Biofilm structure and mass transfer in a gas phase trickle-bed biofilter


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Abstract: Mass transport phenomena occurring in the biofilms of gas phase trickle-bed biofilters are investigated in this study. The effect of biofilm structure on mass transfer mechanisms is examined using experimental observation from the operating of biofilters, microelectrode techniques and microscopic examination. Since the biofilms of biofilters used for waste gas treatment are not completely saturated with water, there is not a distinguishable liquid layer outside the biofilm. Results suggest that due to this characteristic, gas phase substrates (such as oxygen or volatile organic compounds) may not be limited by the aqueous phase because transport of the compound into the biofilm can occur directly through non-wetted areas. On the other hand, for substrates that are present only in the liquid phase, such as nitrate, the mass transfer limitation is more serious because of the limited liquid supply. Microscopic observations show that a layered structure with void spaces exists within the biofilm. Oxygen concentration distributions along the depth of the biofilms are examined using an oxygen microelectrode. Results indicate that there are some high dissolved oxygen zones inside the biofilm, which suggests the existence of passages for oxygen transfer into the deeper sections of the biofilm in a gas phase trickle-bed biofilter. Both the low gas-liquid mass transfer resistance and the resulting internal structure contribute to the high oxygen penetration within the biofilms in gas phase trickle-bed biofilters.

Keywords: Biofilter; diffusion; microelectrode; nitrate; oxygen; VOC

Introduction

Biofiltration is fast becoming a promising air pollution control technology for the removal of volatile organic compounds (VOCs) from waste gas streams, such as gaseous emission from wastewater treatment plants. However, the acceptance of this technology in the United States is still uncertain due to limited fundamental information. Theoretically, the treatment of VOCs in trickle-bed biofilters involves the following basic processes: (1) transport of the VOC and oxygen from the gas phase into the liquid phase; (2) transport of the VOC, oxygen, and nutrients from the liquid phase to the surface of the biofilm; (3) simultaneous diffusion and biotransformation of VOC, oxygen and nutrients within the biofilm. However, unlike biofilm systems used for wastewater treatment, biofilters for waste gas treatment are not completely saturated with water. The addition of nutrients in an aqueous feed is required for trickle-bed biofilters employing inert synthetic media. But this small water flow may not form a distinguishable liquid layer outside the biofilm, causing direct mass transfer of gaseous compounds into the non-wetted biofilm. This type of biofilm, which is not completely covered by water, could have pores and passages that allow for air flow into the biofilm, as represented in Figure 1. The structure and mass transfer processes for such a biofilm have not been well understood.

The importance of the non-saturation feature of the biofilms in gas phase biofilters was observed from various experiments performed in a pilot-scale trickle-bed biofilter system used for the treatment of ether. Experimental results showed that the rate of diffusion of nitrate into the biofilm was the rate limiting process in the biodegradation of VOC, and that oxygen was not a rate limiting factor under the COD volumetric loading rates used (Zhu et
al., 1996, Rihn et al., 1997). These findings were attributed to the structure of the unsaturated biofilms. A study of the effect of the aqueous phase on biofilter performance after medium backwashing showed that a longer draining period after backwash or less water content in the reactor resulted in better ether removal efficiency (Zhu et al., 1998a, 1998b). These improvements in biofilter performance were explained with a combination of biological and physical effects. However, all these studies were based on observations of the response of the biofilter to operating conditions. What is the internal structure of the biofilm in a gas phase biofilter and how this structure affects the mass transfer of VOC, oxygen and nitrate remains unclear. Only a limited number of fundamental experimental studies examining mass transfer phenomena have been reported. Kirchner et al. (1992) investigated the effects of VOC solubility and oxygen diffusion rate on biofilter performance and found that the diffusion of oxygen in the biofilm is rate limiting. Hartmans and Tramper (1991) studied the effect of the liquid phase flow rate on dichloromethane removal in a trickle-bed biofilter and found the biofiltration process to be mass transfer limited. De heyder et al. (1994) showed that the biodegradation of ethene, a poorly water soluble compound, in a packed granular activated carbon bioreactor improved after drying of the bed. They concluded that the water layer was limiting the mass transfer of ethene into the biofilm. However, Diks and Ottengraf (1991) found that gas-liquid mass transfer resistance was negligible in a system treating methylene chloride.

Recently, microelectrode techniques have been developed and effectively used to experimentally examine the internal structures and functions of biofilms (Zhang, 1994). Due to their small size, microelectrodes allow the investigator to measure concentration change over the interval of micrometres and have been used for oxygen, sulfide, pH, and redox potential analysis within biofilms (Fu, 1993; Yu and Bishop, 1997). All these experiments showed that most biofilms are spatially heterogenous with respect to the distributions of biotic and abiotic components. However, current studies are all focused on using microelectrodes to examine wastewater biofilms. No work has been reported on utilizing microelectrode techniques to investigate biofilms in gas phase biofilters.

The objective of this research is to investigate the distinctive structure of biofilms in gas phase trickle-bed biofilters attributed to the non-saturation of the biofilm with water. Special attention is given to how the biofilm structure affects mass transfer mechanisms in the biofilm. Mass transfer phenomena that affect oxygen transport in the biofilm system are studied utilizing microelectrode techniques.

Materials and method

Biofilter system

A schematic diagram of the biofilter system is presented in Figure 2. The experimental apparatus consists of two independent, parallel trickle-bed biofilters which are designated...
as Column A and B. Each reactor is constructed of seven circular glass sections (Ace Glass Inc., Vineland, NJ) with an internal diameter of 76 mm and a total length of 130 cm. Each section is equipped with a sampling port that extends to the centre of the column. The reactor is packed with 6 mm porous ceramic pellets (Celite R-635 Bio-catalyst Carrier) to a depth of about 61 cm. The biofilters are housed in a constant temperature chamber. The temperature in this chamber can be controlled in the range of 5–40ºC. The temperature is maintained at 27ºC during the experiments described here. The air supplied to the biofilters is purified with complete removal of water, oil, carbon dioxide, VOCs, and particles. After purification, the air flow to each biofilter is controlled by mass flow controllers. Liquid VOC is injected via a syringe pump into the air stream where it is vaporized and enters the biofilter through the topmost port. The nutrient feed is delivered into each biofilter through a spray nozzle that is controlled by a timing device. Each biofilter is operated in a co-current mode with the air and nutrient flows directed downward.

Reagent grade diethyl ether ($C_2H_5OC_2H_5$) was used as the sole model VOC. An enriched aerobic microbial culture with diethyl ether degrading microorganisms, taken from an activated sludge system utilizing diethyl ether as one of the carbon sources, was used for seeding the two biofilters. The nutrient solution contained all necessary macro-nutrients, micronutrients, and buffers as described by Rihn et al. (1997). Sodium nitrate was used as the sole nitrogen source and sodium phosphate monobasic as the sole phosphorus source.

Diethyl ether concentrations were measured by a gas chromatograph (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID) (Hewlett-Packard, San Fernando, CA). Nitrate nitrogen concentrations in the aqueous effluent were measured by a diode array spectrophotometer (HP8452, Hewlett-Packard, Palo Alto, CA). Phospholipid content inside the biofilm, which is a measure of the amounts of viable biomass present, was analyzed according to the procedure proposed by Findlay et al. (1989). Biofilm samples were also observed using a microscope (Nikon, SMZ-2T).

Oxygen microelectrode and biofilm sample measurements

The oxygen microelectrode is a solid-state oxygen electrode. It is suitable for amperometric measurement of dissolved oxygen (DO) concentrations in aqueous solutions. The fabrication of this oxygen microelectrode was based on the method developed and modified by Dowben and Rose (1953), Whalen et al. (1967), Linsenmeier and Yancey (1987),
and Fu (1993). The tip diameter of this oxygen microelectrode is 10 µm. The reference microelectrode is a Ag/AgCl reference electrode. The tip diameter of this reference microelectrode is five µm.

Biofilm samples grown on the ceramic pellets were taken from the biofilters and held on a small diamond holder. The diamond holder was tightly fixed at the centre of a plexiglass tray. The sample and tray were placed under a microscope (Nikon, SMZ-2T) for observation. A fiber optic light source (Dolan-Jenner Industries, 190-1) was used to illuminate the measurement area.

The oxygen microelectrode and the reference microelectrode were each fastened to a micromanipulator (World Precision, M3301). Using the micromanipulator, the tip of the reference microelectrode was placed inside the biofilm sample. The tip of the oxygen microelectrode was first positioned on the surface of the biofilm and then advanced in increments of 50 µm or 100 µm into the biofilm sample to measure the dissolved oxygen along the depth of the biofilm. Both microelectrodes were connected to a picoammeter for taking the readings. A Faraday cage was used to shield the measurement system from possible electromagnetic interference (Yu and Bishop, 1997).

Results and discussion
In a non-saturated biofilm system, if the limiting reactant is in the gas phase, and mass transfer resistance in the biofilm is significant, less wetting may result in increased biofilter performance. On the other hand, if the limiting reactant is in the liquid phase, more wetting may result in better biofilter performance. To investigate how the biofilm structure affects mass transfer mechanisms in the biofilters, this study was conducted in three phases. The first phase of this research investigated the effects of the concentration of nitrate (a compound in the aqueous phase) and oxygen (a gaseous and aqueous substrate) on biofilter performance. In the second phase, the influence of liquid flow rate was examined to further investigate the impact of the liquid phase. In the third phase, microelectrode techniques were used to analyze the mass transfer of oxygen in the biofilm, in order to get a better understanding of biofilm structure. The biofilm structure was also observed using a microscope.

Effect of oxygen and nitrate
The effect of a gas/liquid phase substrate (oxygen) and a liquid phase substrate (nitrate) on biofilter performance was investigated to determine how the biofilm structure in a gas phase trickle-bed biofilter affects mass transfer mechanisms. The two trickle-bed biofilters were operated at an empty bed retention time (EBRT) of 25 seconds, inlet gas flow rate of 8.64 m³/day, and nutrient liquid flow rate of 1 L/day. The influent ether concentrations were 67 ppmv and 133 ppmv, resulting in COD loading rates of 1.8 and 3.6 kg/m³-day for Column A and Column B, respectively.

The first experiment investigated the effect of the concentration of nitrate on biofilter performance, a substrate that exists only in the liquid phase. Four different influent nitrate concentrations were sequentially used: 33, 67, 133 and 267 mg NO₃-N/L. For both columns the ether removal efficiency increased when the influent nitrate concentration was increased. Figure 3 shows the effect of the logarithmic mean concentration of nitrate on ether removal in Column B. The log mean concentration \((\ln(C_{\text{in}}/C_{\text{out}}))\) is a measure of average mass flux or the mean driving force for diffusional mass transfer within a biofilter (Bird et al., 1960). It can also be seen that the ether removal efficiency and elimination capacity increased steadily with the increase in the nitrate diffusional driving force. This indicates that mass transfer resistance for nitrate in the biofilter is rate limiting. Nitrate was found in the aqueous effluent throughout this experiment. It can be seen from Figure 3...
that the log mean concentration of nitrate was always higher than 5 mgN/L. A nitrate kinetic study showed that heterotrophic biodegradation rates are not nitrate limited when the nitrate concentration was higher than 1 mgN/L, which again suggested that the diffusion of nitrate into the biofilm is rate determining. The second study was conducted to investigate the effect of oxygen (Figure 5). The influent concentration of oxygen was increased from 21% (ambient air), to 50% and 100%, while maintaining an influent ether concentration at 133 ppmv and a feed nitrate concentration at 67 mg/L. The results showed that the biofilter performance was not significantly affected, which indicates that oxygen was not limited in the biofilm under these conditions, and therefore, the nitrate was rate limiting as a growth nutrient rather than an electron acceptor. A complete description of the experimental results can be found in Zhu et al. (1996). A mathematical model was also used to simulate the biofilter performance and support the conclusion obtained from the experimental results (Alonso et al., 1997).

To interpret the experimental results, an estimate of the diffusivities of nitrate and ether in the biofilm was calculated. The same equation traditionally used for oxygen limitations (Williamson and McCarty, 1976) was used in this case. For the simplest case of steady state biofilm with no decay and for a biofilm to have nitrate mass transfer limitations the following relationship must hold:

$$Y_i x_a \frac{D_{wS}}{D_{wN}} r_S S_s > 1$$

where \( Y \) is the yield coefficient, \( i x_a \) is the fraction of nitrogen in biomass, \( D_{wS} \) and \( D_{wN} \) are the diffusion coefficients in water for ether and nitrate, \( r_S \) and \( r_N \) are the ratio between the diffusivities in the biofilm and in water for ether and nitrate, and \( S_s \) and \( N_s \) are the concentrations of ether and nitrate at the biofilm-water interface. The diffusivity of nitrate and ether in water were estimated as \( 2 \times 10^{-5} \) cm²/s, and \( 0.9 \times 10^{-5} \) cm²/s, respectively. Based on experimental results in this study, the average of \( Y_i x_a \) was 0.008 mg NO₃⁻N/mg ether-COD and the average of the log mean concentrations for ether and nitrate were 0.97 mg ether-COD/L and 80.2 mg NO₃⁻N/L.

After these values were substituted in the equation, a relation of \( r_S/r_N > 625 \) was obtained, suggesting that the diffusivity of ether is proportionally higher than that of nitrate in the biofilm. This result suggests that in gas phase biofilters, the mass transfer of substrates in the gas phase (such as ether and oxygen) may not be limited by the liquid phase because direct mass transfer to a non-wetted biofilm may occur. On the other hand, since substrates in the liquid phase like nitrate can only be transported into the biofilm through the wetted areas, the mass transfer limitation is more serious.

![Figure 3](https://iwaponline.com/wst/article-pdf/43/1/285/428561/285.pdf)

**Figure 3** Effect of log mean nitrate concentration on ether removal at COD loading of 3.6 kg/m³-day
Effect of liquid phase
Since mass transfer limitations for substrates in the aqueous phase are greater than those in the gas phase, further investigation on the influence of the liquid phase was carried out. Our previous studies revealed that high water content in trickle-bed biofilters due to flooding of the bed may cause mass transfer limitation in the biofilters (Zhu et al., 1998b). However, under normal operating conditions, the water content in trickle-bed biofilters is much lower than that after flooding. Water content in trickle-bed biofilters is controlled through manipulating the liquid flow rate. This study was to investigate the effect of liquid flow rate on biofilter performance.

Two identical trickle-bed biofilters were started at nutrient liquid flow rate of 1 litre per day. Throughout this study, both reactors were operated at an influent ether concentration of 333 ppmv, a gas flow rate of 6 L/min or 8.64 m³/day, and an empty bed retention time (EBRT) of 25 seconds, resulting in an ether loading of 7.1 kg COD/m³-day. The nitrate concentration in the nutrient feed was kept at 1067 mg NO₃-N/L. Under these conditions, nitrate concentration would not be a limiting factor (Zhu et al., 1996). The overall performance of the two biofilters with respect to ether removal is shown in Figure 4. Ether removal efficiencies in both columns reached 90% within two weeks of the start-up. During the first two weeks of operation, Column A and Column B were operated and performed in a similar manner, which established a base reference state to properly evaluate and compare variations of operation in the subsequent experiments.

On Day 14 of operation, the liquid flow to Column B was increased to 20 L/day and the liquid flow to Column A remained 1 L/day. As can be seen from Figure 4, liquid flow rates did not have a significant effect on ether removal for about a week. Ether removal efficiencies for both reactors were 92% in average. Afterwards, ether removal improved significantly in Column B. Between day 22 and 69 of operation, the average ether removal efficiency was 98% in Column B and 91% in Column A.

Biomass examination was then conducted during this period. Biofilm samples were taken for phospholipid content analysis. The result shows that the average phospholipid content within the biofilm from Column B was 81 nmol/ mgVSS, much higher than that in Column A, which was 54 nmol/mgVSS, indicating that there was more viable biomass within the biofilm in the column with higher liquid flow rate. Observation of microorganism through a microscope showed that the microbial communities between the two columns were very different. In the biofilter with the higher liquid flow rate, many more filamentous organisms were observed. These results indicate that a higher liquid flow rate leads to an improved biofilter performance through the change of biofilm formation and the improvement of biological activities. The results also confirmed our previous findings that biofilms in trickle-bed biofilters are not completely covered by water. The mass transfer of
substrates in the gas phase may not be limited by the liquid phase because direct mass transfer to a non-wetted biofilm may occur. That explains why there was no immediate effect after the increase of liquid flow rate. However, substrates in the liquid phase, like nutrients, can be transported into the biofilm only through the wetted areas. Increasing liquid flow may enhance their mass transfer into the biofilm, resulting in more active biomass and better biofilter performance.

To investigate whether this biological change under different liquid flow rates is repeatable and reversible, on day 73 of operation, the liquid flow rates in the two biofilters were switched. The nutrient liquid flow rate in Column A was increased from 1 L/day to 20 L/day and that in Column B was decreased from 20 L/day to 1 L/day. Again, the biofilter performance did not exhibit significant change initially. However, after approximately one week, ether removal started to increase in Column A and decrease in Column B. Between day 82 and 139 of operation, the average ether removal efficiency was 97% in Column A, which is similar to the performance of Column B under the same conditions. And the average ether removal efficiency dropped to 88% in Column B, which is also similar to the performance of Column A at the same liquid flow rate during the previous stage (Figure 4). The biomass properties also changed or switched in the two biofilters. These results indicate that the change in biofilm properties and biofilter performance indeed resulted from the change in the nutrient liquid flow rate.

Oxygen penetration within the biofilms

Oxygen microelectrodes were used to measure the distribution of oxygen within the biofilms. Microscopic observations were also conducted to further investigate the biofilm structure in a gas phase biofilter and its effects on mass transfer. The biofilm samples were taken from the biofilter operated at the high liquid flow rate (20 l/day). Sampling locations were at the top, middle and bottom of the column. Oxygen concentration distributions along depth of the biofilms were measured immediately using the oxygen microelectrode.

Figure 5 shows profiles of oxygen concentration within a thick biofilm taken from the top of the biofilter. The thickness of this biofilm was approximately 2.2 mm. Four profiles were obtained from the same pellet and the four analysis points were at least 1 mm apart to minimize interference. As can be seen, the DO concentrations at the surface of the biofilm were close to the saturation concentration which is 8.5 mg/L. The DO concentrations decreased rapidly along the depth of the biofilm to between 0.1 and 0.9 mg/L at the interface of biofilm and the support pellet (the substratum). It is very interesting to see that there...
are two types of DO profiles within the biofilm. In one pattern (point 1 and 4), oxygen concentration decreased continuously and then stabilized after 1000 µm into the biofilm surface. The second pattern (point 2 and 3) shows that the oxygen concentration fluctuated in the deeper section of the biofilm. This indicates that there are some high DO zones inside the biofilm, which suggest that there may exist certain passages for oxygen transfer into the deeper sections of the biofilm in a gas phase trickle-bed biofilter. The latter type of profile also had a higher DO concentration at the substratum. Similar results were obtained from analysis of a few more pellets. It should be pointed out that the fluctuation of DO concentration within the biofilm was not likely caused by analysis errors. The analytical standard deviation for the microelectrode is much smaller than the range of the observed DO fluctuation.

Biofilm samples were observed using a microscope to further examine the biofilm structure. It was found that the biofilms had a layered structure and that void spaces existed between the layers. The existence of high DO zones within the biofilm as evidenced using the microelectrode measurements may be attributed to this special biofilm structure. However, it is still not clear how this layered structure was formed.

To determine the external mass transfer resistance, a test of the liquid effect on oxygen penetration was conducted. The result shows that adding small amounts of water on top of biofilm pellets has little effect on oxygen penetration within the biofilm, which suggests the gas-liquid mass transfer resistance can be negligible in our biofilter system. To better understand the effect of the liquid phase in the mass transfer process in a gas phase biofilter, an investigation was conducted to examine the oxygen penetration for a biofilm submerged in a DO saturated nutrient solution and to compare the DO profiles for the same biofilm pellet when it was open to the air. As can be seen in Figure 6, there was a diffusion layer outside the biofilm surface when the biofilm was submerged in water. The oxygen concentration dropped dramatically before reaching the biofilm surface. This demonstrates why oxygen limitation is a much more serious problem for wastewater biofilm systems than gas phase biofilm systems. It can be seen that the DO concentration did not continue to drop inside the biofilm when the pellet was submerged in the water. This was probably because oxygen analysis was conducted immediately after the biofilm was submerged in the water. The DO content inside the biofilm was still very high. There was a slight drop in DO concentration with time among the three measurements.

Oxygen penetration along the depth of the biofilter was also investigated. The oxygen concentration within the biofilm increased along the medium depth from the top to the bottom of the biofilter. This is because the biofilm became thinner and was subject to less ether substrate or less oxygen consumption from the top to the bottom of the biofilter. Unlike most wastewater biofilms, in which oxygen is often depleted within a shallow layer, usually less than 0.5 mm into the surface (Fu et al., 1993), our biofilms with thickness as high as 2.2 mm still have full penetration of oxygen. This can be attributed to both the negligible gas-liquid mass transfer resistance and the internal structure which may have passages that facilitate oxygen transfer.

Summary and conclusions
Unlike biofilm systems used for wastewater treatment, biofilters for waste gas treatment are not completely saturated with water. Results from this study suggest that for biofilms from gas phase biofilters, the mass transfer of substrates in the gas phase (such as ether and oxygen) may not be limited by the aqueous phase as reported in wastewater biofilm systems, because gaseous compounds can be transported into the biofilm through non-wetted areas. On the other hand, for substrates that are present only in the liquid phase, such as nitrate, mass transfer limitations become more serious.
Microscopic observations revealed that the biofilm had a layered structure and void spaces exist within it. Microelectrode techniques employed in this study enabled us to measure the oxygen profile within the biofilm. Results showed that there are some high DO zones inside the biofilm. This suggests the existence of passages for oxygen transfer into the deeper section of the biofilm. High oxygen penetration within the biofilms in gas phase trickle-bed biofilters can be attributed to both the low gas-liquid mass transfer resistance and the layered and porous internal structure.

References


