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Biotrickling filtration of complex pharmaceutical VOC emissions along with chloroform

P. Balasubramanian, Ligy Philip *, S. Murty Bhallamudi

Environmental and Water Resources Engineering Division, Indian Institute of Technology Madras, Chennai 600 036, India

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ABSTRACT

Biodegradation of chloroform along with a mixture of VOCs (methanol, ethanol, acetone and toluene) commonly found in pharmaceutical emissions using a biotrickling filter (BTF) was evaluated. The performance of the BTF was evaluated for both steady and transient conditions, for different inlet loading rates (ILR), empty bed residence time (EBRT) and inlet chloroform concentrations. Among the VOCs studied before chloroform feeding, toluene removal was the least, under all the operating conditions. Complete removal of all pollutants was achieved up to a chloroform loading rate of 14.22 g/m^3/h. Increase in loading rate of chloroform adversely affected the removal efficiency of toluene and declined the overall performance of BTF. The results suggest that biodegradation of VOCs is influenced by the inlet loading rate and complexity of pollutants in the inlet air stream. Results from studies on shock loading and starvation indicated that the system was highly resilient to transient operating conditions.

1. Introduction

Volatile organic compounds (VOCs) are an important class of emerging atmospheric pollutants due to their ozone depletion and global warming potential and toxicity. They are also carcinogenic. In particular, chlorinated VOCs (CVOCs) are of prime concern due to the severe impact they have on ecosystems. Application of biofiltration techniques such as biofilters (BF), bioscrubbers (BS), biotrickling filters (BTF) to control these emissions have gained attention in recent past due to their cost effectiveness and ability for complete mineralization of toxic pollutants (Dorado et al., 2008). A number of studies have been carried out to assess the viability of these technologies at an industrial scale (Sempere et al., 2011). Rene et al. (2012) investigated removal of styrene removal in a single and two phase BTF (without and with the addition of silicone oil) inoculated with fungi (*Sporothrix variecibatus*) under steady and transient state conditions. The transient nature of industrial gaseous emissions, with complex mixture of highly degradable and relatively recalcitrant VOC compounds, makes the process complicated (Atoche and Moe, 2004). Most of the earlier biofiltration studies have focused on the treatment of a single pollutant, mixtures of aromatic compounds such as benzene, toluene, ethyl benzene, and *o*-xylene (BTEX) (Chen et al., 2010; Mohammad et al., 2007), hydrophobic and hydrophilic compounds (Paca et al., 2007; Sempere et al., 2010) and mixture of hydrophobic VOCs and sulfur compounds (Lebrero et al., 2012). However, biofiltration studies for mixed pollutant removal along with chlorinated solvents are scant.

Feasibility of conventional biofiltration techniques such as BF and BTF for controlling various chlorinated compounds was demonstrated at laboratory scale by a few researchers. Studies on biodegradation of chlorinated compounds in BTF as single primary substrates such as chlorophenols (Nicolella et al., 2009), dichloromethane (Ravi et al., 2010), monochlorobenzene (Mpanias and Baltzis, 1998) and a mixture of monochlorobenzene and dichlorobenzene (Seignez et al., 2004) were reported earlier. These studies demonstrated that BTF is suitable for the effective treatment of CVOCs since the presence of trickling liquid retards the possible accumulation of toxic and acidifying compounds on the fixed bed. Higher order chlorinated compounds cannot contribute sufficient energy for metabolic activity during biodegradation (Field and Alvarez, 2004). The biodegradation of higher order CVOCs occurs mostly under cometabolic conditions in presence of primary substrates such as methane, propane, phenol and toluene. Although many studies have been carried out on aerobic biotransformation of chlorinated ethanes such as trichloroethene (TCE) and perchloroethene (PCE), not much work has focused on aerobic biotransformation of chlorinated methanes such as chloroform (CF) and carbon tetrachloride (CT). Hecht et al. (1995) have found that the removal efficiency of TCE in a column bioreactor varied between 30–80% when the inlet concentration of TCE was in the range of 0.07–0.40 mg/L. Removal efficiency was affected in presence of phenol as a primary substrate. It has also been found that the presence of chlorinated solvents can change the kinetics of pri-

* Corresponding author. Tel.: +91 44 22574274; fax: +91 44 22574252.
E-mail address: ligy@iitm.ac.in (L. Philip).

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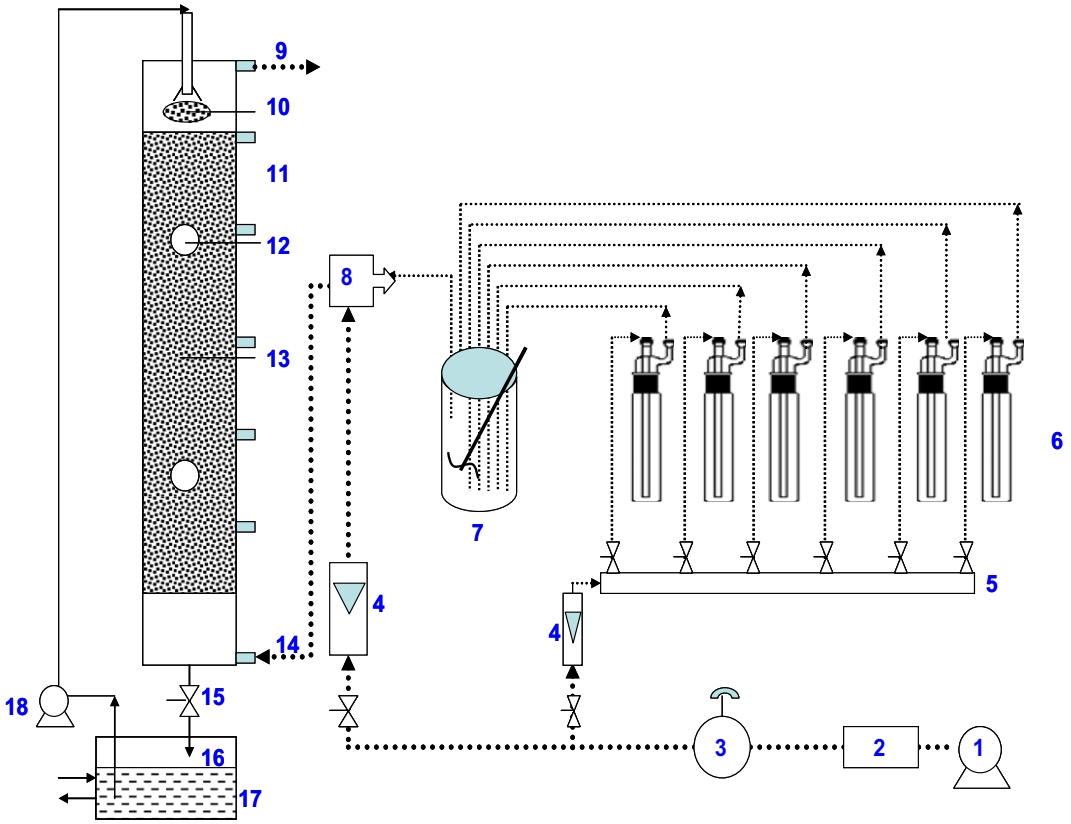

1) Aquarium air pump; 2) Air filter; 3) Air regulator; 4) Air flow rotameters (0.5 LPM & 15 LPM); 5) Air distribution chamber; 6) Impingers for various solvents; 7) Mixing chamber for solvents; 8) Connector for main air stream; 9) Gas outlet port; 10) Nutrient sprayer; 11) Gas sampling port; 12) Media sampling port; 13) Packing media; 14) Gas inlet port; 15) Flow controller; 16) Leachate; 17) Nutrient solution; and 18) Peristaltic pump.

Fig. 1. Schematic diagram of biotrickling filter.

mary substrate degradation and thus decreasing mineralization rate of chlorinated solvents (Cox et al., 1998). Jung and Park (2005) investigated the performance of various microorganisms and substrates such as toluene, cresol or phenol to co-metabolize TCE from contaminated air streams. Besides conventional biofiltration techniques, several other technologies such as hollow fiber membrane bioreactor (Zhao et al., 2011) and foamed emulsion bioreactor (Kan and Deshusses, 2006) were also applied for the removal of TCE.

Very limited studies have demonstrated the feasibility of treating gas streams contaminated with chlorinated solvents using bioreactors. Wilson et al. (1988) performed a detailed study on biodegradation of TCE and 1,1,1-trichloroethane (TCA), in presence of *n*-butane, using mixed culture. Speitel and McLay (1993) investigated the suitability of biofilm reactors for the treatment of gas streams containing chlorinated solvents. Yoon and Park (2002) evaluated the performance of a biofilter packed with peat compost for treatment of a VOC mixture with concentration as follows (g/m^3): benzene (4.5), toluene (15), *m*-xylene (15), *o*-xylene (15), styrene (15), chloroform (7.5), TCE (10), isoprene (4.5), and dimethyl sulfide (5). At an EBRT of 1.5 min and 32 °C, the removal efficiency was highest for isoprene (93%), and lowest for chloroform (84%). Earlier, Todd et al. (1996) also reported similar results. Den et al. (2003) investigated the transient and steady-state performance of a bench-scale biotrickling filter for the removal of an organic mixture of acetone, toluene, and trichloroethylene. Although many studies have been carried to improve the performance of BTF treating various pollutants, comprehensive studies have not been conducted for the performance evaluation of BTF treating mixtures of VOCs in pharmaceutical emissions. Also, the effect of chlorinated compounds such as chloroform on the performance of BTF treating hydrophobic and hydrophilic VOCs has not been studied.

This study attempts to evaluate the performance of a BTF for the treatment of chloroform along with quaternary mixture of VOCs in emissions from pharmaceutical industries. The selected mixture includes representative members of hydrophilic and hydrophobic compounds, with different physical and chemical properties, commonly found in pharmaceutical industries. The compounds employed in the present study include methanol, ethanol (representative of alcohols), acetone (representative of ketones) and toluene (representative of aromatic compounds). The effects of starvation, shutdown and shock loads on performance of BTF were also investigated.

2. Materials and Methods

2.1. Materials

2.1.1. Microorganism and culture media

The BTF was inoculated with a mixed microbial consortium previously utilized for the biodegradation of various groups of pesti-

Table 1
Operational schedule of biotrickling filter treating mixed pollutants.

Phase	Time, days	EBRT, s	Inlet concentration		Volumetric flow rate, m^3/h	Theoretical loading rate, $g/m^3/h$
			VOC g/m^3	Chloroform g/m^3		
Start up of BTF						
I	0–57	68.6	1	–	0.09	52.42
Performance evaluation of BTF without chloroform						
II	58–97	51.5	2	–	0.12	139.78
III	98–121	41.2	2	–	0.15	174.72
IV	124–142	34.4	2	–	0.18	209.67
V	143–161	34.4	3	–	0.18	314.50
VI	162–178	25.0	3	–	0.24	419.34
Performance evaluation of BTF with chloroform						
VII a	179–185	34.4	2	0.05	0.18	214.91
VII b	186–195	34.4	2	0.10	0.18	220.15
VII c	196–203	34.4	2	0.25	0.18	235.88
VII d	204–210	34.4	2	0.50	0.18	262.09
VII e	211–213	34.4	2	1.00	0.18	314.50
VII f	215–219	34.4	2	0.00	0.18	209.67
Shutdown and restart						
VIII a	220–221	34.4	2	–	0.18	209.67
VIII b	223–224	34.4	2	–	0.18	209.67
VIII c	227–236	34.4	2	–	0.18	209.67
Shock loads						
IX	239–263	68.6–20.6	1–4	0.05–1.0	0.09–0.30	52.42–528.89

cides (lindane, methyl parathion, carbofuran) by Ramakrishna and Philip (2009) and for biodegradation of various groups of VOCs (alcohols, ketones, aromatics, chlorinated solvents) by Balasubramanian et al. (2011). The consortium consisted of aerobic and facultative anaerobic bacterial species with predominant strains of *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: $Na_2HPO_4.2H_2O$ (3.5), KH_2PO_4 (1), $(NH_4)_2SO_4$ (0.5), $MgCl_2.6H_2O$ (0.1), $Ca(NO_3)_2.4H_2O$ (0.05), trace elements I (1 mL). Trace elements I contains: EDTA (0.5), $FeSO_4.7H_2O$ (0.2) and trace elements II (100 mL). Trace elements II contains: H_3BO_3 (0.3), $MnCl_2.4H_2O$ (0.03), $CoCl_2.6H_2O$ (0.2), $ZnSO_4.7H_2O$ (0.1), $Na_2MoO_4.2H_2O$ (0.03), $NiCl_2.6H_2O$ (0.02) and $CuCl_2.2H_2O$ (0.01).

2.1.2. Packing media

The packing media (Fujino spirals, India) was made up of polyvinyl chloride. The average size of the packing media was 13 mm, with a maximum surface area around 600 m^2/m^3. The average weight of one piece of the packing media was 700 ± 58 mg and it ranged from 645 to 800 mg. The specific gravity and density of the packing media were 1.30 and 210 g/L, respectively. The number of packing media utilized in this study was 425 and the overall weight of the packing media and wetted water in the reactor were 350.3 and 177.9 g, respectively. The initial porosity of the packed bed before inoculation of microbes was 0.79.

2.2. Analytical procedures

2.2.1. VOC analyses

Liquid samples were analyzed using PerkinElmer 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 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 per the standard method suggested by Lodge (1991). The liquid samples were 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 every day and the standard deviation was less than 4%. Air samples of 0.5 mL were drawn from inlet and outlet sampling ports with a 1.0 mL gas-tight syringes (SGE, Australia) fitted with 3-way Luer-Lock (BD Connecta, Sweden), and directly injected into GC.

2.3. Biotrickling filter operation

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. The minor stream was bubbled through a series of glass bubblers filled with methanol, ethanol, acetone, toluene and chloroform and then mixed with the major part of the air stream. By regulating the volumetric flow rates of two streams, synthetic air streams loaded with different concentrations of CF vapor were obtained. The streams were combined in a mixing chamber and fed to the bottom of the BTF column in a counter-current flow mode.

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

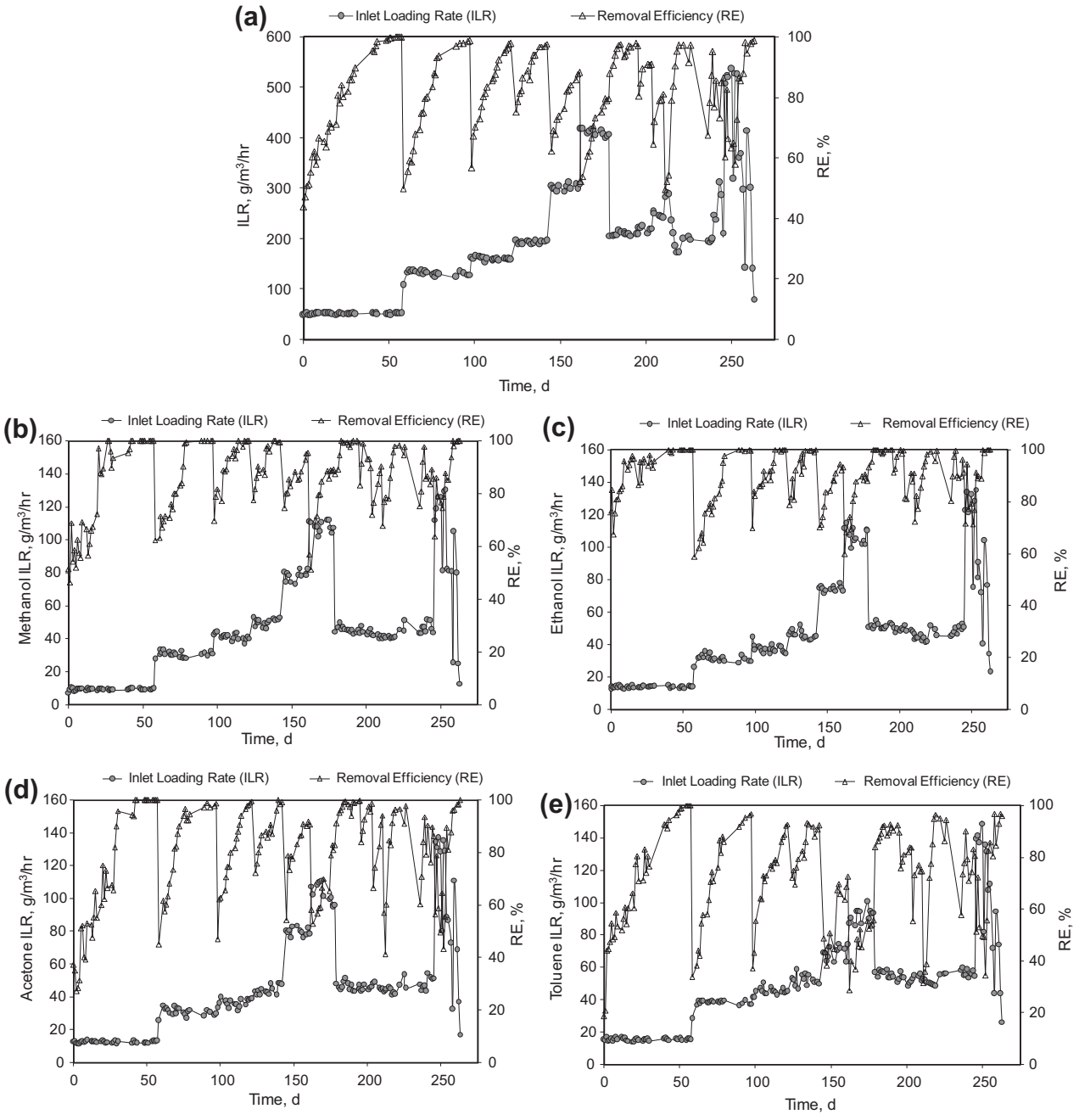

Fig. 2. Overall performance profile of (a) total VOCs (b) methanol, (c) ethanol, (d) acetone and (e) toluene in the biotrickling filter while treating mixture of pollutants.

measured by GC analysis. Concentrations of VOC 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 using a balance (National instrumentation, India) with a precision of 0.5 g once the recycle medium was drained for 30 min. The performance of the BTF was studied for 263 days including 28 days of the acclimatization period. The BTF performance during the period day 29 to day 178 was evaluated without chloroform. Following this performance of the BTF was evaluated for chloroform removal for 40 days and shutdown and shock loads for the next 44 days.

2.4. Start up, operation and performance evaluation of BTF

Prior to BTF start up, the packing materials were sterilized and soaked in a nutrient solution for overnight. Later, BTF was drained and the inoculum (50 g of concentrated biomass in 1 L of mineral salt medium) was recirculated at a flow rate of 1 L/h for 12 h. After draining the inoculum from the columns, the contaminated air stream was supplied to each bioreactor. During the first 28 days of operation, the reactor was operated in a closed loop mode. The liquid was changed once in every four days in order to maximize the cell adhesion to the packing. In order to shorten the start-up stage of the experiment, 1 g/L liquid phase mixed pollutant was added to the cycled nutrient medium and gas with 1 g/m^3 of mixed pollutant concentration was fed to the BTF at the same time.

Table 2
Overall performance of biotrickling filter treating chloroform along with mixed pollutants.

Phase	Time, days	Range	Inlet conc., g/m^3		Outlet conc., g/m^3		Removal efficiency, %		Loading rate, g/m^3/h		Elimination capacity, g/m^3/h	
			Total	CF	Total	CF	Total	CF	Total	CF	Total	CF
VII a	179–185	Min	1.9531	0.0531	0.0471	0.0010	87.83	56.56	204.75	5.57	180.97	3.34
		Max	2.0576	0.0581	0.2392	0.0245	97.68	98.24	215.71	6.09	210.05	5.88
		Ave	1.9929	0.0561	0.1200	0.0102	93.93	81.82	208.92	5.88	196.34	4.82
VII b	186–195	Min	1.9668	0.1217	0.0441	0.0030	93.48	55.37	206.19	12.76	195.82	7.14
		Max	2.0534	0.1356	0.1339	0.0549	97.79	97.53	215.27	14.22	204.19	12.96
		Ave	1.9964	0.1281	0.0824	0.0197	95.89	84.69	209.30	13.43	200.66	11.37
VII c	196–203	Min	2.0197	0.2542	0.1853	0.0577	80.49	61.54	211.73	26.65	178.47	16.97
		Max	2.1474	0.2778	0.4126	0.1012	90.92	77.31	225.12	29.12	201.43	21.35
		Ave	2.0972	0.2643	0.2551	0.0744	87.87	71.88	219.86	27.71	193.13	19.91
VII d	204–210	Min	2.3067	0.5133	0.4348	0.1883	64.46	50.13	241.82	53.81	163.49	28.43
		Max	2.4195	0.5457	0.8600	0.2698	81.15	63.32	253.65	57.21	196.24	35.56
		Ave	2.3562	0.5326	0.5876	0.2184	75.17	59.04	247.01	55.83	185.41	32.93
VII e	211–213	Min	2.7059	0.9973	1.2531	0.5875	49.51	39.03	283.67	104.55	140.46	40.80
		Max	2.7619	1.0254	1.3661	0.6081	54.36	42.71	289.54	107.50	156.48	45.91
		Ave	2.7378	1.0145	1.3136	0.6002	52.01	40.82	287.02	106.35	149.31	43.43
VII f	214–219	Min	1.6538	0.0000	0.0707	0.0000	79.05	0.00	173.37	0.00	159.26	0.00
		Max	2.2520	0.5011	0.4718	0.1198	95.73	98.95	236.09	52.53	186.63	39.97
		Ave	1.8668	0.1817	0.2350	0.0339	88.13	51.88	195.71	19.04	171.07	15.49

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 (ILR, g/m^3/h) and empty bed residence times (EBRT, 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. Outlet VOC concentration was 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 operational history of the BTF is presented in detail in Table 1.

2.5. Starvation and shock loads of BTF

The effect of transient state conditions such as starvation and shutdown on BTF was assessed under three different conditions: (i) short term starvation (2 days experiment), when only air was supplied to the reactor without any VOCs for 2 days to simulate the shutdown conditions; (ii) short term shut down (2 days experiment) and (iii) long term shut down (9 days experiment). On these shutdown experiments both air and VOC supplies were terminated for the respective days.

3. Results and discussion

3.1. Start up and performance evaluation of the biotrickling filter before chloroform loadings

During the start up of the experiments, the reactor was operated in a closed loop mode with respect to liquid to maximize cell adhesion to the packing media. The inoculation of the biomass through trickling liquid helped in accelerating the establishment of an active microbial population in the packed bed. A bacterial consortium adapted for degradation of chlorinated and non chlorinated organic solvents were utilized in this study. Inoculation of BTFs for mixed pollutant removal by communities adapted to those contaminants has been shown to shorten the start-up period considerably as outlined by Veiga and Kennes, (2001). As shown in Fig. 2, the influent VOC concentrations fluctuated slightly during the loading period but were close to the target values. Effects of inlet concentration and EBRT on EC and RE were evaluated. The net inlet concentration was varied from 1 to 4 g/m^3 to achieve ILR variation between 52 and 419 g/m^3/h. The EBRT was varied from 25 to 69 s. Almost complete removal of all the pollutants was achieved up to an ILR of 240 g/m^3/h, while treating mixed pollutants. Among the four pollutants studied, toluene was the most resistant to degradation. Most of the alcoholic compounds degraded in the first 30 cm of the BTF. It was also observed that the RE achieved at different EBRTs, for each pollutant in the BTF, was highly dependent on the ILR and nature of the pollutants.

The inlet concentration was maintained at 2 g/m^3 and the air flow rate was varied to study the effect of EBRT on the performance of BTF treating mixed pollutants. The variation in air flow rate resulted in different EBRTs of 51.5, 41.2 and 34.4 s. As evident from Fig. 2, the BTF performed quite satisfactorily even when the EBRT was low. This is because of high concentrations of acclimatized biomass within the BTF as the time progressed. Maximum removal efficiencies of 98.69%, 97.85% and 97.70% were observed for EBRTs of 51.5, 41.2 and 34.4 s, respectively, when the inlet concentration was maintained at around 2 g/m^3. In phase-III, the porosity of the packed bed decreased from 0.8 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 packed bed reactor was backwashed by filling trickling liquid to two-thirds height of the BTF while simultaneously air was blown for 5 min to remove excess biomass. After the backwash, biomass concentration in BTF reduced from 1067 to 736 g, and

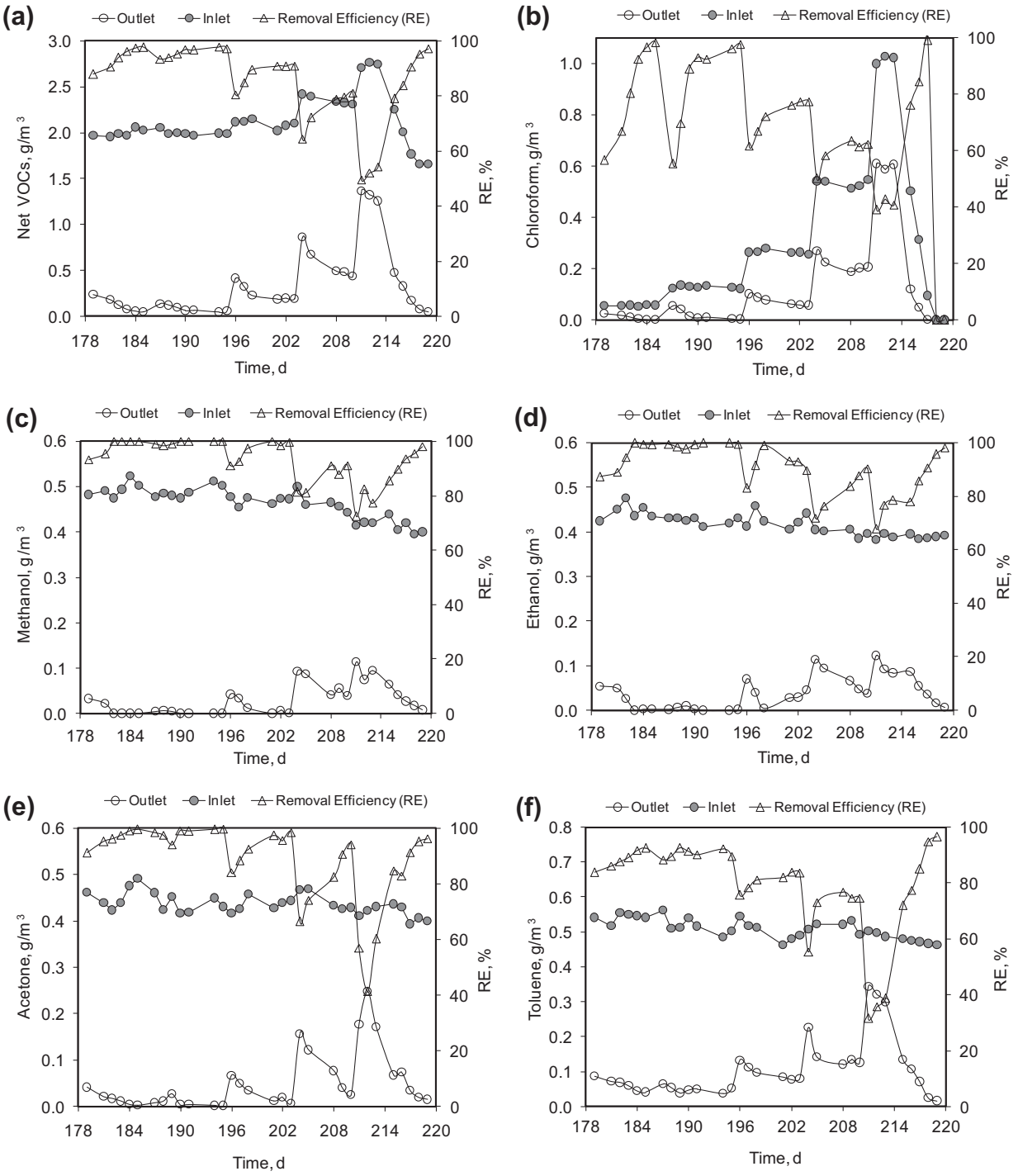

Fig. 3. Performance of biotrickling filter with respect to removal of (a) total VOCs, (b) chloroform, (c) methanol, (d) ethanol, (e) acetone and (f) toluene during chloroform feeding along with mixture of pollutants.

pressure drop across the bed reduced from 2 to 1 cm of H_2O. The porosity after the backwash was 0.74. The system performance declined significantly to 88.13% for higher inlet concentrations (3 g/m^3) and lower residence times (25 s). The effect of gas flow rate on removal efficiency of various individual concentrations for a total inlet concentration of 2 g/m^3 of mixed compounds before chloroform feeding is presented in Fig. 2. It has been found that the inlet concentration and the amount of biomass present in the reactor were the most influencing parameters for the BTF performance.

3.2. Performance evaluation of the biotrickling filter during chloroform loadings

The main objective of this study was to understand the effect of chloroform on the removal of mixed pollutants in a BTF. Therefore, the concentration of the chloroform alone was varied and all other parameters were kept constant throughout this phase. The inlet load of mixed pollutants were maintained around 209 g/m^3/h as almost complete removal was achieved up to an ILR of 240 g/m^3/h. The mass loading rate of chloroform was increased gradually

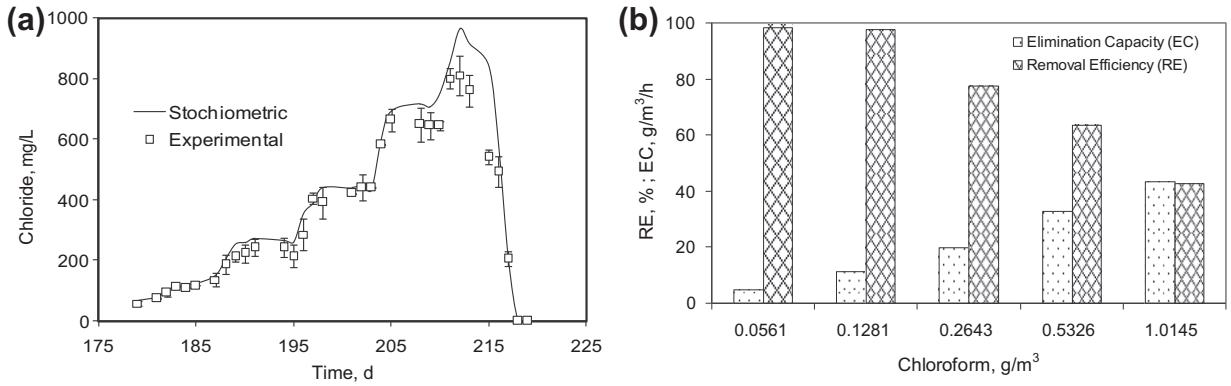

Fig. 4. (a): Stoichiometric and experimental chloride concentrations in the trickling liquid during biotrickling filtration of chloroform. (b): Effect of inlet chloroform concentration on removal efficiency and elimination capacity.

by increasing the gaseous inflow concentration to the bubbler containing chloroform. The EBRT during this phase was also kept constant at 34.4 s as in phase IV. The overall performances of biotrickling filter treating chloroform along with mixed pollutants were summarized in Table 2.

In phase VII (day 179 to 219), the BTF was subjected to different loading rates of chloroform to study the performance of the reactor while treating chloroform along with mixture of compounds. The performance of the BTF with respect to removal of chloroform and VOCs during this phase is shown in Fig. 3. Before chloroform loading was initiated, the system had a biomass of around 1065 g as wet weight and the pressure drop was 1.8 cm of H_2O. On day 179 (the first day of chloroform feeding), CF removal efficiency of 56.56% was observed. The system was already effective in toluene removal by the secretion of oxygenases enzymes, which might have triggered the cometabolic biodegradation of chloroform. Das et al. (2011) reported toluene as the main substrate for oxygenase enzyme responsible for removal of toluene and TCE.

At this stage, the RE of total VOCs dropped from 100% to 87.83% due to the presence of chloroform in the feed. REs of methanol and ethanol were almost 94%, while they were 91.13% and 83.83% for acetone and toluene, respectively. The performance of the system with respect to chloroform removal improved steadily and reached the maximum value of 98.24% within five days. At this stage, REs for methanol and ethanol were almost 100%, while REs for acetone and toluene were 99.51% and 92.50%, respectively. The biomass was 1094 g and the pressure drop was of 1.8 cm of H_2O. Fig. 4 (a) shows the theoretical and measured chloride concentrations in the trickling fluid over 40 days of the BTF operation. The chloride ion concentration in the trickling liquid correlated stoichiometrically with the chloride concentration in chloroform supplied to the BTF. Theoretical values of chloride concentrations were calculated assuming that complete mineralization of chloroform occurred for the reported efficiency of biodegradation in BTF. The experimental value matched well with the theoretical value up to the chloroform loading rate of 14.22 g/m^3/h where 100% RE was observed. At higher chloroform loading rates, there was significant mass balance error (17%) for free chloride ion. In the case of biological degradation of chlorinated compounds, the released hydrochloric acid should be effectively neutralized/removed in order to avoid a pH reduction and/or too high ionic strength, leading to a reduction in metabolic activity (Seignez et al., 2004). Degradation of chloroform acidifies the trickling liquid by releasing hydrochloric acid. However, in this study, highly buffered nutrient medium was used as trickling liquid to maintain the pH at 7.0 ± 0.2. However, at high inlet chloroform concentrations, the pH dropped to 6.7 in some instances.

The overall performance of the BTF with respect to removal of individual compounds during phase VII is presented in Fig. 3. Removal efficiency of 100% was achieved for inlet chloroform loading rates of 5.88 and 14.22 g/m^3/h. The RE for mixed VOCs was around 97.79% for these chloroform loading rates and REs for individual VOCs remained almost the same. As the chloroform loading rate increased beyond 14.22 g/m^3/h; complete removal of chloroform could not be accomplished at the corresponding mixed VOC loading rate of 209 g/m^3/h. At high chloroform loading rates, removal efficiencies of alcohols such as methanol and ethanol were not affected significantly, while REs of toluene and acetone reduced significantly (Fig. 3).

As the inlet CF loading rate was further increased to 27.71 and 55.83 g/m^3/h, RE gradually decreased. REs of chloroform for these two loading rates were 77.31% and 63.32%, respectively. Corresponding mixed VOC loading rates were 225.12 and 253.65 g/m^3/h and REs for total VOCs dropped to 90.92% and 81.15%, respectively. The biomass growth during this phase was only 50 g and there was no significant increase in pressure drop. Except for toluene, all other compounds achieved 99% removal. RE for toluene was 84.02% for an inlet mixed VOC loading of 225.12 g/m^3/h. Thus along with chloroform, the net system performance was around 90.92%. When the net inlet loading rate of VOCs was increased to 253.65 g/m^3/h by increasing CF loading rate to 57.21 g/m^3/h, REs for individual pollutants, except toluene were above 90%. RE for toluene was 76.85%. The RE of chloroform was only 42% when the CF loading rate was further increased to 107.5 g/m^3/h. The corresponding VOC loading rate was 289.54 g/m^3/h and the RE for total mixed VOCs was 54.36%, while REs of individual compounds like methanol, ethanol and acetone dropped significantly to 67.84%, 72.32%, and 41.36%, respectively. In addition, the toluene removal was also affected considerably and the RE dropped to 39.03%. High mass loading rate of chloroform to the BTF deteriorated the system performance. However, the system could be rejuvenated after the discontinuation of chloroform loading. Maximum REs achieved for methanol and ethanol were 78.54% and 82.24%, respectively, while REs of acetone and toluene reduced significantly to 42.71% and 38.69%, correspondingly. The biomass concentration at this stage was around 1250 g and the pressure drop was 2 cm of H_2O. The effect of inlet chloroform concentration on removal efficiency and elimination capacity of chloroform is shown in Fig. 4(b). The poor removal efficiency at higher CF loading rate can be attributed to low residence time for CF biodegradation as well as to substrate inhibition. Similar observations were earlier reported by Kocamemi and Cecen (2007) while studying TCE degradation.

One substantial problem concerning the use of BTF for the control of chlorinated solvents is the rapid deactivation of the

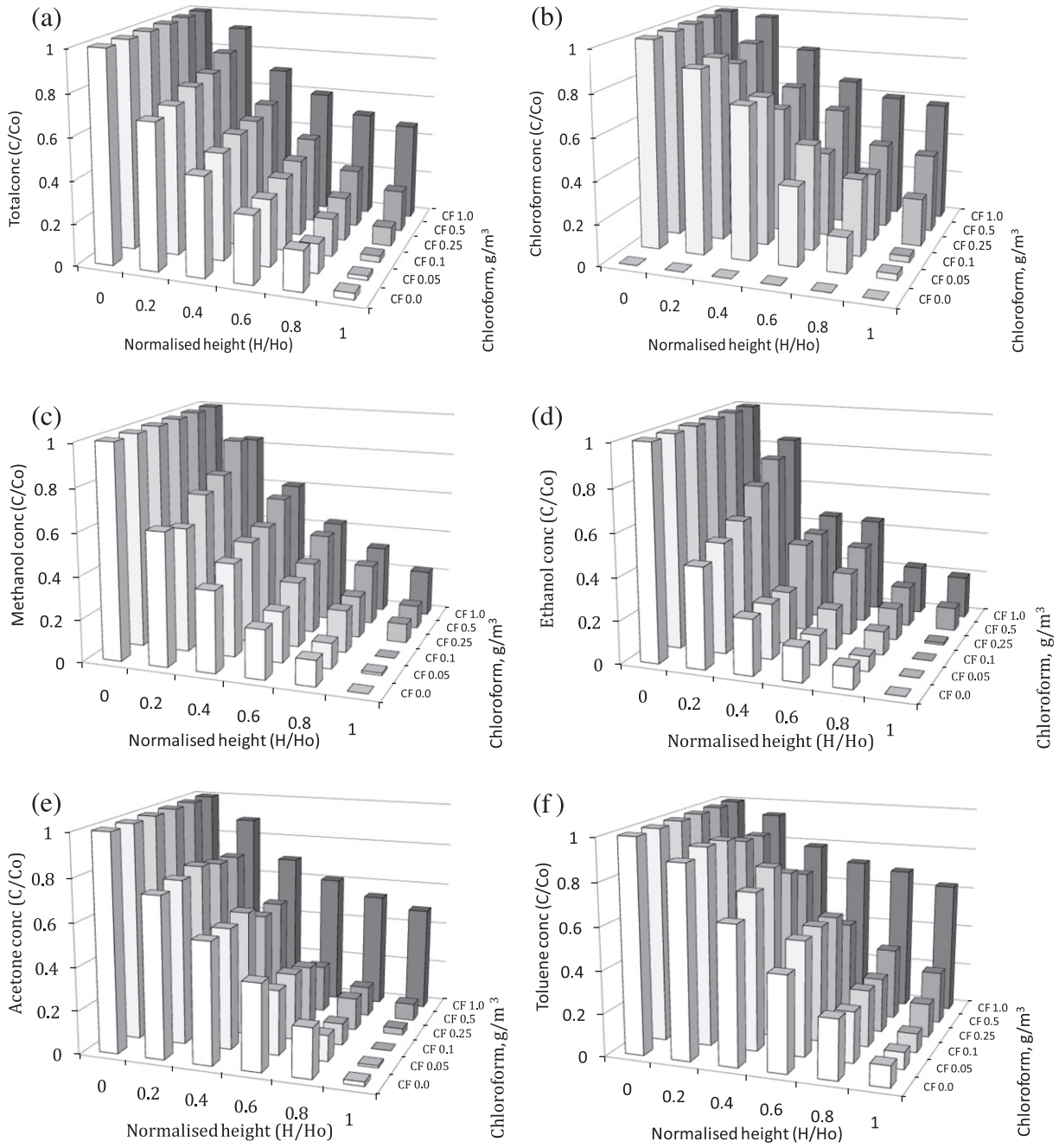

Fig. 5. Concentration profile of (a) total VOCs, (b) chloroform, (c) methanol, (d) ethanol, (e) acetone and (f) toluene along the height of the biotrickling filter treating chloroform along with mixture of compounds.

biomass due to its toxicity from either parent/metabolites or sudden drop in pH (Lee, 2003). The effect of substrate interactions on the biofiltration efficiency, due to the presence of chlorinated solvents among other volatile pollutants, has also been studied by Yoon and Park (2002) and Den et al. (2004). A consortium of microorganisms is normally required to achieve high RE for each compound. It has been demonstrated that mixed bacterial consortium reduced the toxicity of chlorinated solvents and its by-products as the consortium would increase the stability of the biomass and enables efficient and long term operation (Den et al., 2004). It is observed from the present study that the applicability of cometabolism for the degradation of CVOCs is limited due to the decreased cell activity, resulting from the toxic effect of intermediates and the competitive inhibition by primary substrates.

Cox et al. (1998) found temporary toxicity effect due to increase in the TCE concentration in a BTF. This further reduced the toluene degradation efficiency because increased toluene concentration resulted in competitive advantage of toluene that inhibited TCE degradation. In the present study, toluene and chloroform removals were comparable. Among the mixed VOCs fed to the BTF, biodegradation of toluene and acetone might have triggered the secretion of monoxygenases enzyme which simultaneously biodegraded chloroform. Similar observations were reported by other researchers for biodegradation of chloroform with toluene as a growth substrate (Balasubramanian et al., 2011; Chauhan et al., 1998).

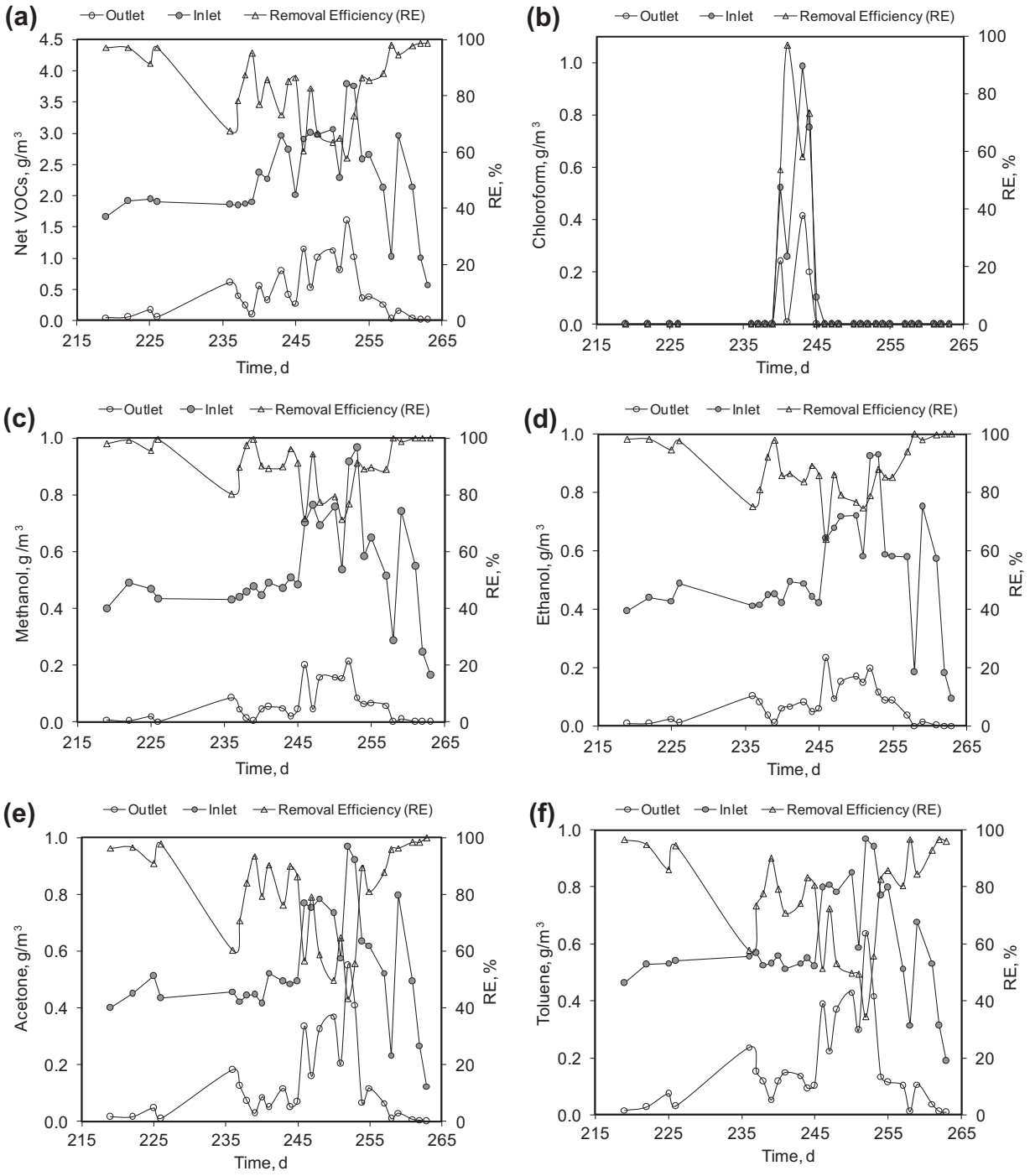

Fig. 6. Effect of shock loads on removal of (a) total VOCs, (b) chloroform (c) methanol, (d) ethanol, (e) acetone and (f) toluene in the biotrickling filter treating chloroform along with mixture of VOCs.

3.3. Degradation variation along the bed height of the BTF

Concentration profiles of CF and other individual VOCs along the depth of the BTF, for various CF inlet loading rates during pseudo steady state conditions are presented in Fig. 5. Atleast 50% of total VOC was removed at a height of almost 30 cm from the inlet of the column for a chloroform loading rate of 5.88 g/m^3/h. It can be observed from Fig. 5 that 74% of removal was achieved within the first 30 cm of BTF for ethanol; where as only 50% of acetone and methanol were removed. Chloroform and toluene degraded up to 25% in this portion. However, at the exit of the column, solvents other than toluene were below detectable limit. Similar trend was observed when the chloroform loading rate was 14.22 g/m^3/h. Further increase in chloroform loading rate to 27.71 g/m^3/h did not have much impact on the total RE of the mixed pollutant. However, 16% and 23% of the toluene and chloroform remained untreated at the outlet of the column. Further increase in chloroform loading rate to 55.83 and 107.85 g/m^3/h severely affected the RE of both chloroform as well as the total pollutants. The high removal near the inlet of column is due to the higher growth rates achieved near the gas inlet, generating biomass stratification along the bioreactor. Similar observations were reported by many researchers

especially in the reactors treating multiple pollutants. Sun and wood (1997) reported similar biomass stratification during TCE mineralization in a fixed film bioreactor. Mathur et al. (2006) studied the removal kinetics of mono-chlorobenzene vapour from waste gases using a trickle bed air biofilter and found that the removal was more in the bottom of the filter and the concentration profiles decreased along the bed from the inlet to outlet (i.e. from bottom to top) due to biodegradation.

3.4. Performance evaluation of the biotrickling filter during starvation

Performance of the BTF for starvation, shut down and shock load conditions was also evaluated in order to depict the real life scenarios. The effect of transient state conditions on the BTF performance was evaluated for three different conditions: (i) short term starvation, (ii) short term shut down and (iii) long term shut down. EBRT of BTF was maintained at 34.4 s and inlet total VOC loading rate was 209.67 $g/m^3/h$ during this study. The overall effects of starvation on performances of BTF treating mixture of VOCs and for individual pollutant removal for various starvation periods are shown in Fig. 6. As anticipated, the RE of toluene and acetone were affected more severely than that of alcohols.

In short term starvation study, where only air was supplied to the reactor without any VOCs for two days, the BTF regained its performance within 2 h of startup. The overall RE of the BTF after 2 days of starvation reduced to 93.54%, which is much lower than that before starvation (98.25%). However, the system performance improved within 2 h of feeding and the RE increased to 98.57%. Alcohols achieved 100% removal within 5 h. The continuous supply of air might have kept the microbial population alive and active in the biofilm, which helped in fast recovery of the elimination capacity.

During the second starvation study, both air and VOC supplies were terminated for 2 days. In this case, the reactor took 6 h to approach the normal efficiency upon restart. The RE of total VOCs reduced to 81.14% from its earlier value of 99%. REs of methanol, ethanol, acetone and toluene were 85.52, 89.70, 78.41 and 71.87%, respectively. In the third starvation study, the reactor was kept devoid of air and VOC supply for 9 days and the system took almost 72 h to regain the original efficiency after restart. The overall RE reduced drastically to 63.57% with more than 70% removal efficiency for alcohols. REs of acetone and toluene were 56.43 and 49.59% due to this sudden loading after the prolonged starvation.

3.5. Performance evaluation of the biotrickling filter during shock loads

BTF performance was also evaluated for shock load conditions, in which the inlet VOC loading rate was varied instantaneously, to assess the robustness of the BTF following periods of shock loads. Second phase of transient-state experiments were carried out from day 240 to day 263. The transient state conditions consisted of rapid change in the mass loading rate. The performance of the BTF with respect to removal of overall RE of VOCs and chloroform during shock loads is shown in Fig. 6.

Once the system regained to its original performance after shutdown for nine days, on day 240, inlet chloroform loading rate was increased suddenly to 55 $g/m^3/h$ and the corresponding total VOC loading rate was 247.71 $g/m^3/h$. Due to this sudden loading of chloroform, the system performance for the total VOC removal reduced to 76.81% from its steady state RE value of above 95%. At this loading rate, the chloroform removal was only 53.68% which is much lower than that of 63.32% achieved during previous stage. RE of alcohols was above 80%, while the acetone and toluene attained around 80% removal efficiency. This indicates that the BTF performance was moderately affected by this shock load. Following this sudden shock load, the chloroform concentration was further varied randomly on successive days to 0.25, 1.0, 0.75 and 0.1 g/m^3 (corresponding chloroform loading rates were 26.65, 106.35, 57.21 and 14.22 $g/m^3/h$) to assess the system performance. It was observed that the system performed well for lower concentrations of chloroform. For chloroform loading rates of 0.25 and 1.0 g/m^3, the BTF achieved chloroform removal of 96.97% and 58.10%. REs for total pollutants were 85.62% and 73.23%, respectively. Subsequently, the BTF was subjected to various mixed pollutant loads without chloroform from day 245 until the end of the study period to assess the system performance for mixed pollutants removal for dynamic conditions. Limitations of carbon and energy sources during the starvation and shutdown periods might have caused the loss of viable microbes, resulting in temporary decline in performance during transient state. Similar behavior was reported by many other researchers. For instance, Den et al. (2003) experienced efficiency recovery of BTF treating TCE within 2 days after a two fold increase of total hydrocarbon concentration. The performance of the BTF with respect to removal of various individual compounds during shock loads is shown in Fig. 6. The order of biodegradability of the individual compounds during steady state and transient state experiments were as follows: ethanol > methanol > acetone > toluene > chloroform. The bioreactor was resilient to shock load ranges tested in our experiments and the BTF regained its original performance within few hours. The EC increased simultaneously with increase in ILR.

4. Conclusions

Steady and transient state performance of a lab scale biotrickling filter for the treatment of waste gas emissions from pharmaceutical industry was evaluated. Complete removal of all the pollutants was achieved up to an inlet chloroform loading rate of 14.22 $g/m^3/h$ and mixed VOCs loading rate of 209 $g/m^3/h$, with residence time of 34.4 s. Increasing chloroform loading rate significantly affected the degradation efficiency of aromatic compounds. BTF was highly resilient to transient operating conditions. Results from this study will help in evolving better operational strategies for BTFs treating a wide range of pollutants, including chlorinated solvents.

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