Biological treatment characteristics of benzene and toluene in a biofilter packed with cylindrical activated carbon

G.-W. Li, H.-Y. Hu, J.-M. Hao and H.-Q. Zhang
ESPC, Department of Environment Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract The biodegradation of toluene and benzene in a biofilter using cylindrical activated carbon as the filler materials was studied. Three gas flow rates, i.e. 0.25, 0.50 and 0.75 m³/h, corresponding to empty bed gas residence of 75, 37.5 and 25 s, respectively, and total organic load lower than 400 g/m³·h were tested. The biofilter proved to be highly efficient in biodegradation of toluene and benzene, and toluene was more easily degraded than benzene. When each inlet load was lower than 150 g/m³·h, removal rate increased with inlet load and reached a maximum, which was 150 and 120 g/m³·h for toluene and benzene, respectively. For inlet load higher than the maximum removal capacity conditions, the removal rate decreased with inlet load. Carbon dioxide concentration profile through the biofilter revealed that the mass ratios of carbon dioxide produced to the toluene and benzene removed were 2.15 g(CO₂)/g(toluene) and 1.67 g(CO₂)/g(benzene), which furthermore, confirmed the biodegradation performance in biofilter. The observation of biotic community demonstrated that the microbes consisted of bacillus, spore bacillus and fungi, of which the spore bacillus was dominant.

Keywords Benzene; biofilter; cylindrical activated carbon; toluene; VOCs

Introduction
In response to the growing concern about volatile organic compounds (VOCs), biofiltration is rapidly becoming a promising technology for removing VOCs in waste gas, such as gaseous discharging from wastewater treatment facilities (Leson, 1991). In this process, the organic compounds are aerobically degraded by aerobic heterotrophic microbial species (Togna and Sing, 1994). The use of biofilters to degrade VOCs from waste gas has occurred only within the last few years, and has been shown to be effective for treating aromatics such as styrene and toluene, aliphatics such as propane and isobutene, and more easily degraded compounds such as esters and alcohols. Various natural materials such as peat, compost and wood bark are frequently used as filtering material. These materials offer many advantages including a rich variety of microbial species, lower prices and larger surface areas (Zhu et al., 1998). However, biofilters filled with these materials may be subject to operating problems such as channeling and compaction. Recently, some synthetic materials including granular activated carbon (GAC), activated carbon fiber and polystyrene has been used to improve the performance and increase the useful life of the filter bed (Li et al., in press).

In this study, the biofiltration of benzene and toluene was investigated using biological cylindrical activated carbon (BAC), the performance of BAC for the removal of benzene and toluene was compared. Because of their higher vapor pressure and large quantity of discharge, toluene and benzene were selected as the representatives of VOCs in this study.

Methods
Material and apparatus
The main component of the biofilter used in this study is shown in Figure 1. The biofilter consisted of a 1,200 cm tall cylindrical column (Plexiglass) with an inner diameter of 100
It was filled with cylindrical activated carbon (CAC, $\varnothing \times 6$ mm, surface area per gram is 979 m$^2$, stacking density is 40 kg/m$^3$) to a total height of 80 cm. The column was divided into four sections evenly with five threaded 0.8 cm i.d. ports for gas sampling and four 2.0 cm i.d. ports for biofilm sampling. Plexiglass mesh was placed above each gas sampling port to support the filter medium and distribute gas flow over the cross-section of the filter bed. The inflow gas was supplied tangentially at the top of the biofilter, meanwhile, the nutrient solution was sparged over the filter material discontinuously to maintain medium humidity and avoid the drying effect on the filter bed by the air flow.

**VOC preparation and delivery**

The gaseous benzene and toluene were generated as follows. First, compressed air from the laboratory distribution system was passed through an oil-water separator to remove oil, water and particulate, then, the filtered air passed through a cylinder filled with cylindrical activated carbon (CAC) to adsorb residual organics. Next, two fractions of the air stream were saturated with benzene and toluene, respectively, and mixed together with the main air stream, the mixed stream then flowed into the biofilter. Flow rates of the main fraction of the air stream and the fraction saturated with benzene and toluene were measured by gas flowmeters in order to obtain the desired benzene and toluene inlet concentration (the concentration ratio is about 1) and gas flow rate through the biofilter. All tube and connections after the introduction of benzene and toluene were stainless steel, Teflon and glass to minimize VOCs sorption.

The biofilter was operated according with the following parameters. Gas flow rates were 0.25, 0.50 and 0.75 m$^3$/h corresponding to empty bed gas residence time of 75, 37.5 and 25 s, respectively. Benzene and toluene concentrations varied between 200 and 3,000 mg/m$^3$. Total organic load was lower than 400 g/m$^3$.h. The moisture content of the filler was maintained around 55–65%. pH varied from 6.5 to 7.5. During 4 months of operating, the operating conditions mentioned above were tested. The performance of the biofilter evaluated by the removal rate ($-r$, g/m$^3$.h), the removal efficiency ($R$, %) and the mass of carbon dioxide produced per unit of time and filler volume ($r_{\text{CO}_2}$, gCO$_2$/m$^3$.h.).

**Analytical techniques**

Gas samples were analyzed for benzene and toluene by direct injection into a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a HP capillary column (30 m $\times$ 0.53 mm $\times$ 6 $\mu$m, filled silicon) and a flame ionization detector (FID). Output from the FID was calculated by HP integrator. Carbon dioxide concentration in the gas phase at each gas sample pore was also analyzed using a CO$_2$ analyzer with a continuous sampling pump. The gas analysis equipment was calibrated before the sample concentration was measured.
standards for calibrating the GC were produced by diffusing a known quantity of benzene and toluene into a known volume vessel. Also, a small part of the filler was withdrawn from solid sample ports at the middle of each section of the filter beds for bacterial identification and counting analysis. The bacterial identification and counts on the filter material samples were performed using standard culture methods.

Results and discussion

Adsorption and biodegradation of toluene

In order to compare the adsorption of dry CAC with the biodegradation of BAC, influent and effluent toluene gas concentration profiles were compiled before and after sparging water over a 15 day period with gas flow rate of 0.50 m³/h (retention time 37.5 s) and toluene concentration 1,800~2,400 mg/m³ (Figure 2). During start-up, CAC was dry, effluent concentrations were controlled primarily by the adsorptive capacity of dry CAC. Differences between influent and effluent concentrations were at maxima. As adsorption went on, effluent concentrations rose until the CAC column was saturated. The adsorbing capacity was 0.179 kg(toluene)/kg(CAC), the transmittance height was 12.7 cm and the saturated adsorption time was 190 hours (Li et al., 2000). Soon afterwards, pure water (no nutrients and bacteria) was added into the column. Because the CAC was humid and the toluene molecule competed with the H₂O molecule on the surface of CAC, part of toluene molecule adsorbed in CAC was desorbed, so the effluent concentration was slightly higher than the influent concentration. With the system operating, effluent concentration tended to equal the influent concentration. The CAC was then taken out of the column and immersed into the activated sludge taken from refinery wastewater plant and acclimatized by benzene and toluene. The granular samples were collected and the surfaces of carbon were observed until there was a layer transparent film (about 1~1.5 mm) over the carbon. And then, the carbon covered by microorganism called BAC was refilled into the biofilter column, with the system running again, effluent concentration declined and CO₂ concentration increased gradually. At about 60 hours after restarting the system, the biodegradation reached steady state. All these showed the removal of VOCs was biodegradation rather than adsorption in a humid situation in the biofilter.

Removal rate and efficiency

The VOCs removal rate is dependent on: (i) transport of organic carbon source to the biofilm around BAC, and (ii) utilization of the carbon source by the microbes. It is obvious that the carbon source must move from the gas phase to the liquid/solid phase and then be utilized by the microbes. Diffusion is the primary driving force and is dependent upon the concentration gradient, so the inlet concentration is the most important parameter in the biofiltration. Also, the high inlet concentration in the gas phase enhances the biomass
production, which increases the volume of the biofilm surrounding the BAC, decreases the porosity of the filter bed and causes restriction to the airflow and channeling in the filter bed. On the other hand, the gas flow rate is another key parameter.

Figure 3a shows removal efficiency (R) of benzene and toluene versus the corresponding inlet concentration for the various tested gas flow rates, i.e. 0.25, 0.50 and 0.75 m$^3$/h. Removal efficiency decreases with inlet concentration and the removal efficiency of toluene ($R_{tolu}$) is always slightly higher than that of benzene ($R_{benz}$). When inlet benzene and toluene concentrations are lower than 1800 and 2600 mg/m$^3$, respectively, at a gas flow rate of 0.25 m$^3$/h, $R_{tolu}$ and $R_{benz}$ are higher than 90% and their decreasing rates with inlet concentration are very slow. When toluene concentration increases from 2,600 to 4,300 mg/m$^3$, and benzene concentration increases from 1,800 to 3,500 mg/m$^3$, $R$ decrease from 90 to 70%. Figure 3a also shows similar trends of variation of $R$ with inlet concentration at gas flow rates of 0.5 and 0.75 m$^3$/h, but at these two flow rates, $R$ decreases with inlet concentrations rapidly. The decreasing rate of $R$ increases with gas flow rate. Figure 3b presents their removal rate ($-r$) as function of inlet load for the same condition with Figure 3a. When inlet loads of toluene and benzene are smaller than 170 g/m$^3$.h, respectively, toluene removal rate ($-r_{tolu}$) and benzene removal rate ($-r_{benz}$) increase with their load linearly, at about 170 g/m$^3$.h, $-r_{tolu}$ and $-r_{benz}$ are constant at the maximum value of 150 and 120 g/m$^3$.h respectively and then decrease at higher load. When the load is higher than 170 g/m$^3$.h, removal rate decreases with the increase of load.

The results show that a higher gas flow rate decreases the contact time between the pollutants and the microbial film and consequently lowers the filler efficiency and removal rate. The increase of toluene and benzene inlet concentration enhances their transfer rate from gas phase to the biofilm, so that more microorganisms participate in the biodegradation activity. This behavior can be described as a diffusion limitation regime. At the maximum removal rate, the entire active microbial pollution is involved in the biodegradation and diffusion limitation does not occur for these operating conditions. When load increases above the upper limit of the diffusion limitation regime, removal rate first remains constant to the maximum value and then decreases for higher load. Increase in the toluene and benzene concentrations above their maximum removal rate conditions cause significant decreases in both removal rate and removal rate. Such behavior was not expected since previous research on the biodegradation of toluene or/and benzene reported a constant removal rate with increase of pollutant inlet load in the reaction limitation, i.e., in the absence of diffusion limitation regime.

**Carbon dioxide produced rate**

In the biodegradation, VOCs are aerobically degraded to carbon dioxide (CO$_2$) and water by microorganisms and exploited as a carbon source for the microbial growth. So, the
profile of CO₂ concentration along with gas flow direction provides valuable information on the biofilter performance. Figure 4 shows the outlet CO₂ concentration versus the inlet benzene and toluene concentration for gas flow rate of 0.50 m³/h. In tested operating condition, the concentration of CO₂ at the exit of the biofilter increases with the inlet benzene and toluene concentrations. The outlet CO₂ concentration is always higher than inlet concentrations indicating and confirming the biodegradation of benzene and toluene in the biofilter. Figure 5 presents the linear response relationship between CO₂ generation rate ($r_{CO₂}$) and toluene and benzene removal rate, i.e. $r_{CO₂,tolu} = 2.15(-r_{tolu})$, $r_{CO₂,benz} = 1.67(-r_{benz})$. This indicates that the mass of CO₂ produced per mass of benzene and toluene degraded is on average equal to 2.15 g(CO₂)/g(toluene) and 1.67 g(CO₂)/g(benzene), respectively, which are lower than theoretical oxidation value: 3.35 g(CO₂)/g(toluene) and 3.30 g(CO₂)/g(benzene). The reason for the deficit in $r_{CO₂}$ is that in case of biodegradation of VOCs, not all organic carbon is completely oxidized to CO₂ and water, but a fraction of consumed organic carbon is used for microbial growth. In addition, in the biodegradation process, the CO₂ produced may partly accumulate in biofilm as its solute species, H₂CO₃, HCO₃⁻ and/or CO₂ which can also cause a deficit in CO₂ in the gas phase. The relationship between $r_{CO₂}$ and removal rate can be efficiently used to describe the biofilter performance.

### Microorganisms

In the biofilter, several groups of microorganisms, which are predominantly on heterotrophic organisms such as bacteria, actinomycetes, and fungi, are known to be involved in the biodegradation of organic carbon. The species and amount of microorganisms also influence biofilter performance. Three types of microbes: bacilli, spore bacilli and fungi, were identified in the biofilter. Figure 6 presents the bacteria counts in the CAC and in the BAC withdrawn from each section of the filter bed at different operating stages (start-up and steady state). This result indicates that there were only a few bacilli in CAC, their number remains at constant of $10^4$ CFU/g(humid filler). Three days after inoculating, fungi and spore bacilli were observed throughout the filter, the number are $10^5$ and $10^{5.5}$ CFU/g(humid filler), respectively, bacillus number is a little higher than that of CAC. Along with the system operating, the number of these microorganisms grows rapidly and then remains constant at maximum values of $10^5$, $10^6$, $10^{6.5}$ CFU/g(humid filler), respectively, and spore bacilli is the preponderant colony. Microorganisms profile shows that bacteria number decreases with the increasing of filter media height along the gas flow direction. Namely, the aerobic heterotrophic bacteria counts were always slightly higher in the first section of the filter bed, which can be related to the higher removal rate and efficiency at this section in comparison with the other three sections.
Conclusions

The biological treatment performance of benzene and toluene was investigated in a biofilter packed with granular activated carbon. The conclusions are summarized as follows.

1. The biofilter system was capable of efficiently biodegrading toluene and benzene. Toluene was more easily degraded than benzene.

2. The biofiltration performance both in terms of removal rate and removal efficiency decreased with the increasing of gas flow rates for all tested inlet concentrations. At low inlet load, removal rate increased linearly with inlet load and reached a maximum. The maximum elimination capacity of toluene and benzene was 150 and 120 g/m$^3$h, respectively, and did not vary with the change of gas flow rate. For inlet load higher than the maximum elimination capacity conditions, the removal rate decreased with increasing of inlet load.

3. The quantity of carbon dioxide from the biodegradation of toluene and benzene was directly proportional to their elimination capacities, the ratio to toluene and benzene was 2.15 g(CO$_2$)/g(toluene) and 1.67 g(CO$_2$)/g(benzene), respectively.

4. The observation of biotic community demonstrated that the microbes consisted of bacillus, spore bacillus and fungi. The spore bacillus was dominant.

References


