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A comparative study for destruction of n-hexane in Trickle Bed Air Biofilters

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ABSTRACT

Trickle Bed Air Biofilter (TBAB) could be an attractive treatment option for removal of hydrophobic Volatile Organic Compounds (VOCs) from air streams. In this study, three independent parallel laboratory-scale TBABs were run simultaneously to degrade n-hexane, a hydrophobic VOC known to be difficult to degrade. The loading rate of n-hexane varied from 13.4 and 47.7 g/(m^3 h) (1.14–4.04 kg COD/(m^3 day)).

The experimental plan was designed to operate one TBAB at pH 7, another at pH 7 utilizing surfactant for enhancing the solubility of n-hexane, and finally a third one operating at pH 4 to promote fungi growth. Elimination capacities up to 38.7 g/(m^3 h) (3.28 kg COD/(m^3 day)) were observed with a removal efficiency of 90% for the TBAB operating at pH 4. The operating conditions for the TBABs include 120 s of Empty Bed Residence Time (EBRT), 1.4 L/min air flow rate and fixed temperature of 20 °C. Biomass control within the TBAB was investigated through two strategies, namely, stagnation (off flow for 2 days/week) and flow switching.

1. Introduction

Air pollution has recently been the center of attention due to the increasing public awareness about global warming and green house gas emissions. The most preferable option to combat air pollution is green technology. Pollution prevention should be used when applicable by exchanging the materials used, however, conventional air pollution, end of the pipe strategies, are of need when green technologies cannot be used [1]. Biological treatment represents cheap and environmental friendly option for air pollution as compared to incineration, catalytic oxidation and adsorption. It has several advantages like minimal power consumption, few byproducts and cost effectiveness. On the other hand, the main disadvantage is the need of continuous and experienced operation [2,3].

There are several challenges facing biological treatment processes. Monitoring of the microorganism behavior and providing the optimum growth conditions has to be done continuously to avoid any downtimes. Variability of flow rate and composition of contaminants from industries are other challenges facing biological treatment processes [4,5]. Furthermore, hydrophobic compounds are not readily available for the microorganisms, creating a deficiency for the use of biological treatment in the industry. The solubility of Volatile Organic Compounds (VOCs) in water which is related to the Henry's law constant is the most important characteristics that affects the performance of biofilters [6]. Since the microorganisms are present only in the biofilm surrounding the packing material of the bed, transport of the VOC from the gas phase to the biofilm, which is composed of more than 90% water, could be rate limiting. Kim et al. [7] demonstrated that hydrophilic compounds were degraded easily and deposited additional cell mass in the biofilter, while degradation of hydrophobic compounds was retarded until biological cultures produced a sufficient RNA or enzyme/protein to utilize these compounds.

Surfactants can be introduced in the biofiltration system as means for enhancing solubility. A surfactant is a service active agent, a compound with a hydrophilic group attached to a hydrophobic segment, typically a hydrocarbon chain or fatty acid [8]. Nonionic and anionic surfactants have been extensively studied to enhance mobilization and bioavailability of hydrophobic compounds in contaminated soils and sediments [9]. Fewer studies however have been conducted for gas treatment bioreactors. The utilization of surfactant Brij35 was successfully applied to enhance the biodegradation of toluene in a bead biofilter to 26 g/(m^3 h) [10]. Another study [11] used the surfactant Tween 81 for the stabilization of erratic loadings in a jet loop reactor treating toluene. In a previous study [12], Aly Hassan and Sorial investigated the impact of the utilization of surfactant on increasing the solubility of n-hexane. It was found that higher elimination capacities could be achieved using a non-toxic surfactant (Tomadol® 25-7).

Several studies have been made to biologically treat n-hexane. n-Hexane is difficult to degrade because of its hydrophobicity. At a loading rate less than 12 g/(m^3 h) (1 kg COD/(m^3 day)) the maximum removal efficiency reached was 70% [6,13–16]. A full scale industrial biofilter in Germany is operating for the elimination of n-hexane and a removal efficiency of 68% is only achieved [17]. The first study concerning the biodegradation of n-hexane in biofil-

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ters was performed by Van-Groenestijn and Lake [13]. The study focused on utilization of silicon oil in the range of 10–30% mixed with water in the nutrient tank. Although the study was promising in utilizing a relatively high loading rate of 100 g/(m^3 h), the Empty Bed Residence Time (EBRT) used was 10 and 20 min which are not economically feasible for field scale. On the other hand, the study of Van-Groenestijn et al. [18] suggested that hexane used as a substrate with a low pH does not encourage fungi to grow. In a later study, Aspergillus Niger fungi isolated from soil next to gas stations proved to be effective strain for biodegradation of n-hexane [19]. In the biofilter it was observed that bigger variability of fungi emerged. Loading rates of up to 300 g/(m^3 h) were tested with removal efficiency as low as 50%. The study was still not practical in their choice of 26.6 min EBRT.

Testing of different media within the bed and having the nutrient liquid feed maintained at pH 7 lead to removal rates of 25 g/(m^3 h) and 40 g/(m^3h) [14]. Arriaga and Revah [20], used fungi with a relatively feasible EBRT of 1–2.8 min. Very high elimination capacities up to 150 g/(m^3h) were reported at loading rate of 600 g/(m^3h). This elimination capacity though very high was attained at a very low removal efficiency (almost 25%), which makes the utilization of the biofilter not practical. On the other hand, the results reported in this study were observed only for 48 h after stabilization leaving some doubt of reliability for a longer term performance. Another study [21] was performed for n-hexane using silicone oil for improving the biodegradation. The study had the same pitfall of a long EBRT of 10 min and a very short run time of just 70 days of operation.

According to Van-Groenestijn et al. [18], replacing the working consortium in a biofilter from Bacteria to fungi has several advantages: (1) fungi are more resistant to acidification and drying out, which is a major advantage of the natural media biofilters but does not necessary count as an advantage in TBABs and (2) the aerial mycelia of fungi form a larger surface area in the gas phase than bacterial biofilms, which may facilitate the uptake of hydrophobic volatile compounds overtaking the rate limiting step. In the same study fungi was utilized in the operation of a traditional biofilter for the treatment of toluene. In a later study [22], the degradation of alkylbenzenes in a TBAB was performed using new isolated fungal strains.

In this study, three independent parallel TBABs were run continuously for a period of almost a year to degrade n-hexane. The loading rate of n-hexane varied from 13.41 and 47.69 g/(m^3 h) (1.14–4.04 kg COD/(m^3 day), respectively). The experimental plan was designed to operate three TBABs designated as “A”, “B” and “C” at different conditions: without surfactant at pH 7, utilization of surfactant at pH 7, and operated at pH 4 to allow growth of fungi, respectively. Other operation strategies for biomass growth limitation are investigated in this study like stagnation (off flow for 2 days/week) and flow switching. The biomass control strategies were chosen to mimic the changes that might occur in industrial facilities.

2. Materials and methods

2.1. Volatile Organic Compounds

The VOC tested in the study was n-hexane (Fisher Scientific, Fair Lawn, N.J., pure 85%). Henry’s Law Constant (HLC) for hexane was reported at 20 °C by different authors in the range of: 0.883 atm m^3/mol [23], 0.014 atm m^3/mol [24] and 0.122 atm m^3/mol [25]. Three different TBABs were employed in this study. TBAB “A” received continuous feed of n-hexane with nutrient flow that did not include surfactant. TBAB “B” was fed continuously with the same flow of n-hexane but with surfactant concentration of 150 mg/L in the nutrient feed. The surfactant used was Tomadol® 25-7 (Tomah products, LA), based on results obtained from a previous study [26]. TBAB “C” operated at the same n-hexane loading rate but the nutrient feed was buffered at pH 4. TBABs “A” and “B” were operated at loading rates of 13.4–21.5 g/(m^3 h) (1.14–1.82 kg COD/(m^3 day), respectively) corresponding to a concentration range from 50 to 200 ppmv, while TBAB “C” operated at loading rates of 13.41–47.69 g/(m^3 h) (1.14–4.04 kg COD/(m^3 day), respectively) corresponding to a concentration range from 125 to 450 ppmv.

2.2. Trickling Bed Air Biofilter

TBABs “A” and “B” were used in pervious runs [26] and continued to run without acclimation while TBAB “C” needed an acclimation period of 11 days. Each TBAB is constructed of seven cylindrical glass sections with an internal diameter of 7.6 cm and a total length of 130 cm. Each reactor is packed with pelletized diatomaceous earth biological support media to a depth of about 60 cm (Celite® 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA). The TBABs were run at constant operating temperature of 20 °C and operated in a co-current gas and liquid downward flow mode.

The air flow was set up at the rate of 1.36 L/min for each TBAB with corresponding EBRT of 2.00 min. This EBRT was chosen to overcome the reluctance of n-hexane for biodegradation, by exposing it for more contact time with the water phase in order to overcome the barrier of the diffusion as it is the rate limiting step. This EBRT was also chosen based on previous research performed on benzene in a similar TBAB [27]. Benzene is expected to be more biodegradable as compared to n-hexane. Liquid n-hexane was injected via a syringe pump and vaporized into the air stream. Buffered nutrient solution at the target pH (four or seven) was supplied at a rate of 2.0 L/day, the composition of the nutrient solution is the same as used by Sorial et al. [28]. The intermittent nutrient flow contained 17.1 mmol NO_3–N/day. The nutrient solution for TBABs “A” and “B” is buffered at pH 7 using sodium bicarbonate. The feed for TBAB “C” was buffered at pH 4 using hydrochloric acid and sodium formate.

2.3. Strategies of biomass control

The TBAB operation was tested with two different experimental strategies. The first strategy involves the study of the performance of a TBAB under flow switching. The second strategy used is stagnation. In addition to the previous mentioned strategies, it was proven that adding a surfactant might limit the microbial growth within the TBAB [29].

Flow switching. This experimental strategy involves switching the direction of the gas flow once weekly, i.e., for a 3 week period, the direction of the gas flow for the first week was co-current with the nutrient liquid flow downwards then countercurrent on the second week upwards and finally co-current on the third week downwards.

Stagnant period. This experimental strategy reflects no flow (VOC, nutrient, and air) passing through the TBAB. The duration and frequency for this strategy were 2 days per week for a period of 3 weeks at each VOC loading rate.

2.4. Analytical methods

The concentrations of VOC in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). Effluent gas phase sample for CO_2 analysis were also taken by using gas-tight syringes through sampling ports in the TBAB. A GC (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with

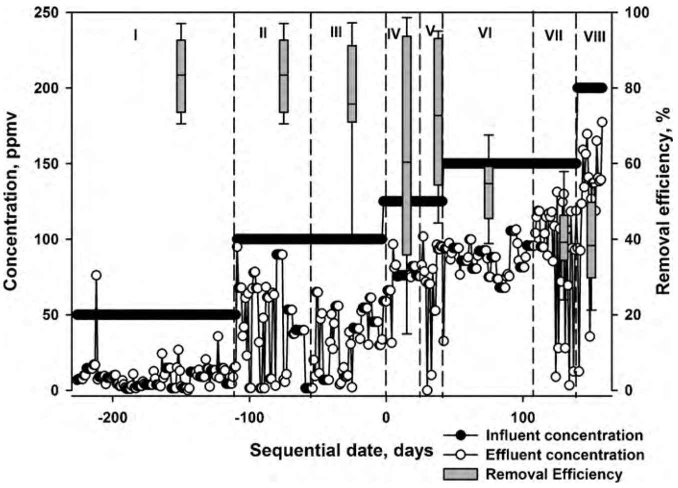

Fig. 1. TBAB “A” performance under continuous loading condition at pH 7 without surfactant (performance prior to day 0 are obtained from a previous publication by the authors [26]).

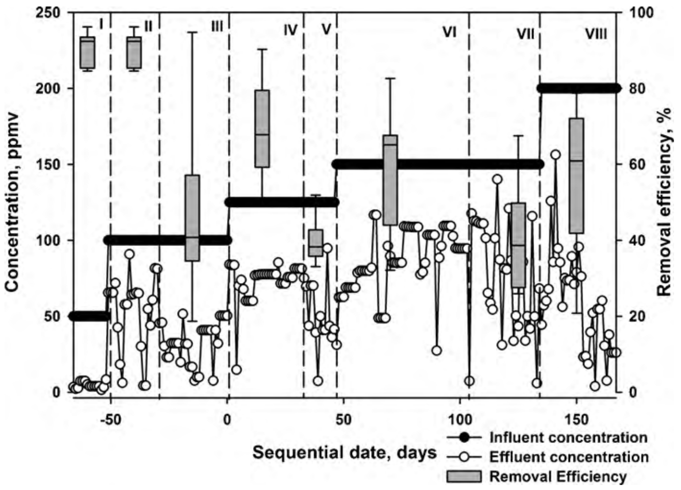

Fig. 2. TBAB “B” performance under continuous loading condition at pH 7 with surfactant (performance prior to day 0 are obtained from a previous publication by the authors [26]).

a thermal conductivity detector (TCD) was used for determining the CO_2 concentrations in the effluent gas phase. Liquid phase samples were analyzed for NO_3^-–N, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. NO_3^-–N was determined according to Standard Methods 4500-NO_3^- [30] by using a Shimadzu UVmini 1240 UV–vis spectrophotometer (Shimadzu Corp., Tokyo, Japan). TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 [30]. The VSS concentrations in the effluent and the backwashing water were determined according to Standard Methods 2540 G [30].

3. Results

3.1. TBAB performance

3.1.1. Performance of TBAB “A”

TBAB “A”, which is the control TBAB, was operated in the n-hexane concentration range from 125 to 200 ppmv, corresponding to 13.4–21.5 g/(m^3 h) (1.14–1.82 kg COD/(m^3 day)). It showed very low removal efficiency at every concentration level, but its performance was needed for comparison purposes. The details of operation for TBAB “A” are given in Table 1 where at every phase of operation the corresponding influent concentration, loading rate and days of operation are provided. The table also summarizes the results of the TBAB including average removal efficiency and its standard deviation and the elimination capacity. The daily results are displayed in details in Fig. 1. The figure illustrates the influent and effluent concentration of n-hexane on the different days of operation and presents the removal efficiency as a box plot for the different phases of operation. The box plot summary indicates the 25th and 75th percentiles by the borders of the box, the median by the line within the box, and the 90th and 10th percentiles by the error bars.

This TBAB was previously acclimated to n-hexane at lower concentration levels up to 100 ppmv [26]. The TBAB was then run at125 ppmv providing a loading rate of 13.4 g/(m^3 h) (1.14 kg COD/(m^3 day)) on a flow switching technique only. The sequential days were set to start from this loading rate. The TBAB with this configuration was working at 41% removal efficiency; however, the fluctuation was limited to 9% standard deviation. On day 30, stagnation technique was coupled with flow switching at the same concentration level. This technique did not have significant improvement on the TBAB performance. The removal efficiency increased to 43%, however, the standard deviation was 24%. In general, the removal efficiency showed relatively good performance after restart from the stagnation period but deteriorated throughout the week.

The same pattern in the performance was realized at an influent concentration of 150 ppmv corresponding to a loading rate of 16.1 g/(m^3 h) (1.36 kg COD/(m^3 day)). On day 45, the influent concentration was increased and flow switching was applied as the only biomass control strategy. The average removal efficiency was observed to be 41 ± 9%. On day 121, when the stagnation was coupled with the flow switching at the same concentration level, the removal efficiency had a small jump to 43% while the standard deviation tripled to 28%. On day 143, the concentration was increased again to 200 ppmv corresponding to 21.46 g/(m^3 h) (1.82 kg COD/(m^3 day)). At this level the removal efficiency decreased to 37 ± 21% by coupling stagnation with flow switching. This was the maximum loading rate applied for this TBAB because of its inefficient performance at such low concentration.

3.1.2. Performance of TBAB “B”

The strategy of operation for TBAB “B” exactly followed the sequence applied for TBAB “A” with its details summarized together with the average performance parameters in Table 2. Fig. 2 represents the corresponding daily influent and effluent concentrations in addition to box plots for the removal efficiency. Similar to TBAB “A” this TBAB was previously acclimated to n-hexane at lower concentration levels up to 100 ppmv [26]. The TBAB was then run at a concentration level of 125 ppmv with a loading rate of 13.4 g/(m^3 h) (1.14 kg COD/(m^3 day)) and only flow switching technique applied. The sequential days were set to start from this loading rate. The removal efficiency was 41 ± 10%. This value matches the performance of TBAB “A” under the same conditions. The effect of surfactant got visible after day 32, when stagnation was coupled with flow switching at the same concentration level. The removal efficiency jumped to 59 ± 18%. This is almost 1.3 times the removal attained by the control TBAB “A”. However, the same pattern was realized, the removal efficiency was very high after restart from stagnation and kept deteriorating with time.

On day 46, the influent concentration was further increased to 150 ppmv corresponding to a loading rate of 16.1 g/(m^3 h) (1.36 kg COD/(m^3 day)). The same removal efficiency pattern was seen, i.e., the removal efficiency kept deteriorating throughout the week. Applying flow switching technique only led to a removal efficiency of 42% which matches the performance of TBAB “A” operating

Table 1
Experimental conditions and results of TBAB “A” at pH 7 without surfactant.

Phases of operation	I[a]	II[a]	III[a]	IV	V	VI	VII	VIII
Experimental conditions								
Influent concentration, ppmv	50	100	100	125	125	150	150	200
Loading rate, g/(m^3 h)	5.5	10.4	10.4	13.4	13.4	16.1	16.1	21.5
(kg COD/(m^3 day))	(0.45)	(0.88)	(0.88)	(1.14)	(1.14)	(1.36)	(1.36)	(1.82)
Operating condition[b]	CO	CO	FS	FS	FS & St	FS	FS & St	FS & St
Days of operation	116 days	54 days	54 days	1–29	30–44	45–120	121–142	143–161
Average removal efficiency (%)	82.1	57.3	66.5	41.2	43.4	40.6	43.1	36.9
Standard deviation (%)	17.3	30.1	19.8	9.1	24.7	8.9	28.1	21.2
Elimination capacity, g/(m^3 h)	4.4	5.9	7.0	5.5	5.9	6.6	7.0	8.0
(kg COD/(m^3 day))	(0.37)	(0.5)	(0.59)	(0.47)	(0.49)	(0.56)	(0.59)	(0.68)

[a] These results are obtained from a previous publication by the authors [26].
[b] Operating conditions: CO, continuous operation; FS, flow switching; S, surfactant; St, stagnation.

Table 2
Experimental conditions and results of TBAB “B” at pH 7 with surfactant.

Phases of operation	I[a]	II[a]	III[a]	IV	V	VI	VII	VIII
Experimental conditions								
Influent concentration, ppmv	50	100	100	125	125	150	150	200
Loading rate, g/(m^3 h)	5.4	10.4	10.4	13.4	13.4	16.1	16.1	21.5
(kg COD/(m^3 day))	(0.45)	(0.88)	(0.88)	(1.14)	(1.14)	(1.36)	(1.36)	(1.82)
Operating conditions[b]	CO & S	CO & S	S & FS	S & FS	S & FS & St	S & FS	S & FS & St	S & FS & St
Days of operation	15 days	23 days	27 days	1–31	32–45	46–111	112–134	135–167
Average removal efficiency (%)	82.2	68.0	71.0	41.4	58.7	41.9	54.6	58.2
Standard deviation (%)	22.0	19.0	13.1	10.3	17.5	15.8	23.0	12.6
Elimination capacity, g/(m^3 h)	4.4	7.1	7.4	5.6	7.9	6.8	8.8	12.6
(kg COD/(m^3 day))	(0.37)	(0.60)	(0.63)	(0.47)	(0.67)	(0.57)	(0.74)	(1.06)

[a] These results are obtained from a previous publication by the authors [26].
[b] Operating conditions: CO, continuous operation; FS, flow switching; S, surfactant; St, stagnation.

under the same conditions. When stagnation was coupled with flow switching at the same concentration level on day 112, the removal efficiency jumped to 55% providing the same ratio of enhancement of 1.3 times if compared to TBAB “A” operating under the same conditions. On day 135, the concentration was further increased to 200 ppmv corresponding to 21.46 g/(m^3 h) (1.82 kg COD/(m^3 day)). At this level the removal efficiency was at 58 ± 13% by utilization of stagnation in addition to flow switching having. The performance ratio of TBAB “B” to “A” increased at this concentration level to 1.6 times.

3.1.3. Performance of TBAB “C”

Prior to operation of TBAB “C” an enriched solution of microorganisms was prepared. This solution contained the liquid effluent of TBAB “A” which already contained n-hexane degrading microorganisms and was acclimated at pH 4 by using formate buffer with HCl. An air stream containing n-hexane was bubbled through the solution for 45 days until the growth of new biomass was visible. The pH was continuously monitored and it did not increase above 4 during this period. TBAB “C” was then seeded with this solution by pouring the solution on the media and leaving the solution intact within the media for 120 min and then drained.

As shown in Table 3, which describes the details of operation of TBAB “C”, the first influent concentration level applied to the TBAB was 125 ppmv corresponding to a loading rate of 13.4 g/(m^3 h) (1.14 kg COD/(m^3 day)). The same operational procedures conducted for the previous TBABs were applied to TBAB “C”. Daily results for TBAB “C” are presented in Fig. 3. Using flow switching alone resulted in a removal efficiency of 71 ± 14%. This removal efficiency is far higher than performance results obtained from both previous TBABs, although the initial acclimation that took a week is still counted within this value. On day 20, stagnation was applied in addition to flow switching at the same influent concentration. This resulted in an average improved performance of 81%.

On day 77, the influent concentration was increased to 150 ppmv corresponding to a loading rate of 16.1 g/(m^3 h) (1.36 kg COD/(m^3 day)). Starting at this concentration level and higher, all runs were performed by applying stagnation and flow switching together. Both strategies were applied because TBABs “A” and “B” showed the superiority of this technique as compared to flow switching alone. The removal efficiency was 84 ± 13%. This value is almost double and 1.6 times the performance in TBAB “A” and TBAB “B”, respectively. On day 133, the influent concentration was raised to 200 ppmv corresponding to 21.46 g/(m^3 h) (1.82 kg COD/(m^3 day)), where the other two TBABs already failed. The removal efficiency at this level further increased to 90%. The increase in removal efficiency with increasing loading rate could be explained by the nature of fungi that needs much longer time to grow than bacteria [18]. This means as time passes more fungal cultures were building up within the bed enabling enhancement

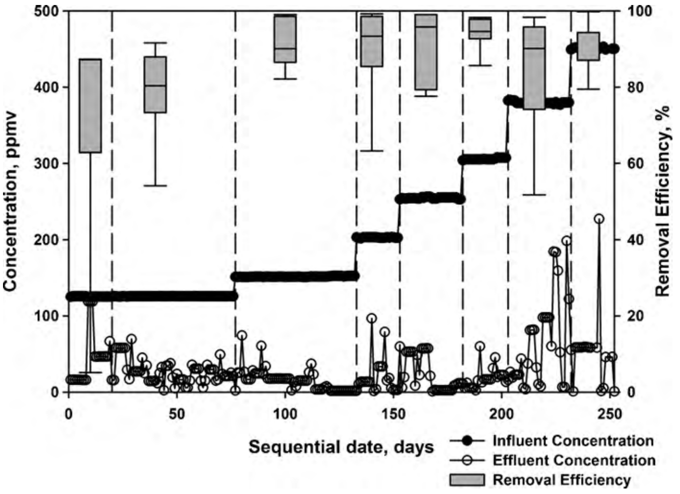

Fig. 3. TBAB “C” performance under continuous loading condition at pH 4 without surfactant.

Table 3
Experimental conditions and results of TBAB "C" at pH 4 without surfactant.

Phases of operation	I	II	III	IV	V	VI	VII	VIII
Experimental conditions								
Influent concentration, ppmv	125	125	150	200	250	300	380	450
Loading rate, g/(m^3 h)	13.4	13.4	16.1	21.5	26.8	32.2	40.1	47.7
(kg COD/(m^3 day))	(1.14)	(1.14)	(1.36)	(1.82)	(2.27)	(2.73)	(3.39)	(4.04)
Operating conditions[a]	FS	FS & St	FS & St	FS & St	FS & St	FS & St	FS & St	FS & St
Days of operation	1–19	20–76	77–132	133–152	153–181	182–202	203–231	232–252
Average removal efficiency (%)	71.1	81.6	83.9	90.0	90.7	94.1	85.0	79.9
Standard deviation (%)	14.2	10.0	13.1	12.5	9.3	4.5	13.1	24.8
Elimination capacity, g/(m^3 h)	9.6	11.0	13.6	19.6	24.8	30.9	34.8	38.7
(kg COD/(m^3 day))	(0.81)	(0.93)	(1.15)	(1.65)	(2.1)	(2.62)	(2.95)	(3.28)

[a] Operating conditions: FS, flow switching; St, stagnation.

of the performance. When the loading rate was further increased to 26.83 g/(m^3 h) (2.27 kg COD/(m^3 day)) with an influent concentration of 250 ppmv on day 153, the removal efficiency was almost constant at 91%. On day 182, the concentration was further increased to 300 ppmv corresponding to 32.19 g/(m^3 h) (2.73 kg COD/(m^3 day)). The removal efficiency was still improving and peaked at a level of 94 ± 5%. On day 203, the influent concentration was further increased to 380 ppmv corresponding to 40.06 g/(m^3 h) (3.39 kg COD/(m^3 day)). The removal efficiency started to decline to 85%. The decline continued after day 232 at the next concentration level of 450 ppmv corresponding to 47.69 g/(m^3 h) (4.04 kg COD/(m^3 day)). The removal efficiency dropped to 80%, which could be considered as the maximum loading capacity of this TBAB. It is worthwhile mentioning that this removal efficiency is still far higher than the removal efficiency of the previous two TBABs. This clearly indicates the superiority of the fungi TBAB over traditional bacterial TBABs even if a surfactant is added.

4. Discussion of the results

4.1. Performance comparison for TBABs "A", "B" and "C"

Generally, for both TBABs "A" and "B" fluctuations in performance was noticed. The fluctuation in removal efficiency was reported previously without known reason [16]. The overall standard deviation in the removal efficiency was 29% which is a very high rate as compared to other contaminants degraded in similar TBABs [31].

Fungi utilization greatly enhanced the performance of the TBAB as compared to TBAB "A" and "B". The switch of microorganisms to fungi has shown superior performance in several studies. Styrene was treated successfully with fungi at a maximum elimination capacity of 67 g/(m^3 h) [32]. The same research group could reach elimination capacities up to 336 g/(m^3 h) using newly isolated fungus Sporothrix variecibatus [33]. In a biofilter treating xylene, fungi were isolated and were identified as the active species in the biofiltration process [34]. The percent removal efficiency in the current study increased significantly and reached the upper 80% level. Fig. 4 shows the different loading rates applied for each TBAB versus the elimination capacity obtained with error bars representing the standard deviation. The theoretical 100% removal line corresponds to the maximum theoretical elimination capacity that could be obtained for each loading rate. The maximum loading rate applied for each TBAB is determined when its performance line starts to deviate from the 100% line. TBABs "A" and "B" had similar performance up to 5.4 g/(m^3 h) with a removal efficiency of 82% for both TBABs. Both TBABs deviated from the 100% line to have the same performance at 10.4 g/(m^3 h). When the loading rate increased further the difference in performance started to be visible favoring better performance for TBAB "B". It is worthwhile to note that the concentration level of the surfactant could play a negative effect in the biodegradation process by inhibiting microbial growth [29]. However, this was not observed in the current study under concentration level of surfactant considered (150 mg/L). The enhanced performance beyond the 10.4 g/(m^3 h) could be explained by the effect of surfactant, while at loading rates below 10.4 g/(m^3 h) the solubility of n-hexane was not a rate limiting factor. It is worthwhile to note that the behavior of TBAB "B" is very similar to the reported performance of toluene in a bead biofilter using surfactant Brij35 [10], although it could be expected that toluene could perform better than n-hexane. The surfactant used in this study, Tomadol 25-7, has shown superior performance in the biodegradation of n-hexane if compared to other surfactants like Triton X-100 [26]. Another recent study [35] exploring the effect of four different surfactants on n-hexane's Henry's Law Constant showed that the highest solubility was achieved using Triton X-100. However, Tomadol 25-7 was not included in this study.

TBAB "C" started at an initial loading rate of 13.4 g/(m^3 h) and the superiority of performance of this TBAB is clearly seen in Fig. 4. It started to deviate from the 100% line only beyond 32 g/(m^3 h). Some improvements need to be accomplished for narrowing the fluctuations in the removal efficiency. It is anticipated that the use of integrated two bed cyclic adsorption/desorption unit together with the TBAB will ease these fluctuations, as demonstrated in our previous study [36].

4.2. Kinetics of n-hexane removal in the three TBABs

The removal performance as a function of depth was measured weekly. This was conducted one day following stagnation at the sampling ports located along the depth. The sampling ports are located at 7.6, 23, 38, 53 and 60 cm measured from media top. These

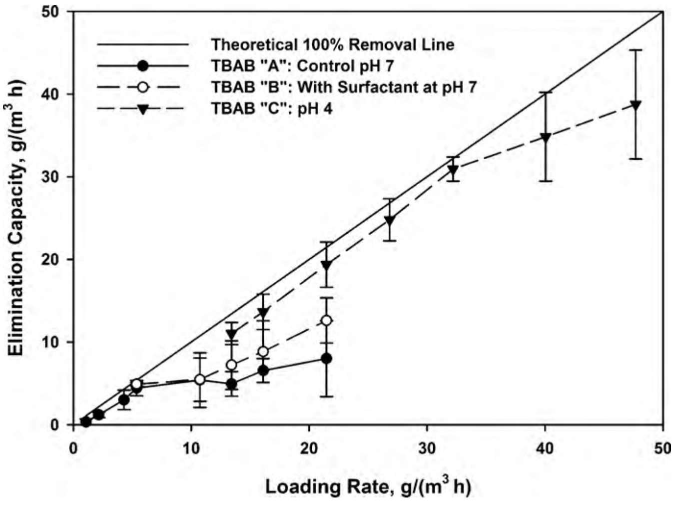

Fig. 4. Elimination capacity versus loading rate for the three TBABs "A", "B" and "C".

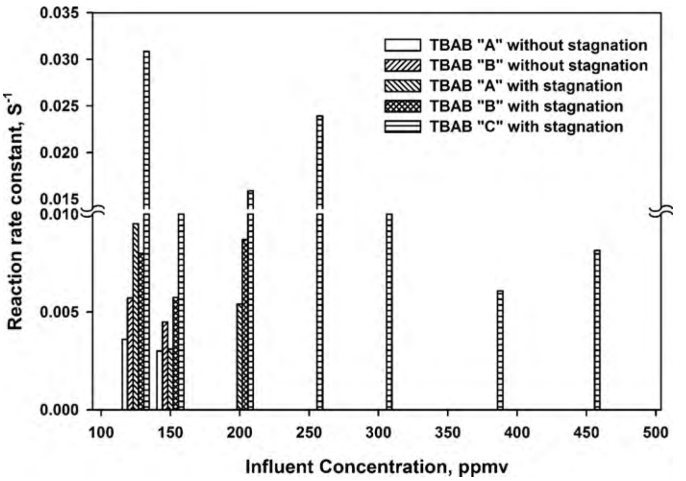

Fig. 5. Pseudo first order reaction rate constant for the different TBABs and influent concentrations.

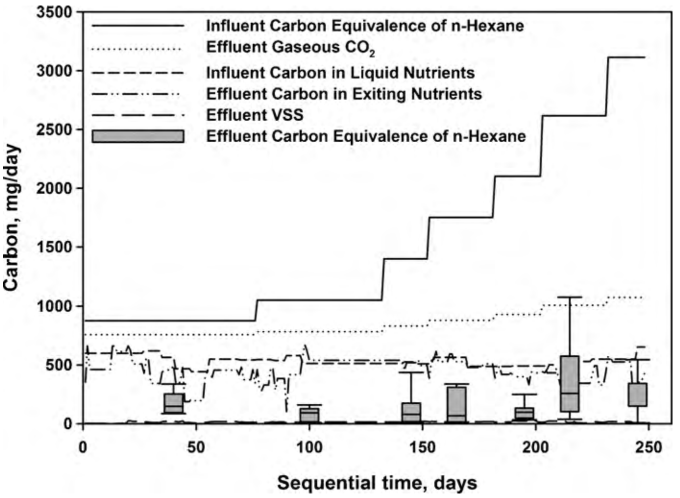

Fig. 7. Carbon mass balance for TBAB "C".

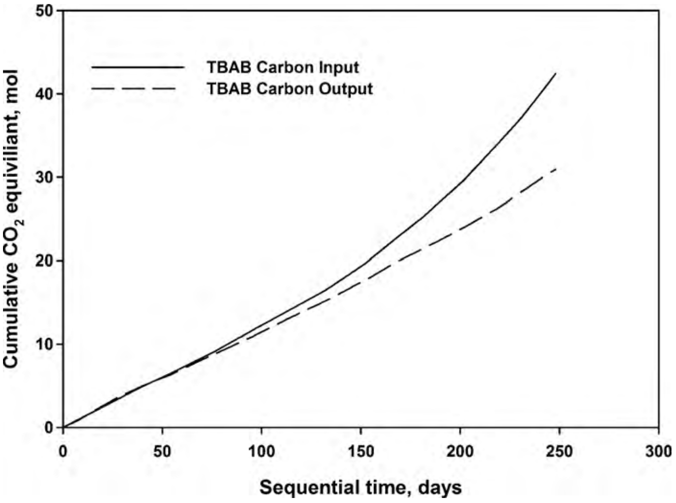

Fig. 6. Cumulative carbon input/output as CO_2 equivilant in mol for TBAB "C".

data were used to develop the pseudo first order reaction rate constant as a function of time. The reaction rate constant is calculated by assuming pseudo first order reaction occurring in a plug flow reactor. All sampling data at every concentration level (minimum of 3 dataset) was fit with a linear model with the independent variable, time (seconds), and the dependant variable, $\log_e(C/C_0)$, where C is the effluent concentration and C_0 is the influent concentration. Fig. 5 clearly shows the advantage of fungi utilization in the TBAB which is indicated by a higher reaction rate constant as compared to the other two TBABs at the same influent concentration. n-Hexane reaction rate constant decreased as the influent loading increased. This could be due to the excess biomass held within the TBAB bed. The reaction rate constant values for TBAB "C" ranged from 0.006 to 0.03 s^{-1}, while the maximum reaction rate constant for TBAB "A" and "B" were 0.0095 and 0.0087 s^{-1}, respectively.

Further analysis of the data were conducted by fitting the daily performance data to a plug flow model in order to estimate the TBAB reaction kinetics during the different operation strategies. The following assumptions for the model were made: (1) the TBAB is running at steady state condition; (2) the pressure drop through the bed is negligible; (3) the area of flow is constant; and (4) one single oxidation reaction is occurring through the bed. Based on these assumptions a simplified plug flow equation can be derived which takes the following form:

$$\mathrm{EC} = \mathrm{LR} \times (1 - 10^{-kt}) \tag{1}$$

where EC: elimination capacity in g/(m^3 h); LR: loading rate in g/(m^3 h); k: first order reaction rate constant; t: time in hours

The first order pseudo reaction rate constants were found to be 6.71, 10.88 and 26.58 h^{-1} for the three TBABs, respectively. These values are very close to the lower end values obtained from the depth removal kinetics. The equation, therefore, could reasonably predict the worst performance that could occur in the TBAB.

4.3. Carbon mass balance

The cumulative CO_2 equivalent of n-hexane in the influent was compared to the same equivalent in the effluent for all biofilters. The influent cumulative CO_2 consists of influent gaseous concentration and influent aqueous inorganic and organic carbon. The effluent CO_2 equivalent includes the effluent aqueous inorganic and organic carbon, effluent VSS, gaseous CO_2 and effluent n-hexane concentration. Fig. 6 presents the cumulative influent and effluent for TBAB "C" as an example. The difference between the influent and effluent carbon on average was 9.6% with a standard deviation of 8.8%. A difference of 29.3 and 19.3% with standard deviations of 3 and 3.1% was obtained for TBABs "A" and "B", respectively (data not shown). The amount of biomass retained in TBAB "C" was on average 528 mg C/day while the amount retained in TBABs "A" and "B" was 195 and 345 mg C/day, respectively. It is postulated that the loss in carbon between influent/effluent was retained as biomass within the TBAB. This hypothesis was tested by comparing the loss in carbon to the biomass amount accumulated in the TBAB which was calculated using the daily nitrate consumption for all loading rates for the different biomass control strategies. A typical cellular composition for a heterogeneous microorganism is represented as $C_9H_{15}O_5N$ [37,38] was used as the basis for relating the nitrate consumed in building up new biomass in order to estimate the amount of biomass retained within the TBAB. The results of the t-test ranged from 0.006 to 0.05. This indicated that the difference between the losses in carbon to the biomass accumulated in the TBAB was significant with a p-value < 0.05.

It is worthwhile to note that the main carbon contributors are the gas phase concentrations: Influent and effluent n-hexane concentrations, and effluent gaseous carbon dioxide. The amount of carbon in the liquid phase due to VSS, influent and effluent organic carbons can be considered to be negligible since the total aqueous carbon did not exceed 5% of the total carbon in the system (gaseous and liquid phases). An example of the contribution of the different components could be found in Fig. 7 for TBAB "C". All the different components contributing to the carbon balance are represented as daily measurements with exception to the effluent carbon equivalence of n-hexane which is represented as box plot for each concentration level. It is worthwhile to note that flow switching of the gas flow did not cause n-hexane to escape in the liquid phase when the gas and liquid phases were run counter-currently.

5. Conclusions

This study investigated the effect of surfactant and fungi on TBAB performance for removal of n-hexane. Using Tomadol® 25-7 successfully enhanced the biodegradation process of n-hexane in the TBAB and provided more stable performance by having smaller standard deviation in the removal efficiency as compared to the control TBAB "A". The added stability in performance could put more trust in the biological treatment of hydrophobic compounds as industries prefer installing more expensive options to ensure compliance with regulatory rules. The stability of the results was more pronounced by using flow switching together with stagnation technique. This strategy could successfully replace backwashing for low microbial yield compounds such as n-hexane.

The fungi TBAB showed a significant performance enhancement as compared to the other two TBABs. Operation at acidic pH enhanced greatly the performance providing a removal efficiency around the 90% level. Using Fungi culture led to higher loading rates that could not be achieved by microbial culture operated at neutral pH. Nevertheless, some more improvements are needed to further narrow the fluctuation in the removal efficiency. The elimination capacities reported in this paper at long duration of performance and controlled operational conditions set new performance standards for biodegradation of hydrophobic compounds generally and n-hexane specifically as compared to previous studies and existing biofiltration units.

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