



Effect of methanol on the biofiltration of n-hexane

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ABSTRACT

This study investigated the removal of recalcitrant compounds in the presence of a hydrophilic compound. n-Hexane is used as a model compound to represent hydrophobic compounds. Methanol has been introduced in mixture with n-hexane in order to increase the bioavailability of n-hexane in trickle-bed-air-biofilters (TBABs). The mixing ratios investigated were: 70% methanol:30% n-hexane, and 80% methanol:20% n-hexane by volume. n-Hexane loading rates (LRs) ranged from 0.9 to 13.2 g m⁻³ h⁻¹. Methanol LR varied from 4.6 to 64.5 g m⁻³ h⁻¹ and from 2.3 to 45.2 g m⁻³ h⁻¹ depending upon the mixing ratio used. Biofilter performance, effect of mixing ratios of methanol to n-hexane, removal profile along biofilter depth, COD/nitrogen consumption and CO₂ production were studied under continuous loading operation conditions. Results have shown that the degradation of n-hexane is significantly enhanced by the presence of methanol for n-hexane LR less than 13.2 g m⁻³ h⁻¹. For n-hexane LR greater than 13.2 g m⁻³ h⁻¹, even though methanol had impacted n-hexane biodegradation, its removal efficiency was higher than our previous study for biodegradation of n-hexane alone, in presence of surfactant, or in presence of benzene. On the other hand, the degradation of methanol was not impacted by the presence of n-hexane.

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1. Introduction

The passage of the 1990 Amendments to the Clean Air Act had led to the development of more stringent regulations, standards, guidelines and codes of volatile organic compounds (VOCs) emissions. It also paved the way to the development of processes aimed at reducing air pollution. Since VOCs contribute greatly to air pollution, several techniques were applied for VOCs abatement such as physico-chemical, adsorption, scrubbing, condensation, oxidation processes, and biofiltration [1].

Recently, biofiltration systems have emerged as an effective technique for non-methane hydrocarbon removal from air operating under dynamic VOCs loading rates and stressed conditions. Combined by its cost effectiveness, it is an attractive option for controlling VOCs emissions from various industrial processes [2]. More interestingly, trickle-bed-air-biofilters (TBABs) offer more optimal and controllable operations which result in low maintenance costs over traditional biofilters. Thus, they are more efficient in treating VOCs that do not engender acidic by-products [2].

The performance of TBABs is significantly affected by the VOCs solubility in water and their Henry's law constant [3]. Hydrophilic compounds, water soluble ketones and esters, are easily biodegradable than hydrophobic ones, such as aromatic hydrocarbons. The later are more resilient to degradation, as VOC mass transfer from gas to liquid phase is rate limiting in TBABs. Thus, an increase in bioavailability of VOCs in the liquid biofilm phase will facilitate their biodegradation by microorganisms. Several processes were tested for addressing the bioavailability of hydrophobic contaminants, like introducing surfactants [4], providing favorable conditions for fungi [5–9], and the utilization of two-phase reactors [10–13].

Several studies were reported on biofiltration of n-hexane as a single solute. An elimination capacity (EC) of 38.7 g m⁻³ h⁻¹ was obtained at a loading rate (LR) of 47.7 g m⁻³ h⁻¹ for a TBAB operating at pH 4. While for TBABs operating at pH 7 with and without surfactant, the ECs were 12.6 and 8.0 g m⁻³ h⁻¹, respectively, at a LR of 21.5 g m⁻³ h⁻¹ [5]. Other researchers obtained results with high elimination capacities but either low removal efficiencies were attained or a short testing period was evaluated which could raise questions about meeting the strict emission levels as well as their practical industrial use. For instance, Arriaga and Revah [14] obtained a maximum EC of 130 g m⁻³ h⁻¹ for n-hexane LR of about 560 g m⁻³ h⁻¹ in a perlite packed biofilters corresponding

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Table 1
Summary of methanol biofiltration as reported in literature.

Reactor medium	Substrate treated	Elimination capacity ($\text{g m}^{-3} \text{h}^{-1}$)	Loading rates ($\text{g m}^{-3} \text{h}^{-1}$)	EBRT (s)	Reference
Compost and wood chips	Methanol	15.8–139	31–147	30–50	[19]
	α -Pinene	13.9–17.5	14.6–26.7	30–50	
Lava rock	Methanol	7.5	7.8	80	[20]
	Formaldehyde	41.2	46.2	71.9	
Nova inert	Methanol	80	140	40	[24]
	Dimethyl Sulfide	2.5	10	40	
Polypropylene pall rings (inert)	Methanol	380	480	16	[25]
	H_2S	85–95	141	16	

to a removal efficiency (RE) of 23% and an effluent concentration of 8.8 g m^{-3} which did not meet the emission criteria of 1.8 g m^{-3} [15]. van Groenestijn and Lake [16] used a mixture of silicone oil and water as the trickling medium for n-hexane removal and obtained an EC of $80 \text{ g m}^{-3} \text{ h}^{-1}$ at LR of $97 \text{ g m}^{-3} \text{ h}^{-1}$. However, according to the authors, this value was obtained by changing the medium each month of two biofilters connected in series. Furthermore, there was increase in liquid phase viscosity and phase inversion combined by high empty bed residence time (EBRT) (6.28 and 13 min) would render its field application not practical. Hernández-Meléndez et al. [7] obtained an EC_{max} of around $70 \text{ g m}^{-3} \text{ h}^{-1}$ for n-hexane LR of $177 \text{ g m}^{-3} \text{ h}^{-1}$, inlet n-hexane concentration of 12.5 g m^{-3} and an EBRT of 4.4 min corresponding to an effluent concentration of about 7.5 g m^{-3} which is above 1.8 g m^{-3} set by the Occupational Safety and Health Administration (OSHA) [15]. In general, although researchers obtained high EC, the RE of n-hexane, as a sole VOC, was either low which could provide an effluent stream at levels beyond the emission standard or the evaluations were done for a short period of time. On the other hand, biofiltration of n-hexane in mixture with other VOCs, to the best of our knowledge, is rarely reported in literature except our previous work in treating n-hexane with benzene [17]. It is worth to note that air emissions are always mixture of gases rather than a sole VOC.

The high biodegradation of methanol raised interest in initiating studies on biofiltration of VOCs in its presence [18–24]. Table 1 summarizes methanol behavior in a binary mixture as reported in the literature. The main objectives of these studies were either to study the effect of methanol on biofiltration of other VOCs such as toluene, dimethyl sulfide, formaldehyde, hydrogen sulfide, α -pinene, or to study the effect of nutrients limitation on these mixtures. The addition of methanol to other VOCs might have neutral [24], positive [19,25] or negative [18,20] effect depending on the VOCs and their loading rates, type of media used, nutrients availability, biomass control strategies, pH, and temperature.

The aim of the current study is to study the bioavailability of n-hexane in the presence of methanol. Both VOCs are hazardous air pollutants included in the 1990 Clean Air Amendment list [26]. Introducing a mixture of n-hexane and methanol has the potential of exposing the biofilm to increased n-hexane concentrations which might lead to overcome the mass transfer limiting step. The effect of methanol to n-hexane mixing ratio on removal efficiency of n-hexane is evaluated. Two independent TBABs “A” and “B” were operated at homogeneous mixing ratios of 70:30% and 80:20%, methanol:n-hexane by volume, respectively. The TBABs were fed with a nutrient solution buffered at pH 7. The effect of step-increase in the influent concentration of the mixture on the EC of the biofilter is also evaluated. The control of biomass growth was achieved by using a combination of stagnation and flow-switching and periodical backwashing. A further illustration of these techniques is provided in previous publications [5,17,27–29] and is described briefly later.

2. Experimental

2.1. VOCs

n-Hexane was obtained from Fisher Scientific (Fair Lawn, NJ) with 95% purity, while methanol was obtained from Tedia (Fairfield, OH) with 99.9% purity. The reported dimensionless Henry's law constants at 25°C for n-hexane are 40.7 ± 2.78 [30] and 48.4 [31], while for methanol is 1.9×10^{-4} [32].

The mixing ratios, considered 70:30 and 80:20 – methanol:n-hexane, were based on emissions from industrial applications. In printing and publishing, polymer and man-made fiber, pulp and paper, and organic chemical industries the release ratios of methanol to n-hexane is varying from about 70% to 96% [33].

2.2. Trickle-bed-air-biofilter

Two TBABs, “A” and “B”, were run in parallel in this study. Both TBABs were made up of seven cylindrical glass sections with an internal diameter of 7.6 cm and a total length of 130 cm. They are packed with palletized 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 schematic of the TBAB setup had been previously provided [34]. TBAB “A” was fed with a mixing ratio of methanol:n-hexane of 80:20% by volume; while TBAB “B” was fed with a mixture 70:30%. Furthermore, each TBAB received an increasing step-change in influent concentrations. The TBABs continued to run for an initial three weeks acclimation period with weekly backwashing.

The methods used to control biomass growth were a combination of stagnation and flow-switching for n-hexane loading rates below $5.3 \text{ g m}^{-3} \text{ h}^{-1}$, stagnation alone and later periodical backwashing for n-hexane loading rates above $5.3 \text{ g m}^{-3} \text{ h}^{-1}$. Flow switching consists of changing the flow of the gas from co-current flow with the liquid nutrients to counter-current flow or vice versa after every one week of operation. Such a process might spread the biomass distribution within the entire biofilter media. While stagnation is a complete shutdown of air, VOCs and buffer nutrient flows for two days per week. Backwashing consists of fluidization of the media bed to ensure adequate removal of excess biomass that might cause channeling within the biofilter. All these techniques were previously applied in the biofiltration of hydrophilic and hydrophobic VOCs and were proven to be very effective in biomass control [5,17,27–29]. Table 2 summarizes the biomass control strategy applied for each phase of the study.

The air flow was set up at the rate of 1.36 L min^{-1} with a corresponding EBRT of 120 s. The liquid mixture of n-hexane and methanol was injected via a syringe pump and vaporized into the air stream. Buffered nutrient solution containing sodium bicarbonate (pH 7) was supplied at a rate of 2.0 L d^{-1} , the composition of the nutrient solution is similar to that reported by Sorial et al. [35].

Table 2
Operating conditions for TBABs “A” and “B”.

	Experimental conditions	I	II	III	IV	V	VI	VII
TBAB “A”	Influent n-hexane concentration (ppmv)	9.1	22.8	34.1	50.9	76.7	102.0	127.0
	Influent n-hexane concentration (g m^{-3})	0.03	0.08	0.12	0.2	0.3	0.4	0.5
	n-Hexane loading rate ($\text{g m}^{-3} \text{h}^{-1}$)	0.9	2.4	3.5	5.3	8.0	10.6	13.2
	Influent methanol concentration (ppmv)	119.5	298.8	447.4	668.5	1007.6	1339.4	1668.2
	Influent methanol concentration (g m^{-3})	0.2	0.4	0.6	0.9	1.3	1.7	2.2
TBAB “B”	Methanol loading rate ($\text{g m}^{-3} \text{h}^{-1}$)	4.6	11.5	17.3	25.8	38.9	51.7	64.5
	Influent methanol concentration (ppmv)	59.0	197.9	293.9	390.1	586.0	781.3	974.9
	(g m^{-3})	0.1	0.3	0.4	0.5	0.8	1	1.3
	Methanol loading rate ($\text{g m}^{-3} \text{h}^{-1}$)	2.3	7.6	11.4	15.1	22.6	30.2	37.7
	Day of operation	1–21	22–49	50–119	120–139	140–170	171–204	205–240
	Operating conditions ^a	S&FS	S&FS	S&FS	S	S	S	B

^a Operating conditions: B, backwashing; FS, stagnation and flow switching; and S, stagnation.

2.3. Analytical methods

Gas phase samples were taken with gas-tight syringes through low-bleed and high-puncture-tolerance silicone gas chromatograph (GC) septa installed in the sampling ports. Samples for n-hexane and methanol were immediately analyzed by using GC (Agilent 6890 Series, Foster City, CA) equipped with flame ionization detector (FID) and $30.0 \text{ m} \times 320 \mu\text{m} \times 0.25 \mu\text{m}$ column (HP-5. 5% phenyl methyl siloxane). The GC oven was programmed isothermal at 60°C , the carrier gas helium (He) flowrate was set at 2.7 mL min^{-1} . The FID was used with He make-up gas at a flowrate of 45 mL min^{-1} , a fuel gas flow (H_2) of 35.3 mL min^{-1} , and an oxidizing gas flow (air) of 450 mL min^{-1} . The detector temperature was 250°C . Retention time of 1.1 min and 1.3 min were obtained, under these conditions for methanol and n-hexane, respectively. Carbon dioxide samples 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 a thermal conductivity detector (TCD) was used for determining the CO_2 concentrations in the effluent gas phase. The detection limit was 0.001 vol.% CO_2 . Detailed description of the analytical method is provided in a previous publication [34].

Liquid phase measurements included influent and effluent concentrations of nitrate, dissolved total carbon (TC), dissolved inorganic carbon (IC), and volatile suspended solids (VSS). Nitrate (NO_3^-) concentration was determined by measuring UV absorption at 220 nm wavelength using a Shimadzu UV mini 1240 UV-Vis spectrophotometer (Shimadzu Corp., Tokyo, Japan). TC and IC contents of the aqueous samples were determined by using a Shimadzu TOC 5000 analyzer (Shimadzu Corp., Tokyo, Japan). The VSS analysis was carried out according to Standard Methods 2540G [36].

3. Results and discussion

3.1. Performance of TBAB “A” (methanol:n-hexane = 80:20)

TBAB “A” started up with n-hexane influent concentration of 9 ppmv and methanol concentration of 119.5 ppmv with a corresponding n-hexane LR of $0.9 \text{ g m}^{-3} \text{ h}^{-1}$ and methanol LR of $4.6 \text{ g m}^{-3} \text{ h}^{-1}$. The operating conditions and different phases of operation are summarized in Table 2. It is worth noting that the removal efficiency of methanol was always above 98% for the entire loading rates conditions studied. Therefore, emphasis will be placed on the performance of the TBAB with respect to n-hexane. Daily performance of the TBAB with respect to influent and effluent concentrations of n-hexane in addition to a statistical summary of the removal efficiency at different loading rates is presented in Fig. 1. The removal efficiencies are displayed in box plots to increase the visibility. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the

boundary of the box furthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. During phases I, II, and III, for influent n-hexane concentrations 9.0, 22.8, and 33.1 ppmv, respectively corresponding to influent methanol concentrations of 119.5, 298.8, and 447.4 ppmv, respectively, TBAB “A” maintained consistently high n-hexane RE of more than 95%. This efficiency was maintained while applying flow switching and stagnation technique as means of biomass control.

Starting from day 120, flow switching was stopped due to an increase of total organic carbon (TOC) from about 350 to around 650 mg L^{-1} in the effluent water which implies that larger quantity of methanol was escaping through the water phase. It was then decided, for further increase in the influent concentration only stagnation technique will be applied as means for biomass control. It is worthwhile to note that the TOC measurements indicated that inorganic carbon was the sole contributor to the total carbon in the liquid phase which clearly specifies no degradation by products were in the liquid phase.

Phase IV started after backwashing the TBAB. The influent concentrations of n-hexane and methanol were increased to 50.9 ppmv and 668.5 ppmv, respectively. The overall performance for n-hexane elimination increased further to achieve 95.3% with a standard deviation of 6.4%. On day 141 (phase V), after backwashing, the influent concentrations of n-hexane and methanol were increased to 76.8 ppmv and 1007.6 ppmv, respectively. The removal efficiency of n-hexane decreased to 91%. Fig. 1 indicates that the effluent concentrations for n-hexane up to this phase were generally low.

On day 171, after backwashing, phase VI was started. The RE of n-hexane declined to 74.8% during this phase at an influent concentration of 101 ppmv for n-hexane and 1339.4 ppmv for methanol,

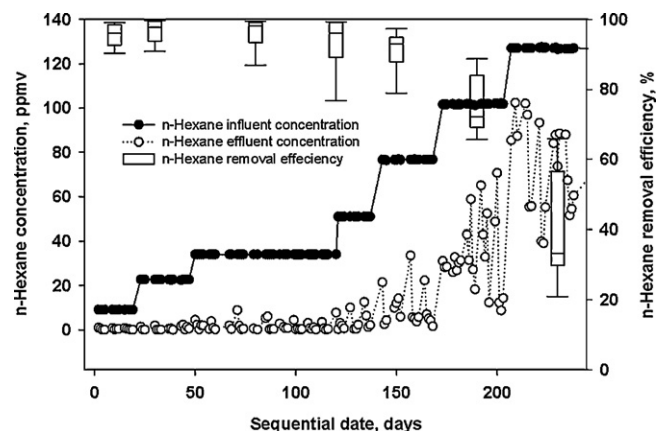


Fig. 1. Performance of TBAB “A” with time for degrading n-hexane in the presence of methanol.

respectively. More fluctuations in n-hexane RE became noticeable due to the negative impact of methanol on the biodegradation of n-hexane. However, the RE of methanol was still maintained at the same level above 98%. At the end of this phase, a thick layer of biomass was visible on the surface of the media, and within the TBAB. With the increase of VOCs' LR, specifically methanol more biomass was accumulating on the surface of the media within the TBAB. This finding could be an indication that cell synthesis and methanol oxidation were simultaneous processes in the upper section of the TBAB. Cell synthesis in the upper section of the TBAB and VOC oxidation within the whole bed was reported in biofiltration of toluene [37] and was also confirmed by Song and Kinney [38]. It was thus decided that for subsequent runs backwashing should be applied weekly as the only biomass control technique. The same observation had been noticed by Cai et al. [34] for removing methyl ethyl ketone and by Sologar et al. for the biofiltration of hydrogen sulfide and methanol [24].

In phase VII, n-hexane RE deteriorated drastically to 41% when the influent concentration was increased further to 127 ppmv while methanol RE was still maintained at high levels above 98%. During this phase backwashing was applied weekly. Weekly backwashing was accompanied by high loss of biomass which might have been the cause for the drastic decrease in the removal efficiency of n-hexane. It is speculated that not enough time was allowed for the growth of microorganisms responsible for n-hexane degradation. This is in accordance with previous studies by Delhoménie et al. [39] and Kim et al. [27] where they observed that decrease in biofilter performance due to biomass loss after biomass control is common. Furthermore, methanol seems to be an easy accessible carbon source for the microorganism, which could be the cause of inhibition of the biodegradation of n-hexane at high methanol loads. Similar inhibitions were encountered by Prado et al. [19] in biofiltration of waste gases containing a mixture of formaldehyde and methanol.

3.2. TBAB "B" performance (methanol:n-hexane = 70:30)

The same operating conditions with respect to n-hexane for TBAB "A" was applied to TBAB "B" as can be seen from Table 2. The biofilter was started up at 9.1 ppmv n-hexane corresponding to 59.0 ppmv of methanol with a corresponding LR of $0.9 \text{ g m}^{-3} \text{ h}^{-1}$ and $2.3 \text{ g m}^{-3} \text{ h}^{-1}$ for n-hexane and methanol, respectively. In phase I, TBAB "B" maintained consistently high n-hexane RE of 90% as well as for subsequent phases II and III, for influent concentrations of n-hexane of 22.8 and 34.1 ppmv.

In phases IV and V, n-hexane RE decreased to 88.6% and 88%, respectively. In the following phase as the LR was increased further to provide an influent concentration of 102 ppmv for n-hexane, n-hexane RE decreased to 75.4% which was slightly higher than that of TBAB "A". Further increase of the influent concentration, with weekly backwashing as means of control of biomass, led to the removal efficiency of n-hexane to drop to 63.4%.

TBAB "B" influent and effluent concentrations together with the removal efficiency as box plots at every concentration level are illustrated in Fig. 2. The same behavior seen previously in Fig. 1 was observed here, high effluent concentration occurred at the start of every concentration change. Specifically, more fluctuations are

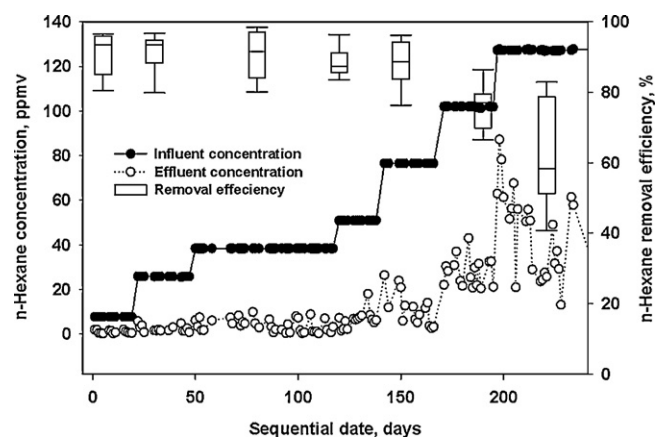


Fig. 2. Performance of TBAB "B" with time for degrading n-hexane in the presence of methanol.

seen during phases VI and VII, i.e., at high methanol loading rates. The maximum EC was $8.4 \text{ g m}^{-3} \text{ h}^{-1}$ for n-hexane (see Table 3). The high methanol LR affected n-hexane RE of the TBAB "B", but to a less extent as compared to TBAB "A".

It is generally seen in this study, for an influent concentration of n-hexane up to 102 ppmv, the RE for both TBABs was not fluctuating as previously reported [40].

Comparing the performance of both TBABs, TBAB "A" had more stable and slightly higher removal efficiencies, especially for loading rates less than $10.6 \text{ g m}^{-3} \text{ h}^{-1}$, but both had similar fluctuations in performance and unexplained high standard deviations especially for the last phase of the experiment. In previous studies, higher standard deviations in n-hexane removal efficiency were common without any reason [40]. On the other hand, both TBABs had overall higher performance in degrading n-hexane in the presence of methanol as compared to a previous study for degrading n-hexane alone, with surfactant, or in mixture with benzene [17].

The degradation of n-hexane in the presence of methanol was greatly enhanced as compared to our previous published literature for n-hexane loading rate less than $10.2 \text{ g m}^{-3} \text{ h}^{-1}$. As a sole VOC, Aly Hassan and Serial [5,40] reported 82.1, 57.3, 66.5 and 41.2% n-hexane RE for LR of 5.4, 10.4, 10.4 (using flow switching) and $13.4 \text{ g m}^{-3} \text{ h}^{-1}$, respectively. In this study we obtained 88.6, 75, and 63.4% in RE for TBAB "B" and 95.3, 74.8 and 41.1% in RE for TBAB "A" for a corresponding n-hexane LR of 5.3, 10.6, and $13.2 \text{ g m}^{-3} \text{ h}^{-1}$, respectively.

It has not escaped our mind that the results obtained for elimination capacities obtained in oil-amended and two phase liquid biofilters were higher than the results obtained in this study. However, the drawback of treating n-hexane as a sole VOC in oil-amended biofilters as mentioned previously were high effluent concentration levels and relatively short period of time of operation which was accompanied by high instability and frequent drop in removal capacity. Furthermore, it is worth noting the n-hexane emission is usually in the presence of other VOCs where methanol is the major component [33,41]. Treating mixture of hydrophilic and hydrophobic in oil-amended systems will not be possible as

Table 3
Biofiltration performances of TBABs "A" and "B".

		I	II	III	IV	V	VI	VII
TBAB "A"	n-Hexane elimination capacity ($\text{g m}^{-3} \text{ h}^{-1}$)	0.8	2.3	3.3	5.0	7.3	7.9	5.4
	Methanol elimination capacity ($\text{g m}^{-3} \text{ h}^{-1}$)	4.5	11.1	16.6	24.8	38.0	50.8	63.7
TBAB "B"	n-Hexane elimination capacity ($\text{g m}^{-3} \text{ h}^{-1}$)	0.8	2.2	3.1	4.7	7.0	7.9	8.4
	Methanol elimination capacity ($\text{g m}^{-3} \text{ h}^{-1}$)	2.2	7.3	10.7	14.4	21.7	29.1	37.1

toxicity and inhibitory effects will surge during the first stage of operation [13,42–46].

Aly Hassan and Sorial [17] reported lower removal efficiencies for n-hexane in the presence of benzene indicating that the presence of benzene impacted the degradation of n-hexane. The current results reported in this paper are consistent with the findings in other studies where methanol addition played an important role in the biofiltration of dimethyl sulfide [25] and in formaldehyde removal [19].

3.3. Effect of methanol to n-hexane mixing ratio

Mixing ratio of methanol to n-hexane was very critical in the biodegradation of n-hexane especially at n-hexane loading rate of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$. Methanol performance was not influenced by the presence of n-hexane for both TBABs (see Tables 2 and 3). This implies that the existence of n-hexane did not hinder the biodegradation of methanol, in contrary to the findings for n-hexane in the presence of benzene [17]. For this study, the data obtained for n-hexane biodegradation showed that methanol had positive effect on the performances of both TBABs. For LR less than $13.2 \text{ g m}^{-3} \text{ h}^{-1}$, TBAB "A" always had a relatively consistent higher performance over TBAB "B". This result could be explained by the fact that the relatively high methanol loading rate in TBAB "A" could trigger more n-hexane to be bioavailable as compared to TBAB "B". On the other hand, for n-hexane LR of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$, the RE for TBAB "A" dramatically decreased to 41% while for TBAB "B" the decrease was not so sharp (from 75% to 63%). The sharp depletion in n-hexane RE might be due to higher methanol loading rate in TBAB "A" $64.5 \text{ g m}^{-3} \text{ h}^{-1}$, as compared to $37.7 \text{ g m}^{-3} \text{ h}^{-1}$ for TBAB "B". The decrease in RE of hydrophobic VOCs in presence of hydrophilic VOCs had been previously reported. Zhu et al. [47] reported significant decrease in the removal rate of hydrophobic VOCs in presence of hydrophilic VOCs. Song et al. [48] confirmed that biodegradation of toluene and p-xylene was severely inhibited by the presence of readily degradable constituents while the presence of aromatic VOCs did not influence the biodegradation of methyl propyl ketone, ethyl 3-ethoxy propionate, or n-butyl acetate. For a mixture of hydrophobic VOCs with methanol, Mohseni and Allen [18] reported that methanol suppressed the growth of α -pinene degrading microbial community and therefore reduced the α -pinene removal efficiency. Jin et al. [20] observed that methanol reduced the efficiency of hydrogen sulfide biodegradation.

A plot of EC vs. LR for n-hexane in both TBABs is provided in Fig. 3. It can be seen from the figure that for n-hexane LR less than $10.6 \text{ g m}^{-3} \text{ h}^{-1}$ both TBABs had approximately the same ECs. Afterward, due to the high loading rate of methanol in TBAB "A"

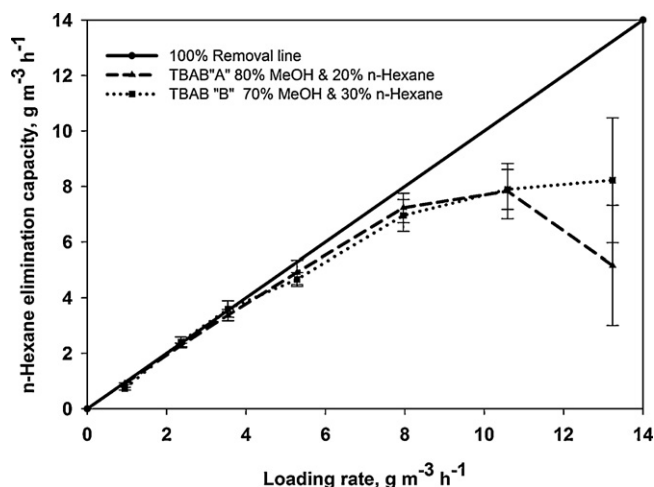


Fig. 3. n-Hexane elimination capacity vs. loading rate.

at n-hexane LR of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$ the EC of TBAB "A" dropped considerably to $5.2 \text{ g m}^{-3} \text{ h}^{-1}$ while it slightly increased for TBAB "B" to reach the value of $8.4 \text{ g m}^{-3} \text{ h}^{-1}$. This confirms the previous observation, where further increase in methanol LR caused a drop of n-hexane EC. It should be noted that both TBABs maintained very high methanol EC indicating that not only the critical LR of methanol was not attained, but also both nutrients and oxygen were not rate limiting [24]. This is further illustrated by daily effluent CO_2 gas analysis and residual $\text{NO}_3\text{-N}$ in the effluent waters.

3.4. Carbon mass balance

Fig. 4 shows cumulative CO_2 equivalent of n-hexane and methanol at the influent as well as at the effluent of both TBABs. Since n-hexane and methanol are the only source of energy and electron donors, the influent carbon represented in carbon dioxide equivalence constitutes VOCs influent gaseous concentrations and the influent aqueous carbon constitutes the influent CO_2 in the liquid nutrients. While the effluent cumulative CO_2 was made up of VOCs effluent gaseous concentrations, effluent aqueous carbon (TC), effluent gaseous CO_2 , and the carbon equivalence of effluent volatile suspended solids (VSS). The carbon recovery rate was $63 \pm 7\%$ and $66 \pm 4\%$ for both TBABs "A" and "B", respectively. The recovery rates found are smaller than that reported earlier for n-hexane as single VOC with surfactant [17], which was ranging from 72% to 78%. The loss between influent and effluent carbon was produced as biomass within the TBABs [17]. In

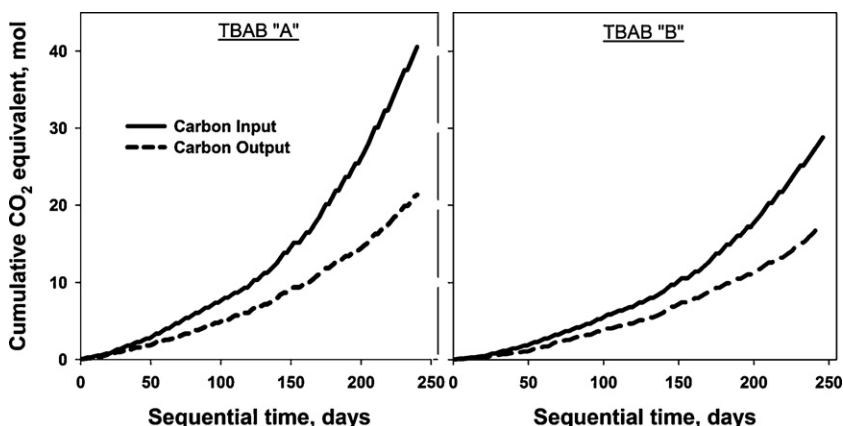


Fig. 4. Cumulative carbon input/output as CO_2 equivalent for TBABs "A" and "B".

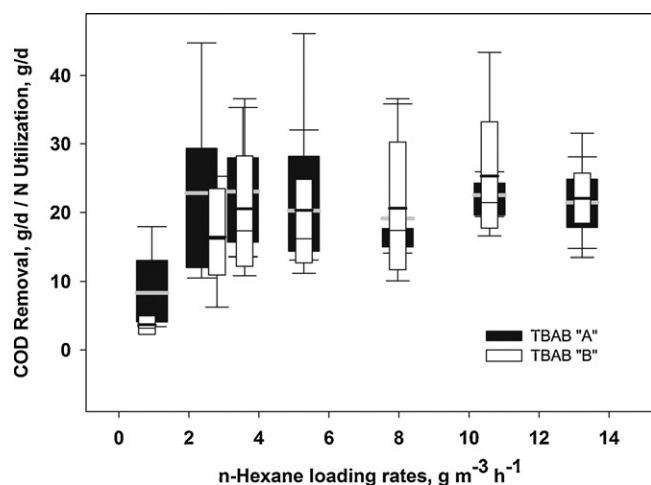


Fig. 5. COD removal per nitrogen utilization for TBABs "A" and "B".

support of this hypothesis, a comparison of the loss in carbon to the biomass amount accumulated in the TBABs was computed. While computing the amount of biomass retained within the bed several assumptions were made (1) biodegradation of n-hexane and methanol occurs independently and (2) $C_5H_7O_2N$ is a typical representation of heterogeneous microorganism in computing the biomass retained within the TBABs [17]. The daily nitrate consumption for all loading rates was used as the basis of this calculation. The results of the t-test, for each phase of the experiments, ranged from 4.3×10^{-6} to 4.7×10^{-2} and from 6.3×10^{-7} to 3.8×10^{-2} for TBAB "A" and TBAB "B", respectively. This indicated that the difference between the losses in carbon to the biomass retained within the TBABs was significant as indicated by a p-value <0.05.

3.5. Nitrogen utilization and VOCs removal

Nitrogen is a critical operational parameter in sustaining biomass development in biological treatment processes [49,50]. Daily analyses for influent and effluent concentrations of $NO_3^- - N$ were performed. $NO_3^- - N$ was used as the only source of nitrogen. The net nitrogen utilization was computed by subtracting the amount of the $NO_3^- - N$ in the effluent water from the influent nutrient liquid. The net chemical oxygen demand (COD) was calculated as the difference between COD of the feed and the COD of the effluent gas and liquid streams. The CODs were theoretically computed using the equivalent carbon values from the different carbon contributors. Fig. 5 shows dimensionless COD/N ratios plotted against the LR of n-hexane for both TBABs "A" and "B" as box plots. It is seen from Fig. 4 that there is a noticeable dependency on the employed LR. Initial increase in loading rates was accompanied by an increase in the nitrate utilization. From loading rate of n-hexane of $5.3 \text{ g m}^{-3} \text{ h}^{-1}$, the nitrate utilization increased to 0.14 g d^{-1} and 0.11 g d^{-1} for TBABs "A" and "B", respectively, without any change in the influent $NO_3^- - N$ which could be attributed to the high methanol LR (see Table 2). This behavior provided a decrease in the COD removal/N utilization ratio. For n-hexane LR of $8.0 \text{ g m}^{-3} \text{ h}^{-1}$, the influent $NO_3^- - N$ was increased further to 0.3 g d^{-1} in order to avoid depletion of $NO_3^- - N$ in the effluent waters. The COD removal/N utilization ratio increased consequently to an average value of 19.1 and 20.6 for TBABs "A" and "B", respectively. At n-hexane LR of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$, $NO_3^- - N$ in the feed was increased further to 0.59 g d^{-1} to maintain sustainable residual $NO_3^- - N$ in the effluent waters. The nitrogen utilized increased to 0.53 g d^{-1} and 0.3 g d^{-1} for TBAB "A" and "B", respectively. It is worth mentioning

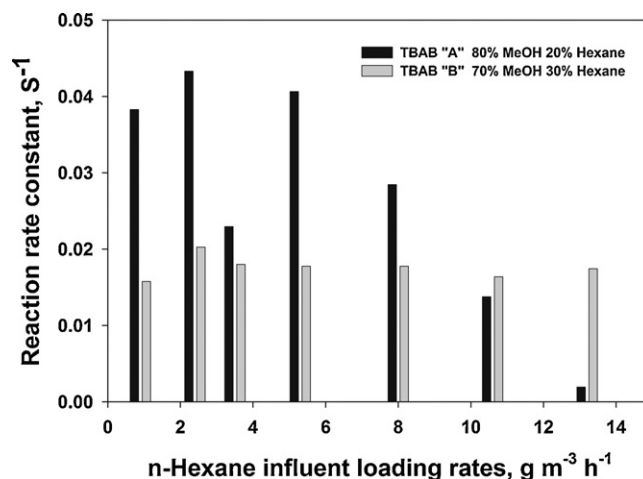


Fig. 6. Reaction rate constants for n-hexane at different loading rates.

that the use of methanol, a high yield VOC, contributed greatly to the high nitrogen consumption.

3.6. Kinetics of n-hexane removal in TBABs "A" and "B"

The removal of both TBABs with respect to n-hexane as a function of depth was measured weekly, one day following stagnation for both TBABs. The sampling ports were located at 7.6, 23, 38, 53 and 60 cm measured from media top. These data were used to develop the pseudo first order reaction rate constant as a function of time. In order to compute the reaction rate constant it is assumed that the TBABs can be modeled as a plug flow reactor [51]. The data were fit with a linear model with the independent variable, time (seconds), and the dependent variable, $\log_e(C/C_0)$, where C is the effluent concentration and C_0 is the influent concentration.

Fig. 6 clearly shows that TBAB "A" had higher reaction rate constant as compared to TBAB "B" up to n-hexane LR of $8.0 \text{ g m}^{-3} \text{ h}^{-1}$. This indicates that the availability of methanol had a crucial role in the performance of n-hexane in the TBABs. Later on, specifically at n-hexane LR of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$ the reaction rate constant for TBAB "A" dropped considerably. This corresponds well with the decrease of the RE noticed in TBAB "A".

It is worth noting that the reaction rate constants for n-hexane obtained in this study are higher than those obtained in our previous research [40] in treating n-hexane with or without surfactant where the maximum values obtained were 9.5×10^{-3} and $8.8 \times 10^{-3} \text{ s}^{-1}$, respectively. As for methanol, since over 90% of the methanol is removed at the top part of the TBAB, it was not possible to evaluate the reaction rate constant. The same observation was made in our previous study [52].

4. Conclusions

This study investigated the effectiveness of methanol in enhancing the degradation of n-hexane in TBABs. The volumetric ratio of methanol to n-hexane were 80:20% and 70:30% for TBABs "A" and "B", respectively. n-Hexane influent LR varied from 0.9 to $13.2 \text{ g m}^{-3} \text{ h}^{-1}$ for both TBABs while for methanol the influent LR varied from 4.6 to $64.5 \text{ g m}^{-3} \text{ h}^{-1}$ for TBAB "A" and from 2.3 to $37.7 \text{ g m}^{-3} \text{ h}^{-1}$ for TBAB "B". The maximum n-hexane EC for TBAB "A" was $7.9 \text{ g m}^{-3} \text{ h}^{-1}$ for an influent LR of $10.6 \text{ g m}^{-3} \text{ h}^{-1}$, while for TBAB "B" the maximum n-hexane EC was $8.4 \text{ g m}^{-3} \text{ h}^{-1}$ for a LR of $13.2 \text{ g m}^{-3} \text{ h}^{-1}$. TBAB "A" had always high and consistent n-hexane RE for LR less than $10.6 \text{ g m}^{-3} \text{ h}^{-1}$. This is due to high bioavailability of n-hexane in TBAB "A" in presence of methanol as compared to TBAB "B". However, for high methanol LR, $64.5 \text{ g m}^{-3} \text{ h}^{-1}$ for TBAB

“A” as compared to only $37.7 \text{ g m}^{-3} \text{ h}^{-1}$ for TBAB “B”, n-hexane EC decreased drastically for TBAB “A” as compared to TBAB “B”. The decrease in n-hexane RE at high methanol LR might be due to applying weekly backwashing as well as to inhibitory effect of methanol on n-hexane degrading microorganisms.

It is worth noting that treating n-hexane in presence of methanol is accompanied by high nitrogen consumption of 0.53 and 0.3 g d^{-1} for TBAB “A” and “B”, respectively. This entails that, for the current operation conditions, nitrogen concentration in the influent nutrient need to be maintained in the range of 0.59 g d^{-1} -N. Maintaining a sustainable residual of nitrogen in the effluent waters will ameliorate the ratio COD/N consumed.

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