Biodegradation of Benzene, Ethylbenzene, and Xylene Mixture in a Date Palm Tree Bark-based Upflow Biofilter

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The performance of a date palm tree bark-based biofilter inoculated with mixed microbial consortia was investigated for the removal of a benzene-ethylbenzene-xylene mixture at a total inlet loading rate range of 38.0 to 612.0 g/m^3·h. The influences of the inlet pollutant concentration and air flow rate were studied. The maximum elimination capacities attained for benzene, ethylbenzene, and toluene were 79.51, 77.47, and 57.08 g/m^3·h, respectively. The removal efficiencies were evaluated and found to vary inversely with the inlet pollutant concentration. The VOC conversions were demonstrated by the difference in inlet and exit concentrations. The axial removal performance of the biofilter was studied, and the contribution of the lowest part was comparatively more than those of the upper sections because of the different biomass growth patterns. Temperature monitoring in the biofilter confirmed the exothermic nature of the biodegradation.

Keywords: Benzene; Elimination; Date palm tree; Removal efficiency

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INTRODUCTION

Increased industrial activity and the requirement for greater fuel production have significantly contributed to the deterioration of air quality. Pollution control boards and environmental legislation are stringent in enforcing regulatory norms to reduce or control the release of harmful air pollutants. Benzene, ethylbenzene, and toluene are common volatile organic compounds (VOCs) used in the petroleum refining, petrochemical, pharmaceutical industries, and others; these tend to be released into the atmosphere, depleting the ozone layer and causing global warming (Mathur *et al*. 2006; Rajamohan *et al*. 2015a; Rene *et al*. 2015). Improper handling and leakage during storage and transportation within industrial premises also contribute to VOC pollution (Chang *et al*. 2015).

The potential for the removal of individual compounds, or a mixture, using physicochemical and biological methods has been investigated throughout the last few decades. High energy consumption, maintenance costs, and operating costs discourage the use of physicochemical methods (Kennes *et al*. 2009; Mudliar *et al*. 2010). Biological methods of air pollution control have gained importance because of their simple design and ease of operation (Lucero *et al*. 2014). In addition, biological methods do not require excessive chemicals and generate lower quantities of secondary wastes (Alfonsin *et al*. 2015). This method has advantages, such as the use of one or more of the following reactor configurations for the degradation of the target compound: biofilter, bio-trickling filter, bio scrubber, and membrane bioreactor. Biofiltration is a process in which the air contaminated with a VOC is circulated through a packed column with an immobilized microbial culture on its inert filter media. The presence of a highly active biofilm is considered the main factor contributing to the removal performance of any bioreactor (Priya and Ligy 2015). The microbial culture, pure or mixed, is responsible for mineralizing the VOC into carbon dioxide, water vapor, and new biomass (Lucero *et al*. 2014; Rajamohan *et al*. 2015a). Biofilters offer a wide range of biofilter media choices, from naturally available biomass to industrial waste products (Saravanan and Rajamohan 2009; Eldon *et al*. 2012).

The performance of biofilters has been found to be influenced by the effectiveness of biofilm formation inside the column. Recent studies have reported that bacterial biomass is much more effective than fungal biomass at degrading VOCs (Estrada *et al*. 2013). Biofiltration experiments on pure benzene and toluene in a compost biofilter (Rene *et al*. 2005; Rene *et al.* 2009; Saravanan *et al.* 2013), xylene in a press mud-based biofilter (Saravanan and Rajamohan 2009), ethylbenzene in nutshell biofilter (Volckaert *et al*. 2013), and in a date palm tree bark-based biofilter (Rajamohan *et al.* 2015b) have been successfully conducted. However, few studies on the treatment of VOC mixtures have been conducted. The bacterial and fungal biofiltration of propanal, methyl isobutyl ketone, toluene, and hexanol have been studied, and their mineralization ratios were found to be in the range of 43% to 63%, respectively (Estrade *et al*. 2013). Biofiltration of a mixture of ethylene, ammonia, n-butanol, and acetone gases in a bio-trickling filter using perlite and polyurethane foam as packing media was investigated (Lee *et al*. 2013). There has been no specific study on the removal of a benzene-ethylbenzene-xylene mixture using a biofilter, and no interaction effects between these three compounds have been investigated.

The main objectives of this study were to investigate the biofiltration performance of a date palm tree bark-based biofilter in the removal of the mentioned benzene-ethylbenzene-xylene mixture and to study the effect of operating variables, namely the inlet VOC concentration and the air flow rate. In addition, the effect of the biofilter height was observed and the temperature was monitored.

EXPERIMENTAL

Biofilter

This experimental study utilized a biofilter column constructed using acrylic. It was operated in an upflow mode with influent air entering in the bottom. The configuration of the date palm tree bark-based biofilter used in this study was the same as described in previously published works (Rajamohan *et al*. 2015a,b). The density of the date palm tree bark was determined as 0.44 g/ mL, which is comparable with other biofilter media employed. The moisture content inside the biofilter column is essential for better microbial activity and is partly influenced by the water holding capacity of the filter media. The water-holding capacity of the tree barks was found to be 30% (w/w %), and the maintenance of moisture content was partially achieved through periodic addition of nutrient media (Rajamohan *et al.* 2015c).

The biofilter reactor had a height-to-diameter (H:D) ratio of 20:1, column diameter of 5 cm, and height of 100 cm. Collection of the treated gas was performed within the 10-cm headspace, and nutrient feed addition and a 10-cm bottom space for leachate collection were provided. A schematic of the experimental setup is shown in Fig. 1. The column consisted of four individual modules, each 25 cm in height and able to be dismantled for maintenance whenever required. The packing media were loaded in the column section-wise, and a perforated plate, permitting only air flow, was present at the bottom of the each section. In order to collect gas samples and monitor various parameters, two sampling ports at the tail end of each section, from the direction of the flow of air, were provided. The nutrient media, which were autoclaved at 120 °C for 20 min, were added at periodic intervals to the top of the column using a nutrient distribution system, which utilized a peristaltic pump to pump the nutrient solution from the storage tank. The benzene-ethylbenzene-xylene (B-EB-X) stream was generated using compressed air.

The air stream was divided into two streams, denoted the primary and secondary streams. The primary air stream was passed into the storage tanks containing the benzene (99% purity), ethyl benzene (99% purity), and xylene (99% purity) and then passed through the humidifier to maintain sufficient relative humidity. The primary air stream loaded with VOC was mixed with the secondary air stream in the mixing chamber to attain the desired VOC concentration and fed into the biofilter reactor in an upflow mode. Gas sampling was done at the reactor inlet, outlet, and sampling ports located at heights of 25, 50, and 75 cm in the respective tail ends of the individual sections.

The biofilter start-up and acclimatization was performed as explained below. The biofilter employed for the treatment of ethylbenzene-xylene mixtures was fed with an equal proportion of benzene at a low flow rate of 0.025 m^3/h. The benzene concentration was in the range of 0 to 2 g/m^3. The biofilter required 10 d for acclimatization and reached steady state removal efficiency after preliminary fluctuations. This phenomenon confirmed the development of a VOC-resistant biofilm in the column. In the first phase of experiments, the inlet VOC concentrations were maintained at 1.0 g/m^3, individually, for benzene, ethylbenzene, and xylene. The inlet loading rates were calculated and summed to determine the total inlet loading rate. The experimentation period was 24 d, and the flow rates were studied in the range of 0.025 to 0.10 m^3/h.

In the second phase of experimentation, the inlet concentrations were increased to 2.0 g/m^3 benzene, ethylbenzene, and xylene, and the flow rates were tested identically to in the first phase. The third and fourth phases followed the same procedures but the individual VOC concentrations were 3.0 and 4.0 g/m^3, respectively.

The performance of the biofilter was investigated in terms of the removal efficiency (% RE) and elimination capacity (EC) in g/m^3·h (Devinny *et al.* 1999). These parameters are defined as,

$$\%RE = \frac{C_0 - C_t}{C_0} \, x \, 100 \tag{1}$$

$$EC = \frac{Q(C_0 - C_t)}{V} \tag{2}$$

where C_0 and C_t represent the exit and inlet concentrations of the individual VOC, benzene, ethyl benzene, or xylene, respectively (g/m^3); Q is the flow rate of the benzene, ethyl benzene, or xylene (m^3/h); and V is the volume of the biofilter (m^3). In addition, two total parameters, the total elimination capacity and the inlet loading rate, were estimated by adding the individual values of the components chosen and utilized in the studies to describe the overall removal performance of the biofilter.

The empty bed residence time (EBRT) is defined as,

$$EBRT = \frac{V}{Q} \, (\mathrm{h}) \tag{3}$$

The inlet loading rate (ILR) is defined as,

$$ILR = \frac{QC_0}{V}\ (\frac{\mathrm{g}}{\mathrm{m^3 h}}) \tag{4}$$

Microbial Culture and Filter Media

Mixed microbial cultures collected from the activated sludge system of the municipal waste water treatment plant were used to inoculate the biofilter column. Date palm tree barks, produced from the tree *Phoenix dactylifera* commonly found in the Arabian gulf, was utilized as the biofilter media. The inoculum was cultured in an aerated batch reactor and diluted as explained in another work (Saravanan and Rajamohan 2009).

Analytical Methods

Air samples were collected at periodic intervals for analysis for residual benzene, ethylbenzene, and xylene contents. The residual VOC concentration in the gas samples was measured using a gas chromatograph (Perkin Elmer, USA) equipped with a FID and a capillary column. The temperatures at the GC injector, oven, and detector were prescribed as stated in previous works (Saravanan and Rajamohan 2009; Rajamohan *et al*. 2015b), and high-purity helium (99%) was used as the carrier gas at a fixed flow rate.

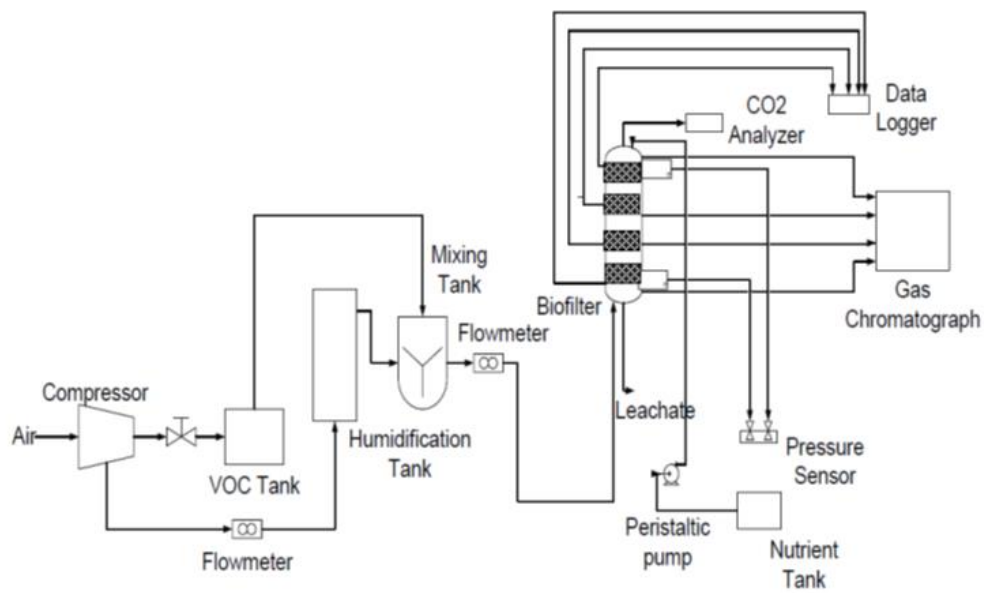

Fig. 1. Biofilter reactor and its components

RESULTS AND DISCUSSION

Biofiltration Studies at Various Inlet Mixture Concentrations and EBRTs

The performance of the biofilter was assessed in terms of the removal efficiency and the individual removal efficiencies. The inlet and exit VOC concentrations are presented in Figs. 2, 3, and 4 for benzene, ethylbenzene, and xylene, respectively.

Figure 2 shows the removal performance of benzene at fixed inlet concentrations of 1.0 g/m^3 for each of the VOCs at different flow rates as explained. The inlet loading rate applied during the first phase was in the range of 12 to 22.5 g/m^3 h. The equilibrium removal efficiency of benzene decreased from 95% to 74% when the flow rate was increased from 0.025 to 0.10 m^3/h. The benzene removal efficiency as analyzed over the entire 96-d period confirmed that the removal efficiency decreased with increased inlet concentration. The maximum removal efficiencies obtained at inlet benzene concentrations of 1.0, 2.0, 3.0, and 4.0 g/m^3 were 69%, 77%, 86%, and 95%, respectively, at the lowest operating air flow rates.

Figure 3 shows the removal performance of the biofilter with respect to ethyl benzene. The exit ethyl benzene concentrations were low at the lowest air flow rate, 0.025 m^3/h, and increased at higher flow rates. Correspondingly, the removal efficiency decreased at higher flow rates. The maximum ethylbenzene removal efficiency attained was 85% when the inlet VOC concentration was 1.0 g/m^3. The minimum was 56% at 4.0 g/m^3 inlet concentration.

Figure 4 shows the experimental removal efficiency and exit concentration of xylene observed over the concentration range of 1.0 to 4.0 g/m^3 at the flow rates used in the previous experiments. The removal efficiency of xylene was high at low flow rates and inlet concentrations, with a maximum value of 75% at an inlet xylene concentration of 1.0 g/m^3 and flow rate of 0.025 $g/m^3 \cdot h$. The efficiency decreased to 49% when the inlet concentration was increased to 4.0 g/m^3.

During all experiments, the efficiency was inversely related to both the inlet concentration and the air flow rate. This phenomenon could be possibly explained by the threshold concentration concept applicable to all microbial species (Rene *et al.* 2015). The mixed microbial culture has limited tolerance to increases in the inlet loading rate. The requirement of low flow rates justifies the need for more contact time between the VOC substrate and the biofilm to achieve better mass transfer. Moreover, the removal efficiency observed in this study, involving the treatment of mixtures, was comparatively lower than the pure component removal efficiencies reported elsewhere (Rajamohan *et al.* 2005a; Saravanan and Rajamohan 2009; Eldon *et al.* 2010). This could be because of the interaction effects in the substrate utilized by the mixed culture. Similar observations were reported in biofiltration studies on benzene, toluene, xylene, and methyl tert-butyl ether mixtures (Hwashim *et al.* 2006) and a benzene-toluene mixture (Eldon *et al.* 2015).

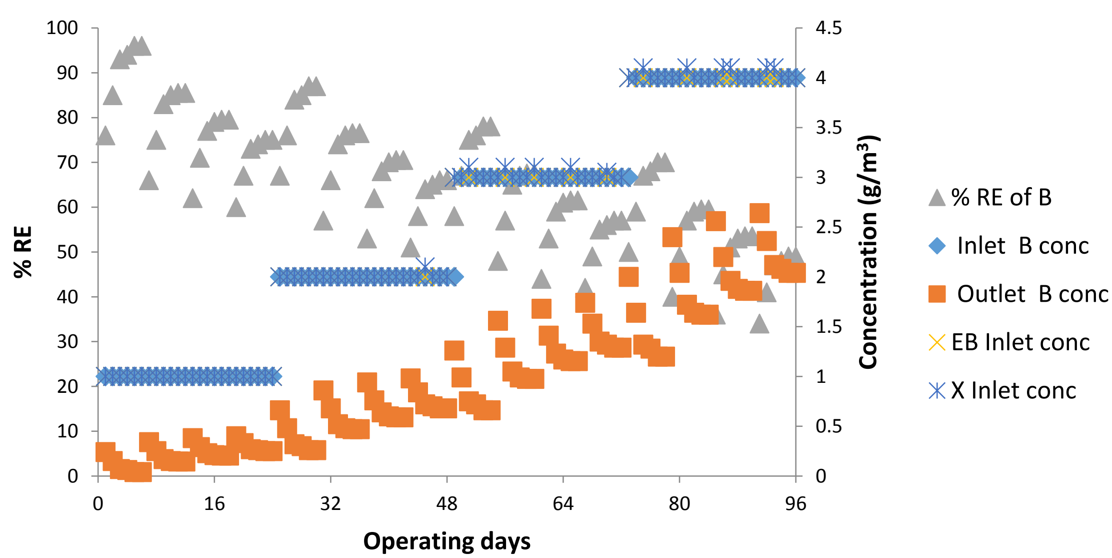

Fig. 2. Biofiltration performance for benzene removal from benzene-ethylbenzene-xylene mixture

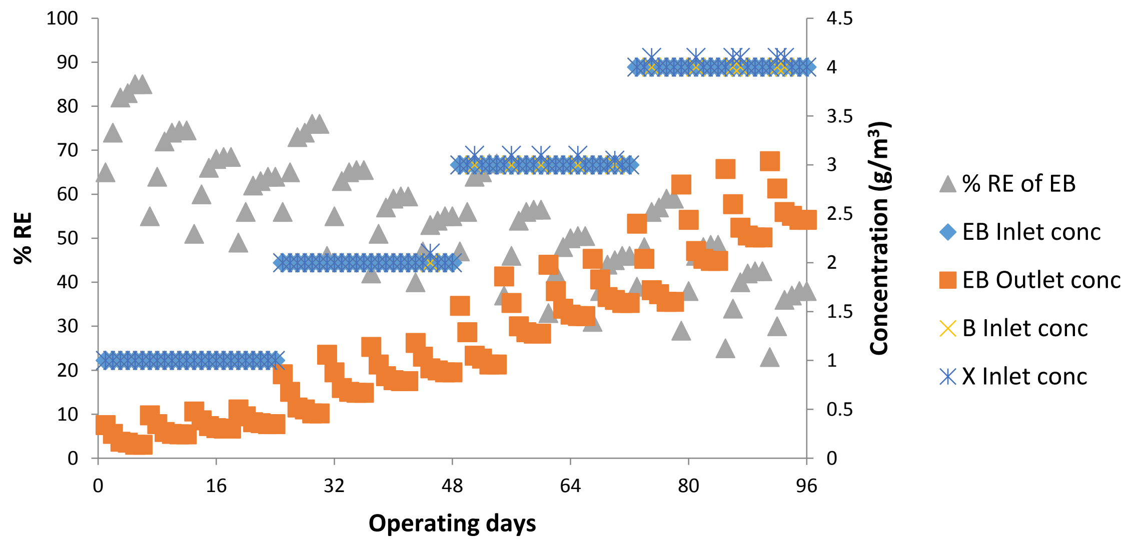

Fig. 3. Biofiltration performance for ethylbenzene removal from benzene-ethylbenzene-xylene mixture

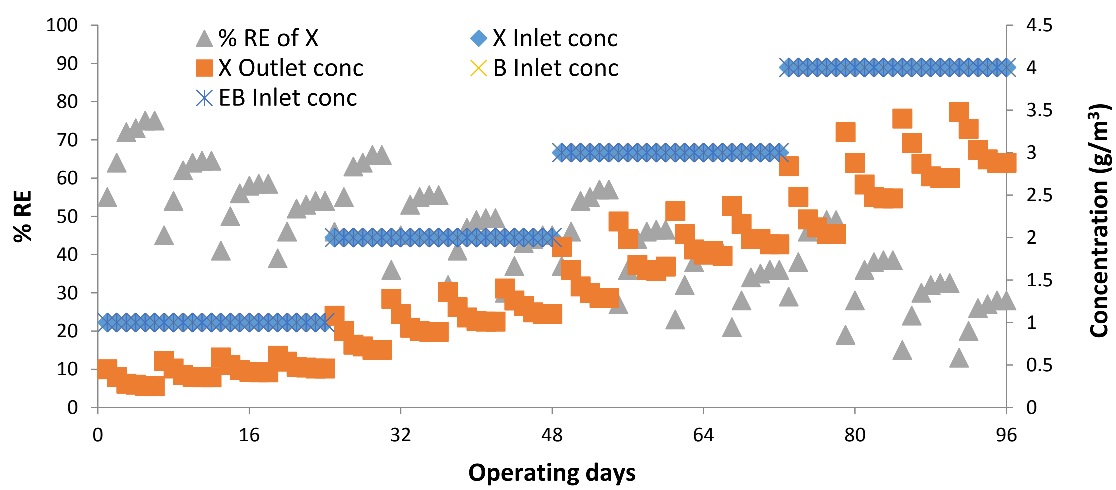

Fig. 4. Biofiltration performance for xylene removal from benzene-ethylbenzene-xylene mixture

Effect of Inlet Loading on Elimination Capacity

One of the vital input parameters representing the interactive effect between the inlet concentration and the flow rate on the biofiltration performance is the inlet loading rate. In this experimental study, the individual inlet loading rates tested were in the range of 12.0 to 51.0, 25.0 to 102.0, 38.0 to 152.0, and 50.0 to 204.0 g/m^3·h during experimental phases I, II, III, and IV, respectively. The total inlet loading rate was determined from the individual VOC loading rates and plotted against the total elimination capacity in Fig. 5. The maximum total elimination capacity obtained was 214.1 g/m^3·h at a total inlet loading rate of 611.6 g/m^3·h. The high load-withstanding capacity of the biofilter and the VOC tolerance of the mixed microbial biofilm were demonstrated by these results. Biofiltration studies on xylene-, ethylbenzene-, and benzene-toluene mixtures found similar relationships between the inlet loading rate and the elimination capacity (Saravanan and Rajamohan 2009; Rajamohan *et al.* 2015; Rene *et al.* 2015).

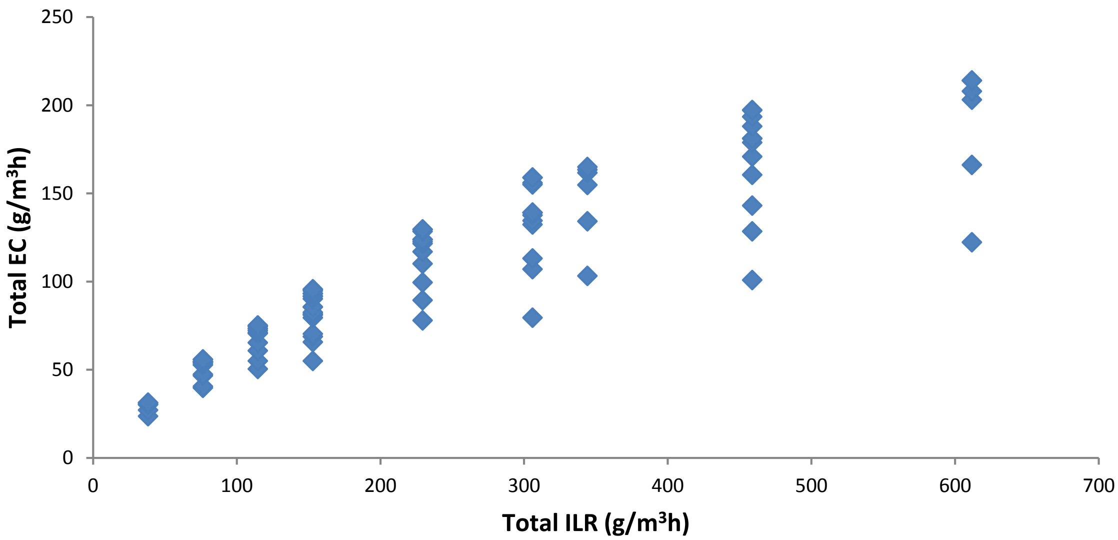

Fig. 5. Effect of inlet loading rate on the combined elimination capacity

Effect of Biofilter Height

Biofiltration performance was assessed axially, and the concentration profile of the VOC was determined by sampling at the tail ends of each section of the biofilter column. The removal efficiencies were estimated section-wise and are plotted in Fig. 6 at chosen VOC concentrations of 1.0 and 2.0 g/m^3 at the maximum removal flow rate conditions.

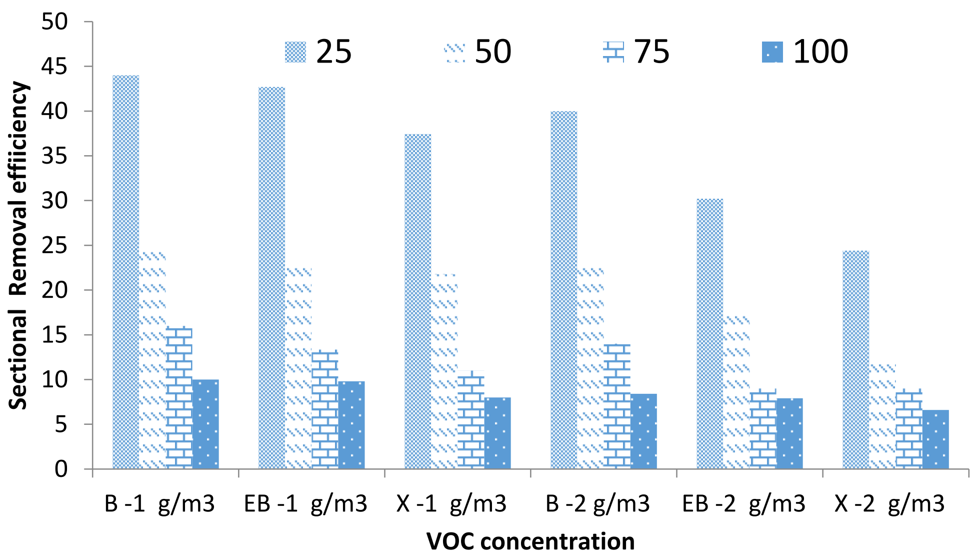

Fig. 6. Effect of the height of the biofilter on the sectional removal efficiency

It was observed that the lowest part of the biofilter was responsible for nearly 40% of the total removal efficiency and that the efficiencies of the other sections decreased along the height of the reactor. The removal contribution of second section was found to be in the range of 10% to 14% of the total efficiency. The contribution of the top-most section was the least of all of the sections. This variation in removal efficiency could be attributed to the localized substrate concentration gradient existing throughout each section. In addition, nutrient limitation and temperature variations during biofiltration could have contributed. Biofiltration studies on ethylbenzene degradation in a mesophilic biofilter (Volckaert *et al.* 2015) and mixtures of ethylene, ammonia, n-butanol, and acetone gases (Lee *et al.* 2013) reported identical removal profiles along the biofilter height. Higher contributions of the lowest section of the biofilter were also reported in xylene removal using a biofilter employing a mixed culture (Saravanan and Rajamohan 2009).

Temperature Profile

Biofiltration experiments involve microbial degradation reactions that lead to the reductive cleavage of VOCs and form carbon dioxide and water vapor as the end products. The extent of the biochemical reaction could be determined by observing the temperature variations during the experimental stages. Temperature monitoring was performed, and the average bed temperature was plotted against time for different elimination capacities, as shown in Fig. 7. Temperature variations followed a similar pattern to the elimination capacities. Increases in the observed temperatures confirmed the exothermic nature of the biodegradation reaction occurring in the biofilter. The temperature range observed was between 25.1 and 30.2 °C. The biofilter attained consistent removal efficiencies and was found to be stable during the entire test period; the mixed microbial consortia withstood the variations in temperature. Increases in temperature improve the rate of diffusion, facilitating better mass transfer.

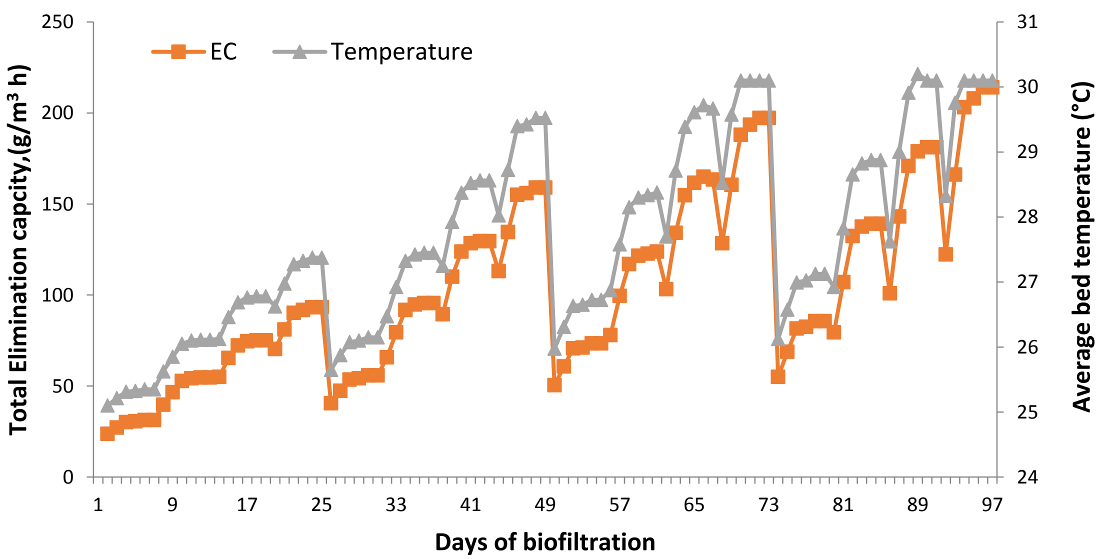

Fig. 7. Elimination capacity *versus* bed temperature during biofiltration

The biodegradation of ethylbenzene-xylene-polluted air was investigated in a date palm tree bark-based biofilter employing a mixed microbial culture. The removal efficiency of the bioreactor was studied over 13 weeks at different loading rates, and the maximum total elimination capacity, 148.8 $g/m^3 \cdot h$, was achieved at a total inlet loading rate of 407.7 $g/m^3 \cdot h$. Ethylbenzene was degraded better than xylene, with removal efficiencies of 89% and 78% for toluene at an inlet concentration of 1.0 g/m^3 and an EBRT of 0.078 h. The axial concentration of the VOC was monitored and the lowest part of the column was found to contribute more than 40% of the overall removal efficiency. The temperature and biomass profiles were recorded during the entire experimental period. The carbon dioxide production rate was estimated and was correlated with the elimination capacity.

CONCLUSIONS

1. Biofiltration of air contaminated with a benzene-ethylbenzene-xylene mixture, using a date palm tree bark-based biofilter containing immobilized, mixed microbial consortia, was investigated.
2. The effect of the inlet VOC concentration and the flow rate on the removal performance was studied. A maximum total elimination capacity of 214.1 $g/m^3 \cdot h$ was achieved.
3. Benzene was degraded better than the other two contaminants were.
4. The concentration profile of VOC degradation was recorded along the height of the biofilter. The lowest part of the column was found to contribute most to the removal efficiency.

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