

Article

Removal Characteristics of Gas-Phase D-Limonene in Biotrickling Filter and Stoichiometric Analysis of Biological Reaction Using Carbon Mass Balance

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Abstract: Volatile organic compounds (VOCs) pose significant risks to human health and environmental quality, prompting stringent regulations on their emissions from various industrial processes. Among VOCs, d-limonene stands out due to its low threshold and contribution to malodorous emissions. While biofiltration presents a promising approach for VOC removal, including d-limonene, a comprehensive understanding of its performance and kinetics is lacking. This study aims to comprehensively assess the performance of a lab-scale biotrickling filter in treating gas-phase d-limonene. The experimental results indicate that the biotrickling filter efficiently removed d-limonene, achieving a critical loading rate of $19.4 \text{ g m}^{-3} \text{ h}^{-1}$ and a maximum elimination capacity of $31.8 \text{ g m}^{-3} \text{ h}^{-1}$ (correspondingly, up to 85% removal) at the condition of 94.2 s of EBRT. Microbial activity played a significant role in biotrickling filter performance, with a strong linear correlation being observed between CO_2 production and substrate consumption. The Michaelis–Menten model was employed to represent enzyme-catalyzed reactions, suggesting no inhibition during biotrickling filter operation.

Keywords: biofiltration; d-limonene; stoichiometric analysis; microbial kinetics



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1. Introduction

Volatile organic compounds (VOCs) are widely recognized for their adverse impacts on human health due to their inherent toxicity, serving as precursor pollutants for the secondary formation of organic aerosol and ozone upon release into the atmosphere [1–5]. The emissions of VOCs, primarily originating from various industrial processes, are subject to increasingly stringent regulations worldwide [6].

Of all the VOCs, d-limonene has a relatively low threshold of 0.05 to 7.3 mg/m^3 [7–9], giving rise to environmental concerns associated with the generation of malodorous emission. This compound is generated from both anthropogenic sources, including sewage treatment plants, composting processes, landfill gas treatment processes, and biogas production processes, and natural sources such as urban forests and street trees [10–13]. Gaseous limonene concentrations from wastewater treatment plants were reported to reach up to $232.6 \text{ }\mu\text{g/m}^3$ [14]. Zarra et al. [15] found the highest concentration of limonene to be $111.21 \text{ }\mu\text{g/m}^3$ in the sludge treatment plant. Yuya et al. [12] examined the concentrations of limonene in landfills in China and Japan, which ranged from 0.25 to 259 mg/m^3 . Nie et al. [10] investigated ozone formation potential from the sewage sludge composting plant, revealing a propene-equivalent concentration of limonene ranging from $32.47 \text{ }\mu\text{g/m}^3$ to $1565.28 \text{ }\mu\text{g/m}^3$. Terpenes including limonene can contribute to indoor secondary pollution by generating compounds such as formaldehyde, even in the presence of ozone at a low concentration ranging from 17.2 to 21.4 ppb [16].

In comparison to other treatment processes such as adsorption, absorption, and catalytic oxidation, biological methods prove effective and economical for biodegradable

odorants and organic compounds. A biotrickling filter is a well-established biological process, and is particularly effective for removing VOCs, including d-limonene [3,17]. In the biotrickling filter, polluted air passed through a microbial-rich packed bed, facilitating the transfer of contaminants to microorganisms for subsequent biodegradation [18]. Compared to conventional biofiltration, biotrickling filters can effectively control excessive biomass accumulation and enhance the efficiency of biofiltration through regulating the pH, temperature, moisture content, and other parameters [1,17,19–23]. This approach represents a reliable means for addressing odorous and hazardous pollutants, ultimately resulting in the formation of odorless and harmless products. In particular, hydrophobic VOCs control processes using biotrickling filters are becoming more widely used [24–29]. Hong et al. [30] reported that the removal efficiency of methyl isobutyl ketone in a tubular-type biotrickling filter ranged from 70% to 99% at a maximum elimination capacity (EC_{max}) of about $200 \text{ g/m}^3 \cdot \text{h}$. And Chen et al. [25] reported that the removal efficiency of toluene in a tubular biofilter ranged from 52.2% to 99% at a maximum elimination capacity (EC_{max}) of $83.0 \text{ g/m}^3 \cdot \text{h}$.

Terpene-like volatile organic compounds are typically characterized as being hydrophobic. In particular, limonene is highly hydrophobic, with a solubility in water of 13.8 mg/L at 25°C and a Henry's constant of $0.0111 \text{ atm} \cdot \text{m}^3/\text{mol}$ at 25°C . In a study conducted by van Groenestijn and Liu [31], alpha-pinene exhibited removal efficiencies ranging from 50% to 90% in a biofilter, with an inlet loading of 24 to $38 \text{ g/m}^3 \cdot \text{h}$. Cabeza et al. [32] reported that in the biofilter system, alpha-pinene removal was less than 60% at a higher inlet loading of $180 \text{ g/m}^3 \cdot \text{h}$. Another study by Viswanathan et al. [33] demonstrated that applying limonene and beta-pinene to a compost biofilter resulted in 85% and 45% removal, respectively, at an inlet loading rate of $55 \text{ g/m}^3 \cdot \text{h}$. Fatih and Mark [13] reported that a biotrickling filter for limonene and methane showed 83% removal at an inlet loading of $35.5 \text{ g/m}^3 \cdot \text{h}$. While several studies have reported on terpene removal in biofilters, the overall performance, including kinetics and microbial activity, remains incompletely understood. Therefore, further study should be conducted to comprehensively assess the performance of terpene removal, focusing on kinetics and microbial activity. A comprehensive analysis of the activity and kinetics of microorganisms within a biotrickling filter is required to ascertain the operational parameters, including the influent load, gas flow rate, and backwash conditions, for the biofilter operation. Moreover, it is essential to conduct further research into the scientific and engineering fundamentals of biotrickling filters, with a particular focus on the removal of malodorous compounds, including limonene. This study presents a comprehensive application of both stoichiometric and kinetic analyses to elucidate the biological reactions involved in d-limonene treatment. This methodological approach facilitates a deeper understanding of microbial activity and substrate kinetics, which has been insufficiently addressed in prior research.

The objective of this study is to comprehensively assess the performance of a lab-scale biotrickling filter in treating gas-phase d-limonene. The evaluation involves kinetic and stoichiometric analyses to elucidate the characteristics of the biological reactions occurring in the biotrickling filter. Specifically, the study aims to determine the biotrickling filter's critical loading rate and maximum elimination capacity (EC_{max}) and to understand the biological behavior through the application of two biokinetic models (Michaelis–Menten model and Haldane model). Additionally, the carbon mass balance over six months operation of the biotrickling filter was established to analyze carbon utilization and the biological reaction.

2. Materials and Methods

2.1. Biofilter Setup

The laboratory-scale biotrickling filter was setup as shown in Figure 1. It consisted of 7 cylindrical PMMA (Polymethyl methacrylate) parts with an internal diameter of 100 mm, a total length of 1500 mm, and a total volume of 8.25 L (a packed bed volume of 4.71 L). Polyurethane foam (PUF) was used as the packing materials for this experiment because it

has advantages of high surface area, good gas permeability, and efficient moisture distribution, and it performs better than ceramic or activated carbon carriers [34] (Juntai Plastic, Hangzhou, China). The PUF was cut into a cubic structure of 15 mm × 15 mm × 15 mm, a packing depth of 600 mm, and a packing volume of 4.71 L. The pore size and porosity of PUF were 1–2 mm and 96–97.5%, respectively. A mineral salts medium (MSM) tank was placed to supply moisture and nutrients to the biotrickling filter. The air was consistently supplied through mass flow controllers (MFC), while d-limonene was provided as the sole carbon source through a syringe pump. Table 1 presents the specific operating conditions for each reactor. Backwashing was performed when the compression of more than 15% of the bed volume was observed with the naked eye.

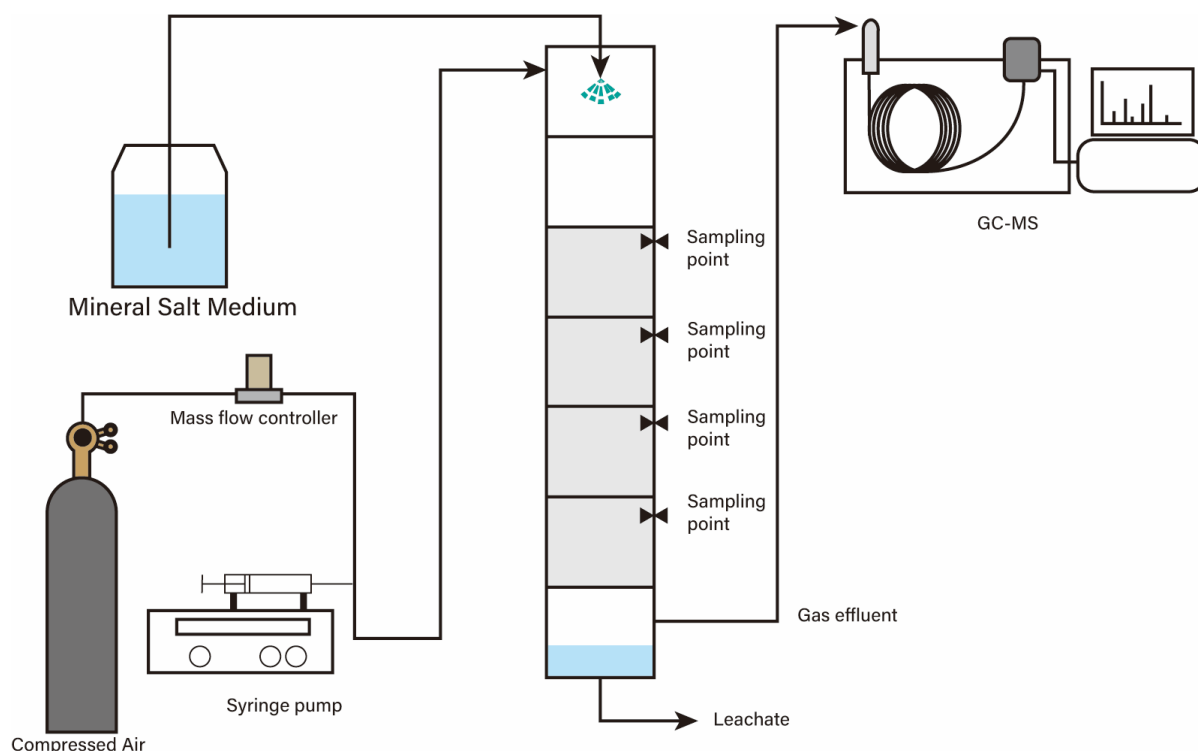


Figure 1. Schematic diagram of biotrickling filter setup in this study.

Table 1. Experimental conditions for the biotrickling filter.

	Acclimation	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5
Operational periods	Day 1–14	Day 15–33	Day 34–66	Day 67–94	Day 95–136	Day 137–174
Loading (g/m³·h)	3.1	3.1	6.0	12.0	23.8	35.7
Concentration (ppm)	14	14	28	56	112	168
EBRT (s)	94.2					

2.2. Microbials Inoculation and Nutrient Medium

The microbial inoculum for the biotrickling filter was prepared using activated sludge from the aeration tank in the wastewater treatment plant located in Uijeongbu City, Republic of Korea. The supernatant of the activated sludge was acclimated to d-limonene as the sole carbon source through aeration for one week. To facilitate microbial growth, nitrogen and phosphorus were supplied in the form of NaNO₃ and NaH₂PO₄·H₂O, respectively,

according to the d-limonene concentration. The ratio of COD:N:P was maintained at 100:5:1, and NaHCO_3 was used as a buffer solution. Trace elements were supplied for microbial growth, including FeCl_3 , MgCl_2 , CaCl_2 , KHSO_4 , CoCl_2 , CuCl_2 , MnCl_2 , and ZnCl_2 . All chemicals were purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO, USA).

2.3. Analysis Methods

2.3.1. Biotrickling Filter Performance

Gas samples were collected from the sampling point of the biotrickling filter through gas-tight syringes. D-limonene was analyzed using gas chromatography-mass spectrometry (GC-MS, YL-6500GC, YoungIn, Anyang City, Republic of Korea) equipped with a DB-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). The temperature of the injector, ion source, and oven were set to 250, 200, and 50 to 125 °C, respectively. The method detection limit of d-limonene analyzed using GC-MS was 1.26 ppb with 98.5% accuracy and 9.2% RSD repeatability. CO_2 was analyzed using GC-FID with a methanizer (YL-6100GC, YoungIn, Anyang City, Republic of Korea) equipped with a Porapak N column ($1.83 \text{ m} \times 2 \text{ mm}$, mesh 80/100). The injector, detector, and oven temperature were set to 120, 250, and 50 °C, respectively. Helium gas was used as the carrier gas at a flow rate of 20 mL/min for GC-FID with a methanizer and 1 mL/min for GC-MS, respectively. Liquid samples were collected from the effluent of the biofilter for volatile suspended solids (VSS) and total organic carbon (TOC) analyses. The activity of the microbial in the biofilter was indirectly assessed via analyzing the amount of VSS. The total organic carbon was measured using a TOC analyzer (TOC-L, Shimadzu, Kyoto, Japan).

2.3.2. Microbial Kinetic

In order to understand the dynamic behavior of microorganisms and their biochemical reactions in the biotrickling filter, two microbial kinetics, i.e., the Michaelis–Menten model and Haldane model, were employed to offer distinct perspectives on enzyme–substrate interactions and microbial growth. The Michaelis–Menten model is a microkinetic representation of enzyme-catalyzed reactions, which can be rearranged for applications in biotrickling filters as follows [35]:

$$C_{ln} = \frac{C_{in} - C_{out}}{\ln(C_{in}/C_{out})} \quad (1)$$

$$EC = \frac{EC_{max} C_{ln}}{K_S + C_{ln}} \quad (2)$$

where C_{ln} is the logarithmic average concentrations of the biotrickling filter, EC_{max} is the maximal elimination capacity, and K_S is the saturation constant.

The Haldane model is an extension of the classical Michaelis–Menten equation, which into account the inhibitory effects of a substance on the enzyme activity. This equation can be applied to a biotrickling filter as follows [36]:

$$EC = \frac{EC^* C_{ln}}{K_S' + C_{ln} + (C_{ln}^2/K_I)} \quad (3)$$

where EC^* is the maximal EC in the absence of inhibition, K_S' is the saturation constant, and K_I is the inhibition constant of the Haldane model.

2.3.3. Mass Balance Analysis

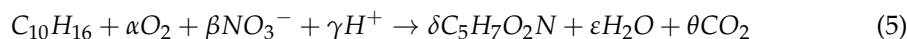
The following mass balance equation can describe the behavior of the substrate of the biotrickling filter:

$$C_{removed} = C_{CO_2} + C_{VSS} + C_{TOC} + C_{unknown} \quad (4)$$

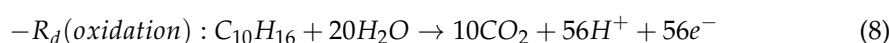
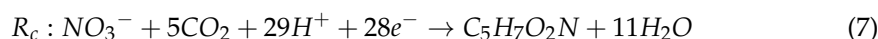
where $C_{removed}$ is the removed carbon amount of d-limonene, C_{CO_2} is the CO_2 of effluent gas, C_{VSS} is the VSS of the effluent liquid, C_{TOC} is the total organic carbon of the effluent

liquid, and $C_{unknown}$ is the unrecovered carbon, and all terms can be converted into carbon mole. A typical cellular composition for a heterogeneous microorganism in the biotrickling filter can be represented as $C_5H_7O_2N$ [37].

The overall reaction for the aerobic biodegradation of d-limonene in the biotrickling filter under steady state conditions without the accumulation of intermediate products and nitrate used as nitrogen sources can be thus given by the following equation:



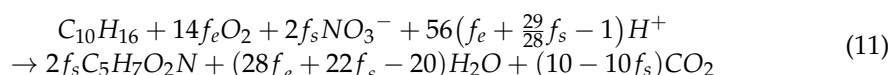
The overall reaction for the aerobic biodegradation of d-limonene can be determined using the following half reaction (half-reaction of an electron receptor, R_a ; an electron donor, R_d ; and a cell synthesis, R_c) because the biological activity could be due to cell synthesis and energy production.



The fraction of electrons used for cell synthesis and energy generation in the overall reaction can be expressed as f_s and f_e , respectively. The overall reaction equation taking into account the electron fraction is as follows:

$$f_e + f_s = 1 \quad (9)$$

$$R = f_e R_a + f_s R_c - R_d \quad (10)$$



The assumptions of this stoichiometric interpretation are as follows: The d-limonene was supplied in a steady state. There was no endogenous respiration and denitrification reaction involving microorganisms. The intermediate step of d-limonene degradation was not considered. There was no inhibition by oxygen or the substrate.

3. Results and Discussion

3.1. Biotrickling Filter Performance

Figure 2 shows the performance of the biotrickling filter with respect to the d-limonene inlet concentration and the removal efficiency (RE). The biotrickling filter was started with an influent d-limonene concentration of 14 ppmv, with a corresponding loading rate of $3.1 \text{ g m}^{-3} \text{ h}^{-1}$. The inlet loading was then stepwise increased as planned in Table 1. Although the overall performance was unstable during the acclimation period, the biotrickling filter reached an RE up to 95%. The RE then remained above 99% until a loading rate of $23.8 \text{ g m}^{-3} \text{ h}^{-1}$. The corresponding pH in the effluent liquid from the biotrickling filter remained stable at around 8.0 during these loading rates. However, when the loading rate exceeded $23.8 \text{ g m}^{-3} \text{ h}^{-1}$, the RE dropped to below 85%. On day 148, a bed compression was observed, which may have been caused by the overgrowth of biomass in the biotrickling filter bed. However, no significant pressure drop was found during operation. It should be noted that PUF cubic media is preferred due to its low pressure drop property. The impact of biomass overgrowth on performance may vary depending on the condition of the biotrickling filter, including the packing media [31].

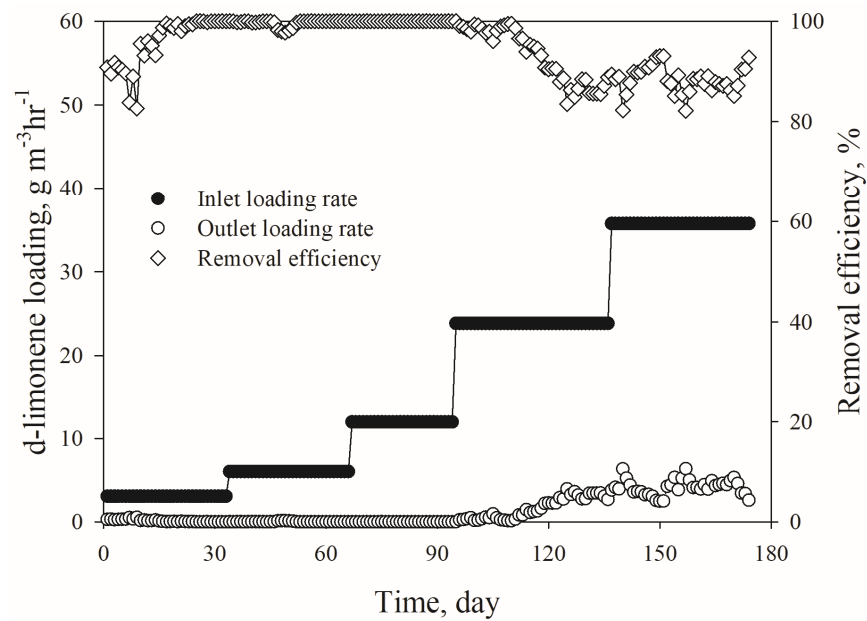


Figure 2. Biotrickling filter performance with respect to d-limonene removal.

Figure 3 presents the elimination capacity (EC) of the biotrickling filter as a function of the loading rate of d-limonene. This confirms that relatively high loading rates above $23.8 \text{ g m}^{-3} \text{ h}^{-1}$ lead to the substantial deteriorating of the biotrickling filter performance. The critical loading rate was found to be about $19.4 \text{ g m}^{-3} \text{ h}^{-1}$, and the maximum elimination capacity (EC_{max}) was $31.8 \text{ g m}^{-3} \text{ h}^{-1}$ under the given condition of biotrickling filter operation.

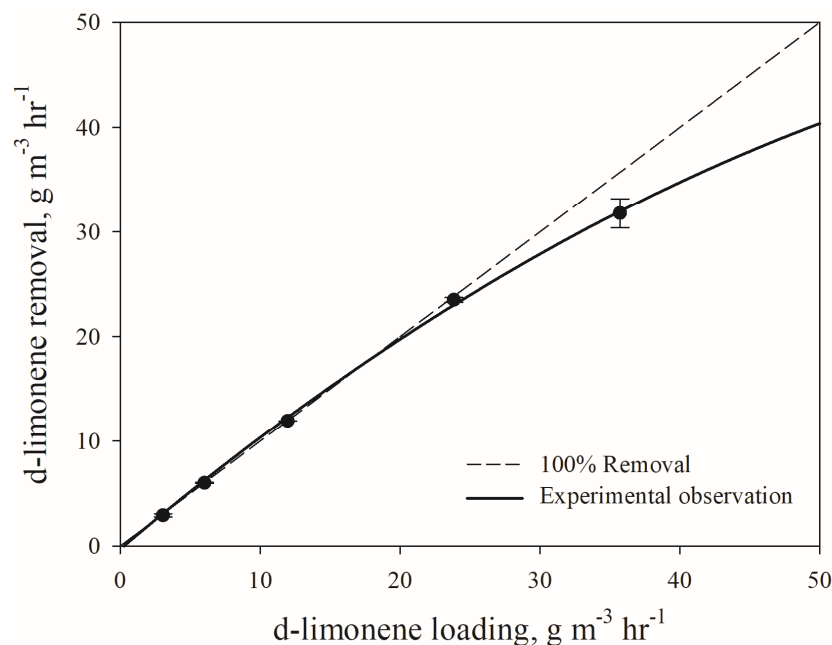


Figure 3. D-limonene removal capacity of d-limonene with respect to its loading rate.

3.2. Kinetic Analysis

Microorganisms play a significant role in the biotrickling filter performance because the removal capability is mostly dependent on the microbial activity [38]. It is therefore necessary to understand the biochemical reaction and the removal behavior of the substrate in the biotrickling filter. Different models have been studied to evaluate microbial kinetics

and substrate degradation [35,36,39]. In addition, several studies have been carried out to analyze the mass balance through measuring the biomass growth and CO₂ production in the biotrickling filter, as well as assessing the operating characteristics of the biotrickling filter [40,41].

Figure 4 shows the elimination capacity of the loading of the biotrickling filter using the logarithmic mean of the substrate concentration and microbial activity in the biotrickling filter, as demonstrated in the Michaelis–Menten and Haldane models. The Michaelis–Menten and the Haldane models (denoted as EC_{max} and EC* for each model) provided maximum removal efficiencies of 32.0 g m^{−3} h^{−1} and 26.0 g m^{−3} h^{−1}, respectively, whereas the experimentally observed value was 31.8 g m^{−3} h^{−1}. It can be deduced from Figure 4 that there was no substrate inhibition during the biotrickling filter run. The reduced performance may be due to limitations in mass transfer. As limonene is highly hydrophobic, some research is investigating the addition of surfactants or the use of fungi to improve the removal of hydrophobic compounds. Other possible causes of reduced performance could be the saturation of microbial capacity or changes in the microbial community. This is beyond the scope of this study, but is worth considering for future studies. Therefore, further investigation is necessary to determine the reason for the observed decrease in the removal efficiency with an increase in d-limonene loading.

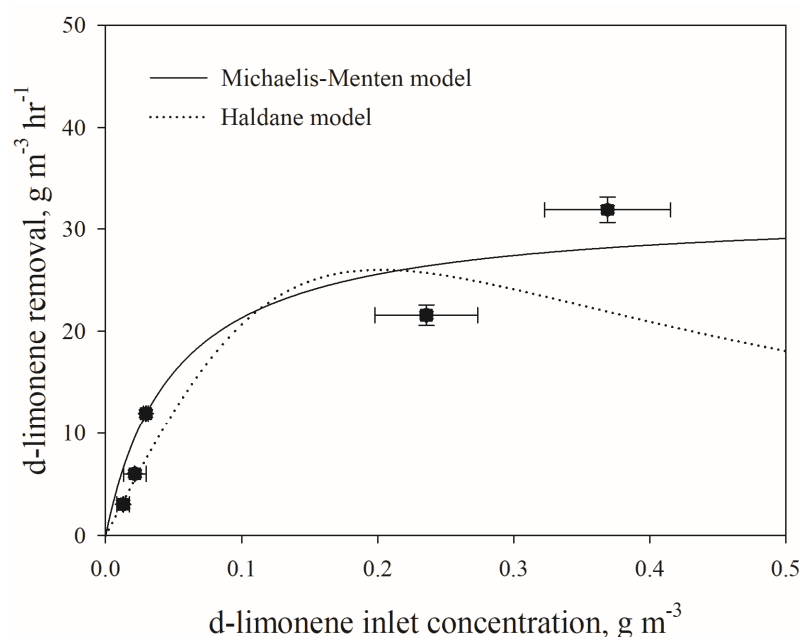


Figure 4. Elimination capacity according to the logarithmic average of d-limonene concentration for the biotrickling filter.

It can be deduced that oxygen transfer to the biofilm was inhibited during the biotrickling filter operation. To prevent biofilter failure, excess oxygen must be allowed to pass through the entire biofilm as an electron acceptor. The maximum practical concentration of d-limonene in the biofilm at the air–biofilm interface can be estimated from the maximum equilibrium concentration of oxygen in the biofilm, as suggested by Williamson and McCarty [42].

$$S_{\text{substrate}} > \frac{v_{\text{substrate}} D_{\text{oxygen}} MW_{\text{substrate}}}{v_{\text{oxygen}} D_{\text{substrate}} MW_{\text{oxygen}}} S_{\text{oxygen}} \quad (12)$$

where S is a concentration of d-limonene and O₂ (8.3 mg L^{−1} of water solubility at 25 °C and 1 atm) at the biofilm surface, v is a stoichiometric reaction coefficient for d-limonene and O₂, MW is the molecular weight of d-limonene and O₂, and D is the diffusion coefficient of d-limonene and O₂. The diffusion coefficient can be calculated through the Wilke–Chang equation [41]. The ratio of $D_{\text{oxygen}}/D_{\text{substrate}}$ was 3.03 for d-limonene. The

maximum practical concentration of d-limonene ($S_{\text{substrate}}$) in the biotrickling filter can be calculated as 1698 ppmv. At the given experimental conditions, the d-limonene loading rate corresponded to $360.83 \text{ g m}^{-3} \cdot \text{h}^{-1}$. Since the observed value of the elimination capacity (EC_{max}) was $31.8 \text{ g m}^{-3} \text{ h}^{-1}$, it can be speculated that oxygen was not limited in the biotrickling filter bed in this study.

Another possible reason for the decrease in the removal efficiency with an increase in d-limonene loading is that d-limonene has a low water solubility (7.57 mg L^{-1} , 25°C) [7], which limited the mass transfer between the gas and biofilm. This, in consequence, would inhibit the performance of the biotrickling filter [36]. It should be noted that the effectiveness of the biotrickling filter may be correlated with their physical and chemical properties of VOCs [41].

3.3. CO_2 Generation and Biomass Yield

The biotrickling filter essentially operates as an aerobic biological process, with CO_2 production serving as a useful indicator of the biological activity resulting from the aerobic oxidation of organic matters and endogenous respiration. In a biotrickling filter, biomass can accumulate and sometime endogenous respiration may occur [41]. Therefore, the carbon mass balance can be expressed as a CO_2 production rate, which was suggested by [41,43], as follow:

$$R_{\text{CO}_2} = R_{\text{sub}} - R_{\text{biomass}} + R_{\text{endo}} \quad (13)$$

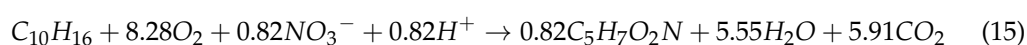
where R_{CO_2} is the CO_2 production rate, R_{sub} is the substrate consumption rate, R_{biomass} is the biomass production rate, and R_{endo} is the endogenous respiration rate of microbes. Moreover, this equation can be interpreted by the biomass yield coefficient (Y , mole C as biomass/mole C as the substrate) as follows:

$$R_{\text{CO}_2} = (1 - Y)R_{\text{sub}} + R_{\text{endo}} \quad (14)$$

Figure 5 shows the CO_2 production rate as a function of consumed d-limonene. The regression line in Figure 5 represents a term of $(1 - Y)$ in Equation (14), while the y-intercept represents the endogenous respiration rate. The observed biomass yield coefficients (mole biomass/mole carbon as the substrate) were 0.437, which corresponds to $0.363 \text{ g biomass/g substrate}$ (dry weight basis) if a molecular formula for biomass $\text{C}_5\text{H}_7\text{O}_2\text{N}$ is considered. The endogenous respiration rate was low (0.013), indicating that endogenous microbial activity was less significant during the operation period. This observation is consistent with those found in Section 3.2, where we assumed that the oxygen inhibition did not occur during the operation period.

Figure 5 also highlights a strong linear correlation between CO_2 production and substrate consumption. This observation indicates that the biological activity within the biotrickling filter was consistently maintained under pseudo-steady state conditions, regardless of the variations in substrate inlet loadings applied.

Figure 5 provides information on carbon recovery as CO_2 at different substrate loadings, from which f_e (the fraction of energy generation) and f_s (the fraction of cell synthesis) can be derived from Equation (11). As a result, the stoichiometric reaction in the biotrickling filter (Equation (15)) represents the biological response at a critical substrate loading. In general, the biological response of a biofilter can vary depending on the depth of the reactor and the duration of the operation. However, the stoichiometric equation for the biological degradation of d-limonene using the biotrickling filter obtained in this study can be useful for a comprehensive understanding of the substrate-dependent biological response.



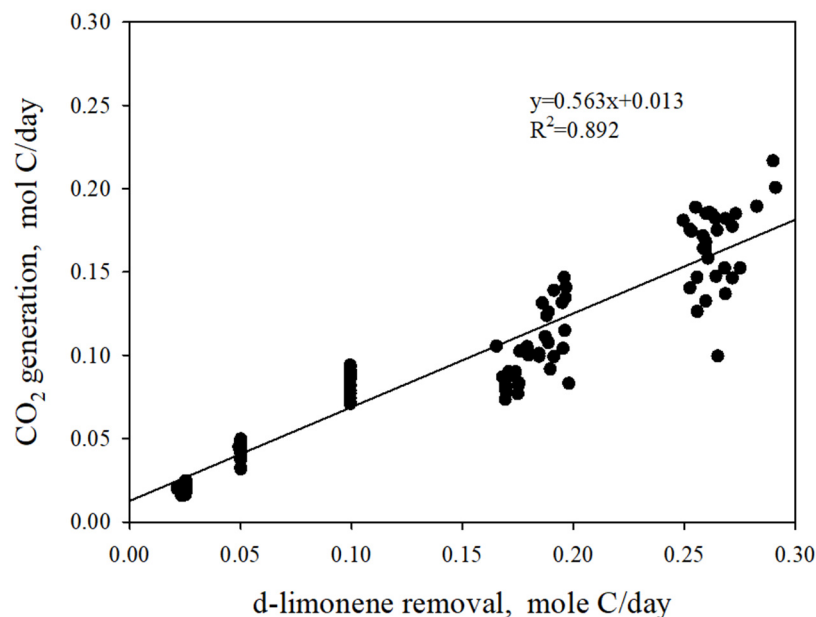


Figure 5. CO₂ production as a function of d-limonene consumption (CO₂ production rate and d-limonene consumption rate were calculated on a carbon-mole basis).

4. Conclusions

This study presents the performance and kinetics of a biotrickling filter system for the removal of gas-phase d-limonene. The specific conclusions and recommendations that can be drawn from this study include the following:

- (1) The biotrickling filter with concurrent gas–liquid downflow demonstrated the efficient removal of d-limonene, with a critical loading rate of $19.4 \text{ g m}^{-3} \text{ h}^{-1}$ and a maximum elimination capacity of $31.8 \text{ g m}^{-3} \text{ h}^{-1}$. Loading rates above this threshold resulted in a substantial deterioration of the biotrickling filter performance, possibly due to bed compression caused by biomass overgrowth.
- (2) Microbial activity plays a significant role in biotrickling filter performance, with biochemical reactions and substrate degradation being key factors. Michaelis–Menten and Haldane kinetic models have been studied to understand microbial kinetics and substrate degradation, providing insights into the biological response of the biotrickling filter to varying substrate concentrations. The Michaelis–Menten model was employed to represent the enzyme-catalyzed reactions in this biotrickling filter, given that no inhibition was observed during the biotrickling filter operation.
- (3) The study observed a strong linear correlation between CO₂ production and substrate consumption, with the observed biomass yield coefficients being 0.437 mole biomass/mole carbon as the substrate. The stoichiometric equation for the biological reaction provided a comprehensive understanding of the substrate-dependent biological response in the biotrickling filter.

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