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BIOLOGICAL CONTROL OF BENZENE AND ETHYLENE

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Abstract : The objective of this study was to investigate the biodegradation of gaseous benzene and ethylene in biofilters filled with granular activated carbon. As the results of this study, the benzene biofilter was capable of achieving benzene removal efficiency as much as 96% at a residence time of 2 min and an inlet concentration of 220 ppm. During operation with an inlet benzene of 220 ppm, the maximum elimination capacity of the biofilter was 483 g of $C_6H_6/m^3 \cdot$ day. The ethylene biofilter was capable of achieving ethylene removal efficiency as much as 100% at a residence time of 14 min and an inlet concentration of 290 ppm. During operation with an inlet ethylene of 290 ppm, the maximum elimination capacity of the biofilter was 34 g of $C_2H_4/m^3 \cdot$ day. The biofilter could provide an attractive treatment technology for removing individual and mixed benzene and ethylene.

Key Words : activated carbon, benzene, biofilter, degradation, ethylene, filter media

INTRODUCTION

Emission sources of benzene (C_6H_6) and ethylene (C_2H_4) are industrial processes, petroleum refining, petroleum marking, containers, and storage tanks. Benzene has been detected in contaminated groundwaters and soils.[1] Ethylene is reported to be produced by biosynthesis in soils.[2] Both benzene and ethylene are volatile and odor compounds. Benzene is known to be carcinogenic.[1] Ethylene has an effect on plant physiological processes such as ripening, senescence, and aging.[2] In addition, accumulation of ethylene in plants may occur in horticultural storage facilities due to endogenous production by the plant material.[3] In order to remove the odor compounds, scrubbers or incineration are widely used in storage facilities. Disadvantages of the scrubbers and incineration are high operation costs and replenishing a removing agent. Especially, it is very difficult to treat ethylene by adsorption methods.[4]

Biofiltration has been widely applied to the treatment of odor compounds containing volatile organic compounds (VOCs). Biofiltration has been known to be a reliable and cost-effective technology for the treatment of odor and VOCs. Several researchers reported the control of benzene or ethylene using different filter media and biomass.[5,6] Elsgaard[7] studied ethylene removal using a peat/soil biofilter with an immobilized pure culture. After starting operation with 117 ppm of ethylene, the concentration was reduced to 0.04 ppm.

In this study, activated carbon biofilter was introduced as a medium for biofiltration because granular activated carbon provides several advantages, such as greater surface area and porosity.[8] The objective of this study was

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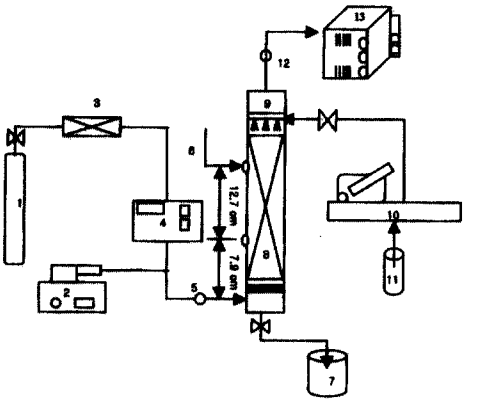
to investigate benzene and ethylene degradation in the activated carbon biofilter, inoculated with benzene-degrading microorganisms or ethylene-degrading microorganisms, under different operation conditions. In addition, biofilter performance of mixed compounds at different residence times was studied.

MATERIALS AND METHODS

Materials

Benzene, as an inlet vapor source, was purchased from Fisher Scientific, USA. For the preparation of benzene standards, a benzene solution with 100 ppm was obtained from Chem Service, USA. Ethylene was purchased from a local gas company in Korea. The inlet ethylene concentrations of 99, 290, 310, and 452 ppm were fixed with pure air (free of carbon dioxide). In order to pack the biofilter with filter media, granular activated carbon was obtained from Shin Ki Chemical, Korea. Before the carbon was transferred into the biofilter, the carbon was washed with tapwater, graded with USA ASTM No.8 and No.32, and dried at room temperature.

Microbial consortium was obtained from raw wastewater at the Nam-Hae Wastewater Treatment Plant in the City of Mokpo, Korea. The microbial consortium was continuously acclimated to benzene or ethylene as a primary substrate with a nutrient solution in a cultivation reactor having 29.2 cm ID and 50 cm long under aerobic conditions. Inlet concentrations of aqueous benzene and ethylene were 1,000 mg/L and 452 ppm, respectively. Added amount of the benzene was 5 mL/day, whereas the ethylene was continuously added to the reactor for three weeks. The nutrient solution had the following compositions: 50 mg NaH_2PO_4, 85 mg KH_2PO_4, 165 mg K_2HPO_4, 100 mg NH_4Cl, 0.1 mg $MgSO_4 \cdot 7H_2O$, 0.12 mg $FeSO_4 \cdot 7H_2O$, 0.036 mg $MnSO_4 \cdot H_2O$, 0.03 mg $ZnSO_4 \cdot 7H_2O$, 0.01 mg $CoCl_2 \cdot 6H_2O$, 0.1 mg $CaCl_2 \cdot 2H_2O$, and 0.5 mg yeast extract in 1 L distilled water



1. Air of ethylene
2. Syringe pump
3. Filter
4. Mass flow controller
5. Inlet gas sampling port
6. Sampling port
7. Drainage
8. Filter media
9. Water distributor
10. Metering pump
11. Water & nutrients
12. Outlet gas sampling port
13. Gas chromatograph

Figure 1. Schematic diagram of biofilter-setup.

Methods

Figure 1 shows a schematic diagram of a lab-scale biofilter. Two biofilters were made of PVC having 6.7 cm ID and 62.5 cm long. The depth of the activated carbon in the biofilter was 24.4 cm, and its weight was 500 g. Benzene vapor and ethylene were fed into the biofilters using a ¼ inch OD Teflon tubing and fittings. Pure air, as the oxygen source, was supplied from a cylinder. The inlet benzene vapor concentration was controlled by a syringe pump (Cole-Parmer, USA) and with the flow rate of the air by a mass flow controller (Unit Instruments, USA). The nutrient solution in distilled water was introduced at the top of the biofilter through a Tygon tubing using a Cole-Parmer metering pump at a rate of 400 mL/day.

Gaseous samples were collected using 1.6-L tedlar gas sampling bags with on/off and septum valves. The on/off valve was used for collecting gaseous samples, and the septum valve for needle injections. It took more than 20 min to collect gaseous samples. Before each sampling, the bags were filled with air and evacuated by a vacuum pump several times. Gaseous benzene concentrations were analyzed

with a GC/MSD (Shimadzu QP-5050A, Japan), fitted with a DB-1 widebore column (60 m). The Henry's law constant of the compound was 0.562 KPa · m^3/mol.[9] Ethylene and carbon dioxide were analyzed with a GC (Shimadzu 14A, Japan) installed with TCD and a Porapak-Q column. Helium was used as a carrier gas at a flowrate of 30 mL/min. Gaseous samples were directly injected into the injection port using a 1-mL Pressure-Lok gas syringe (Series A-2) with a push-button valve.

RESULTS AND DISCUSSION

Before benzene-degrading microorganisms and ethylene-degrading microorganisms were inoculated into each biofilter, biodegradation of gaseous benzene and ethylene by each microorganism was monitored in 250-mL amber bottle. As results of experiment, it was found that the gaseous benzene or ethylene dissolved in mixed liquor suspeded solids was well consumed. After the microorganisms were inoculated into each biofilter, biofiltration based on different inlet concentrations and residence times (t) were conducted. Degradation of individual compound will be presented at first, and then degradation of mixed compounds will be followed.

Benzene Biofilter Performance

The evaluation of biofilter performance in terms of different inlet concentrations is presented as summarized in Table 1. Figure 2 shows variations of inlet and outlet concentrations of benzene with different operation conditions. In the beginning of operation, the average gas flow rate was 200 mL/min through the biofilter, resulting in an average gas residence time of 4.3 min, and average inlet concentration was 1,280 ppm during 45 days of operation. Inlet benzene concentrations ranged from 958 to 1,718 ppm, whereas outlet concentrations ranged from 7.3 to 300 ppm. After changing the inlet concentration to 300 ppm while maintaining the same residence

Table 1. Operation conditions of each biofilter

	Gas flow rate (mL/min)	Residence time (min)	Inlet conc. (ppm)	Mass of media (g)
Benzene	430	2.0	220	500
	200	4.3	300	500
	200	4.3	1,280	500
Ethylene	61	14	99	500
	61	14	290	500
	61	14	452	500

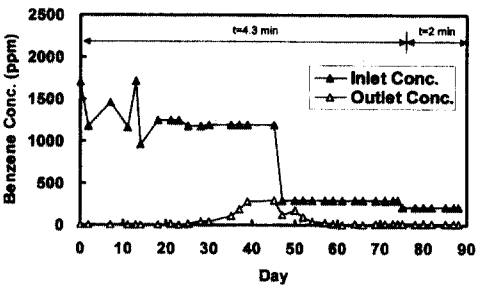


Figure 2. Benzene removals according to different inlet concentrations and residence times.

time, outlet benzene was gradually decreased and benzene removal efficiency increased to 96% in 15 days, as shown in Figure 2.

Second, the evaluation of biofilter performance in terms of a different residence time is presented. Figure 2 illustrates variations of inlet and outlet concentrations of benzene after the change in residence times from 4.3 to 2 min. Inlet benzene concentration was 220 ppm in the gaseous phase. At this residence time, up to 96% of the benzene was removed.

The pure air supply, with variable pressure from an air cylinder, was connected to the benzene vapor source. Such an arrangement produced varying negative pressures on the downstream side of the source, which resulted in fluctuations in the inlet benzene concentration during the beginning of the biofilter operation. A consistent inlet benzene concentration was maintained using a syringe pump and a mass flow controller as shown in Figure 2. The removal efficiency is determined by the concentration of gaseous benzene removed by the biofilter, and expressed as a percentage of

the inlet benzene concentration. Initially, more than 90% benzene removal was observed as it might be adsorbed to biofilms and was degraded by the benzene-degrading microorganisms. However, the removal efficiency of the biofilter decreased to 75% after 35 days. The benzene-degrading microorganisms could not degrade a relatively high benzene concentration due to removal capability. The inlet concentration needed to be lowered because of low removal efficiency. After changing the inlet concentration to 300 ppm, a maximum of 98% of the benzene was degraded. In addition, with an inlet benzene concentration of 220 ppm and a residence time of 2 min, up to 96% of benzene was removed. Improved performance in subsequent days may have occurred because necessary microbial enzymes were induced and initially small populations of benzene-degrading microorganisms grew.

In Oh and Bartha's study,[6] benzene removal was below 50% at an inlet concentration of 157 ppm and a residence time of 40 sec using a peat biofilter. They suggested that benzene concentration needed to be lowered or residence time needed to be increased in order to achieve higher benzene removal. The study of Ergas et al.[5] employed a compost biofilter inoculated with *Pseudomonas putida* to remove gaseous benzene, and obtained 22~99% removal efficiency at low concentrations (282~469 ppb). The biofilter study was evaluated in terms of the benzene elimination capacity, defined as the amount of benzene degraded per unit of reactor volume and time. With an inlet concentration of 300 ppm at a residence time of 4.3 min, maximum elimination capacity was 314 g of $C_6H_6/m^3 \cdot$ day. By this study, it was found that the maximum elimination capacity of this study was 483 g of $C_6H_6/m^3 \cdot$ day under the condition of an inlet benzene of 220 ppm. Significant variation of the elimination capacity was observed with varying different residence times. With a relatively high concentration of benzene used in this study, more than 96% was removed at residence times ranging from 2 to 4.3 min. The relatively high concentration was applied to the biofilter in this study because it is typically encountered in off-gas emission. This study showed that the use of an activated carbon biofilter inoculated with the benzene-degrading microorganisms provides a more attractive treatment technology for removing gaseous benzene at a relatively high concentration than peat or compost biofilters.

Carbon Dioxide Production from Benzene Biofilter

Figure 3 shows the concentrations of carbon dioxide produced in the benzene biofilter with different operation conditions. For all the conditions, the inlet gas was free of carbon dioxide. An increase in the carbon dioxide concentration of up to 3,140 ppm was found at an average inlet concentration of 1,280 ppm. With an inlet concentration of 300 ppm at the same residence time, similar concentration ranges of carbon dioxide were investigated. Carbon dioxide concentrations ranging from 468 to 726 ppm were produced at a residence time of 2 min during 14 days of operation (inlet benzene concentration=220 ppm).

Carbon dioxide and water vapor are produced as a result of benzene degradation with benzene-degrading microorganisms. As a result of the benzene degradation, a biofilm would have grown, and more microbial activity would have occurred gradually. The outlet carbon dioxide concentration was significantly higher than the inlet carbon dioxide concentration, demonstrating a mineralization of the benzene in the biofilter. With the lower inlet concentration (300 ppm) at a residence time of 4.3 min, almost all of the benzene was degraded because the biofilter was capable of removing all inlet benzene quickly. The average carbon dioxide concentration at the outlet port was 1,241 ppm during 28 days of operation, as shown in Figure 3. With an inlet concentration of 220 ppm at a residence time of 2 min, it was found that carbon dioxide was produced at a rate of 608 mg/day, which corresponded to a volume of 0.35 L/day.

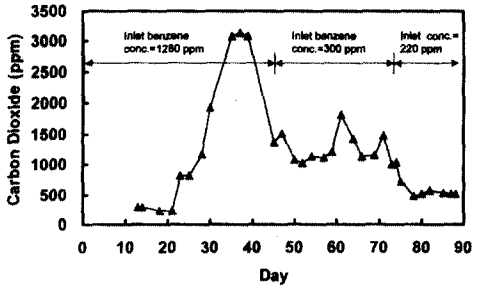


Figure 3. CO_2 concentrations of the outlet gas from the benzene biofilter: t=4.3 min for average inlet conc.=1,280 ppm and inlet conc.=300 ppm, t=2 min for inlet conc.=220 ppm.

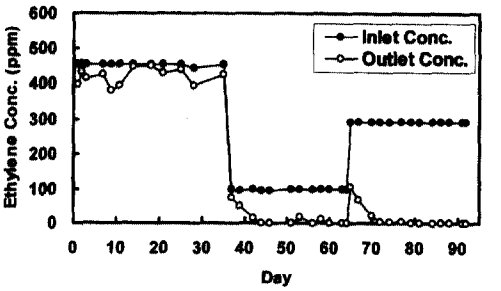


Figure 4. Ethylene removals according to different inlet concentraions at a residence time of 14 min.

Table 2 summarizes mass balances of carbon based on inlet and outlet benzene concentrations, and carbon dioxide produced in the biofilter with different operation conditions. It is difficult to calculate mass balance of carbon by carbon dioxide production because of inconsistent microbial activity in the biofilter. But a rough mass balance of carbon using stoichiometry was attempted. Theoretically, 1 ppm of benzene will be converted to 6 ppm of carbon dioxide. For the benzene biofilter, less carbon dioxide was measured because some of benzene might be removed by adsorption. During operation with an inlet benzene of 300 ppm, a slight different outlet concentration of carbon dioxide between the measured and calculated was observed.

Ethylene Biofilter Performance

Biofilter performance in terms of different inlet concentrations: 452, 290, and 99 ppm, at the same residence time of 14 min, is presented. Figure 4 shows variations of inlet and outlet concentrations of ethylene during 92 days of operation. Low removal efficiency, 10 ~15%, was observed because the ethylene was refractory to biodegradation at the relatively higher concentration. After changing the inlet concentration to 99 ppm while maintaining the same residence time, the ethylene removal efficiency increased to 90% in 6 days. Thereafter, outlet ethylene was gradually decreased and a maximum of 100% of ethylene was degraded. With an inlet concentration of 290 ppm, 100% removal efficiency was also observed.

The removal efficiency of the biofilter was lowest at an inlet concentration of 452 ppm. As previously mentioned, the ethylene was difficult to be degraded biologically at the relatively higher concentration. Because ethylene is an extremely volatile and slowly adsorbed compound, sufficient time for microbial adaptation to the ethylene may be required. The inlet concentration needed to be lowered because of poor removal efficiency. With the lower inlet concentrations, a maximum of 100% of ethylene was removed as it was

Table 2. Mass balance of carbon in biofilters

	Inlet conc. (ppm)	Measured outlet CO_2 conc. (ppm)	Calculated outlet CO_2 conc. (ppm)	Removal (%)
Benzene	220	515~726	1,270	96
	300	1,010~1,820	1,760	98
	1,280	1,280~3,140	5,280	75~98
Ethylene	99	328~354	200	100
	290	409~611	580	100
	452	71~140	100	10~15

adsorbed onto biofilm and degraded on filter media by the ethylene-degrading microorganisms. Improved performance in subsequent days may have occurred because necessary microbial enzymes were induced and initially small populations of ethylene-degrading microorganisms grew.

In comparison, van Ginkel et al.[10] reported the removal of ethylene by a compost biofilter inoculated with *Mycobacterium* strain E3. With an inlet concentration of 2 ppm, 87% removal efficiency was achieved during operation for 8 weeks. Elsgaard[7] employed a peat-soil biofilter inoculated with ethylene-degrading bacterial strain RD-4 to remove ethylene, and obtained 99% removal efficiency at an inlet concentration of 117 ppm. With a relatively high concentration of ethylene used in this study, a maximum of 100% was removed. The biofilter study was evaluated in terms of the ethylene elimination capacity, defined as the amount of ethylene degraded per unit of reactor volume and time. During operation with an inlet ethylene of 290 ppm, it was found that the maximum elimination capacity of this study was 34 g of $C_2H_4/m^3 \cdot$ day, whereas the capacity of Elsgaard's study was 21 g of $C_2H_4/m^3 \cdot$ day. This capacity was slightly higher than that calculated for Elsgaard's biofilter study. This could be due to the selection of activated carbon. The surface of activated carbon was excellent for colonization by microorganisms.[11] Microbial growth on the activated carbon was an expected consequence of the attractive environment. Observable features of the microorganisms were also investigated with scanning electron microscopy analysis.[11] It is likely that biofilm as result of active microbial growth on the activated carbon may improve the removal of ethylene. As previously mentioned, ethylene is not well treated by adsorption process.[4] Adsorption on the activated carbon was ignorable because the previous research has already reported the adsorption was minor compared to biodegradation.[12] The activated carbon may be biocoated granular media.

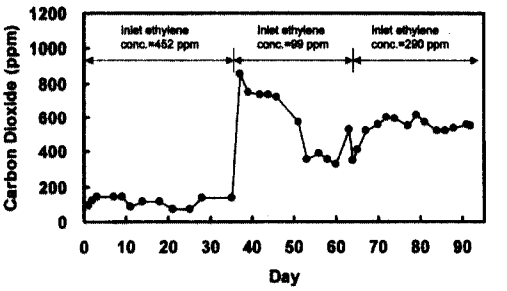


Figure 5. CO_2 concentrations of the outlet gas from the ethylene biofilter.

This relatively high concentration was applied to the biofilter because it is frequently encountered in industrial emission sources. This study showed that the use of an activated carbon biofilter inoculated with ethylene-degrading microorganisms provides an alternative and more attractive treatment technology for ethylene removal at a relatively high concentration. This study also suggested that ethylene from industrial point sources or horticultural storage facilities could be reduced to low range when the biofilter is applied.

Carbon Dioxide Production from Ethylene Biofilter

Figure 5 shows the concentrations of carbon dioxide produced in the biofilter with different operation conditions. Carbon dioxide concentrations ranging from 328 to 354 ppm were found at an inlet concentration of 99 ppm. With an inlet concentration of 290 ppm at the same residence time, similar concentration ranges of carbon dioxide were investigated. Carbon dioxide concentrations ranging from 71 to 140 ppm were produced at an inlet concentration of 452 ppm.

As previously mentioned, ethylene degradation might have resulted in growth of biofilm and a mineralization of ethylene in the biofilter. With the lower inlet concentration, almost all of the ethylene was degraded because the biofilter was capable of removing inlet ethylene quickly. Higher carbon dioxide production rates were obtained at the lower inlet concentrations due to high removal

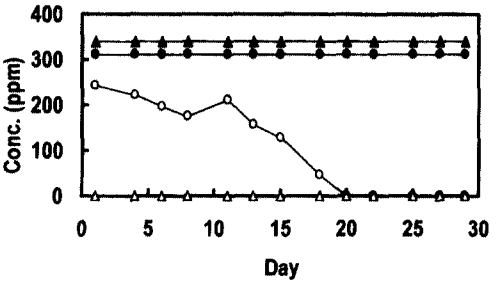


Figure 6. Removal of mixed benzene and ethylene concentrations at a residence time of 15 min: inlet benzene (▲), outlet benzene (△), inlet ethylene (●), outlet ethylene (○).

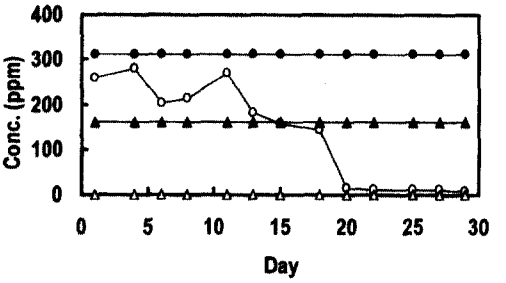


Figure 7. Removal of mixed benzene and ethylene concentrations at a residence time of 10 min: inlet benzene (▲), outlet benzene (△), inlet ethylene (●), outlet ethylene (○).

efficiency. With an inlet concentration of 290 ppm at a residence time of 14 min, it was found that carbon dioxide was produced at a rate of 87 mg/day, which corresponded to a volume of 0.05 L/day.

As summarized in Table 2, the carbon dioxide concentrations of the measured were similar to those of the calculated. With an inlet concentration of 99 ppm, more carbon dioxide was measured because previously adsorbed ethylene at an inlet concentration of 452 ppm might be degraded.

Biofilter Performance for Mixed Compounds

Figure 6 illustrates inlet and outlet concentrations of mixed benzene and ethylene during 29 days of operation. Benzene with ethylene was fed to the ethylene biofilter. With an residence time of 15 min, inlet benzene and ethylene concentrations were 336 and 310 ppm, respectively. Complete removals of both benzene and ethylene were noticed. As shown in Figure 7, another biofilter performance was conducted at a gas residence time of 10 min and an inlet ethylene concentration of 310 ppm. Inlet benzene concentration was 158 ppm. Two channels of a syringe pump could not control the same inlet concentration of benzene. About 96~97% of ethylene was degraded at this residence time. For the benzene, 100% removal efficiency was achieved at residence times of 10~15 min. Eventually, a good biofilter performance with mixed compounds was also studied.

CONCLUSION

The following conclusions can be drawn based on the findings of this study:

1. The biofilter was capable of achieving benzene removal efficiency as much as 96% at a residence time of 2 min and an inlet concentration of 220 ppm.
2. With an inlet concentration of 220 ppm at a residence time of 2 min, maximum elimination capacity of this study was 483 g of $C_6H_6/m^3 \cdot$ day. And carbon dioxide was produced at a rate of 608 mg/day, with a volume of 0.35 L/day.
3. The biofilter was capable of achieving ethylene removal efficiency as much as 100% at a residence time of 14 min and an inlet concentration of 290 ppm.
4. During operation with an inlet ethylene of 290 ppm, it was found that the maximum elimination capacity of this study was 34 g of $C_2H_4/m^3 \cdot$ day. And carbon dioxide was produced at a rate of 87 mg/day, with a volume of 0.05 L/day.
5. For the mixed compounds, approximately 96~100% of the ethylene was degraded, whereas complete removal of benzene was achieved at residence times of 10~15 min.

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