

REMOVAL OF BTEX FROM PRODUCED WATERS USING SURFACTANT-MODIFIED ZEOLITE

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ABSTRACT

We tested the effectiveness of surfactant-modified zeolite (SMZ) for removal of BTEX with batch and column experiments using waters with BTEX concentrations that are comparable to those of produced waters. The data from our experimental investigations showed that BTEX sorption to SMZ can be described by a linear isotherm model, and competitive effects between compounds were not significant. The SMZ can be readily regenerated using air stripping. We field-tested a prototype SMZ-based water treatment system at produced water treatment facilities and found that the SMZ successfully removes BTEX from produced waters as predicted by laboratory studies.

INTRODUCTION

Water produced by oil and gas wells accounts for a significant portion of waste in the United States and the world. According to 1991 figures presented by Neff and Sauer (1), over 250 million gallons of produced water were discharged daily in the Gulf of Mexico and North Sea, with this number expected to rise significantly throughout the coming years. This water contains various pollutants and may have high quantities of dissolved organic molecules such as benzene, toluene, ethylbenzene, and xylenes (BTEX). Although nearly 90% 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 certain cases, reinjection is not affordable and surface discharge is the only option available for disposal of this water. Discharge to the surrounding water is the most cost-effective means of disposal for offshore wells. The water produced by wells in arid environments may be a valuable resource for agricultural purposes such as irrigation and livestock watering. Produced water discharge is currently excluded from several federal and state laws concerning water quality. Increasing regulations on this water will necessitate the development of additional treatment options (2).

Surfactant-modified zeolites (SMZ) have been shown to be effective sorbents for removal of organic contaminants from groundwater. Zeolites are aluminosilicate minerals that have a cage-like structure with high surface areas and high cation exchange capacities. Positively charged inorganic counterions neutralize the zeolite's negative charge, but these cations can be replaced by larger surfactant molecules, such as hexadecyltrimethylammonium chloride (HDTMA-Cl), that have greater affinity for the zeolite surface. The presence of the surfactant molecules imparts hydrophobic properties to the zeolite surface and allows the zeolite to sorb organic compounds such as BTEX (3). The cost of SMZ is low (\$460 per metric ton), increasing their appeal for use in water treatment systems (4). It has been shown that SMZ saturated with volatile organics can be regenerated using an air-sparging technique (5).

These properties of SMZ make it a promising alternative for removing organics from produced water. We investigated the use of SMZ to remove BTEX from produced water, and present the results of laboratory and field prototype experiments. The specific objectives of this study were to 1) Determine the sorption capacity of SMZ for BTEX; 2) Determine the ability to regenerate spent SMZ; 3) Build a prototype SMZ treatment system and field test it at a produced water facility.

MATERIALS AND METHODS

Zeolite

The zeolite used in this study is a natural clinoptilolite-rich zeolite from the St. Cloud mine near Winston, NM. The mineral content of the zeolite is 74% clinoptilolite, 5% smectite, 10% quartz plus cristobalite, 10% feldspar, and 1% illite. The zeolite has an internal cation exchange capacity (CEC) of 800 meq/kg, and an external cation exchange capacity (ECEC) of 90-110 meq/kg. The external surface area is 15.7 m²/g (3).

The zeolite was ground and screened to two different grain sizes: 14-40 mesh (1.4 to 0.4 mm) for the field columns and 80-100 mesh (0.18 to 0.15 mm) for the laboratory columns.

SMZ Preparation

The SMZ used for the laboratory sorption experiments was produced by treating zeolite with HDTMA-Cl in the proportions of 60 g of zeolite with 180 mL of a 0.10 M HDTMA-Cl solution. After shaking at 25°C for 24 hr, the HDTMA-zeolite was rinsed with two 180 mL aliquots of type I water and air dried.

The SMZ used for the field sorption experiments was bulk-produced at the St. Cloud mine. The procedure used to prepare the SMZ is described by Bowman et. al. 2001 (4).

Laboratory Experiments

A study was performed using a column scaled from a proposed field setup using rapid small-scale column test (RSSCT) design equations. This method uses relationships between empty bed contact time, particle diameter, and superficial velocity to scale between large and small columns. The assumed field design called for a flow rate of 3000 L/d with a benzene influent concentration of 8.35 mg/L. The field column was intended to have a service life of one day before benzene saturation, while the hydraulic loading rate would be maintained at 2 gpm/ft² to insure good hydraulic flow. With these design criteria set, the RSSCT equations were used to determine the SMZ particle size and laboratory column dimensions with the assumption of constant diffusivity.

A glass column 270-mm long with a 4-mm radius was selected for the laboratory tests and was packed with SMZ (80-100 mesh). The column was purged with CO₂ for 24 hr in order to flush out any air remaining in the column, followed by saturation with purified water (reverse osmosis).

The influent BTEX solution (with a concentration of 16 mg L⁻¹ for each of the six compounds) was prepared in a collapsible 10-L (12" x 19") Tedlar® Gas Sampling Bag (Alltech) with a barbed on/off valve. The BTEX solution was introduced into the saturated column at a flow rate of 1.19 cm min⁻¹. Influent and effluent samples were taken to monitor the BTEX concentrations flowing into and out of the column. Flow was terminated when the BTEX effluent concentrations were equal to the influent concentrations; the column was then sealed prior to regeneration.

The spent SMZ was regenerated by air-sparging. A 65-mm, single-float flowmeter (Cole Parmer) and compressed gas tank (air) were attached to the influent end of the column for the regeneration step.

The compressed air tank was set to 20 psi and the flowmeter was used to control flowrate through the column. Flowrate was set at 2.3 ml min⁻¹. Using a 1.0-mL glass gas-tight syringe, samples periodically were taken by withdrawing gas through a sampling port at the effluent end of the column. The air-sparging experiment was continued until the BTEX mass coming off of the column was negligible.

The regenerated SMZ was again saturated with the aqueous BTEX solution. The input BTEX concentration and flow rate were the same as for the original saturation. However, for this experiment the SMZ-filled column was not purged with CO₂ or saturated with pure water prior to introducing the BTEX solution.

Field Test of Prototype SMZ System

The columns selected for use in the field trials were provided by a local Culligan distributor in Austin, TX. Originally designed for use in ion exchange systems, the columns were readily adapted to the needs of this study by substituting the ion exchange resin with SMZ. The columns were constructed from fiberglass and PVC and were designed to operate with the influent stream dispersing at the top of the resin and flowing down to the bottom. Inside the column, the influent port contained a coarse filter to prevent large debris from fouling the column. At the bottom of the column, a perforated collector plate funneled the water up a 1" PVC pipe through the middle of the column to the effluent port.

Two of these columns were used in the field. The first column was 14" in diameter and 48" in height, while the second had a diameter of 12" and was 44" in height. The available volumes of these columns were approximately 3.6 ft³ and 2.4 ft³ respectively. The 14" column was filled to the top with 192.0 lbs. of 14-40 mesh SMZ, while the 12" column contained approximately 4" of headspace and held 132.25 lbs of 14-40 mesh SMZ.

The site chosen for the field study is operated by Crystal Solutions, LLC., and is located in an oil producing region just outside of Wamsutter, WY. The facility is set up to receive produced water from the region by tanker truck. The water is unloaded from the trucks into an oil/water separation tank. Overflow from this tank flows into a second separation tank. Both tanks are identical, and measure approximately 20' in height and 10' in diameter. Oil is sent into an oil condensate tank for later processing. As the second separation tank fills with water, it flows into a lined separation pond. From the separation pond, water is pumped through a series of lined evaporation ponds.

Previous analysis had shown this produced water contained approximately 16 mg/L of benzene, 27 mg/L of toluene, 2 mg/L ethylbenzene, 9 mg/L m-&p-xylene, and 3 mg/L o-xylene (10). The field columns were connected to the second separation tank at a 4" valve located about 2' from the bottom. This connection point provided approximately 15' of head, driving water flow through the SMZ system. Just downstream of the tank valve was a strainer to prevent large debris from entering the system. The 4" line was reduced to a 1" PVC pipe that ran to a flow meter, sample port, and influent port of the column. The effluent pipe from the column consisted entirely of 1" PVC, contained a sample port for effluent sample collection, and led into the lined separation pond. Regeneration was attempted in the field using a portable air compressor provided by the field operators. The same setup was used, except the influent water connection was replaced with an air connection, and an air flow meter was used. The effluent line remained in place until the column was drained. The effluent pipe was then replaced with tygon tubing so air samples could be collected easily.

Influent and effluent water samples were collected from the sample ports periodically. A portable photoionization detector (PID) was used to estimate total

concentrations of volatiles in water and air during produced water treatment and SMZ regeneration. Air samples were collected during regeneration by placing the tygon tubing of the effluent air into the bottom of the vial and filling until all the original air in the vial had been displaced. The vial was then quickly closed and sealed as the tygon tubing was being removed.

The 14" column was the first column connected and run from the separation tank. This column was operated for about 46 hours with a few minutes downtime to repair a minor leak. During the operation, the flow rate averaged 25 gph but was dropping throughout the course of the run to 17.5 gph. It is believed this drop in flow rate was caused by clogging of the SMZ pores inside the column by particles in the water. BTEX concentrations were constant throughout the trial at levels similar to those of the previous analysis.

The 12" column was put into service next and was in operation for approximately 45 hours, with 1 hour of stoppage for repairs. The average flow rate during this run was 19 gph. However, once again there was a drop in flow rate as the trial progressed, reaching as low as 12.5 gph. A large increase in BTEX influent concentrations occurred during the last 36 hours of operation, when BTEX concentrations jumped to the highest concentrations observed during the testing. Toward the end of the run with the 12" column, most BTEX concentrations had fallen from these peaks, but were still high. It is believed that these elevated measurements were caused by the discharge of one or more trucks carrying produced water with these high BTEX levels into the separation tanks.

Regeneration was intended to occur for approximately 12 hours, or until the PID gave insignificant readings from the effluent air. However, due to compressor failure, regeneration had to take place sporadically with active regeneration taking place for about 8.5 hours at air flow rates between 3.0 and 3.5 scfm.

Although the regeneration was not complete, the 14-inch column was run a second time for nearly 48 hours, with an average flow rate of 20 gph. Once again, flow rate dropped with time, reaching as low as 16.5 gph. The BTEX concentrations were consistent during this operation, at levels slightly higher than the 14-inch column trial with virgin SMZ. The concentrations averaged: benzene- 20 mg/L, toluene- 40 mg/L, ethylbenzene- 30 mg/L, m-&p-xylene- 30 mg/L, and o-xylene-5 mg/L.

Analysis

Aqueous BTEX concentrations from the laboratory columns were measured using a Hewlett-Packard (HP) Model 7694 headspace sampler attached to a HP Model 5890A gas chromatograph (GC) with a 30 m 0.53-mm ID Megabore® high resolution column (J&W, model GS-Q) and flame ionization detector (FID) with helium as the carrier gas. The GC was calibrated during each run with five BTEX standards of varying concentrations over the linear response range. p-xylene and m-xylene were not resolved by this method and were treated as a single compound.

Aqueous BTEX concentrations from the field columns were measured using a Tekmar 7000 headspace sampler attached to an HP 5890 GC equipped with a 30 m 0.53-mm ID Restek capillary column (RTX-624) and FID. Nitrogen was an auxiliary gas, and helium was the carrier gas.

The BTEX concentrations in gas samples from air-sparging were analyzed by direct injection into the HP 5890A GC. The GC was calibrated using gaseous BTEX standards prepared for this purpose.

RESULTS AND DISCUSSION

Laboratory Experiments

Figure 1 shows the results of the breakthrough of BTEX on virgin SMZ. Because of its low octanol-water partition coefficient (K_{ow}) and high solubility in water, benzene breakthrough occurs first, while compounds with higher K_{ow} and lower water solubility breakthrough later. The estimated amount of BTEX mass sorbed to the SMZ and estimated distribution coefficient (K_d) values are shown in Table 1. The K_d values determined in this experiment are similar and in some cases higher than those determined from batch experiments (7). A higher K_d indicates enhanced sorption of the compound.

Figure 2 shows the cumulative masses of BTEX removed by air-sparging after the first column experiment. The compounds with the lowest K_{ow} were the most readily removed. While air sparging was effective in stripping all of the benzene and toluene from the column, not all of the ethylbenzene and the xylenes were removed under these conditions (data not shown).

BTEX breakthrough in the regenerated column is shown in Figure 3. The estimated mass of BTEX sorbed to the SMZ and estimated K_d values are shown in Table 1. The breakthroughs of benzene and toluene for the regenerated SMZ are similar to their breakthroughs with virgin SMZ. Figure 4 shows a comparison of benzene breakthrough in the two columns. The breakthrough curves for ethylbenzene and the xylenes seem to plateau at a relative concentration of 0.8. We hypothesize the low plateau concentrations to be a result of enhanced cosorption effects in the regenerated columns. Others have noted that an increase of bound organic carbon due to BTEX sorption will enhance partitioning of additional BTEX (8, 9). These effects would be more significant in the regenerated column since there is a higher hydrocarbon content on the SMZ, as not all of the BTEX mass was removed during air-sparging. These effects are most pronounced on the compounds with highest K_{ow} and lowest S_w . Because the relative concentrations indicate that equilibrium between the SMZ and these compounds was not reached, K_d values were not calculated for ethylbenzene and xylenes in the regenerated column.

Field tests of Prototype SMZ System

The BTEX concentrations in the produced water used in the field testing varied over time. Table 2 shows the average and range of values of the BTEX component concentrations throughout the duration of the test of the field-scale columns. The breakthrough of BTEX in the virgin 14-inch field system is shown in Figure 5. The effluent concentrations of all compounds remained below the influent concentrations for the duration of the test. Little ethylbenzene or xylene had appeared in the effluent after 80 pore volumes. Benzene and toluene concentrations in the effluent appeared to plateau at relative concentrations of 0.8 and 0.6, respectively. A possible reason for the failure of

benzene and toluene to reach saturation may be the cosorption described above. The dissolved organic carbon of this produced water was 470 mg/L, of which only 110 mg/L was BTEX, thus providing additional hydrocarbons that were not present in the laboratory experiments. These additional, primarily higher molecular weight hydrocarbons may have added to the cosorption effects. Laboratory batch tests comparing BTEX sorption to SMZ in both pure and produced waters showed similar results. The K_d values were higher in produced water, which contained higher dissolved organic carbon (10).

Figure 6 shows a comparison of benzene sorption between the lab trial and 14-inch column field trial, both with virgin SMZ. Benzene breakthrough is later in the field column and does not reach the influent value. The results of the 12-inch column with virgin SMZ are similar. Figure 7 shows a comparison of toluene sorption between the lab trial and 12-inch field column with virgin SMZ.

Regeneration of the 14-inch column showed results similar to regeneration of the lab column, as shown in Figure 8. Benzene was the first to be removed, and was the only compound that fully stripped from the column. As mentioned above, air-sparging of the field column was terminated sooner than desired due to equipment failure.

Figure 9 shows the breakthrough of BTEX in the regenerated 14-inch column. The relative concentrations of all of the compounds except for benzene are above background (and higher for ethylbenzene and the xylenes than during any stage of the initial sorption experiment). We believe the high initial concentrations were due to the incomplete regeneration of the SMZ. During regeneration, air was pushed into the column in the same flow direction as water. Therefore, the influent end of the column was regenerated first and the BTEX was pushed toward the effluent end of the column. The compounds with higher K_{ow} are less readily air sparged from the SMZ and were not completely removed from the column when regeneration terminated, but instead concentrated near the effluent end. Thus, when produced water was again flushed through the column, these higher concentrations eluted. If flow was reversed during regeneration, residual BTEX would be concentrated towards the influent end of the column and less readily eluted during the next saturation step.

Except for the high initial concentrations, the regenerated SMZ was even more effective than the virgin SMZ at BTEX removal. A comparison of toluene removal from the virgin and regenerated 14-inch column trials is shown in Figure 10. As was noted in the lab columns, the regenerated column removes higher amounts of BTEX from the water than the original column.

CONCLUSIONS

Field-scale tests support laboratory column tests showing that SMZ will successfully remove BTEX from produced water. The BTEX components break through the columns in order of increasing K_{ow} and decreasing solubility in water. SMZ can be regenerated by air-sparging, and regenerated SMZ will continue to remove BTEX from produced water. Further studies will be completed on this SMZ system in an attempt to determine the role that enhanced cosorption plays in the removal of BTEX, and to determine the useful life of SMZ in the treatment system.

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Table 1. Amount of BTEX sorbed in laboratory columns and Kd values.

	Mass sorbed to virgin SMZ (mg)	Kd (L/kg) virgin SMZ	Mass sorbed to regen. SMZ (mg)	Kd (L/kg) regen. SMZ	Kd (L/kg) batch (7)
Benzene	1.9	7.8	1.8	8.2	9.9
Toluene	4.4	23	4.2	23.0	27
Ethylbenzene	15.5	85	12.6	--	69
p&m-xylene	15.1	90	12.8	--	75
o-xylene	16.1	85	12.8	--	66

Table 2. Average and range of BTEX component concentrations in WY Produced Water.

	Average concentration in WY Produced water (mg/L)	Range of concentration (mg/L)
Benzene	25.1	18.9-36.4
Toluene	40.7	31.0-61.3
Ethylbenzene	4.7	1.8-19.9
p&m-xylene	30.6	8.8-78.9
o-xylene	9.5	3.7-40.8

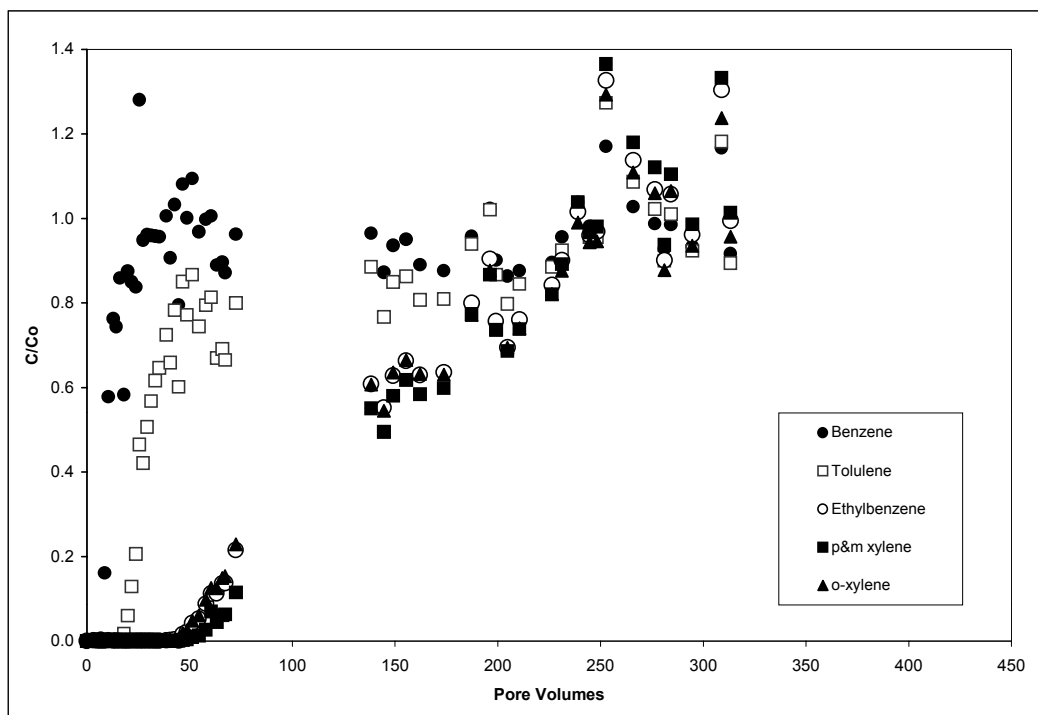


Figure 1. BTEX Breakthrough in the lab column with virgin SMZ.

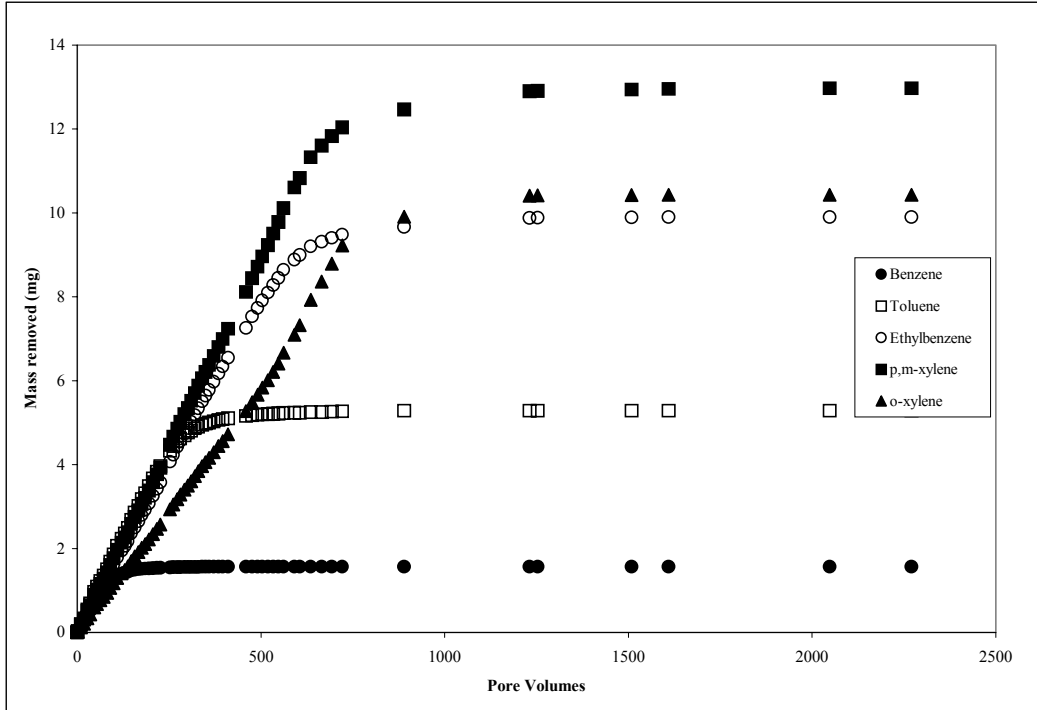


Figure 2. BTEX mass removed from SMZ in the lab column by air-sparging.

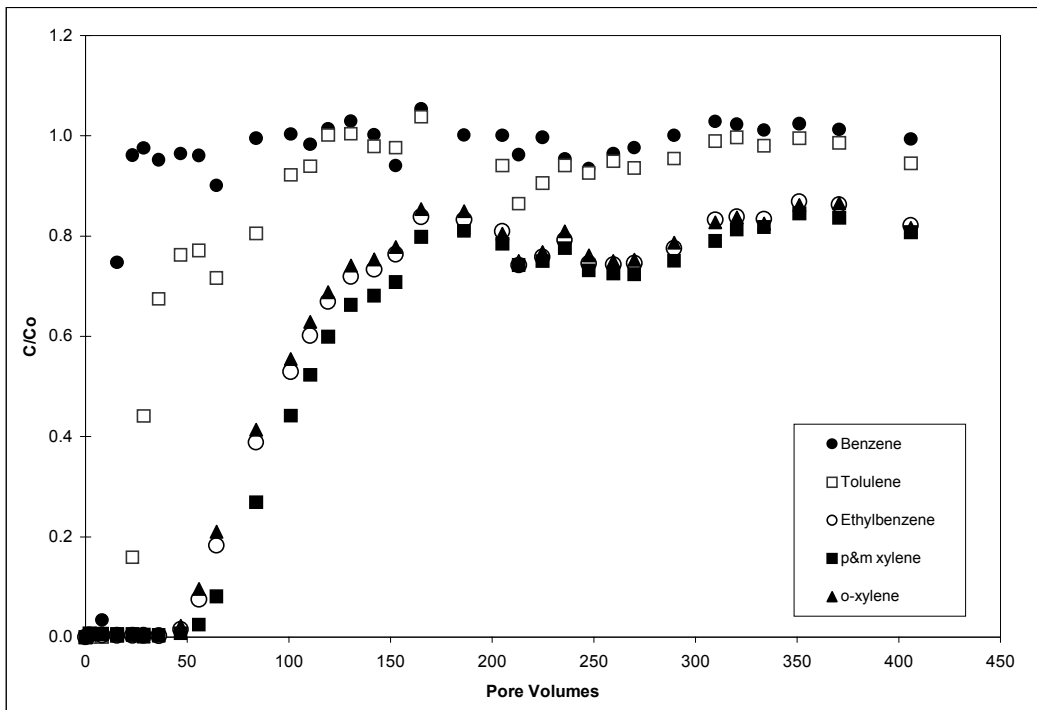


Figure 3. BTEX Breakthrough in the lab column with regenerated SMZ.

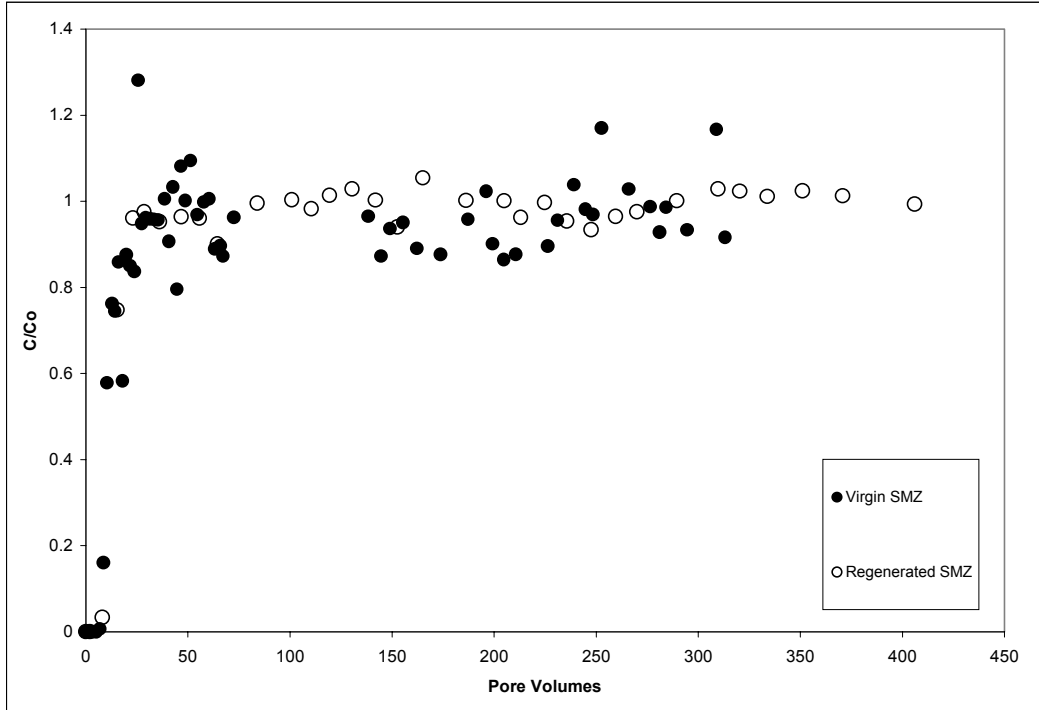


Figure 4. Comparison of benzene breakthrough in lab column with virgin and regenerated SMZ.

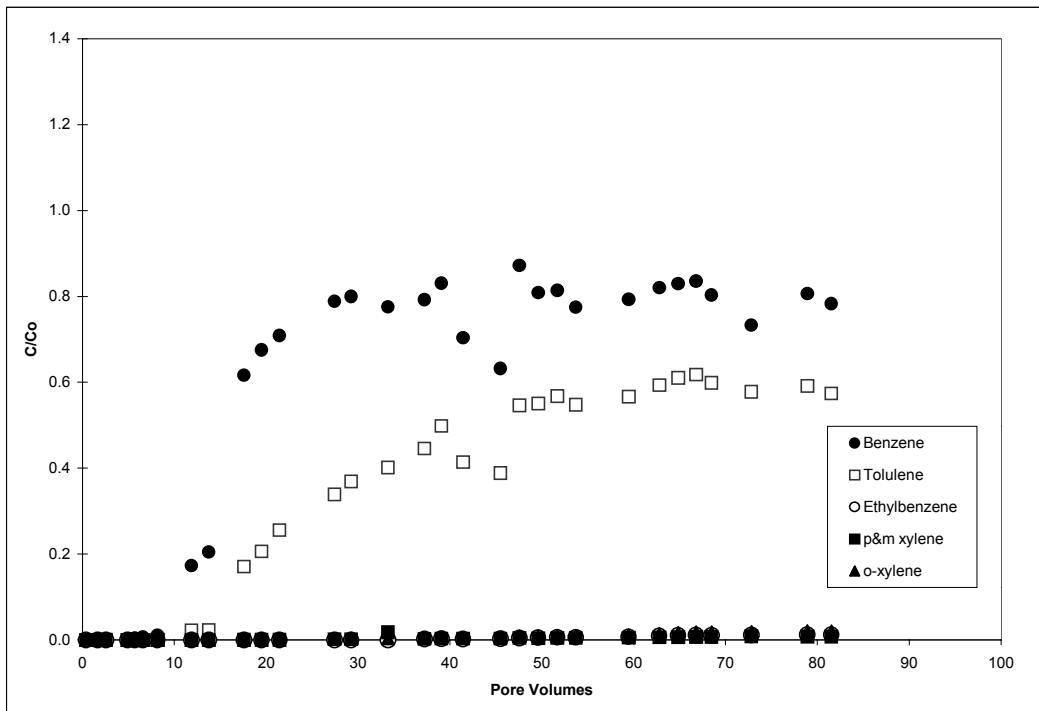


Figure 5. BTEX breakthrough in the 14-inch field column with virgin SMZ.

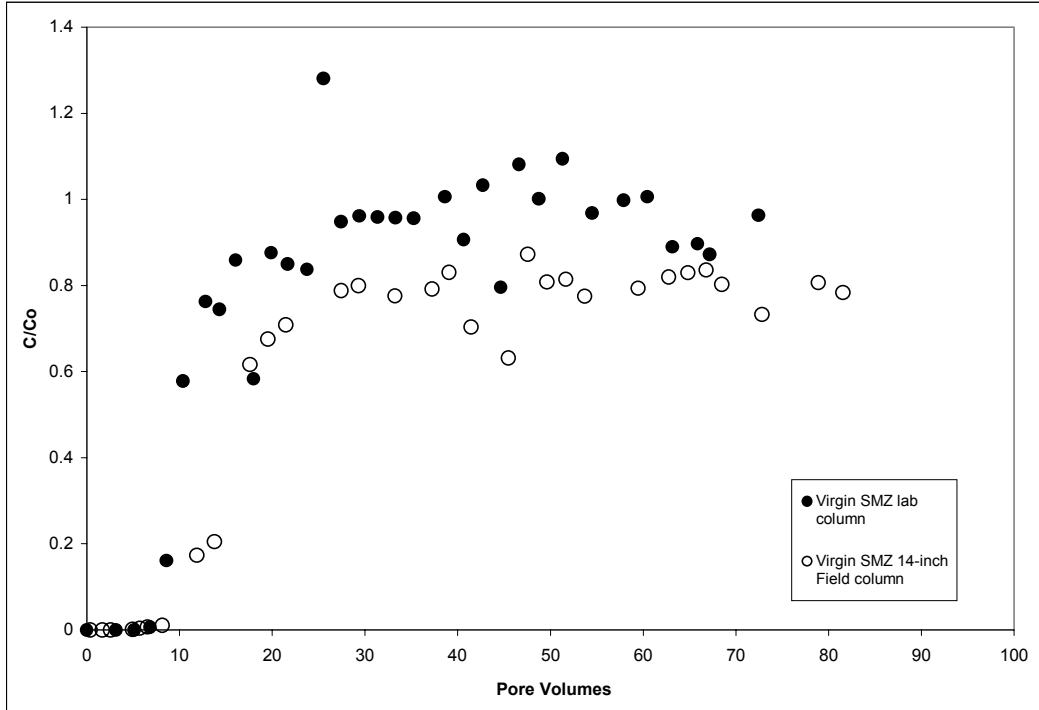


Figure 6. Comparison of benzene breakthrough in lab column with virgin SMZ and 14-inch field column with virgin SMZ.

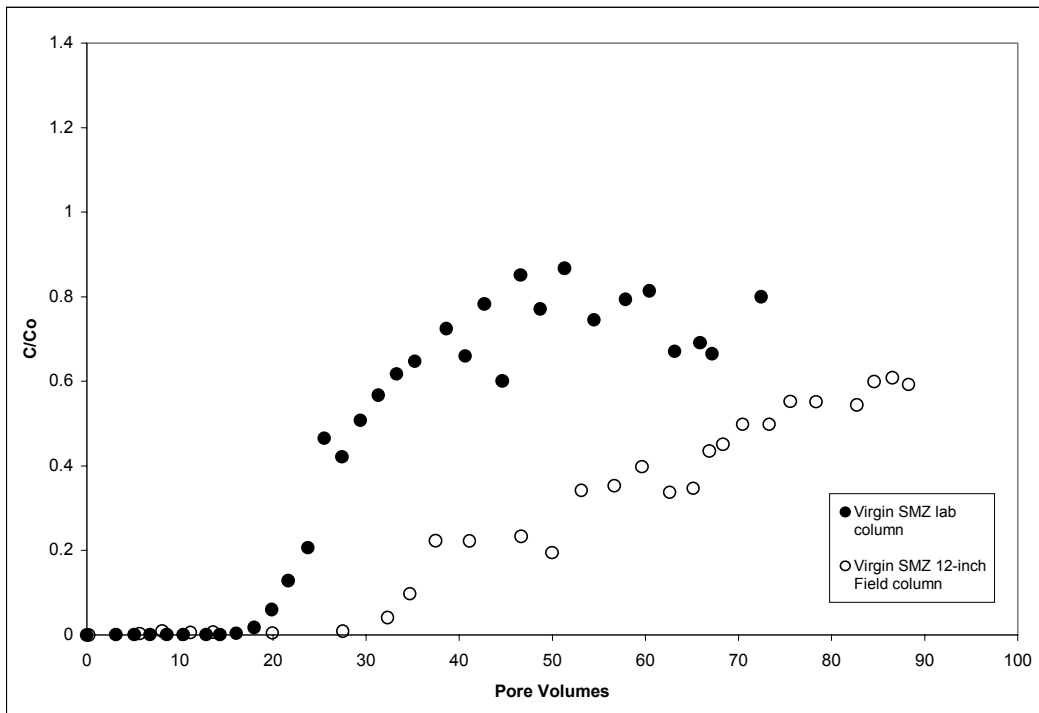


Figure 7. Comparison of toluene breakthrough in lab column with virgin SMZ and 12-inch field column with virgin SMZ.

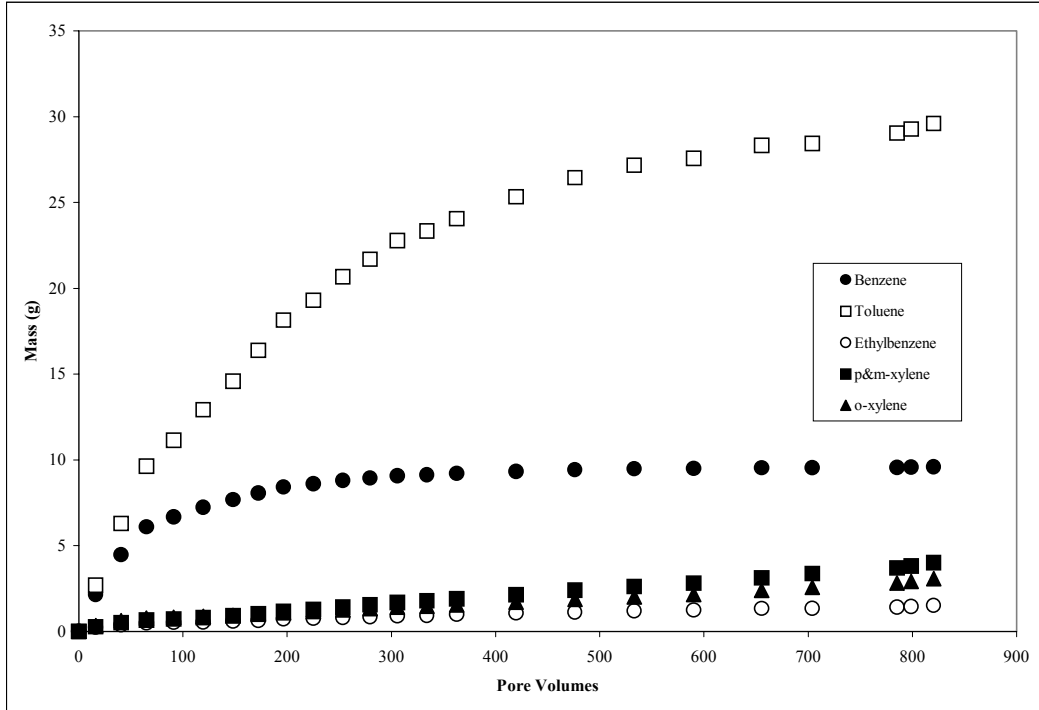


Figure 8. BTEX mass removed from SMZ in 14-inch field column by air-sparging.

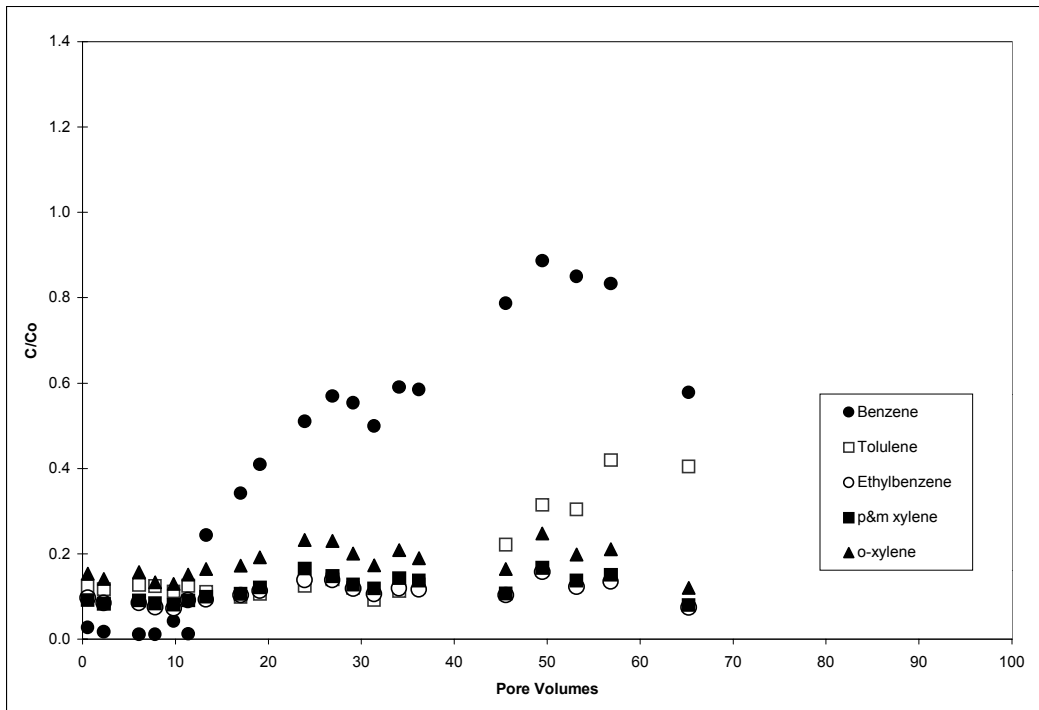


Figure 9. BTEX breakthrough in 14-inch field column with regenerated SMZ.

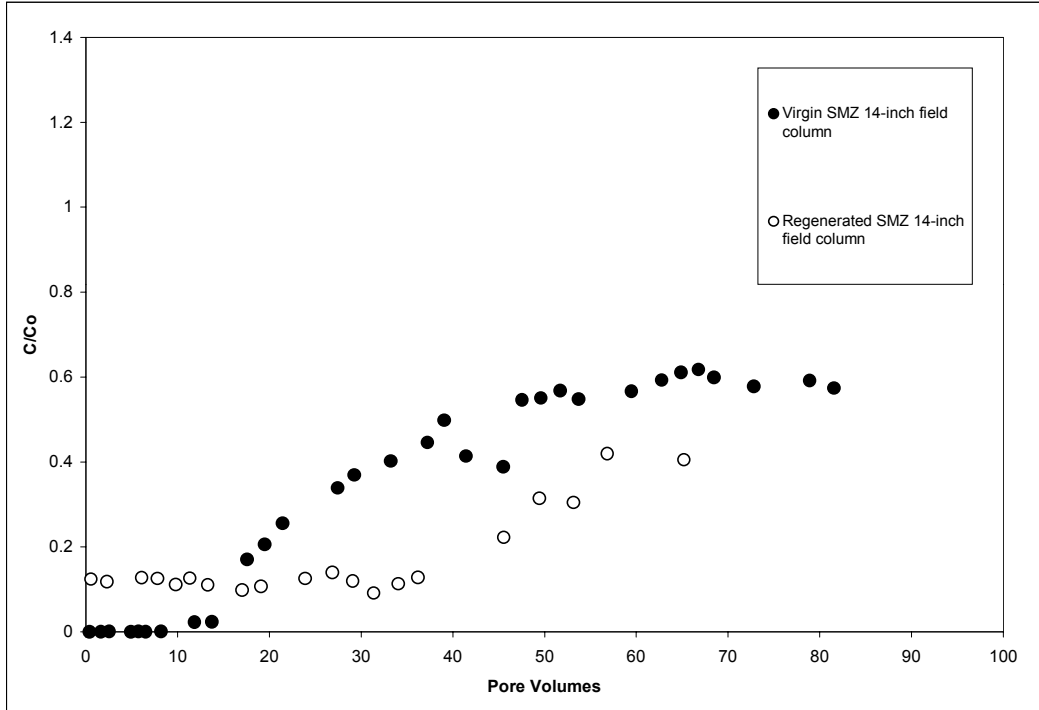


Figure 10. Comparison of toluene breakthrough in 14-inch field column with virgin SMZ and 14-inch field column with regenerated SMZ.