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Effective Removal of Gaseous BTEX Using VPB During Treatment of Briny Produced Water

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VPB를 이용한 효율적인 Gas 상태의 BTEX 제거에 관한 연구

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Abstract

Billions of barrels of briny produced water are generated in the United States every year during oil and gas production. The first step toward recovering or reusing this water is to remove the hazardous organics dissolved in the briny produced water. Biological degradation of hazardous volatile compound could be possible regardless of salinity if they were extracted from briny water. In the current work, the effectiveness of a vapor phase biofilter to degrade the gas-phase contaminants (benzene, toluene, ethylbenzene and xylenes, BTEX) extracted from briny produced water was evaluated. The performance of biofilter system responded well to short periods when 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 a Surfactant-Modified Zeolite (SMZ) bed. Results of these experiments indicate that although the BTEX removal efficiency declined under these conditions, it stabilized at 75% overall removal even when the biofilter was provided with BTEX-contaminated air only 8 hours out of every 24 hours. Benzene removal was found to be the most sensitive to time varying loading conditions. A passive, granular activated carbon bed was effective at attenuating and normalizing the peak BTEX loadings during SMZ regeneration over a range of VOC loads. Field testing of a SMZ bed coupled with an activated carbon buffering/biofilter column verified that this system could be used to remove and ultimately biodegrade the dissolved BTEX constituents in briny produced water.

keywords : Biofilter, Briny produced water, BTEX, Surfactant-Modified Zeolite (SMZ)

1. Introduction

Co-produced water from the oil and gas industry accounts for a significant waste stream in the United States. For each barrel of oil produced, an average of 7.6 barrels of water is generated for an annual total of approximately 21 billion barrels (Clark and Veil, 2009). Produced water has a high TDS (Total Dissolved Solids) content and typically contains dissolved organic constituents, oil and grease, heavy metals, radionuclides, and chemicals added during the oil-production process (Stephenson, 1992). Among the wide variety of organics present in the water, the concentration of hazardous substances such as benzene, toluene, ethylbenzene, and xylenes (BTEX) can reach 600 mg/L and the concentration of non-hazardous carboxylates can be as high as 10,000 mg/L (API, 2002).

Over 90% of onshore produced water is currently disposed of by reinjecting it into the subsurface (API, 2000), while the remaining water is discharged onto the surface via irrigation, evaporation pits, or application to roads (US EPA, 2000). In some areas, however, re-injection is geologically infeasible and for small producers, it can be economically prohibitive. Also, regulations governing the disposal of produced water are tightening and interest in reusing treated produced water is increasing in the United States particularly in regions with scarce water supplies (Burnett, 2004). In order to reuse produced water, removal of both the inorganic dissolved solids and hazardous organics such as BTEX is necessary.

The high salinity levels typical of produced water can pose a challenge to direct biological treatment of produced water (Gilbert et al., 2005; Raterman et al., 1993) although recently such treatment has been demonstrated (Scholz et al., 2005; Tellez et al., 2005). However, biological destruction of the pollutants is relatively straightforward if the organic

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contaminants are removed from the produced water prior to the biological treatment step. One approach is to utilize a SMZ (Surfactant Modified Zeolite)/VPB (Vapor Phase Biofilter) system (Fig. 1) which combines adsorption and biological treatment technologies into one integrated system. Produced water passes through adsorbent beds containing SMZ, which has high selectivity for the organics typically found in produced water. In a previous study, Rank et al. (2005) demonstrated successful removal of BTEX from produced water by adsorption on virgin and regenerated SMZ. Others have verified that there was no significant reduction of sorption capacity of the SMZ for BTEX over 100 sorption/regeneration cycles (Altare et al., 2007). Spent SMZ can be regenerated simply by passing ambient air through the drained SMZ column but subsequent treatment of the organic-laden air is required. One possibility is to direct the waste air to a vapor phase biofilter (VPB) where the stripped organics are degraded to nontoxic products. In this way, biological degradation of the pollutants occurs in the VPB free of the high TDS levels present in the produced water.

While this coupling of an abiotic adsorption system with a VPB holds promise for rapidly treating the dissolved organics in produced water, the intermittent and variable inlet organic load to the biofilter may overwhelm the degradation capacity of a biofilter. As noted in numerous studies, biofilters often respond poorly to sudden changes in the VOC concentration of the influent gas stream (Deshusses, 1997; Dirk-Faitakis and Allen, 2003; Wright, 2005). Most field tests report a wide range of VOC removal efficiencies in biofilters subjected to transient VOC loadings, even when the average removal is relatively high (Chang et al., 2001; Choi et al., 2004; Ergas et al., 1995; Leson and smith, 1997). Blending an adsorbent material such as GAC into the biofilter packing media can be used to buffer transient VOC loadings although the effectiveness of this approach has been mixed (Chang et al., 2001; Medina et al., 1995). Another method to address transient loadings is to place a separate fixed bed adsorption column in front of the biofilter bed. Such a buffering system has been demonstrated to improve the performance of a downstream biofilter subjected to step feeding conditions in which a constant VOC load is provided during each feed period (Moe and Li, 2005; Weber and Hartmans, 1995); however the response of such a system to varying concentrations during the feed period has not been examined. Another common problem in the field is frequent shutdowns of the biofiltration system. Loss of biomass activity during carbon-deprived conditions can lead to reduced performance of VPBs upon restart of the system (Martin and Loehr, 1996; Moe and Qi, 2004) although generally complete recovery is observed after a variable lag period.

The objective of the current study was to determine if a biofilter could successfully treat the BTEX-laden waste gas stream produced during the SMZ regeneration process. To this end, a series of experiments were conducted with a compost-based biofilter to determine the response of the system to the discontinuous and dynamic feed conditions

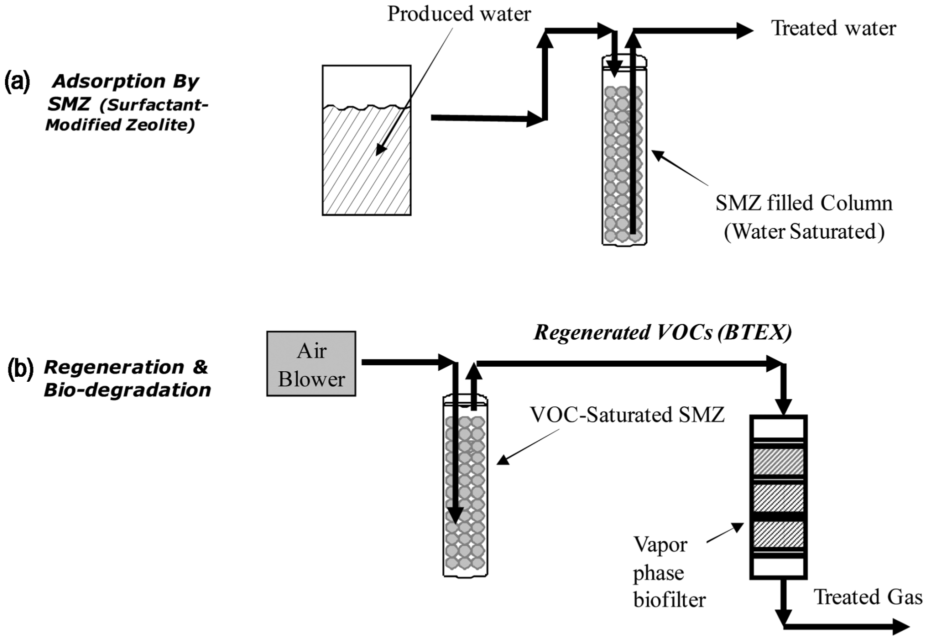


Fig. 1. Schematic diagram of SMZ (Surfactant-Modified Zeolite) /VPB (Vapor Phase Biofilter) system for treating produced water. Note that SMZ is drained of water but is still VOC-saturated.

expected when the system is coupled with a SMZ bed. Finally, a field test was completed to verify that the combined SMZ/VPB system could remove and biodegrade the dissolved BTEX constituents in produced water.

2. Materials and Methods

The experimental biofilter column (ID 16 cm) consisted of three individual sections bolted together, and packed with 12 L of compost-based materials that were inoculated with a BTEX-degrading microbial consortium. The compost filter media consisted of the following materials (by volume): 60% compost (sieved to remove particles less than 2 mm), 36.5% perlite, and 3.5% crushed oyster shell. The compost (Dillo Dirt™) is produced from dewatered municipal sludge and bulking agents such as tree trimmings and yard waste. Perlite was added to improve the air flow through the packing media and to reduce compaction of the packing media mixture. Crushed oyster shell was added to the media to act as a pH buffer. Before packing the media into the column, it was mixed with a BTEX-degrading microbial consortium. The original culture was obtained from an activated sludge sample collected from the South Austin Wastewater Treatment Plant. One mL aliquots of the original activated sludge culture were placed into sealed 250 mL-glass bottles containing 100 mL nutrient medium and 10 μL of either benzene, toluene, ethylbenzene or xylenes (*para-, meta-, and ortho-*). After the original aliquot of each organic was degraded, the bottles were aerated and another 10 μL of the appropriate organic chemical was injected into each bottle. After this process was repeated a total of four times, the individual cultures were mixed together prior to being used to inoculate the compost biofilter. This enrichment technique in which separate cultures were developed to degrade each of the BTEX constituents was used to maximize the microbial diversity of the inoculum for the VPB (Park, 2004).

To ensure the packing media would have enough nitrogen for an extended operating period, it was mixed with one liter 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 KNO_3 by a factor of ten to 101 g/L. The modified hydrocarbon minimal medium (HCMM) consisted of 2.72 g/L KH_2PO_4, 1.42 g/L Na_2HPO_4, 3.96 g/L $(NH_4)_2SO_4$, 10.1 g/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 $ZnSO_4 \cdot 7H_2O$, 0.025 g/L $Na_2MoO_4 \cdot 2H_2O$, and 0.02 g/L $NiCl_2 \cdot 6H_2O$.

The BTEX contaminants were injected into a small slip air stream using a syringe pump (Model 44, Harvard Apparatus, South Natick, MA). This contaminated air was mixed with humidified air in a mixing chamber prior to being introduced to the top of the biofilter. 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 at a steady BTEX feed, and the empty bed contact time (EBCT) in the biofilter was maintained at one minute. The ratio of each component in the BTEX mixture was selected to match the ratio expected in the waste gas produced during the SMZ regeneration process (Ranck et al., 2005).

Table 1 summarizes the operating conditions for each of the experimental phases following a 25 day start up period. In Phase 1, 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 a humidified air stream

Table 1. Operating conditions for the VPB (Vapor Phase Biofilter) during each study phase

Test phase	Operating conditions	EBCT$^{(2)}$	Introduced VOCs	Total Conc. (ppm_v)
1	Shut down test (1 & 2.8 day)	60 sec. (VPB)	BTEX$^{(3)}$	130 ppm_v during feed period
2	Spike loading	60 sec. (VPB)	BTEX	Variable (Max. 380 ppm_v)
3	GAC$^{(1)}$ Buffering test	1 sec. (GAC)	Toluene	Variable (Max. 1000 ppm_v)
4	Field test	73 sec. (VPB) 1,5 sec. (GAC)	BTEX + Other VOCs	Variable (Max. 1120 ppm_v)

(1) Granular Activated Carbon
(2) Empty Bed Contact Time
(3) Benzene, Toluene, Ethyl benzene, Xylenes (*para-, meta-, and ortho-*)

was supplied as usual. Following each shutdown test, the BTEX feed to the biofilter was reestablished at a steady concentration of 130 ppm$_v$. The recovery of the biofilter following each shutdown test was monitored until the removal efficiency across the biofilter exceeded 90%.

In Phase 2, a series of BTEX spike experiments were conducted. During these experiments, the inlet BTEX concentration was increased rapidly to approximately 380 ppm$_v$ and then decreased to zero in an exponential fashion over an eight hour period. The relative composition of each BTEX component in the waste gas feed was consistent with the volume ratio utilized during the continuous feed experiments (e.g., benzene 9.2%, toluene 18.5%, ethyl benzene 24.6%, *p&m*-xylene 16.9%, *o*-xylene 30.8%, by volume). 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 an SMZ system that is 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.

Based on previous SMZ regeneration studies, it was expected that the BTEX concentrations during the initial regeneration period would be high and that a supplementary, load equalization system would be necessary to attenuate VOC concentrations entering the VPB and prevent the variable load from overwhelming the VOC degradation capacity of the biofilter. Granular activated carbon (GAC) was investigated as an adsorbent to attenuate the peak VOC loadings during Phase 3.88 mg of BPL GAC (4-6 mesh, Calgon Carbon Corp., Pittsburgh, PA) was packed in a fixed bed adsorption column (ID 10.16 cm, PVC). BPL GAC has a reported surface area of 1040 m^2/g (Vidic, 1997). Contaminant-free air (average RH below 10%) flowed through a pressure regulator at 12 L/min resulting in a one second-EBCT in the fixed bed adsorption column. All experiments were conducted at the ambient laboratory temperature of 23°C. Fresh GAC was completely saturated by introducing 1000 ppm$_v$ of toluene continuously, and then regenerated by clean air until the exit toluene concentration from the fixed bed adsorption column declined below 0.01 ppm$_v$. Following the pre-saturation/regeneration step to precondition the GAC, a series of toluene transient feed tests were conducted. In each transient feed test, an initial peak concentration (1,000 ppm$_v$) of toluene was supplied to the biofilter for a period of 15 minutes; the toluene concentration in the inlet waste gas stream was then reduced exponentially over the next 8 hours. After eight hours, the toluene feed to the column was discontinued, and the outlet concentration from the fixed bed adsorption column was measured continuously to monitor desorption of toluene from the GAC. To determine how the system would respond to repetitive cycles of toluene transient feeds, this 8-hours on/16-hours off pattern was repeated several times.

In the final study phase, a field test of the coupled GAC buffering/VPB system was completed at a salt water disposal facility in New Mexico. Two Culligan fiberglass tanks (0.36 m in diameter, 1.22 m in height) were packed with SMZ to a total packed capacity of 104.8 L (Culligan International Company). The same compost-based VPB (i.e., 12 L of total packing volume with three individual sections) and GAC-fixed bed adsorption column, operated in the laboratory tests above were used in the field test. One additional section containing 4 L of fresh compost packing media was added to the existing biofilter to increase the total packed volume of the VPB to 16 L. During the field test, produced water was passed through the two SMZ adsorption columns placed in series. Three different produced water flow rates were evaluated (102.2, 37.9, and 18.9 L/hr). When the first SMZ column reached the target VOC breakthrough for a given test (e.g., 30% to 100%), the water flow to the first column was terminated, and the SMZ column was drained and regenerated by air sparging. During regeneration, 13 L/min of ambient air (temperature = 20 ~ 28°C, RH = 26~ 70%) was supplied via an air blower to regenerate the drained SMZ column. Regeneration periods ranging from 4.9 hours to 44 hours were evaluated. For the load equalization of VOC concentrations, the regenerated gas stream from the SMZ column was passed through a fixed bed adsorption column containing GAC. Finally, the buffered gas stream passed through a humidifier and then flowed into the VPB, which was operated at an EBCT of 73 seconds.

In the laboratory experiments, gas samples were collected with 0.5-mL gas tight syringes from sampling ports located along each column and immediately analyzed on a Hewlett-Packard 5890 gas chromatograph (GC) fitted with a 30 m Restek capillary column (RTX-624; ID 0.53; DF 3.0) and flame-ionization detector (FID). *para*- and *meta*-Xylenes were not be distinguished from each other so the sum of the *para*- and *meta*-xylene concentrations were determined. For the GAC-fixed bed adsorption tests, a sample of the gas entering and exiting the fixed bed adsorption column was diverted to a total hydrocarbon (THC) analyzer (3000 HD heated FID, K2BW Environmental Equipment Co.) and monitored automatically. The relative humidity and temperature of the gas stream were measured by a traceable hydrometer/thermometer (Fisher Scientific, Pittsburgh, PA).

For the on-site analysis of BTEX concentrations in gaseous samples during the field test, a 0.5 mL gas-tight syringe was used to extract gaseous samples from the inflow and outflow sampling ports of the VPB and GAC-fixed bed adsorption column. Gaseous samples were then injected into a HP Model 5890 Series II GC with a 30 m Restek capillary column (RTX-5; ID 0.53; DF 1.5).

3. Results and Discussion

Within two weeks of start up in the laboratory, the biofilter achieved greater than 98% removal of the BTEX contaminants. These results are consistent with others reported in the literature (Abumaizar et al., 1998; Sorial et al., 1997) for biofilters treating steady concentrations of BTEX and indicate that, under steady feed conditions, the biofilter was capable of achieving and maintaining high BTEX removals (Fig. 2). Mixing of a concentrated nutrient solution during the biofilter start up ensured high removals of BTEX for extended periods without external nutrient addition.

3.1. Shutdown Experiments

Unlike many laboratory studies where stable conditions are maintained, field conditions are often quite variable and VPBS are subjected to transient pollutant load (Dirk-Faitakis and Allen, 2003). One challenge to field application of biofilters is frequent system shutdowns. These shutdowns may result from unintentional maintenance problems or may be intentional as part of scheduled shutdowns resulting from the operating schedule of the facility.

To determine how the biofilter would respond to periodic shutdowns in inlet BTEX load, a series of discontinuous feed experiments were conducted. Immediately after a 24 hour-shutdown period, the removal of benzene in the biofilter decreased to 84% and *p&m*-xxylene decreased below 95%, but the removal of the other chemicals remained above 95% (Fig. 3(a)). However, the removal of benzene recovered quickly and within approximately six hours, the removal efficiency exceeded 95%. These results indicate that

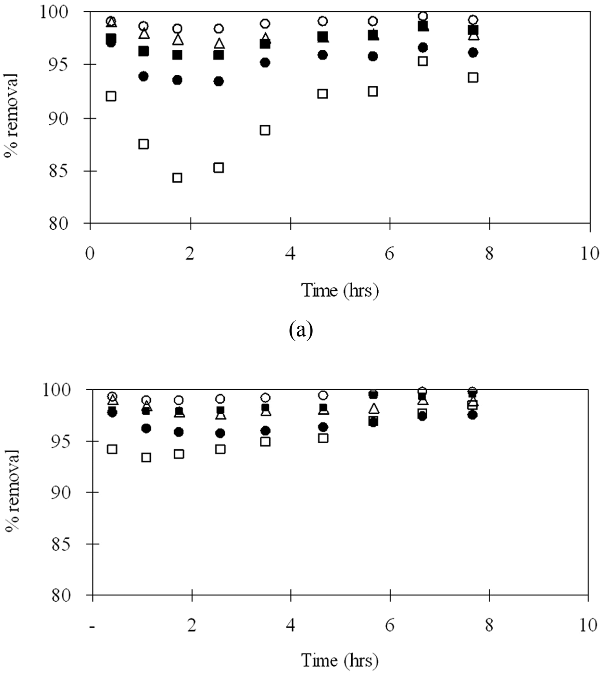


Fig. 3. BTEX removal efficiency in the vapor phase biofilter during cyclic operation in which the BTEX supply was interrupted for a 24 hour period every 72 hours. (a): After first shut down and (b): After third shut down. □ ; Benzene, ■ ; Toluene, ○ ; Ethyl benzene, ● ; *p&m*-Xylene, △ ; *o*-Xylene. Ratio of BTEX components introduced (by volume); Benzene 9.2%: Toluene 18.5%: Ethyl benzene 24.6%: *p&m*-Xylene 16.9%: *o*-Xylene 30.8%.

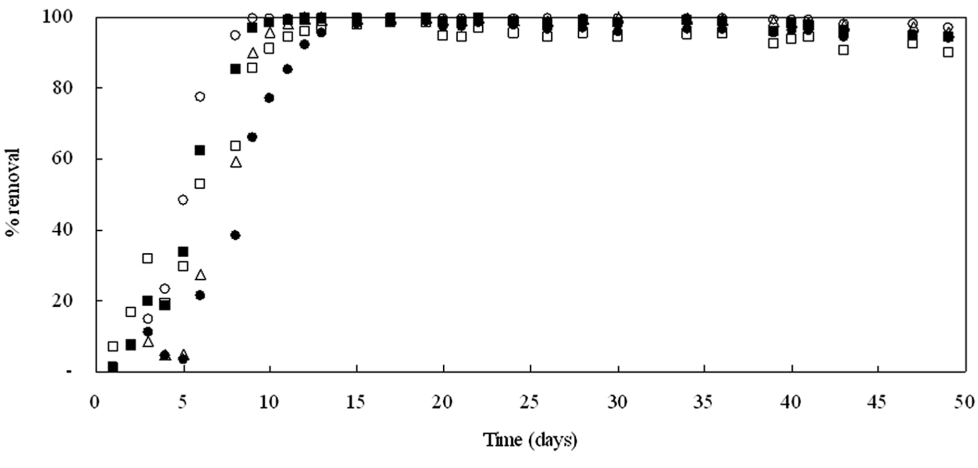
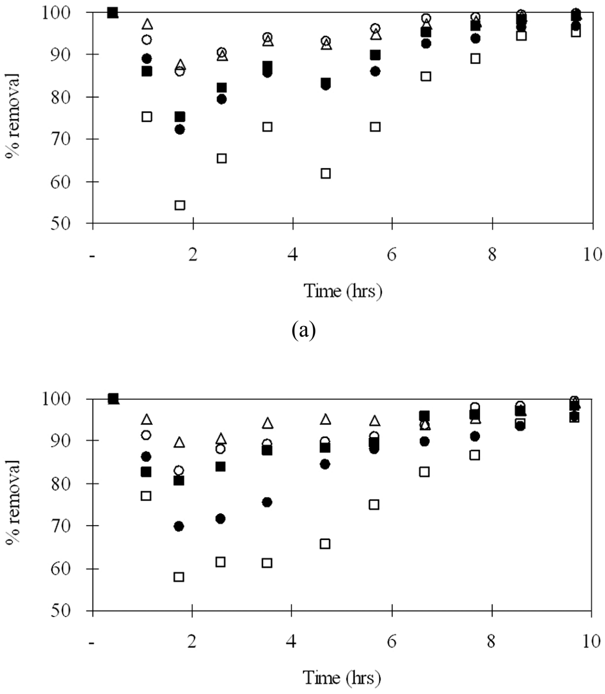


Fig. 2. BTEX removal efficiency in the compost biofilter. (□ ; Benzene, ■ ; Toluene, ○ ; Ethylbenzene, ● ; *p&m*- Xylene, △; *o*-Xylene)

a biofilter that has been provided with a continuous VOC supply can handle short periods without a carbon source as noted in previous studies (Park and Kinney, 2001). The same one-day shutdown test was repeated several times to investigate the bioreactor response to periodic shutdowns. Fig. 3(b) shows the recovery of VOC removal efficiency after the third one-day shutdown test. Higher removal efficiencies for each of the BTEX constituents were observed following the third shutdown test than were observed following the first shutdown test. These results imply that the biomass in the compost biofilter can adapt well to repeated system shutdowns that are short in duration. One possible reason for this resiliency is that the biofilter packed with compost can provide the microbial community with alternative carbon sources during the shutdown periods. However, this same recovery pattern was also observed in an identical biofilter that was packed with polyurethane foam cubes (1.5 cm) suggesting that the organics present in the compost were not responsible for the biomass response (data not shown).

The response of the system following resumption of the BTEX feed after a 2.8-day shutdown period was also examined (Fig. 4). Compared to the one-day shutdown tests, the BTEX removal was more seriously affected by the longer term shutdown test. The percent removal of benzene following the shutdown test decreased to 54% with lower declines observed for *p&m-* xylene and toluene. However, the overall BTEX removal efficiency recovered to 90% within eight hours (Fig. 4 (a). Unlike the one-day shutdown tests, no improvement in BTEX removal efficiency was observed after repeated 2.8-day shutdown tests (Fig. 4 (b)).

The experiments demonstrated that biofilter could recover rapidly from one-day and 2.8-day shutdowns indicating that this system was resilient to short term, discontinuous feed conditions. This result is consistent with previous results. Dirk-Faitakis and Allen (2003) observed no difference of biofilter performance in treatment of alpha-pinene-laden waste gas in both continuous and 24hr-cycle shutdown period operations. Martin and Loehr (1996) demonstrated that it took only 8 hours to recover full toluene removal capacity after 3 days of starvation. It is interesting to note, however, that in both the one-day and 2.8-day shutdown tests, the biofilter in this research required similar time period (approximately 8 hours) to recover the VOC removal efficiency observed prior to each shutdown test. In general, the time required for biofilter reacclimation after shutdown is proportional to the duration of the shutdown. However, the packing material, compound and concentration of pollutants also affect the reacclimation time (Cox and Deshusses, 2002; Martin and Loehr, 1996). Therefore, it is speculated that the tested shutdown periods of one-day and 2.8-day in this study were minor factors in reacclimation time in given conditions compared to other factors.



(a)

(b)

Fig. 4. BTEX removal efficiency in the vapor phase biofilter during cyclic operation in which the BTEX supply was interrupted for a 2.8-day period every 72 hours. (A): After first shut down and (B): After third shut down. □ ; Benzene, ■ ; Toluene, ○ ; Ethyl benzene, ● ; *p&m*-Xylene, △ ; *o*-Xylene.

3.2. Response of Biofilter to Variable Loading Conditions

In addition to frequent system shutdowns, variations in the VOC concentration in the waste gas streams are another challenge for VPBs. In the SMZ regeneration process, ambient air is sparged through the saturated SMZ column to remove the adsorbed BTEX contaminants. During regeneration, the initial contaminant concentrations (particularly benzene and toluene) in the gas stream are high (on the order of thousands of ppm$_v$) but drop off exponentially as the sparging process continues (Fig. 5).

A single variable feed test was done to determine how the system would respond to variations in BTEX concentration. The maximum BTEX concentration detected in the exit gas stream from the biofilter was 57 ppm$_v$ when the inlet BTEX concentration was increased rapidly to 380 ppm$_v$ (See Fig. 6). While short term, such a breakthrough would not be acceptable for application to a field system.

To determine how the biofilter would respond to cyclical variations in inlet BTEX concentration as would be expected when it is coupled with the SMZ columns, the biofilter was

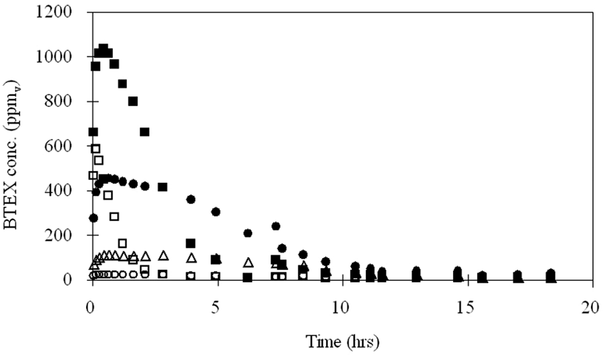


Fig. 5. Typical concentration profile of gas phase effluent during regeneration of saturated SMZ (Surfactant Modified Zeolite) column. Air flow rate for the regeneration was 7.5 mL/min. ☐ ; Benzene, ■ ; Toluene, ○ ; Ethyl benzene, ● ; *p&m*-Xylene, △ ; *o*-Xylene. Column dimensions; 0.4 cm (radius) × 10 cm (length). SMZ size ; 0.15-0.18 mm.

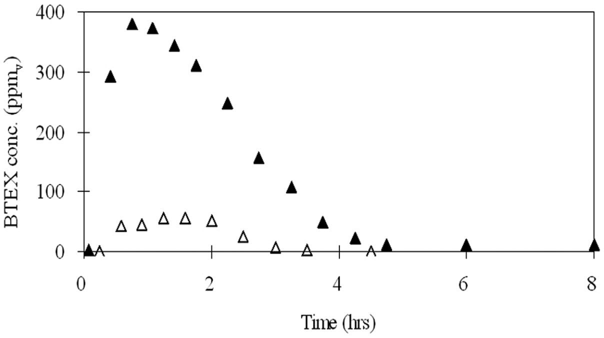


Fig. 6. Response of vapor phase biofilter to a BTEX spike loading. The total inlet BTEX concentration to the VPB was suddenly increased to 380 ppm_v, and then decreased exponentially. ▲ ; BTEX concentration introduced to VPB, and Δ ; effluent BTEX concentration from VPB.

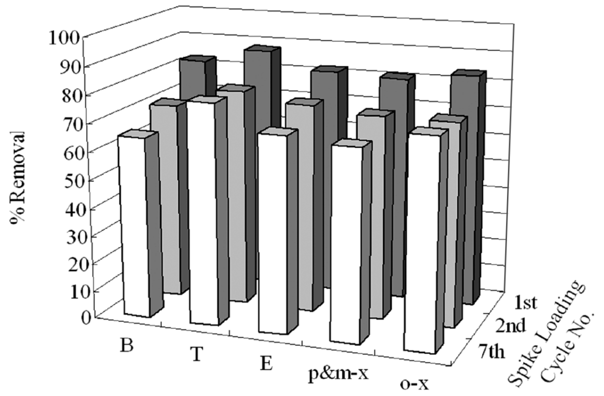


Fig. 7. Response of vapor phase biofilter to repeated BTEX spike loading cycles. In each 24 hour cycle, a high loading of BTEX was provided for 8 hours as shown in Fig. 6. During the remaining 16 hours of each cycle, clean air was passed through the biofilter. B ; benzene, T ; toluene, E ; ethyl benzene, *p&m*-x ; *para & meta* xylene, *o*-x ; *ortho* xylene.

subjected to repeated variations in VOC loadings (8 hours on /16 hours off per day). Results showed that the maximum outlet BTEX concentration on the second day of the variable loading test increased to approximately 95 ppm_v where it remained for the rest of the cycles. Thus, the overall BTEX removal efficiency at the point of maximum outlet concentration was approximately 75% (Fig. 7). Benzene removal was most adversely affected and toluene removal was found to be the least sensitive to the variable loading.

Observed result of poor performance of biofilter during the peak loading period are well expected, since the peak loading is beyond the normal biofilter capacity, and the biomass had not enough time to accustomed to new circumstances. This is a common situation in field application of biofilter, and most field tests report a wide range of VOC removal efficiencies subjected to transient VOC loadings, even though the average removal is relatively high (Chang et al., 2001; Choi et al., 2004; Ergas et al., 1995; Leson and Smith, 1997). These results indicate that a supplementary, load equalization system would be necessary to attenuate the inlet VOC concentrations and prevent VOC breakthrough the biofilter.

3.3. Buffering by GAC

Fig. 8 shows the response of the GAC-fixed bed adsorption column to a sudden variation in inlet toluene concentration. The maximum outlet concentration from the fixed bed adsorption column remained below 30 ppm_v and this value remained relatively constant over 40 hours of operation, even though the maximum inlet toluene concentration was 1,000 ppm_v. This result implies that the GAC column can effectively buffer the peak VOC concentrations and prevent overloading of a downstream biofilter. The gradual release of the adsorbed toluene also ensures that a downstream biofilter would receive a steady VOC supply even if the SMZ regeneration process does occur on a cyclical basis.

However, one concern with the results presented in Fig. 8 is the question of how well the GAC column would handle repeated variations in VOC feed. Fig. 9 presents the outlet toluene concentrations from the GAC-fixed bed adsorption column over several toluene adsorption/air regeneration cycles. As evident in Fig. 9, the GAC effectively buffered the transients in inlet toluene concentration with a maximum breakthrough concentration of 65 ppm_v despite a peak inlet concentration of toluene of 1,000 ppm_v. Even though the outlet concentration from the GAC-fixed bed adsorption column increased during the first five transient cycles (due to insufficient air stripping of the toluene), its increase was slowed as the transient feed tests continued. This result indicates that the buffering capacity of the GAC could

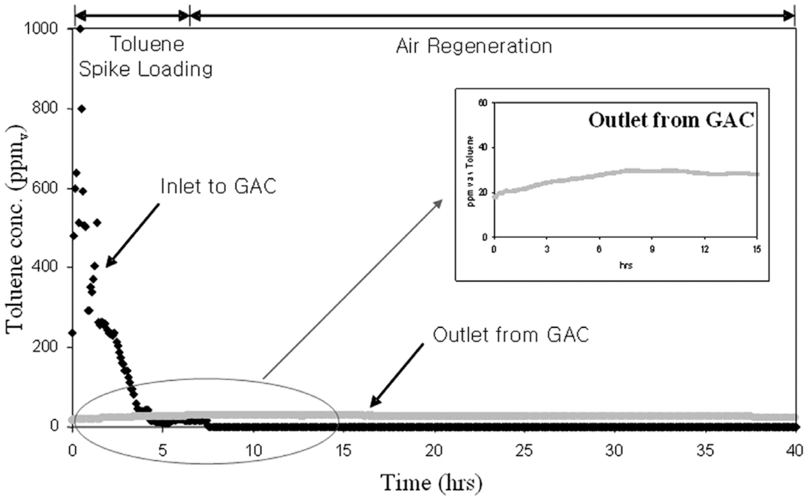


Fig. 8. Response of the GAC (Granular Activated Carbon) buffering column to a toluene spike. Toluene was supplied for 8 hours as a transient load followed by 32 hours of clean air. GAC (BPL 4 × 6 mesh, Cargon Carbon Corp.) was used as buffering agent, and empty bed contact time in buffering column was one second.

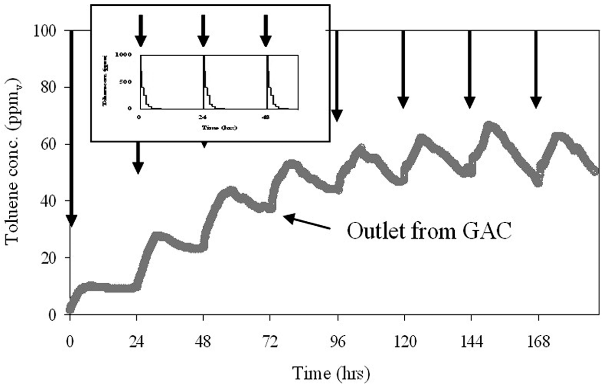


Fig. 9. Response of the GAC (Granular Activated Carbon) buffering column to repeated toluene spikes. As depicted in the inset, each toluene spike was supplied for 8 hours followed by 16 hours of clean air. Each arrow represents the start of a spike loading period.

diminish when sorbed VOCs were not regenerated sufficiently in a given regeneration period over repeated adsorption/air regeneration cycles. Overall results in this section suggest that a small passive GAC-fixed bed adsorption column operated at a short EBCT can help buffer peak VOC concentrations as high as 1,000 ppm$_v$.

To our knowledge, this study is the first attempt to assess the effectiveness of passive and separate GAC-fixed bed adsorption column to variable loading conditions which are encountered in field application. Some researchers (Moe and Li, 2005; Weber and Hartmans, 1995) have tried similar approaches, however, these studies focused on step feeding, in which a constant VOC loading was provided during each feed period. Those experiments can't mimic truly the field situation since actual contaminant concentrations in the field often change dynamically even during the loading period. Still several factors must be considered in order to apply the load equalization system in the field. One of them is competitive adsorption effects between compounds, which affect the adsorption/regeneration of VOC constituents on the adsorbent (Crittenden et al., 1985; Yang, 1987). The other factor that must be considered is the humidity of the gas streams. Werner (1985) observed that TCE adsorption at a RH of 85% was only 9% of the amount adsorbed at a RH of 5% when 300 mg/m3 of TCE was applied to a GAC column. Crittenden et al. (1988) also observed that RH values greater that 45% in a gas streams significantly decreased the adsorption of TCE on GAC. Cal et al. (1996) found that water vapor in a gas streams had little effect on benzene (500 ppm$_v$) adsorption onto the activated carbon cloth until the RH exceeded 65%, at which point a rapid decrease in adsorption capacity was observed.

3.4. Field application

Based on the lab tests of the VPB and GAC-fixed bed adsorption column, a field test of the load equalization and VPB system was completed as part of a field evaluation of an SMZ/VPB unit treating produced water. The total VOC concentrations in the produced water were approximately 20 mg/L; toluene, *p&m*-xylene, acetone, benzene, and *o*-xylene represented approximately 80 percent of this total.

Of the BTEX components present in the produced water, benzene had the lowest adsorption affinity for the SMZ and thus controlled the sorption cycle length. Regeneration of the SMZ using air sparing was found to be sufficient in the field to maintain the SMZ adsorption capacity and to allow continuous operation of the system. Fig. 10 represents the performance of GAC buffering column and following VPB

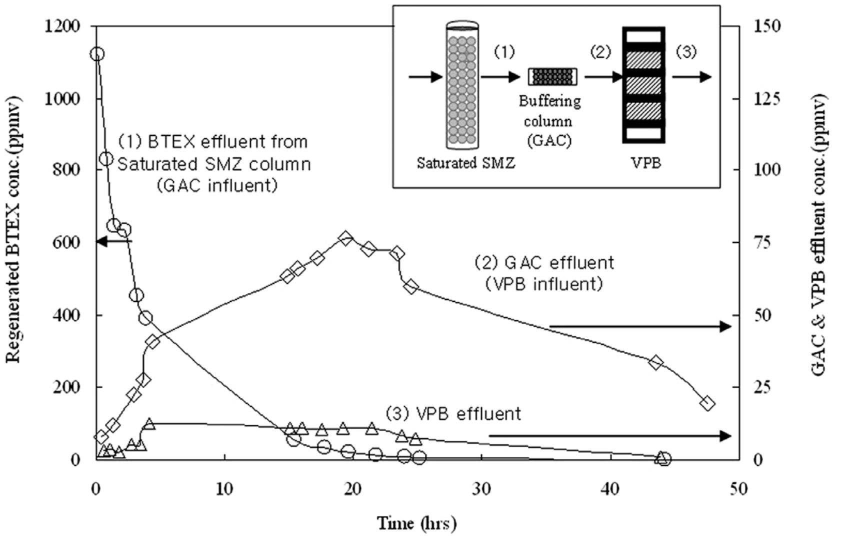


Fig. 10. Performance of the GAC buffering column and VPB during the regeneration of the saturated SMZ field column. Schematic diagram in the inset represents the treatment process. Water flow rate to SMZ column was 1.58L/min and disconnected when benzene breakthrough occurred. Air flow rate during regeneration was 13L/min which resulted in a 1 second EBCT in the buffering column and a 73- second EBCT in the VPB. ○, ◇, and Δ represent the GAC influent (1), GAC effluent (2) and VPB effluent (3), respectively.

for the regenerated gas stream of SMZ. As expected, the BTEX concentration in the regeneration off gas streams was initially very high as 1,120 ppm$_v$. However, a GAC-fixed bed adsorption column placed upstream of the VPB reduced the peak BTEX concentrations to acceptable levels for the VPB (76 ppm$_v$) and a decrease in buffering efficiency was not observed after repeated adsorption/regeneration cycles under the conditions evaluated in the field test. As a result, the VPB was able to maintain performance over the entire SMZ regeneration period despite the intermittent nature of the feed. Benzene was found to be the chemical controlling removal rates during SMZ adsorption and regeneration, GAC-load equalization, and biodegradation in the VPB. Further researches are necessary regarding the competitive adsorption and relative humidity effect on the adsorbent of load equalization system in the application to the real field.

4. Conclusions

Experiments conducted with a vapor phase biofilter (VPB) packed with compost based material in treatment of gaseous BTEX mixture indicated the following:

1) 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, and VPB showed improved removal efficiency after periodic shutdown.
2) When the biofilter was subjected to periodic spikes in BTEX concentration, it was found that the total BTEX removal efficiency stabilized at 75% despite the fact that the biofilter was only fed BTEX contaminants 8 hours per day.
3) A short, fixed bed adsorption column containing GAC can be used to attenuate and smooth the gas-phase VOC concentrations entering a downstream biofilter. The fixed bed adsorption system can be operated in a passive mode such that VOCs adsorb to the GAC during periods of high inlet concentration, and desorb VOCs during periods of low inlet concentration.
4) Field application of the GAC buffering/VPB system verified that it could be used successfully to treat the regenerated gas stream from an SMZ adsorption column during the treatment of actual produced water. These results implies that GAC buffering/VPB system could be used broadly to treat the transient loading of biodegradable VOCs frequently encountered in numerous sites.

국문요약

Oil이나 Gas생산시 발생하는 Produced water의 양은 미국 내에서만 연간 수십억 배럴에 육박한다. 이러한 Produced water의 재이용을 위한 첫 번째 과제는 유해 유기물질을 제거하는 것으로, 본 연구에서는 수중의 BTEX를 가스상태로 변화시킨 후 Vapor phase biofilter (VPB)로 분해, 제거 효능을 평가하였다. VPB 시스템은 짧은 기간의 시스템 shutdown에는 거의 영향을 받지 않는 것으로 나타났다. 그러나 주입되는 농도가 Peak 형태를 가질때는 제거효능의 저하가 관찰되었으며, 이중 Benzene이 가장 민감하게 반응하였다. 이를

위한 해결책으로 GAC로 충진된 Buffering Column이 사용되었으며, 이는 peak 형태의 유입농도 Profile을 완만한 형태로 buffering하는 역할을 하였다. 현장 적용을 통하여, 본 시스템이 Produced water내에 존재하는 용존 BTEX를 효과적으로 제거할 수 있음을 확인하였다.

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