REPORT TITLE: Treatment of Produced Waters Using a Surfactant Modified Zeolite/Vapor Phase Bioreactor System
REPORT TYPE: Semi-Annual Technical Report
REPORT PERIOD: 1 April 2004 – 30 September 2004
PRINCIPAL AUTHORS: Lynn E. Katz, Kerry A. Kinney, R.S. Bowman**,** E.J. Sullivan
REPORT ISSUE DATE: December 2004
DOE AWARD NUMBER: DE-FC26-02NT15461

Treatment of Produced Waters Using a Surfactant Modified Zeolite/Vapor Phase Bioreactor System

Semi-Annual Technical Report
1 April 2004 – 30 September 2004
DOE AWARD NUMBER: DE-FC26-02NT15461

Lynn E. Katz
Project Manager

Abstract

This report summarizes work performed on this project from April 2004 through September 2004. Our previous work demonstrated that a polyurethane foam biofilter could successfully biodegrade the BTEX contaminants found in the SMZ regeneration waste gas stream. However, establishing the biomass on the polyurethane foam packing was relatively time consuming and daily recirculation of a concentrated nutrient solution was required for efficient operation of the foam biofilter. To simplify the start up and operating requirements of the biofilter system, a simple, compost-based biofilter was investigated for its ability to treat the BTEX contaminants generated during the SMZ regeneration process.

The investigation of the compost biofilter was divided into three experimental phases that spanned 180 days of biofilter operation. During Phase 1, the biofilter was continuously supplied a BTEX-contaminated waste gas stream. During Phase 2, a series of periodic shutdown tests were conducted to assess how the biofilter responded when the BTEX feed was discontinued for periods ranging from 1 day to 2.8 days. The Phase 3 experiments focused on determining how the biofilter would handle periodic spikes in inlet BTEX concentration as would be expected when it is coupled with an SMZ column. Results from the continuous feed (Phase 1) experiments demonstrated that the compost biofilter could maintain BTEX removals of greater than 98% within two weeks of startup. Results of the shutdown experiments indicated that benzene removal was the most sensitive to interruptions in the BTEX feed. Nevertheless, the BTEX removal efficiency exceeded 95% within 6 hours of reestablishing the BTEX feed to the biofilter. When the biofilter was subjected to periodic spikes in BTEX concentration (Phase 3), it was found that the total BTEX removal efficiency stabilized at approximately 75% despite the fact that the biofilter was only fed BTEX contaminants 8 hours per day. Finally, the effects of nutrient supply and EBCT on compost biofilter performance were also investigated. The bioreactor maintained greater than 95% removal efficiency for over 40 days without an additional supply of nutrients when a 10X concentrated HCMM was mixed with the compost packing at the beginning of the experiments. Results also suggest that an EBCT greater than 30 seconds is required to maintain high BTEX removal efficiencies in the compost biofilter system.

TABLE OF CONTENTS

List of Figures

1. Introduction

The United States oil and gas industry generates more than three billion tons of wastewater annually (API, 1987). This is by some estimates the largest single waste stream in the country, aside from nonhazardous industrial wastes. This water is often called 'produced water' and can be generally characterized as saline water that contains various amounts of pollutants, including soluble and insoluble organics as wells as many inorganic species. Several of the dissolved contaminants, namely benzene, toluene, ethylbenzene, and xylenes (BTEX), are known to be hazardous at low concentrations. Although as much as 95% of this produced water is disposed via reinjection, the remaining amounts that are discharged on the surface are significant. Environmental and cost considerations make surface discharge of this water a more practical means of disposal in many instances. In addition, reinjection is not always a feasible option because of geographic, economic, or regulatory considerations. In these situations, it may be desirable, and often necessary from a regulatory viewpoint, to treat produced water before discharge. It may also be feasible to treat waters that slightly exceed regulatory limits for re-use in arid or drought-prone areas, rather than losing them to re-injection.

Current treatment methods for produced water focus on the recovery of insoluble oil and grease that are of economic value to the producer. These include separation tanks, flotation methods, and hydrocyclones. These treatment procedures are ineffective at removing dissolved organic and soluble inorganic compounds. Large-scale on-shore producers are required to re-inject this contaminated water into non-drinking water aquifers. Small-scale producers (less than 10 bbl per day) are exempt from this requirement. Although this water is frequently collected and concentrated in evaporation pits, many small-scale producers dispose of this water via surface discharge. Due to the harmful constituents remaining in produced water after oil/water separation, members of the industry feel that regulation of all types of produced water disposal will soon become more stringent. Therefore, the need for innovative treatment methods exists (Lawrence et al., 1995). Moreover, many oil and natural gas production operations are located in arid environments, where water is extremely valuable. Therefore, the ability to reuse produced water in agricultural and transportation operations would be of great benefit to local communities. Although some innovative treatment methods have been explored (i.e., phytoremediation, filtration, and carbonaceous sorbents), they are generally cost prohibitive or do not provide a reusable product. This research focuses on the use of a surfactant modified zeolites (SMZ) to treat produced waters.

Zeolites are naturally occurring aluminosilicate minerals with high porosities and large cationic exchange capacities. Cationic surfactants can adsorb to the external exchange sites on zeolite to produce a material that is capable of sorbing anions, cations, and non-polar organics. SMZ's relatively low cost and ease of regeneration makes it a promising option for field-scale treatment of produced waters, as well as many other multi-component waste streams (Janks and Cadena, 1992; Li & Bowman, 1998, 2000; Gupta, 2001; Tan, 2002, Ranck et al., 2003).

Field studies conducted in Wyoming have shown that regenerated SMZ has a greater affinity for BTEX compounds compared to virgin SMZ (Ranck et al., 2003). It was theorized that less volatile compounds present in produced water remained on the surface of SMZ through the regeneration process. This increased organic phase was believed to provide a larger sorption capacity for BTEX sorption. Batch experiments conducted in this phase of the project were to determine the impact of semi-volatile compounds on sorption of BTEX to virgin SMZ, and to evaluate the potential of SMZ for removal of semi-volatile compounds and inorganic contaminants from produced water.

A key feature required for successful application of SMZ to the treatment of produced water is regeneration of the SMZ. Studies completed by the PIs indicate that SMZ can be readily regenerated for BTEX compounds simply by sparging ambient air through the SMZ column. This process generates a moist air stream contaminated with volatile organic compounds (VOCs) including BTEX. Because these VOCs are biodegradable, a vapor phase bioreactor (VPB) can be used to destroy the pollutants generated in the SMZ regeneration step. Recent experiments completed by the PIs indicate that a polyurethane foam biofilter can successfully biodegrade the BTEX contaminants found in the SMZ regeneration waste gas stream. The biofilter was also found to tolerate short periods without a feed waste gas stream. This feature will be important when the biofilter is coupled to the SMZ beds and only receives a waste gas when an SMZ bed is actually being regenerated. Despite the effectiveness of the foam biofilters, it would be desirable to simplify the start up and operating requirements of the biofilter system. To this end, a simple, compost-based biofilter was investigated for its ability to treat the BTEX contaminants generated during the SMZ regeneration process. The results of these experiments are presented and discussed below.

2. Experimental Methods

Results of our previous experiments demonstrated that a biofilter packed with polyurethane foam could effectively treat the waste gas stream generated when a saturated SMZ bed is regenerated. However, establishing the biomass on the polyurethane foam packing was relatively time consuming and daily recirculation of a concentrated nutrient solution was required for efficient operation of the foam biofilter. Since it is anticipated that coupled SMZ/vapor phase bioreactor systems may be deployed in remote locations, it would be desirable to simplify the operational and maintenance requirements associated with the biofilter module. The objective of the most recent series of experiments was therefore to determine if a simpler biofilter system packed with a compost-based media could also successfully treat the BTEX-laden waste gas stream that would be expected from the SMZ regeneration process. To this end, a series of experiments were conduced with a compost-based biofilter to determine the response of the system to continuous operation as well as to discontinuous feed conditions expected when the system is coupled with a SMZ bed. Finally, the ability of the biofilter to handle the spikes in BTEX concentration that would be expected during the SMZ regeneration cycle was evaluated. Finally, the nitrogen requirements of the biofilter system over long term operation were examined.

2.1 Vapor Phase Bioreactor Design and Operation

The experimental reactor consisted of an 11.75 L biofilter packed with a compost-based material (see Figure 2-1). The experimental reactor was similar to that used in the biofilter experiments described previously (DOE Semiannual Report 15461R04) except that it was packed with a compost-based material. The compost filter media used to pack the columns consists of the following materials (by volume): 60% compost, 36.5% perlite, and 3.5% crushed oyster shell. The compost, known as Dillo Dirt™, is produced from dewatered municipal sludge and bulking agents such as tree trimmings and yard waste. Prior to mixing the compost with the other ingredients, the compost was sieved to remove particles less than 2 mm. Perlite was added to improve the air flow through the packing media and to reduce compaction of the packing media mixture. The oyster shell was added to the media to act as a pH buffer.

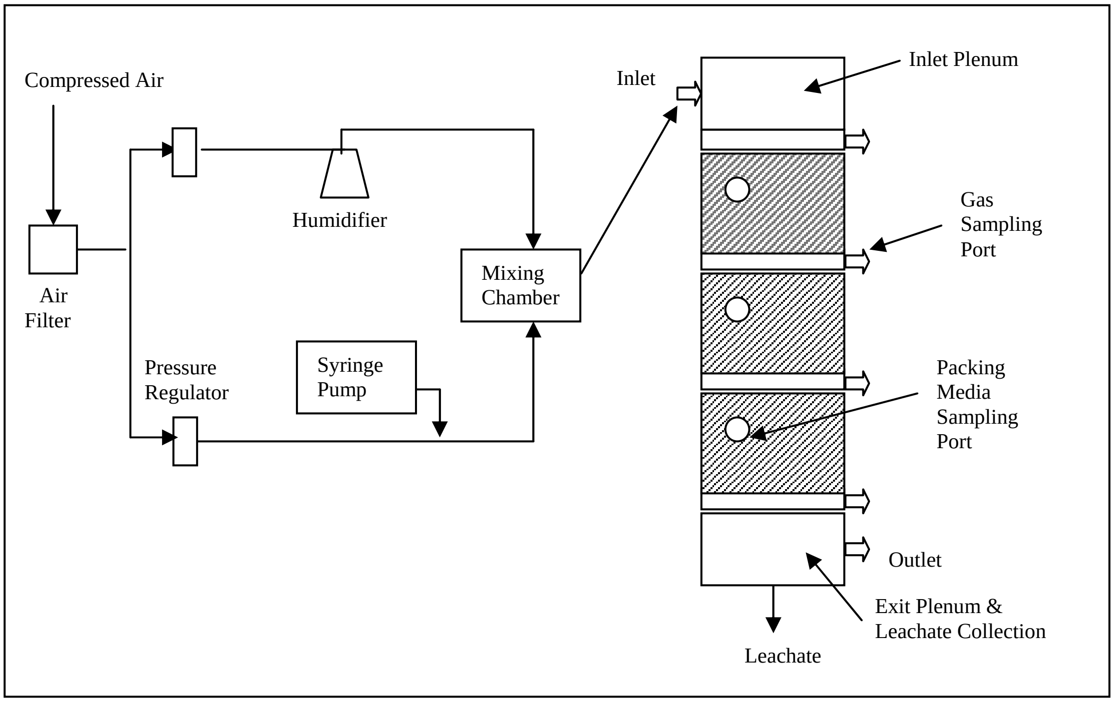


Figure 2.1 – Schematic diagram of experimental vapor phase biofilter.

Before packing the media into the column, it was inoculated with a BTEX-degrading microbial consortium. The inoculum was developed from an activated sludge culture as described previously (DOE Semiannual Report 15461R04). To ensure the packing media would not be nitrogen limited during the start up period, the packing media was mixed with 1L of a concentrated nutrient solution prior to being placed in the biofilter column. The concentrated nutrient solution consisted of a hydrocarbon minimal medium (HCMM) solution that was modified by increasing the concentration of each component by a factor of ten. The modified HCMM consisted of 2.72 g/L KH_2PO_4, 1.42 g/L Na_2HPO_4, 3.96 g/L $(NH_4)_2SO_4$, 10.1g/L KNO_3, and 1 mL/L of trace metal solution.

The trace metal solution was composed of: 50 g/L $MgSO_4 \cdot 7H_2O$, 14.7 g/L $CaCl_2 \cdot 2H_2O$, 2.5 g/L $FeSO_4 \cdot 7H_2O$, 2.86 g/L H_3BO_3, 1.54 g/L $MnSO_4 \cdot H_2O$, 0.041 g/L $CoCl_2 \cdot 6H_2O$, 0.027 g/L $CuCl_2 \cdot 2H_2O$, 0.044 g/L $ZnSO4 \cdot 7H_2O$, 0.025 g/L $Na_2MoO_4 \cdot 2H_2O$, and 0.02 g/L $NiCl_2 \cdot 6H_2O$.

To introduce the BTEX contaminants into the biofilter, a liquid BTEX mixture were injected into a small slip air stream using a syringe pump. This contaminated air stream was mixed with humidified air in a mixing chamber prior to being introduced to the top of the biofilter (see Figure 2-1). Throughout most of the first 180 days of biofilter operation, the bed contact time (EBCT) in the biofilter was maintained at one minute except for a period from Day 108 to Day 133 when the EBCT was reduced to 30 seconds. The total BTEX concentration in the inlet gas stream was maintained at 130 ppm_v (benzene 12, toluene 24, ethyl benzene 32, *p&m*-xylene 22, *o*-xylene 40 ppm_v) for the first 25 days of operation when the biofilter was operated with a steady, continuous BTEX feed (Phase 1 experiments). During the second study phase (Days 26 through 33), a series of discontinuous feed experiments were conducted to determine the response of the biofilter to periodic shutdowns. In these experiments, the BTEX feed to the compost bioreactor was discontinued for periods ranging from 1 to 2.8 days. During each shutdown test, no VOCs were provided to the column but the air flow rate and humidity were supplied as usual. Following each shutdown test, the BTEX feed to the biofilter was reestablished at a steady concentration of 130 ppm_v.

During the third phase of biofilter operation (Day 177 to Day 189), a series of BTEX spike experiments were conducted. During these experiments, the inlet BTEX concentration was increased rapidly to approximately 400 ppm_v and then decreased to zero in an exponential fashion over an eight hour period. After each spike test, the VOC feed to the biofilter was discontinued for 16 hours although the humidified air supply was continued during this period. These spike tests were intended to mimic the off-gas concentration profiles that would be expected from the SMZ system when it was being regenerated with air for 8 hours per day. The remaining 16 hours in which the biofilter received no contaminated air represented the period when the SMZ column(s) would be treating produced water and no contaminants would be fed to the downstream biofilter.

2.2 Analytical Methods

Gas samples were collected from sampling ports located in each column to determine the VOC removal profiles along the bioreactor column. Samples were collected with gas-tight syringes and immediately analyzed using a gas chromatograph equipped with a flame ionization detector.

To determine the nutrient concentration along the column, samples of packing media were collected periodically from each section in the column. Deionized water was added to sample which was homogenized in a vortexer and then sonicated to remove the biomass from the packing material. The samples were equilibrated overnight to allow separation of the compost particles from liquid. The liquid ammonium concentration was then determined with an ammonium electrode probe (Orion 95-12, Orion Research Inc., MA). Nitrate measurements were performed in a similar manner using a nitrate combination electrode (Accumet, Fisher Scientific, NJ).

The pressure drop across the column was measured periodically using a pressure gauge (Magnehelic, Dwyer Instrument Inc., IN). The gauges were directly connected to the inlet and outlet gas sampling ports, and the pressure difference was measured in inches of H_2O. Media moisture content was determined gravimetrically. During sampling, a media sample of approximately 0.5 g was obtained directly from the bioreactor, placed on the dish, and weighed. The dish and sample were then dried for 24 hours in a 105°C oven. After cooling the dry dish and sample to room temperature in a dessicator, the dry dish and sample were reweighed. The pH of leachate samples was measured using an Accument™ pH meter (Fisher Scientific, Model 50). The pH meter was calibrated daily with standard pH solutions of 4 and 7 (Fisher Scientific).

3. Results and Discussion

The compost biofilter was operated for over 180 days. During the first phase of operation, the compost biofilter was continuously supplied a waste gas stream with a total BTEX inlet concentration of 130 ppm_v. A series of periodic shutdown experiments were then conducted during the second study phase to see how the biofilter system would respond when the BTEX feed was discontinued for periods ranging from 1 day to 2.8 days. Finally, a series of experiments were conducted to determine how the biofilter would respond to periodic spikes in BTEX concentration as would be expected when it is coupled to an SMZ bed treating produced water.

3.1 Start Up and Continuous Feed Experiments

Within two weeks of starting the VOC feed to the biofilter, the compost biofilter achieved greater than 98% removal of the BTEX contaminants in the waste gas stream. This start up period compares favorably with that observed in the polyurethane foam biofilter which required more than a month and several adjustments to the nutrient feed system before high BTEX removals were achieved. Initially, the BTEX removal profiles along the compost biofilter column were rather linear as evident in Figure 3-1(A). However, the removal profiles improved over time and eventually became exponential indicating that the biofilter had achieved optimal removal of the contaminants (Figure 3-1(B)).

(A)

(B)

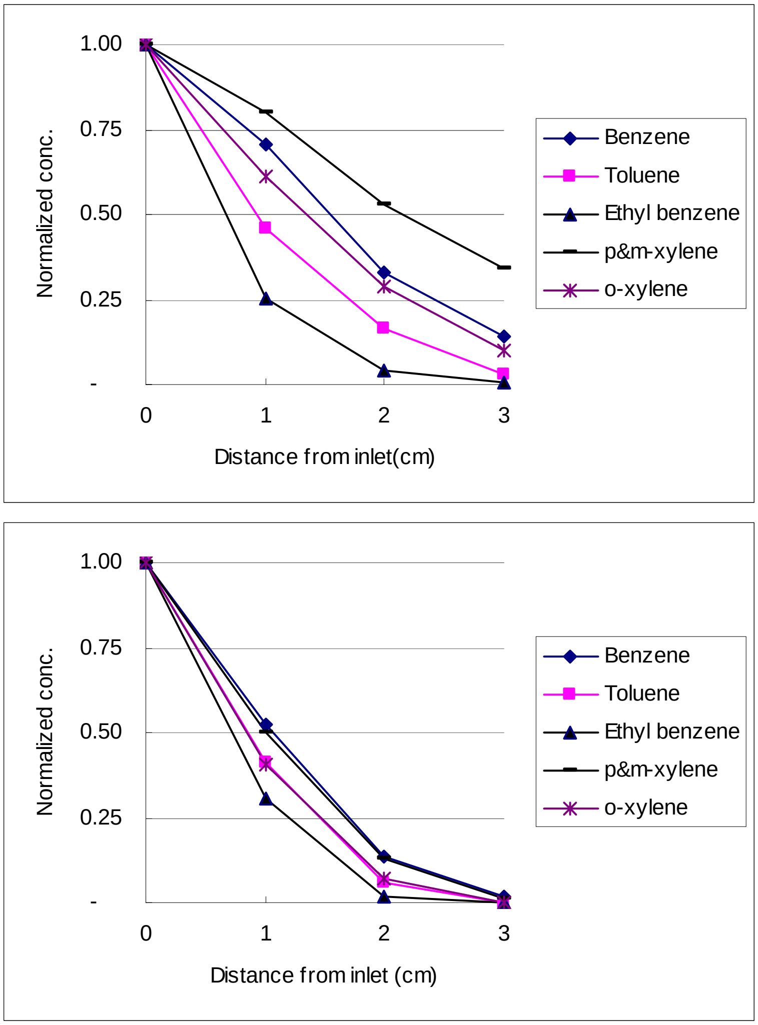


Figure 3-1. Normalized VOC removal profiles along the compost biofilter column on (A) Day 9 and (B) Day 19.

3.2 Discontinuous operation – Shutdown Experiments

To determine the response of the biofilter to periodic shutdowns, the BTEX feed to the compost bioreactor was discontinued for periods ranging from 1 to 2.8 days. During each shutdown test, no VOCs were provided to the column but the air flow rate and humidity were supplied as usual. The recovery of the biofilter following each shutdown test was monitored until the removal efficiency across the biofilter exceeded 90%. Figure 3-2 shows the results of the one-day shutdown test in the compost-based biofilter. For comparison purposes, the results of the one-day shutdown experiment for the polyurethane foam biofilter are also shown.

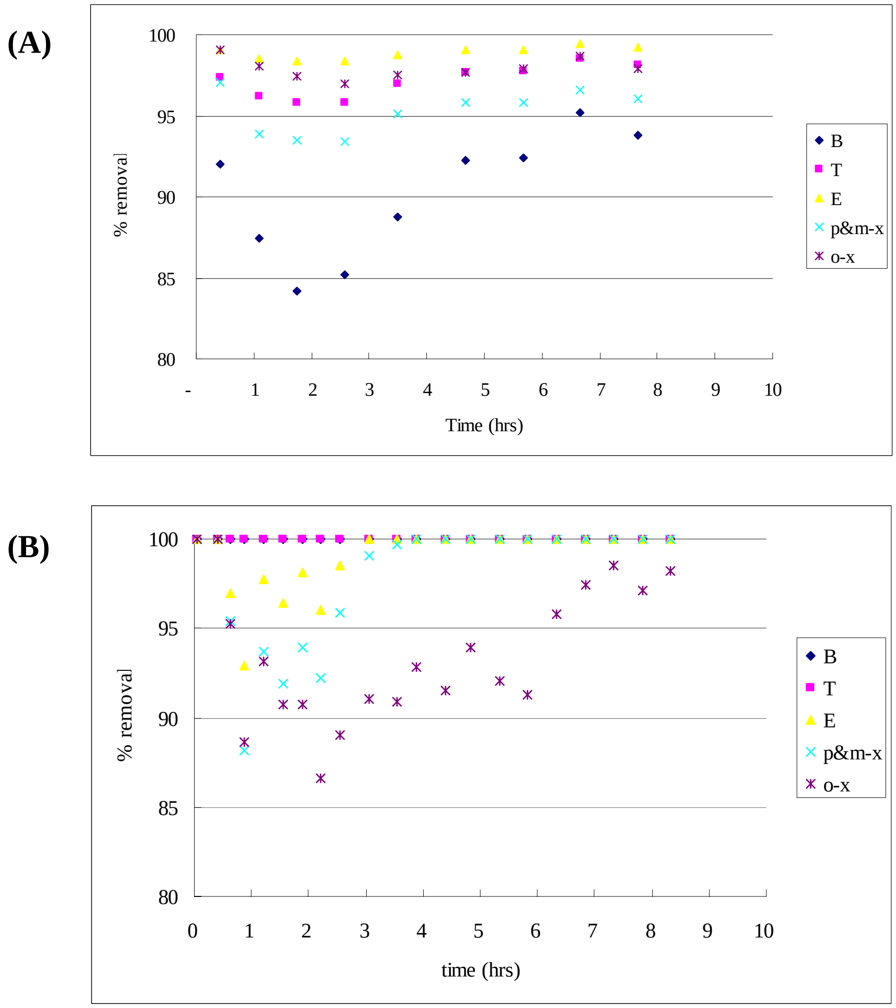
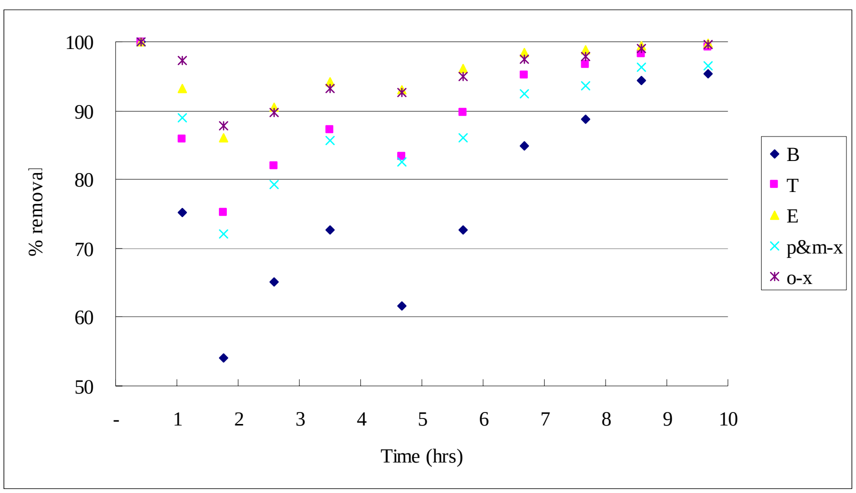


Figure 3-2. BTEX removal efficiency after a 24 hour shutdown period. (A): compost biofilter and (B): polyurethane foam biofilter

As is evident in the figure, the recovery period for both biofilters was nearly identical. However, the contaminant that broke through the biofilter first upon resumption of the BTEX feed differed between the biofilters. In the polyurethane foam biofilter, *o*-xylene removal was most adversely affected by the one-day shutdown period while in the compost biofilter, benzene removal was found to be the most sensitive to the shutdown. In either case, the biofilters recovered rather quickly and within approximately 6 hours, the removal efficiency exceeded 95%. These results indicate that a biofilter that has been provided a continuous VOC supply can handle short periods without a carbon source.

The response of the compost biofilter to a 2.8-day shut down period was also examined. The response of the system following resumption of the BTEX feed is presented in Figure 3-3. Again, for comparison purposes, the response of the polyurethane foam biofilter is also shown. As can be seen in the figure, the overall BTEX removal efficiency recovered to 90% removal in the compost biofilter within eight hours whereas the polyurethane foam biofilter only required approximately 5 hours. In this case, the polyurethane foam biofilter made a more rapid recovery than the compost biofilter. This result may have been due to the high levels of biomass that were present in the polyurethane biofilter at the time of the shutdown tests.

(A)



(B)

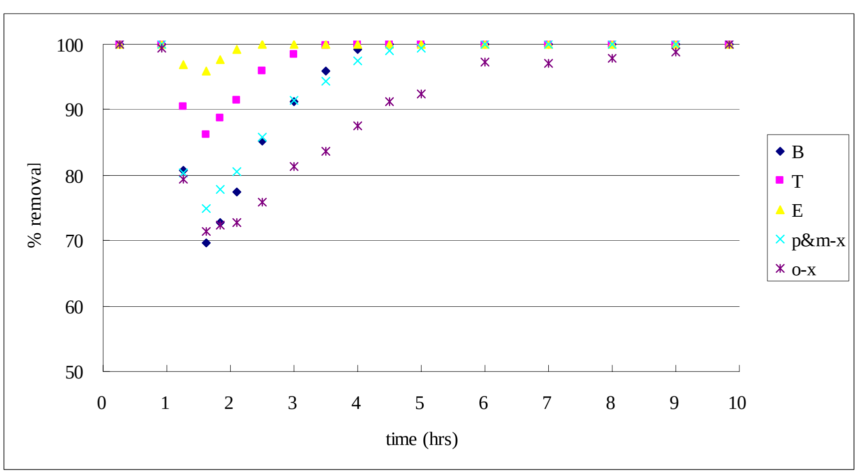


Figure 3-3. – BTEX removal after a 2.8-day shutdown period: (A) compost based biofilter and (B) polyurethane foam based biofilter.

3.3 Biofilter Response to Periodic Spikes in BTEX Concentration

A single spike feeding test was completed on Day 38 of biofilter operation to determine how the system would respond to the variations in BTEX concentration expected during a single SMZ regeneration cycle. To mimic the off-gas stream from a saturated SMZ column, the BTEX inlet concentration was suddenly increased to 275 ppm_v and then decreased exponentially over a six hour period. The maximum BTEX concentration detected in the exit gas stream from the biofilter was only 23 ppm_v indicating that greater than 90% removal was achieved at all times in the biofilter (see Figure 3-4).

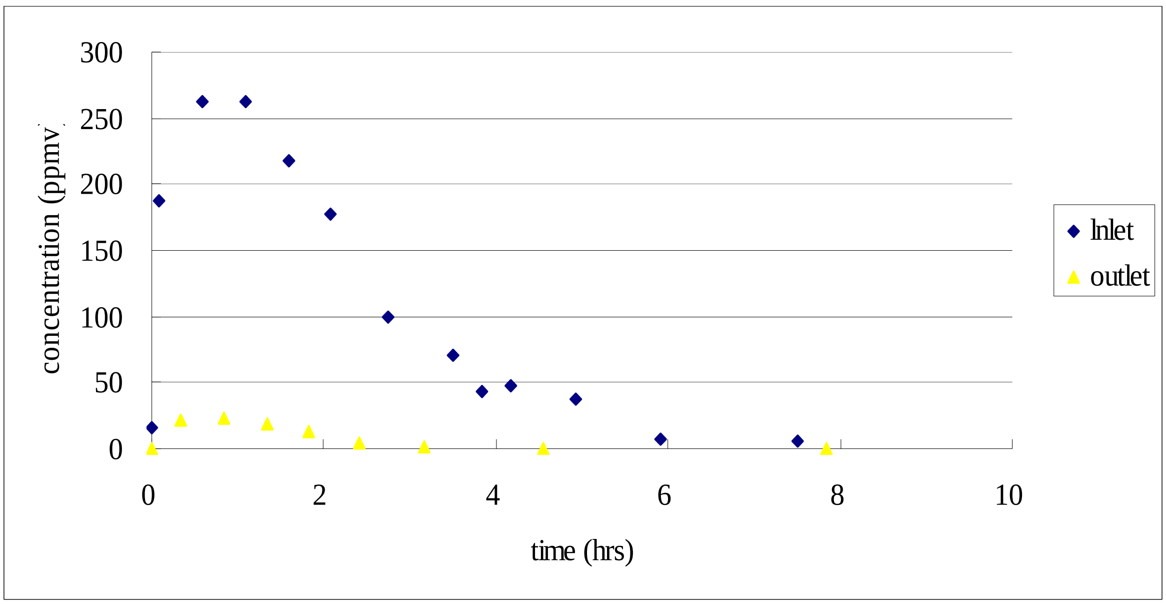


Figure 3-4. – BTEX removal during the single spike feeding test.

The results of the single BTEX spike experiment indicate that the biofilter can handle moderate spikes in inlet BTEX concentration. However, the previous history of the biofilter is expected to affect its response to spikes in inlet concentration. Prior to conducting the single spike test, the biofilter had been continuously supplied a waste gas stream contaminated with 130 ppm_v BTEX and thus the biomass in the system would be expected to be quite active. In an actual field situation, the biofilter may only receive VOCs in the waste gas stream as little as 8 hours per day and thus the biodegradation capacity of the biomass may be diminished. The actual period that the biofilter will receive a VOC-laden waste gas stream will depend on the regeneration frequency of the SMZ columns and how they are coupled to the downstream biofilters. Thus, it is important to determine how the biofilter would respond to cyclical spikes in inlet BTEX concentration as would be expected when it is coupled with the SMZ columns. To address this issue, a series of experiments were conducted in which the inlet concentration to the biofilter was increased rapidly to approximately 370 ppm_v and then decreased exponentially to zero over an 8 hour period. For the remaining 16 hours per day, the biofilter was only supplied humidified air to mimic the maximum starvation period we would expect in a 24 hour period for a coupled SMZ/biofilter system. The results of these experiments are summarized in Figure 3-5. The outlet BTEX concentration on the first day of the spike test was approximately 50 ppm_v but the BTEX concentration increased to approximately 95 ppm_v for the remainder of the cycles. Thus, the total BTEX removal efficiency stabilized at approximately 75% despite the fact that the biofilter was only fed VOCs 8 hours per day.

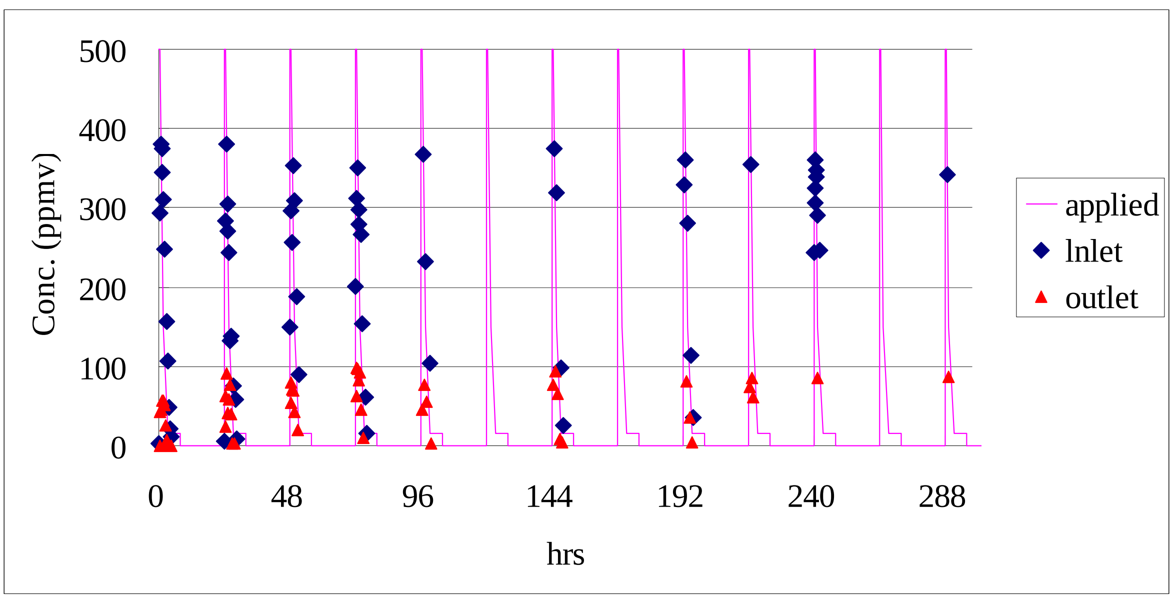


Figure 3-5. – BTEX removal efficiency during the cyclical spike feeding experiments.

3.4 Effect of Nitrogen Supply and EBCT

One potential advantage of compost biofilters over polyurethane foam biofilters is that they may require less frequent nutrient additions to maintain biofilter performance. Indeed, the compost biofilter investigated in this study was able to operate for extended periods without a frequent nutrient supply. Just prior to starting up the compost biofilter, a 10X concentrated HCMM was mixed with the compost packing to increase the nutrient concentration of the media. The bioreactor maintained greater than 95% removal efficiency for over 40 days without any additional supply of nutrients (Figure 3-6). However, the nitrogen supply eventually became depleted and the removal dropped below 60%. Due to the characteristics of compost, addition of too much nutrient solution can result in compaction, channeling, and washout of media. For this reason, a small quantity (440 mL) of a 5X concentrated HCMM solution was evenly distributed on the top of the column on Day 85. After the addition of the concentrated nutrient solution, the BTEX removal efficiency recovered rapidly and exceeded 99% within two days.

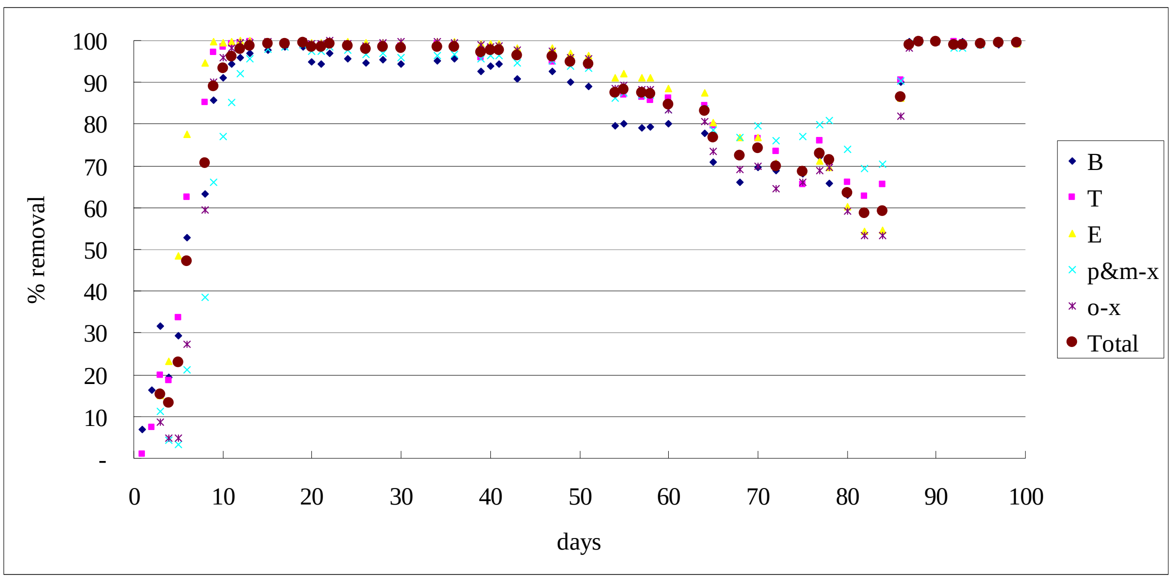


Figure 3-6. – Effect of nutrient addition on BTEX removal efficiency. A concentrated nutrient solution was added on Day 85 of Operation.

In addition to nutrient supply, another concern that must be addressed when designing the biofiltration system is the EBCT that is required for the gas phase system since this will ultimately determine the size of the biofilter unit required. An experiment was therefore conducted to determine the effect of reducing the EBCT from 1 minute to 30 seconds. As evident in Figure 3-7 below, halving the EBCT to 30 seconds reduced the BTEX removal efficiency. The BTEX removals fluctuated from 60 to 90% and more frequent nitrogen additions were required to maintain high BTEX removals. These results suggest that an EBCT greater than 30 seconds is required to maintain high BTEX removal efficiencies in a compost biofilter system.

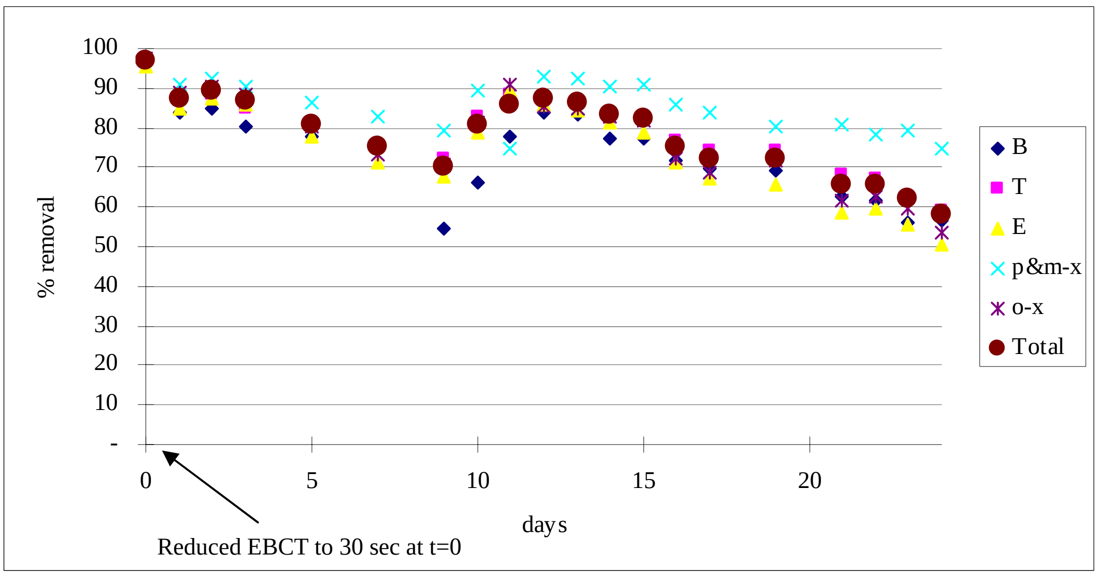


Figure 3-7. Response of the compost biofilter to reducing the gas-phase EBCT from 1 minute to 30 seconds. The total inlet BTEX concentration was maintained at 130 ppm$_v$.

4. Summary

A series of experiments were conducted to assess how well a simplified compost biofilter could treat a BTEX-contaminated waste gas stream that would be expected when the air used to regenerate a saturated SMZ column is fed to a downstream biofilter. When the compost biofilter received a constant supply of air contaminated with 130 ppmv BTEX, the biofilter could remove greater than 98% of the contaminants from the waste gas stream. The system also responded well to short periods where the BTEX feed to the biofilter was discontinued. To challenge the system further, the biofilter was subjected to periodic spikes in inlet BTEX concentration as would be expected when it is coupled to an SMZ bed. Results of these experiments indicate that although the BTEX removal efficiency declined under these conditions, it stabilized at 75% removal even when the biofilter was only provided the BTEX-contaminated air 8 hours out of every 24 hours. A series of experiments are now underway to determine if a gas-phase adsorption column can be used to buffer the spikes in BTEX concentration that occur during the regeneration of a saturated SMZ bed. It is anticipated that this buffering system will reduce the peak BTEX concentrations reaching the biofilter and thus enhance the ability of the biofiltration system to degrade the BTEX contaminants.

5. References

American Petroleum Institute. "Proceedings: Workshop to Identify Promising Technologies for the Treatment of Produced Water Toxicity." Health and Environmental Sciences Departmental Report No. DR351. Parsons Engineering Science, Fairfax, Va. (1995).

Janks, J.S.; Cadena, F. "Investigations into the Use of Modified Zeolites for Removing Benzene, Toluene, and Xylene From Saline Produced Water." Produced Water. Eds. J.P. Ray and F.R. Engelhart. Plenum Press. New York, NY. 1992. 473-487.

Lawrence, A.W.; Miller, J.A.; Miller, D.L.; Hayes, T.D. "Regional Assessment of Produced Water Treatment and Disposal Practices and Research Needs." Presented at SPE/EPA Exploration and Production Environmental Conference. Houston, TX. March 27-29. 1995. SPE 029729.

Li, Z.; Bowman, R.S. "Sorption of Perchloroethylene by Surfactant-Modified Zeolite as Controlled by Surfactant Loading." Environmental Science and Technology. 32 (15) (1998) 2278-2282.

Li, Z.; Anghel, I.; Bowman, R.S. "Sorption of Oxianions by Surfactant-Modified Zeolite." Journal of Dispersion Science and Technology. 19 (6&7) (1998) 843-857.

Li, Z.; Burt, T.; Bowman, R.S. "Sorption of Ionizable Organic Solutes by Surfactant-Modified Zeolite." Environmental Science and Technology. 34 (17) (2000) 3756-3760.

Lide, D.R. CRC Handbook of Chemistry & Physics. 75th Edition. CRC Press, Boca Raton, FL. (1994)

Lo, I.M.C.; Lee, S.C.H.; Mak, R.M.K. "Sorption of Polar and Non-Polar Organics on Dicetyldimethylammonium-Bentonite." Waste Management and Research. 16 (2) (1998) 129-138.

Ranck, J.M.; Bowman, R.S.; Weeber, J.L.; Katz, L.E.; Sullivan, E.J. "BTEX Removal from Produced Water Using Surfactant-Modified Zeolite." Submitted to Journal of Environmental Engineering. (2003)

Tan, G. "Sorption of Benzene, Toluene, Ethylbenzene, and Xylenes onto Surfactant-Modified Zeolite: Effects of Temperature and Produced Water." Thesis, University of Texas at Austin, 2002.