

Elimination of Toluene Vapors in Biotrickling Filters: Performance and Carbon Balances

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Huub H.J. Cox, Tranquoc T. Nguyen and Marc A. Deshusses

Department of Chemical and Environmental Engineering

University of California

Riverside, CA 92521

ABSTRACT

Performance of two toluene-degrading biotrickling filters was systematically investigated under different conditions of supply of toluene (0, 1 or 2 g/m³) and nutrients (feed of phosphate buffer or mineral medium). The focus of the investigation was on quantification of biomass growth and determination of the influence of biomass growth on filter performance. Treatment of 1 g/m³ toluene at a volumetric load of 64 m³/(m³.h) while feeding a mineral medium to support growth resulted in an increase of wet biomass at a rate of 3.2-9.8 kg/(m³ reactor.day). Biomass accumulation in the reactor resulted in decreasing toluene elimination capacities, i.e., from about 40 g/(m³.h) at 0.3 kg wet biomass/(L reactor) to 20 g/(m³.h) at 0.7 kg/L. When using 2.5 cm Pall rings as packing, a sharp increase of the pressure drop may be expected at 0.5 kg wet biomass/(L reactor). Carbon mass balances show that on average 69% of C-toluene degraded was oxidized to C-CO₂, whereas 21% was incorporated into biomass and 6% washed out via the liquid purge. It is estimated that decreasing performance due to clogging of these reactors may be expected after 3 months of operation with continuous feed of mineral medium. Changing to a nutrient-limited environment resulted in a loss of toluene elimination capacity of 25-50% within two weeks. Although nutrient limitation may delay biomass accumulation, larger reactor volumes are required to compensate for the loss of microbial activity. Endogenous respiration resulted in an average CO₂ production of 2 g C-CO₂/(m³.h). Under starvation conditions, an average loss of wet biomass of 2.2 kg/(m³ reactor.day) was observed. Periods of starvation to maintain a constant amount of biomass is not a realistic option for these reactors as this would require shut-down of the biotrickling filter for two to five days per week depending on the biomass accumulation rate at nutrient-rich conditions.

INTRODUCTION

Biotrickling filters for waste air treatment have increasingly been studied over the past ten years. Most studies deal with optimization of pollutant elimination capacities and/or modeling of reactor performance. As biotrickling filters rely on pollutant degradation by microorganisms, remarkable little attention has been paid to the microbial population inside biotrickling filters and the accumulation of biomass. Recently, Alonso *et al.*¹ addressed the question of how much biomass is enough in biotrickling filters, but quantification was not possible as not only the amount is important but also its accessibility for pollutant removal. Zuber² found that increasing amounts of biomass did not result in increasing pollutant degradation rates in methylene chloride-degrading biotrickling filters. Accumulation of dead/inactive biomass as well as the development of secondary population are likely to occur. Results of Pedersen *et al.*³ obtained with a toluene-degrading biotrickling filter indicate that cell death is already significant during

the start-up of the filter. Because biomass accumulation compromises the stability of biotrickling filters over the long term due to clogging, several biomass control strategies such as back-washing, washing with chemicals, nutrient limitation and protozoan predation are currently being investigated.^{4,5,6,7}

Deshusses⁸ discussed the complexity of processes taking place in biofilms in biofilters, which includes mass transfer of pollutants and oxygen, pollutant degradation by the primary culture, cell death and lysis, cryptic growth and predation by higher organisms. To improve our understanding of biotrickling filters, it is essential to relate biomass accumulation in the reactor and biotrickling filter performance. Quantification of the fate of carbon and closure of the carbon balance is required to predict the long-term performance of these filters.

In the present contribution, we present results of our investigation of toluene degradation in biotrickling filters. Over a seven month period, the performance was investigated at zero, intermediate and high toluene loadings with either continuous supply of a mineral medium or phosphate buffer to simulate growth and nutrient-limited conditions, respectively. Analyses of the gas phase and the liquid purge and determination of the biomass accumulation rate allowed the calculation of carbon mass balances and the determination of the influence of biomass accumulation on reactor performance.

MATERIALS AND METHODS

Experimental Set-Up

Biotrickling filter performance was investigated under different conditions of toluene and nutrient supply as shown in Table 1. A specific set of conditions was maintained until a steady-state was obtained as judged from constant toluene and CO₂ concentrations in the outlet gas. Toluene degradation, CO₂ production, biomass accumulation, pressure drop and carbon discharge via the liquid purge were determined on a daily basis over a steady-state period of several days and average values were calculated. When changing to a new liquid source, the existing liquid in the entire system (i.e., reactor, tubing and liquid vessel) was replaced. Each set of conditions was examined at least four times over a seven-month period at different amounts of wet biomass in the reactor, varying between 5.1 and 19.3 kg (total bed volume 23.6 L).

Equipment and Operation

Two biotrickling filters were investigated in parallel under identical conditions throughout this study, and thus performances of the reactors were considered to be directly comparable. A detailed description of the equipment as well as operational conditions has been given elsewhere.⁹ In summary, the reactors with a length of 1.3 m, a diameter of 0.152 m and filled with 2.5 cm Pall rings were operated concurrently with a constant volumetric gas load of 64 m³/(m³.h). Liquid was recirculated from a vessel (effective liquid volume of 1.8 L) over the filter bed at a superficial velocity of 7.9 m/h and fresh mineral medium or phosphate buffer was continuously supplied to the liquid vessel at a rate of 273 mL/h. Toluene was supplied to air stream at concentrations of 1 and 2 g/m³ by a metering pump.

Analytical Techniques

Toluene and CO₂ gas phase concentrations were determined in triplicate by gas chromatography using FID and TCD, respectively. Wet biomass in the reactor was determined as the difference in weight of the reactor after allowing the liquid to drain for ten minutes and the clean reactor

without biomass. Pressure drop was measured over 1.3 m filter bed at a volumetric load of $64 \text{ m}^3/(\text{m}^3 \cdot \text{h})$ while circulating liquid. Total carbon in the liquid was determined in duplicate using a TOC-analyzer.

Calculation of Carbon Balances at Steady State

The amounts of carbon entering and leaving the reactor were calculated from toluene and CO_2 gas phase concentrations, total carbon in the liquid purge and gas flow and liquid dilution rates. At steady state, a linear increase or decrease (depending on the conditions) in time of the amount of wet biomass was assumed and calculated by linear regression using the least squares method. C-biomass in the reactor was calculated from wet biomass using conversion factors of $0.046 \text{ g dry biomass}/(\text{g wet biomass})$ and $0.44 \text{ g C}/(\text{g dry biomass})$.⁹

RESULTS AND DISCUSSION

Steady State

A true steady state in biotrickling filters will never be obtained because the amount of biomass will change in time, and changes in the microbial population may occur even after 500 days of operation.¹⁰ However, when monitoring reactor performance at constant toluene inlet concentration and constant nutrient feed, a pseudo steady state can be defined when outlet concentrations are approximately constant, and a constant rate of biomass accumulation is observed. In the present case, pseudo steady state was generally observed within a few days, but it occasionally took as long as seven to ten days. An example of the latter case is shown in Figure 1, where, at time zero, the liquid was changed from mineral medium to phosphate buffer while maintaining a toluene inlet concentration of $1 \text{ g}/\text{m}^3$. Toluene degradation and CO_2 production were still declining at the end of this experiment, albeit at a lower rate than at the beginning of the experiment. Calculation of average 'steady state' parameters over day 7-9 showed a toluene elimination capacity of $12.9 \text{ g}/(\text{m}^3 \cdot \text{h})$, a CO_2 production rate of $9.7 \text{ g C-CO}_2/(\text{m}^3 \cdot \text{h})$ and a wet biomass accumulation rate of $0.115 \text{ kg}/(\text{m}^3 \cdot \text{day})$ (Figure 1). As the toluene elimination capacity and CO_2 production were still slowly declining over day 7-9, actual steady state values may have been somewhat lower than the calculated values from this example. Possible explanations for delayed steady state when changing from mineral medium to phosphate buffer will be discussed in later sections.

Influence of the Biomass Concentration in the Reactor on Biotrickling Filter Performance

The performance of the reactor at different amounts of biomass is shown in Figure 2, where toluene elimination capacities at $1 \text{ g}/\text{m}^3$ toluene in the inlet are plotted versus the biomass concentration in the reactor. Clearly, the toluene elimination capacity decreases with increasing amounts of biomass in the reactor, which indicates that over the long term, biotrickling filter performance will decrease unless preventive action is taken to control biomass accumulation. Figure 2 also gives the true gas residence time, which was calculated by taking the volume of biomass (density $1 \text{ kg}/\text{L}$), bed porosity of the clean packing (estimated to be 0.9) and the dynamic liquid hold-up (on average 1.3 L) into account. Although elimination capacity and actual gas residence time appear to be correlated, calculations by Alonso *et al.*¹ indicate that lower elimination capacities at high biomass concentration in the reactor are due to a decrease of the biofilm specific surface area, rather than a decrease of the actual gas residence time or void volume as such. This is supported by calculation of the toluene elimination capacity per void

volume, which showed a rapid increase with increasing amounts of biomass in the reactor (Figure 3). Apparently, at increasing biomass concentration in reactors packed with Pall rings, the void volume decreases more rapidly than the biofilm specific surface area.

The influence of biomass content in the reactor on pressure drop is presented in Figure 4. A good agreement was found for the two reactors. Up to a wet biomass concentration of 0.5 kg/L, the pressure drop over the filter bed remained relatively constant, between 5-10 cm H₂O. It increased rapidly at higher biomass concentrations. Comparing Figures 2 and 4, it appears that loss of pollutant elimination capacity due to biomass accumulation occurs at earlier stage than pressure drop build-up. Decreasing pollutant elimination capacity is therefore the primary concern when biotrickling filters containing a high-porosity packing such as Pall rings are getting clogged.

Carbon Mass Balance Studies

By daily weighing of the reactor, it was possible to determine the rate of biomass accumulation under different conditions and to close carbon mass balances. Results obtained at 1 g/m³ toluene in the inlet and with continuous feed and recirculation of mineral medium are presented in Figure 5. Total recovery of carbon was calculated as the sum of C-CO₂ produced, C-biomass produced (assuming a constant dry matter and C-content of wet biomass throughout the reactor) and C washed out via the liquid purge (assuming that total carbon in the liquid is mainly C-biomass) as a percentage of C-toluene degraded. Recoveries of carbon varied between 80 and 107%. The fate of degraded carbon was approximately the same at different wet biomass concentrations in the reactor (Figure 5). On average, 69% was oxidized to CO₂, 21% was incorporated into biomass in the reactor and 6% was discarded via the liquid purge. The wet biomass accumulation rate at 1 g/m³ toluene and continuous feed of mineral medium varied between 3.1 and 9.8 kg/(m³.day) with a declining trend at higher biomass concentrations in the reactor (Figure 6). These high biomass accumulation rates emphasize the need of biomass control in biotrickling filters to ensure long-term stability. In our reactors, decreased performance due to clogging may be expected after about three months.

Replacement of the mineral medium by phosphate buffer to limit growth resulted in a reduction of both the toluene degradation and CO₂ production rate (e.g., see Figure 1). Wet biomass accumulation rates in the absence of nutrients fluctuated between 1.5 and 9.1 kg/(m³.day) as determined in three experiments (Figure 6). As zero growth is expected when no nutrients are supplied, we suspect that circulation of a phosphate buffer for maximal two weeks did not result in a steady state with respect to biomass accumulation. A possible explanation could be that growth occurred on nutrients still present in the biofilm, and hence a decrease of the biomass accumulation rate may only be observed at extended circulation of phosphate buffer. Nutrient limitation has been shown to extend the life span of biotrickling filters and biofilters.^{5,6,11,12} However, the pollutant elimination capacity will decrease as the cells shift from growth to maintenance metabolism. This is illustrated in Figure 7, where toluene degradation at 1 and 2 g/m³ toluene in air and with and without nutrients is plotted versus the wet biomass concentration in the reactor. Within two weeks, the toluene elimination capacity decreased 25-50% when changing to nutrient limitation by circulating and feeding a phosphate buffer and perhaps a further reduction may be expected when a true steady state is obtained. Consequently, biotrickling filters operated under nutrient limitation require a larger volume to effectively treat polluted waste gases. In this respect it should be investigated whether operation of biotrickling filters under nutrient limitation is more cost effective than operation of high-performance

biotrickling filters (i.e., with continuous nutrient supply) with regular removal of excess of biomass.

Endogenous Respiration

CO₂ production rates in the absence of toluene are shown in Figure 8. Values fluctuated widely with no apparent correlation with the wet biomass concentration in the reactor, or with the presence or absence of nutrients. A maximal endogenous CO₂ production rate of 3.9 g C-CO₂/(m³.h) was observed. Starvation has been suggested a means to control biomass in biotrickling filters.¹³ Obviously, it is only a realistic option for biotrickling filters that are operated discontinuously. For the reactors studied in this investigation, it was calculated that an average endogenous CO₂ production of 2.0 g C-CO₂/(m³.h) corresponds to the removal of wet biomass at a rate of 2.4 kg/(m³.day). Actual determination of biomass during starvation showed biomass reduction rates of 0.04-5.9 kg/(m³.h). From seven independent experiments, an average value of 2.2 kg/(m³.day) was found which is very close to the expected rate of biomass loss as calculated from the average endogenous CO₂ production. These results imply that maintaining a constant amount of biomass by starvation would require shut-down of these biotrickling filters for 1.7 to 5.4 days per week, depending on the biomass accumulation rate under normal operation (3.1-9.8 kg/(m³.day) as found with continuous feed of mineral medium and 1 g/m³ toluene in air).

CONCLUSION

From quantification of the clogging process in toluene-degrading biotrickling filters and determination of carbon mass balances we conclude the following:

1. Under nutrient-rich conditions, decreased performance due to biomass accumulation in these reactors will cause reduced performance in about three months.
2. When using a high-porosity packing such as Pall rings, a decrease of the toluene elimination activity is the main concern. Pressure drop build-up occurs at a later stage.
3. A significant decrease of the toluene elimination capacity is observed when changing from nutrient-rich to nutrient-limited conditions. Cost analyses are required to decide between operation of relatively small, high-performance biotrickling filters with regular removal of excess biomass versus operation of relatively large biotrickling filters with extended stability due to nutrient limitation.
4. Biomass removal by endogenous respiration during periods of starvation is not a realistic option for the biotrickling filters investigated in this study. To maintain a constant amount of biomass, the period of shut down would exceed the time of normal operation.

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Table 1. Experimental set-up.

Toluene inlet (g/m ³)	Liquid phase ^a
2	Mineral medium
2	Phosphate buffer
1	Mineral medium
1	Phosphate buffer
0	Mineral medium
0	Phosphate buffer

a Mineral medium contained per liter: 1 g KH₂PO₄, 1 g K₂HPO₄, 1 g KNO₃, 1 g NaCl, 0.2 g MgSO₄, 0.26 g CaCl₂·2H₂O, 1 ml trace-elements solution, pH 6.7. Phosphate buffer contained per liter: 1 g KH₂PO₄, 1 g K₂HPO₄, pH 6.7.

Figure 1. Toluene elimination capacity, CO₂ production and biomass accumulation in the reactor after replacing mineral medium by phosphate buffer on day 0 while maintaining a toluene inlet concentration of 1 g/m³ (solid lines show calculations by assuming that a steady state over day 7-9 was obtained with a constant toluene elimination capacity and CO₂ production, and a constant daily increase of wet biomass in the reactor).

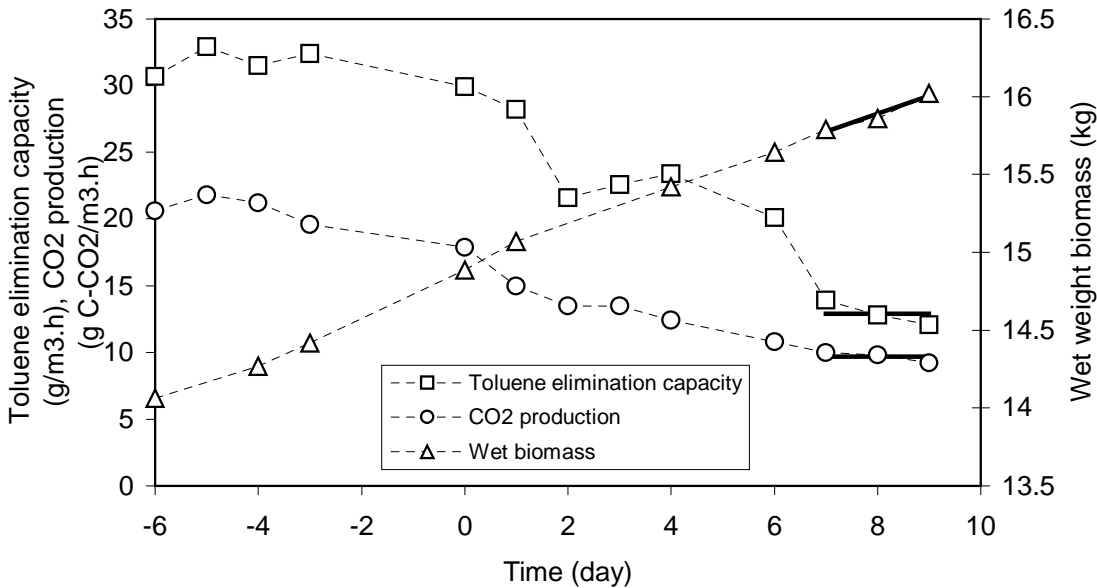


Figure 2. Influence of the biomass concentration in the reactor on the toluene elimination capacity (1 g/m^3 toluene in inlet, volumetric load $64 \text{ m}^3/(\text{m}^3 \cdot \text{h})$) and the actual gas residence time.

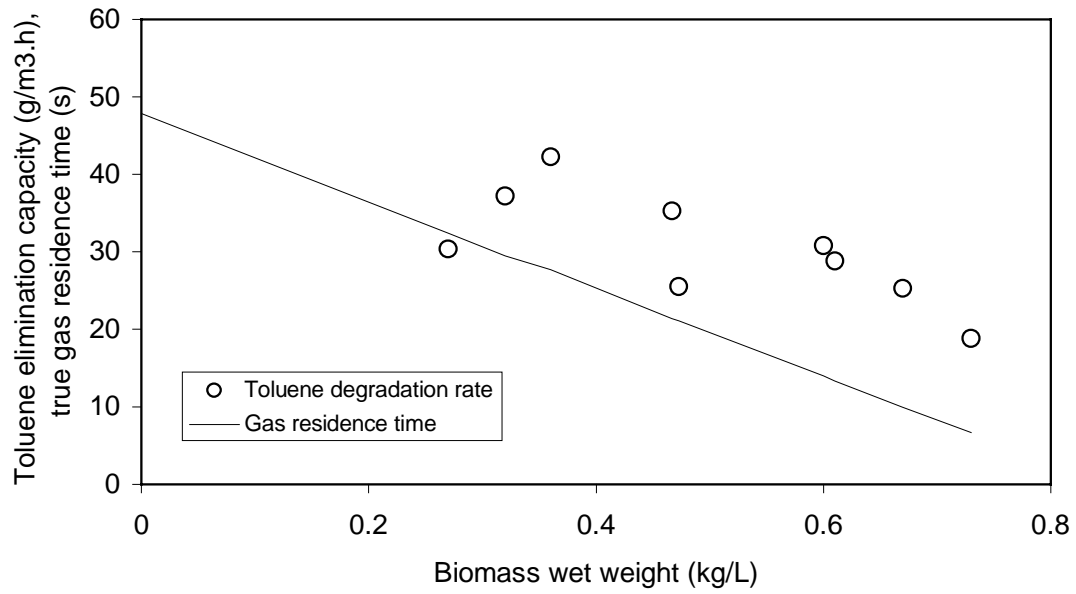


Figure 3. Plot of the toluene elimination capacity, expressed per void volume, versus the biomass concentration in the reactor.

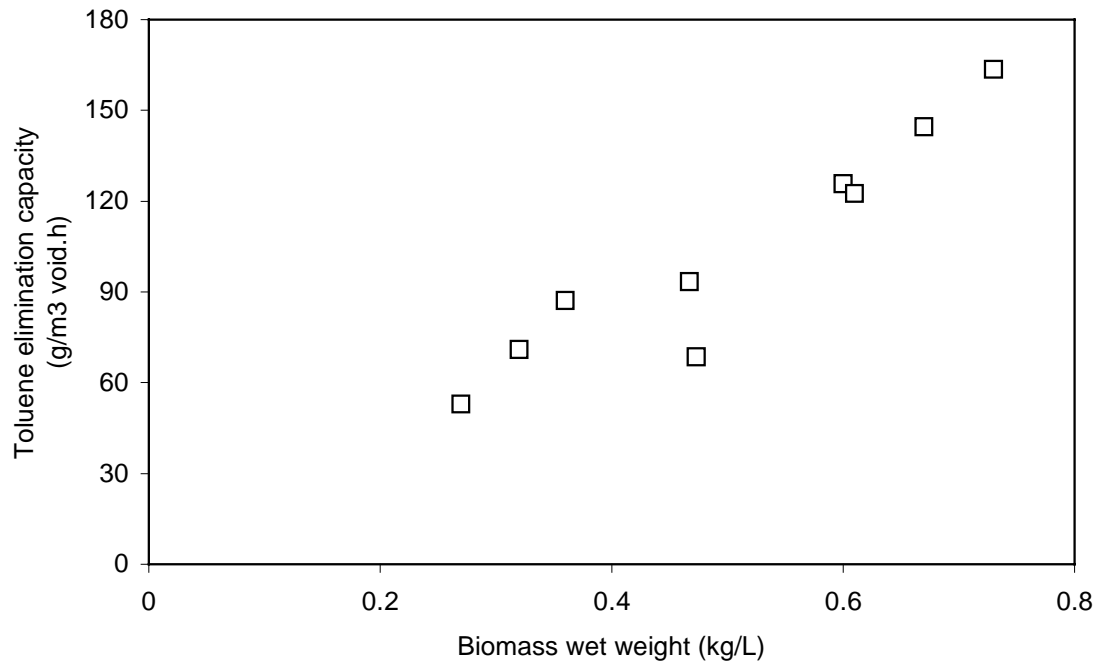


Figure 4. Influence of the biomass concentration in the reactor on the pressure drop (1.3 m filter bed, superficial gas velocity 82.7 m/h, superficial liquid velocity 7.9 m/h).

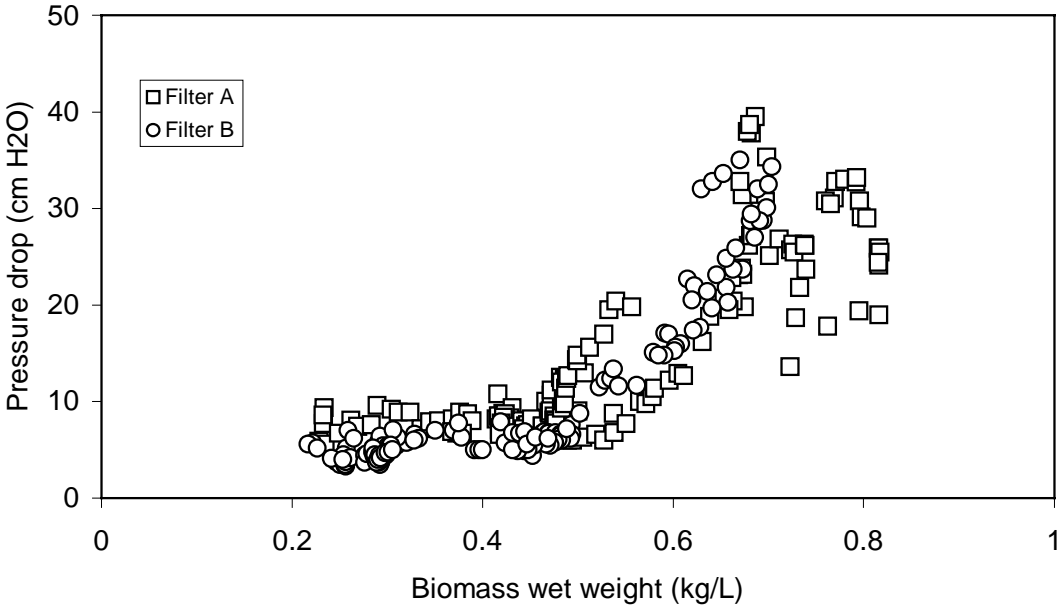


Figure 5. Fate of carbon as percentage of C-toluene degraded at different biomass concentrations in the reactor.

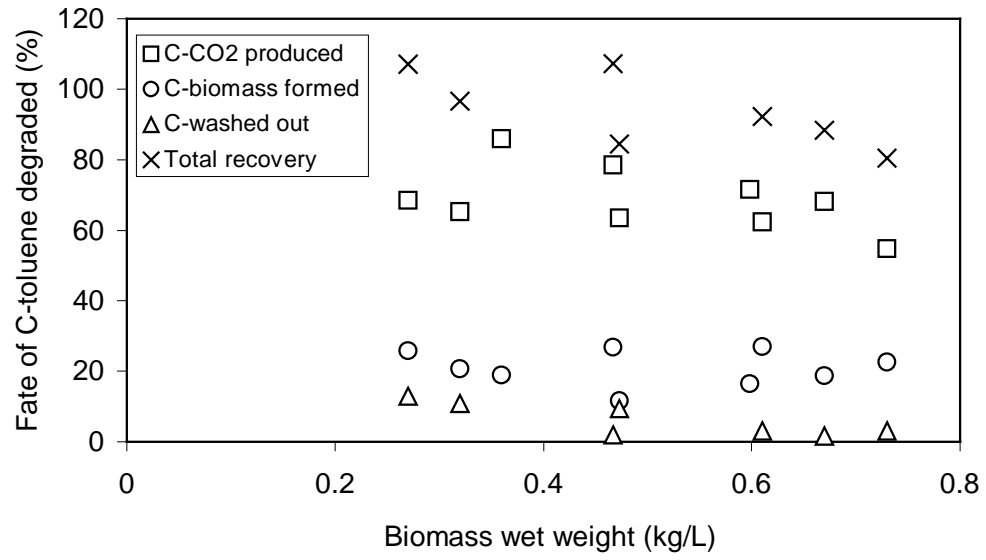


Figure 6. Biomass accumulation in the reactor in the presence and absence of nutrients (1 g/m^3 toluene).

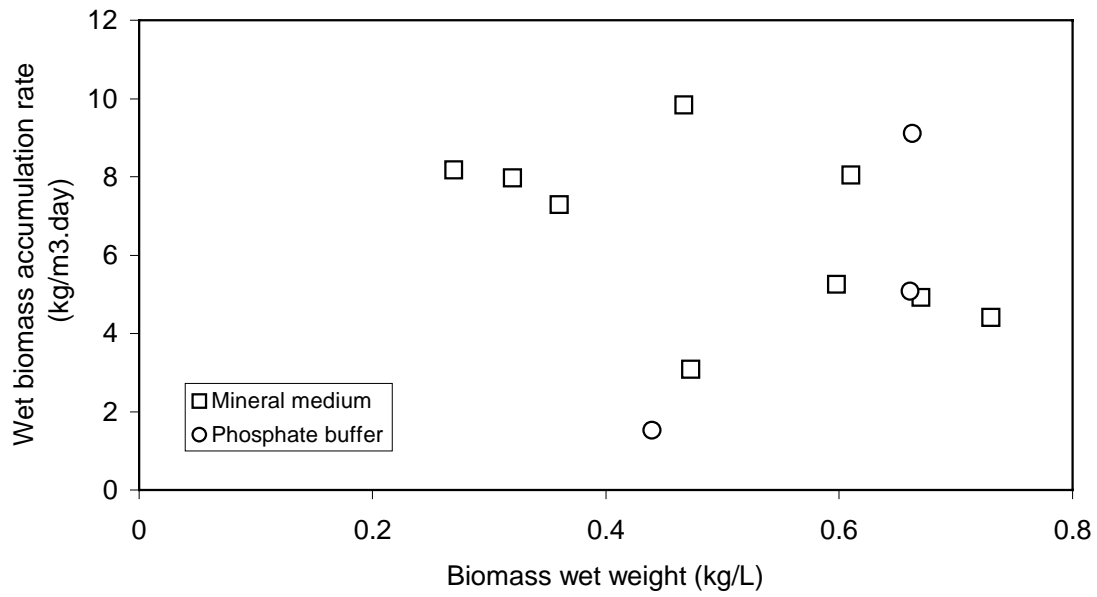


Figure 7. Comparison of the toluene degradation rate at continuous supply of mineral medium (MM) or phosphate buffer (KP) and at 1 or 2 g/m³ toluene in the inlet gas.

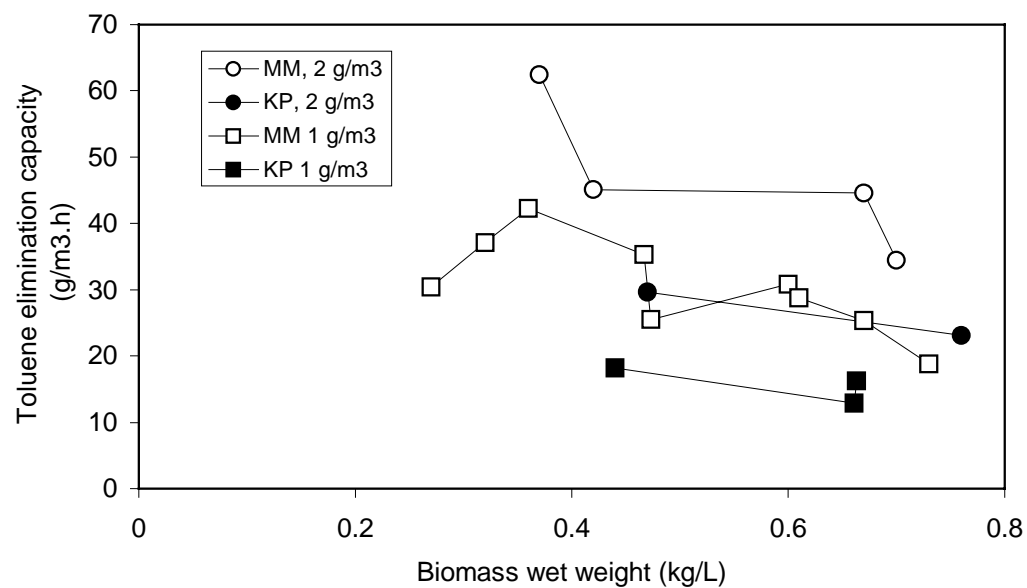


Figure 8. Endogenous CO₂ production at various wet biomass concentrations in the reactor and in the presence of mineral medium or phosphate buffer.

