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# Biotrickling filtration of VOC emissions from pharmaceutical industries

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## HIGHLIGHTS

- Performance of biotrickling filter treating a mixture of VOCs was evaluated.
- Methanol, ethanol, acetone and toluene were the pollutants studied.
- Effects of ILR and EBRT on EC and removal efficiency were evaluated.
- EC (100%) was achieved for ILRs of 320 g/m$^3$/h and 240 g/m$^3$/h for single and mixed pollutants respectively.
- Toluene was the most resistant compound to degrade.

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## ABSTRACT

In this study, the performance of a biotrickling filter (BTF) treating complex mixtures of VOCs from pharmaceutical industries was evaluated. Effects of inlet loading rate (ILR) and empty bed residence time (EBRT) on elimination capacity (EC) and removal efficiency (RE) were evaluated. Methanol, ethanol, acetone and toluene were taken as model pollutants. The net inlet concentration was varied from 1 to 4 g/m$^3$ to achieve an ILR variation from 52 to 419 g/m$^3$/h, while the EBRT was varied from 25 to 69 s. The BTF was able to completely degrade the VOCs up to an ILR of 240 g/m$^3$/h, while treating mixed pollutants. On the other hand, 100% RE was achieved for ILRs up to 320 g/m$^3$/h in case of single pollutants and the corresponding maximum elimination capacity ($EC_{max}$) for ethanol and acetone was 380 g/m$^3$/h. However, the $EC_{max}$ was only 320 g/m$^3$/h for the BTF treating mixed pollutants. Competitive interactions between different pollutants resulted in significantly lower $EC_{max}$ for individual pollutants in a mixed pollutant system than those in a single pollutant system. Toluene was the most resistant to degradation, followed by acetone, among the four pollutants studied. It was found that much of the degradation of ethanol and methanol occurred in the first 30 cm of BTF. It was also observed that the ILR and nature of the pollutants significantly affected the RE achieved at different EBRTs. Results from this study help in selecting the operational parameters for optimal performance of a BTF treating complex mixtures of VOCs emitted from pharmaceutical industries.



## 1. Introduction

A wide range of organic solvents are used as raw materials in pharmaceutical industries [1]. These are used in chemical synthesis, formulation, filtering to concentrate or removal of impurities, extraction of valuable products, facilitation of waste-stream clean-up and by-product recovery. The gaseous emissions arising from various pharmaceutical operations have a cocktail of organic solvents. These waste streams contain a wide variety of solvents at varying concentrations, generally too low for viable, cost-effective recovery [2]. Therefore, economically viable and environmentally friendly treatment technologies are most preferred in such cases. Presently, biological treatment is the most preferred approach for the treatment of contaminants in waste streams.

Biological systems such as biofilters (BFs), bioscrubbers (BSs) and biotrickling filters (BTFs) have been well established in odor control. They have been widely accredited as promising alternatives to other conventional volatile organic compound (VOC) control technologies [3]. Among the various biological waste gas treatment techniques, BTFs are preferred in many instances because of their low capital expenditure, stable operation [4], high removal rates [5] and better pH control [6]. However, they are prone to excess biomass accumulation in the bed [7].

Most of the biofiltration studies in the recent past have focused on the treatment of a single pollutant [4,8]. Target contaminants included hydrocarbons (e.g., benzene, styrene, hexane, toluene, and naphthalene), oxygenated hydrocarbons (e.g., methanol, ethanol,), ketones (e.g., acetone and methyl ethyl ketone), chlorinated

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hydrocarbons (e.g., chlorobenzene and o-dichlorobenzene), and sulfur compounds (e.g., hydrogen sulfide). These studies have focused on single pollutant removal with an aim to maximize elimination capacities (ECs). They also attempted to elucidate effects of operating conditions and media characteristics on BTF performance. However, gaseous effluents emitted into the atmosphere by industries are a complex mixture of VOCs [9,10]. Applying BTF techniques to treat VOC mixtures is challenging as the pollutants can be involved in complex interactions with the microbial system [11]. A number of biofiltration studies have been carried out with mixtures of aromatic compounds such as benzene, toluene, ethyl benzene, o-xylene (BTEX) [12,13], hydrophobic, and hydrophilic compounds [5,6]. Earlier studies have indicated that substrate interactions in a mixture are mostly system dependent and may have both positive and negative impacts on the performance of reactor. For instance, presence of ethanol significantly increased the o-dichlorobenzene removal rates [14], while high ethanol concentration had a negative effect on toluene and benzene degradation as it caused oxygen limitations [15].

Though many studies have been reported on control of VOC mixtures from microelectronics industry [16], paint industry [4,5,17], pulp and paper industry [18,19], very little attention has been paid to the control of VOC mixtures from pharmaceutical industries. Pharmaceutical industries emit a complex mixture of readily degradable and relatively recalcitrant compounds. Therefore, it is necessary to study the complexities that may occur during the biodegradation of these mixtures in BTF due to substrate competition/inhibition. To the best of authors' knowledge, very few studies have focused on the biodegradation of an individual compound, when it exists in a mixture. Moreover, profiles of biodegradation for each individual compound as a function of height of the biotrickling filter have not been studied extensively, especially in case of VOC emissions from pharmaceutical industries. Relatively less information is available about how the coexisting substrates affect the biodegradation kinetics of individual organic constituent, by a mixed microbial community. There is a need to gain insight into these aspects in order to apply biofiltration techniques for the treatment of VOC emissions from pharmaceutical industries. Hence, the objective of this present study was to evaluate the simultaneous degradation of the individual hydrophilic and hydrophobic components in a pharmaceutical solvent mixture comprising of methanol, ethanol (representative of alcohols), acetone (representative of ketones) and toluene (representative of aromatic compounds). Though a few earlier studies [20,21] have focused on the removal of these compounds in binary mixtures using biofiltration, no studies, to the knowledge of authors, have been conducted on the degradation all these compounds in a quaternary mixture using a biotrickling filter.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Chemicals

Methanol (Thomas Baker, India, 99.8%), ethanol (Changshu Yangyuan, China, 99.9%), acetone (Rankem, India, 99.8%) and toluene (Rankem, India, 99.5%) were utilized in this study. Ethanol was of analytical grade and all other chemicals were of High Performance Liquid Chromatography (HPLC) grade.

#### 2.1.2. Microbes

Microbes used for the inoculation of biotrickling filter were previously isolated and enriched by Ramakrishna and Philip [22], for the degradation of various groups of pesticides (lindane, methyl parathion, carbofuran), consisted of aerobic and facultative anaerobic bacterial species. The predominant bacterial strains isolated from the consortium were identified as *Pseudomonas aeruginosa* (MTCC 9236), *Bacillus* sp. (MTCC 9235) and *Chryseobacterium joostei* (MTCC 9237). Minimal Salt Medium (MSM) with following composition (quantity of chemicals are given in g/L in parentheses) was utilized in this study: $Na_2HPO_4{\cdot}2H_2O$ (3.5), $KH_2PO_4$ (1), $(NH_4)_2SO_4$ (0.5), $MgCl_2{\cdot}6H_2O$ (0.1), $Ca(NO_3)_2{\cdot}4H_2O$ (0.05), trace elements I (1 mL). Trace elements I contains: EDTA (0.5), $FeSO_4{\cdot}7H_2O$ (0.2) and trace elements II (100 mL). Trace elements II contains: $H_3BO_3$ (0.3), $MnCl_2{\cdot}4H_2O$ (0.03), $CoCl_2{\cdot}6H_2O$ (0.2), $ZnSO_4{\cdot}7H_2O$ (0.1), $Na_2MoO_4{\cdot}2H_2O$ (0.03), $NiCl_2{\cdot}6H_2O$ (0.02) and $CuCl_2{\cdot}2H_2O$ (0.01). The culture was grown at 30 °C in MSM and further acclimatized with major chlorinated and non-chlorinated solvents emitted from pharmaceutical industry [23].

#### 2.1.3. Packing media

The packing media (supplied by Fujino spirals, India) was made up of polyvinyl chloride. The average size of the packing media was 13 mm and had a spiral shape, with a surface area of 600 $m^2/m^3$. The average weight of one piece of the packing media was 700 ± 58 mg. The specific gravity and density of the packing media were 1.3 and 210 g/L, respectively. The number of packing media utilized in the column was 425. The weight of the packing media and liquid film in the reactor were 350.3 g and 177.9 g, respectively. The initial porosity of the packed bed was 0.8.

### 2.2. Analytical procedures

#### 2.2.1. Gas chromatographic analysis

Liquid samples were analyzed using Perkin Elmer Clarus 500 gas chromatograph with flame ionization detector (GC–FID). GC was equipped with an auto sampler, an on-column, split/split less capillary injection system, and a capillary column (Perkin Elmer Elite (PE)-624, 30 m × 0.53 mm × 0.5 mm film thickness). During the analysis, the column was held initially at a temperature of 50 °C for 20 min. Temperatures of injector and detector were maintained at 150 and 300 °C, respectively. Nitrogen was used as the make-up and carrier gas at a flow rate of 60 and 1.5 mL/min, respectively. Injections were made in the split mode with a split ratio of 1:20. Standard graphs for respective solvents were prepared individually by injecting known amounts of respective compound into a sealed bottle equipped with Teflon septum as suggested by Lodge [24]. The liquid samples were then transferred to GC vials and analyzed by GC–FID. Gas samples were analyzed by manual injection with the same program except that the split ratio was 1:2. At standard operating conditions, influent and effluent streams were analyzed in duplicate once in a day.

### 2.3. Experimental studies

#### 2.3.1. Biotrickling filter

Experiments were carried out in lab-scale biotrickling filter columns made of 3 mm thick plexi glass (Fig. 1). These columns had an outer diameter of 6.0 cm. The reactor was packed with open pore spirals (supplied by Fujino spirals, India). The total height of the reactor was 100 cm and the bed height was 75 cm. The nutrient solution was continuously sprayed over the top of the column at 1 L/h by a peristaltic pump (Masterflex L/S, USA). The filtered air stream was split into two parts: minor and major air streams. The primary air stream was passed through water columns in order to increase the relative humidity of inlet air. Air flow rates were controlled and measured using rotameters (Placka Instrumentation, India). The total gas flow rate was varied to achieve different empty bed residence times (EBRTs) in the reactor.

VOC contaminated air stream, corresponding to that commonly found in pharmaceutical air emissions was synthesized by diverting

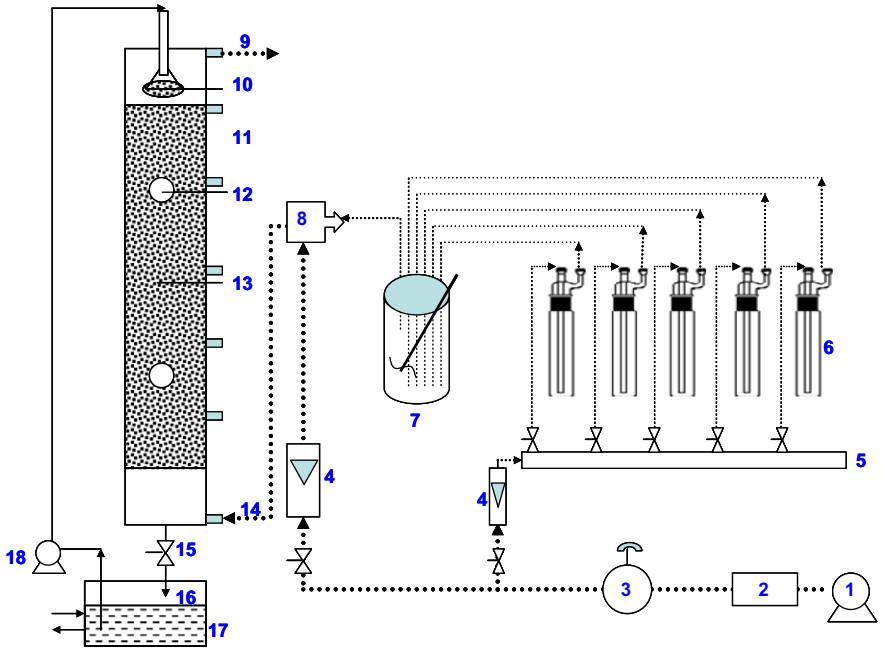


**Fig. 1.** Schematic of the biotrickling filter.

the compressed air of minor stream through glass bubbler unit of 200 mL of volume containing pure liquid of target pollutants, at room temperature. This VOC stream was then well mixed with the primary air stream by passing both streams through a mixing chamber. The resulting gas mixture was fed from the base of the BTF reactor. Sampling ports were provided at every 15 cm interval along the height of the reactor, from the base, to facilitate sampling. Gas samples were also collected from influent and effluent sampling ports with gas-tight syringes (SGE, Australia) fitted with 3-way Luer-Lock (BD Connecta, Sweden), and VOC concentrations were measured by GC analysis. Concentrations of VOCs in the synthetic gas stream were varied by changing the air flow rate through the bubbler. The pH of the re-circulating liquid collected in the reservoir (as shown in Fig. 1) was monitored periodically using a Eutech cyberscan portable pH meter (Eutech Instruments, Singapore). Pressure drop in the gas phase across the fixed-bed reactor was measured using a water filled U-tube manometer. Weight of the reactor was also measured periodically.

### 2.3.2. Procedure for estimating weight of packing media, porosity and liquid hold up

The weight of empty BTF reactor (A) was measured first and it was then filled with packing media. The weight of BTF along with packing media (B) was measured. The difference between A and B gives the weight of packing media. Then the reactor was filled with water up to the top of packing media, and the volume of water utilized was recorded to estimate the porosity. Water was then allowed to drain for 30 min and volume of drained water collected was used in determining the liquid hold up capacity.

### 2.3.3. Biomass and liquid content in the packing bed

The inoculum for BTF was prepared by suspending 50 g wet biomass (in 1 L MSM) obtained from mixed microbial culture acclimatized with target VOCs. This biomass solution was circulated through BTF for 12 h (1 L/h) in order to facilitate the attachment of the microbial culture to the packing media, followed by a 30 min draining time. The initial weight of BTF with packing media alone was deducted from the final weight of BTF containing packing media along with microbial culture. The difference in weight was taken as the initial biomass amount. The accumulation of wet biomass was estimated by periodically measuring the total mass of the BTF. For this, the gas and liquid flows to the BTF were stopped, the reactor was allowed to drain for 30 min and then weighed (with a precision of 0.5 g) using a balance (National Instruments, India). The difference between the above weight and the empty wet weight of the reactor gave the total wet biomass for the corresponding time. Dry biofilm weight was estimated by weighing wet and oven dried (105 °C) samples of biofilm collected at various depths of BTF.

### 2.4. Performance evaluation of BTF

The performance of the BTF was evaluated in terms of removal efficiency (RE, %) and elimination capacity (EC, g/m$^3$/h), for different inlet loading rates (ILRs, g/m$^3$/h) and empty bed residence times (EBRTs, s). ILR is the VOC mass applied to bioreactor per unit volume of medium per unit time. EC is the normalized measure of VOC removal capacity at a given mass loading. EC is defined as the VOC mass removed per unit volume of medium per unit time. EBRT is the relative measure of gas residence time within the reactor medium. ILR, EC, EBRT and RE were calculated using the following equations:

$$\text{Mass inlet loading rate, ILR} = \left(\frac{C_{in}}{V}\right) * Q \quad (1)$$

$$\text{Elimination capacity, EC} = \left(\frac{C_{in} - C_{out}}{V}\right) * Q \quad (2)$$

$$\text{Empty bed residence time, EBRT} = \frac{V}{Q} \quad (3)$$

$$\text{Removal efficiency, RE} = \left(\frac{C_{in} - C_{out}}{C_{in}}\right) * 100 \quad (4)$$

where $Q$ is the gas flow rate (m$^3$/h), $V$ is the volume of the biotrickling filter (m$^3$), $C_{in}$ and $C_{out}$ are the inlet and outlet concentrations (g/m$^3$) of VOC, respectively. Inlet and outlet VOC concentrations were monitored continuously. Once a pseudo-steady state was attained, substrate concentrations were increased to proceed to the next stage of operation with higher inlet loading rate. Studies were

also performed for various EBRTs. The overall operation history of the BTF is presented in detail in Table 1.

## 3. Results and discussion

### 3.1. Performance of BTF for single pollutant degradation

#### 3.1.1. Start-up and acclimatization

BTF was used to treat ethanol and acetone individually. During the start up of these experiments, the reactor was operated in a closed loop mode with respect to liquid to maximize the cell adhesion to the packing media. The liquid was changed every 4 days. In case of ethanol, the start up period was 20 days, while it was 12 days for acetone. One g/L of ethanol or acetone was added to the nutrient medium while 1 g/m$^3$ ethanol or acetone was passed through the BTF in gaseous phase during the start up. The pH of the nutrient medium was measured periodically during start up and it was maintained between 7.0 and 7.3.

During the start up phase, an ILR of 52.5 g/m$^3$/h (mass as total concentration and not in terms of carbon) and a gas flow rate of 0.09 m$^3$/h were maintained and the corresponding EBRT was 68.7 s. The presence of organic compounds in the air stream enhanced the biomass production. Uniform and stable operation with high RE (>90%) was observed in BTF treating ethanol from day 32 onwards, after which a steady state was attained. In case of BTF treating acetone, steady state was attained after 26 days. An increase in pressure drop was noticed after 10 weeks in the BTF while treating ethanol or acetone. During the steady state operations, ethanol or acetone concentration in the outlet gas stream was below detectable limit.

#### 3.1.2. Performance of BTF treating ethanol during different phases of operation

During the Phase-I of operation (day 21 to day 46), an EBRT of 68.7 s and an ILR of 52.4 g/m$^3$/h were maintained in the system. The flow rate of trickling water was maintained constant at 1 L/h through out the study. Initially, the removal efficiency was 45% and this increased gradually to 100% on day 37. The same level of performance was observed until day 46. During Phase-II to Phase-IV operation (day 47 to day 109), the minor stream gas flow rate was doubled as compared to that during Phase-I in order to achieve an inlet ethanol concentration of approximately 2 g/m$^3$. The ILR was varied by changing the major stream air flow rate to the humidifier. EBRTs of 68.7, 41.2 and 29.5 s were maintained during Phase-II, Phase-III and Phase-IV, respectively. The corresponding ILRs were 104.8, 174.7 and 244.6 g/m$^3$/h, respectively. Due to the sudden increase in ILR on day 47, the RE of BTF dropped to 52%. However, the RE gradually increased with increase in time and attained a steady state value of 95% by day 65 and remained constant until the end of Phase-II on day 70, as shown in Fig. 2a. Biomass increased rapidly and reached a value of 762 g (wet weight in the total BTF volume of 1.7 L) at the end of first 12 weeks of operation. Dry weight of the biomass in the biotrickling filter was 4.3 ± 0.3% of the wet weight. However, the pressure drop across the packed bed was negligible during this period. This might be due to the fact that the volume occupied by biomass was less compared to the effective pore space.

On day 71, the flow rate in the main air stream was increased from 0.09 m$^3$/h to 0.15 m$^3$/h in order to achieve an EBRT of 41.2 s in Phase-III (day 71 to day 93) operation of BTF. The RE decreased suddenly to 54% on day 71. However, it increased gradually and reached a steady state value of 99% on day 90 and remained almost constant until further change in operating conditions on day 94. In Phase-IV (day 94 to 109), the air flow rate was further increased to 0.21 m$^3$/h on day 94 to achieve an EBRT of 29.4 s, corresponding ILR was 244.6 g/m$^3$/h. On day 94, the RE reduced to 50% and then increased gradually to reach a steady state value of 98% on day 107. Several analyses of the trickling liquid at steady state showed no intermediates, i.e., the parent compound was completely mineralized in both the cases. At this stage, the biomass concentration was around 935 g (wet weight) and the pressure drop increased to 0.7 cm of $H_2O$. The increase in pressure drop might be due to either the increase in air flow rate or increase in biomass.

In Phase-V (day 110 to day 121), the inlet concentration of pollutant was increased to 3 g/m$^3$, corresponding to an ILR of 419.3 g/m$^3$/h, which resulted in EBRT of 25 s. The RE dropped to 46% and regained the performance to achieve an RE of 78%. Further increase in loading rate in Phase-VI (day 122 to 130) was achieved by increasing the inlet concentration of ethanol to 4 g/m$^3$. The inlet air flow rate was maintained at 0.24 m$^3$/h, as in Phase-V. This resulted in an ILR of 559.1 g/m$^3$/h with EBRT of 25 s. The RE decreased suddenly to 42% on day 122. However, it increased gradually and remained almost constant at a value of 68% on the last 3 days of this phase (Fig. 2a). Though the biomass appeared to have attained a constant value during this phase, the pressure drop increased to 1.1 cm of $H_2O$. This could be due to change in the gas flow rate.

**Table 1**
Operation history of BTF treating: (a) ethanol, (b) acetone and (c) mixed pollutants.

| Phase | Time, days | Gas rate, LPM | EBRT, s | Ethanol conc., g/m$^3$ | Volumetric flow rate, m$^3$/h$^1$ | Inlet loading rate, g/m$^3$/h$^1$ |
|---|---|---|---|---|---|---|
| I | 0–46 | 1.5 | 68.7 | 1 | 0.09 | 52.4 |
| II | 47–70 | 1.5 | 68.7 | 2 | 0.09 | 104.8 |
| III | 71–93 | 2.5 | 41.2 | 2 | 0.15 | 174.7 |
| IV | 94–109 | 3.5 | 29.4 | 2 | 0.21 | 244.6 |
| V | 110–121 | 4.0 | 25.0 | 3 | 0.24 | 419.3 |
| VI | 122–130 | 4.0 | 25.0 | 4 | 0.24 | 559.1 |
| Phase | Time, days | Gas rate, LPM | EBRT, s | Acetone conc., g/m$^3$ | Volumetric flow rate, m$^3$/h$^1$ | Inlet loading rate, g/m$^3$/h$^1$ |
| I | 0–32 | 1.5 | 68.7 | 1 | 0.09 | 52.4 |
| II | 33–52 | 2.0 | 51.5 | 2 | 0.12 | 139.8 |
| III | 53–70 | 3.0 | 34.3 | 2 | 0.18 | 209.7 |
| IV | 71–84 | 4.0 | 25.0 | 2 | 0.24 | 279.5 |
| V | 85–93 | 4.0 | 25.0 | 3 | 0.24 | 419.3 |
| VI | 94–101 | 4.0 | 25.0 | 4 | 0.24 | 559.1 |
| Phase | Time, days | Gas rate, LPM | EBRT, s | Inlet conc., g/m$^3$ | Volumetric flow rate, m$^3$/h | Inlet loading rate, g/m$^3$/h$^1$ |
| I | 0–57 | 1.5 | 68.6 | 1 | 0.09 | 52.4 |
| II | 58–97 | 2.0 | 51.5 | 2 | 0.12 | 139.8 |
| III | 98–121 | 2.5 | 41.2 | 2 | 0.15 | 174.7 |
| IV | 124–142 | 3.0 | 34.4 | 2 | 0.18 | 209.7 |
| V | 143–161 | 3.0 | 34.4 | 3 | 0.18 | 314.5 |
| VI | 162–178 | 4.0 | 25.0 | 3 | 0.24 | 419.3 |

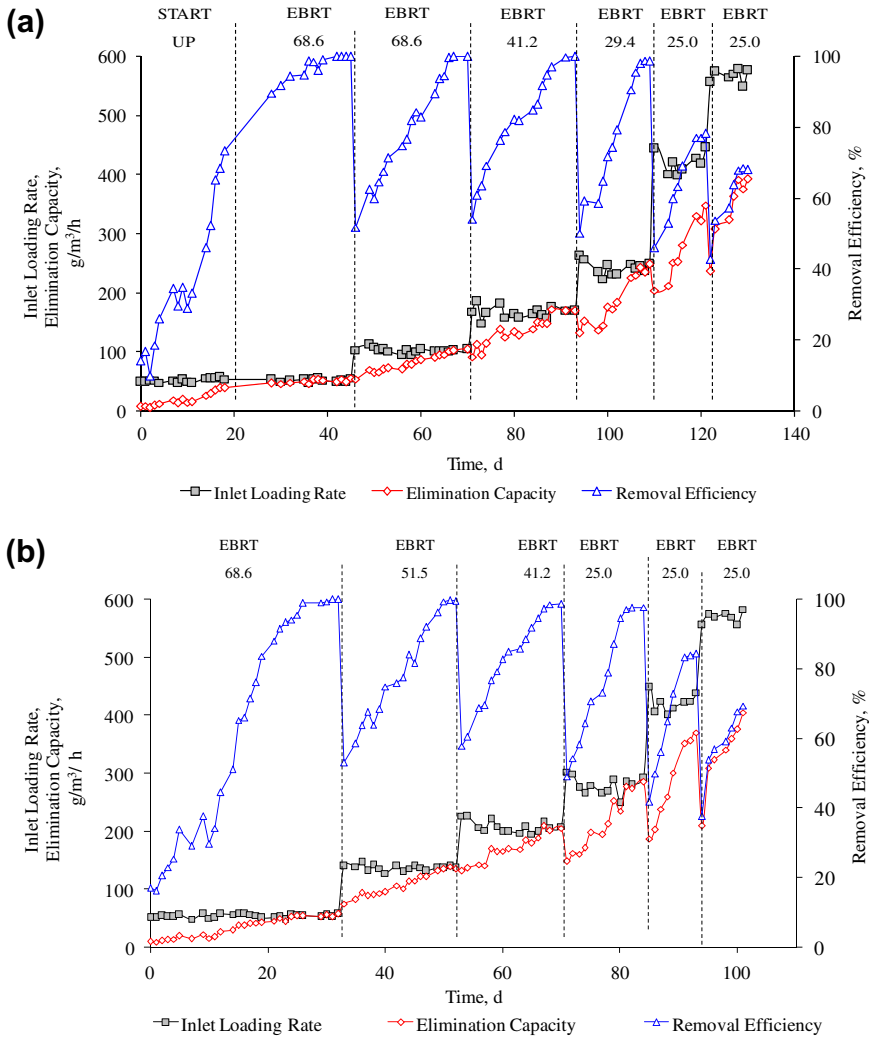


**Fig. 2.** Performance of biotrickling filter treating (a) ethanol and (b) acetone during various phases of operation.

*3.1.3. Performance of BTF treating acetone during different phases of operation*

During the Phase-I of operation (day 13 to day 32), an EBRT of 68.7 s and an ILR of 52.4 g/m$^3$/h were maintained in the system. The flow rate of trickling water was maintained constant at 1 L/h through out the study. Initially, the removal efficiency was 45% and this gradually increased to 100% on day 26. The same level of performance was maintained until day 32. During Phase-II to Phase-IV operations (day 33 to day 84), the minor stream gas flow rate was twice that during Phase-I in order to achieve an acetone concentration of approximately 2 g/m$^3$. However, the ILR was varied by changing the major stream air flow rate to the humidifier. EBRTs of 51.5, 34.4 and 25 s were maintained during Phase-II, Phase-III and Phase-IV, respectively. The corresponding ILRs were 139.8, 209.7 and 279.6 g/m$^3$/h, respectively. Due to the sudden increase in ILR on day 33, the RE of BTF dropped from 99.7% to 53%. However, the RE gradually increased with increase in time and attained a steady state value of 95% on day 45. It remained constant until the end of Phase-II on day 52, as shown in Fig. 2b. The biomass concentration at this phase was 368 g/L.

On day 53, the air flow rate in the main air stream was increased from 0.12 m$^3$/h to 0.18 m$^3$/h in order to achieve an EBRT of 34.4 s in Phase-III (day 53 to day 70) operation of BTF. The RE decreased suddenly to 58% on day 53. However, it increased gradually and reached a steady state value of 99% on day 66 and remained almost constant until further change in operating conditions on day 70. In Phase-IV (day 71 to 84) the air flow rate was further increased to 0.24 m$^3$/h on day 94 to achieve an EBRT of 25 s. Corresponding ILR was 279.6 g/m$^3$/h. On day 71, the RE reduced to 49% and then increased gradually to reach a steady state value of 98% on day 81. Several analyses of the trickling liquid during steady state showed no intermediates. In Phase-V (day 85 to day 93), the inlet concentration of acetone was increased to 3 g/m$^3$, corresponding to an ILR of 419.3 g/m$^3$/h. The EBRT was maintained at 25 s. The RE dropped to 42% and regained the performance to achieve an RE of 82%. Further increase in loading rate in Phase-VI (day 94 to 101) was achieved by increasing the inlet concentration of acetone to 4 g/m$^3$. However, the inlet air flow rate was maintained at 0.24 m$^3$/h, as in Phase-V. This resulted in an ILR of 559.1 g/m$^3$/h with EBRT of 25 s. The biomass concentration reached a value of 592 g/L and the corresponding pressure drop was 1 cm of $H_2O$. The RE decreased suddenly to 38% on day 94. However, it increased gradually and remained almost constant at 69% on the last 3 days of this phase (Fig. 2b).

*3.1.4. Effect of ILR on EC of ethanol and acetone*

Fig. 3a and b shows the variation of elimination capacity with ILR for ethanol and acetone, respectively. Two distinct stages in elimination capacity can be observed from Fig. 3: (a) diffusion limited region (up to 330 g/m$^3$/h of ILR); and (b) reaction limited

region (for ILRs greater than 330 g/m$^3$/h). EC was directly proportional to the inlet load during the diffusion limited stage. At higher loads, the BTF performance was reaction limited. Similar trend was observed by Ottengraf [25]. Cox et al. [26] investigated the performance of BTF for ethanol removal for inlet load ranging from 70 to 320 g/m$^3$/h. They observed an $EC_{max}$ of 200 g/m$^3$/h at an inlet ethanol concentration of 5 g/m$^3$. Przybylska et al. [27] investigated the acetone biodegradation in a BTF inoculated with *Burkholderia cepacia* and *Acinetobacter baumannii* on plexi glass chips and reported an $EC_{max}$ of 77.8 g/m$^3$/h at an air flow rate of 36 m/h. Tang et al. [28] reported an $EC_{max}$ of 82 g/m$^3$/h for acetone in a laboratory scale biofilter with a mixture of compost and porous clay particles as the filter material. In the present study, $EC_{max}$ was 380 g/m$^3$/h for both acetone and ethanol.

### 3.2. Performance of BTF for mixed pollutant degradation

#### 3.2.1. Start-up and acclimatization

During start up and acclimatization phase (day 1 to day 20), the net inlet concentration of mixed pollutants were maintained at 1.0 g/m$^3$ with a gas flow rate of 0.09 m$^3$/h. It resulted in an inlet loading rate of 52.4 g/m$^3$/h and an EBRT of 68.7 s. On day 4, a thin layer of biofilm growth was observed on the packing material. Within 20 days of operation, 350 g of wet biomass was developed in the system. The porosity of the packing media reduced to 0.77 from 0.8. However, pressure drop was less than 0.1 cm of $H_2O$. After this start-up period (20 days), the BTF was tested for its performance under different operating conditions (Phase-I to Phase-VI) as per the operational schedule given in Table 1. The temporal variations of inlet and outlet concentration of mixed pollutants are shown in Fig. 4.

#### 3.2.2. Performance evaluation of the biotrickling filter for various loading rates

During the Phase-I of operation (day 21 to day 57), an EBRT of 68.7 s and an ILR of 52.4 g/m$^3$/h were maintained in the system. The flow rate of trickling water was maintained constant at 1 L/h throughout the study. Initially, the removal efficiency was 45% and this gradually increased to 100% by day 42. The same level of performance was maintained until day 57. RE for methanol and ethanol were slightly higher than RE for acetone and toluene during Phase-I, which could be due to the simple chemical structure of compounds like methanol and ethanol, making them more easily biodegradable than acetone and toluene. The wet biomass was 619 g at the end of Phase-I, which decreased the porosity to 0.74. The pressure drop across the packed bed at the end of Phase-I was 0.3 cm of $H_2O$.

During Phase-II to Phase-IV operation (day 58 to day 142), the minor stream gas flow rate was doubled as compared to that during Phase-I in order to achieve a total gaseous pollutant concentration of approximately 2 g/m$^3$. However, the ILR was varied by controlling the major stream air flow rate to the humidifier. EBRTs of 51.5, 41.2 and 34.4 s were maintained during Phase-II to Phase-IV. The corresponding ILRs were 139.8, 174.7 and 209.7 g/m$^3$/h, respectively. Due to the sudden increase in ILR as well as decrease in residence time from 68.7 s to 51.5 s on day 58, the RE of BTF reduced from 100% to 49%. However, the removal efficiency gradually increased with increase in time and attained a steady state value of 95% by day 89 and remained constant until the end of Phase-II on day 97, as shown in Fig. 5. The maximum RE for the mixed pollutant as a whole in this phase was 98.67%, while for methanol; ethanol, acetone and toluene the REs were 100%, 100%, 98.7% and 96.8% respectively. Though the inlet concentration of mixed pollutants is doubled in Phase-II, the RE obtained was almost the same as that in Phase-I. This is because of the presence of large quantity of acclimatized active microbial consortium in the packed bed of the BTF. It was observed that the removal efficiency was more than 99%, at an ILR of 139 g/m$^3$/h, in both cases of BTF treating individual (acetone/ethanol) and mixed pollutants. However, it may be emphasized that the individual loading rates of ethanol and acetone in the mixed pollutant were around 35 g/m$^3$/h. As

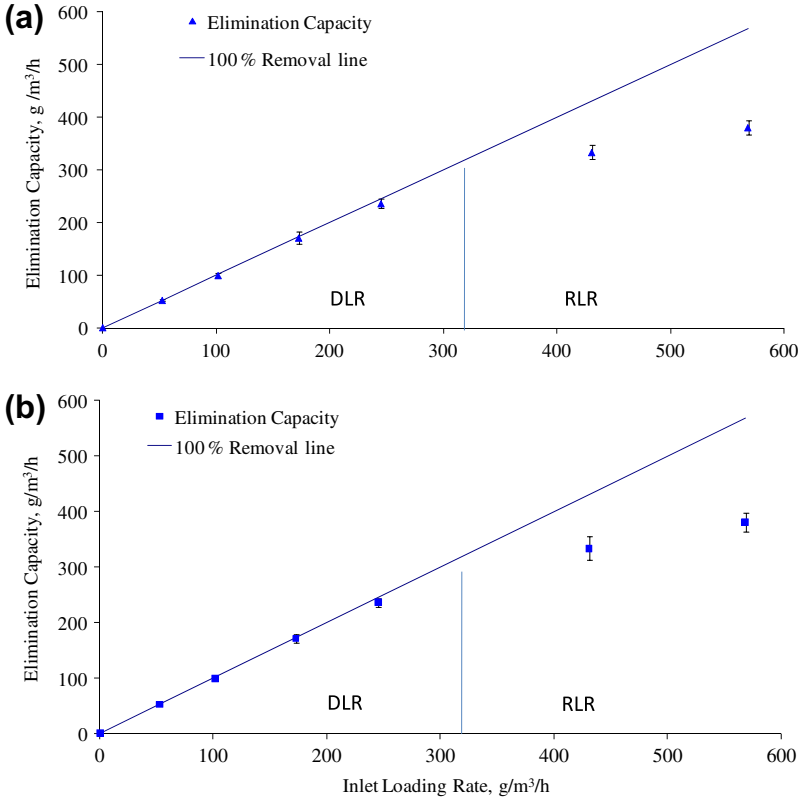


**Fig. 3.** Effect of inlet loading rate on elimination capacity of biotrickling filter treating: (a) ethanol and (b) acetone.

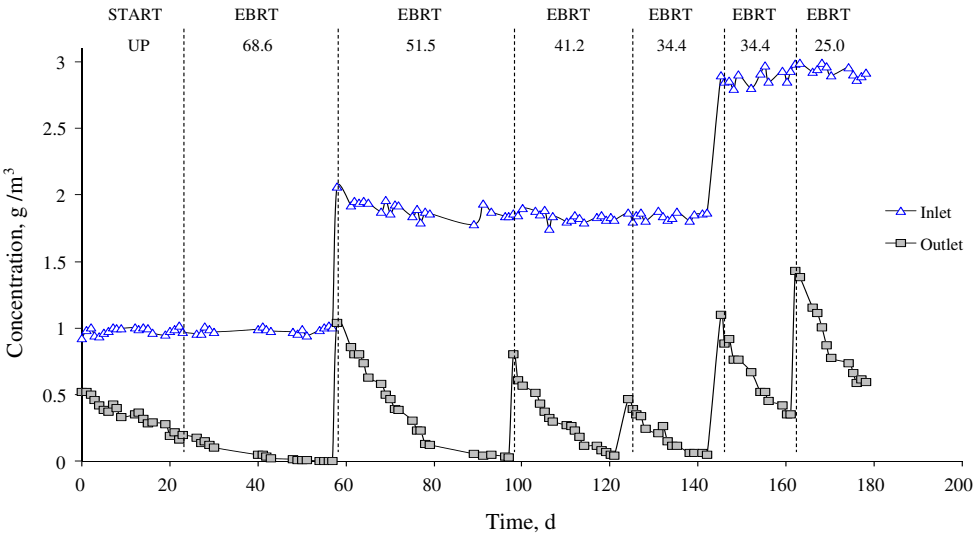


**Fig. 4.** Inlet and outlet concentrations of VOCs in the biotrickling filter treating mixture of pollutants during various phases of operation.

the ILR increased in subsequent phases, the biomass in the reactor also increased. The microbial mass increased from 619 g in Phase-I to 856 g in Phase-II, and the porosity of packed bed reduced to 0.68, while the pressure drop increased to 1.0 cm of $H_2O$ on day 78.

On day 98, the air flow rate in the main air stream was increased from 0.12 $m^3$/h to 0.15 $m^3$/h in order to achieve an EBRT of 41.2 s in Phase-III (day 98 to day 121) operation of BTF. The RE decreased suddenly to 56.7% on day 98. However, it increased gradually and reached a steady state value of 97.8% on day 118 and remained almost constant until further change in operating conditions on day 124. The maximum RE for the mixed pollutant in this phase was 97.85% and corresponding REs for methanol, ethanol, acetone and toluene were 100%, 100%, 99.6% and 92.7%, respectively. In Phase-III, the porosity of the packed bed decreased to 0.61 and the pressure drop increased to a high value of 2 cm of $H_2O$ on 111th day, leading to clogging of the reactor. Therefore, the reactor was backwashed with water and pressurized air was employed to control the clogging. After the backwash, the biomass concentration in BTF reduced from 1067 g (wet weight) to 736 g (wet weight), and the pressure drop across the bed reduced from 2 cm to 1 cm of $H_2O$. The porosity after the backwash was 0.74.

In Phase-IV (day 124 to 142) the air flow rate was further increased to 0.18 $m^3$/h on day 124 to achieve an EBRT of 34.4 s, corresponding ILR was 209.7 g/$m^3$/h. On day 124, RE reduced to 75% and then steadily increased to reach steady state value of 98% on day 138. The maximum RE for methanol, ethanol, acetone and toluene were 99.4%, 100%, 99.2% and 92.4%, respectively. Analyses of the trickling liquid during steady state showed no intermediates, indicating that all the pollutants were completely mineralized. At the end of Phase-IV, the biomass was 904 g, with a pressure drop of 1.2 cm of $H_2O$ and a porosity of 0.73.

In Phase-V (day 143 to day 161), the inlet concentration of mixed pollutant was increased to 3 g/$m^3$, corresponding to an ILR of 314.5 g/$m^3$/h. The EBRT was maintained at 34.4 s, as in Phase-IV. On day 143, the RE dropped to 62% and then gradually increased to reach a steady state value of 88% on day 155 and it was maintained until further variation in loading rates. The maximum RE for mixed pollutants in this phase was 88.1% while for methanol, ethanol, acetone and toluene were 95.3%, 93.2%, 90.7% and 72.5%, respectively. The BTF could not completely eliminate the pollutants supplied to the reactor in this phase, since the system could have reached reaction rate limiting stage. The biomass increased to

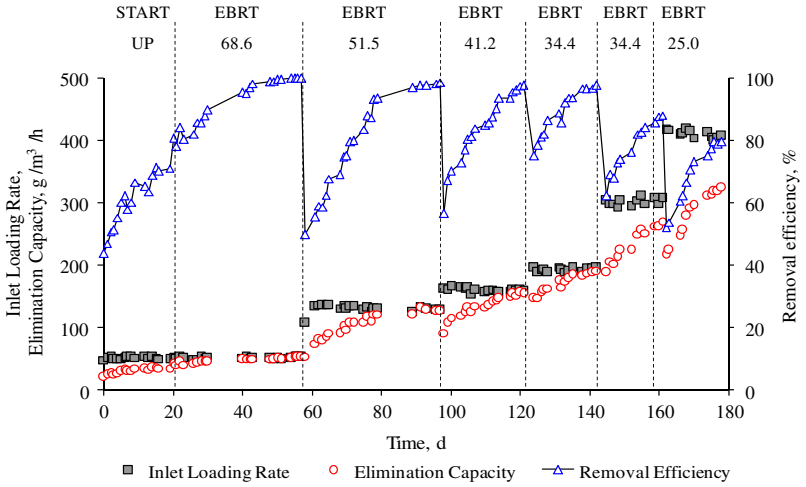


**Fig. 5.** Performance of biotrickling filter treating mixture of pollutants during various phases of operation.

1018 g from 904 g and the porosity decreased to 0.70, resulting in slight increase of pressure drop to 1.5 cm of $H_2O$. In Phase-VI (day 162 to 178), the inlet concentration of mixed pollutant was maintained at 3 g/m$^3$ as in the previous phase. However, the inlet air flow rate was increased to 0.24 m$^3$/h. This resulted in an ILR of 419.3 g/m$^3$/h with EBRT of 25 s. The maximum RE for the mixed pollutants in this phase was 79.6% and the maximum RE for methanol, ethanol, acetone and toluene were 89.2%, 87.9%, 82.9% and 55.7%, respectively. Since the biomass growth during this phase was only 50 g, there was not much significant variation in the pressure drop and porosity. It was observed that the maximum RE achieved for different EBRTs, for each pollutant in the BTF was highly dependent on the ILR and nature of the pollutants. From Fig. 6, it was observed that the RE has reduced significantly in case of aromatics and ketones as compared to that for alcohols, when the ILR was increased. This clearly indicates the effect of nature of pollutants on degradation. During the mixed biodegradation total $EC_{max}$ was observed to be 324 g/m$^3$/h while $EC_{max}$ for acetone and ethanol in the single pollutant systems were 380 g/m$^3$/h. The $EC_{max}$ for acetone and ethanol in mixed pollutant system were 96 g/m$^3$/h and 78 g/m$^3$/h, respectively. This shows that the RE of each pollutant during different EBRTs, depended not only on the concentration of individual pollutant, but also on the concentrations of other pollutants in the mixture since interaction effects play a major role in determining the removal of a given compound in the mixture. Rene et al. [29] made similar observations regarding interactions among individual compounds in biodegradation of mixed pollutant system.

### 3.2.3. Effect of inlet loading rate on the elimination capacity

The variation of elimination capacity with respect to inlet loading rate, for the BTF treating mixed pollutant, is presented in Fig. 7. As discussed earlier for BTF treating single pollutant, the behavior of the BTF with respect to EC can be divided into (a) diffusion limited region (DLR) [up to an ILR of 240 g/m$^3$/h] and (b) reaction limited region (RLR) [for ILR greater than 240 g/m$^3$/h]. In the DLR phase, BTF completely degraded the pollutants; the only limitation was the rate of diffusion of pollutants into the biofilm as EC was directly proportional to ILR. In the RLR phase, biodegradation rate was the limiting factor. The microbial population was unable to degrade the pollutants completely since ILR was very high. In this phase EC was not directly proportional to ILR. For compounds having high water solubility, the EC may be subjected to diffusion control in the wet biofilm region of the packed bed in BTF. As the load increased significantly, the BTF performance became reaction limited as outlined by Ottengraf [25]. An increase in ILR generally would enhance the transfer rate of the VOCs from the gas phase to the biofilm and thus activates more microbes to biodegrade in DLR. However, high concentrations may produce inhibitive effects on the metabolic activity of the microbial population and hence EC did not increase significantly after the ILR of 240 g/m$^3$/h.

The variation of elimination capacity with ILR for individual compounds in the mixed pollutant system is shown in Fig. 8. The BTF treating individual pollutants achieved a maximum EC of 380 g/m$^3$/h for ethanol as well as acetone. The BTF treating the mixture of pollutants was able to achieve an $EC_{max}$ of 320 g/m$^3$/h. Among the mixture of four individual pollutants, the value of DLR in terms of EC was in the order as follows: ethanol (70 g/m$^3$/h) > methanol (65 g/m$^3$/h) > acetone (60 g/m$^3$/h) > toluene (45 g/m$^3$/h). At higher inlet loadings, the ECs of the alcohols did not deviate much from the 100% removal line as shown in Fig. 8. However, EC of acetone showed a slight deviation, whereas EC of toluene deviated significantly from the 100% removal line. This indicated the difficulty in degradation of toluene, which affected the overall

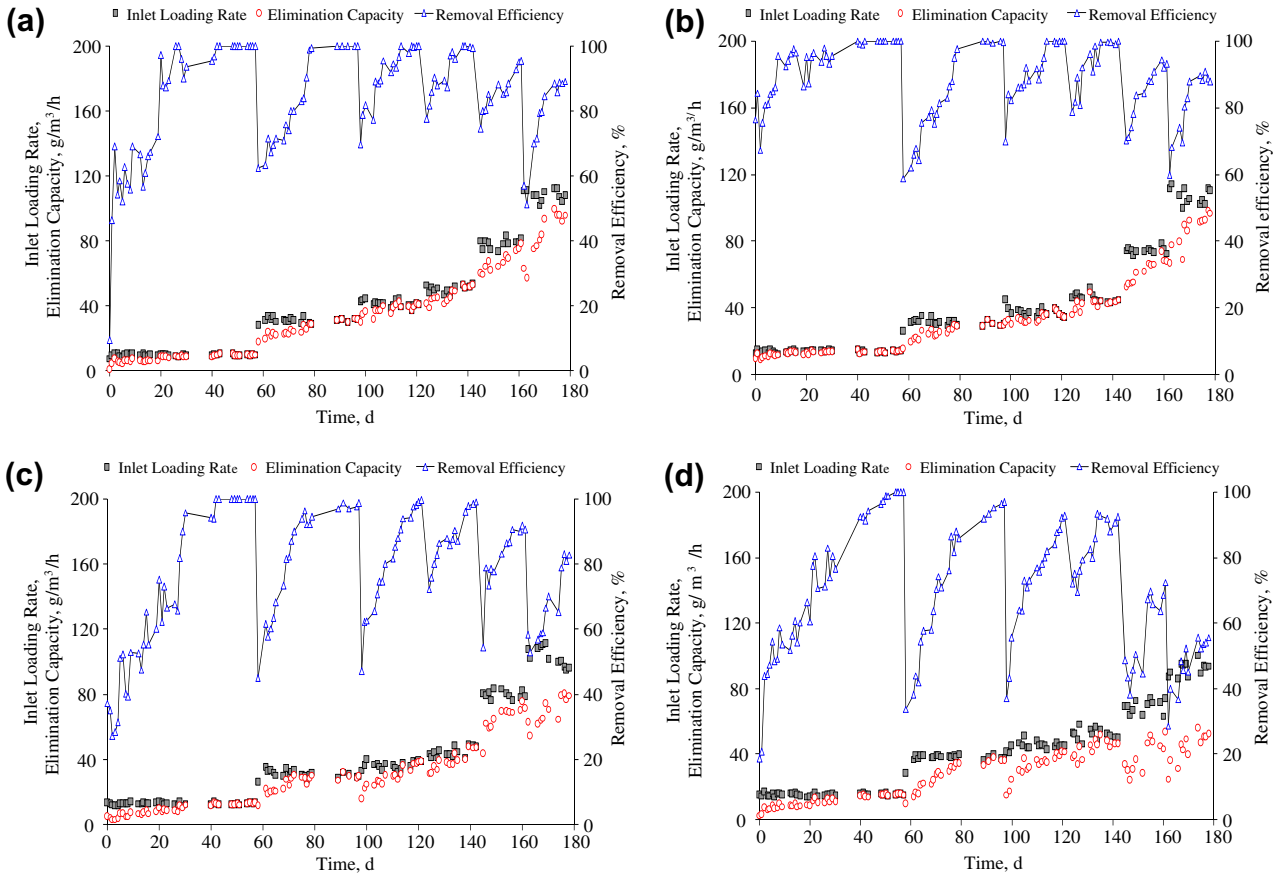


**Fig. 6.** Removal efficiency and elimination capacity for individual compounds [(a) methanol, (b) ethanol, (c) acetone and (d) toluene] in the BTF treating mixture of pollutants.

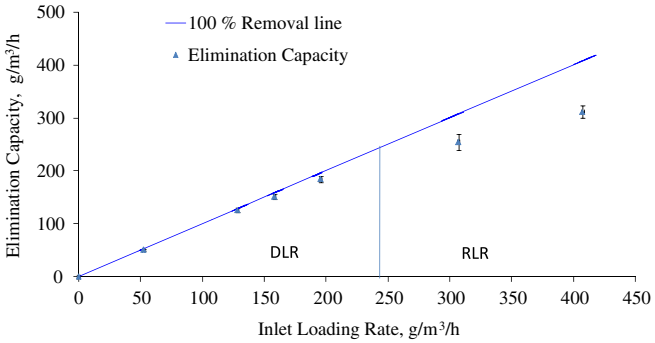


**Fig. 7.** Effect of inlet loading rate on elimination capacity of biotrickling filter treating mixture of pollutants.

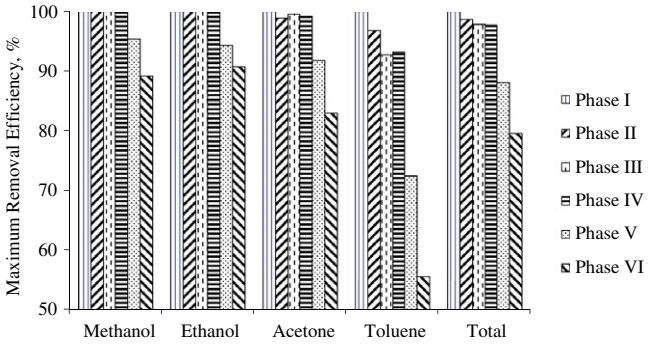


**Fig. 9.** Maximum removal efficiencies of individual pollutants in the biotrickling filter treating mixture of pollutants during various phases of operation.

RE of the system while treating mixed pollutants. The critical load i.e., the load beyond which the RE was less than 100%, observed in the present study was around 240 g/m$^3$/h for mixed pollutants, while for single pollutant removal the critical load was 320 g/m$^3$/h. The $EC_{max}$ achieved in this study were comparable to the results obtained by other researchers for toluene (125 g/m$^3$/h) [20]; methanol (82 g/m$^3$/h) and ethanol (150 g/m$^3$/h) [30], based on degradation studies on single and/or mixed VOCs. Earlier biotrickling filtration studies with methanol, ethanol, acetone and toluene reported an $EC_{max}$ of 200, 200, 100 and 100 g/m$^3$/h, respectively while treating them individually [26–28,31].

### 3.3. Effect of inlet loading rate on the removal efficiency

Total pollutant removal efficiency (Fig. 9) was maintained constant above 98% with increase in inlet loading rate up to Phase-IV. The BTF was able to degrade the pollutant up to a certain inlet loading rate and as the loading rate increased, RE also increased since the degradation followed the first-order reaction. However, as the inlet loading rate increased beyond a critical value, the RE decreased. The RE of BTF decreased gradually either due to the inhibition effect of pollutants on the bioreactor or because the inlet loading rate was higher than the degradation capacity of the biofilm. Variation of RE with respect to the inlet loading rate was different for different individual pollutants. This may be due to the fact that the individual pollutant degradation depends not only on inlet loading rate but also on the nature of pollutants. Moreover, there are competitive interactions between the individual pollutants while they exit as a mixture and the earlier studies by Balasubramanian et al. [23] outlined these interactions.

Chetpattananondh et al. [21] studied the biofiltration of methanol and toluene as single and mixed compounds with mixture of palm shells and activated sludge as inoculum and achieved an

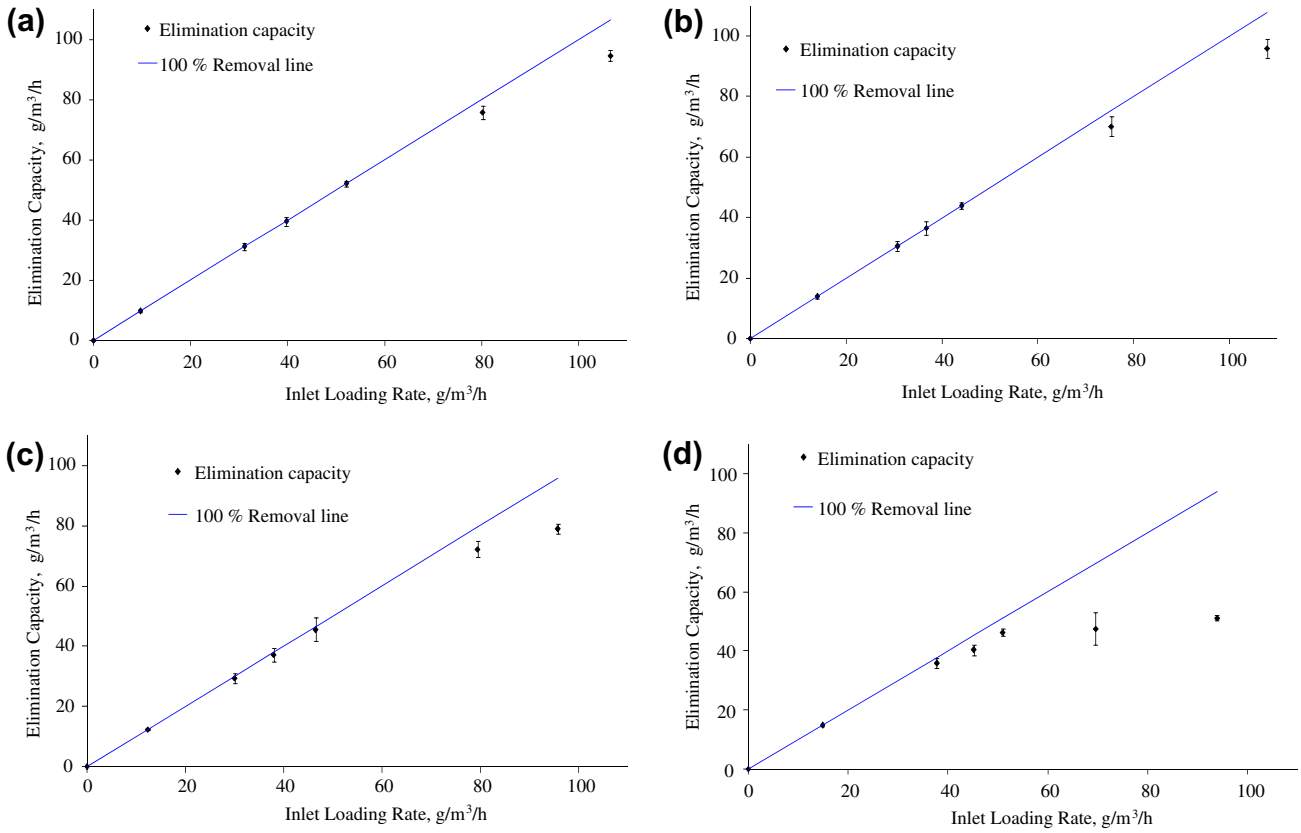


**Fig. 8.** Effect of inlet loading rate on elimination capacity of individual pollutants [(a) methanol, (b) ethanol, (c) acetone and (d) toluene] in the biotrickling filter treating mixture of pollutants.

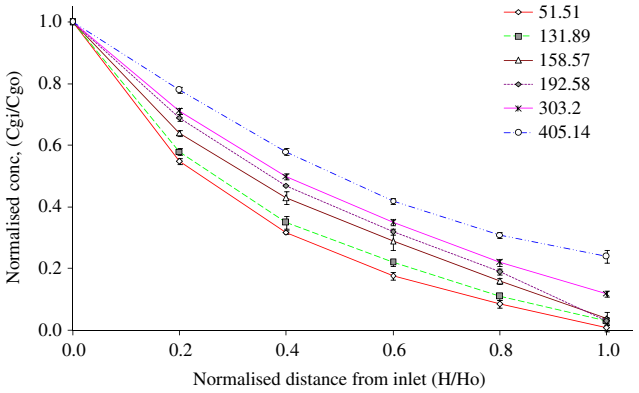


**Fig. 10.** Variation of concentration along the height of the biotrickling filter treating mixture of pollutants as a function of inlet loading rate.

$EC_{max}$ of 230 and 181 g/m$^3$/h for methanol and toluene, respectively. Further, they found that the presence of toluene had negligible effect on the removal rate of methanol while methanol had significant effect on the removal rate of toluene. This might have occurred due to competition phenomena. Similar observations were made by the authors in their earlier batch scale studies [23]. Chang and Lu [20] investigated the biodegradation of binary mixtures of acetone and toluene in a BTF and achieved RE greater than 90% for an ILR of toluene and acetone below 125 and 15 g/m$^3$/h, respectively. Lee et al. [32] investigated the biodegradation of acetone and MEK as individual and mixed compounds using a biofilter packed with a ceramic type medium and achieved an $EC_{max}$ of 200 g/m$^3$/h for acetone removal.

### 3.4. Degradation variation along the bed height of the BTF

Variations in degradations of individual pollutants in the mixture along the height of the BTF column were monitored. Results for normalized concentrations as a function of normalized distance from the inlet are presented in Fig. 10. Complete elimination was achieved up to Phase-IV. During Phase-IV, for an ILR of 200 g/m$^3$/h, almost 50% of total pollutant removal occurred within 30 cm height from the inlet and the remaining 50% of removal occurred in the remaining part of the BTF. The RE achieved for ethanol within 30 cm height from the inlet was 74% and for toluene it was only 35%. In case of methanol and acetone, REs achieved within 30 cm height from the inlet of the BTF were 62% and 44%, respectively. The above variation in removal rates may be attributed to the fact that the degradation of aromatic compounds (toluene) is much more complex as compared to that of oxygenated compounds and therefore, the microbes tend to utilize the preferential carbon source first. It is interesting to note that the removal of aromatic compounds occurred only after most of the alcohols were removed from the gas stream. This suggests that alcohols have a competitive effect on aromatics degradation in the bioreactor. Khammar et al. [33] showed that oxygenated compounds were removed efficiently and preferably as compared to aromatic and halogenated compounds.

In case of BTF with single pollutant, for an ILR of 200 g/m$^3$/h, REs at 30 cm height from the inlet of the BTF were 52% and 45% for ethanol and acetone, respectively. It was also observed visually that

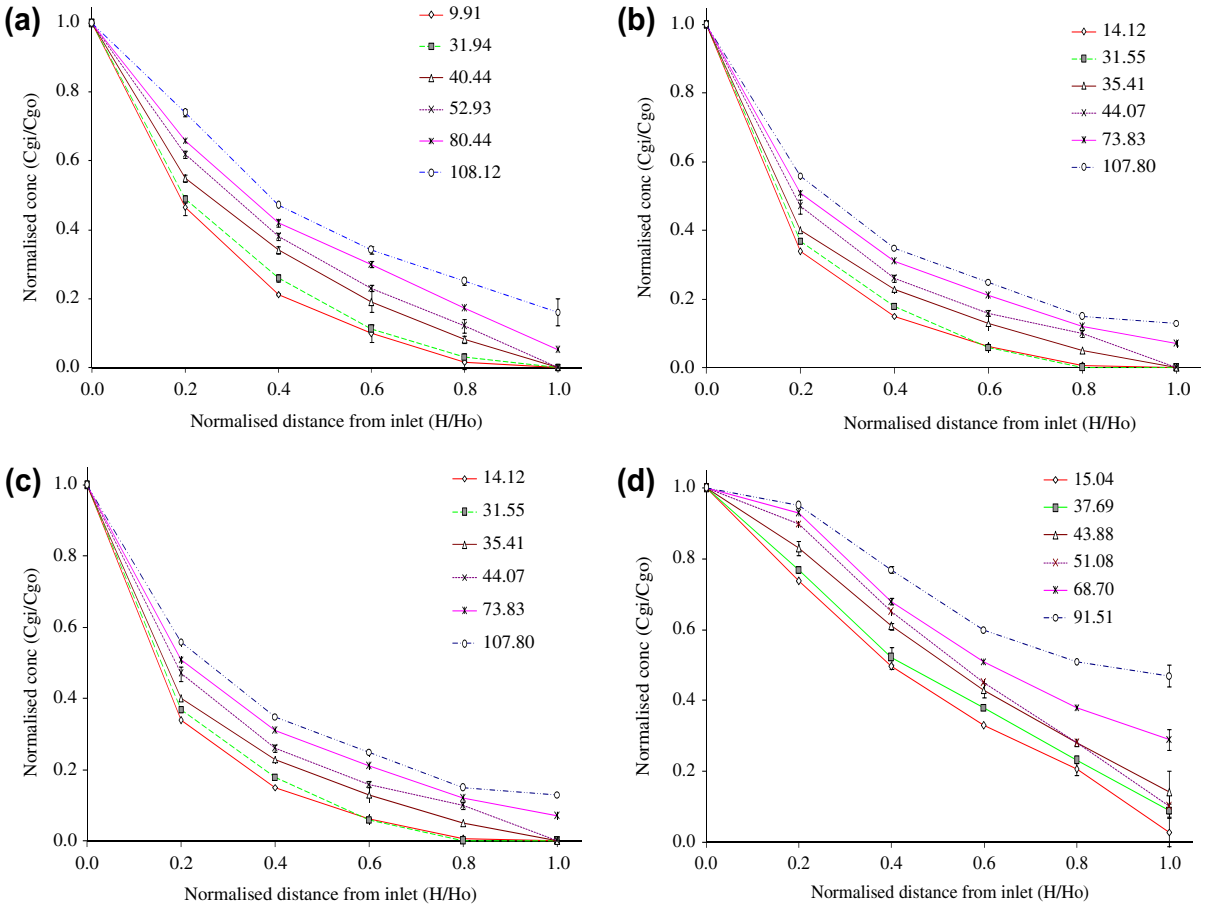


**Fig. 11.** Variation of concentrations of individual pollutants [(a) methanol, (b) ethanol, (c) acetone and (d) toluene] along the height of the biotrickling filter treating mixture of pollutants as a function of inlet loading rate.

there was a dense microbial population in the lower part of BTF than that in the upper part. It can be seen from Fig. 11 that with the increase in inlet concentration, Cgi/Cg0 increased significantly at the same height of BTF column. This may be due to the fact that large quantities of pollutants were available for the same microbial mass in the column, resulting in reaction limited operation of the BTF.

Mathur and Majumder [17] studied the degradation of a mixture of pollutants from paint industry in a BTF and their degradation profile along the height of BTF. Most of the MEK degradation occurred within the first 30 cm length of the BTF, where as o-xylene required the entire length of the BTF. Mohseni and Allen [31] studied transient and long-term performance of methanol and α-pinene mixture and found that most of the methanol was removed in the top portion of the biofilter, while degradation of α-pinene occurred over the entire biofilter depth. Aizpuru et al. [34] developed a biofilter packed with peat to treat a complex mixture of VOCs (oxygenated, aromatic, and chlorinated compounds). They reported that the oxygenated compounds were metabolized before the aromatic and halogenated ones. The oxygenated compounds were eliminated in the first 50 cm of column, while the aromatic and halogenated compounds were eliminated in the last 80 and 70 cm of the column, respectively.

## 4. Conclusion

The aim of the present study was to evaluate the performance of a BTF treating complex mixtures of VOCs from pharmaceutical industries. Effects of inlet concentration and EBRT on elimination capacity and removal efficiency were evaluated. Almost complete removal could be achieved up to an ILR of 240 g/m$^3$/h, while treating mixed pollutants. For individual pollutants, 100% RE was achieved for ILRs up to 320 g/m$^3$/h. The $EC_{max}$ for ethanol and acetone were 380 g/m$^3$/h, in a BTF treating individual pollutants, while $EC_{max}$ was only 320 g/m$^3$/h for the BTF treating mixed pollutants. The $EC_{max}$ for individual pollutants was much lower in a mixed pollutant system than that in a single pollutant system, due to competitive interactions. Among the four pollutants studied, toluene was the most resistant to degradation. Most of the alcoholic compounds degraded in the first 30 cm of biofilter. It was also observed that the RE achieved at different EBRTs, for each pollutant in the BTF, was highly dependent on the inlet loading rate (ILR) and nature of the pollutants. The inhibitory effect of aromatic compounds on the removal of aliphatic compounds has also been observed. Results from this study provide an insight into the interactive effects occurring during the biological treatment of a complex gaseous mixture containing organic hydrophilic and hydrophobic pollutants. They also help in selecting the operational parameters for BTF treating complex mixtures of VOCs emitted from pharmaceutical industries.

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