Dichloromethane removal using mixed cultures in a biofilter and a modified rotating biological contactor – start up studies

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ABSTRACT

Dichloromethane (DCM) is a widely used organic solvent which is considered to be hazardous air pollutant. Regulatory standards in many countries require its removal from waste gas streams. Biological waste gas treatment is an attractive and environmental-friendly alternative to physicochemical methods. Volatile organic compounds (VOCs) in waste gases can serve as energy source and/or carbon source for the microbial metabolism. Biofilters and biotrickling filters, the widely used bioreactors, suffer from limitations such as control of operating parameters, pH, humidity and nutrient supply and clogging due to overgrowth of biofilm.

To overcome these drawbacks, a modified rotating biological contactor (RBC) has been proposed which can retain the advantages of conventional systems. A conventional RBC system containing 20 acrylic discs 21 cm diameter and 5mm thickness with a disc spacing of 10 mm was modified by adding a leak tight cover and baffles between disks to avoid short circuiting of flow. The biofilm was formed on the discs with inoculum pre acclimatized to DCM at low concentration.

The RBC was operated at an inlet concentration of 0.15 - 0.2 g/m³ at a gas flow rate of 0.06 m³/h corresponding to an empty bed residence time (EBRT) of 2.5 min for 38 days resulting in a steady state removal of 84%. The residual DCM concentration in liquid phase was 5ppm and dissolved oxygen level was 3-4 ppm. pH decreased from 7 to 4.5 in the media, which indicated biodegradation and formation of acidic metabolites.

The performance of RBC was compared with that of a biofilter packed with a mixture of garden compost and ceramic beads. The biofilter was operated at an inlet concentration of 0.15 - 0.21 g/m³ and at a gas flow rate of 0.06 m³/h corresponding to an empty bed residence time (EBRT) of 1.47 min for 90 days to reach steady state removal efficiency of 88%. Thus RBC system seems to be a potentially alternative to biofilter.

1 INTRODUCTION

With the increasing usage of synthetic chemicals, particularly the petrochemicals, a new class of air pollutants, the Hazardous Air Pollutants (HAPs) have become a matter of concern in recent years. The list of hazardous air pollutants includes a number of volatile organic compounds (VOCs) which are commonly used as industrial solvents. Dichloromethane (DCM) is an important VOC used primarily for metal degreasing and paint removal. Due to its low boiling point (40.1° C) and high vapor pressure (47 Kpa at 20° C) significant amounts of DCM reach the environment (Wang *et al.*, 2006). DCM is difficult to remove from contaminated water and air (Machey and Cherry, 1989) and shows high persistence in water (half life over 700 years) and atmosphere (half-life 79 days). The solvent DCM is known to be toxic to central nervous system at high exposure levels and there is suspected carcinogenicity in human liver and kidney (Green, 1991).

Conventional VOC control techniques such as adsorption, absorption, scrubbing and condensation, thermal and catalytic incineration are generally energy intensive, ineffective and economically nonviable. Biological treatment systems are ecologically compatible alternatives to physicochemical methods (Kennes and Veiga, 2001). VOCs in waste gases can serve as energy source and or carbon sources for the microbial metabolism. DCM has been shown to be utilized by both aerobic and anaerobic bacteria as a sole carbon and energy source (Brunnel *et al.*, 1980; Ritman, 1980; Krausova *et al.*, 2003). A reasonable good number of studies have been carried on DCM biodegradation using pure culture (Dicks *et al.*, 1994; Herbst *et al.*, 1995).

Biofiltration is a popular technique for removal of VOCs from contaminant air. It utilizes a support matrix packed in a column for microbial growth. The contaminants in the air stream are absorbed and metabolized by the microorganisms in the biofilm. Most biofilters that are in operation today can treat odors and VOCs effectively with efficiencies greater than 90%. A major limitation of biofilters is the increasing pressure drop during operation due to overgrowth of biofilm which requires periodical clean up. A potential alternative to overcome this limitation is to use rotating biological contactors (RBC) commonly used for waste water treatment. The RBC combines the advantages of low energy consumption and better control of biofilm growth.

Ruediger (1999) first used RBC for waste gas treatment using DCM as the model pollutant. Vinage and von Rohr (2003) have assessed the long term performance of an RBC system for toluene removal at different loading rates, achieving an elimination capacity of 60 g/m³.h. It has been shown that microbial metabolism on the disc surface occurs through a series of phenomenological steps consisting of adsorption, absorption, diffusion and biodegradation. The present study focuses on the biodegradation of DCM in modified RBC and its comparison with a biofilter.

2 MATERIALS AND METHODS

2.1 CHEMICALS

All Chemicals used in this study were of laboratory grade: Dichloromethane (>99%), was purchased from Merck Limited, India.

2.2 MICROBIAL CULTURE AND MEDIA COMPOSITION

The microbial mixed consortium was obtained from a municipal sewage treatment plant. The final inoculum was obtained by series of repeated inoculation in a mineral salt medium (MSM) that had the following composition: $(NH_4)_2SO_4 - 2.0 \text{ g/L}, \text{KH}_2PO_4 - 2.0 \text{ g/L}, \text{NaCl} - 0.5 \text{ g/L}, \text{MgSO}_4 \cdot 7H_2O - 0.025 \text{ g/L}$ (Krausova, *et al.*, 2003). The pH of the mineral salt media was adjusted to (7±1).

2.3 EXPERIMENTAL

The schematic of the experimental setup is given in Figure 1. The VOC vapor generated by passing air at controlled rate through a VOC reservoir was mixed with humidified air in a glass mixing chamber to obtain the desired concentration of the feed gas stream.

The biofilter consisted of a poly-acrylic tube (5'70 cm) having 6 sampling ports sealed with a rubber septa at 10 cm interval along the biofilter height. It was loosely packed with a mixture of compost and polystyrene spheres. A perforated plate at the bottom provided the support for the packing and also ensured uniform distribution of the vapor stream. The moisture content of the filter bed was maintained by prehumidifying the incoming vapor and by periodically sprinkling fresh media from the top of the biofilter.

The modified RBC was made from two semi-cylindrical poly-acrylic parts with flanges to get a leak free operation. It contained 20 poly-acrylic discs each of 21 cm diameter, 5 mm thickness with 10 mm spacing between the discs. The discs were mounted on a stainless steel shaft and rotated slowly with variable speed motor. Baffles fixed to the top cover allowed the gas flow to pass through each chamber and increase the residence time of the gas in the reactor.

The experimental runs were performed by passing the VOC vapor at different concentration and flow rates to vary the influent organic load. Samples were collected at the inlet and outlet at different intervals using gas tight syringe and analyzed for residual VOC concentration.

2.4 Analytical methods

Residual concentration of DCM in the aqueous phase was measured in cell free samples using a Gas Chromatograph (AIMIL, India) fitted with a flame ionization detector and a (10% FFAP) packed column. Nitrogen was used as the carrier gas at a



Figure 1. Schematic of the experimental setup.

flow rate of 25 mL/min. The temperatures of injector, oven and detector were 200, 120 and 220°C respectively and retention time was 1.4 mins.

3 RESULTS AND DISCUSSION

3.1 Startup and acclimatization of biofilter and rotating biological contactor (RBC)

Startup studies were initiated with both biofilter and RBC in order to develop the required biofilm acclimatized to DCM as the main carbon source.

3.1.1 BIOFILTER STARTUP

Through a diverse microbial population exist in the compost, an external microbial consortium acclimatized to DCM in batch culture was added to the biofilter. Acclimatization is critical for successful operation of any biofilter and it depends on the activity of the microorganisms present in the compost. The biofilter was initially operated at an inlet concentration of 0.15 - 0.21 g/m³ and at a gas flow rate of 0.06 m³/h corresponding to an empty bed residence time (EMBRT) of 1.47 mins. The removal efficiency profiles were monitored continuously for 90 days till they achieved steady state. Figure 2 and 3 show the concentration profile of DCM and its removal efficiency in the biofilter. The removal efficiency during the first few days was high, which could be mainly due to the absorptive and adsorptive capacity of the compost. After this initial sorption phase, the biofilter efficiency decreased to 49%. However, there was a slow gain in the efficiency after 4 days. Zhu et al. (1998) have reported similar observation during the treatment of benzene vapors in biofilters containing compost and granular activated carbon as the packing material. Hodge and Devinny (1994) and Arulneyam and Swaminathan (2004) have also reported similar adsorption and biodegradation phases during startup operation in biofilters handling ethanol and methanol vapours. The removal mechanism shifted towards biodegradation and during this phase, the removal efficiency progressively increased with fluctuations, until becoming constant at about 88%.



Figure 2. Startup operation of the biofilter treating DCM vapors.



Figure 3. Removal efficiency of the biofilter treating DCM vapors.

3.1.2 STARTUP WITH RBC

The RBC was initially inoculated with a seed culture acclimatized to DCM and operated at an inlet concentration of 0.25 - 0.3 g/m³ at a gas flow rate 0.06 m³/h for 10 days. It was observed that fairly thick and uniform biofilm was formed on the disc surface. As the removal efficiency was observed to be low, the DCM concentration in the feed was reduced to 0.15 - 0.2 g/m³ and the study was continued. The removal efficiency profiles were monitored continuously till they achieved steady state. Figures 4 and 5 show the concentration profile and the removal efficiency in RBC. The removal efficiency increased from 19% to 54% when the RBC was operated at high concentration. After decreasing the concentration, the removal efficiency increased rapidly and reached about 85% in 32 -35 days. The shorter time to achieve the steady state may be due to the thick growth of biofilm in the RBC. The total biomass in the RBC may be more than in the biofilter. The fact that such a thick biofilm can develop in RBC with DCM as the only carbon source proves the potential application of RBC for VOC removal.

4 CONCLUSIONS

The RBC system was found to be a potentially attractive configuration for gas phase biodegradation of VOC. For comparative organic load, both RBC and biofilter gave reasonably high (>80 %) removal of DCM, but RBC was able to reach it in shorter time.



Figure 4. Startup operation of the RBC treating DCM vapors.



Figure 5. Removal efficiency RBC treating DCM vapors.

References

- Arulneyam, D. and Swaminathan, T. (2004) Biodegradation of mixture of VOC's in a biofilter. J. Environ. Sci. 16(1): 30-33.
- Brunner, W., Staub, D. and Leisinger, T. (1980) Bacterial degradation of dichloromethane. *Appl. Environ. Microbiol.* 40: 950-958.

- Diks, R., Ottengraf, S.P.P. and Vanden Oever, A.H.C. (1994) The inflence of NaCl on the degradation rate of dichloromethane by *Hyphomicrobium sp. Biodegradation* 5: 129-141.
- Green, T. (1991) Human exposure. Toxicol. 16: 2981-2985.
- Herbst, B. and Wiseman, U. (1996) Kinetics and reaction engineering aspects of the biodegradaton of dichloromethane and dichloroethane. *Wat. Res.* 30(5): 1069-1076.
- Hodge, D.S. and Devinny, J.S. (1994) Biofilter treatment of ethanol vapours. *Environ. Prog.* 13: 167-173.
- Wang, J. and Chen, J.M. (2006) A Removal of dichloromethane from waste gases with a biocontact oxidation reactor. *Chemical Eng. J.* 123(3): 103-107.
- Krausova, V.I., Robb, F.T. and Gonzalez, J.M. (2003) Bacterial degradation of dichloromethane in cultures and natural environments. *J. Microbiol. Methods* 54: 419-422.
- Kennes, C. and Veiga, M.C. (2001) Conventional Biofilters. *In: Bioreactors for Waste Gas Treatment*, Kennes, C. and M. C. Veiga (Eds.) Kluwer Academic Publisher, Dordrecht, pp. 47-98.
- Machay, D.M. and Cherry, J.A. (1989) Ground water contamination pump-and-treat remediation. *Environ. Sci. Technol.* 23: 630-636.
- Rittmann, B.E. and McCarty, P.M. (1980) Utilization of dichloromethane by suspended and fixedfilm bacteria. *Appl. Environ. Microbiol.* 39(6): 1225-1226.
- Rudiger, P. (1999) Abluftreinigung in Biofilmreaktoren mit inerten Tragern. Diss. ETH No: 13229, ETH Zurich.
- Vinage, I. and Rudolf Von Rohr, P. (2003) Biological waste treatment with a modified rotating biological contactor. I. Control of biofilm growth and long-term performance. *Bioprocess Biosyst. Engin.* 26: 49-57.
- Zhu, L., Abumaizar, R.J. and Kocher, W.M. (1998) Biofiltration of benzene contaminated air streams using compost activated carbon filter media. *Environ. Prog.* 17(3): 168-172.