

Chemical Removal of Excess Biomass in Clogged Biotrickling filters by Hypochlorite Treatment

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Huub H.J. Cox and Marc A. Deshusses

Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521. Email: mdeshuss@enr.ucr.edu

ABSTRACT

Biomass overgrowth is a major problem for the development of high-performance biotrickling filters for air pollution control. Biotrickling filters clogged with biomass show reduced performance and high pressure drop over the reactor. Biomass control strategies should try to extend the operational stability without reducing the pollutant removal rate. Various options have been tested to slow down the growth of biomass in biotrickling filters, such as nutrient limitation, addition of growth inhibitors and the use of predators that prey on bacteria. So far, none of these strategies has fully succeeded in both extending the stability and maintaining a high pollutant elimination capacity. One relatively unexplored alternative is to periodically remove excess biomass using chemical washes. We investigated the use of NaOCl to remove biomass from a toluene-degrading biotrickling filter with a volume of 23 L and packed with 1” polypropylene Pall rings. Initial experiments with addition of a large batch of NaOCl indicated that large amounts of biomass were removed, but at an uncontrolled rate. Better process control was achieved by metering the supply of NaOCl using a pH control unit (pH 9.2) during chemical wash. A total amount of 11 L of 5.25% commercial bleach sufficed to remove 10.9 kg of wet biomass from the reactor, thus reducing the wet biomass content from 77 to 31% by volume. However NaOCl is a bactericide that inhibits the restart of the biotrickling filters if it is not completely removed. Rinsing the reactor with large amounts of water was not sufficient as low concentrations of chlorine were detected in the recycle liquid up to 5 days after the washing. However, residual chlorine could effectively be removed by rinsing the reactor with a solution containing sodium thiosulfate. This enabled to fully recover the performance within 2-3 days.

INTRODUCTION

Rapid biomass growth and potential bed clogging is a recognized problem in the development of biotrickling filters for waste air treatment. High-performance biotrickling filters require frequent supply of nutrients in order to maintain an actively growing process culture. Over the long term, however, continuous biomass growth in biotrickling filters causes a reduced performance and an increase of the pressure drop over the reactor (Cox and Deshusses, 1998^a). A plausible explanation for the negative effect of high biomass concentrations on the pollutant removal rate is the reduction of the biofilm surface area available for pollutant mass transfer (Alonso *et al.*, 1997). Various options have been tested to slow down the growth of biomass in biotrickling filters, e.g., by nutrient limitation (Weber and Hartmans, 1996; Wübker and Friedrich, 1996; Holubar *et al.*, 1999), by addition of growth inhibitors (Diks *et al.*, 1994; Schönduve *et al.*, 1996), and by the use of predators that prey on bacteria (Cox and Deshusses, 1999^a). Neither of these strategies has fully succeeded in both extending the stability and maintaining a high

pollutant elimination capacity (Cox and Deshusses, 1998^b). One alternative to the above mentioned options is to allow growth of the process culture and periodically or continuously remove the excess of biomass. This can possibly be done mechanically (by scouring or using high hydrodynamic shear stress) or using chemicals that remove biomass. Chemical washing of the excess biomass is attractive as it can be done in a short time-span and without complex or expensive equipment. Previously, we developed a rapid test protocol to assess the efficiency of various chemicals to remove biomass by chemical washing (Cox and Deshusses, 1999^b). From 18 compounds or combinations of compounds tested, sodium hypochlorite (NaOCl) was found to be the most efficient. Further demonstration of the use of sodium hypochlorite in a clogged biotrickling filter was warranted. Aspects that needed further investigation included the determination of the rate of biomass removal, closure of carbon and biomass balances during the chemical wash, and pollutant elimination performance after restart and means to minimize the downtime after restart time.

MATERIALS AND METHODS

Biotrickling Filters

NaOCl treatment was tested in two toluene-degrading biotrickling filters, which were used at the time in a study on the effect of toluene loading and nutrient supply on the biomass growth (Cox and Deshusses, 1998^a). The packing was 1" polypropylene Pall rings, the bed had a height of 1.3 m and a diameter of 0.152 m (volume 0.0236 m³). The gas flow was downflow with an empty bed gas residence time of 57 s. Liquid was continuously recycled at superficial velocity of 7.9 m/h. During actual toluene treatment, the biotrickling filters were operated at 0, 1 or 2 g/m³ toluene in the inlet air and with continuous supply (275 mL/h) of a mineral medium (Cox and Deshusses, 1998^a) or a phosphate buffer. Standard operation before and after the chemical treatment to remove biomass was at 1 g/m³ toluene and a volumetric loading of 63 m³/m³.h and supply of mineral medium. Under these conditions, the expected elimination capacity of the reactor (unclogged) was about 35 g/m³.h, i.e., a removal of 44%. Depending on the input, decreasing performance due to clogging was observed within a few months of operation. The specific performance during standard operation will not be discussed in this paper, since the paper deals only with biomass control issues.

Treatment with NaOCl

The efficiency of NaOCl treatment was optimized in two experiments. In the first run (batch mode), NaOCl was recirculated (~ 8 m/h) over the packing from a large, external reservoir with 16 L of 1.3% w/v NaOCl (5.25% household bleach, diluted with tap water). This treatment lasted for 2.5 hours, after which the hypochlorite solution was drained from the reactor. The reactor was then rinsed to lower the residual chlorine by connecting tap water to the top of the reactor and use a one pass flow for a 2-5 hours. Standard operation was continued after adding the original recycle liquid, that had been saved prior to NaOCl treatment.

In the second run (continuous mode), the washing liquid was recirculated from a reservoir of 4 L to which 5.25% NaOCl was continuously added to maintain a pH of 9.2 (model 5654-28 pH controller from Cole-Parmer) in the washing liquid. The total washing liquid volume was kept constant at 5 L (i.e., 4 L + ~1 L of dynamic liquid hold-up) by using an overflow outlet. This

treatment lasted for 4 hours, during which period the biomass content in the reactor and the pH, the oxidation/reduction potential (ORP), suspended solids and dissolved carbon in the washing liquid were regularly determined. The treatment was stopped by removing all washing liquid and the efficiency of biomass removal was determined. Post-treatment consisted of recirculation of 4 L of a sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) solution for 18 hours to neutralize residual chlorine in the biotrickling filter. Thiosulfate was added at several occasions and in different amounts as based on the ORP in the recycle liquid during post-treatment. Subsequently, the thiosulfate solution was removed and standard operation of the biotrickling filter was continued by adding the original recycle liquid from before treatment.

Analytical methods

The following parameters were determined in either the chemical washing solution during removal of biomass and/or in the recycle liquid during standard biotrickling filter operation:

pH: direct measurement with an Accumet model 15 pH/ORP meter and a Ag/AgCl electrode (Fisher) or with a pH controller, model 5654-28 (Cole-Parmer, Chicago, IL).

ORP: direct measurement with an Accumet model 15 pH/ORP meter and a platinum combination electrode from Corning.

Suspended solids: known amounts of liquid sample (~40 mL) were centrifuged in a weighed tube for 10 min at ~5,000 g and the pellet was dried overnight at 95°C and weighed.

Total dissolved carbon: after centrifugation of suspended solids, the supernatant was analyzed in triplicate with a TOC-5050 total carbon analyzer (Shimadzu, Tokyo, Japan).

Free chlorine: free and bound chlorine were determined in the supernatant after centrifugation of suspended solids, using the DPD ferrous titrimetric method (APHA *et al.*, 1985).

Biomass in the reactor: for estimation of the decline of the biomass content in the biotrickling filter during chemical treatment, the reactor was suspended from a scale and the total weight (± 5 g) was regularly recorded. The wet biomass content was calculated by subtracting the known weight of the dry and clean reactor. This assumes that the dynamic liquid hold-up during treatment was approximately constant, which is reasonable. The overall efficiency of biomass removal was calculated from the wet biomass content before and after treatment, as determined by first allowing the liquid to drain from the reactor for 10 min. The same procedure was used to determine the biomass content during standard operation of the biotrickling filters.

Toluene concentration, pressure drop: toluene concentrations and pressure drop during biotrickling filtration were determined using gas chromatography and a U-tube, respectively as previously reported (Cox and Deshusses, 1999^a).

RESULTS

Experiment 1: Batch Mode

The first test was done after 190 days of continuous operation of the biotrickling filter. The wet biomass content in the reactor was at this time 18.8 kg, corresponding to 80% of the packed bed volume. Severe clogging problems were observed. The toluene elimination capacity had declined from about 35 g/m³.h to less than 7 g/m³.h, for a toluene loading of 63 g/m³.h at a volumetric loading of 63 m³/m³.h. The pressure drop across the packing was up to 60 cm H₂O.

The effect of recirculation of 16 L of a 1.3% NaOCl solution is presented in Figure 1. The initial reaction rate was fast and appeared to be uncontrolled as a rapid decline of the wet biomass content in the reactor was observed and excessive amounts of foam were produced. At the same time, the concentration of suspended solids and dissolved carbon in the washing liquid increased, indicating biomass removal from the packing by detachment and dissolution (Figure 2). After about 2.5 hours, the biomass content in the reactor became constant and a total amount 5.26 kg wet biomass was removed. Examination of the data for the pH and concentration of free chlorine in the washing liquid during treatment shown in Figure 3, reveals that the slow down of biomass removal at 2.5 hours coincided with the depletion of NaOCl (Figure 3).

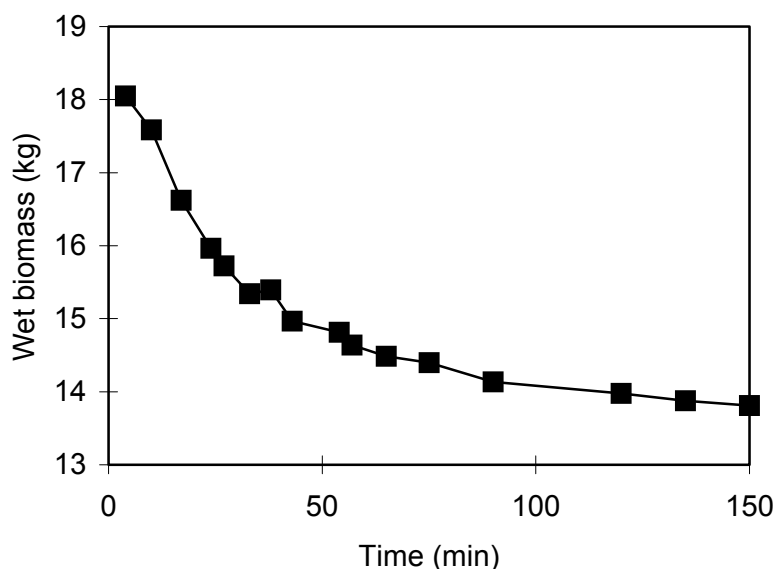


Figure 1. Biomass removal by recirculation of a 1.3% NaOCl solution (batch mode, total liquid volume of 16 L). The biomass wet weight includes ~500 mL liquid hold-up.

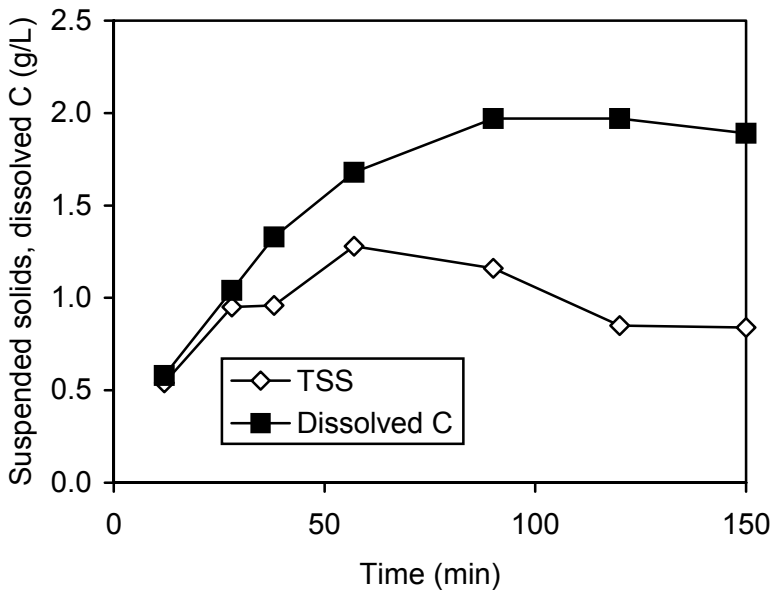


Figure 2. Suspended solids and total dissolved carbon in the washing liquid during batch treatment with 16 L of 1.3% NaOCl.

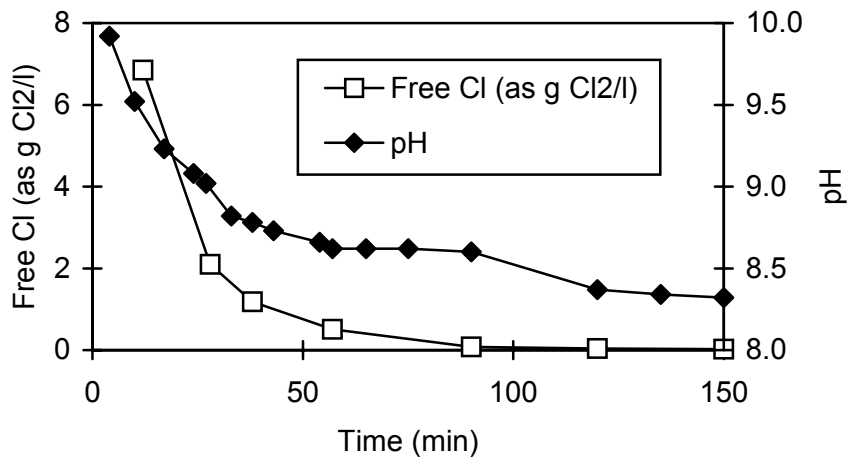


Figure 3. pH and free chlorine in the washing liquid during batch treatment with 16 L of 1.3% NaOCl.

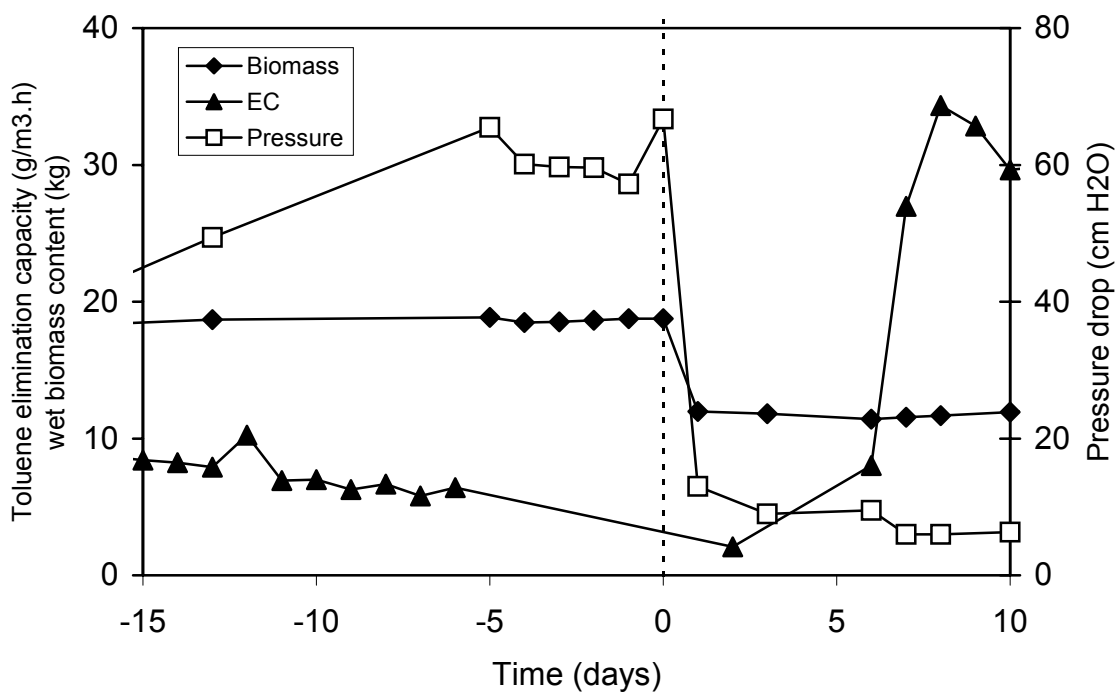


Figure 4. Performance of the biotrickling filter before and after biomass removal by batch treatment (on day 0) with NaOCl. The normal elimination capacity of the unclogged system under the standard conditions is about 32-35 g/m³.h.

The performance of the biotrickling filter before and after treatment is presented in Figure 4. This figure demonstrates the efficiency of the hypochlorite treatment in reducing both the wet biomass content and the pressure drop across the reactor and in restoring the toluene elimination capacity to a level observed when clogging problems are not present. However, detailed examination of Figure 4 reveals that it took seven days before a complete recovery of the maximum toluene removal performance was obtained. In a separate experiment it was found that the recycle liquid after the treatment contained significant concentrations of residual chlorine. The concentration of free and bound chlorine declined from 14 mg/L (as Cl₂) one day after treatment to below the detection limit after six days of operation. Because chlorine (as NaOCl, or Cl₂ or in a bound form) is a strong inhibitor of microbial growth and of microbial activity, it can be reasonably assumed that recovery of toluene removal was inhibited by residual chlorine. Presumably, the attached biomass not removed by the treatment absorbed chlorine during the treatment and post-treatment by flushing the reactor for a few hours with tap water was not sufficient for complete removal of the residual chlorine. Analysis of residual chlorine (not shown) revealed that about six days of standard operation with continuous medium feed and recycle liquid were required to purge completely and leach out residual chlorine from the biotrickling filter. Attempts to shorten the restart time were warranted.

Experiment 2: Continuous Mode

The second experiment was conducted in an attempt to solve two problems encountered with biomass removal using the batch mode: 1) the initial reaction was too fast and uncontrolled,

causing excessive foaming, 2) obtaining full pollutant treatment capacity after chemical treatment took six days, which is too long for application in an industrial setting. Hence, the addition of hypochlorite and the post-treatment flushing procedures were modified. First NaOCl addition was metered rather than a one-time addition. For the addition of NaOCl, either the oxidation-reduction potential (ORP) or the pH could potentially be used as a parameter for the feed-back control metering of NaOCl. As pH control will be a standard equipment on most industrial biotrickling filters, the latter option was selected. Second, to possibly shorten the downtime after NaOCl treatment, a post-treatment consisting of recirculating a sodium thiosulfate solution instead of tap water was implemented.

The experiment proceeded as follows. Before treatment, the biotrickling filter contained 17.455 kg wet biomass, the pressure drop across the reactor was 25 cm water column, and the toluene elimination capacity was as low as 17 g/m³.h. For the actual chemical wash, a 5.25% NaOCl solution was metered into the recycle liquid triggered by a pH controller set to maintain a pH of 9.2 (the actual measured value ranged from 9.2 to 9.6). In contrast to the batch mode, the initial biomass removal rate was slow but it increased over time (Figure 5). The same trend was observed for the consumption of the NaOCl solution. One can speculate that as biomass was removed, the biofilm area available for reaction of NaOCl increased, thus facilitating a faster reaction rate. The ORP in the recycle liquid remained constant during treatment at 700-825 mV. After 4 hours of treatment, 10.56 kg wet biomass had been removed from the biotrickling filter, corresponding to a removal efficiency of 60%. Total suspended solids and dissolved carbon in the washing liquid at the end of the treatment had increased to 3.7 and 3.5 g/L, respectively.

After the NaOCl treatment, effective neutralization of residual chlorine was achieved by recirculating a sodium thiosulfate solution. The neutralization of chlorine was indirectly assessed by measuring the ORP in the washing liquid during post-treatment (Figure 6). These measurements indicated that addition of a total 60 g Na₂S₂O₃.5H₂O was sufficient for complete neutralization. Although the post-treatment lasted for 18 h, Figure 6 indicates that post-treatment for 2 hours would probably have been sufficient, since concentrations of free and bound chlorine in the washing liquid decreased to below the detection limit after the last addition of sodium thiosulfate.

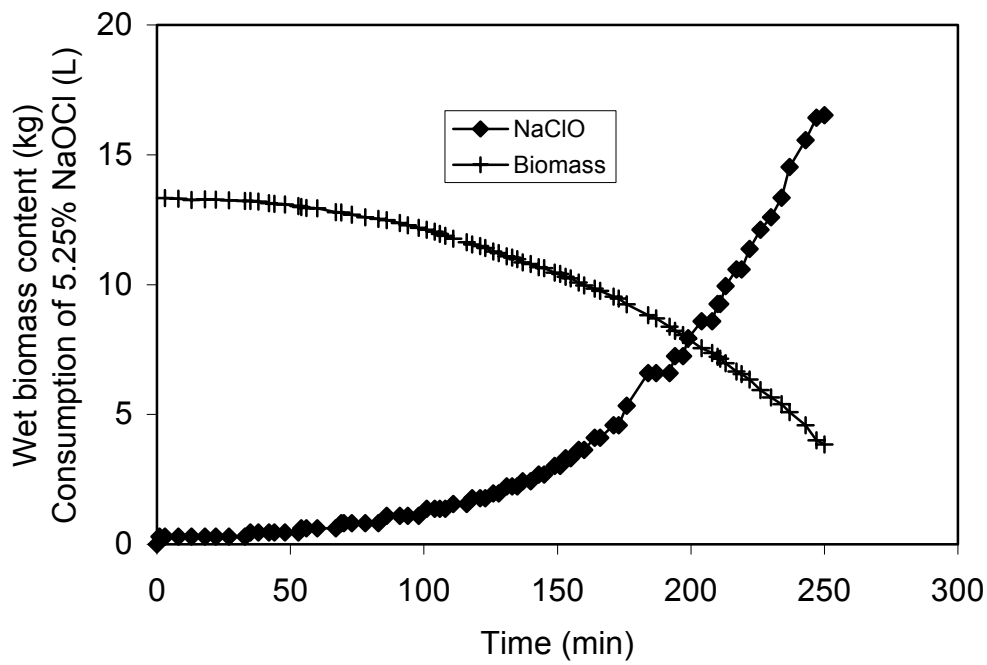


Figure 5. Biomass removal and hypochlorite consumption in the treatment with continuous addition of 5.25% NaOCl (continuous mode, regulation of the washing liquid pH at 9.2).

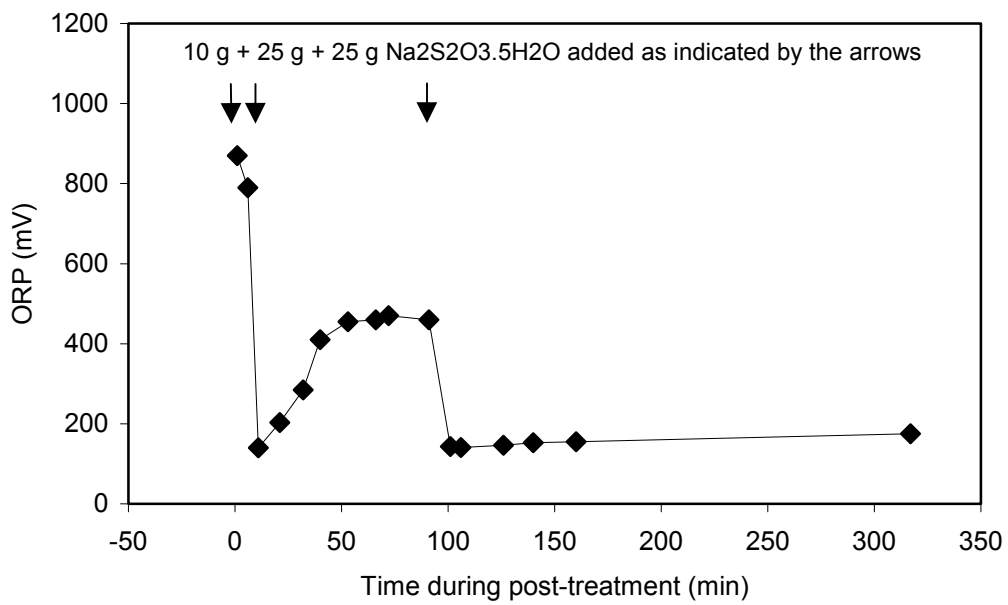


Figure 6. Post-treatment by recirculation of 4 L of a sodium sulfate solution. The ORP in the washing liquid is an indirect measure of residual chlorine.

In Figure 7, the performance of the biotrickling filter before and after the chemical treatment is presented. The first measurement after treatment shows a decrease in the elimination capacity which is likely due to the temporary and partial inactivation of the process culture. Thereafter, in a similar manner to Experiment 1 (Figure 4), biomass removal resulted in improved performance with a significantly higher toluene elimination capacity and a lower pressure drop. The post-treatment with sodium thiosulfate was successful in reducing the time required for the biotrickling filter to recover from the NaOCl treatment. Toluene removal was completely restored after two days of operation (Figure 7), instead of the six days required after post-treatment by washing with tap water only (Figure 4).

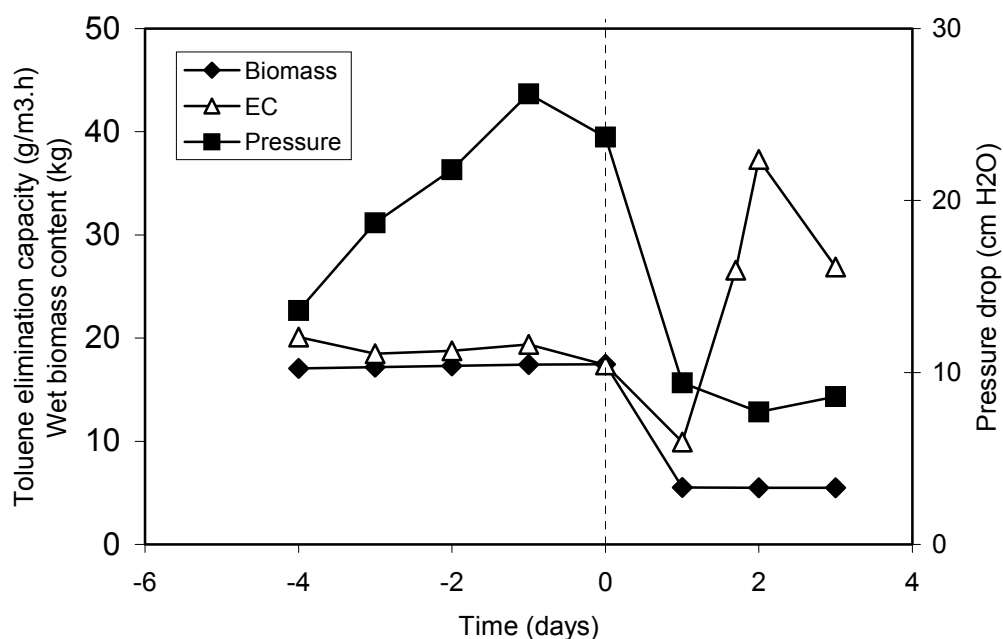


Figure 7. Performance of the biotrickling filter before and after biomass removal by continuous treatment with NaOCl and post treatment with sodium thiosulfate (on day 0).

Carbon Balances for Biomass Removal

Table 1 summarizes biomass removal for the batch and continuous mode of treatment. Biomass removal efficiencies of 28 and 60%, respectively were calculated. These values clearly depend on the amount of NaOCl added (batch mode), and/or the duration of treatment (continuous mode), hence greater efficiencies may be obtained than demonstrated in these experiments. The continuous treatment appeared to consume twice the amount of NaOCl required in the batch treatment, per amount of wet biomass removed. A plausible explanation is that during continuous treatment part of the added NaOCl is purged before reaction with the biomass. The data in Table 1 show that about 40-80 g of NaOCl is required to remove 1 kg of wet biomass.

Table 1. Mass balances of biomass removal from toluene-degrading biotrickling filters (packed bed volume 23.6 L) using hypochlorite in the batch and continuous mode of treatment.

Parameter	Batch mode ^b	Continuous mode ^c
Wet biomass in the reactor		
Before treatment	18.765 kg	17.455 kg
After treatment	13.505 kg	6.895 kg
Removal efficiency	28%	60%
<i>Recovery of removed biomass in the washing liquid^a</i>		
As suspended solids	6%	ND
As dissolved carbon	28%	ND
NaOCl consumption		
Ratio of NaOCl consumed to wet biomass removed	40 g/kg	82 g/kg

^a Conversion factors for biomass immobilized on the Pall rings (Cox and Deshusses, 1999^b): 0.046 g dry biomass/g wet biomass, 0.44 g carbon/g dry biomass.

^b Total washing liquid volume of 16 L of 1.3% w/v NaOCl.

^c Addition of 16.5 L of 5.25% NaOCl over 4 hours of treatment, constant washing liquid volume of 4 L by overflow purge.

Attempts to close the mass balance of biomass removal by analysis of the washing liquid revealed that a large fraction of carbon was missing. For example, in the batch treatment, suspended solids and dissolved carbon accounted for respectively 6 and 28% of the amount of biomass removed. This indicates that gaseous compounds are the main products of reaction between NaOCl and biomass, and that biomass detachment or production of water soluble organic compounds are not the main routes of biomass removal by NaOCl. At this time, the composition of the gaseous compounds is unknown. One expects of course a large fraction of the biomass to be oxidized to carbon dioxide, but halomethane formation can not be excluded.

DISCUSSION

Until biotrickling filters that combine a high elimination capacity and a slow clogging rate are developed, periodical removal of biomass by chemical treatment appears to be attractive technique for long-term, stable operation of biotrickling filters. The advantage is that biotrickling filter performance can be maximized by ample supply of nutrients, thereby reducing the required reactor volume and the investment costs (Deshusses and Cox, 1999^c). Furthermore, chemical treatment requires no structural changes to the biotrickling filter construction or expensive equipment other than a vessel to contain the washing liquid. In this respect, experience will show whether the benefits of restarting the biotrickling filter with the original liquid is significant. If not, the holding tank would not be required. While biomass removal using NaOCl appears promising, there are a few points that require further consideration:

1. Chemical treatment should remove large amounts of biomass in a short time-span. Previously, Weber and Hartmans (1996) demonstrated biomass removal by treatment with 0.4% NaOH. It can be estimated from their data that this treatment removed about 3.2 kg dry biomass/m³ reactor (i.e., 70 kg wet biomass/m³ reactor), which would be insufficient for biotrickling filters that rapidly clog (Cox and Deshusses, 1999^b). The present results demonstrate the effectiveness of NaOCl. Treatment using the continuous mode at pH 9.2

removed 12.3 kg dry biomass/m³ reactor in 4 hours (i.e., 270 kg wet biomass/m³ reactor), a larger amount can be expected when prolonging the treatment.

2. The concentration of NaOCl used during these treatments is several orders of magnitude higher than usually used for disinfection purposes (White, 1972). This will not only kill the biomass remaining after the NaOCl treatment, but residual chlorine may slow down the restart after treatment. These effects were minimized by the post-treatment with thiosulfate and by restarting the biotrickling filter with the original recycle liquid (containing suspended biomass) from before treatment as an inoculum. Since toluene is easily biodegradable, these procedures proved sufficient to reduce the total down-time to three days (one day of treatment, two days of recovery). However, for pollutants more difficult to biodegrade, longer periods of recovery may be expected, similar to as observed for the start-up of biotrickling filters after construction.
3. The mass balances of biomass removal (Table 1) indicate that a major part of biomass is converted into unidentified products. Especially the potential formation of volatile chlorinated compounds is of concern. These products need to be identified and quantified, and evaluated with respect to the toxicity and emission standards.
4. As previously discussed (Deshusses and Cox, 1999^c), the cost of biomass control in high-performance biotrickling filters (i.e., requiring frequent treatment) by NaOCl treatment may constitute up to 40% of the total treatment costs. A major part is related to the purchase of NaOCl. Although the continuous mode of treatment is preferable with respect to controlling the reaction rate and the time required for effective biomass removal, this treatment requires a relatively large amount of NaOCl (Table 1) and further optimization is required to reduce the treatment costs.

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Key Words

biofilter, biotrickling filter, VOC treatment, biomass control