameters reported by (Lu *et al.*, 2004) are used for simulation of the present model, which are given in Table 1. Eq. (8-10) that constitutes gas phase equations, are solved by finite difference technique to obtain the gas phase concentration at different positions of trickle bed air biofilter. The concentration profiles are then obtained by using the final gas phase concentrations obtained.

Table 1: Model parameters value for simulation (Lu *et al.*, 2003)

| Parameter | Value |
|--|-----------------------|
| A_S , biofilm surface area per unit volume of packing material, cm^{-1} | 3 |
| C_{O_i} , initial VOC concentration, g/cm^3 | 2.75×10^{-5} |
| D_A , mass diffusivity of ACE in liquid, cm^2/s | 1.15×10^{-5} |
| D_I , mass diffusivity of IPA in liquid, cm^2/s | 1.11×10^{-5} |
| D_O , mass diffusivity of oxygen in liquid, cm^2/s | 2.41×10^{-5} |
| m_A , thermodynamic distribution coefficient of ACE, (-) | 0.0016 |
| m_I , thermodynamic distribution coefficient of IPA, (-) | 0.000347 |
| m_O , thermodynamic distribution coefficient of oxygen, (-) | 34.4 |
| $f(X_V)$, | |
| K_{SA} , substrate half saturation constant for ACE, g/cm^3 | 9.48×10^{-5} |
| K_{SI} , substrate half saturation constant for IPA, g/cm^3 | 3.54×10^{-4} |
| K_{AI} , cross-inhibition constant for IPA expressing interaction with ACE (-) | 2.58×10^{-3} |
| K_{IA} , cross-inhibition constant for ACE expressing interaction with IPA (-) | 4.37×10^{-3} |
| K_{iA} , inhibition coefficient of ACE, g/cm^3 | 5.44×10^{-4} |
| K_{iI} , inhibition coefficient of IPA, g/cm^3 | 1.86×10^{-3} |
| K_{OI} , oxygen half saturation constant for IPA, g/cm^3 | 2.67×10^{-7} |
| K_{OA} , oxygen half saturation constant for ACE, g/cm^3 | 2.67×10^{-7} |
| H, height of TBAB column, cm | 85 |
| R, radius of coal particle, cm | 1 |
| X_V , biofilm density, g/cm^3 | 0.07-0.28 |
| Y_A , yield coefficient of ACE, g of biomass produced/g of ACE consumed | 0.40 |
| Y_I , yield coefficient of IPA, g of biomass produced/g of IPA consumed | 0.29 |
| Y_{OA} , yield coefficient of ACE on oxygen, g of biomass produced/g of O_2 consumed | 0.24 |
| Y_{OI} , yield coefficient of IPA on oxygen, g of biomass | 0.14 |

| | |
|---|-----------------------|
| produced/g of O ₂ consumed | |
| μ_{mI} , maximum specific growth rate of IPA, s ⁻¹ | 5.15X10 ⁻⁵ |
| μ_{mA} , maximum specific growth rate of ACE, s ⁻¹ | 1.11X10 ⁻⁴ |
| δ , biofilm thickness, cm | 0.008-0.025 |

Results and Discussion

The model described above is used to obtain the VOCs concentration along the biofilm thickness. The concentration profiles for IPA and ACE along the biofilm is shown in Fig. 8. The VOCs concentration is decreasing along the biofilm thickness from outside surface to inside surface of biofilm. This is validated with the theoretical phenomena occurring within the biofilm (Den and Pirbazari, 2002). The VOCs concentrations obtained at the interface of liquid and gas is used to obtain the bulk gas phase concentration. The bulk gas concentration is obtained at different heights of TBAB, which is shown in Fig 9. The result shows that the concentration of VOCs in the gas phase is decreasing continuously along the bed height, which is in good agreement with those reported in the literature (Amanullah *et al.*, 1999). Based on the results obtained by the present model, which are showing the good agreement with the results as reported in the literature, the simulations are carried out using the present model for a systematic parametric study. The simulations are carried out by varying different important parameters such as specific growth rate, empty bed residence time and specific surface area of biofilm per unit of packing material.

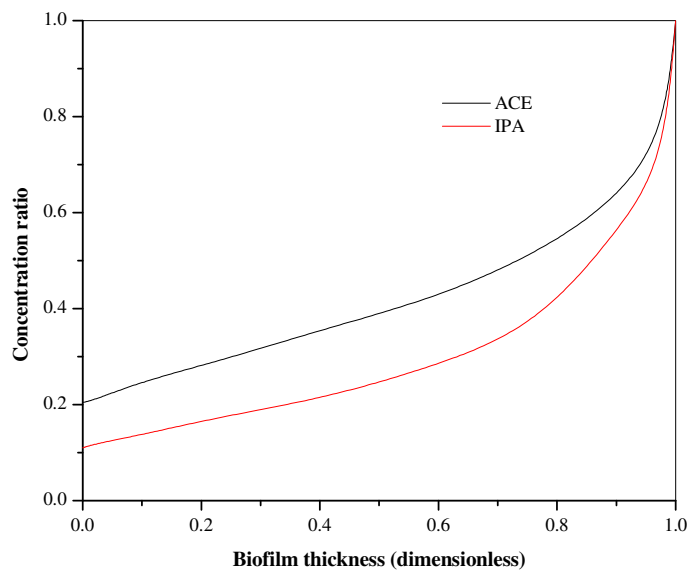


Fig. 8: Concentration profile of VOCs inside the biofilm

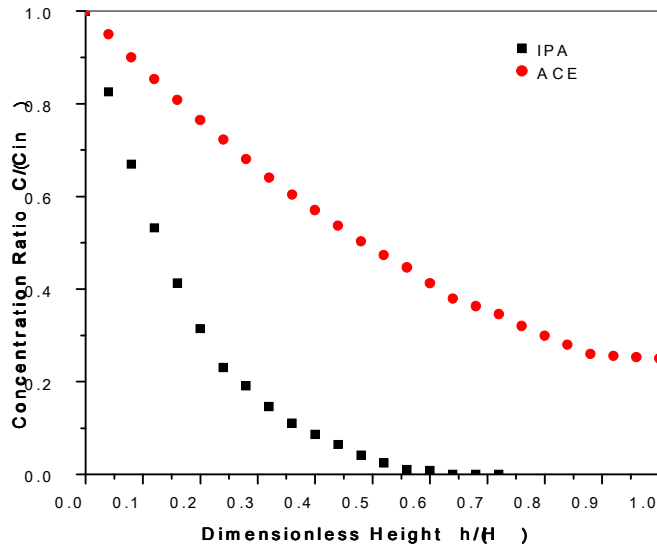


Fig. 9: Gas phase Concentration profiles for IPA and ACE against biofilter length

Effect of Empty Bed Residence Time (EBRT)

Figs. 10 & 11 show that, with the increase of EBRT, the removal efficiency of VOCs by the microorganisms increases. This is because with increase in EBRT, contact time increases between microbes and VOCs, and microbes get more time to consume VOCs and that result in increased removal efficiency of VOCs.

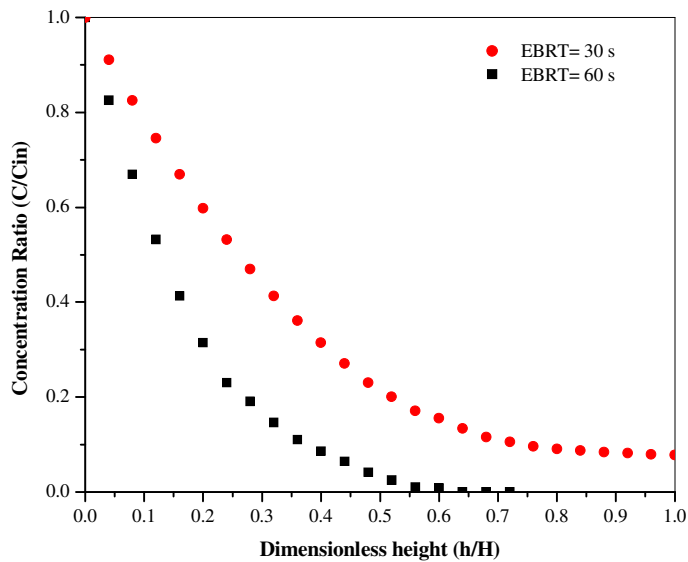


Fig. 10: Effect of EBRT on gas phase concentration profile of IPA

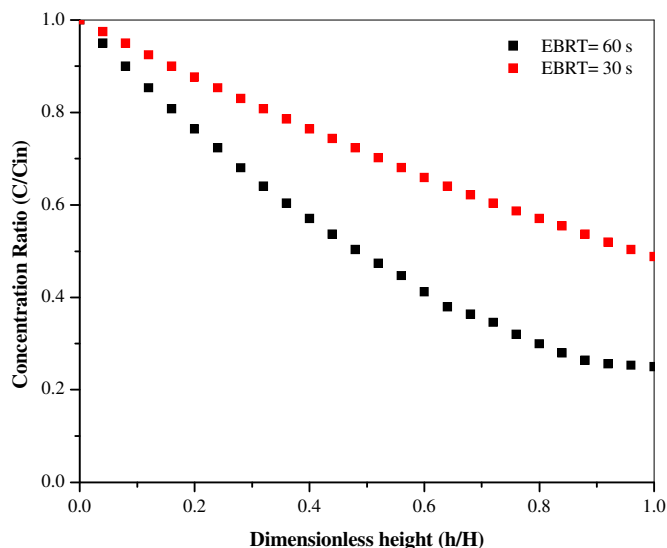


Fig. 11: Effect of EBRT on gas phase concentration profile of ACE

Effect of biofilm on surface area per unit volume of packing material (A_s)

Figs. 12 & 13 shows that the effect of surface area per unit volume of packing material on concentration profiles of IPA and ACE along the bed length. A sensitivity analysis of A_s is carried out from 1 to 5 cm^{-1} . The increase in A_s gives more surface area for mass transfer to take place from gas phase to air / biofilm phase and thus removal efficiency increases with the increasing value of A_s . The removal efficiencies of IPA and ACE is increased from 83.46 to 100 % and from 37.23 to 100% respectively with an increase in A_s from 1 to 5 cm^{-1} .

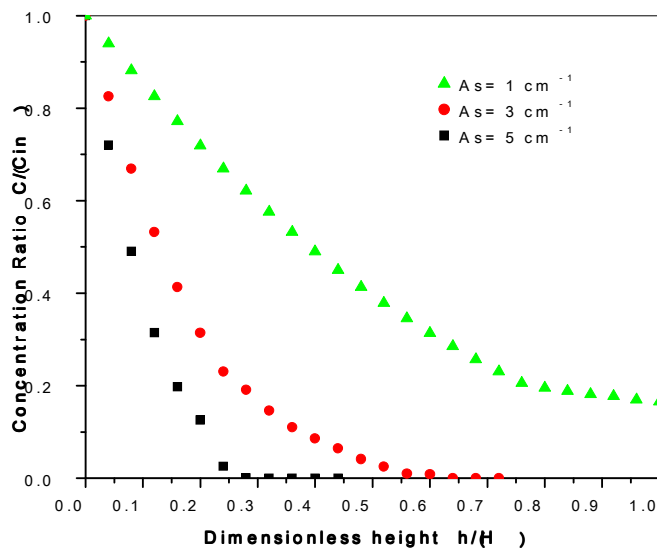


Fig. 12: Effect of A_s on gas phase concentration profile of IPA

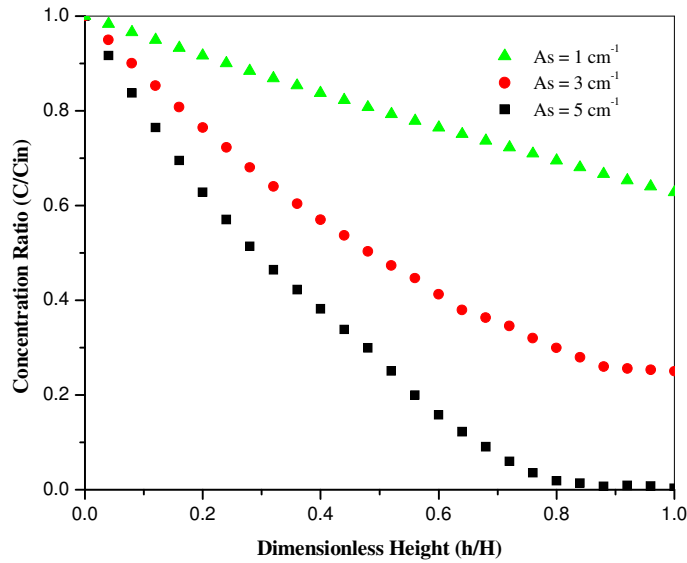


Fig. 13: Effect of A_s on gas phase concentration profile of ACE

Effect of Maximum specific growth rate (μ_m)

The removal efficiencies are higher for higher μ_m value. Figs 14 & 15 show that with the increase of μ_m , the removal efficiency of VOCs by the microorganisms increases. This is because, high μ_m means more is the microbes production and more microbes produced will consume the VOCs more rapidly. Therefore theoretically the model is validated for high μ_m values. The removal efficiencies of IPA and ACE is increased from 75.41 to 100% respectively with increase in value of μ_{mA} from 1.11×10^{-4} to $5 \times 10^{-4} \text{ s}^{-1}$.

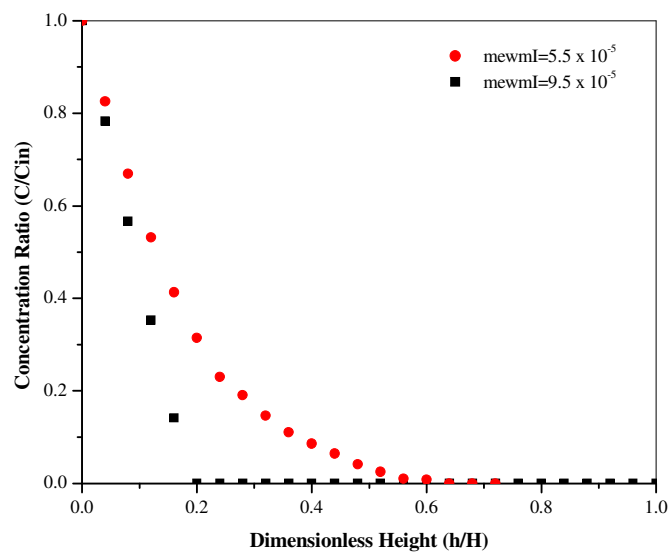


Fig. 14: Effect of μ_m on gas phase concentration profile of IPA

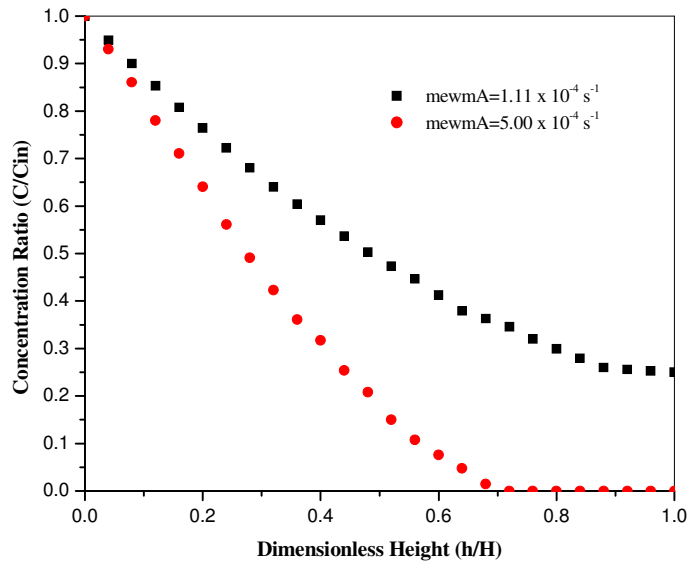


Fig. 15: Effect of μ_m on gas phase concentration profile of ACE

Conclusions

A mathematical model is developed and theoretically validated by the reported literature. The impacts of the important parameters are studied such as maximum specific growth rate constant (μ_m), empty bed residence time (EBRT) and surface area of biofilm per unit volume of packing material (A_s). The conclusions drawn are given as following.

1. The VOCs concentration is decreasing along the biofilm thickness from outside surface to inside surface of biofilm.
2. The maximum specific growth rate is identified as the important parameter, which strongly influences the removal efficiency as the microbes growth rate depends on the value of μ_m .
3. The other parameters such as EBRT and A_s also results in achieving better removal efficiency of VOCs with increase in their respective values.

10. Experimental Work on Biofiltration

Case Study 2: Biofiltration for the Removal of Methyl Isobutyl Ketone (MIBK) (Raghuvanshi and Babu, 2006)

Bulk organic chemicals such as MIBK and Methyl Ethyl Ketone (MEK) are used as solvent in many process industries (Raghuvanshi and Babu, 2006). The primary sources of MIBK are the industries that manufacture it or use it in production. Some of the industries that use it in production are chemical industry, rubber manufacturers, pharmaceutical industry, the semiconductor industry, and the manufacturers of paints, varnishes and lacquers. Workers in the industries that use or produce MIBK are at risk of exposure. Breathing MIBK for short periods of time (i.e. painting in a poorly ventilated area) can affect the nervous system. The effects may be headaches, dizziness, nausea,

numbness in the fingers and toes, and unconsciousness and even death (if the exposure is prolonged). MIBK vapor irritates the eyes, nose, and throat. Prolonged contact with the skin will cause irritation. Therefore, MIBK has been designated as high priority toxicity chemicals (Deshusses *et al.*, 1995, Geoghegan *et al.*, 1997).

Physical and chemical methods such as incineration, ozonation, combustion, and adsorption, are expensive and require elaborate equipment and/or fuel. These processes also generate secondary pollutants that require further treatment because they simply convert target material into another phase (Babu and Raghuvanshi, 2003). Compared to the above conventional processes, biofiltration is a very cost-effective process that degrades VOCs to non-toxic materials such as carbon dioxide (CO₂), water (H₂O) and biomass which can be used as manure. The microbes take the VOCs as the carbon source (food) for their growth and hence do not cause any sludge handling problem. Therefore, there is no need of any secondary treatment process.

Biofiltration is a technology, which is used for the treatment of gas streams contaminated with biologically degradable compounds (Babu and Raghuvanshi, 2006). Biofilters are those bioreactors in which a mixed culture is attached to a stationary support material such as compost, soil, peat, granular activated carbon or other porous media capable of adsorbing gaseous compounds and support biological growth. Contaminants pass into a wet biofilm layer surrounding the support particles and are aerobically degraded to carbon dioxide and water. The bed's moisture is maintained at constant level by introducing humid air to maintain a biologically active layer surrounding the media which is known as "biofilm". VOCs streams containing airstreams are transported to the air/biofilm interface where VOCs are adsorbed by biofilm and used as carbon / or energy sources by microorganisms.

The ketones are not so far extensively studied as far as biodegradability is concerned. Aerobic biodegradation tests have shown that, it is in general relatively easily biodegraded (Bridie *et al.*, 1979, Price *et al.*, 1974). In the present study, the biodegradability of MIBK was established by carrying out a wide range of batch experiments. The final well acclimatized culture with MIBK was prepared from the microbial culture obtained from the Municipal Sewage Treatment Plant, BITS Pilani. The batch biodegradation of MIBK was studied and biomass concentration was obtained for a concentration of 400 mg/l in 250 ml Erlenmeyer flasks. The optical density (OD) of microbial culture was obtained using UV Spectrophotometer.

Materials and methods

Materials

MIBK and other chemicals were used which were of Merck grade. The 250 ml Erlenmeyer flasks were used for carrying out the experiments.

Preparation of Media

The media (Mineral Salt Medium, MSM) was prepared which had the following composition (in g/l): K₂HPO₄ – 0.8, KH₂PO₄ – 0.2, CaSO₄.2H₂O – 0.05, MgSO₄.7K₂O –

0.5, $(\text{NH}_4)_2\text{SO}_4$ – 1.0, FeSO_4 – 0.01 in distilled water. 100 ml of MSM was taken in 250 ml Erlenmeyer flask and autoclaving was carried out to make it free from all the impurities. Stock glucose solution was prepared by dissolving 10 g of glucose in 100 ml distilled water.

Microorganisms Culture

The microbial mixed culture was obtained from the Municipal Sewage Treatment Plant, BITS Pilani and acclimatized with MIBK as the carbon source in a mineral salt medium (MSM). The sludge was kept for settling for almost 3-4 hours in cool place (away from sunlight). 10 gm of settled sludge was taken and was thoroughly mixed with 100 ml of distilled water. The shaking was carried out gently and then sludge was allowed to settle. The 50 ml of supernatant was taken and centrifugation was carried out for 2 minutes at 10,000 rpm in the Centrifuge. The pellet achieved after the centrifugation was further used for the microbial growth and supernatant was discarded.

Immobilization Procedure

The immobilization was carried out in laminar hood chamber. The autoclaved MSM solution was added with 1 ml of 1000 ppm glucose solution. Then $1\mu\text{l}$ of MIBK was added to maintain 9 ppm concentration of MIBK. After that, a loop full of sludge which was obtained after centrifugation was added. The solution was then kept in the rotary shaker at 37°C for around 48 hours. After obtaining sufficient microbial culture, the glucose utilizing culture was acclimatized with MIBK by slowly increasing its concentration and decreasing the concentration of glucose in the mixture. This was carried out by a series of transfers at 48 hour intervals for a period of more than 3 weeks to obtain a final well acclimatized mixed culture grown in MIBK. The MSM solution was prepared fresh for carrying out each transfer after every 48 hours. The final microbial culture obtained was containing the microorganisms trained with MIBK

Batch Experiments

To obtain the optical density of microbial culture, prepared from the culture obtained from the municipal sewage treatment plant, 100 ml of MSM solution was autoclaved and added with 1 ml of stock solution of glucose to maintain the glucose concentration of 1000 ppm in the solution. Then a loop full of sludge was added. The solution was then kept in the rotary shaker at 37°C . The absorbance of this solution was measured after every 24 hours for the period of 7 days.

The batch experiments were carried out for the measurement of biomass concentration and biodegradation of MIBK. This study was carried out for a concentration of 400 mg/l of MIBK in 250 ml Erlenmeyer flasks. In these experiments, 100 ml of MSM was prepared and autoclaved to remove impurities. This MSM solution was added with $46\mu\text{l}$ of MIBK to maintain 400 mg/l concentration and was inoculated with 5 ml of pre-cultured suspension. Then it was kept in a rotary shaker at 150 rpm at 37°C . Flask was sealed with stopper to minimize VOCs loss. Samples collected at regular intervals were analyzed for biomass and residual MIBK concentration. The culture was passed through a filter. The filter was dried at 90°C for 6 hours and cooled in a dessicator prior to weighing.

The concentrations of MIBK in aqueous samples were determined by using a Model 5700 series gas chromatograph (Nucon Engineers) fitted with 2 m long stainless steel column with a poropak packing and a flame ionization detector. The injection port was maintained at 150⁰ C, detector port at 150⁰ C and oven temperature was maintained at 200⁰ C. Nitrogen was used as the carrier gas. Injections of known volumes of MIBK which varied from 1 to 5 µl were introduced manually to obtain the calibration plot. Then concentration of residual MIBK which was collected at different intervals was analyzed by using gas chromatograph with help of calibration plot.

Results and discussion

Optical Density (OD)

The OD of the microbial culture was measured at 540 nm in 10 mm cuvette with a model 119- Systronics UV-VIS Spectrophotometer with respect to distilled water. The maximum absorbance value of 0.369 was achieved at 540 nm after 1 day. This shows that MIBK and glucose of amounts mentioned above was consumed by mixed culture in 1 day.

Biomass Concentration

Culture dry weights were obtained to calculate the value of biomass concentration. Growth kinetics were obtained for microbial culture in aerobic environment showing three phases. Fig. 16 shows the variation of biomass concentration with time. It can be categorized into three phases such as lag, log and stationary phase. Initially, there was no increment in the biomass concentration with time giving the lag phase. In log phase, concentration of biomass was increased with time and after sometime (in stationary phase) there was no increment in biomass concentration. The maximum biomass concentration was found to be 257 mg/l. The Fig. 16 was obtained between biomass concentration and time. The lag phase was observed up to 4 hours and corresponding biomass concentration was 60 mg/l. The log phase was observed up to 8 hours and biomass concentration was found to be increased to 240 mg/l. After that, the stationary phase was observed from 8 to 12 hours and corresponding biomass concentrations was found to be 257 mg/l. Fig. 16 shows that after 8 hours there was no increase in biomass concentration which indicates that MIBK (400 mg/l) was consumed completely by microbial culture. After that, there was no increase in biomass concentration because of the non availability of the carbon source. The experimental result obtained validated the biodegradability of MIBK as mentioned in the literature (Deshusses *et al.*, 1995, Geoghegan *et al.*, 1997).

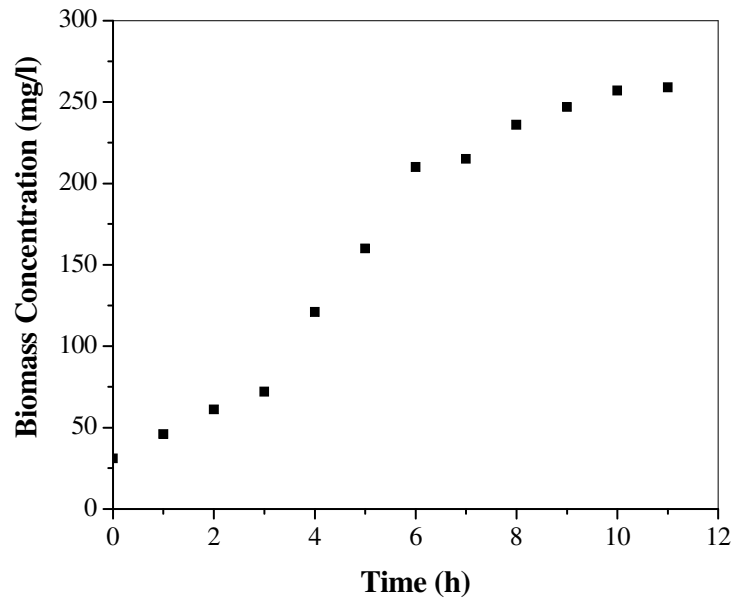


Fig. 16: Biomass Concentration (mg/l) Vs Time (h)

Dissolved Ketone Analyses

The Fig. 17 shows the calibration plot for MIBK concentration in aqueous phase. Fig. 18 was plotted between concentration of MIBK and time. In the Fig. 18, it was observed that the initial concentration of MIBK was more than 400 mg/l. It was because of the presence of MIBK in precultured solution. The MIBK concentration was found to be decreasing from 400 to 10 mg/l in 10 hours. It shows that the 400 mg/l of MIBK was completely consumed by microorganisms within 10 hours. That means the biodegradability was found to be good.

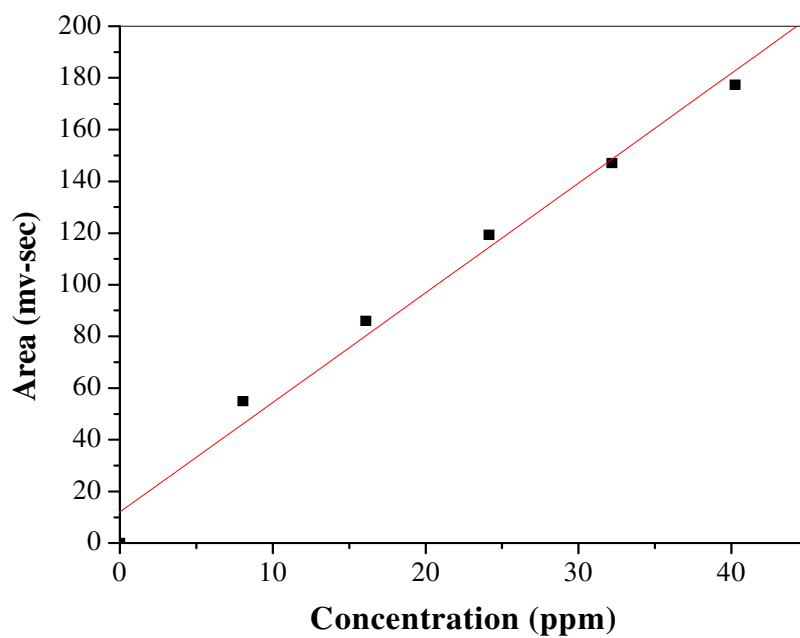


Fig. 17: Calibration Plot for MIBK

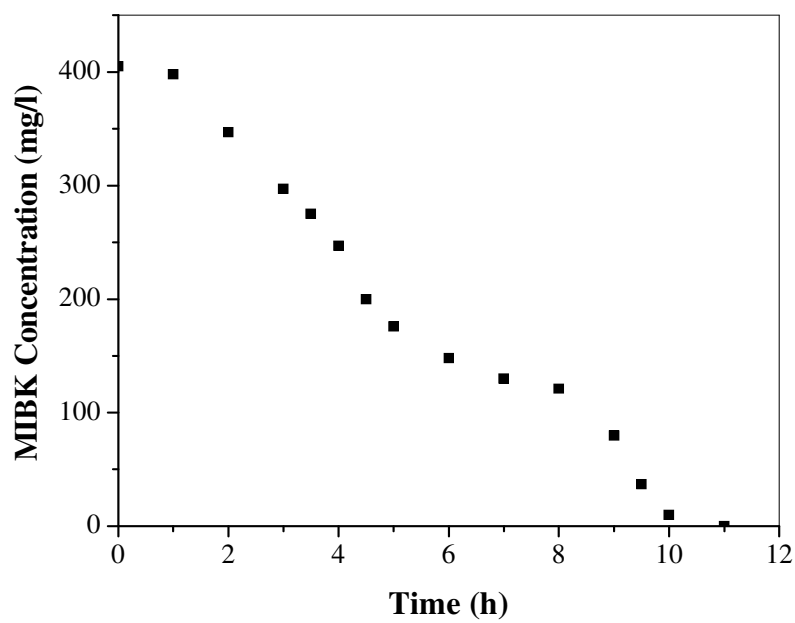


Fig. 18: MIBK Concentration (mg/l) Vs Time (h)

Conclusions

The present study has shown that the concentration of biomass increases with time and then becomes constant showing that growth stops once the substrate (MIBK in this case) is consumed completely. It also concludes that the microbes take some time to acclimatize to the new environment. The growth of the microbial culture follows the lag, log and stationary phases and the batch studies carried out for MIBK biodegradation has also followed the same growth curve. The MIBK concentration was found to be 10 mg/l from initial concentration of 400 mg/l showing that biodegradation of MIBK has taken place by the acclimatized mixed culture. The performance of cultures needs to be understood well in order to carry out the further detailed studies. The results obtained were matching with those available in the literature.

Nomenclature

| | |
|----------|--|
| A_S | biofilm surface area per unit volume of packing material, cm^{-1} |
| C | gas phase concentration |
| D | mass diffusivity in liquid |
| f | correction factor for the mass diffusivity within the biofilm |
| H | height of TBAB packed with media |
| h | position along TBAB column |
| K_S | substrate half saturation constant |
| K_{AI} | cross-inhibition constant for IPA expressing interaction with ACE |
| K_i | inhibition constant |
| K_{IA} | cross-inhibition constant for ACE expressing interaction with IPA |
| K_O | oxygen half saturation constant |
| m | thermodynamic distribution coefficient |
| R | radius of the coal particle |
| r | radial distance from the center of the coal particle |
| S | liquid phase concentration |
| u_g | superficial air velocity |
| X_V | biofilm density |
| Y | yield biomass on substrate |
| Y_O | yield biomass on oxygen |

Greek letters

| | |
|----------|------------------------------|
| μ | specific growth rate |
| μ_m | maximum specific growth rate |
| δ | biofilm thickness |

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