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Study on Rate-Limiting Factors with a Heavy Loaded Biofilter

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Abstract

Feasibility test for a biofilter was performed to treat VOCs. The applied loading rate to the biofilter was calculated between 60 to 3,700 kg COD/m^3. Trimethyl-pentene and trimethyl-hexene were the two most dominant compounds and they occupy about 85 percent. During the acclimation period, it is desirable for a biofilter to receive relatively lower VOCs concentration and flow rate, until it can adjust to new substrate and operational environment. Temperature at various points inside the biofilter reactor was observed with more than 23 temperature sensors. With steam heating, temperatures of the top sections of the media were greater than those of bottom sections. Without steam heating, intermediate stages generally had higher temperature measurement than those of bottom and top stages. Because the pH values for different biofilter materials vary significantly, measurement of the pH for the mixture of different combinations of biofilter materials is necessary. Based on the types and brands of media, the measured pH ranged from 5.38 to 9.10. The range of measured pH of different mixtures with perlite, compost, saw dust, peat moss, limestone, vermiculite was 7.05 to 8.62.

Key words : Biofilter, Temperature, VOC, Trimethyl-pentene, pH

1. INTRODUCTION

Research on the biofiltration system has been performed to treat VOCs from chemical manufacturing factory, located in Ulsan Industrial Complex, Korea. The company produces variety of chemical products, including PVC, polyurethane, polyester, biphenol, agrochemicals, etc. A pilot-scale biofilter was installed outdoor in the factory and tested from the middle of January until early March. The objective of this paper is to investigate the effects of some selected rate-limiting factors in a pilot-scale biofilter.

Wani *et al.* studied hydrogen sulfide (H_2S) treatment under pulse loading lasted about thirty minutes at a concentration of approximately twice the baseline load level. It took about 1.5 ~ 2.5 hours for the biofilters to reach the original removal capacity after the H_2S pulse. Deshusses *et al.* (1996) performed methyl-ethyl-ketone (MEK) pulse tests which lasted 2 minutes at a loading rate of 1.28 g/m^3 which was approximately 1.5 times the baseline load level. It took about an hour for the biofilter to achieve the original removal capacity after the MEK pulse. A methyl-isobutyl-ketone (MIBK) pulse test by Deshusses *et al.* (1996) showed similar results. Based

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on different loading rates and duration of a pulse, different recovery times are expected for a biofilter to achieve original removal capacity after the pulse input.

Longer periods of biofilter non-use result in longer re-acclimation periods (Wani *et al.*, 1998; Martin and Loehr, 1996). Martin and Loehr (1996) and Wani *et al.* (1998) reported that when humidified air, rather than no air, was passed through the biofilter during the period of non-use (without chemical flow), the re-acclimation period was shorter and initial removal efficiency was higher. Martin and Loehr (1996) reported that transition between different chemicals resulted in acclimation periods shorter than initial acclimation periods.

Wright *et al.* (1997) operated four identical compost biofilters for the treatment of gasoline vapor. For the summer months operation, two out of four biofilters were shaded from solar heating while the other two were not shaded. Often, outlet gas temperatures from the unshaded biofilters were 10°C warmer (up to 38°C) than the outlet gas temperatures from the shaded ones. Biofilters with higher outlet gas temperatures could achieve higher removal efficiencies (89% and 92%). The other Biofitlers with lower outlet gas temperatures had lower reported removal efficiencies of 64% and 67%.

Swanson and Loehr (1997) recommended 35°C as the optimal temperature for the aerobic microorganisms in biofilters. Cox *et al.* (1997) reported that styrene degradation rates at biofilter were similar between 22.5 and 33°C. However, decrease was observed at higher temperatures. More research is needed for the optimum temperature range for the biofilter operation with various operating conditions.

Most natural environments have pH values between 5 and 9, and for the majority of microorganisms, the pH optimum for growth is between 6 and 8. Only a few species can grow at pH values of less than 2 or greater than 10. Fungi as a group tend to be more acid-tolerant than bacteria. Many fungi grow optimally at pH 5 or below, and a few grow well at pH values as low as 2 (Madigan *et al.*, 1997).

Wani *et al.* (1998), Cox *et al.* (1997), and Webster *et al.* (1997) reported pH reduction during biofilter operation. Devinny and Hodge (1995) reported that pH reduction was caused by intermediate acid accumulation in the biofilter. System overload caused accumulation of acid intermediates which resulted in reduction of the pH. This caused removal efficiency to decrease. Biodegradation of certain pollutants, such as chlorine-, sulfur-, and nitrogen-containing compounds, can produce acid intermediates or end products that can lower media pH (Chou and Shiu, 1997; Swanson and Loehr, 1997). Microbial activity in the biofilter may be inhibited at low pH (Gribbins and Loehr, 1998; Chou and Shiu, 1997; Swanson and Loehr, 1997). However, Cox *et al.* (1997) reports that decreased pH levels (<3) did not have an adverse effect on biofilter performance. Webster *et al.* (1997) also observed that a biofilter could tolerate very low pH (≥ 2.0).

Chou and Shiu (1997) reported a gradual pH increase in a methylamine degrading biofilter. As methylamine is degraded ammonia was accumulated in the biofilter media. When the pH was over 8.8, treatment by the biofilter was inhibited. The majority of researchers have tried to maintain a neutral pH in biofilters.

The following pH buffer media have been used in previous studies; dolomitic lime (Wani *et al.*, 1998), limestone (Deshusses *et al.*, 1996), and crushed oyster shell (Zhu *et al.*, 1998; Leson and Smith, 1997; Sorial *et al.*, 1997). Swanson and Loehr (1997) and Chou and Shiu (1997) report buffering solution is an another effective method to control pH.

2. MATERIALS AND METHODS

2.1 Biofilter design

The body of the biofilter reactor was constructed with steel with an internal diameter of 230 cm and a height of 260 cm. The Biofilter consisted of the following sections, from top to bottom.

1) A headspace for housing the water spray nozzle.

2) A section containing biofilter media. The height of the biofilter media was one meter and the size of the media was about 4.3 m^3. Conceptually, the biofilter was divided into five different consecutive

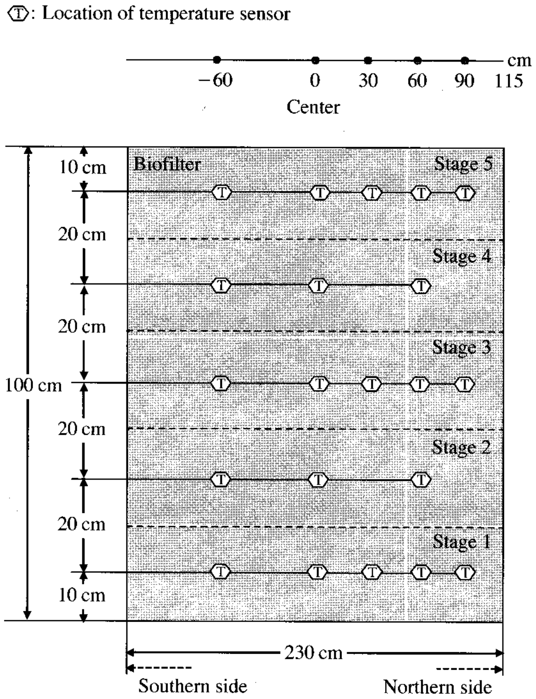

Fig. 1. Locations of temperature sensors inside biofilter media.

stages. The height of each stage was 20 cm.

3) A bottom space to collect leachate from biofilter.

Inlet and outlet relative humidity ($R.H._1$ and $R.H._2$) were measured using a model DUO humidity indicator and a model Capacitive RH Sensor (rbr-Computertechnik, Germany). Relative humidity of inlet air stream was maintained almost 100% for most of the experimental period. The body of the humidifying water chamber was constructed with steel with an internal diameter of 76 cm, and a height of 130 cm. Water was sprayed through nozzles inside the humidification chamber against the air flow and relative humidity was measured for the entire experimental periods.

Temperatures of the biofilter media at five different consecutive stages (stage #1, #2, #3, #4, and #5) were measured using a model 865F thermistor meter and model OL-710-PP probes (Omega Engineering Inc., Stamford, CT). Temperature sensors were spaced throughout the media: 3 to 5 sensors were spaced at 30 cm to 60 cm intervals at various heights throughout the biofilter media (see Fig. 1 for details).

As the pilot-scale biofilter was installed outdoor and operated during winter time (from middle of January until early of March), temperature management for the biofilter was needed. To overcome the outside freezing cold weather, 7 cm thick fiber glass insulation and 150°C steam heating was used. Seven millimeter diameter copper pipe circulated the main body of the biofilter reactor for steam heating. Total height of the biofilter reactor body was 2.6 meter and the height of media was one meter. Around middle section of the wall of the biofilter reactor where the media attached inward, copper pipe circulation was installed at 10 cm interval. At the lower and upper sections of the wall of the biofilter reactor (where the media is not attached inward directly), it was installed at 20 cm interval. Fiber glass insulation covered the outside of the reactor body over the copper pipe circulation. In the case of humidifying water chamber, only fiber glass insulation was made without steam heating.

2.2 VOC analysis

Inlet and outlet air samples from each stage of the biofilter (S_1, S_2, S_3, S_4, S_5, and S_6) were collected in one liter Tedlar sample bags. The concentrations of VOCs were measured using a Varian Saturn-3 Gas Chromatography/Mass Spectrometry (GC/MS). Five hundred micro-liters from the Tedlar bag sample were injected into the GC injection port with a Hamilton Gastight #1750 syringe. For species separation, a 0.25-mm ID*30 m DB5 capillary column (J & W Scientific, Folsom, CA) containing 0.25 μm film thickness was used. Helium (He) was used as the carrier gas at a flow rate of 8 mL/min. The injection temperature was 220°C and the transfer line temperature to Mass Spectrometry was set at 220°C. Total sample run for each VOC analysis was 28 minutes in duration. For the initial 5 minutes, the GC oven temperature was maintained at 30°C and then the temperature was increased until 130°C with the rate of 10°C/min, then it was increased until

250°C with the rate of 15°C/min. At 250°C, the GC oven temperature was maintained for 5 minutes. A single point external standard calibration method was used. All results are given in parts per million (ppm) by volume.

2.3 Loading rate

Volatile organic compounds (VOCs) COD loading rate (kg COD/m^3) to the biofilter was calculated based on the individual stage volume (0.83 m^3). During the experiment, only on the day 2 to 7, 14, 15, 37, and 38, the contaminated air stream was provided to the biofilter system. On other days, ambient air was supplied to the system to maintain proper operational condition.

3. RESULTS AND DISCUSSION

3.1 Compost media and initial acclimation period

Compost media biofilter is one of the most important biological processes applied to treat waste gases. Instead of using large amounts of thermal energy to destroy pollutants, or removing pollutants via transfer from one phase to another, biofilter systems harness the natural abilities of microorganisms to degrade organic and inorganic contaminants biochemically into environmentally harmless end-products. Composting material was used as the biofilter media. It was manufactured from the local composting facility (Jung-Won Farm, Changwon, Korea). The compost was produced with two different types of hardwood saw dust and cow manure after 30 days of composting retention. Saw dust was purchased from a local carpenter shop and was used as received without further sieving. It was consisted of a variety of wood wastes, but was predominantly from white pine and chestnut. The ratio for the raw materials of saw dust and cow manure was about 50% each. The compost manufacturing process was conducted aerobically. Usually, it took about 40 days for the composting facility to produce their final products. However, in the case of the compost used for the experiment, it took only 30 days, be-cause of their hectic production schedule. Therefore, relatively immature material could be used for the tests. The pH of the compost was 7.2 ($\pm$0.1). The content of nitrogen in the compost material was 0.92% and the content of phosphorous was 0.87% by weight, respectively.

Compost possesses a large diversity and density of microorganisms. Among them, bacteria and fungi are the two dominant microorganisms groups in biofilters. Most biofilms will contain substantial numbers of both, but their relative abundances can vary widely. Bacteria have the advantage of rapid substrate uptake and growth. According to Yadav and Reddy (1993), benzene, toluene, ethylbenzene, and xylenes could be degraded by fungi (*Phanerochaete chrysosporium*) in the liquid culture in serum bottle. However, although the reports of Yadav and Reddy (1993), fungi may not be as competitive as bacteria in degrading certain types of substrates (like ethylbenzene) in the biofilter environment, where the alternative food source (like composting material) is available.

Microorganisms exposed to a new substrate may require a period of acclimation before they begin vigorous degradation. Excessive pollutant loading may cause a significant decrease of removal efficiency in the biofilter. Therefore, when new substrate is provided, or significant operational conditions and/or microbial growth environment are changed, an acclimation period is necessary. The acclimation period is defined as time needed for the biofilter to adjust to the new operational environment and remove substrate effectively. During the acclimation period, it is desirable for a biofilter to receive relatively lower VOCs concentration and flow rate, until it can adjust to new substrate and operational environment.

3.2 Fluctuated loading rate and removal efficiency

Average concentration to the biofilter was 7,283 ppm and trimethyl-pentene and trimethyl-hexene were the two most dominant compounds and they were about 85 percent (Fig. 2). The total removal efficiency of the system fluctuated on the days when polluted air stream was provided (Fig. 3). Until day

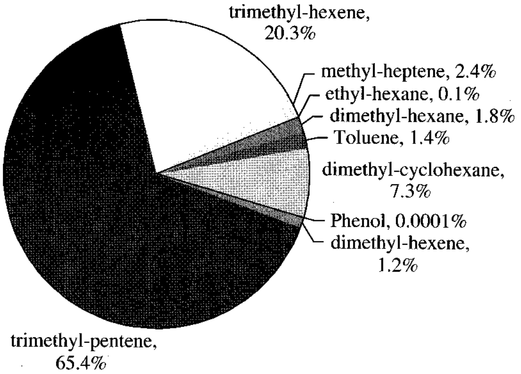

Fig. 2. Percent ratio of the inlet air flow to the biofilter system.

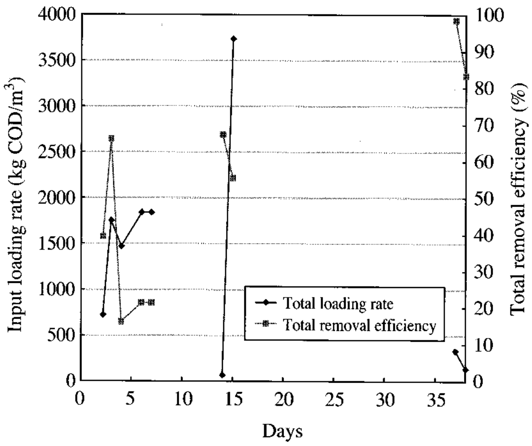

Fig. 3. Total loading rate and total removal efficiency of the biofilter system.

7, about 1,500 kg COD/m^3 was provided to the biofilter system. As it was too heavy for the biofilter, ambient air was provided from day 8. On day 14 and 15, the polluted air stream was provided to the biofilter system. The loading rate was 65 and 3,700 kg COD/m^3 and removal efficiency was about 67 and 55 percent. Particularly, the loading rate on day 15 was extremely heavy and it made serious shock to the biofilter. Therefore, another period of ambient air supply was made until day 36. On day 37 and 38, polluted air stream was provided (330 and 140 kg COD/m^3) and removal efficiency was 99% and

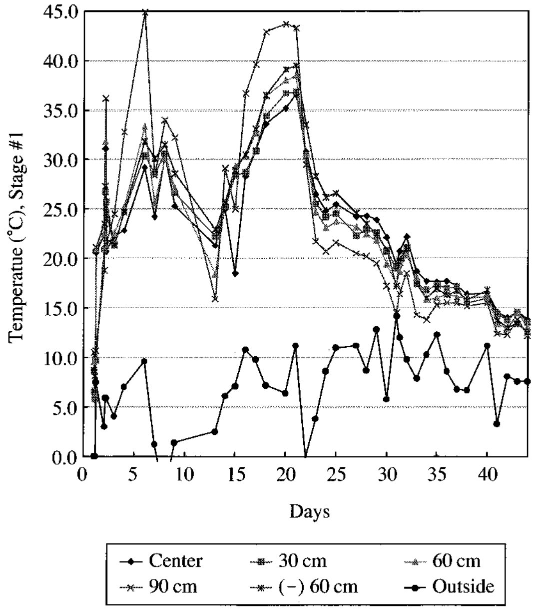

Fig. 4. Temperature of stage #1 at different locations from center.

83% each. Unfortunately, VOC measurement was not available from day 40 until day 44, because of mechanical problem of GC/MS.

3.3 Temperature measurement

The pilot-scale biofilter was installed outdoor and the experiment was performed from middle of January until early of March. For temperature management of the biofilter reactor, 7 cm thick fiber glass insulation and 150°C steam heating was used. In the case of steam heating, it was provided until day 21 and resulted in general increase of temperatures inside the biofilter reactor. With steam heating, temperatures of the top sections of the media were greater than those of bottom sections. Without steam heating, intermediate stages (like stage #3) generally had higher temperature measurement than those of bottom and top stages.

Fig. 4 shows temperature measurements at different locations at the same depth in stage # 1. Range of temperature of stage # 1 at different locations was from 6°C to 45°C during the experiment. As

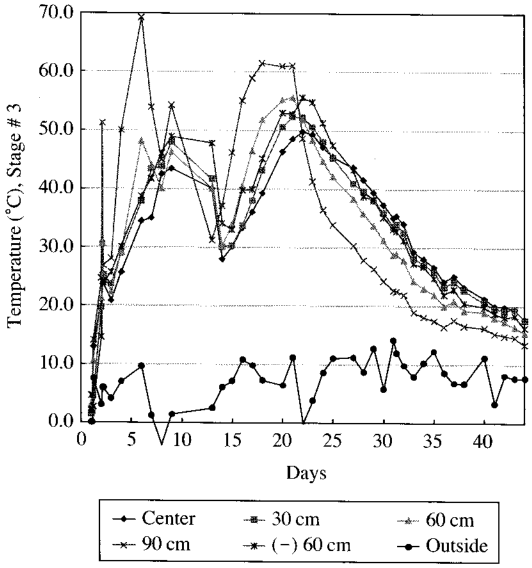

Fig. 5. Temperature of stage #3 at different locations from center.

mentioned previously, the outside wall of the biofilter reactor body was circulated with steam heating copper pipe. Among temperature measurement points inside biofilter media, location (90 cm) was positioned outer most from center. Therefore, with steam heating, the highest temperature measurement at the same depth was observed at location (90 cm). The next high temperature measurements were observed in the order of location (60 cm), (30 cm), and (center). However, without steam heating, temperature at location (center) was the highest and temperature at location (90 cm) was the lowest. Temperature difference between the location (90 cm) and (center) was 15.7°C on day 6 and −1.3°C on day 44.

Fig. 5 shows temperature measurements at different locations at the same depth in stage #3. Like stage #1, until day 21 with steam heating, temperature measurement of location (90 cm) was the highest and location (center) was the lowest. Without steam heating, temperature at location (center) had the highest measurement and temperatures at location (90 cm) had the lowest. Range of temperature of stage #3 at different locations at the same depth

Table 1. pH of the different type of biofilter media.

Media	pH
Compost A	7.24
Compost B	6.47
Perlite A	7.45
Perlite B	8.30
Saw dust	4.98
Peat moss	5.50
Vermiculite	7.16
General fertilizer A	6.05
General fertilizer B	7.61
Acid-loving fertilizer	5.38
Limestone	10.58

was measured from 13°C to 69°C after day 2. Temperature difference between the location (90 cm) and location (center) was 34.8°C on the day 6 and −3.2 °C on the day 44. Compared to other stages, temperature difference of locations at (90 cm) and (center) of stage #3 was the biggest.

In the case of stage #5, the range of temperature at different locations was measured from 11°C to 65 °C after day 2. Temperature difference between the location (90 cm) and location (center) was 18.8°C on day 6 and −3.8°C on day 44.

3.4 pH

A combination of natural organic media, inert synthetic media, and fertilizer is also often used for biofilter media. Because the pH values for these materials vary significantly, measurement of the pH for the mixture of different combinations of these materials is necessary. The pH was measured for several different biofilter media candidates (Table 1). Since the media is different, ranging from natural to synthetic media, the measured pH is different. Even the same type of organic/synthetic media but with different brand names had different pH values. Supplementary nutrients for the high loading operations are often required, consequently nutrients often in the form of fertilizer are added to the media. Based on the types and brands of media, the measured pH ranged from 5.38 to 9.10. The pH of different mixtures was also investigated in the laboratory. The range of measured pH of different mixtures with perlite, compost, saw dust, peat moss, limestone, vermiculite was 7.05 to 8.62.

4. CONCLUSIONS

A biofilter was tested for 44 days to treat VOCs in contaminated air stream from chemical manufacturing process. Trimethyl-pentene and trimethyl-hexene were the most dominant compounds and they occupy about 85 percent. Extremely heavy loading rate and severe fluctuation of loading rate (60 to 3,700 kg COD/m^3) was applied and became a severe shock for the biofilter to operate properly. Therefore, only for nine days out of 44 test days, the contaminated air stream from the manufacturing line was provided to the biofilter. More acclimation time and test period was needed to determine the maximum loading rate for the pilot-scale biofilter to operate properly with given operating condition.

Temperature was measured for the entire experimental periods. The pilot-scale biofilter was installed outdoor and the experiment was performed during winter season. For temperature management of the biofilter reactor, 7 cm thick fiber glass insulation and 150°C steam heating was used. In the case of steam heating, it resulted in general increase of temperatures inside the biofilter reactor. Steam heating affect the temperatures at headspace and bottomspace most significantly. With steam heating, temperature measurement of stage #5 was the highest. However, without steam, it decreased gradually and was measured second lowest from day 28 until the end of the experiment. Also, with steam heating, the highest temperature measurement at the same depth was observed at location (90 cm). The lowest temperature measurement was observed at location (center).

Because the pH values for different biofilter materials vary significantly, measurement of the pH for the mixture of different combinations of biofilter materials is necessary. Based on the types and brands of media, the measured pH ranged from 5.38 to 9.10. The range of measured pH of different mixtures with perlite, compost, saw dust, peat moss, limestone, vermiculite was 7.05 to 8.62.

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