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

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Abstract

This report summarizes work performed on this project from April 2005 through September 2005. In previous work, a series of laboratory scale experiments were conducted to determine the feasibility of using a SMZ system coupled with a VPB to remove and ultimately destroy the organic pollutants found in produced water. Based on the laboratory scale data, a field test of the process was conducted at the McGrath Salt Water Disposal facility in July and August of 2005. The system performed well over repeated feed and regeneration cycles demonstrating the viability of the process for long term operation. 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 sparging was found to be sufficient in the field to maintain the SMZ adsorption capacity and to allow continuous operation of the system. As expected, the BTEX concentrations in the regeneration off gas stream were initially very high in a given regeneration cycle. However, a granular activated carbon buffering column placed upstream of the VPB reduced the peak BTEX concentrations to acceptable levels for the VPB. In this way, the VPB was able to maintain stable performance over the entire SMZ regeneration period despite the intermittent nature of the feed.

TABLE OF CONTENTS

List of Figures

1. Introduction

Results of our previous laboratory scale investigations indicate that the SMZ/VPB process can be an effective system to remove organic pollutants such as benzene, toluene, ethylbenzene and xylenes (BTEX) from produced water. For instance, regeneration of the SMZ with air was shown to restore the sorption capacity of the SMZ for BTEX compounds. Similarly, experiments with the VPB indicated that it could effectively degrade the BTEX mixture found in the off gas generated during SMZ regeneration. However, the peak BTEX concentrations observed initially during the regeneration process exceeded the biodegradation capacity of the VPB. This problem was solved by placing a granular activated carbon buffering column upstream of the VPB to attenuate the BTEX concentrations entering the bioreactor. The VPB effectively degraded the BTEX constituents exiting the buffering column indicating that the coupled SMZ/VPB treatment technology could effectively remove and biodegrade the BTEX contaminants found in produced water.

The next step of the project is to verify the performance of the coupled SMZ/VPB technology in the field. More specifically, the objectives of the field test were to evaluate the performance of the coupled SMZ/VPB system treating actual produced water over a range of flow rates and over multiple sorption regeneration cycles. The field scale test was conducted at the McGrath Salt Water Disposal facility in July and August 2005. The following sections summarize the materials and methods employed during the field test and the results obtained.

2. Materials and Methods

2.1 Pilot SMZ/VPB System

The pilot system consisted of two SMZ columns in series treating produced water and one VPB treating the off-gas produced during the regeneration of the SMZ columns (Figure 1). The pilot scale SMZ columns were constructed of fiberglass, each 14” in diameter and 48” in height with a combined packed capacity of 3.7 ft^3 (Culligan International Company). Each column was filled with approximately 170 lbs of 14-40 mesh SMZ, leaving a 3” headspace below the inlet manifold. Sampling ports were installed in the 1” pipelines entering and exiting each column. Several quick-disconnect valves were added to the system to allow a given SMZ column to be disconnected from the produced water flow when it was ready for regeneration via air sparging.

In addition to the two SMZ columns, the system consisted of a compost-based vapor phase biofilter (VPB) and a granular activated carbon (GAC) buffering column placed upstream of the VPB. The packing media was inoculated as described earlier (semi-annual report 15461R06) and the total packed volume of the VPB was 16 L. During regeneration of a SMZ column, the regenerated gas stream from the SMZ column was first passed through an activated carbon buffering column to attenuate the inlet volatile organic compound (VOC) concentration. This buffered gas stream was humidified and then introduced to the top of the biofilter. The empty bed contact time (EBCT) in the VPB was 73 seconds while the GAC buffering column was operated at an EBCT ranging from 1 to 5 seconds.

2.2 Field Test of the Pilot System

A schematic diagram of the operation of the SMZ system during the sorption phase of the process is shown in Fig. 1(a). An 8,800 gallon feed tank of produced water was filled daily with water that had been filtered through the micron-filtration system present at the field site. Flow from the storage tank was controlled by an electrical pump and was delivered through PVC pipelines to the pilot SMZ/VPB system. A total flowmeter and a real-time flowmeter were installed between the pump and the pilot system. The system was operated continuously at a specific flow rate until the upstream column reached the target breakthrough of the BTEX compounds. The target breakthrough varied during the field trial. During the initial experiments with virgin SMZ, one SMZ column was operated until it was completely saturated with benzene and toluene and complete breakthrough occurred for these compounds. In subsequent runs, the SMZ columns were operated until the benzene concentration in the effluent was approximately 20% of the inlet concentration. In each case, after breakthrough was reached, the upstream SMZ column was disconnected and regenerated while the downstream column remained online treating produced water. Once the upstream column was regenerated, it was placed back on-line downstream of the other SMZ column.

The process flow diagram for the regeneration phase of operation is shown in Fig. 1(b). Before regenerating a saturated column, the water in the off-line column was removed using a peristaltic pump. Ambient air, provided by blowers (GAST REGENAIR Model R1102), was purged through the SMZ column countercurrent to the direction of produced water flow. Waste gas produced during regeneration flowed through the GAC passive buffering column and a humidifier before entering the VPB. The effluent air stream from the VPB was routed through an activated carbon drum to capture any residual VOCs that escaped the VPB during the field test. The air flow rate during regeneration was 13 L/min resulting in a 73 second EBCT in the VPB. Although the flow rate was held constant, the period of regeneration for each SMZ column was varied to examine the effect of regeneration time on VOC removal from the SMZ column.

To verify SMZ performance over multiple sorption/regeneration cycles and a range of produced water flow rates, three flow rates (27gph, 10gph, and 5gph) were tested to examine the sorption capacity of the SMZ system under field conditions. During the field test, influent and effluent water samples were collected from the sampling ports to capture the breakthrough of the contaminants through the upstream SMZ column prior to saturation. Analyses of water samples were performed at the field site as well as in the laboratory. The field site analyses included measuring BTEX concentrations present in the produced water as well as those in the contaminated air stream generated during the SMZ regeneration process. Laboratory analyses of the produced water included analyzing volatiles organic compounds (VOCs), semi-volatiles organic compounds (SVOCs) and organic acids concentrations.

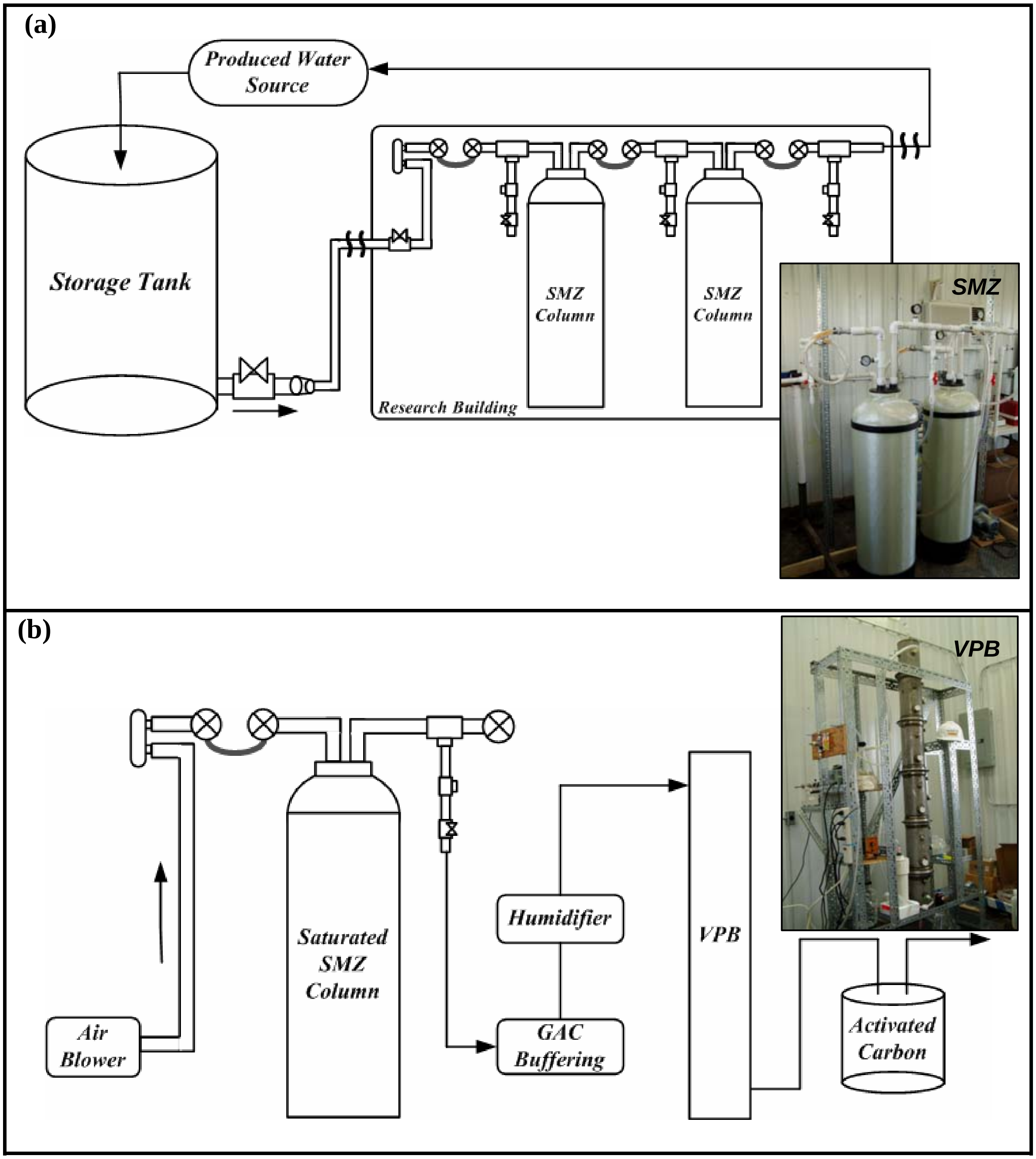

Fig. 1. Schematic diagram of the coupled SMZ/VPB system used in the field test. (a) Treatment of produced water using the SMZ columns. (b) Treatment of off-gas from a saturated SMZ column during regeneration with air.

2.3 Analytical Methods

BTEX concentrations of aqueous samples were analyzed in the field using an on-site Gas Chromatograph (GC) equipped with a flame-ionization detector (FID). A 2.5 mL aliquot of each water sample was placed in a 10mL headspace vial fitted with a Telflon-faced butyl septum. The vials were placed in a heating block and equilibrated at 80°C for 15 minutes. Gas-tight syringes (0.5 mL) were used to extract gaseous samples from the headspace vials as well as gaseous samples from the inflow and outflow sampling ports of the VPB during regeneration. Gaseous samples were injected into a HP Model 5890 Series II Gas Chromatograph (GC) with a 30 m Restek capillary column (RTX-5; ID 0.53; DF 1.5) and flame-ionization detector (FID). Helium carrier gas was used at a flow rate of 1 mL/min. The FID was supplied with 30 mL/min ultra high purity (UHP) nitrogen, 30 mL/min UHP hydrogen, and 300 mL/min air. The analyses were performed at an initial oven temperature of 40°C for 1 minute followed by 20°C/min to 85°C, and then increased at 0.5°C/min to a final temperature of 90°C which was maintained for 1 minute. The temperatures of the injector and the detector were 250°C and 275°C, respectively.

Aqueous concentrations of BTEX, phenols and naphthalenes, and C1-C5 carboxylic acids were also measured in the Environmental and Water Resources Engineering (EWRE) laboratory at the University of Texas at Austin. BTEX concentrations were measured using a Tekmar 7000 headspace sampler attached to a HP Model 5890 GC with a 30 m Restek capillary column (RTX-624; ID 0.53; DF 3.0) and FID. The headspace sampler and GC operating conditions were described previously by Ranck et al (2005). Samples were selectively measured for semi-volatile concentrations (EPA Method 8270C) using a Thermo Gas Chromatograph/Mass Spectrometer (GC/MS) using an Autosampler AS3000 attached to a Finnigan TraceGC Ultra with a 30m Restek capillary column (RTX-5MS; ID 0.25; DF 0.25) and a Finnigan Polaris Q Ion Trap MS. Prior to quantifying SVOCs in the GC/MS, aqueous semi-volatiles were extracted into dichloromethane (adapted from EPA Method 3510C). One microliter of extracted liquid was injected into the GC in splitless mode. The initial oven temperature was held at 40°C for 5 minutes, then increased at 7°C/min to 250°C, and ramped at 10°C/min to a final temperature of 300°C which was held for 2 minutes. Helium was used as carrier gas at the flow rate of 1 mL/min. The injector temperature was 200°C while the MS transfer line temperature was 300°C.

Organic acids concentrations were measured using Dionex AS 40 autosampler attached to DX-600 Ion Chromatograph (IC). The IC was equipped with a Dionex CD25A conductivity detector, an ASRS ULTRA 4mm suppressor, an EG50 eluent generator and an IonPac AS11-HC analytical column. The oven temperature was maintained at 30°C for each run, the suppressor current was set at 300 mA, and the flow rate of the eluent (KOH) through the column was 1 mL/min. The eluent concentration was set as follows: 1 mM for the first 4 minutes, 2 mM from 4.2 to 13.2 minutes, 10 mM from 13.5 to 28 minutes, 2 mM form 28.5 to 30 minutes, 30 mM from 30.5 to 40 minutes, and 0.5 mM from 40.5 to 44 minutes.

3. Field Test Results

3.1 SMZ Breakthrough

The breakthrough curves of selected organic compounds in produced water through the virgin SMZ columns are shown in Fig. 2. At the 27 gph flow rate, the upstream column was disconnected when benzene reached complete breakthrough and the downstream column remained online until toluene reached complete breakthrough. The corresponding K_d values calculated for benzene and toluene are 11.4 L/kg and 20.9 L/kg, respectively. The other volatile compounds, ethylbenzene, *p&m*-xylene and *o*-xylene exhibited similar breakthrough curves to benzene and toluene. Two of six monitored semi-volatile organics (SVOC), phenol and 2-methylphenol, were also detected in the SMZ effluent. The remaining SVOCs (4-methylphenol, 2,4-dimethylphenol, naphthalene and 2-methylnaphthalene) never broke through the column. The concentrations of organic anions (formate, acetate, propionate, butyrate, and valerate, oxalate, malonate, succinate and gultarate) in the influent and effluent of the system were similar indicating that the SMZ has low sorption capacity for the organic anions found in produced water (data not shown).

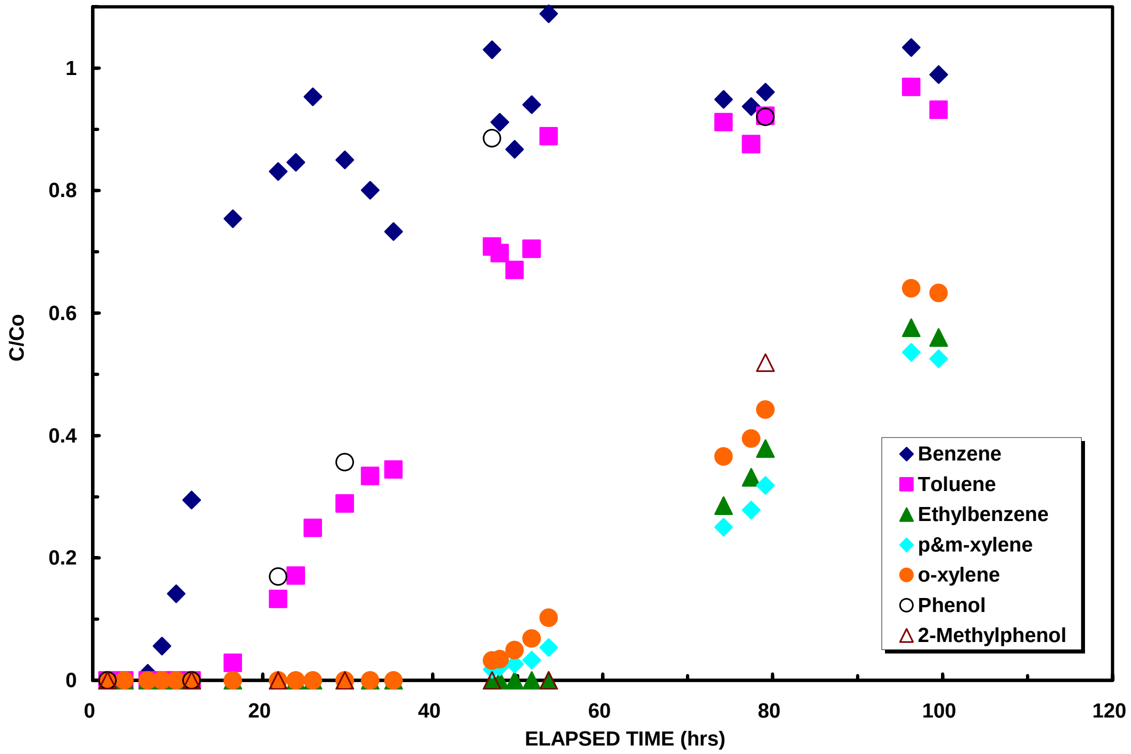

Fig. 2. Breakthrough curves of selected organic compounds in produced water through virgin SMZ at a flow rate of 27 gph**.**

The performance of the virgin and regenerated SMZ columns were examined during the field test to determine how the adsorption capacity of the SMZ was affected by regeneration. Figure 3 compares the benzene breakthrough profiles from a virgin SMZ column to that observed from a SMZ column that had been saturated and then regenerated with air. As evident in the figure, BTEX was observed in the effluent from the regenerated SMZ column immediately after it was placed back online. It is believed that residual water remained in the SMZ column even after the previous regeneration cycle because the configuration of the SMZ columns did not allow all of the water to be drained from the columns during regeneration. As a result, this BTEX laden water was carried over to the next sorption cycle when the SMZ column was reconnected to the system and produced water flowed through it again. Despite this initial spike in effluent concentration, the regenerated SMZ provided higher sorption capacity for benzene (Fig. 3.) and toluene (data not shown) than did the virgin SMZ during the first 30 pore volumes.

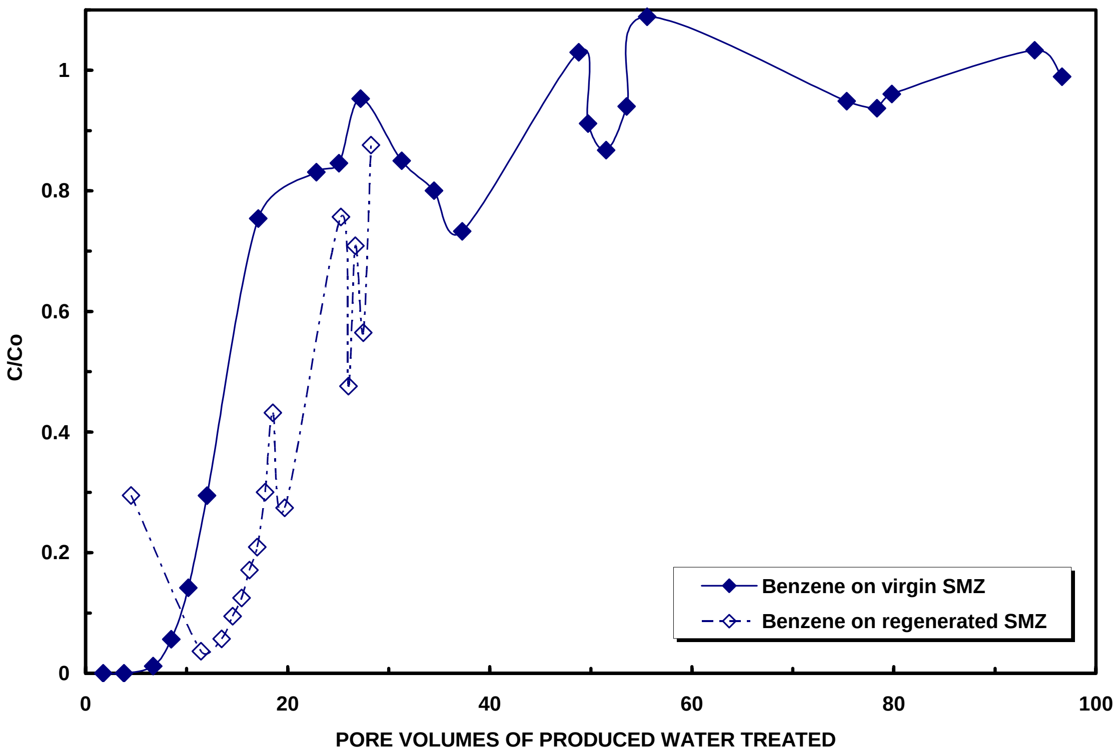

Fig. 3. Comparison of benzene breakthrough curves on virgin and regenerated SMZ with flow rates of 27 and 10 gph, respectively.

The performance of the pilot SMZ system was investigated at three produced water flow rates: 27 gph, 10 gph and 5 gph. As evident in Figure 4, the flow rate had no affect on SMZ performance for the first 10 pore volumes indicating that liquid phase mass transfer was not limiting under the conditions evaluated in the field test. The greatest difference in sorption is evident at later times when the SMZ column operated at 10 gph continued to sorb benzene and the virgin SMZ column operated at 27 gph became saturated. This difference in sorption is not likely a result of the different flow rates but rather due to the fact that the SVOCs and other organics that sorbed onto the SMZ column during the initial runs actually increases the sorption capacity of the SMZ for organics such as benzene.

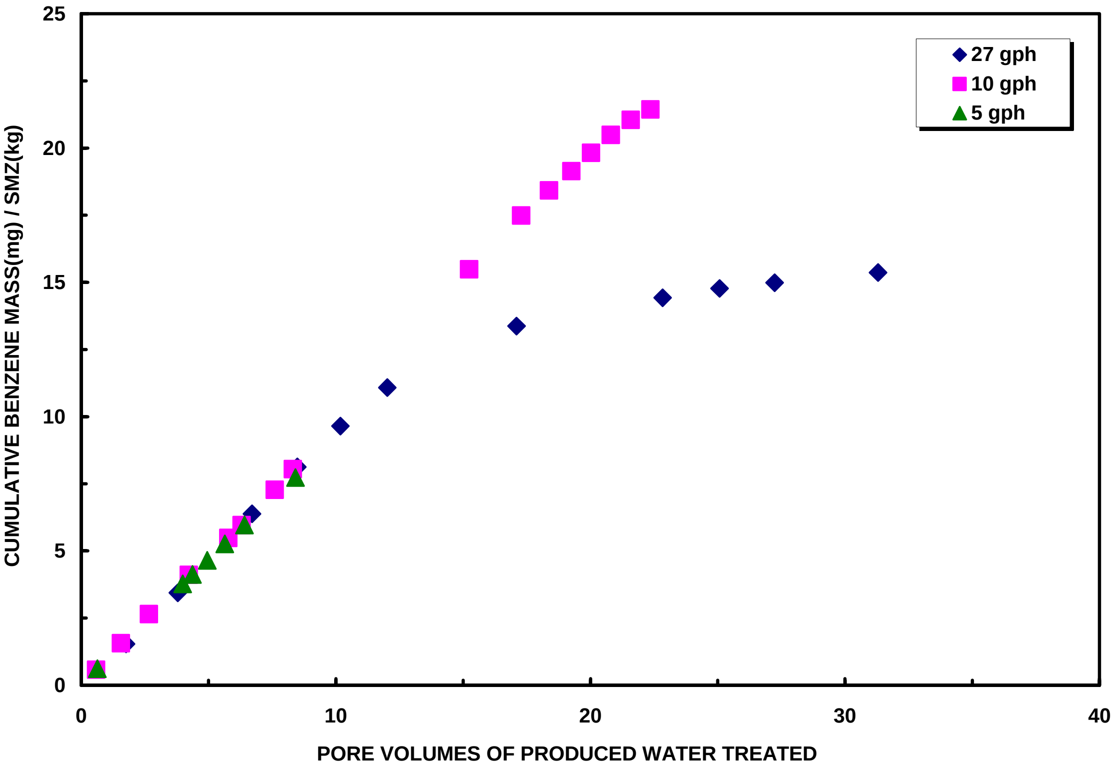

Fig. 4. Cumulative mass of benzene on SMZ over different flow rates used in the field test

In the field test, SMZ performance over two sorption/regeneration cycles was examined at a produced water flow rate of 5 gph. The goal of this test was to demonstrate that it was possible to treat produced water continuously in the SMZ/VPB system. After saturating the first SMZ column, the saturated column was pulled offline and regenerated with air. The second SMZ column remained on line treating produced water until the benzene concentration in the effluent reached 205 of the influen benzen3e concentration. At this point, the regenerated SMZ column was placed back online as illustrated in Figure 5. The breakthrough of BTEX through the SMZ columns over two complete cycles are shown in Fig. 5. During the test, the effluent BTEX concentrations remained below 20 % of influent concentrations, except for two transitory effluent spikes in benzene concentration that occurred due to the carryover problem described earlier.

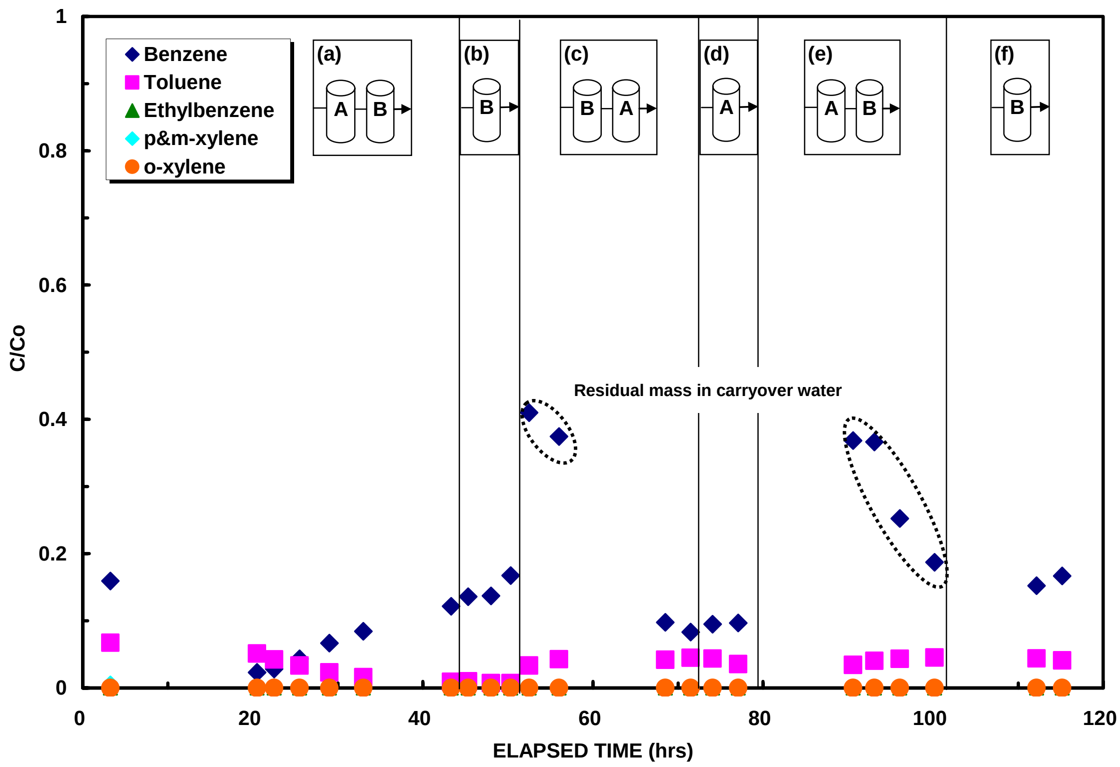

Fig. 5. Breakthrough curves of BTEX compounds on regenerated SMZ over two sorption/regeneration cycles at the flow rate of 5 gph. In stages (a), (c), (e): two columns (noted as A and B) were in line. In the stages of (b), (d), (f): one column was in line while the other column was regenerated.

3.2 Treatment of Regeneration Off-gas in the VPB

Regeneration of Saturated SMZ.

A typical BTEX concentration profile observed in the regenerated gas stream during the field test is presented in Figure 6a. Lab-scale regeneration results obtained previously are presented in Fig. 6(b) for comparison. In both cases, benzene desorption occurred very rapidly compared to the other chemicals. In the laboratory tests, the SMZ column was completely saturated with BTEX before regeneration was initiated. However in the field test, the SMZ sorption cycle was generally terminated when benzene reached 100% breakthrough even though the breakthrough percentages of the other components were only approximately: toluene 70%, *o*-xylene 15%, ethyl benzene and *p&m*-xylenes < 10%. As a result, the concentration of benzene in the regenerated gas stream was higher than the other compounds during the field test. Toluene levels were similar to the benzene levels indicating that the downstream VPB would have to treat high levels of benzene and toluene initially if no buffering system was in place.

GAC Buffering

During the field test, the regenerated gas stream was buffered by a load equalizing column containing a granular activated carbon sorbent. As shown in Figs. 6(a) and 6(b), benzene and toluene were the major components present in the regenerated gas stream. The concentrations of these two chemicals in the gas stream entering and exiting the GAC column during a regeneration cycle are presented in Fig. 7. The results indicate that the GAC columns effectively reduced the toluene and benzene concentration sin the gas stream. The GAC system was more effective at the 5 s EBCT where it reduced the benzene concentrations to below 100 ppmv, a ideal level for successful biodegradation in the VPB.

VPB Performance

After passing through the GAC buffering column, the VOC-laden gas stream from the SMZ regeneration process was fed to the VPB. Fig. 8 shows the subsequent removal of benzene and toluene in the VPB for two different operating conditions. During the beginning of the field trial, the VPB was operated with a microbial community that had been adapted to an inlet benzene concentration of only 12 ppm_v. As a result, the benzene removal efficiency observed in the VPB was very poor when subjected to an inlet benzene concentration of 170 ppm_v, as shown in Fig. 8(a). The toluene removal was better even when it was subjected to an inlet concentration of 110 ppmv. To improve the performance of the VPB and acclimate the microbial population to a higher benzene concentration, a surrogate BTEX feed was provided to the VPB during the shut down periods and the benzene concentration in this feed was increased to 90 ppmv. As a result, the biomass in the VPB became accustomed to 90 ppm_v benzene levels and could remove more than 95 % of the benzene introduced to the column during the regeneration process (Fig. 8(b)). These results along with similar results obtained in the SMZ sorption and regeneration experiments indicate that benzene will control the design and operation of the coupled SMZ/VPB for BTEX removal from produced water.

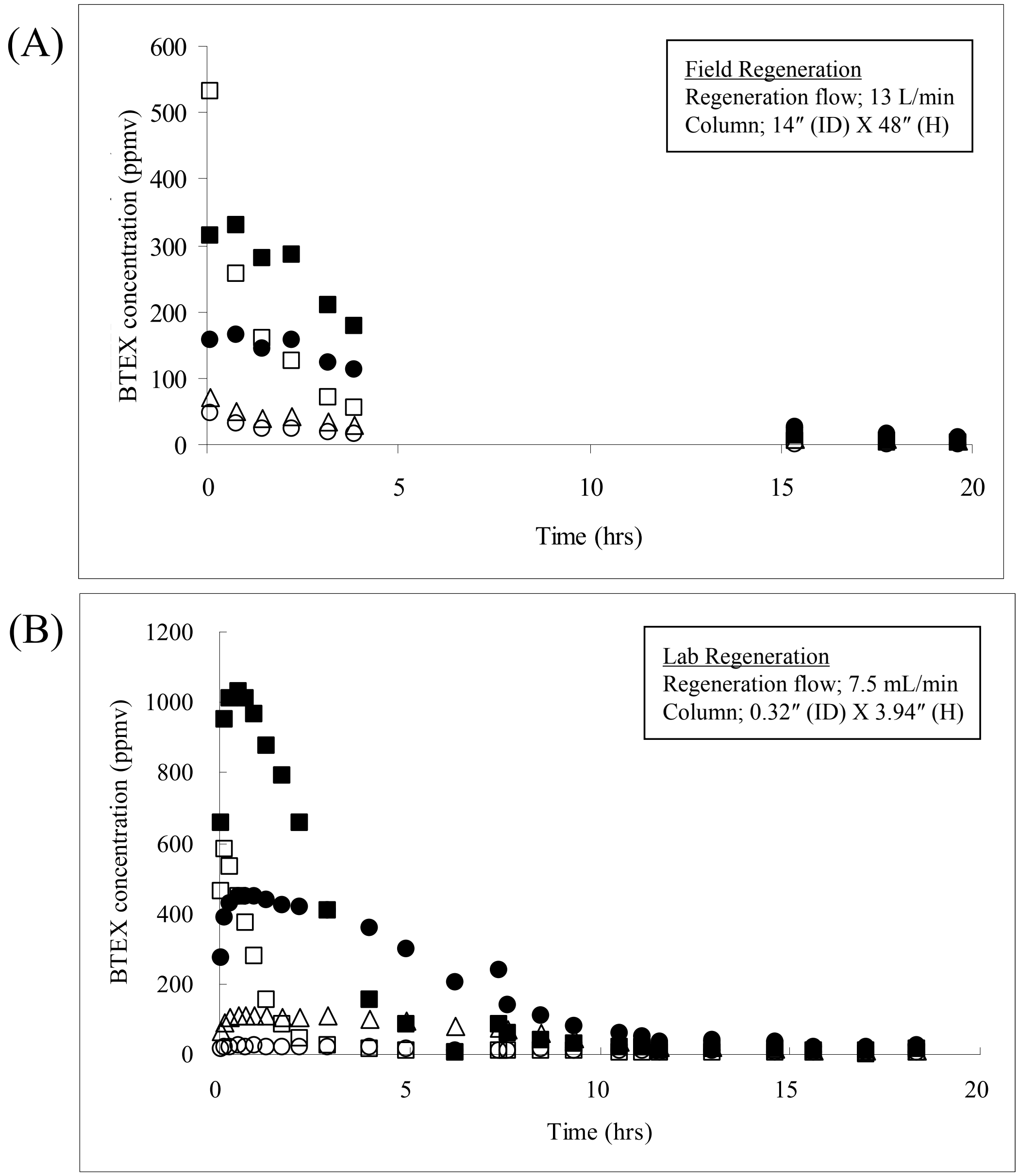

Fig. 6. BTEX concentration profile of gas phase effluent during regeneration of SMZ column: (a) Regeneration in the field, and (b) regeneration in the lab. □: Benzene, ■: Toluene, ○: Ethyl benzene, ●: *p&m*-xylene, Δ: *o*-xylene.

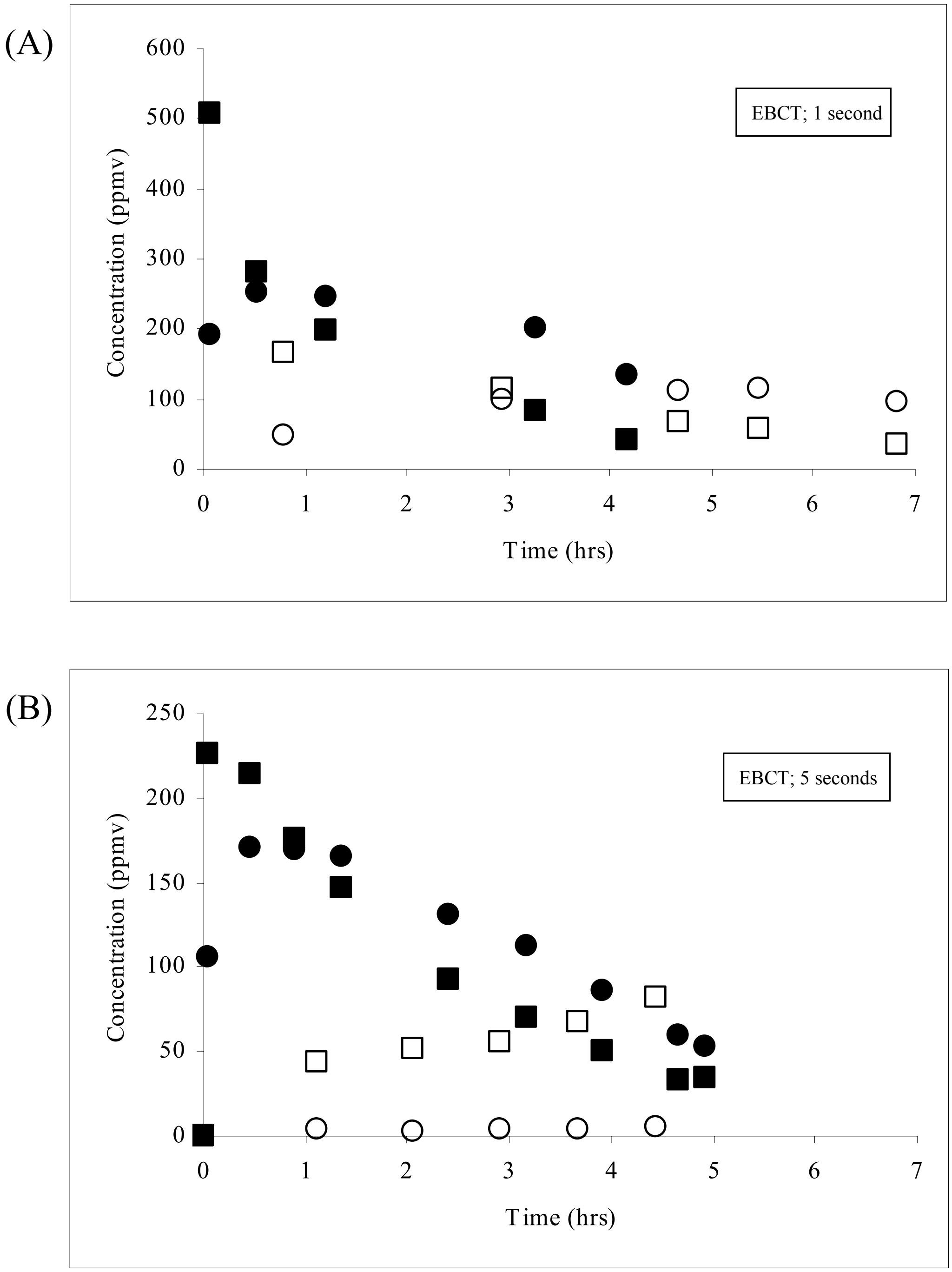

Fig. 7. Benzene and toluene concentrations in the gas stream entering and exiting the GAC buffering column during SMZ regeneration. (a) 1 second EBCT in the buffering column, and (b) 5 second EBCT in the buffering column. ■: Benzene influent to buffering column, □: Benzene effluent from buffering column, ●: Toluene influent to buffering column, ○: Toluene effluent from buffering column.

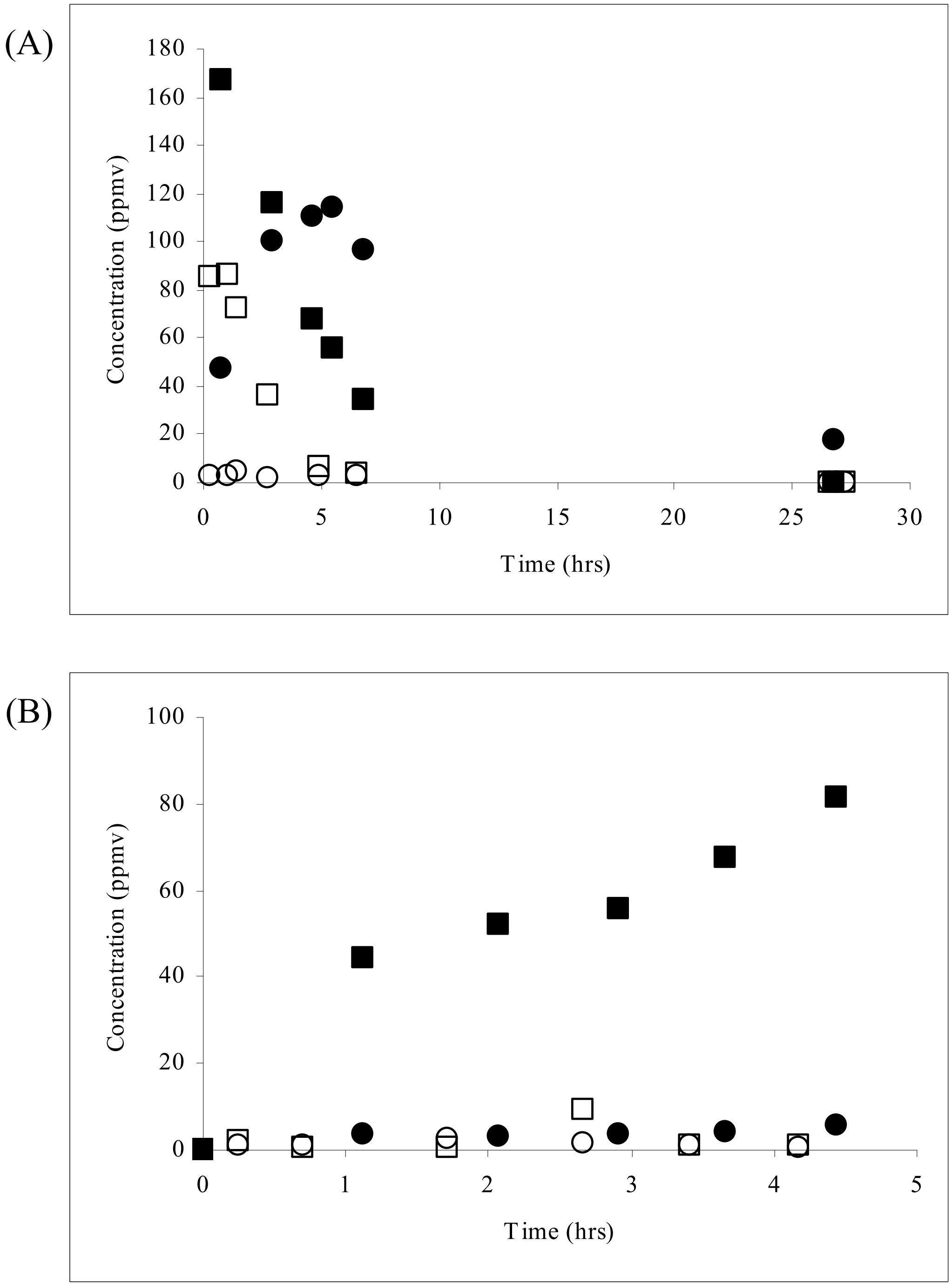

Fig. 8. Removal of VOCs in the VPB during the field test at two different operating conditions: (a) Biomass accustomed to low concentration (12 ppm$_v$) of benzene, and (B) biomass accustomed to high concentration (90 ppm$_v$) of benzene. ■: Benzene influent to VPB, □: Benzene effluent from VPB, ●: Toluene influent to VPB, ○: Toluene effluent from VPB.