TREATMENT OF BENZENE –TOLUENE MIXTURE IN A BIOFILTER USING A MIXED MICROBIAL CULTURE

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Abstract- Biofiltration of benzene-toluene gas mixtures was investigated in a biofilter operated in an up-flow mode using mixed microbial cultures immobilized in a novel filter medium. The effect of inlet load of benzene-toluene mixtures on the biodegradation performance of the biofilter was studied. The maximum elimination capacities of 162.08 g/m^{3}h for benzene and 110.09 g/m^{3}h for toluene were obtained at a total inlet loading of 611.62 g/m^{3}h.Inhibition of toluene degradation by the presence of benzene was observed in this study. The relationship between elimination capacity and inlet loading rate was studied. The carbon dioxide gas production rate was recorded and related to elimination capacity. Temperature variations during the biofiltration experiments were monitored. Axial variation of pollutant concentration in the biofilter bed was studied and the lowest part of the biofilter column was found to remove approximately 40 % of the total removal which was due to enhanced biomass density.

Keywords- Biofiltration, Removal Effeciency, Elimination Capacity, Volatile Organics.

I. INTRODUCTION

Different air pollutants which deteriorate the atmospheric air quality are released from various sources that are industrial production units, waste treatment facilities and biogenic origins. Exposure to excess concentrations poses dangerous effects to human health in addition to environmental impacts like global warming. Air pollution control of these contaminants has become inevitable in order to ensure a safe environment for living[1]. Several physico-chemical methods like condensation, absorption, cryo condensation and membrane separation have been used for the treatment of polluted air. The choice a depollution method depends on the operating conditions like pollutant concentration, stream flow rate, temperature and humidity. Most of these above mentioned methods suffer from demerits like lower conversions, secondary pollutant generation, high cost and poor selectivity [2].Biological methods have proved to be an alternative for the treatment of volatile organic compounds and the most popular and oldest bioreactor configuration is the biofilter. Biofilters have been reported to be more suitable for handling a wide range of gas flow rates with a concentration span of 0 -10 g/m^3 [3]-[4].Benzene and Toluene are volatile hydrocarbons present in gasoline and are reported to be two common air pollutants released into the environment from refineries , oil wells and storage vessels [5].Many studies on biological treatment of single air pollutants like ethyl benzene [6],toluene [7] ,xylene [8] and styrene [9] have been investigated. Studies on mixtures of volatile organics, namely Benzene, Toluene Ethylbenzene and Xylene (BTEX) as a whole or any combination of the member components are comparatively less and needs more attention as the possibility of the co-existence of two pollutants are high in an industrial environment. In this back ground, the present study is aimed to degrade the benzene –toluene mixture in a biofilter operated in an upflow media with a novel biofilter media. The effect of process variables like influent gas concentration and flow rate on the removal performance of the biofilter is studied. The axial variation in removal efficiency was monitored to understand the role of biofilter height on the removal patterns. Temperature variations were recorded to observe the nature of biochemical reactions.

II. MATERIALS AND METHODS

A. Biofilter Set Up and Operation

The biofilter unit consists of a column with a height of 100 cm and an inside diameter of 5 cm and made of acrylic polymer. Four sampling points were provided at at 0 cm (inlet), 25 cm (section-1), 50 cm (section-2), 75 cm (section-3) and 100 cm (exit), for treated gas sampling and another set of ports for temperature measurements along the height of the biofilter. The nutrient media was added at periodic intervals through a nutrient distribution system at the top. Treated gas was collected at the reactor headspace and a 10 cm bottom space was utilized for leachate collection. Fig. 1 shows the biofilter reactor unit with its components. A carbon dioxide gas sensor (Extox, Germany) was connected at the exit to determine the quantity of gas produced. The influent air stream was generated by injecting a compressed air stream into the storage vessel containing the respective volatile organic compound. In this study, the air is bubbled successively through two tanks filled with benzene and toluene respectively. The air stream loaded with benzene and toluene was adjusted for its concentration by mixing with the humidified pure air stream in the mixing chamber and fed into the biofilter reactor in an

upflow direction. The operating parameters are varied in the ranges: inlet benzene concentration-1.5 to 6.0 g/m^3 and inlet toluene concentration - 1.5 to 6.0 g/m^3 and flow rate 0.25 – 1.0 m^3/h and the samples were collected at periodic intervals for analysis for residual volatile organic compounds. The nutrient solution, Basal salts medium, used has the following composition: K_2HPO_4 – 0.91 g; $Na_2HPO_4.2H_2O$ -2.39 g; $(NH_4)_2SO_4$ – 1.97 g; $FeSO_4$. $2H_2O$ – 0.2 g; $MgSO_4.7H_2O$ – 2.0 g; $MnSO_4$. 7 H_2O – 0.88 g; Na_2MoO_4. 2 H_2O – 1.0 mg; $CaCl_2$– 3.0 mg; $ZnSO_4$. $7H_2O$ – 0.04 g and $CoCl_2.6H_2O$ -0.04 mg per Litre of water .The biofilter media used in this study was date palm tree barks.

B. Estimation of Concentration And Biofilter Parameters

The benzene and toluene concentrations in gas samples were measured by gas chromatograph (Perkin Elmer, USA) equipped with a FID and a capillary column. The temperature conditions were 160°C for injector and 280°C for detector .The oven temperature was set at 60°C for the first 5 min and increased at a rate of 15°C per minute to reach 180 °C and held at 4 min. Helium was used as a carrier gas at a flow rate of 2 ml/min. The temperature of the filter bed was measured using temperature sensors connected to a data logger. The removal effect of the biofilter was measured in terms of the removal efficiency (% RE), elimination capacity (EC), g/m^{3}h,and carbon dioxide production rate (CPR), g/m^{3}h. These parameters are defined as given below:

$$\%RE = \frac{S_0 - S_t}{S_0} \times 100 \quad (1)$$

$$EC = \frac{Q(S_0 - S_t)}{V} \quad (2)$$

$$CPR = \frac{Q(C_{CO_2 out} - C_{CO_2,in})}{V} \quad (3)$$

The Empty Bed Residence Time (EBRT) is defined as

$$EBRT = \frac{V}{Q}(h) \quad (4)$$

The Inlet Loading Rate (ILR), g/m^{3}h, is defined as

$$ILR = \frac{Q(S_0)}{V} \quad (5)$$

Where S_0 and S_t represent the inlet and exit concentrations of benzene or toluene or total (g/m^3), Q is the flow rate of the benzeneor toluene (m^3/h), V is the volume of the biofilter (m^3) ,$C_{CO_2 out}$ and $C_{CO_2,in}$ represent exit and inlet concentrations of carbon dioxide (g/m^3).

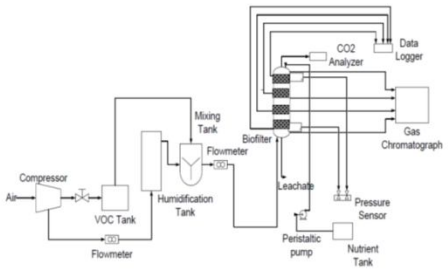


Fig. 1 Bioreactor set up with its components

III. RESULTS AND DISCUSSION

A. Biofilter performance for the treatment of benzene-toluene mixture

Design and hydrodynamics of biofilter reactor depends on two important process variables, namely, inlet concentration and Empty Bed Residence Time (EBRT). The biofilter was operated for a period of 64 days during which the inlet concentrations of benzene and toluene were changed along with EBRT (or flow rates). During the first stage of experimentation, the individual inlet concentrations of benzene and toluene were maintained at 1.5 g/m^3 corresponding to a total inlet loading of 38.23 g/m^3 h. In order to acclimate the microbial culture gradually, the start up residence times were maintained at 283 s and the removal performance was studied for 4 days till it attain equilibrium efficiency. The removal efficiency achieved varied from 78% from day 1 to 89% in day 4. The attainment of higher removal efficiency was attributed to a well-established biomass inside the biofilter column. In the case of the second pollutant in the mixture, toluene, the removal efficiencies achieved were comparatively lesser than the benzene with 68% in day -1 and increased to 79% in day-4.The reasons attributed for this behaviour were the inhibitive interaction effect of benzene and the complex structure of toluene which made the biodegradation difficult. Also, VOC hydrophobicity could play an important role in removal pattern [10].The total elimination capacity, which represents the treatment capacity of the biofilter, achieved was in the range of 27.9- 32.1 g/m^3 h. The inlet loading to the reactor was increased gradually by varying the flow rate and keeping the inlet concentration constant. The flow rate was increased to 0.05m^3/h with an EBRT of 142 s and the removal performance was assessed in the inlet loading rate of 76.45 g/m^{3}h.

Benzene removal efficiency achieved was in the range of 88 -93 % while toluene removal efficiency was in the range of 68 -74%.The elimination capacity obtained was in the range of 26 – 28 g/m^3 h. During the stage 3 of the experimental period, the inlet loading rate was increased to 114.68 and the removal efficiencies were found to decrease compared to the earlier phase. The total elimination capacities achieved during day 9 -12 were in the range of 76 – 82.5 g/m^3 h. During the next stage of operation, the maximum inlet loading of 152.91 g/m^3 h was imposed on the biofilter and the system responded to yield lower removal percentages for benzene in the range of 67 -71% while toluene efficiency dropped to 57 -61 %.The decreased removal efficiencies at higher flow rates was due to the availability of limited exposure time of pollutants to biofilm. The pollutant is expected to diffuse the microbial film from the bulk of gas phase and contact time is reported as an essential parameter for achieving better biochemical conversions. Biofiltration studies on xylene removal in a bagasse based biofilter employing mixed microbial culture reported a similar

observation [8].The effect of varying concentration of the benzene and toluene iin the gas mixture was studied to verify the withstanding ability of the biofilter to be operated under higher pollutant loading. The inlet concentration of benzene and toluene were increased to 3.0 g/m^3 and the experiments were repeated in a similar pattern to phase 1.The flow rates were increased gradually to obtain an inlet loading rate of 76 – 306 g/m^{3}h. The removal efficiencies obtained were found to vary from 55 -80 % for benzene and 45 – 65 % for toluene. In common with the previous experiments, the lower flow rates always resulted in good removal performances. To identify the threshold capacity of bioreactor, higher inlet concentrations of benzene and toluene at 4.5 and 6.0 g/m^3 were employed and the elimination capacities were recorded. Fig. 1 presents the pollutant removal efficiency observed during the entire experimental phase. Also, the exit concentrations of benzene and toluene are plotted against time. The biofilter performance dropped significantly at higher inlet pollutant loadings and toluene proved more resistant compared to benzene with attainment of lower removal efficiencies.

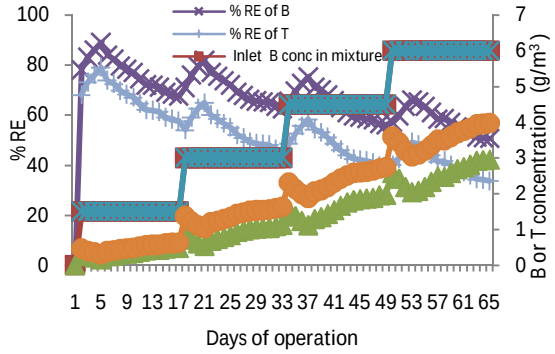


Fig.2 Removal performance of date palm tree bark based biofilter for the treatment of benzene-toluene mixture

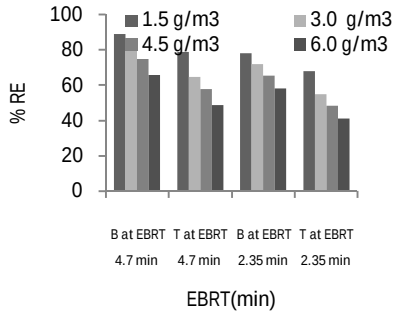


Fig. 3 Effect of initial VOC concentration on the removal efficiency at different EBRT

B. Relationship between Elimination capacity and inlet loading rate

The inlet loading rate which represents the pollutant loading on the biofilter per unit time on is required to be studied for its effect on the removal efficiency of the biofilter. The total inlet loading rate is calculated by summing up the individual loading rates of benzene and toluene and plotted against the total elimination capacity which represents the combined elimination capacities of the two compounds, benzene and toluene. Fig. 4 shows the relation between total inlet loading rate and total elimination capacity. Two different regions, namely a nearly linear first region followed by non-linear second region were observed to exist in the Fig.4. The elimination capacity was found to vary in a linear pattern upto a threshold elimination capacity of 500 g/ m3h and there was a shift in variation pattern at higher inlet loadings. The correlation coefficient value was found to be sufficiently high to prove the linearity in relationship and the following equation represented the relationship between total inlet loading rate and elimination capacity.

$$EC=0.5016\ (ILR) \qquad (6)$$

Biofiltration studies on removal of BTEX mixtures in a thermophilic biofilter reported similar relation between elimination capacity and loading rate [11].

C. Effect of biofilter height

Axial variations in the pollutant concentration were recorded in order to identify the role of biofilter height on the removal performance of biofilter. The biofilter employed in this study had four different sections and the concentrations were found from the samples collected at the tail end of each section through sampling ports located at 25, 50, 75 and 100 cm respectively. The removal efficiency of each section was plotted in terms of normalized concentration ratio (C/C_0) against inlet concentration of the volatile organic compounds. Fig. 5 and 6 shows the variation in removal efficiency section-wise at different inlet concentrations ranging from 1.5- 6.0 g/m3for benzene and toluene respectively. From the Fig.5 and 6, we observed that nearly 40% of the removal was achieved at section-1, the lowest part of the biofilter. The second section contributed roughly to 20% of the efficiency and the average removal efficiencies observed at section-3 and 4 towards the top of the column were in the range of 10 - 14%. Better biomass distribution and higher concentration gradients were found to be the reason for the higher contribution of lower section of the biofilter. The change in temperature during biofiltration experiments could lead to dryness of the bed and could hinder the microbial activity at the upper sections of the biofilter. Similar effects of inlet loading rate on elimination capacity were reported on biodegradation studies on BTEX using a fungal biofilter [12].

D. Temperature variations study

Biochemical reactions are always accompanied by heat release and are exothermic in common. In this biofiltration study, temperatures were recorded during the entire study period and the average bed temperatures were plotted against time .Fig. 7 depicts the variation in temperature at different stages of reactor operation and compared with the changes in

elimination capacity. It was observed that the changes in elimination capacity had a similar impact on temperature resulting in higher temperatures at higher elimination capacities. This fact proved the occurrence of biodegradation of benzene and toluene through biochemical conversion by mixed microbial culture present in the biofilter media. Temperature variations are within the range of 0 – 4 °C during the experiments confirming the exothermic nature of this biochemical destruction.

E. Gas production profile

The possible end products of bio conversion of benzene and toluene are as given carbon di oxide, water vapor and new biomass when some of the organic compounds are consumed by the preexisting microbial culture.

The variation of carbon di oxide production (CPR) was related to the changes in elimination capacity during the biofiltration experiments and a plot was made as shown in Fig. 8.The relationship between carbon dioxide production rate and elimination capacity was found to be directly proportional and the maximum gas production rate was observed as 884.6 g/m^{3}h observed at an elimination capacity of 310.4 g/m3h. The experimental data showed a proportional increase (or decrease) in gas production when the elimination capacity changed in similar pattern. The carbon di oxide mineralization ratio was found to be 2.97 which is lesser than the theoretical value. The theoretical conversion is possible only when all the reactants are completely converted to carbon dioxide with no other carbon compound.

The intercept value of 11.529 g/m3h represents the carbon dioxide gas produced due to endogenous respiration of microbes in the biofilter even when there is no conversion of volatile organic compounds. The differences between the theoretical and actual carbon dioxide production rates were reported to occur at higher loading rates [13].Also, there is a possibility of some of the carbon dioxide formed to be accumulated in the liquid phase as H_2CO_3,HCO^{3-} and CO_3^{2-}[8].

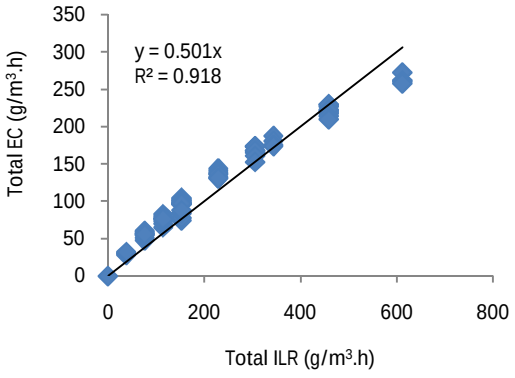


Fig. 4 Effect of Total Inlet loading rate on the Total Elimination capacity of the biofilter

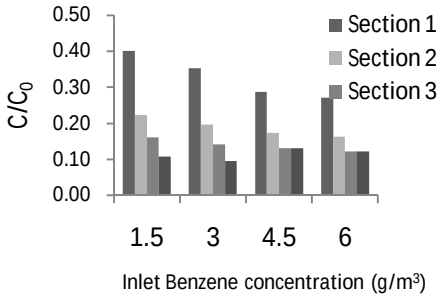


Fig. 5 Effect of biofilter height on the removal efficiency of benzene

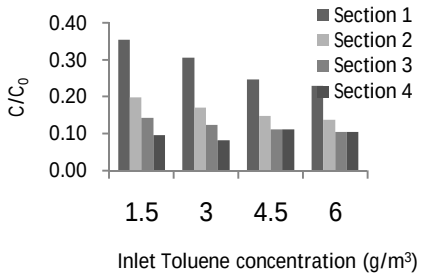


Fig. 6 Effect of biofilter height on the removal efficiency of toluene

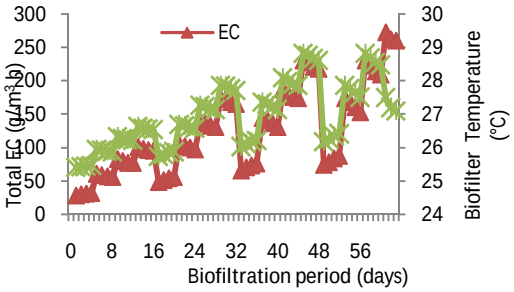


Fig. 7 Temperature profile during the biofiltration experiments

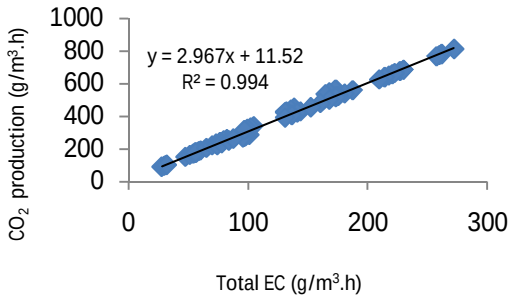


Fig. 8 Carbon dioxide production and the relationship with total elimination capacity

CONCLUSION

Biodegradation of benzene-toluene gas mixtures was successfully demonstrated in an up flow biofilter operated at different loading rates. Higher removal efficiencies were achieved at low flow rates and inlet loading rates. With increase in loading rates couple with decrease in EBRT, the performance of the biofilter reduced. The threshold total loading rate was identified as 76.45 g/m^{3}h in order to achieve individual benzene and toluene removal efficiencies

greater than 80 %.The effect of inlet loading on elimination capacity was found to be nearly linear for most of the operating range. Effect of biofilter height proved better removal efficiencies at the lower sections compared to the upper sections of the biofilter. Temperature profile was recorded and the carbon dioxide conversion ratio was determined.

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