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Biodegradation of methanol vapor in a biofilter

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Abstract: Volatile organic compounds (VOCs) are a new class of air pollutants posing threat to the environment. Newer technologies are being developed for their control among which biofiltration seem to be most attractive. Biofiltration of methanol vapor from air stream was evaluated in this study. Experimental investigations were conducted on a laboratory scale biofilter, containing mixture of compost and polystyrene inert particles as the filter materials. Mixed consortium of activated sludge was used as an inoculum. The continuous performance of biofilter for methanol removal was monitored for different concentrations and flow rates. The removal efficiencies decreased at higher concentrations and higher gas flow rates. A maximum elimination capacity of 85 g/(m^3·h) was achieved. The response of biofilter to upset loading operation showed that the biofilm in the biofilters was quite stable and quickly adapted to adverse operational conditions.

Keywords: biofilter; methanol; removal efficiency; elimination capacity; degradation

Introduction

With increasing public concern about deteriorating atmospheric air quality, stringent regulations are being enforced to control air contaminants. Volatile organic compounds (VOCs) are among the new class of air pollutants generated from a variety of industrial sources, which are attracting serious attention in recent years. Methanol vapors are mainly emitted from chemical industries where methanol is used as a solvent and is also formed as a by-product. The global annual production of methanol is approaching 20 million metric tonnes per year(Shareefdeen, 1993). The U.S. Clean Air Act Amendments of 1990 lists methanol as a regulated hazardous air pollutants. The common air pollution control process applied for control of VOCs are (1) physical treatment, such as adsorption, absorption and UV radiation; and (2) chemical treatment e.g., incineration, catalytic combustion, ozonation, and chlorination. These control techniques may yield, products, which require further treatment before their disposal. Further, these traditional methods are relatively less effective, more expensive and wasteful in terms of energy consumption. Hence, development of alternative control measures is warranted.

Biological waste gas treatment represents a new treatment alternative, although it has sporadically been used since the 1920s(Ottengraf, 1986). In the past few decades biological treatment of waste gases has gained considerable interest as it is seen to be a competitive alternative to the physicochemical treatment technologies, particularly for vapors of organic compounds present in air streams at low concentration. The major advantages of biological waste gas treatment methods are its low cost, high reliability and environmental compatibility. The pollutants are not merely transferred from one phase to another but completely oxidized to CO_2 and H_2O. Among the various biological techniques, biofiltration has attracted considerable attention in the last few years, because of its potential for effectively removing VOCs from contaminated air from variety of sources(Van Groenestijn, 1993). In biofiltration, the gas to be treated is passed through a packed bed of biomass supported on suitable matrices such as compost, peat, humus earth and wood chips. Biodegradable volatile compounds are absorbed by the biofilm and oxidised into harmless end products.

A number of experimental studies (Shareefdeen, 1993; Ottengraf, 1983; 1986; 1991; Van Groenestijn, 1993) have established biofiltration as an efficient treatment process and reliable technology

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for the control of volatile organic compounds. The compounds to be treated must be readily biodegradable and non toxic; thus, biofilters have treated alcohols, ethers, aldehydes, ketones, monocyclic aromatics, organic amines and sulphide in reasonable concentrations. Chlorinated organic compounds can also be treated, but degradation may require the presence of cometabolite and the rates are slow(Van Groenestijn, 1993). Biofiltration of methanol vapor in a bed of a mixture of compost and perlite particles showed an elimination capacity of 112.8 g/(m^3 · h) (Shareefdeen, 1993). Three different packing materials were studied for the biofiltration of ethanol vapor and elimination rates ranging from 53 to 219 g/(m^3 · h) were achieved(Hodge, 1994). This paper examines the performance of continuously operated biofilter for the removal of ethanol vapor at relatively high inlet concentration and the dynamics of the packed bed reactor system on extended operation.

1 Materials and methods

1.1 Organisms and culture medium

Mixed culture microorganisms, obtained from a sewage treatment plant was continuously acclimated to methanol as the carbon source with a nutrient solution in a 250 ml flask. Nutrient solution consisted of (g/L): K_2HPO_4 – 0.8; KH_2PO_4 – 0.2; $CaSO_4 \cdot 2H_2O$ – 0.05; $MgSO_4 \cdot 7H_2O$ – 0.5; $(NH_4)_2SO_4$ – 1.0; and $FeSO_4 \cdot 7H_2O$ – 0.01 in water. Enrichment cultures were developed by serial transfer.

1.2 Filter materials

The packing material for the bed consisted of a mixture (60:40 v/v) of sieved compost (4 mm and 10 mm size granules, 1:1 ratio) and polystyrene inert particles (4 mm size). The inert material severed to increase the bed porosity and to ensure a more homogenous gas distribution across the filter bed. The filter material was inoculated with methanol acclimated mixed microorganisms.

1.3 Experimental set-up

Fig. 1 illustrates the schematic diagram of the biofilter. The biofilter made of transparent polyacrylic tube with an internal diameter of 5 cm. The tube was packed to a height of 50 cm. The filter material was supported by perforated plate. Sampling ports covered with rubber septa allowed collection of samples for analysis. Humidified air and methanol vapor were mixed in a mixing chamber and the mixture was passed through the packed bed. Methanol concentration in the feed stream was varied by adjusting the flow rates of the air stream passing through the water and ethanol solution. The biofilter was operated at different inlet feed concentrations and flow rates. Samples were collected at regular intervals from the top of the biofilter as well as from the sampling ports using a gas tight syringe and analyzed for residual methanol.

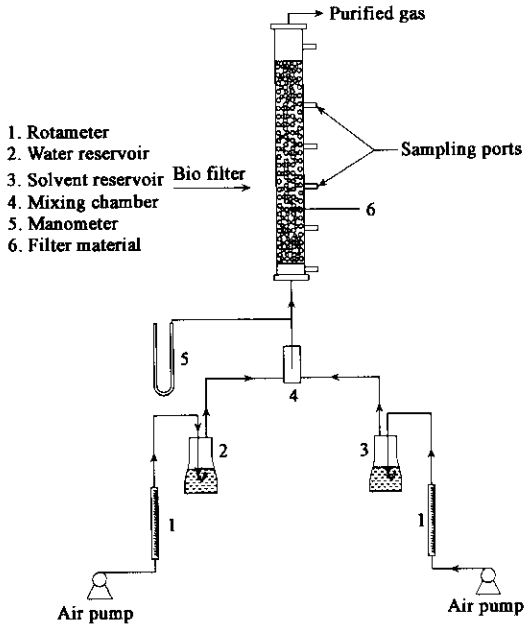

Fig. 1 Schematic diagram of the experimental set-up

1.4 Analytical methods

Ethanol in the samples were analyzed by gas chromatography (NUCON – 5765, GC India) using a chromosorb-101 packed column and flame ionization detector. Nitrogen was used as the carrier gas at a flow rate of 20 ml/min. The temperature of the column was maintained at 150℃. Injector and detector temperatures were 160 and 165℃, respectively. The retention time of ethanol was 2.0 minute under these

conditions.

2 Results and discussion

2.1 Start up operation of biofilter

During the start up, the biofilter was inoculated with a seed culture of methanol acclimated inoculum, and operated at an inlet methanol concentration of 2.0 g/m^3 and gas flow rate of 0.012 m^3/h. As shown in Fig. 2 the reactor performance was monitored over a period of time till the removal efficiency reached steady state. Initially, the filter bed showed complete removal, mainly due to adsorptive and absorptive capacity of the filter material, which has been observed in other studies also (Hodge, 1995; Zhu, 1998; Webster, 1997). Once the adsorptive and absorptive capacity of the filter bed was exhausted, the removal efficiency decreased to 27%, later it gradually increased with fluctuations. A visible biofilm was observed within 15 days, with complete removal of methanol at the outlet. Similar observation has been reported during the treatment of ethanol vapor (Hodge, 1995). Ottengraf (Ottengraf, 1986) has reported acclimation times of one to three weeks for a wide range of bed materials and substrates. Webster *et al*. (Webster, 1997) have stated that adsorption of contaminant to the medium dominates removal during the initial period of any biofilter operation and should not be erroneously counted as part of the biodegradation performance of the system. Allen *et al*. (Allen, 1991) have observed 99% removal efficiency during initial period of operation treating H_2S in a compost biofilter and reported that the high removal efficiency was probably due to physical and chemical processes rather than biological interactions between H_2S and the biofilter materials.

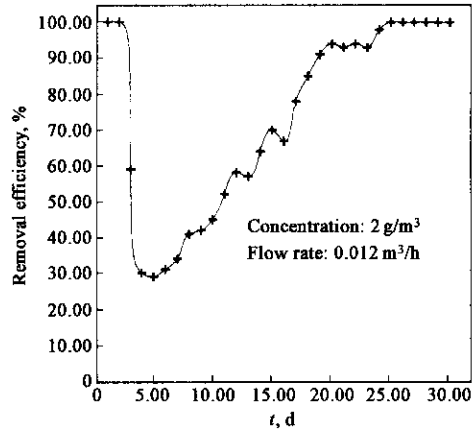

Fig.2 Start up operation of the biofilter

2.2 Removal efficiency

Removal efficiency is the operating parameter, most often used to judge the success of the biofilter. It is dependent not only on the biological activity of the filter but also on the loading applied to the biofilter. Removal efficiencies as high as 95%—99% have been reported in the literature for many VOCs (Ottengraf, 1983; Hodge, 1994; 1995; Zhu, 1998). The effect of flow rate on methanol removal was studies over a range of concentrations up to 8.0 g/m^3. As shown in Fig. 3 the removal efficiency decreased with the increasing flow rate. Higher removal efficiency was achieved, when the flow rates were controlled in the range of 0.012 m^3/h, when the flow rate increased up to a value of 0.026 m^3/h, the removal efficiency dramatically decreased to 30%. The removal efficiency showed a lesser variation at lower flow rate of 0.012 m^3/h, whereas a significant difference was observed when the flow rate increased to 0.026 m^3/h. At higher gas flow rate, the removal efficiency declined rapidly even at relatively lower concentrations. The removal efficiency in the biofilter is mainly controlled by the mass transfer rate of substrate in the biofilm and in the gas phase boundary layer, which in turn is controlled by the residence time in the biofilter. At low flow rate, the residence time being adequate, the decrease in the removal

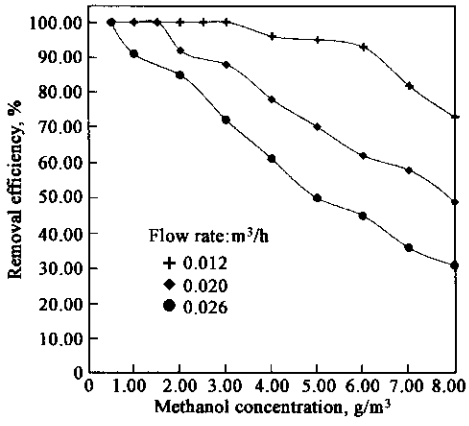

Fig.3 Removal of efficiency of biofilter for methanol biodegradation

efficiency at higher methanol concentration is mainly due to biodegradation limitation of the biofilm. At higher gas flow rates, the inability of the substrate to reach the interface between the gas and the biofilm due to the shorter residence time might have been responsible for the decrease in the removal efficiency. Gas removal in the biofilter consists of two steps, first the gas is removed from the gas phase by diffusing into the liquid film followed by microbial degradation. Similar kind of behaviors have been observed during the treatment of methanol vapor in a biofilter(Shareefdeen, 1993). They have also found that increasing concentration and flow rate decreases the removal efficiency. At a flow rate 0.012 m^3/h they achieved above 90% removal efficiency up to 6 g/m.

2.3 Elimination capacity for methanol

Elimination capacity is defined as the amount of VOC removed in the biofilter per unit volume of biofilter per unit time (e.g., methanol m^{-3} filter h^{-1}). The maximum elimination capacity of the biofilter is the maximum pollutant-loading rate that the biofilter can tolerate without inhibiting its microbial population.

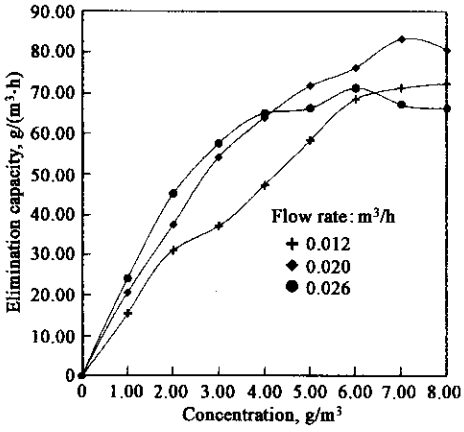

Fig.4 Elimination capacity of the biofilter

The effect of the methanol loading on the elimination capacity of the biofilter is shown in Fig. 4 as a function of the inlet methanol concentration at three different flow rates. The gas flow rate was varied from 0.012 to 0.026 m^3/h and the inlet concentration was varied from 1.0 to 8 g/m^3. It may be observed that at all the gas flow rates the elimination capacity increased with increasing methanol concentration till a threshold concentration after which it remains constant. The threshold concentration varied with the gas flow rate. The initial increase in the elimination capacity can be interpreted to be due to enhanced pollutant transfer to the biofilm and increased rate of biodegradation in the biofilter. At higher concentration, the biofilm get saturated which limits the rate of biodegradation and thus the elimination capacity remains stable. Similar behaviors has been observed during the treatment of toluene or xylene individually in a pilot scale biofilter (Jorio, 1998). A maximum elimination capacity value of 112 $g/(m^3 \cdot h)$ has been reported for the treatment of methanol vapor in biofilter (Shareeffdeen, 1993).

The macrokinetics of the contaminant elimination processes in a biofilter can be described by an absorption process in a wet biofilm accompanied by a simultaneous biodegradation reaction (Ottengraf, 1991). The absorption process is controlled by the diffusion rate which in turn is related to the inlet concentrations. At high inlet concentrations, diffusion rate is relatively high and the contaminant removal process is controlled by the biological degradation reaction. The elimination of biodegradable compounds like alcohol, ketones, esters etc., in a biofilter follows zero order reaction kinetics. At low gas concentration level the elimination rate of the filter bed may shift towards diffusion controlled regime. Hence, as the inlet concentration increases, the elimination capacity reaches a maximum determined by the so called reaction limited regime where in the activity of the biofilm is fully utilized. Further, the elimination capacity may also reach a limiting value due to the oxygen limitation.

2.4 Upset loading operation

The emissions from industries are often under transient conditions. The biofilter should be able to treat the pollutant effectively under different loading conditions. The microorganisms survive in the filter bed must be able to withstand such a loading conditions. So, it is important to study the dynamic behaviors of the filter during upset loading operation. Biofilter performance with upset loading was investigated in two

different upset modes such as change in the inlet concentrations and change in flow rate. The effect of upset loading due to feed concentration change on methanol removal in the biofilter is shown in Fig. 5. In response to a sharp increase in the concentration from 2 to 6 g/m^3 the methanol removal decreased immediately from 85% to 50% during the exposure to higher concentration. When the feed concentration was brought down to the original level the methanol removal also recovered within 2 days to its original value. This result also shows that the methanol degraders are also sensitive to concentration fluctuations but the biofilm was quite stable to withstand the upset load conditions. However, the methanol removal decreased by 30% due to the sudden increase in the flow rate. When the original were restored the methanol removal did not totally recover to its original value.

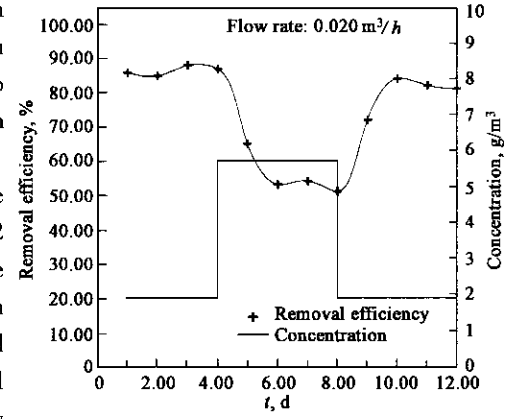

Fig.5 Upset loading effects on bofilter due to abrupt change in concentration

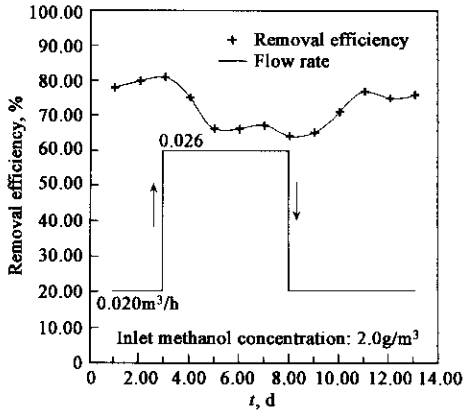

Fig.6 Upset loading effects on biofilter due to abrupt change in gas flow rate

As shown in Fig. 6 the flow rate of the biofiler was changed from 0.02 to 0.026 m^3/h and maintained at that level for 6 days. The removal efficiency of methanol biofilter was reduced from 80% to 60% during the upset condition and recovered to almost the original value within 2 days when the flow rate was reversed to original level. Corsi *et al*. (Corsi, 1995), in their biofiltration studies treating toluene have reported that a small increase in the inlet toluene concentration could only induce the variation of the exit concentration over a very short period of time (20 h), and the original steady state was subsequently reached. Baltzis *et al*. (Baltzis, 1997), have studied the shock loading effects in the biofilter containing peat/perlite particles as the filter material for the treatment of ethanol and butanol and reported that the filter bed never failed completely under shock loading operation. Tang *et al*. (Tang, 1995), have also extensively studied the shock loading effects in toluene removal in biofilter containing different filter material and reported that the performance of biofilter was never affected by the shock loading effects. They also reported that during the shock loading operation, after increase or decrease in concentration and gas flow rate, the filter could reach the previous value within 2 to 4 days. As observed from the results presented by Hodge *et al*. (Hodge, 1995), during the treatment of ethanol vapor in a biofilter, the sudden variations in inlet concentrations resulted in fluctuations in exit concentrations, but the steady state was achieved at every stage.

3 Conclusions

Biodegradation in biofilter containing compost as the main biomass support appears to be a cost effective treatment method for easily biodegradable volatile compound like methanol. Concentrations as high as 8 g/m^3 could be degraded at a gas flow rate of 0.026 m^3/h. Higher concentrations and higher gas flow rates reduced the removal efficiency due to mass transfer limitations and shorter residence times. The elimination capacity of the filter bed is a function of the inlet methanol concentration. A maximum elimination capacity of 85 g/(m^3·h) was achieved, which was comparable to the reported value in the

literature. The response of the biofilter were sensitive to the changes, but the biofilm in the biofilters was quite stable and quickly adapted to adverse operational conditions. The long-term operation of the biofilter showed very little variation in performance.

References:

Allen E R, Y Yang, 1991. Biofiltration control of hydrogen sulfide emissions[C]. Proceedings of the 84th annual meeting of the air and waste management association. Pittsburgh, Pa.

Baltzis B C, S M Wojdyla, M Z Shareefdeen, 1997. Modeling biofiltration of VOC mixtures under steady state conditions[J]. J Envir Eng, 123 (6): 599—605.

Corsi R C, L P Seed, 1995. Biofiltration of BTEX: media, substrate, and loading effects[J]. Environ Prog, 3: 151—158.

Hodge D S, J S Devinny, 1994. Biofilter treatment of ethanol vapors[J]. Environ Prog, 13: 167—173.

Hodge D S, J S Devinny, 1995. Modelling removal of air contaminants by biofiltration[J]. J Envir Engg, 121: 21—44.

Jorio H, K Kiared, R Brzizinski *et al*., 1998 . Treatment of air polluted with high concentrations of tolune and xylere in a pilot scale biofilter [J]. J Chem Technol Biotechnol, 73(3):183—196.

Ottengraf S P P, 1986. Exhaust gas purification[J]. Biotechnology, 8: 426—452.

Ottengraf S P P, 1991. Process technology of biotechniques[J]. LUCHT, 4: 135—144.

Ottengraf S P P, A H C Vander Oever, 1983. Kinetics of organic compound removal from waste gases with a biological filter[J]. Biotechnol Bioeng, 25 : 3089—3102.

Shareefdeen Z B C, Baltzis Y S Oh, R Bartha, 1993. Biofiltration of methanol vapor[J]. Biotechnol Bioeng, 41: 512—524.

Tang H M, S J Hwang, S C Hwang, 1995. Dynamics of toluene degradation in biofilters[J]. Haz Waste Haz Matls, 12: 160—172.

Van Groenestijn J W, P G M Hesselink, 1993. Biotechniques for air pollution control[J]. Biodegradation, 4: 283—301.

Webster T S, J S Devinny, E M Torres *et al*., 1997. Microbial ecosystem in compost and granular activated carbon biofilters[J]. Biotech Bioeng, 53(3): 296—303.

Zhu L, R J Abumaizer, W M Kocher, 1998. Biofiltration of benzene contaminated air streams using compost-activated carbon filter media[J]. Environ Prog, 17 : 168—172.

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