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Biodeodorization of Waste Gas Containing Monochlorobenzene (MCB) in a Bench Scale Biofilter

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MCB is manufactured worldwide by the chlorination of benzene and the process produces MCB and its derivatives, which are separated using distillation as per the requirement for different uses. The production and processing of MCB generates obnoxious odour. Exposure to emissions containing MCB has deleterious health effects and environmental implications. Industrial emissions containing MCB requires proper treatment prior to discharge.

A bench scale biofilter system packed with compost and wood chips seeded with isolated bacterial cultures which is identified as *Acinetobacter calcoaceticus* having biokinetic properties (specific growth rate μ_{max} = 0.18/h, half saturation rate constant K_s = 12.8 mg/L MCB and inhibition constant 81.71 mg/L MCB) was operated for the treatment of waste gas containing MCB. The process parameters viz. startup time for the biofilter system, effective bed retention time (EBRT), MCB load, pH, moisture and microbiological status of the biofilter have been evaluated and the results on these aspects have been presented and discussed in the paper.

1. Introduction

MCB is produced worldwide approximately 647000 MT. MCB is used as an intermediate in dye and pesticide synthesis, solvents, insect repellents, degreasers, deodorants, heat transfer agents etc. The estimated release of MCB to air is above 0.2% of the total production and use. Dow Chemical Company have reported that about 30-50% of their annual MCB produced is released to air (ATSDR, 1990). MCB is identified as a priority pollutant by the USEPA and has several health and environmental implications (ATSDR, 1990).

Several literature reports (Diks, 1992; Diks and Ottengraf, 1991; Haigler, et al., 1988; Namkung and Rittmann, 1987) have reported mineralization of MCB and its derivatives in luquid broth under appropriate conditions in the laboratory by the bacteria isolated from solid and water. The deodorization of waste gas containing MCB has been cited using biotrickling filter (Young and Richard, 1994; Mathur et al., 2006). Thus, biological treatment is considered to be feasible for the deodorization of waste gas containing MCB, which is emitted into the environment from chemical processing industries and other anthropogenic sources. There is limited cited investigation on biodeodorization of waste gas containing MCB in the biofilter. The paper outlines deodorization of waste gas containing MCB in a biofilter packed with compost & wood chips augmeted with seeded culture *Acinetobacter calcoaceticus*.

2. Materials and Methods

2.1 Materials

Biofiltration unit

A scheme of bench scale biofiltration unit is presented in Figure 1. The laboratory scale biofilter was made-up of PVC material. The biofilter set-up consists of a blower, an odour-generating unit, a rotameter (1-10 LPM), bioreactor, a temperature indicator, and manometer for pressure reading as well as sample collection ports. A leachate collection unit with water seal was also provided at the bottom of the biofilter. The biofilter is filled with packing material consisting of compost (% w/w carbon 38, nitrogen 1.3, phosphorous 0.02, potassium 0.71, calcium 1.62, magnesium 0.14 and sodium 0.01; trace elements µg/g: copper 44, manganese 360 and zinc 70) and wood chips in alternate layers. Dimensional details of the bioreactor are given in Table 1.

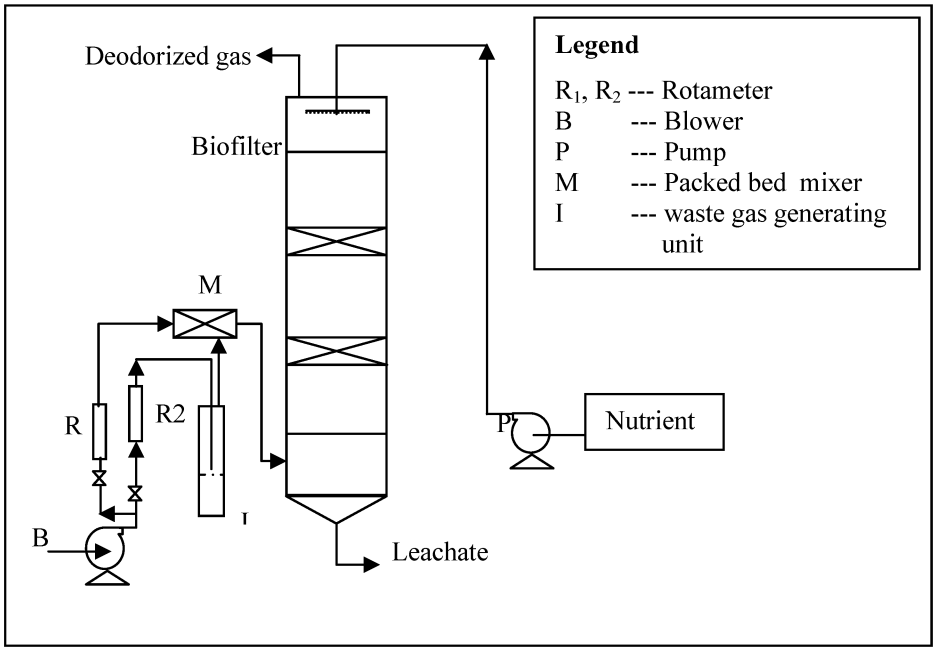

Figure 1: Schematic diagram of air phase biofilter for deodourization of waste gas containing MCB

Table 1: Dimensional details of different units of bench scale biofilter unit

Particulars	Magnitude
Height of the bioreactor	90 cm
Diameter OD/ID of bioreactor	OD=20 cm, ID=19.5 cm
Total volume	27 litre
Volume of packing	12.1 litre
Porosity of packing	0.3
Details of media	
Weight of compost	4269.4 g
Weight of wooden chips	1067.35 g
Odorant generating unit	
Volume of impinger	275 ml
Blower capacity	1.5 m^3/min
Rotameter	0 to 10 LPM

ID - Inner diameter; OD - Outer diameter; LPM - Liters per minute

Equipments

The quantitative estimation of MCB was carried out using Perkin Elmer make Gas chromtograph on a Supelco Equity 5 Fused silica capillary column (Length - 30 m, ID - 0.25 mm x 0.5 µm film thickness). The data was acquired, stored and analyzed with Turbochrome navigator Software attached with the system. pH meter (Thermo make), incubator, hot air oven, centrifuge (IEC model PR-2), rotary shaker (EMENVEE make), suction pump (Rotovac FP2F Model PRM3) , autoclave (P- 95 K, wates no. 191), electronic weighing machine (Schimadzu AX200), muffle furnace (Tempo make) and air compressor (ELGI make) were used in the experiments.

Chemicals

Standard odorant included MCB and solvents of analytical reagent grade were procured from Merck, India.

Media

The supplementaly media for the growth of microbial culture consisted of dipotassium hydrogen phosphate (K_2HPO_4, 0.625 g/L), potassium dihydrogen phosphate (KH_2PO_4, 0.375 g/L), ammonium sulphate [$(NH_4)_2SO_4$, 0.5 g/L]. Magnesium sulphate ($MgSO_4$, $7H_2O$) calcium chloride ($CaCl_2$), copper sulphate ($CuSO_4$,$5H_2O$) and ferrous sulphate ($FeSO_4$).

Bacterial culture

A culture seeded to the biofilter unit for bio-augmentation of deodorization of MCB was isolated using soil enrichment technique. It was later identified as *Acinetobacter calcoaceticus* based on morphological, biochemical, physiological and 16SRNA analysis using standard procedure.

2.2 Methods

All the medium (liquid and solid medium) was prepared as per Standard Method of Water and Wastewater Analysis (APHA, AWWA, WEF, 1990). MCB in the waste gas before and after treatment was analyzed by GC fitted with flame ionization detector (FID) and supelco equity 5 capilary columnhaving length 30 m, ID - 0.25 mm x 0.5 µm film thickness. The oven temperature was maintaned at 100^{o}C for one minute and then programme at the rate 25^{o}C per minute to 200^{o}C. The temperature of the injector and detector was kept at 250^{o}C and 300^{o}C respectivley with nitrogen as the carrier gas.

The waste gas containing MCB was generated usign odour generation unit and with appropriate dilution using air was introduced from the bottom of the biofilter. The nutrient medium along with grown culture of *Acinetobacter calcoaceticus* (10% w/v in 100 ml media) was sprinkled from the top of the biofilter to use as a seed and maintain proper moisture content in order to enhance the growth of microorganism in the compost. The operation of the biofilter resulted in the growth of microorganism and the removal of MCB from the waste gas. Continuous operation of the biofilter was carried out for evaluation of different parameters for degradation of MCB.

The biofilter was operated for more than 365 days on a bench scale on a continuous feed basis, and the parameters, viz. EBRT, MCB loadings at optimal EBRT, requirement of moisture content and pH of the packing medium were evaluated. The EBRT was varied by varying the flow rate of waste gas. The loading of MCB was varied by changing the input concentration of MCB in the waste gas at optimal EBRT. During assessment of the moisture content of the packing medium of the biofilter, the moisture content of the system was varied by manipulating the sprinkling of nutrient medium. All the experimental observations and assessment of the different parameters were made during pseudo steady state of performance of the biofilter.

3. Results and Discussion

3.1 Identification and evaluation of biokinetics of potential culture isolated from degradation of MCB

The molecular identification of the potential culture degrading MCB was carried out using 16SRNA technique. The homology of 16SRNA sequence was matched to NCBI library database through RDPE (FASTA). Depending on the percentage of matches and total mismatches, the strain was identified to be *Acinetobacter calcoaceticus*, which has over 98.417% homology with the 16SRNA of *Acinetobacter calcoaceticus* of NCBI library database. Several aerobic bacteria *Pseudomonas* sp., *Actinomycetes, Rhodococcus, Azotobacter* have been reported in the literature for degradation of MCB (Bhatt et al., 2007). The degradation of aromatic chloro compounds has been reported both in aerobic and anaerobic conditions, sequential use of these processes has an

advantage over using them individually for complete mineralization of chlorobenzenes and its derivatives. The microorganisms are present in both aerobic and anaerobic conditions in the biofilter, therefore, MCB can be mineralized to CO_2 and water.

3.2 Biokinetic constant for degradation of MCB using *Acinetobacter calcoaceticus*

The flask culture experiments using pure culture of *Acinetobacter calcoaceticus* for degradation of MCB was carried out at different concentrations. The value of μ was evaluated by adopting standard procedure and kinetic constants were evluated using modified Monord equaiton. The constants were found to be specific growth rate μ_{max} = 0.18/h, half saturation rate constant K_s = 12.8 mg/L MCB and inhibition constant 81.71 mg/L MCB (unpublished data part, Joshi, 2008).

3.3 Startup of the biofilter

The waste gas containing MCB at a concentration of 2 g/Nm^3 was passed through the biofilter for a period of 10 days. Initially, it was found that MCB was adsorbed to the compost and after 2 days of the operation, the concentration of MCB remained unchanged at the inlet and outlet of the biofilter (Figure 2). Therefore, the potential microorganism *Acinetobacter calcoaceticus* having capacity to biodegrade MCB was grown in the liquid medium and was inoculated in the biofilter. Further, the system was periodically inoculated with the culture biomass at intervals of 5 days for a period of 20 days. Thus, the packing medium of the biofilter got enriched with the microorganisms having potential to degrade the MCB within 45 days as was evident from the level of MCB in the inlet and outlet of the biofilter (Figure 2). This was further supported by the facts that there was an increase in the specific and total counts from 2x10^4 CFU/g to 20x10^4 CFU and 13x10^5 to 22x10^5 CFU/g respectively in the system.

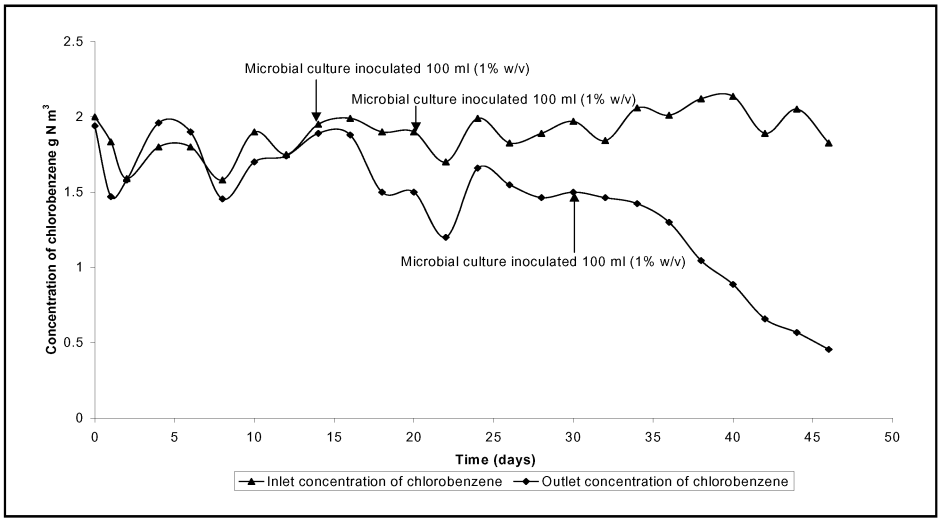

Figure 2: Startup of the biofilter for the deodorization of waste gas containing MCB

3.4 Assessment of EBRT

The waste gas containing a fixed concentration of MCB was introduced from the bottom of the biofilter at different flow rates ranging from 2 to 10 LPM. The performance of the biofilter at different values of EBRT is presented in Figure 3. An EBRT of 1.5 minutes was found to be optimal, resulting in 97% MCB removal efficiency. Generally, the EBRT reported for highly degradable substrates is maximum upto 30 seconds but, for moderate and low degradable substrates the reported EBRTs are as high as 2-3 minutes.

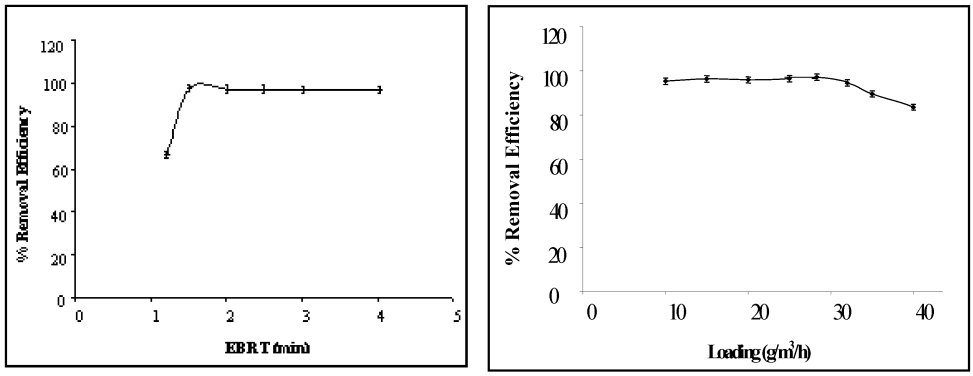

Figure 3 : Assessment of EBRT and loading for MCB biodegradation from waste gas

3.5 Assessment of loading

The MCB load to the biofilter was varied by changing the concentration of MCB in the inlet of the biofilter at a constant flow rate of the waste gas (EBRT of 1.5 min). The loading of MCB in the present investigation was varied in the range of 10 to 60 $g/m^3/h$ and the results of removal efficiency of MCB are presented in Figure 3. A loading of 28 $g/m^3/h$ of MCB exhibited more than 97% removal of MCB from the waste gas. The reported loading range in biofilters for low and moderately degradable odorants is generally in the range of 10-50 $g/m^3/h$.

3.6 Effect of moisture and pH

The system was operated at different moisture and pH content of the packing medium in the range of 50-70% and 5.5 to 9.0 (+0.2) respectively at the optimal EBRT and MCB loading of 28.28 $g/m^3/h$ MCB. The results are presented in Figure 4. The results indicate that the moisture content of 60-65 % of the packing medium is optimum while optimal pH of the system is in the range of 6.2-7.5 with a removal efficiency of 94-95%. The reported optimum moisture content of packing media is in the range of 45-55%. The observed optimum range of 60-65% for MCB in the present investigation may be attributed to lower solubility of MCB and the higher moisture content facilitates higher dissolution in to the packing media for subsequent degradation. Further, the use of compost along with wood chips in the biofilter is advantageous with respect to: easy

availability, inheret buffering capacity, nutrient contents and lower biomass yields for MCB ensure long term stable performance of the biofilter as observed through lower pressure drops. Thus, in the present investigation the pH variation in the packing media is observed to be minimum with insignificant drop of <0.5 pH unit.

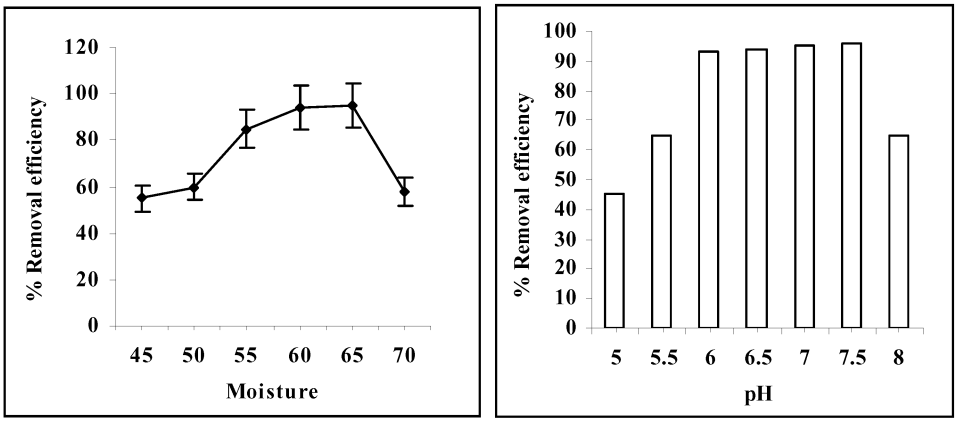

Figure 4: Effect of moisture and pH on deodorization of MCB

3.7 Fate of MCB in the biofilter

During biodegradation of MCB, the chlorine atom in the MCB ring is released as chloride ion. The chloride concentration is often monitored as a measure of MCB biodegradation. In the present investigation on bench scale biofilter for the treatment of MCB, the formation of chloride as byproducts was observed in the range of 50-600 mg/L as chloride ion in the leachate of the biofilter during the operational period.

3.8 Bacteriological status of the biofilter

The compost samples from different heights of the packing in the biofilter were collected during the assessment of different loadings for bacteriological analysis. At the optimal loading of MCB, the biofilter showed a total bacterial count of 111×10^5 CFU/g of compost, while the MCB- degrading bacterial count was 90×10^5 CFU/g of compost. The microbial status of the packing medium of the biofilter indicates that about 80% of the total microorganisms in the biofilter were MCB-degrading population.

Thus the MCB present in waste gas can be mineralized to CO_2 and water with the release of chloride ion in a appropriate biofilter condition. Bacteria metabolise MCB and its derivates to chlorocatechols in consecutive dioxygenase and diol dehydrogenase reactions. The results are comparable with the literature reports (Young and Richard, 1994; Mathur et al., 2006). However, these investigators have used consortium immobilized on porous support in a biotrickling filter. The present system is a conventional system packed with compost and wood chips seeded with *Acinetobacter*

calcoaceticus for bio-augmentation, which does not have similarity with trickling filter. The process parameters generated indicate that system can be used for deodorization of emissions containing MCB for commercial exploitation.

4. Conclusion

The assessment of different parameters showed that slightly higher EBRT of 1.5 minute was required for removal of MCB. Compost based biofilter could remove maximum loading of 28 g/m^3/h MCB at optimal EBRT of 1.5 min with a removal efficiency of 97%. At optimal condition moisture content and pH in the biofilter was found to be in the range of 60-65% and 6.2-7.7 respectivley.

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