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Performance of a biofilter for the removal of high concentrations of styrene under steady and non-steady state conditions

Eldon R. Rene, María C. Veiga, Christian Kennes*

Chemical Engineering Laboratory, Faculty of Sciences, University of La Coruña, Rua Alejandro de la Sota, 1, E-15008 La Coruña, Spain

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ABSTRACT

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Keywords: Volatile organic compounds Biofiltration Styrene Perlite Elimination capacity Removal efficiency Relative humidity Transient operations The performance of a laboratory scale perlite biofilter inoculated with a mixed culture was evaluated for gas phase styrene removal under various operating conditions. Experiments were carried out by subjecting the biofilter to different flow rates $(0.15-0.9 \text{ m}^3 \text{ h}^{-1})$ and concentrations $(0.03-17.3 \text{ g m}^{-3})$, corresponding to inlet loading rates varying from as low as $3 \text{ gm}^{-3} \text{ h}^{-1}$ to as high as $1390 \text{ gm}^{-3} \text{ h}^{-1}$. A maximum elimination capacity (EC) of 382 g m⁻³ h⁻¹ was achieved at an inlet loading rate of 464 g m⁻³ h⁻¹ with a removal efficiency of 82%. The high elimination capacity reached with this system could have been due to the dominant presence of filamentous fungi among others. The impact of relative humidity (RH) (30%, 60% and >92%) on the biofilter performance was evaluated at two constant loading rates, viz., 80 and 260 g m⁻³ h⁻¹, showing that inhibitory effects were only significant when combining the highest loads with the lowest relative humidities. Biomass distribution, moisture content and concentration profiles along the bed height were significantly dependent on the relative humidity of the inlet air and on the loading rate. The dynamic behaviour of the biofilter through vigorous short and long-term shock loads was tested at different process conditions. The biofilter was found to respond apace to rapid changes in loading conditions. The stability of the biomass within the reactor was apparent from the fast response of the biofilter to recuperate and handle intermittent shutdown and restart operations, either with or without nutrient addition.

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1. Introduction

Styrene (C₆H₅CH=CH₂) is an essential and important chemical feedstock, which is used commonly as a raw material for the synthesis of plastics, synthetic resins, butadiene-styrene latex, styrene co-polymers and unsaturated polyester resins [1]. The widespread use of styrene in various industrial operations, its high vapour pressure (0.67 kPa at 20 °C) and high polarity characterized by its water solubility (0.3 g l⁻¹ at 20 °C) warrants its removal from point sources before its emission into the natural environment. It is reported to have significant effect on human health. Exposure to even low concentrations of styrene could cause contact-based skin inflammation, irritation of the eyes, nose and respiratory tract, and may induce narcotism [2]. On the other hand, it has also been reported to pose severe human health issues because of its toxicity and carcinogenicity [3,4].

Biodegradation is a promising alternative for the complete mineralization of volatile organic compounds (VOCs) to innocuous end products. Biotechnological waste gas treatment technologies are efficient, reliable, rather simple to operate, cost effective and do not expend energy/chemicals unlike conventional physico-chemical treatment processes. The most widely used biological processes for waste gas treatment are biofilters and biotrickling filters [5,6]. Biofilters have also proven to be effective in treating large volumes of individual and mixtures of VOC at relatively high concentrations [7,8]. The removal and oxidation rates of these hazardous contaminants count principally on the biodegradability, reactivity and largely on the solubility of the pollutant in the liquid layer of the biofilm. The effectiveness of the organic biofilter depends on the health and effectiveness of microbes in the biofilm at capturing and decomposing the target pollutants. Biofiltration studies have been tested with different packing materials and with a wide variety of pollutants having different degradation rates. Typical examples are biofilters packed with perlite as inert carrier material that have been used to treat styrene or alkyl benzene vapours [7,9,10].

For styrene removal in biofilters, individual or mixed species of bacteria have generally been used according to literature. *Pseudomonas* sp. represents the most common group of isolates capable of styrene degradation and has been shown to produce styrene mono-oxygenase, which plays a major role in styrene degradation [11]. Juneson et al. [12] investigated styrene removal using a styrene enriched culture in a biofilter packed with composted wood bark mixed with yard wastes and observed maximum removal rates of 271 and 334 g m⁻³ h⁻¹ at 60 and 30 s empty bed residence

^{*} Corresponding author. Tel.: +34 981 167000x2036; fax: +34 981 167065. *E-mail address:* Kennes@udc.es (C. Kennes).

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time (EBRT). Similarly, a mixed culture biofilter packed with perlite showed maximum elimination capacity (EC) of 145 g m⁻³ h⁻¹ [13]. [ang et al. [14] used *Pseudomonas* sp. in a biofilter packed with peat and ceramic beads to treat styrene vapours that was able to depict a maximum EC of $170 \text{ g m}^{-3} \text{ h}^{-1}$. Kim et al. [15] used a polyurethane foam biofilter inoculated with activated sludge and achieved EC ranging between 580 and $635 \text{ gm}^{-3} \text{ h}^{-1}$ at a space velocity (SV) of 50–200 h⁻¹. The high elimination capacities achieved in their study was attributed to the presence of a superior bacterium. Pseudomonas sp., IS-5 and polyurethane foam packing material. A perlite biofilter inoculated with Rhodococcus pyridinovorans showed maximum EC of $279 \text{ g m}^{-3} \text{ h}^{-1}$ at a loading rate of $345 \text{ g m}^{-3} \text{ h}^{-1}$ [16]. Dehghanzadeh et al. [17] used a compost based biofilter to treat styrene vapours at different residence times and envisaged that reduction in retention times invariably decreased the EC from 45 to $27\,g\,m^{-3}\,h^{-1}$ and that the kinetics of the system was concentration dependent.

Water content is an important parameter in biofiltration studies. The addition of an aqueous phase is a prerequisite for the successful operation of biofilters, since microorganisms need some minimum water content for optimal growth and activity. In the present work, the performance of the biofilter was evaluated by monitoring the water content profiles of the filter bed due to changes in flow rate and studying the effect of relative humidity (RH) on styrene removal. In practical cases, biofilters handling industrial waste gases often receive sudden fluctuations in pollutant loading rates and are also frequently subjected to intermittent operations such as week-end shutdowns, holiday breaks, facility repairs, etc., depending on the plant operation. An active biofilter should be able to handle such adverse situations in order to provide a sustained maximum removal of the target contaminant [6]. The ability of the biofilter to withstand shock loads and handle intermittent operations however depends on factors such as biomass activity, pollutant loads, nutrient and oxygen availability, pH distribution or interference due to accumulation of by-products. Though there are several studies that have demonstrated the use of biofilters to treat styrene vapours, only few reports pertain to the treatment of styrene under high loading conditions and studying the effect of relative humidity and transient operating conditions



Fig. 1. Schematic of the perlite biofilter.

such as subjection to shock loads and intermittent shut down and restart operations.

In the work described herein, the behaviour of a laboratory scale perlite biofilter inoculated with a mixed culture from a petrochemical sludge was investigated at different initial loading rates of styrene polluted gas. The effects of inlet gas concentration, flow rate and relative humidity changes in the range of 30–92% on the removal efficiency (RE) of styrene were studied. In addition, the reactor performance during transient response to shock loads and periodic shutdowns was studied and explained.

2. Materials and methods

2.1. Microbial seed

A mixed microbial culture obtained from activated sludge collected from a petrochemical refinery was used to inoculate the biofilter. This was done by filling the perlite biofilter with the sludge and draining it after 12 h. The procedure was repeated several times with the same sludge until visible biomass was noticed on the surface of perlite. The dominant fungal population, present after long-term operation, was identified at the CBS (Utrecht, The Netherlands).

2.2. Biofilter

The biofilter was made of glass having an internal diameter (ID) of 10 cm and 70 cm in height, while the filter bed volume was 5 l. The packing in the biofilter consisted of sieved perlite beads (4–6 mm). Perlite has been shown previously to be a highly suitable packing material in biofiltration [5]. A perforated plate at the bottom provided the support for the packing material, while another plate at the top acted as a distributor for gas flow and mineral medium distribution. Gas sampling ports sealed with rubber septa were available at equal intervals (20 cm) along the biofilter height (*H*).

2.3. Experimental

A schematic of the experimental setup is given in Fig. 1. Humidified styrene vapours at constant flow and concentration, controlled through valves were passed through the bed in a down-flow mode. 150 ml of nutrient medium was periodically sprinkled from the top of the biofilter (once every 3 d) and the incoming gas was prehumidified to maintain the relative humidity to values higher than 92%. Samples for estimating bed moisture content and biomass concentration were collected before media sprinkling and these values were averaged for each operational change of RH. The mineral salt medium (pH 5.9) had the following composition per litre of deionised water: 0.5 gK2HPO4, 0.1 g MgSO4·7H2O, 4.5 g KH₂PO₄, 2g NH₄Cl, and 2 ml trace elements and vitamin solutions [7]. Experiments were carried out by varying the flow rates of the styrene vapours and humidified air independently to get different initial concentrations and residence times in the biofilter. Gas samples were collected from different ports and analyzed for styrene and CO₂ concentrations. A glass U-tube water manometer was used to measure the pressure drop across the filter bed height.

2.4. Analytical methods

Styrene concentration in gas samples was measured by gas chromatography on an HP 5890 gas chromatograph, using a 50 m TRACER column and a FID. The flow rates were 30 ml min⁻¹ for H₂ and 300 ml min⁻¹ for air. Helium was used as the carrier gas at a flow rate of 2 ml min⁻¹. The temperatures at the GC injection, oven and detection ports were 150, 150 and 150 °C respectively.



Fig. 2. Start-up of the biofilter and effect of flow rate and concentration on the performance of perlite biofilter.

CO₂ was analyzed with a HP 5890 gas chromatograph equipped with a TCD. The injection and oven temperatures were 90 and 25 °C respectively, with the TCD set at 100 °C. Biomass concentration, as g of dry biomass g^{-1} of perlite and moisture content (%) were measured according to the procedure outlined by Mohammad et al. [8]. Inlet relative humidities were measured using a hand held thermo-hygrometer, model C210 fitted with a flexible sampling probe (G. Lufft Mess-und Regeltechnik, GmbH, Germany). pH was measured with a Crison model GLP 22 pH-meter connected to an Ingold electrode. The temperature of the filter bed was measured using a FlashCheck pocket probe digital thermometer. Perlite samples, immobilized with biomass and exposed to styrene were prepared for observations under the electron microscope according to the procedure described by Jin et al. [18]. Examinations were performed with a JOEL JSM-6400 SEM working at a voltage of 20 kV and a working distance of 15 mm.

3. Results and discussion

3.1. Start-up and performance evaluation

The performance of the biofilter was evaluated in terms of the removal efficiency (RE, %) and the elimination capacity of the filter bed (EC, g m⁻³ h⁻¹) as defined elsewhere [5]. The biofilter was ini-

tially acclimated to styrene by passing low concentrations and low gas flow rates $(0.15 \text{ m}^3 \text{ h}^{-1})$ for 53 d to obtain sufficient biomass in the filter bed. The biofilter was run under these conditions to achieve stable and high removal efficiencies. During the operation, the relative humidity of the air stream was maintained at 92% or more.

After acclimation, the effect of styrene inlet concentration and gas flow rate was investigated in different phases that correspond to decreasing residence times of 2 min, 1 min, 40 s and 20 s respectively (Fig. 2). On day 54, when the concentration was increased at once from 0.5 to 4 g m⁻³, the removal efficiency dropped, but only to about 82%. Later, when the inlet concentration was again increased more slowly and stepwise to values as high as 5 g m^{-3} , the biofilter maintained 100% removal efficiency. Thus, at an EBRT of 2 min, 100% RE could be maintained at an inlet concentration of 5 g m⁻³ corresponding to a load of 150 g m⁻³ h⁻¹. The removals were still high in the next phase when the flow rate was increased to 0.3 m³ h⁻¹ corresponding to an EBRT of 1 min and for inlet loads varying between 80 and $190 \text{ g m}^{-3} \text{ h}^{-1}$. In order to check if still higher EC could be reached, the concentrations were increased from 6.5 to $17.4 \,\mathrm{g}\,\mathrm{m}^{-3}$ by keeping the flow rate at $0.15 \text{ m}^3 \text{ h}^{-1}$ (EBRT-2 min), thereby subjecting the biofilter to loading rates as high as $527 \text{ gm}^{-3} \text{ h}^{-1}$. A maximum EC of $382 \text{ g m}^{-3} \text{ h}^{-1}$ was achieved with 82% removal in this phase.



Fig. 3. Effect of inlet loading rate on the elimination capacity of biofilter (Inset: dependence of critical load at different EBRT).



Fig. 4. Variation of biomass concentration during continuous biofilter operation.

The next two phases of operation were aimed at investigating the biofilter performance under lower residence times of 40 and 20 s. The flow rate and concentration were adjusted to yield loading rates from as low as $50 \text{ gm}^{-3} \text{ h}^{-1}$ to as high as $1400 \text{ gm}^{-3} \text{ h}^{-1}$. The biofilter responded quite effectively by showing high removal efficiencies (>80%) for loading rates up to about $300 \text{ gm}^{-3} \text{ h}^{-1}$. However, there was also a gradually declining performance as the loading rates were increased from nearly 600 to $1300 \,\mathrm{g}\,\mathrm{m}^{-3}\,\mathrm{h}^{-1}$, where at an ILR > $1100 \text{ gm}^{-3} \text{ h}^{-1}$, the RE was just 20%. However, there was a strong relationship between the critical loads to the biofilter and the flow rate. It was observed that the critical load at $2 \min \text{EBRT}$ was $260 \text{ gm}^{-3} \text{ h}^{-1}$ and that it decreased down to $196 \,\mathrm{g}\,\mathrm{m}^{-3}\,\mathrm{h}^{-1}$ when decreasing the EBRT to 20 s. The elimination capacity, which reflects the capacity of the biofilter to remove the pollutants, is plotted as a function of the inlet styrene load in Fig. 3. Though there were fluctuations in the EC values during start-up, under steady state conditions, a linear relation between the two variables was observed with a maximum EC of 382, 380, 348 and $323 \text{ g m}^{-3} \text{ h}^{-1}$ at EBRT of 120, 60, 40 and 20 s respectively. From Fig. 3 it can be observed that near complete pollutant removal could be maintained up to a load of about $260 \text{ gm}^{-3} \text{ h}^{-1}$ at an EBRT of 2 min, while this value dropped to about $200 \text{ g m}^{-3} \text{ h}^{-1}$ at the lowest EBRT of 20 s. Thus, it can be concluded that both the maximum EC and critical load clearly dropped when reducing the EBRT from 2 min to 20 s, although high values were still obtained at the lowest EBRT of 20 s. The results from this study are higher than most EC reported in the literature using biofilters for handling styrene polluted air, which could be due to the dominant presence of fungi, confirmed by observations with a scanning electron microscope and microbiological studies [19]. The main fungal species was later isolated from the biofilter and identified as Sporothrix variecibatus, a white colored yeast like thermally dimorphic fungus (non-published data). It has been reported that fungal dominant biofilters would allow reaching a better performance than usual for hydrophobic VOCs [20]. Fungi are able to grow under acidic conditions and the pH level within the biofilter was maintained almost constant at 5.9 ± 0.1 by periodically sprinkling the media, while the pH of the leachate was 3.4-4.6. It was also observed that the pressure drop values were consistently low and varied between 0.5 and $4.2 \text{ cm H}_2 \text{Om}^{-1}$ bed height depending on the applied superficial gas velocities, which suggests the absence of filter bed compaction and excess biomass growth.

3.2. Biomass concentration

Despite the high loads maintained throughout the experiments, no clogging was observed even after more than 6-month operation. Biomass concentration measured as dry biomass weight per g of perlite is shown in Fig. 4. The biomass concentration was initially low during start-up (0.1 g g^{-1} perlite). It then gradually increased up to 0.7 g^{-1} perlite over a period of 5 months. There was thus a



Fig. 5. Variation of moisture content during continuous biofilter operation.

gradually inclining trend in the biomass concentration measured at two different ports in the biofilter till about 140 d, while the inlet load to the biofilter was gradually increased. This value then remained almost constant and did even drop somewhat (0.6 g g^{-1} perlite), when the EBRT was decreased to 40 and 20 s and when the loading rate was varied drastically during the last two phases of operation.

3.3. Water content

Intermittent drying near the inlet port when applying high flow rates $(0.9 \text{ m}^3 \text{ h}^{-1}$ and EBRT–20 s) was observed after 160 d operation. Optimizing the moisture content within the biofilter is an essential parameter to maintain biomass activity and good performance. The moisture content was monitored periodically by collecting known amounts of samples, taken 2 d after medium addition, from the two sampling ports. It was found that, the moisture levels across the biofilter height varied depending on the flow rate, but remained within a moisture range (45–60%) recommended for biofiltration (Fig. 5) [5]. The lowest moisture content (MC) was found at the shortest EBRT of 20 s, while the highest MC was attained at an EBRT of 2 min, indicating that higher gas flow rates will result in faster water loss.

3.4. Concentration profiles of styrene

The concentration profile (i.e., concentration at different heights of the filter bed) was measured at a constant loading rate. The results indicate that styrene removal was basically constant and linear along the filter bed (Fig. 6). At a flow rate of $0.3 \text{ m}^3 \text{ h}^{-1}$ (EBRT of 60 s), nearly 36% styrene was removed in the first section followed by 30% respectively in the other two sections (Fig. 6a). Such a relatively linear relationship between concentration profile and biofilter height is not always found in biofilters. It can be explained here by a relatively homogenous biomass distribution (Fig. 4) and probably due to down-flow mode of biofilter operation. In general, homogenous biomass distribution is known to improve the reactor's performance compared to non-homogenous profiles [21]. After a somewhat longer operation period of 147 d, when the concentration was $2.45 \,\mathrm{g}\,\mathrm{m}^{-3}$ and the flow rate was increased $(ILR-222 g m^{-3} h^{-1})$, there was more significant variation in concentration profiles along the biofilter (Fig. 6b). It was observed that about 46% of incoming styrene vapours were mineralized in the first section followed by 26% and 24% in the next two sections. This could explain the somewhat higher increase in microbial concentration near upper port than near the lower port between the 99th day and the 147th day of continuous operation. It could have resulted from the better supply of nutrients and higher moisture content in the upper section of the filter bed.

Table 1 Effect of relative humidity on the bed moisture content, biomass concentration and removal efficiency profile in the perlite biofilter.						
RH (%)	MC (%)		BC (gg ⁻¹ perlite)		RE (%)	
	Port 1	Port 2	Port 1	Port 2	ILR (80 g m ⁻³ h ⁻¹)	ILR (260 g $m^{-3} h^{-1}$
>92 60 30	56 ± 0.4 44.3 ± 1.2 23.4 ± 2.8	52 ± 1.9 48.7 ± 2.6 44.3 ± 2.1	$\begin{array}{c} 0.66 \pm 0.02 \\ 0.62 \pm 0.02 \\ 0.52 \pm 0.02 \end{array}$	$\begin{array}{c} 0.64 \pm 0.03 \\ 0.62 \pm 0.02 \\ 0.59 \pm 0.01 \end{array}$	100 97.2 82.3	92.4 86.8 69.8

Note: RH-relative humidity; MC-moisture content; BC-biomass concentration; RE-removal efficiency; ILR-inlet loading rate.



Fig. 6. Removal of styrene and CO₂ evolution profile along the biofilter height. (a) Day 99: inlet concentration -1.2 gm^{-3} ; inlet loading rate $-72.1 \text{ gm}^{-3} \text{ h}^{-1}$; removal efficiency-100%. (b) Day 147: inlet concentration-2.45 g m⁻³; inlet loading rate-222 g m⁻³ h⁻¹; removal efficiency-96.5%.

3.5. Effect of relative humidity (RH) on biofilter performance

A continuous film like aqueous phase may be maintained within the biofilter either through humidification of the waste gas or through the external addition of water phase in the form of media addition to the biofilter [22]. If the filter bed is too dry, it will not support a diverse and robust microbial community. A filter bed that is too wet can become too dense and compact, resulting in reduced porosity, high back pressure and reduced airflow. Besides, biological waste gas treatment is an exothermic process; hence the temperature across the biofilter is expected to increase, which will increase water losses [8]. In the present study, a temperature increase of up to 2.6 ± 0.2 °C was observed along the filter bed. Some authors observed that when the biofilter medium moisture content decreased by 16%, odour and ammonia removal efficiencies decreased by 7% and 23% respectively [23]. Experiments were carried out for 26 d at two inlet loading rates, viz., approximately 80 and 270 g m⁻³ h⁻¹ at a constant gas flow rate $(0.3 \text{ m}^3 \text{ h}^{-1})$ and by varying the RH of the incoming vapour (>92%, 60% and 30%). The results from this study are shown in Fig. 7 as a function of the removal efficiency and elimination capacity of the filter bed. It could be seen that, initially when the loading rates were around 80 g m⁻³ h⁻¹, nearly 100% styrene was removed at RH values greater than 92%. However, when the loading rate was increased to about $260 \text{ g m}^{-3} \text{ h}^{-1}$, the RE dropped by about 5–10% (days 1–9). The bed moisture content and the biomass concentration were maintained at 56% and $0.66 g g^{-1}$ perlite respectively (Table 1). In the subsequent steps of operation, when the RH was reduced to 60%, there was a slight, though not highly significant, decline in the removal profile. The dominant presence of fungi offers the advantage to tolerate fluctuating moisture conditions that commonly occur in biofilters. At similar loading conditions, from days 21 to 26, when decreasing the RH further down to 30%, there was a sharp decline in the removal profiles as well as the moisture content and the biomass concentration within the filter bed. However, under such low RH and moisture content within the filter bed, nearly 70% of the incoming styrene vapour was removed at an ILR of $260 \text{ g m}^{-3} \text{ h}^{-1}$. It has been earlier hypothesised that aerial mycelia of fungi which



Fig. 7. Effect of relative humidity and loading rate on the elimination capacity of the styrene degrading biofilter.



Fig. 8. Styrene removal profiles at different relative humidity and inlet loading conditions: (a) >92% RH, (b) 60% RH and (c) 30% RH. –, concentration profile; ---, removal profile.

are in direct contact with the gas phase pollutant can facilitate more rapid mass transfer of hydrophobic VOCs than can aqueous bacterial biofilms [24].

For better understanding the styrene elimination mechanism within the reactor under changing RH conditions, the concentration profile at different heights was measured under different operating loads, 1 d after medium addition. The results achieved under steady state conditions clearly show the stratification of removal efficiency along the biofilter height. At a RH > 92% and at an inlet load of $90 \text{ g m}^{-3} \text{ h}^{-1}$, approximately 52% of the inlet styrene was degraded in the first section of the biofilter, while only 22% and 26% were removed in the other two parts (Fig. 8a). Additionally, when the inlet load was increased to $314 \text{ g m}^{-3} \text{ h}^{-1}$, though 53% of the incoming styrene vapour was removed in the first section, only 6% was removed in the third section of the filter bed. When experiments were carried out at a RH of 60%, at inlet styrene loading rates of $90 \text{ g m}^{-3} \text{ h}^{-1}$, nearly 40% removal was possible in the

first section followed by 31% and 24% removal in the later sections. However, these removal profiles changed in the third section of the filter bed when the loading rate was increased to $360 \,\mathrm{g}\,\mathrm{m}^{-3}\,\mathrm{h}^{-1}$, where only 11% removal was plausible (Fig. 8b). Such somewhat higher removal rates near the inlet of the biofilter, at relatively high moisture contents were also observed as shown earlier in Fig. 6. A further decrease in the RH by 30%, under styrene loads of 70 and $270 \text{ g m}^{-3} \text{ h}^{-1}$ showed a drastic effect on the removal dynamics within the biofilter (Fig. 8c). At these loading rates, nearly 34% and 25% removal was accomplished in the first section, while the last section of the filter bed removed 16% and 26% of the remaining styrene. A rapid change in stratification that corresponds to differences in removal patterns along the biofilter height under changing RH conditions (from 92% to 30%) and loading rates (77 to $360 \text{ g m}^{-3} \text{ h}^{-1}$) were noticed. At low loading rates, the removal pattern in the first section decreased by about 18%, while at higher loading rates (270 g m⁻³ h⁻¹), the removal dropped by 28%. The different behaviour at the lowest relative humidity compared to higher ones, suggests a higher depletion of water content and the available nutrients near the inlet of the reactor when feeding poorly humidified air. Such effect is more significant at high flow rates, i.e., high styrene loads.

3.6. Effect of transient operating conditions on biofilter performance

3.6.1. Biofilter response to shock loads

The transient behaviour of the perlite biofilter was investigated by subjecting it to different types of shock loads, i.e., short-term shock load of 12 h and long-term shock load of 10 d. Short-term shock loads were studied at a flow rate of 0.15 m³ h⁻¹, in two stages, viz, at a normal ILR of approximately 60 and a shock load of $200 \text{ gm}^{-3} \text{ h}^{-1}$ (low and medium loading rates, L–M), and at a normal ILR of 60 and a shock load of $450 \text{ gm}^{-3} \text{ h}^{-1}$ (low and high loading rates, L-H). The results shown in Figs. 9 and 10 indicate that the styrene laden perlite biofilter was able to maintain a high performance close to 100%, when applying a medium shock load (L-M), however, when a higher, short term, shock load of 450 g m⁻³ h⁻¹ was applied, the removal efficiency dropped suddenly to 70% and then remained constant at such value during the shock load period of 12 h. The response of the biofilter was fast as seen from the immediate decrease in removal profile at high loads and the retrieval in performance (100%), when restoring low loads. The biofilter recovered almost instantaneously after both the medium and the high shock loads. Barona et al. [25] investigated the performance of biofilters to handle H₂S vapours using low and medium shock loads over 36 d of continuous operation. Their biofilter was subjected to an instant shock from 8 to 68 g $H_2Sm^{-3}h^{-1}$ after a brief starvation period of 80 and 25 h, where the EC dropped from 68 to 48 g H_2 S m^{-3} h^{-1} , and a restoration in the RE was reported when the original low loading rates were re-applied. [in et al. [26] conducted long-term shock loading experiments of 1 month, by subjecting a fungal biofilter to multiple medium and high shock loads of α -pinene and observed that the performance of the biofilter quickly recovered after every 4 h shock load, reaching EC values of $60 \text{ g m}^{-3} \text{ h}^{-1}$ with removal efficiency greater than 90% over the 13 h period after the shock load.

The effect of long-term shock loads was investigated for 240 h in three stages at flow rates of 0.15, 0.45 and 0.3 m³ h⁻¹, corresponding to medium and high shock loads varying between 145 and $520 \text{ gm}^{-3} \text{ h}^{-1}$ (Fig. 11). At a flow rate of $0.15 \text{ m}^3 \text{ h}^{-1}$ and at loading rates lesser than $280 \text{ gm}^{-3} \text{ h}^{-1}$, the removal efficiencies were higher than 94% (0–60 h). However, these values of removal profiles gradually declined when both the flow rate and concentration were changed in the subsequent shock loads (72–156 h). At an ILR of 145 gm⁻³ h⁻¹, the RE was 85%, but when the ILR was



Fig. 9. Effect of short-term medium shock load on the removal efficiency of the biofilter.



Fig. 10. Effect of short-term high shock load on the removal efficiency of the biofilter.

increased gradually to $236 \text{ gm}^{-3} \text{ h}^{-1}$, the RE dropped by just 6%. In the last step of this experiment (168–240 h), styrene gas concentrations were increased to as high as 8.6 gm^{-3} corresponding to high shock loads varying between 374 and $520 \text{ gm}^{-3} \text{ h}^{-1}$. It was observed that the RE dropped correspondingly from values higher

than 85% to 76%. However, the original removal profile was almost restored when the concentration of styrene was reduced. These results clearly show the sensitivity of the biofilter to changes in loading rate due to variations in concentration and flow rate. Furthermore it was also evident that a maximum EC of $400 \text{ g m}^{-3} \text{ h}^{-1}$



Fig. 11. Effect of long-term shock loads at different flow rates on the removal efficiency of the biofilter.



Fig. 12. Response of biofilter to intermittent shutdown and restart operations.

was achieved with 76% removal during different shock loading studies and the critical load for 100% removal was found to be $276 \, g \, m^{-3} \, h^{-1}$.

3.6.2. Biofilter response to intermittent operations

The transient behaviour of the perlite biofilter was also investigated in the form of intermittent shut down periods at a flow rate of $0.45 \text{ m}^3 \text{ h}^{-1}$ and a concentration of 2 g m^{-3} that corresponds to a styrene loading rate of $170 \text{ g m}^{-3} \text{ h}^{-1}$ for 25 d. The biofilter operation was stopped twice by closing both air supply and inflow of styrene, viz, 3 d with nutrient addition and 7 d without nutrient addition. The results shown in Fig. 12 indicate that the biofilter was able to maintain its performance after a shutdown period of 3 d. Even under harder conditions, when the biofilter operation was stopped for 7 d without adding nutrients, the system recovered very fast when restarting the feed of styrene polluted air on the 19th day and the RE had decreased only by 10%. The biofilter was able to restore back to its original performance (86%) in a few days. Similar fluctuations in the biofilter performance for VOC removal have been reported in the literature. Jang et al. [27] investigated styrene removal in a biofilter inoculated with Pseudomonas sp. SR-5 through vigorous shutdown experiments (shutdown of styrene; shutdown of styrene, air and moisture; and shutdown of styrene and moisture). Their results showed that, though low loading rates of styrene were passed before shutdown $(36 \text{ g m}^{-3} \text{ h}^{-1})$; nearly 90% styrene was removed on restart after 4 d at an ILR of $115 \text{ gm}^{-3} \text{ h}^{-1}$. Rene et al. [6] reported that an intermittent shutdown period of 9 d in a compost biofilter treating toluene vapours did not pose significant impact on the biofilter performance when similar inlet load $(22 \text{ gm}^{-3} \text{ h}^{-1})$ was supplied during restart. However, they observed a drastic decline in the removal efficiency from 82% to 38%, when 160 g toluene $m^{-3} h^{-1}$ was supplied during the second shut period of 8 d. Halecky et al. [28] reported that, when a perlite biofilter was subjected to low styrene loads of $8 \text{ g m}^{-3} \text{ h}^{-1}$ with an idle period of 95 h, it required just 2.5 h to recover to its original performance during restart. After a 7 d starvation period in a biofilter treating H₂S, Wani et al. [29] observed that 25-30 h were sufficient to achieve their initial RE of 99% at an ILR of $45 \text{ g m}^{-3} \text{ h}^{-1}$.

The EC varied between 103 and $195 \,\mathrm{g}\,\mathrm{m}^{-3}\,\mathrm{h}^{-1}$ during this study. This corroborates well with the fact that biofilm developed in the biofilter was quite stable and the activity of the biofilm was restored rapidly. The activity of the biomass would have been maintained by availability of trace quantities of non-biodegraded styrene and nutrients in the biofilm, which in turn would have helped in restoring the biofilter performance during restart.

4. Conclusions

The results from this experimental study show promising results for the treatment of very high concentrations of off gas emissions containing styrene (-18 gm^{-3}) by means of a biofilter. Complete styrene removal was possible at loading rates less than $200 \text{ gm}^{-3} \text{ h}^{-1}$ irrespective of the gas residence time, which could be attributed to the dominant presence of fungi. Also, it was observed that, the maximum performance and critical load were dependant on the superficial air velocity, i.e., EBRT. The critical load at 20 s EBRT was $196 \text{ g m}^{-3} \text{ h}^{-1}$, while at 2 min EBRT it was 260 g m⁻³ h⁻¹. Though changing relative humidity values from >92% to 60% showed minuscule effect, the performance of the biofilter reduced to values lesser than 80% at 30% RH. The response of the biofilter to low-medium and low-high shock loads was fast, as seen from the immediate decrease in RE at high loads and restoration of removal under low loading conditions. Short-term intermittent shut down (3 d) with nutrient addition apparently had no effect on the biofilter performance during restart, while a 7 d shutdown period with no nutrient addition had reduced the removal by only 10%.

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