REPORT TITLE: Treatment of Produced Waters Using a Surfactant Modified Zeolite/Vapor Phase Bioreactor System
REPORT TYPE: Semi-Annual Technical Report
REPORT PERIOD: 1 October 2003 – 31 March 2004
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REPORT ISSUE DATE: June 2004
DOE AWARD NUMBER: DE-FC26-02NT15461

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

This report summarizes work of this project from October 2003 through March 2004. The major focus of the research was to further investigate BTEX removal from produced water, to quantify metal ion removal from produced water, and to evaluate a a lab-scale vapor phase bioreactor (VPB) for BTEX destruction in off-gases produced during SMZ regeneration. Batch equilibrium sorption studies were conducted to evaluate the effect of semi-volatile organic compounds commonly found in produced water on the sorption of benzene, toluene, ethylbenzene, and xylene (BTEX) onto surfactant-modified zeolite (SMZ) and to examine selected metal ion sorption onto SMZ. The sorption of polar semi-volatile organic compounds and metals commonly found in produced water onto SMZ was also investigated. Batch experiments were performed in a synthetic saline solution that mimicked water from a produced water collection facility in Wyoming. Results indicated that increasing concentrations of semi-volatile organic compounds increased BTEX sorption. The sorption of phenol compounds could be described by linear isotherms, but the linear partitioning coefficients decreased with increasing pH, especially above the pKa's of the compounds. Linear correlations relating partitioning coefficients of phenol compounds with their respective solubilities and octanol-water partitioning coefficients were developed for data collected at pH 7.2. The sorption of chromate, selenate, and barium in synthetic produced water were also described by Langmuir isotherms.

Experiments conducted with a lab-scale vapor phase bioreactor (VPB) packed with foam indicated that this system could achieve high BTEX removal efficiencies once the nutrient delivery system was optimized. The xylene isomers and benzene were found to require the greatest biofilter bed depth for removal. This result suggested that these VOCs would ultimately control the size of the biofilter required for the produced water application. The biofilter recovered rapidly from shutdowns showing that the system was resilient to discontinuous feed conditions therefore provided flexibility on the SMZ regeneration process.

Table of Contents

List of Figures

List of Tables

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.

Building on the experimental methods developed by our previous effort, the sorption of semi-volatile organic compounds, metal cations, and metal oxyanions was also investigated. The additional compounds selected for study were based on characterization of the produced water used in the field experiments conducted at Crystal Solutions, LLC in Wamsutter, Wyoming. Phenol, naphthalene, and methylated variations of these compounds were the only semi-volatile organics found in concentrations greater than 100 μg/L. Inorganic contaminants identified at significant concentrations included barium, chromium, and selenium. Isotherms were developed to describe the sorption of these compounds to SMZ. The sorption of barium onto virgin zeolite was also investigated to determine how surfactant modification altered sorptive behavior of metal cations.

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 relatively low concentrations of volatile organic compounds (VOCs) including BTEX. Because these VOCs are biodegradable and present in dilute concentrations, a vapor phase bioreactor (VPB) can be used to destroy the pollutants generated in the SMZ regeneration step. Products of VPB biodegradation include carbon dioxide, water and new biomass. This technology has several advantages for this application including high destruction efficiencies for many VOCs including BTEX compounds, low operating costs and minimal generation of undesirable byproducts (van Groenestijn and Hesselink, 1993; Deshusses and Webster, 2000). Several VPB configurations are possible for the SMZ application including a biofilter configuration with a stationary liquid film containing nutrients and biomass, and biotrickling filters with a liquid nutrient phase recirculated throughout a synthetic packing material.

The effectiveness of the SMZ/VPB combination may be affected by several factors such as: the interaction of multiple VOCs presented in the inlet gas stream; the interactions of VOCs in the waste gas stream; and the presence of nitrogen. In addition, VPBs prefer a continuous feed stream and thus the operation of the SMZ/VPB system will need to be optimized to match SMZ regeneration and VPB feed cycles.

It is important to note that although many of the organic constituents found in produced water are biodegradable, the high salinity of produced water prevents direct biological treatment of the produced water. Furthermore, direct air stripping of the produced water phase will not remove the less volatile organic contaminants. Thus, treatment of the water via SMZ followed by treatment of the regeneration gas via a VPB allows the removal of organic and inorganic constituents and ultimate destruction of the VOCs without the problems associated with high salinity and the presence of heavier organic species.

2. Experimental

2.1 SMZ Btach Reactors

2.1.1 SMZ Preparation

Surfactant Modified Zeolite (SMZ) was prepared by adsorbing a surfactant to the surface of zeolite; thus altering the zeolite's adsorptive capabilities. The zeolite used in this study was purchased from the St. Cloud Mine in Winston, New Mexico. An X-ray diffraction analysis conduced by Sulivan et al. (1997) found the material to be comprised of 74% clinoptilolite, 10% feldspar, 10% quartz and cristobalite, 5% smectite clay and 1% illite. Calcium and potassium were determined prior to this research to be the major exchangeable cations present on the raw material. The external and internal cation exchange capacities are 90-110 meq/kg and 800 meq/kg (Li and Bowman, 1997). The BET external surface area of the zeolite is 15.7 m2/g (Sulivan et al., 1997).

Hexadecyltrimethylammonium chloride (HDTMA-Cl) was selected as the surfactant because its long hydrocarbon tail and cationic head exhibit ideal characteristics for this sorption study. The cationic head can adsorb to the zeolite surface, while the hydrocarbon tail is capable of absorbing organic molecules. Dependent upon the counterion on the head group, HDTMA is available in many forms; the form used in this study was balanced with chloride. HDTMA's chemical formula is $N(CH_3)_3Cl_6H_{33}$. The critical micelle concentration of HDTMA is 0.9 mmol/L. HDTMA-Cl (25%w in water) surfactant was obtained from Aldrich (Milwaukee, WI).

The preparation of SMZ involves mixing an HDTMA solution and zeolite for several hours, followed by a series of washings with ultrapure water. Ultrapure water was prepared by a filtration system water using a Milli-Q system, Millipore Corp., Bedford, MA. Detailed procedures describing the SMZ preparation procedure are described in Tan (2002). The expected HDTMA sorption capacity was 200 mmol/kg (Li, 1999).

2.1.2 Produced Water

This study focused on the sorption of the primary organic and metal components found in produced water from a collection facility in Wyoming. Of interest were BTEX, phenols, naphthalenes, barium, chromate, and selenate. Primary interest was focused on BTEX, as these compounds are known to be hazardous (Fucik, 1992). The sorption of the semi-volatile compounds phenol and naphthalene, as well as their methylated relatives, were studied to see how they affected BTEX sorption. The average concentrations of the semi-volatile concentrations found in the produced water from Wyoming is listed in Table 2.1.

Table 2.1 – Concentrations of seim-volatile compounds found in the produced water from Wyoming. (μg/L)

compound	concentration
phenol	1573.5
2-methylphenol	1395
4-methylphenol	836
2,4-dimethylphenol	809
naphthalene	291.6
2-methylnaphthalene	438.5

Benzene and ortho-xylene were obtained from J. T. Baker (Phillipsburg, NJ). Toluene was obtained from EM Science (Gibbstown, NJ), ethylbenzene from Mallinckrodt Chemical Inc. (Paris, KY), meta-xylene from Aldrich (Milwaukee, WI), and para-xylene from Fisher Scientific (Fairlawn, NJ). All chemicals were of 99% purity or greater. Their chemical formulas, molecular weight, and water solubilities (25^{o}C, 1 atm) are reported in Table 2.2.

Table 2.2 – BTEX chemical formulas, molecular weights, solubilities, Henry's constants, and K_{ow}s.[1]

	Benzene	Toluene	m-Xylene	p-Xylene	o-Xylene	Ethyl-benzene
Chemical formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}
Molecular Weight (g/mole)	78	92	106	106	106	106
Water Solubility at 25°C (log M)	-1.66	-2.14	-2.72	-2.72	-2.79	-3.03
Henry's Constant (M/atm)	0.18	0.15	0.16	0.16	0.29	0.17
log K_{ow} at 20°C (L octanol/ L water)	2.13	2.69	3.20	3.15	3.12	3.15

[1] Lide et al. (1994)

Table 2.3 lists the semi-volatile compounds found in a sample of produced water from Wyoming. These compounds were selected to represent the semi-volatile components in the synthetic produced water. Phenol, 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, naphthalene, and 2-methylnaphthalene were purchased in solid form from Aldrich (Milwaukee, WI). The molecular weight, pKa, and solubility of each species are shown in Table 2.4.

The only metals found above detection limits in the produced water from Wyoming were barium and selenium. Chromium was also selected for analysis because it is frequently reported to be found in produced water. These metals were chosen for sorption analysis.

Table 2.3 – Approximate semi-volatile concentrations in a sample of produced water (μg/L)

Compound	concentration
Phenol	2383
2-Methylphenol	1440
4-Methylphenol	672
2,4-Dimethylphenol	802
Naphthalene	419.2
2-Methylnaphthalene	717

Table 2.4 – Chemical formulas, molecular weights, pKas, water solubilites, Henry's constants, and log K_{ow}s of the semi-volatiles used in this study.[1]

	phenol	**2-methyl phenol**	**4-methyl phenol**	**2,4-dimethyl phenol**	**naphthalene**	**2-methyl naphthalene**
chemical formula	C_6H_6O	C_7H_8O	C_7H_8O	$C_8H_{10}O$	$C_{10}H_8$	$C_{11}H_{10}$
molecular weight	94	108	108	122	128	142
pKa	9.99	10.3	10.26	10.6	NA	NA
Water Solubility at 25°C (log M)	-0.03	-0.54	-0.67	-1.19	-3.63	-3.68
Henry's Constant (M/atm)	2000	830	1000	410	2.1	2
log K_{ow} at 20°C (L octanol/ L water)	1.48	1.96	1.96	2.30	3.37	4.37

[1] Lide et al. (1994)

A series of separate metal salt solutions were prepared using barium chloride and potassium chromate from MCB Reagents (Cincinnati, OH) and sodium selenate-decahydrate from Aldrich (Milwaukee, WI). Metals standards for ICP analysis were prepared with standards purchased form Fisher Scientific (Fairlawn, NJ). Barium chloride, potassium dichromate, and selenium dioxide were all initially at 1000 ppm.

2.1.3 Background Water Components

Background water was prepared to mimic the saline produced water from Wyoming. Total ion concentrations were used to select appropriate salts that cumulatively would approximately equal the same ion concentrations as the actual produced water; thus mimicking the ionic strength. Six anhydrous salt compounds were used to prepare this solution. Sodium bicarbonate and sodium carbonate were obtained from Fisher Scientific (Fairlawn, NJ). Potassium bromide was obtained from J. T. Baker (Phillipsburg, NJ), calcium chloride from MCB Reagents (Cincinnati, OH), sodium chloride from Mallinckrodt Chemical Inc. (Paris, KY), and sodium sulfate from EM Science (Gibbstown, NJ). Sodium sulfate was also used as a drying agent in aqueous semi-volatile extractions. The preparation of this synthetic salt solution is described in detail later.

2.1.4 Other Chemical Components

Potassium phosphate (mono and dihydrate) was used to buffer organic experiments at pHs typical of produced water. Both were obtained from J. T. Baker (Phillipsburg, NJ).

Methanol and dichloromethane were used as solvents and rinsing agents. These solvents were used to prepare stock solutions of organic compounds, internal standards, and surrogate compounds. Both were purchased in HPLC grade from EM Science (Gibbstown, NJ).

Many variables can occur when using complicated analytical equipment. Some of these variables are the result of the equipment itself, and cannot be mitigated by the researcher. Instead of trying to resolve these problems, internal standards are used to measure the variables and account for them in the analysis.

An internal standard was used during gas chromatography flame ionization detection analyses of BTEX compounds. The internal standard was α,α,α- (TFT) purchased from Restek Corption at an initial concentration of 2500 ug/mL in methanol.

Six semi-volatile surrogate compounds were used to evaluate the effectiveness of semi-volatile extractions from aqueous solution. All were purchased solvated in dichloromethane from Supelco (Bellafonte, PA). The acidic surrogates 2-flurophenol, d6-phenol, and tribromophenol were used to quantify phenol extractions. The base/neutral compounds d10-nitrobenzene, 2-flurobyphenyl, and d12-terphenyl were used to quantify naphthalene extractions.

A six component semi-volatile mix obtained from Supelco (Bellafonte, PA) was used as an internal standard for gas chromatography mass spectrometry analysis. The semi-volatile internal standard (SVIS) mix was solvated in methanol and included d4-dicholorbenzene, d8-naphthalene, d10-acenaphthalene, d10-phenanthrene, d12-chrysene, and d12-perylene.

The metal standards, barium chloride, potassium dichromate, and selenium dioxide, were purchased from Fisher Scientific (Fairlawn, NJ). Scandium carbonate, purchased from Fisher Scientific (Fairlawn, NJ), was used as an internal standard for all metal analysis.

2.1.5 Analytical Methods

2.1.5.1 Produced Water Characterization Methods

The water obtained from Crystal Solutions, LLC located near Wamsutter, Wyoming was used during this study to characterize produced water. This produced water was not used in any experiments in this research; it was only analyzed so that an accurate synthetic water could be prepared. Crystal Solutions is located in the Red Desert near a large natural gas reservoir. Water is collected throughout the region and transported to Crystal Solutions in tanker trucks. The water is pumped through two oil/water separation tanks connected in series. Oil is separated from the top of the two tanks and further processed to recover oil. The denser water is sent to lined evaporation ponds to reduce volume. Water was collected in December 2002 in 55 gallon drums and preserved at 4ºC. Samples were taken after the oil/water separation tanks and prior to the evaporation ponds. This water was taken back to New Mexico where samples were then sent to the University of Texas at Austin in the summer of 2003. Analyses were preformed both in New Mexico and Austin to characterize the water.

Major ion concentrations were determined by the New Mexico Bureau of Geology. Cation concentrations were determined by flame absorption spectroscopy (EPA method 200.0). Anion concentrations were measured by ion chromatography (EPA method 300.0). This information was used to prepare the background synthetic salt water discussed earlier. A summary of these ion concentrations, as well as those in the synthetic water, are listed in Table 2.5. The ionic strength of the Wyoming water was calculated to be 0.183 M. The ionic strength of the synthetic water at pH 7.2 was 0.179 M.

Table 2.5 – Major ion composition in produced water from Wamsutter, Wyoming

Analyte	**Wyoming water concentration** (mg/L)	**synthetic water concentration** (mg/L)
HCO_3^-	3120	3129
Cl^-	4400	4373
Na^+	4100	4051
Br^-	22	90
F^-	57	0
SO_4^{2-}	13	13
K^+	44	44
Mg^{2+}	6	0
Ca^{2+}	30	30

2.1.5.2 BTEX Analysis

BTEX concentrations in the aqueous phase were measured using a gas chromatograph (GC) equipped with a flame-ionization detector. A headspace autosampler was used to analyze the vapor phase of each sample. An eleven point standard curve was made for each compound.

The volatility of BTEX compounds complicates experimental and analytical procedures when water is used as the solvent. Using an organic solvent such as methanol helps to overcome these difficulties by reducing BTEXs' tendency to leave solution. A series of highly concentrated BTEX stock solutions in methanol were used in the preparation of standard curve and batch samples. An initial BTEX solution was made by adding required amount of each chemical to make a 10 g/L stock in methanol. This volume was corrected for density and purity using Equation 2.1.

$$X = \frac{CVP}{\rho} \qquad (2.1)$$

where:
X = volume of BTEX compound required to reach desired concentration (mL)
C = desired concentration (g/L)
V = total volume of final solution (L)
P = purity of BTEX compounds in decimal form
ρ = density of pure BTEX compound (g/mL)

Serial dilutions of 1, 0.2, 0.03, 0.003 g/L were made using glass volumetric pipettes and flasks. The bulk solutions were transferred to 2 mL vials using Pasteur pipettes and were immediately crimped shut with PTFE septa, labeled, and stored in a -18^{o}C freezer.

Standard curves samples were prepared in 22 mL headspace vials (Agilent Technologies; HP5182-0837) by using a 5 mL volumetric pipette to fill each vial with 5 mL of water. Vials were loosely capped to minimize evaporation until BTEX stock solutions were added using gastight syringes. Volumes of the appropriate stock solutions were calculated using Equation 2.2. To avoid co-solvency effects, the amount of methanol in aqueous solutions was kept below 1% by volume (Pinal et al., 1990). Vials were then closed using aluminum crimp caps fitted with PTFE/black butyl rubber septa (Agilent Technologies, HP9301-0976).

$$V_{add} = \frac{C_{final} V_{H_2O}}{C_{final} - C_{stock}} * 10^{-6} \, \mu g / g \tag{3.2}$$

where:
V_{add} = volume of stock solution required (μL)
C_{final} = final aqueous concentration BTEX (g/L)
V_{H20} = volume water (L)
C_{stock} = concentration of stock solution (g/L)

After each vial was prepared, an internal standard was added. The internal standard was used to account for variability in the instrumental apparatus and any volatilization through the septa. α,α,α-Trifluorotoluene (TFT) was used because it eluted from the GC between the benzene and toluene peaks. Each 5 mL vial was injected with 250 μL to yield an internal standard concentration of 1250 μg/L.

The flame-ionization detector becomes saturated for compound concentrations greater than 1500 μg/L. Therefore, the highest standard of each BTEX compound was 1500 μg/L. Eleven standards, prepared in triplicate, were used for every compound in each matrix.

A Tekmar 7000 Headspace Autosampler (HAS) was used for extracting BTEX from the samples. Samples were heated in the HAS to 80ºC and allowed to equilibrate for 15 minutes. This was followed by 10 minutes of mixing, 1 minute of pressurization, 0.25 minutes for pressure equilibration, 1 minute of sample loop filling, and 0.25 minutes for loop equilibration. The 1-mL sample loop was maintained at 170°C to prevent condensation. The sample GC transfer line was also maintained at 170°C. Helium, flowing at 1 mL/min was used as a carrier gas.

A Hewlett-Packard 5890 gas chromatograph fitted with a 30 m Restek capillary column (RTX-624; ID 0.53; DF 3.0) was used to analyze BTEX. The temperature ramping program consisted of an initial oven temperature of 40°C for 1 minute followed by an increase of 20°C/min until 85°C. The oven temperature was then increased at a rate of 0.5°C/min and held at 90°C for 1 minute. The injector temperature was maintained at

250°C and the flame-ionization detector (FID) at 275°C. Helium, flowing at 36 mL/min was used as an inert carrier gas. Hydrogen gas and ambient air with moisture and hydrocarbon traps were used to fuel the FID.

Results were analyzed with EZChrom Chromatography Data System v6.5 (Scientific Software, Inc., San Ramon, CA; (510) 244-6622). The ratio of the amount of BTEX detected to the amount of TFT detected was used to generate the standard curves. The elution times for each BTEX compound and TFT are reported in Table 2.6.

Table 2.6 – BTEX retention times for GC method used in this study.

Compound	Peak Retention Times minutes, (± 0.01)
Benzene	2.89
α,α,α-Trifluorotoluene	3.47
Toluene	4.19
Ethylbenzene	6.03
p- & m-Xylenes	6.25
o-Xylene	6.99

2.1.5.3 Semi-volatiles Analysis

Mass spectrometry was used to measure semi-volatile compounds using EPA Methods 8720C (Semi-Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)). A Hewlett Packard HP5890 gas chromatograph with an OI Analytical 4430 photo ionization detector was used to quantify the semi-volatile concentrations. Due to limitations of the optic equipment, this procedure required aqueous semi-volatiles to be extracted into dichloromethane. The extraction procedure was adapted from EPA method 3510-C (Separatory Funnel Liquid/Liquid Extraction).

Stock solutions of the six semi-volatile chemicals were made in both methanol and dichloromethane. A 10 g/L solution was made by adding approximately 1 g of each chemical to 100 mL solvent. Serial dilutions were prepared so that sample concentrations could be prepared over several orders of magnitude.

An additional solution was prepared of each chemical in methanol at concentrations typical of produced water. The concentrations were representative of samples collected during the summer 2002 study and those collected in December 2002. The concentrations of these two samples were averaged and rounded to the nearest 250 µg/L. The compounds and their respective approximate concentrations are shown in Table 2.7.

Table 2.7 –Average semi-volatile composition of produced water from Wamsutter, Wyoming.

compound	Approximate concentration (µg/L)
phenol	1500
2-methylphenol	1500
4-methylphenol	1000
2,4-dimethylphenol	1000
naphthalene	250
2-methylnaphthalene	500

The acid and base/neutral surrogate compounds were combined and diluted to make 5 and 50 mg/L stock solutions in dichloromethane. An additional 20 mg/L solution of all six surrogates was made in methanol to help evaluate semi-volatile extraction efficiency.

Standard curves were made using 1 mL dichloromethane samples containing all eighteen semi-volatile compounds used in this study. The amount of each stock solution necessary to prepare each 1 mL solution was calculated by Equation 2.3.

$$V_{add} = \frac{V_{final} C_{final}}{C_{add}} \tag{2.3}$$

V_{add} = volume stock solution to add (mL)
V_{add} = volume final solution (mL)
C_{final} = final concentration (mg/L)
C_{add} = stock solution concentration (mg/L)

The required dichloromethane needed to make these exact concentrations was found by subtracted the three stock addition volumes from 1 mL. All components were combined in 2 mL vials with PTFE lined screw caps and closed.

The GC-MS quantification was controlled by EnviroQuant Chemstation software (G1701BA version B.01.00). The initial oven temperature was held at 45ºC for four minutes, and then increased at 15ºC/min to 175ºC, 20ºC/min to 250ºC, and 30ºC to 310ºC. The temperature maintained at 310ºC for approximately 8.5 minutes until the run was completed. Helium was used as the carrier gas at 8.8 mL/min. Due to variability in the GC-MS measurements, each sample was analyzed three times an averaged to reduce error.

2.1.5.4 Batch Experiments of Organic Compounds

Batch experiments using semi-volatile species were always conducted in the presence of BTEX, and therefore preparation was similar to that of BTEX experiments. After 24 hours of tumbling with SMZ and 5 mL water, a constant amount of the synthetic stock solution of phenols and naphthalenes was added to each 22 mL vial prior to any BTEX addition. To account for this additional volume, vials were filled with slightly less water prior to any organic additions. After BTEX was added, the vials were sealed and then tumbled for 24 hours.

The EPA extraction method was altered to apply to a smaller sample volume. The method required 1 L of sample, but due to material limitations only 35 mL of water was used. A comparable water/dichloromethane ratio was maintained. 35 mL of sample was transferred to a 40 mL VOA vial. 110 µL of surrogate solution was added to each sample. The pH was then lowered below 2 by adding 1 mL of 20% sulfuric acid.

After adding 2 mL of dichloromethane to each VOA vial, they were shaken vigorously by hand for two minutes. The denser dichloromethane was then removed with a glass Pasteur pipette and transferred to a 6 mL vial. The 6 mL vials were then sealed with a PTFE lined screw cap. This process was repeated twice; once with 2 mL dichloromethane and once with 1 mL dichloromethane. Any water that solvated into the dichloromethane was removed by adding approximately 0.5 g of sodium sulfate to each 6 mL vial. One mL of each sample was then transferred to 2 mL vials. Before sealing with a PTFE lined cap, 5 µL of SVIS was added to make a 1 mg/L concentration.

After achieving low phenol recovery rates, the water/dichloromethane extraction ratio was decreased from 7:1 to 3:1 to increase recovery efficiency. 30 mL of sample was extracted with five, five and then four mL dichloromethane. Although this was a higher ratio than the EPA method used, better results were obtained.

The produced water from Wyoming had a pH of 7.2. Organic experiments performed at that pH had to be buffered to keep the pH constant. 1 M solutions of monohydrate and dihydrate potassium phosphate were used to keep the pH stable at 7.2.

Sorption experiments were also conducted at several pH units above the pKas of the phenol species. This was done to investigate how these chemicals bind to the SMZ. Instead of buffering the experiment, the pH was initially raised to 12.4 using 5 M sodium hydroxide.

Although semi-volatile isotherm experiments were not conducted, the effects of semi-volatile concentrations on BTEX adsorption were investigated. Two experiments were conducted with multiples of initial semi-volatile concentrations.

2.1.5.5 Batch Experiments of Metal Ion Sorption

Inductively Coupled Plasma (ICP) Emisson Spectroscopy was used to quantify metal concentrations by measuring specific light wavelengths. The advantage of using this instrument is that it is linear over large ranges of concentrations for most compounds. Each metal could also be measured at multiple wavelengths simultaneously. All samples were analyzed with a SPECTRO CIROS ICP spectrometer according to EPA Method 200.7.

All experiments were conducted inside an nitrogen atmosphere controlled glove box.and all water was purged of carbon dioxide prior to use. One molar stock solutions were of each metal ion was initially prepared with barium chloride, potassium chromate, and sodium selenate. Each solution was made with chemicals that had been dried in a 110°C oven overnight. Each one molar solution was then used to make dilutions of 100, 10, and 1 mM solutions.

Standard curve solutions were prepared in a 2% nitric acid background. A 1 mg/L scandium solution prepared in a 2% nitric acid background served as an internal standard. Argon as a carrier gas. The autosampler was programmed to flush the system with 2% nitric acid for 80 seconds between each run.

Batch experiments were conducted in 40 mL PTFE-lined centrifuged tubes. First 3 g of SMZ (or virgin zeolite) was added to each tube. The required amount of stock solution required to achieve the desired concentration was d added with the required amount of carbon dioxide free water to fill the tube to 30 mL. The pH was then adjusted with varying concentrations of sodium hydroxide, hydrochloric acid, and nitric acid. Vials were then tumbled at 11 rpm. The pH of each vial was checked every two hours and altered if necessary before returning to the tumbler. After 24 hours, all tubes were centrifuged at 11,000 rpm for 10 minutes. 15 mL of each sample was transferred to a 15 mL centrifuge tube. The pH was lowered by 0.436 mL 70% environmental grade nitric acid. This made each sample equivalent to the 2% nitric acid standard solution background.

To obtain a pH edge, initial concentrations were set at 1.8 μM. An attempt was made to keep each vial's pH one unit apart from the next in the range of pH from 4 to 10 (typical of produced waters.

Isotherms were generated by starting with a set of samples with initial concentrations ranging over several orders of magnitude. The pH was kept to within 0.05 unit of 7.20 by using the acids and bases mentioned previously.

2.2 Vapor Phase Bioreactors

The experimental reactor consists of a 11.75 L biofilter packed with polyurethane foam that was inoculated with a BTEX-degrading microbial consortium (see Figure 1). Inoculation of the biofilter was accomplished by recirculating a BTEX-degrading microbial culture through the bioreactor packing material for 12 hours. The inoculating solution was then drained from the column and the VOC feed to the biofilter was started. The design empty bed contact time for the gas phase was one minute and the total inlet BTEX concentration for the experiments was 130 ppm_v (Benzene 12, Toluene 24, Ethyl Benzene 32, p&m-xylene 22, o-xylene 40 ppm_v). The BTEX contaminants were injected into a small slip air stream using a syringe pump. This contaminated air was mixed with humidified air in a mixing chamber prior to being introduced to the top of the biofilter. Twice a day, a modified hydrocarbon minimal medium was supplied as an external nutrient source to the biofilter via a nutrient spray system. 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 $(NH_4)_2SO_4$, 10.1g/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 $NiCl_2{\cdot}6H_2O$. The HCMM in the biofilter was replaced every 3 days with fresh solution. In the early stages of biofilter operation, the nutrient spray system inhibited the attachment of biomass to the first section of the packing material. To remedy this problem, the foam packing material in the biofilter was removed, completely mixed and then returned to the biofilter column on Day 60. Fine steel mesh was also placed on top of the column-packing material at this time to reduce the impact of the nutrient spray on the packing and to prevent the wash out of biomass from the column.

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 distribution of biomass along the column, packing materials containing attached biomass 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 COD of the biomass removed was determined via a colorimetric method in Standard Methods (APHA et al., 1992). The liquid ammonium concentration was 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.

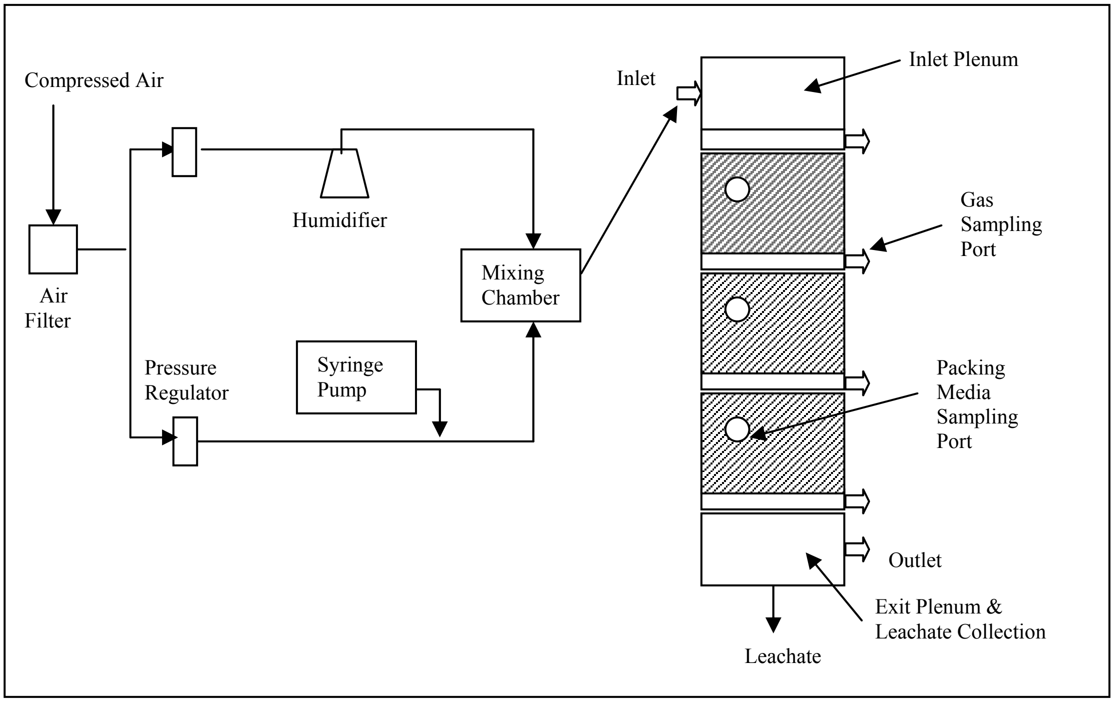

Figure 2.1. – Schematic diagram of experimental vapor phase biofilter design

3. Results and Discussion

3.1 Interaction of BTEX, Semi-volatile Organic Compounds, and SMZ

A number of BTEX isotherm experiments were conducted to evaluate BTEX sorption to SMZ as a function of solution chemistry. Our previous work evaluated the impact of salinity, temperature, and the presence of other BTEX components on sorption capacity. The focus of this phase of the research project was to evaluate effect of semi-volatile compounds and pH on BTEX sorption.

3.1.1 BTEX Isotherms and Comparisons with Previous Studies

Preliminary experiments were conducted in saline water in the absence of semi-volatile components to serve as a baseline for comparison to experiments conducted in the presence of semi-volatile compounds. These experiments were conducted by adding varying amounts of a multi-solute BTEX solution and a constant SMZ mass to water containing approximately 11,000 mg/L TDS and equilibrating the samples for 24 hours. Our previous results showed that the presence of other BTEX components had no impact on the sorption of benzene or toluene. Figure 3.1 shows the results of the multi-solute batch sorption experiments conducted in the synthetic salt solution. Regressions of the data were conducted assuming that the isotherms were linear. As a result, the data for the highest concentration (highest Ce value) dominates the regression statistics. This is evident in the plot shown in Figure 3.1 as the regression lines only pass through the highest data point for each compound . This behavior is often observed for linear isotherms with volatile compounds when the error in the data is not uniform across the concentration range (i.e. losses are greater for higher aqueous concentrations). In some cases, it is possible to weight the error by performing log regressions using the Equation 3.1.

$$\log q = \log C_e + \log K_D \qquad (3.1)$$

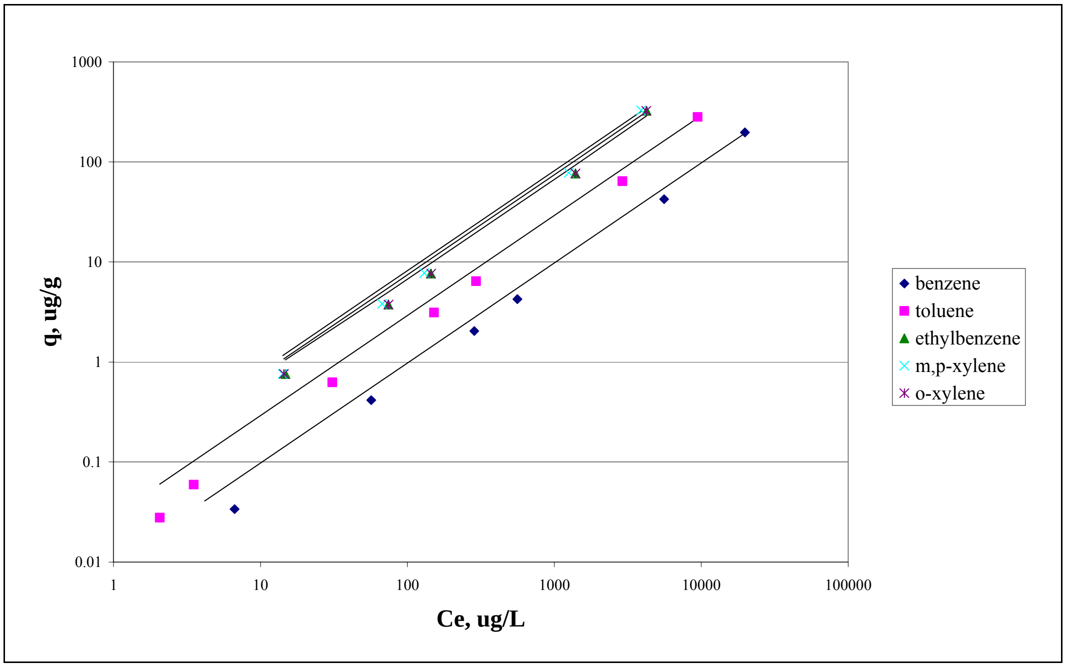

Figure 3.1 – BTEX isotherms in synthetic salt solution.

A log regression was performed on the benzene data generated in this study. The results of this regression are compared to the benzene data obtained in this period of work as well as previous single-solute data in a saline solution containing 30,000 mg/L TDS (Gupta, 2001) in Figure 3.2. Comparison of regressions of the data collected in this period suggested that the log regression fits the data better over the entire concentration range. However, to ensure that isotherms collected in this study were consistent with previous results, K_D values and hypothesis testing were conducted using linear regression. It should be noted that the K_D values obtained using data from previous results (Gupta,2001) did not show significant differences between the two regression techniques.

K_D values obtained from linear regressions of data collected in this experiment and previous work (Gupta, 2001) are shown in Table 3.1. The data from previous work was collected in multi-solute BTEX sorption experiments in ultrapure water. Ionic strength effects in this range of salinities (i.e., less than 30,000 ppm) did not affect BTEX sorption.

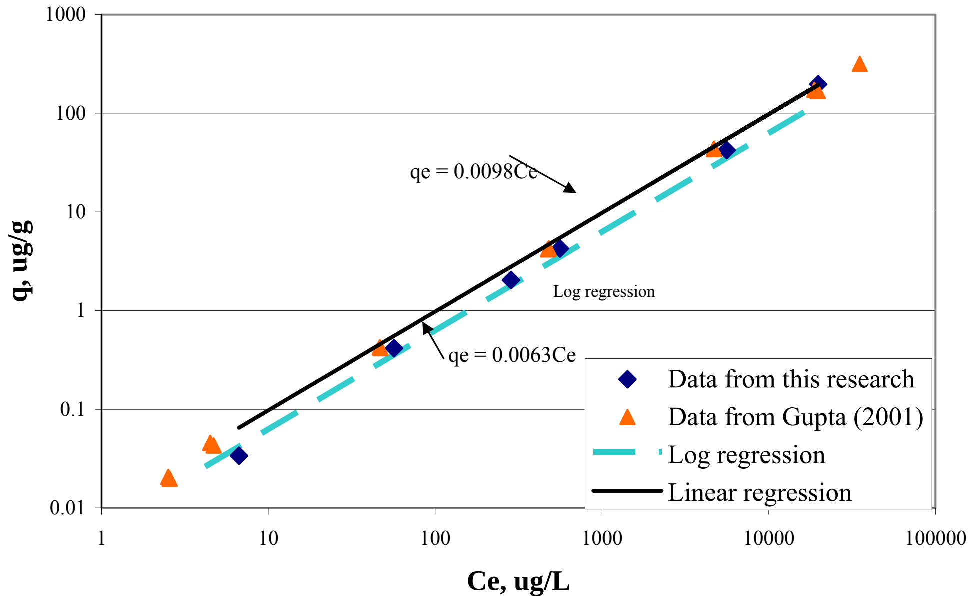

Figure 3.2 – Comparison of regression techniques for benzene sorption in synthetic salt solutions. Data from previous work (Gupta, 2001) provided for reference, but the regressions were performed on data from the current research study only.

Table 3.1 – Comparison of K_D values from this study with those from previous work (Gupta, 2001). Units of K_D are L/g. (Previous data represents batch studies conducted in Millipore water)

compound	**this study**	**R^2**	**Gupta (2001)**	**R^2**
benzene	0.00977	0.9947	0.00982	0.9993
toluene	0.0291	0.9925	0.0270	1.000
ethylbenzene	0.0741	0.9890	0.0692	0.9999
m,p-xylene	0.0818	0.9906	0.0749	0.9999
o-xylene	0.0744	0.9882	0.0664	1.000

compound	**95% confidence limits on slope**	**95% confidence limits on slope**
benzene	0.00921, 0.0103	0.00968, 0.0101
toluene	0.0272, 0.0311	0.0270, 0.0271
ethylbenzene	0.0729, 0.0754	0.0687, 0.0692
m,p-xylene	0.0802, 0.0831	0.0745, 0.0752
o-xylene	0.0731, 0.0758	0.0659, 0.0669

Comparison of the K_D values suggests that the results from our current research are consistent with previous research, although, the 95% confidence limits on K_D values obtained from this experiment were larger than those reported in our previous work. The larger confidence limits are partially the result of the relatively fewer number of samples used in this study. Due to the large sample volume required for semi-volatile extractions required in subsequent isotherms experiments, only one sample was taken for each BTEX batch sample analysis. Although the 95% confidence limits do not overlap for ethylbenzene and xylene, the K_D values should appear similar as shown in Figure 3.3 in which data collected in this research is compared to data collected from previous work. The data collected previously and shown in this figure were conducted in water containing 30,000 mg/L TDS.

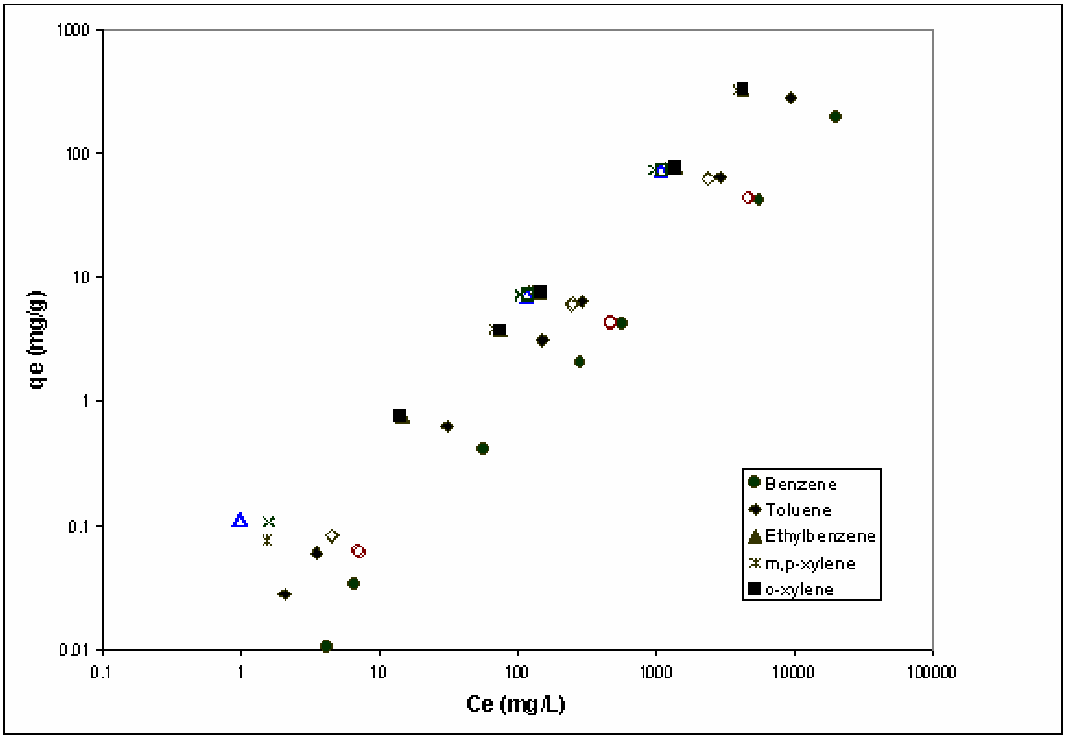

Figure 3.3 – Comparison of BTEX isotherms collected in this research and in previous research (open symbols represent corresponding data collected previously in water containing 30,000 ppm TDS).

The similarities between the data collected in ultrapure water and saline water suggest that the differences between these experiments should reflect the level of error expected between any two experiments. Thus, statistical comparison of these experiments was used to determine the level of confidence to be used in subsequent comparisons of experiments. Specifically, hypothesis testing was used to determine the confidence level where each compound's K_D value was not statistically different between data sets collected previously and data sets collected in this current work. The null hypothesis for comparing the isotherms was that the isotherms are parallel. Since the isotherms are linear and forced to pass through zero, testing for parallelism and coincidence are the same. The T-statistics comparing the K_D values from this and previous reaults are shown in Table 3.2. The null hypothesis that the isotherms are parallel was tested at a 95% confidence level. In some cases, the isotherms were not parallel (the null hypothesis was rejected) at the 95% confidence level. Since the assumption is that these isotherms should be coincident, the level of confidence required to achieve coincidence was calculated for each compound.

Table 3.3 lists the confidence levels required to accept the null hypothesis (the two isotherms are parallel). These levels of confidence establish coincidence between experiments that are believed to be similar. The high required levels of confidence are indications of error in analysis; the lower regression coefficients in this study also reflect this conclusion. The results of the hypothesis testing suggest that using a 95% confidence level for comparing data between experiments would often lead to Type I error in which the null hypothesis would be rejected when the data are not different. However, the data also suggest that selecting a value that is too high (such as that required for concluding that the xylene isotherms are the same) would increase the likelihood of Type II error (concluding that the isotherms are not different when they are truly different). Thus, a compromise was made and subsequent hypothesis testing was performed using a 99.5% confidence level to compare isotherms collected under different experimental conditions.

Table 3.2 – Results for hypothesis testing at of isotherms generated in this research versus those in previous work.

compound	**T-value**	**Result for Null Hypothesis at 95% confidence level**
benzene	-0.19	Valid: isotherm slopes are the same
toluene	4.04	Invalid: isotherm slopes are not the same
ethylbenzene	4.34	Invalid: isotherm slopes are not the same
m,p-xylene	5.69	Invalid: isotherm slopes are not the same
o-xylene	7.32	Invalid: isotherm slopes are not the same

Table 3.3 – Necessary confidence levels to prove isotherm parallelism for isotherms collected in this research versus those from previous work.

compound	**confidence level**
benzene	14.60%
toluene	99.63%
ethylbenzene	99.75%
m,p-xylene	99.95%
o-xylene	99.99%

3.1.2 BTEX With Semi-Volatile Compounds

BTEX sorption experiments were conducted in the presence of a number of semi-volatile compounds identified in produced water to determine whether the presence of these compounds was responsible for field observations suggesting an increase in BTEX sorption after regeneration. The semi-volatile compounds listed in Table 3.2 were added to the synthetic saline water used for the BTEX studies described above. The synthetic water composition was based on analyses of produced water from Wyoming that were conducted in the summers of 2002 and 2003. In addition, water containing higher concentrations (approximately double) of these semi-volatile compounds was also prepared and used to evaluate its impact on BTEX sorption. A summary of the concentrations of the semi-volatile compounds used to evaluate BTEX sorption in the presence of synthetically prepared produced water is presented in Table 3.4.

Table 3.4 – Initial semi-volatile concentrations (µg/L) added to synthetic water

compound	synthetic water	concentrated synthetic water
phenol	1586	3172
2-methylphenol	1593	3186
4-methylphenol	1076	2152
2,4-dimethylphenol	1071	2142
naphthalene	273	546
2-methylnaphthalene	629	1258

3.1.2.1 pH effects

Experiments conducted with the synthetic water containing the semi-volatile compounds were designed to determine whether BTEX sorption to SMZ is affected by the presence of the semi-volatile compounds and to determine whether there was an effect of pH on BTEX sorption in the semi-volatile, saline background water. Three experiments were conducted at three different pH values. pH was altered primarily for semi-volatile analysis, as no significant differences were expected in BTEX sorption. The first experiment was measured to have an equilibrium pH of 10.2 (Figure 3.5). The pH in the second experiment was maintained near 7.2 with a phosphate buffer (Figure 3.4). In the third experiment, the pH was raised to 12.4 with concentrated sodium hydroxide (Figure 3.6). The equilibrium pH after 24 hours was 12.2. K_D values for these experiments are shown in Table 3.5.

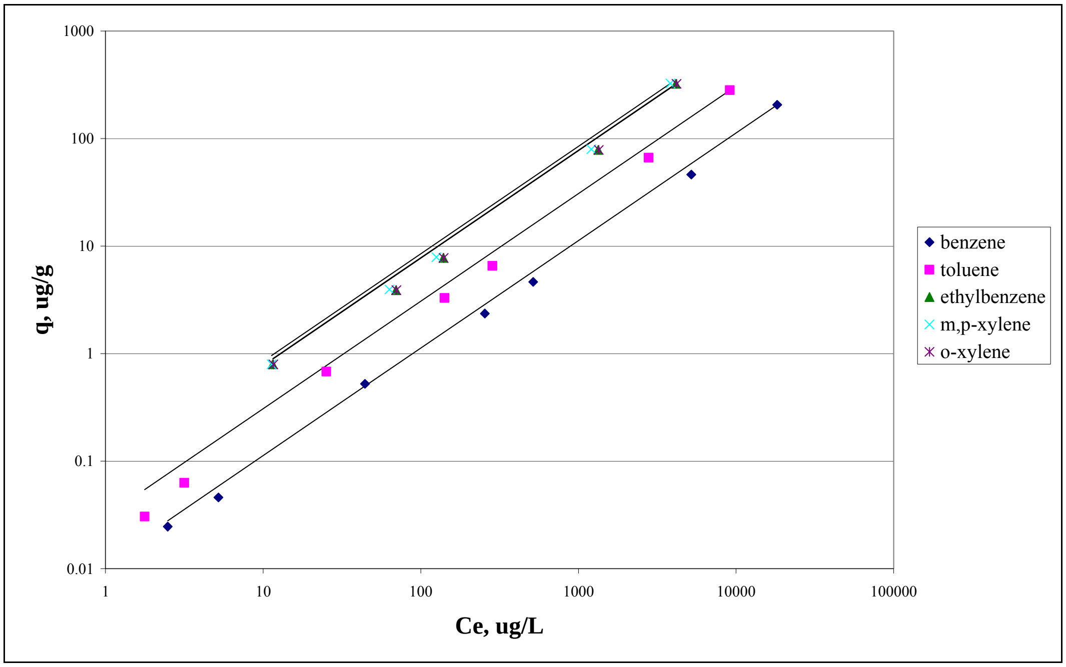

Figure 3.4 – BTEX isotherms in salt water buffered at pH 7.2.

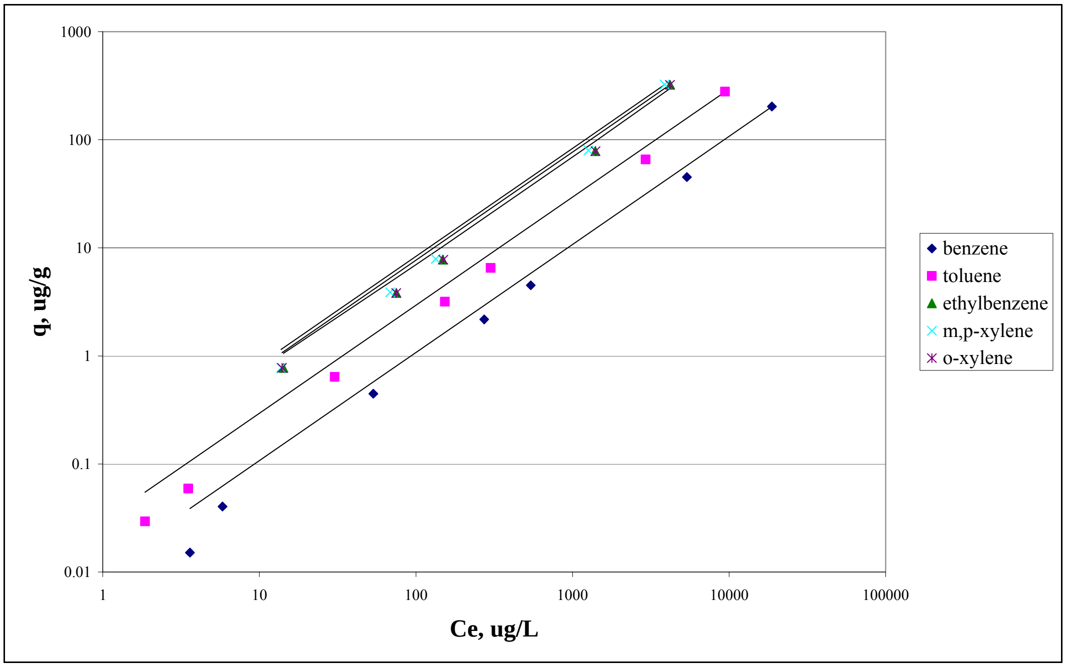

Figure 3.5 – BTEX isotherms in salt water at pH 10.2.

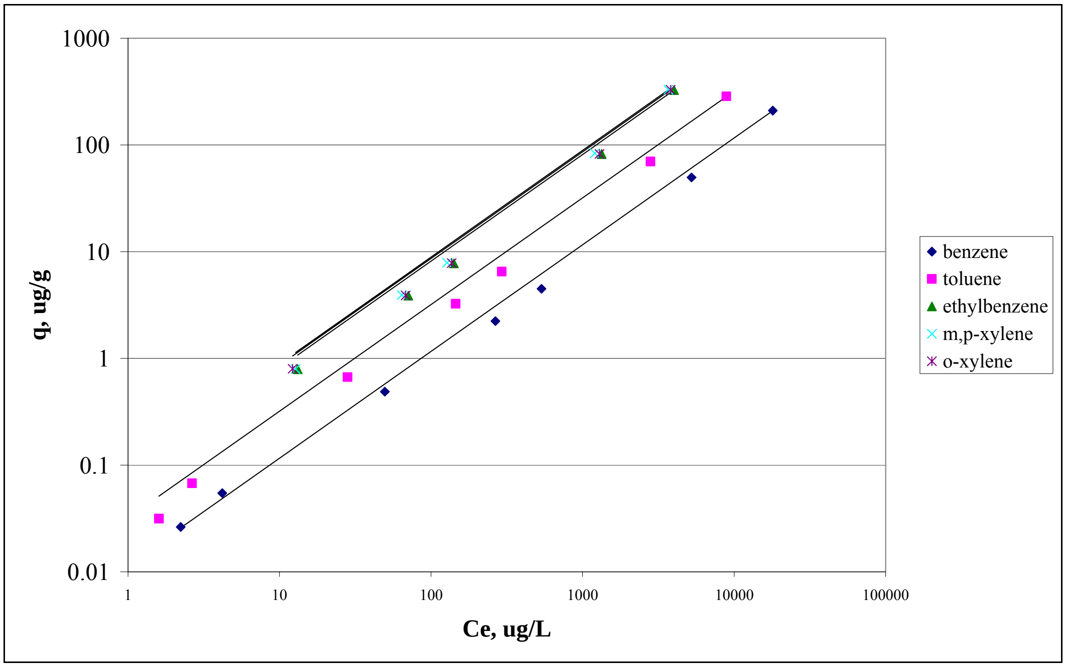

Figure 3.6 – BTEX isotherms in salt water at pH 12.2.

Table 3.5 – Comparison of K_D values at various pHs in the presence of semi-volatiles in synthetic salt water. Units of K_D are L/g.

compound	pH 7.2	R^2	pH 10.2	R^2	pH 12.2	R^2
benzene	0.0112	0.9956	0.0108	0.9952	0.0116	0.9964
toluene	0.0307	0.9942	0.0294	0.9932	0.0310	0.9940
ethyl-benzene	0.0778	0.9916	0.0768	0.9891	0.0806	0.9913
m,p-xylene	0.0846	0.9937	0.0834	0.9919	0.0862	0.9933
o-xylene	0.0770	0.9916	0.0769	0.9888	0.0814	0.9896

compound	95% confidence limits on slope	95% confidence limits on slope	95% confidence limits on slope
benzene	0.0107, 0.0118	0.0102, 0.0113	0.0111, 0.0122
toluene	0.0289, 0.0325	0.0276, 0.0313	0.0291, 0.0329
ethyl-benzene	0.0767, 0.0790	0.0756, 0.0781	0.0794, 0.0818
m,p-xylene	0.0835, 0.0857	0.0821, 0.0846	0.0850, 0.0873
o-xylene	0.0759, 0.0781	0.0757, 0.0782	0.0800, 0.0827

No major differences in sorption were observed for benzene and toluene over the entire pH range tested. As shown in Table 3.5, the slopes of the benzene and toluene isotherms are similar for the three pH values. No trends are apparent in the values of K_D as a function of pH, and the 95% confidence limits overlap for all three experiments. In contrast, greater variation in the K_D values was observed for ethylbenzene and the xylenes. K_D values decreased slightly between pH 7.2 and 10.2, and increased between pH 10.2 and 12.2. 95% confidence limits overlapped for pH values 7.2 and 10.2, but did not for pH values 10.2 and 12.2. The similarity in these trends among the more hydrophobic compounds could be related to the fact that the data were collected in a multi-solute experiment in which a data point for each compound is collected from a single isotherm vial. Losses from a vial should be similar for all of the compounds with similar chemical properties.

One potential explanation for the increase in sorption between pH 10.2 and 12.2 for these more volatile compounds could be the increase in ionic strength caused by addition of base to increase the pH. Table 3.6 lists the approximate ionic strength values for experiments conducted at each pH value. However, our previous work suggested that even at salt concentrations of 30,000 ppm (an ionic strength of approximately 0.53 M), no statistical differences between K_D slopes were observed for any BTEX compound.

Table 3.6 – Approximate ionic strengths of all waters used in pH experiments (M)

pH 7.2	pH 10.2	pH 12.2
0.2	0.26	0.3

Hypothesis testing was performed to further evaluate the significance of the observed differences between isotherm slopes determined as a function of pH. Table 3.7 shows the result of hypothesis testing at a 99.5% confidence level. All benzene, toluene, and m,p-xylene isotherms were determined to be parallel. The isotherm collected for ethylbenzene at pH 7.2 was found to be parallel to ethylbenzene isotherm data collected at pH 10.2 and 12.2, but the pH 10.2 and 12.2 isotherms were statistically different. This result suggests that the level of confidence for comparing the isotherms is not appropriate for these data. Similar conflicting results were also observed for o-xylene. The necessary level of confidence required to accept the null hypothesis that the isotherms are parallel for all of the comparisons presented in Table 3.7 was found to be 99.82% (T-value of 4.21).

Table 3.7 – Results for hypothesis testing of isotherms at different pHs

Compound	T-value	Result for Null Hypothesis
benzene: 7.2, 10.2	1.51	Valid: isotherm slopes are the same
toluene: 7.2, 10.2	2.47	Valid: isotherm slopes are the same
ethylbenzene: 7.2, 10.2	0.98	Valid: isotherm slopes are the same
m,p-xylene: 7.2, 10.2	1.08	Valid: isotherm slopes are the same
o-xylene: 7.2, 10.2	0.1	Valid: isotherm slopes are the same
benzene: 10.2, 12.2	-3	Valid: isotherm slopes are the same
toluene: 10.2, 12.2	-3.02	Valid: isotherm slopes are the same
ethylbenzene: 10.2, 12.2	-3.66	Invalid: isotherm slopes are not the same
m,p-xylene: 10.2, 12.2	-2.48	Valid: isotherm slopes are the same
o-xylene: 10.2, 12.2	-4.21	Invalid: isotherm slopes are not the same
benzene: 7.2, 12.2	-1.48	Valid: isotherm slopes are the same
toluene: 7.2, 12.2	-0.55	Valid: isotherm slopes are the same
ethylbenzene: 7.2, 12.2	-2.68	Valid: isotherm slopes are the same
m,p-xylene: 7.2, 12.2	-1.41	Valid: isotherm slopes are the same
o-xylene: 7.2, 12.2	-4.11	Invalid: isotherm slopes are not the same

Figures 3.7 and 3.8 show comparisons of isotherms at the three pH values for benzene and o-xylene, respectively. All three isotherms appear to be parallel over several orders of magnitude. Previous research conducted by Lo et al. (1998) supports the hypothesis that the isotherms should be similar. The authors investigated the sorption of BTEX onto dicetyldimethylammonium-modified bentonite. They concluded that BTEX sorption was pH independent over larger concentration ranges. Their equilibrium concentrations range from approximately 10 to 120 mg/L. Interestingly, their K_D values were slightly more than an order of magnitude larger than those reported in this study.

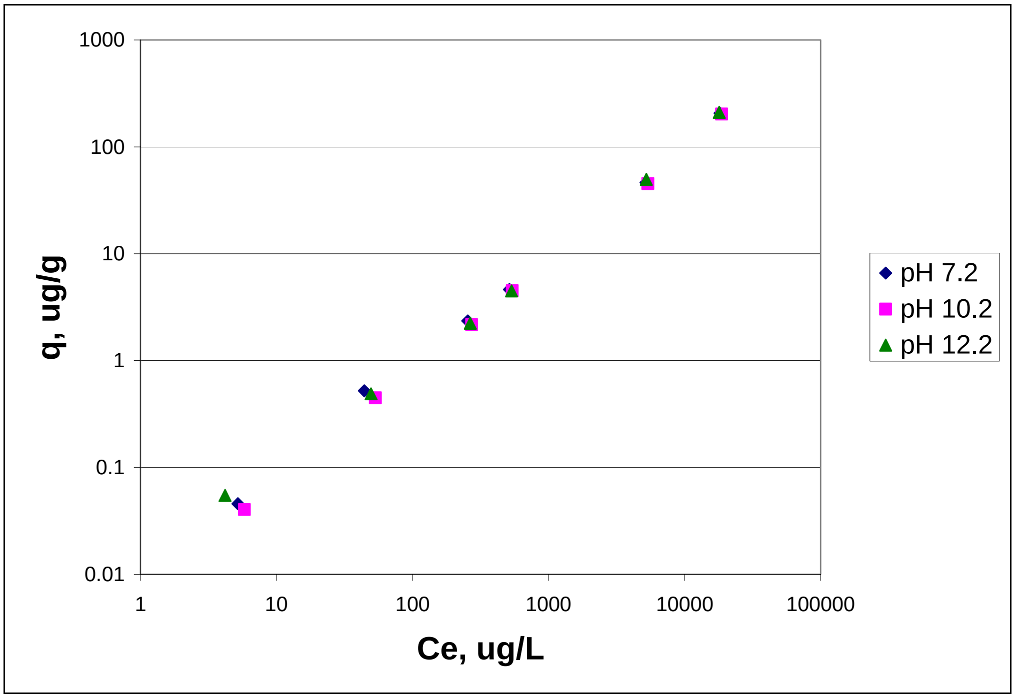

Figure 3.7 –Benzene isotherm data collected in the presence of the synthetic produced water over a range of pH values.

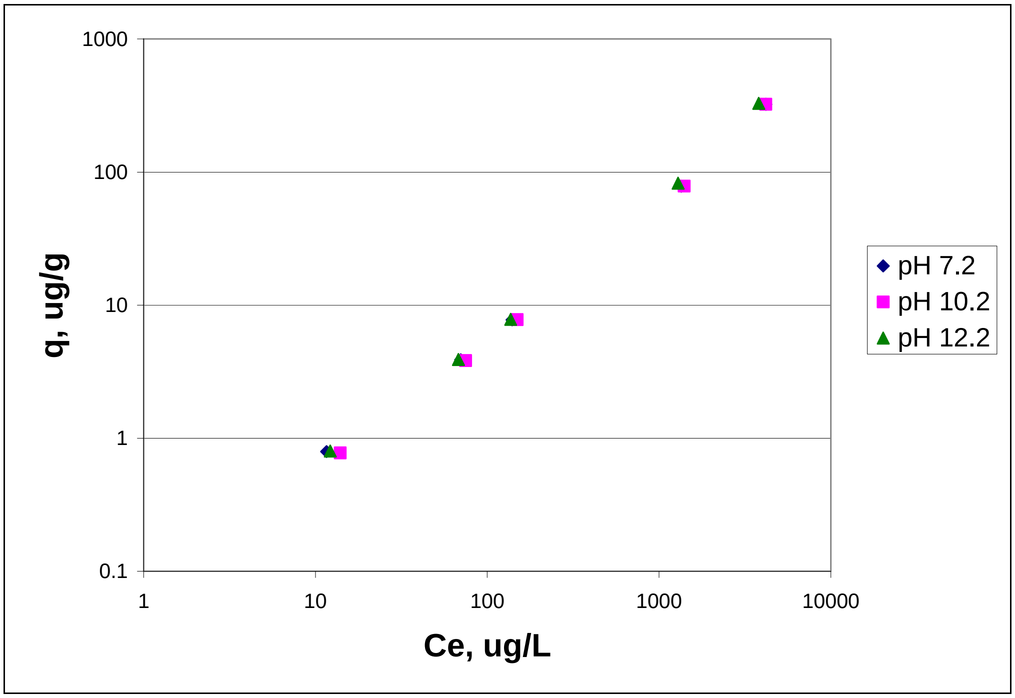

Figure3.8 – o-Xylene isotherm data collected in the presence of the synthetic produced water over a range of pH values

3.1.2.2 Effects of Varying Concentrations of Semi-Volatiles

In previous laboratory and field testing, there was limited evidence provided to support the hypothesis that K_D values for BTEX compounds increase in the presence of produced water constituents (Ranck, 2003; Tan, 2002). The K_D values presented above for the experiments conducted in the synthetic produced water at varying pH values also provides some indication that there is an increase in K_D in the presence of the produced water. To further evaluate the impact of the dissolved semi-volatile organic compounds on BTEX sorption, BTEX isotherms were prepared using a semi-volatile synthetic water of higher concentration. The concentrations of the semi-volatiles components of the synthetic water in these experiments were approximately double those used in the synthetic water experiments (see Table 3.4). Figure 3.9 shows the differences in BTEX sorption for the two semi-volatile concentrations; filled symbols indicate the synthetic water while open symbols indicate the more concentrated semi-volatile background solution.

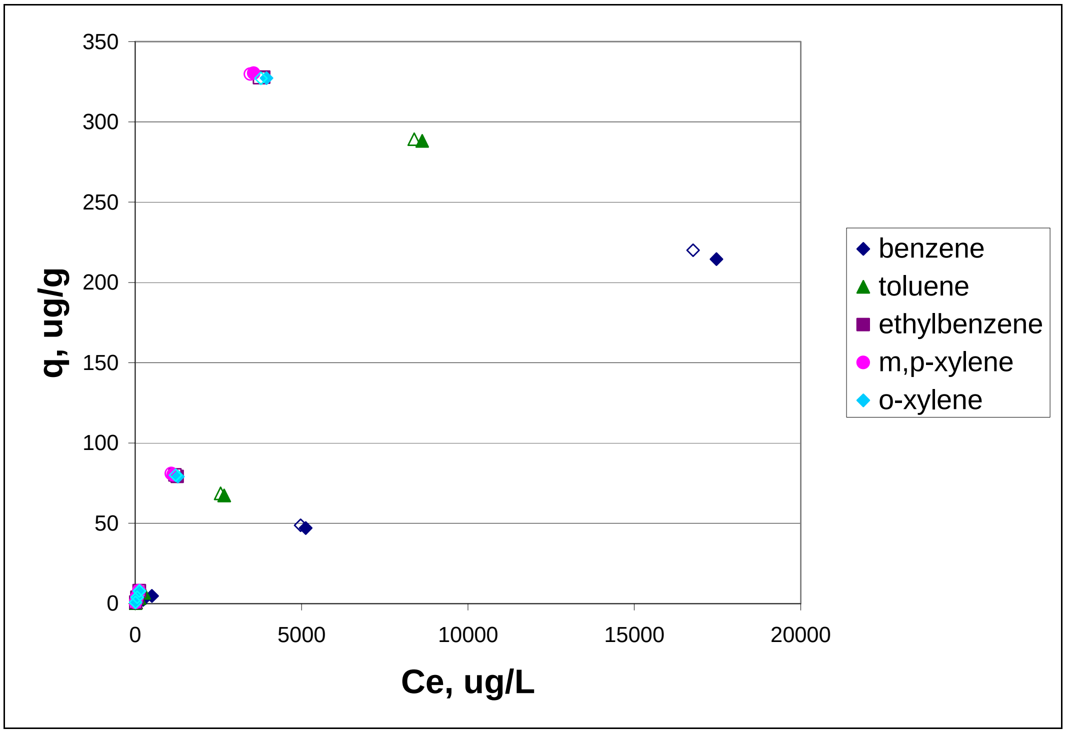

Figure 3.9 – BTEX isotherms in salt water in the presence of synthetic semi-volatile (filled symbols) and more concentrated (open symbols) solutions.

As shown in Figure 3.9, only slight differences were observed between the sorption of BTEX onto SMZ in the presence of the two semi-volatile concentrations when the data is plotted on a linear scale. The differences between the two experiments are only visually observable for benzene and toluene. The differences are more apparent when examining the K_D values for each experiment. Larger K_D values were observed for each BTEX compound in the more concentrated semi-volatile water, as shown in Table 3.8. Differences were greatest for ethylbenzene and xylene. Although benzene and toluene's 95% confidence limits overlap slightly, ethylbenzene and xylenes clearly do not. Hypothesis testing confirmed that each compound's isotherms were statistically different for the two semi-volatile concentrations using a 99.5% confidence level. Table 3.9 presents the results of the hypothesis tests.

Table 3.8 – Comparison of K_D values with varying semi-volatile concentrations. Units of K_D are L/g.

Compound	**synthetic**	**R^2**	**concentrated synthetic**	**R^2**
benzene	0.0113	0.9981	0.0123	0.9989
toluene	0.0294	0.9993	0.0316	0.9995
ethylbenzene	0.0647	0.9973	0.0747	0.9986
m,p-xylene	0.0803	0.9981	0.0862	0.9990
o-xylene	0.0716	0.9976	0.0775	0.9986
compound	**95% confidence limits on slope**		**95% confidence limits on slope**	
benzene	0.0106, 0.0120		0.0118, 0.0128	
toluene	0.0276, 0.0312		0.0301, 0.0334	
m,p-xylene	0.0633, 0.0661		0.0735, 0.0759	
ethylbenzene	0.0789, 0.0817		0.0850, 0.0874	
o-xylene	0.0702, 0.0730		0.0763, 0.0787	

Table 3.9 – Results of hypothesis testing for BTEX isotherms in the presence of different semi-volatile concentrations.

compound	**T-value**	**Result for Null Hypothesis**
benzene	-11.03	Invalid
toluene	-12.08	Invalid
ethylbenzene	-24.59	Invalid
m,p-xylene	-13.4	Invalid
o-xylene	-14.74	Invalid

Semi-volatile analysis indicated ethere was significant adsorption of the naphthalene and phenol compounds. Since the increases in K_D values were relatively small for these two systems, an increase in the organic content and a change in the organic phase may have resulted from the increase in concentrations of the organic components in the synthetic water. Greater sorption of ethylbenzene and xylene could possibly be the result of this larger sorbed organic phase.

Although the isotherms were proven to be statistically different, their overall variations do not appear to be that large. A greater impact of semi-volatile concentrations on BTEX sorption onto SMZ can be seen when their aqueous concentrations are comparable in magnitude to that of BTEX. An additional experiment was conducted in which equal concentrations of all twelve BTEX, phenols, and naphthalenes were added to batch reactors. Initial concentrations of each compound ranged from 0 to 75,000 μg/L. A semi-volatile analysis was not completed, so no equilibrium semi-volatile concentrations were determined. However, the sorption capacity, qe, value was determined for each of the BTEX compounds and single point K_D values were obtained from the data. Table 3.10 presents the single point K_D values for the BTEX compounds from these experiments. To show the maximum impact of semi-volatile concentrations on BTEX sorption, data points used for these calculations were the samples with initial 75,000 μg/L concentrations.

The single point K_D values measured in this study more closely resemble those obtained using produced water from our previous work. The zeolite used in our previous work included 14-40 mesh materials for batch experiments and 80-100 mesh materials for column studies. The experiments in this period of work utilized the 14-40 mesh zeolite. The produced water used in the previous studies was from the same source as the water utilized to select the concentrations of semi-volatile compounds used in the preparation of the synthetic water for this study. The higher single-point K_D values found in this study compared to those reported previously may reflect a larger organic phase created by the much higher semi-volatile concentrations.

Table 3.10 – Single point K_D values describing BTEX sorption in the presence of comparatively large amounts of semi-volatile compounds compared with those from the saline water study. Also shown are K_D values from batch experiments using produced water and lab scale column studies using produced water (K_D in L/g units)

compound	**Semi-volatile Background single point K_D**	**Saline Water Background study K_D**	**Produced Water Background K_D Batch experiments**	**Produced Water Background K_D Column experiments**
benzene	0.00995	0.00977	0.0130	0.0183
toluene	0.0410	0.0291	0.0327	0.0375
ethylbenzene	0.0987	0.0741	0.0794	0.0880
m,p-xylene	0.105	0.0818	0.0926	0.0950
o-xylene	0.0976	0.0744	0.0774	0.0877

Figure 3.10 compares the single point highly concentrated semi-volatile K_D values with corresponding BTEX isotherms conducted in the presence of a saline solution without the presence of semi-volatile compounds. A greater sorption capacity was obtained in the presence of the solutions containing high concentrations of semi-volatile compounds. Direct comparison between data points among the different experiments could not be conducted because each single point K_D value reported for the experiment conducted at high solute concentrations yielded Ce and qe values outside the range of the corresponding isotherm data collected in saline water.

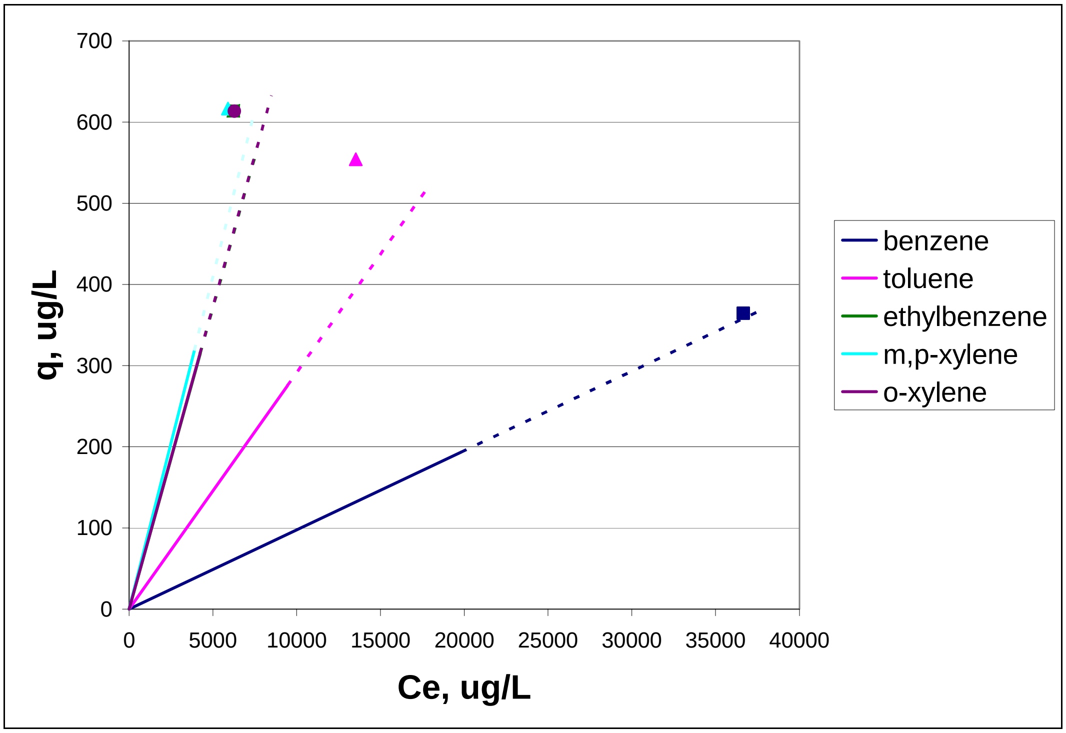

Figure 3.10 – Single point K_D values describing BTEX sorption in salt water in the presence of comparatively large amounts of semi-volatile compounds. Each compound had an initial concentration of 75,000 µg/L. For reference, BTEX isotherms describing sorption in salt water in the absence of semi-volatile compounds are shown. Each isotherm is extended beyond calibrated values with dashed lines.

3.2 Semi-Volatiles Organic Compounds Removal with SMZ

SMZ was also evaluated for its potential to remove semi-volatile compounds from produced water. The two major classes of semi-volatile compounds identified in the produced water from the Wamsutter, Wyoming field site were phenols and napthalenes. As a result, the synthetic produced water used in this research contained naphthalene, methyl naphthalenes, phenol and methyl phenols. In addition to examining the impact of these compounds on BTEX sorption, the removal of the phenols and the napthalenes was also assessed.

3.2.1 Phenols Removal

Phenol sorption was related to the aqueous solubility constant of each compound found in the literature. Figure 3.11 shows a correlation developed to predict this relationship, where K_D is expressed in units of L/kg. Predicted semi-volatile K_Ds are also plotted using a correlation developed by our previous work (Gupta, 2001) to predict BTEX K_D values for SMZ from their corresponding aqueous solubilities. As the solubility decreases, sorption coefficients increase. Although all single point K_D values in this research fit a linear model of a similar slope to the correlation obtained from the previous work (Gupta, 2001), the intercept is much higher. The increase in the intercept of these regressions for phenols compared to the BTEX compounds may relate to the chemical characteristics of the HDTMA surfactant. The polar headgroups of the hemimicelles presumed to be present on the zeolite surface create an environment which is more polar than most natural organic matter, and hence, more conducive to sorption of polar compounds such as phenols.

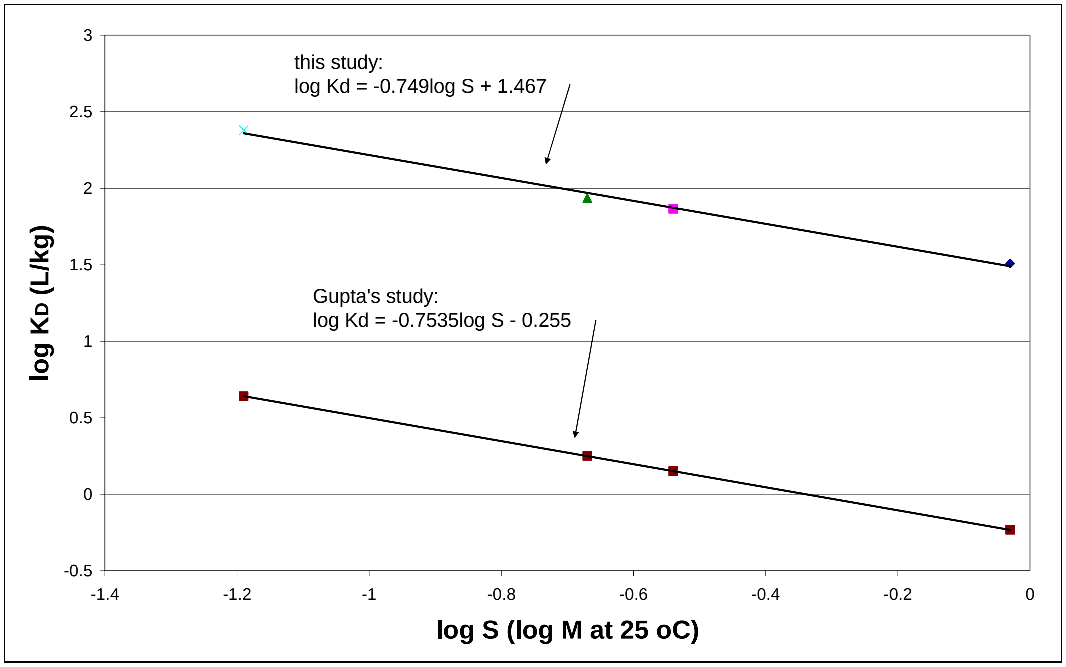

Figure 3.11 – Regression of single point K_D values with respect to aqueous solubiltes for phenol compounds. Also plotted are predicted K_D values using a correlation developed by the previous work (Gupta, 2001).

3.2.1.1 Effects of pH on Phenol Sorption

pH was expected to affect the sorption of phenolic compounds. By increasing the solution pH above the pKas of the phenol species, all of the phenol compounds become negatively charged. If phenol sorption is dependent on the charge of the molecule, then K_D values would be expected to differ at pHs above and below a molecule's pKa. Table 3.11 shows the average single point K_D values measured in experiments conducted at pH 7.2, 10.2, and 12.2. As the pH increases from 7.2 to 10.2 (near the pKas of all four phenol compounds), sorption decreases almost by a factor of two. As the pH increases two units above the pKas of the phenol compounds, sorption continues to decrease. This indicates that as the phenol species become charged they are less likely to adsorb.

Table 3.11 – Average single point K_D values for various equilibrium pH values. Units of K_D are L/g.

Compound	pH 7.2	pH 10.2	pH 12.2
Phenol	0.0322	0.0167	0.0119
2-methylphenol	0.0734	0.0416	0.0217
4-methylphenol	0.0865	0.0474	0.017
2,4-dimethylphenol	0.2395	0.1305	0.0332

Li et al. (2000), however, reported that phenol adsorption increased with solution pH onto SMZ over a pH range of 7 to 10. The authors reported that this was evidence that phenol adsorbed as an ionic species. At high pH, the phenol compounds lose their proton and become charged. Although the authors reported increased sorption at high pH, sorption actually decreased at pH values above phenol's pKa of 10. This was attributed to the increasing ionic strength of the water, although ionic strength values for their research were one to two orders of magnitude smaller than the ionic strength of water in this study. Table 4.6 shows the change in ionic strength for the waters with different pH values used in this experiment. As indicated in the table, there is an increase in ionic strength with increasing pH. Although our previous studies showed that ionic strengths in this range do not affect sorption of BTEX molecules, this evidence suggests that this may not be true for polar organics.

3.2.1.2 Effects of Semi-Volatile Concentrations

BTEX isotherms were conducted in the synthetic salt solution at both synthetic semi-volatile and concentrated semi-volatile concentrations. Analysis of the concentrations of semi-volatile compounds prior to and at the end of the experiment enabled the construction of two point linear isotherms for the four phenol compounds (Figure 3.12). Their K_D values are shown in Table 3.13. pH was not measured in this experiment, but it would be expected to be near neutral based on the results of similar experiments using these waters. If this is the case, then the data correlates well with the average single point K_D values from the pH 7.2 experiment (Table 3.11). The only reported K_D values listed in Li et al. (2000) are for phenol at three different pH values at 7 or above. K_D increased from 0.012 L/g to 0.021 L/g when the pH increased from 7 to 9.8, where it then dropped to 0.016 L/g when the pH increased to 11.2. Even the largest K_D value presented in Li et al. (2000) is only approximately two-thirds the value calculated for the circumneutral pH expected for this experiment. It should be noted that even though the K_D values for phenol determined by Li et al. (2000) are smaller than the values found in this research using a higher ionic strength water, they are also not consistent with the log K_D-log K_{ow} or log Kd-log S relationships developed by the PIs.

Table 3.12 – K_D values for the four phenol compounds used in this study. (Units of K_D are L/g)

compound	K_D
phenol	0.0334
2-methylphenol	0.0888
4-methylphenol	0.0883
2,4-dimethylphenol	0.201

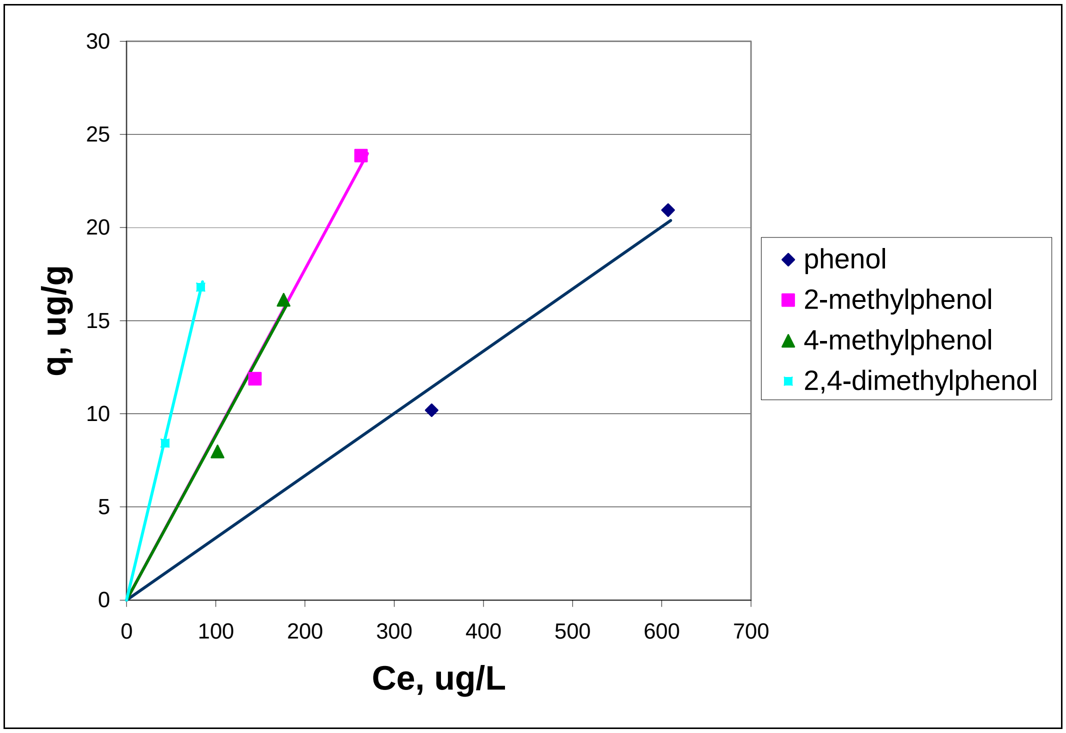

Figure 3.12 – Linear approximations of the two semi-volatile concentration isotherms.

3.2.2 Naphthalenes Removal

GC-MS results suggested that removal of naphthalene from the synthetic water was significant. It was not possible to quantify the extent of removal because the concentrations of naphthalene remaining in solution after sorption were below the detection limit of the GC/MS. The estimated quanteitation limit for EPA method 8270C was 10 µg/L. However, due to a loss of sensitivity during the time period in which this research was conducted, it is not possible to report an accurate value for the method detection level. Based on the calibration data, the practical quantitation limit for the aqueous concentrations of naphthalenes in the experiments was approximately 50 µg/L. Although the GC-MS was able to detect naphthalene and 2-methylnaphthalene during batch experiments, these compounds were never measured within an order of magnitude of the estimated detection limit. The high removals observed for these compounds during the sorption experiments are expected based on their lower solubilities and higher octanol/water partitioning coefficients compared with BTEX compounds. Indeed, a comparison of the solubilities and octanol/water partitioning coefficients of all twelve compounds used in this study (shown in Table 3.13) shows the differences between the napthalenes and the other organic compounds.

Table 3.13 – Water solubilities and octanol/water coefficients for all organic compounds used in this study.

	Water Solubility at 25°C (log M)	**log K_{ow} at 20°C (L octanol/ L water)**
benzene	-1.66	2.13
toluene	-2.14	2.69
m-xylene	-2.72	3.2
p-xylene	-2.72	3.15
o-xylene	-2.79	3.12
ethylbenzene	-3.03	3.15
phenol	-0.03	1.48
2-methylphenol	-0.54	1.96
4-methylphenol	-0.67	1.96
2,4-dimethylphenol	-1.19	2.30
naphthalene	-3.63	3.37
2-methylnaphthalene	-3.68	4.37

Although the two naphthalene compounds could not be accurately measured, K_D values were estimated using correlations with literature values of aqueous solubilities and K_{OW} values. These correlations are shown in Equations 3.2 and 3.3, where K_D is in L/kg units. Table 3.14 summarizes these results.

$$\log K_D = -0.7535 \log S - 0.255 \qquad (3.2)$$

$$\log K_D = 0.8408 \log K_{OW} - 0.807 \qquad (3.3)$$

Table 3.14 – Predicted K_D values using Equations 3.2 and 3.3

compound	Water Solubility at 25°C (log M)	Predicted log K_D from solubility	Predicted K_D from solubility (L/kg)
naphthalene	-3.63	2.48	302
2-methylnaphthalene	-3.68	2.52	330
	log K_{ow} at 20°C(L octanol/ L water)	**Predicted log K_D from K_{OW}**	**Predicted K_D from K_{OW} (L/kg)**
naphthalene	3.37	2.03	106
2-methylnaphthalene	4.37	2.87	734

In 2003, the EPA decided not to consider naphthalene for inclusion in future drinking water quality standards, and therefore does not currently list the compound in either its primary or secondary water quality standards. However, it does list a lifetime health advisory of 100 µg/L. Based on the results of this research and the predicted K_D values for the naphthalenes, it appears that SMZ is capable of reducing naphthalene concentrations well below this level.

3.3 Metals Removal with SMZ

3.3.1 Oxyanions

Chromium and selenium were both found in the produced water obtained from the treatment facility in Wamsutter, Wyoming. Both of these elements are commonly found in the environment as the oxyanions, chromate and selenate. These oxyanions were used to study the impact of background water composition on anion sorption to SMZ. Analyses of chromate and selenate in solutions prior to and following the sorption experiments were measured using ICP. ICP measures total metal concentrations. Therefore, all reported data is in terms of total chromium and total selenium, and no attempt was made to determine whether changes in oxidation state occurred during the course of the experiments. However, changes in oxidation state were not expected based on the redox conditions in the samples.

3.3.1.1 Chromium

Chromium sorption onto SMZ was determined as a function of pH for constant total chromium concentrations added (pH adsorption edges) and as a function of aqueous chromium concentration at constant pH (isotherms). Initial chromium sorption results were very confusing. First, it was apparent that chromium adsorbs to SMZ in ultrapure water, but not in the synthetic salt solution. This was thought to be the result of competition with other ions in the salt solution. Further experimentation indicated that while chromium would adsorb in the salt solution at high pH, it would not at low pH. This is counterintuitive for the sorption of an anionic species to oxide minerals in which sorption typically decreases with increasing pH. In these experiments, nitric acid was used to lower the pH. Further research indicated that nitrate was a strong competitor with chromium for adsorption sites on SMZ (Li et al., 1998). In ultrapure water, very little acid is required to alter the pH, so there was not enough nitrate to hinder chromium sorption. The synthetic salt water required additions of significant amounts of concentrated acid to adjust the pH due to the presence of carbonates. Therefore, at low pH, there was a significant increase in the nitrate concentration, and the nitrate was able to successfully compete with chromium for sorption sites on the SMZ in the synthetic salt water. When hydrochloric acid was used to lower pH, no competitive effects were observed, even though the increase in ionic strengths resulting from the addition of either acid was similar.

A chromium sorption edge was prepared in the synthetic salt solution using hydrochloric acid and sodium hydroxide to adjust pH. 30 mL of 1.8 mM K2CrO4 was added to three grams of SMZ, and the pH was adjusted to a series of vials to produce a pH range from 4 to 11. The results are shown in Figure 3.13. The decrease in anion sorption with increasing pH is typical of adsorption of oxyanions to surface functional groups. The potential functional groups on the SMZ are the positively charged ammonium head groups on the surfactant bilayers and the surface hydroxyl groups of the exposed (surfactant free) external zeolite surface. Cation exchange is the expected removal mechanism for the ammonium head groups on the surfactant, because the positive charge is assumed to be permanent and the charge is initially counterbalanced with chloride ions. In contrast, surface complexation is the expected removal process for the variable charge hydroxyl groups associated with the zeolite surface.

Li (2004) studied chromate uptake by SMZ over a range of pH values. Chromate sorption was described by Langmuir isotherms over a pH range of 3 to 11. The overall sorption capacity remained constant throughout this range, but the sorption intensity or Langmuir distribution coefficient decreased from 42.2 to 4 L/mmol for pH 3 to 11. As a result, anion exchange was favored over surface complexation as the mechanism for sorption. The decrease in sorption intensity was attributed to competition from other ions in solution. As pH increased, chromate sorption decreased and chloride desorption increased. No increase in aqueous HDTMA was measured; therefore, other anions in solution must have had a higher affinity for the surfactant bilayer. The only other anion present in their solution was hydroxide. The decrease in sorption seen in Figure 3.14 begins at pH 6. This is close to the pKa1 of carbonate (6.3). High pH carbonate/hydroxide solutions have been shown to remove as much as 90% of sorbed chromate (Li & Bowman, 2001). Therefore, the lower chromate sorption at high pH observed in this experiment may have resulted from competition from hydroxide and/or carbonate ions. To fully understand how oxyanions sorb to SMZ, a sorption edge was prepared using natural zeolite.

A chromium isotherm was prepared in ultrapure water using hydrochloric acid and sodium hydroxide to maintain the pH at 7.2. This experiment served as a control for a subsequent experiment to determine the impact of background electrolytes on chromate sorption to SMZ. The chromate isotherm data are presented in Figure 3.14. Also shown in the figure is a Langmuir isotherm model fit to the data obtained using nonlinear regression. The approximation is described with Equation 3.4, where Ce is expressed in terms of mmol/L. At low concentrations, the Langmuir isotherm appears to be linear with a K_D value of approximately 0.05 L/g.

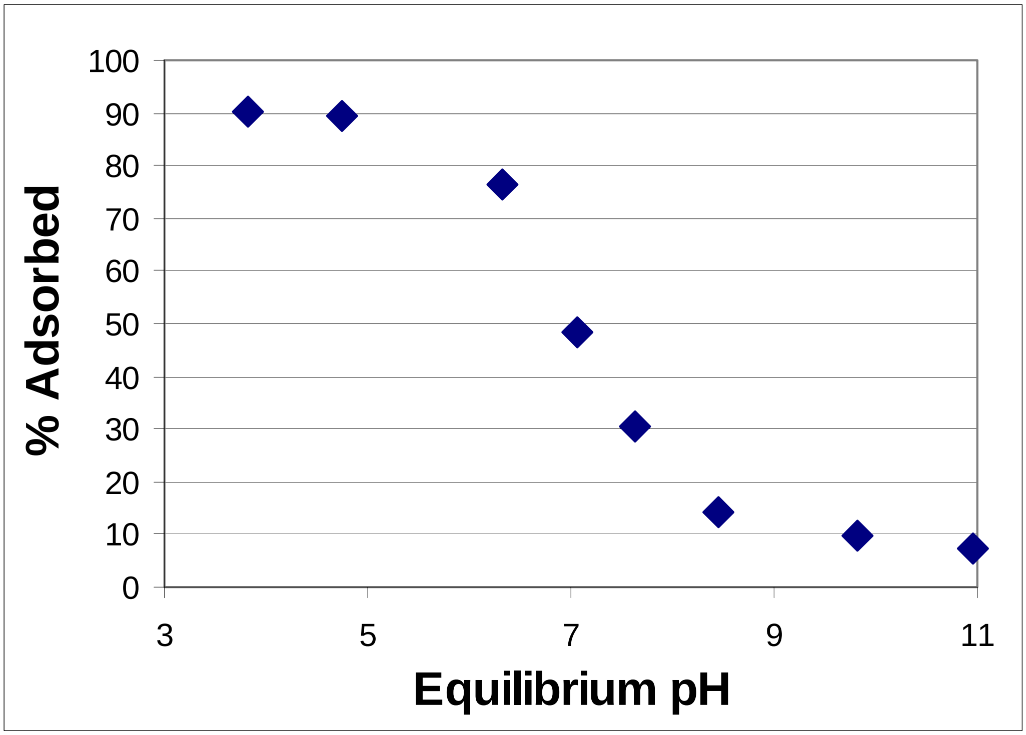

Figure 3.13 – Chromium sorption edge in synthetic salt solution.

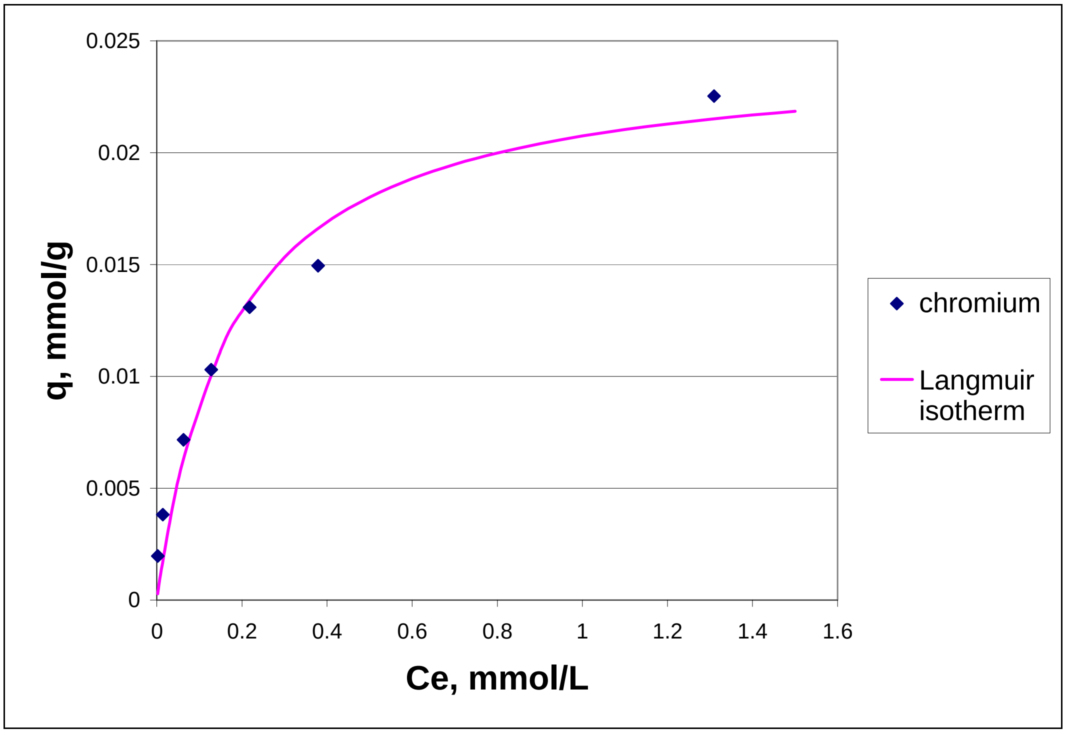

Figure 3.14 – Chromium isotherm in Millipore water at pH 7.2.

These results are consistent with Li et al. (1998). At 200% surface coverage of zeolite with HDTMA, the authors report that chromium sorption follows a Langmuir isotherm, although no constants are given. However, maximum sorption in their isotherm appears to occur approximately at 10 mmol/kg, which is less than half of the 24.5 mmol/kg predicted in Equation 3.4 for this experiment. No description of the water matrix is given. Assuming that Millipore water was used in Li's study, the results in this experiment indicate that much more chromium can be sorbed than was reported in their study.

$$q_L = \frac{q_{\max} b C_e}{1 + b C_e} \qquad (3.4)$$

where:

qmax = 0.0245 mmol/g
b = 5.593 L/mmol when Ce is in mmol/L units

A similar chromium isotherm was prepared in the synthetic salt water using hydrochloric acid and sodium hydroxide to maintain the pH at 7.2. The results are shown in Figure 3.15. The data could be fit to a linear isotherm with an R^2 value of 0.967, shown in Equation 3.5.

$$q = K_D C_e \qquad (3.5)$$

where:

K_D = 0.011 L/g when C_e is in mmol/L

The K_D value is much lower than the linear portion of the Langmuir isotherm describing sorption in ultrapure water (K_D =0.137 L/g). This suggests that there is competition for exchange sites from ions in the salt solution. If the isotherm conducted in saline water was continued at higher concentrations, sorption may level off. This would indicate sorption may be better described with a Langmuir isotherm over large concentration ranges.

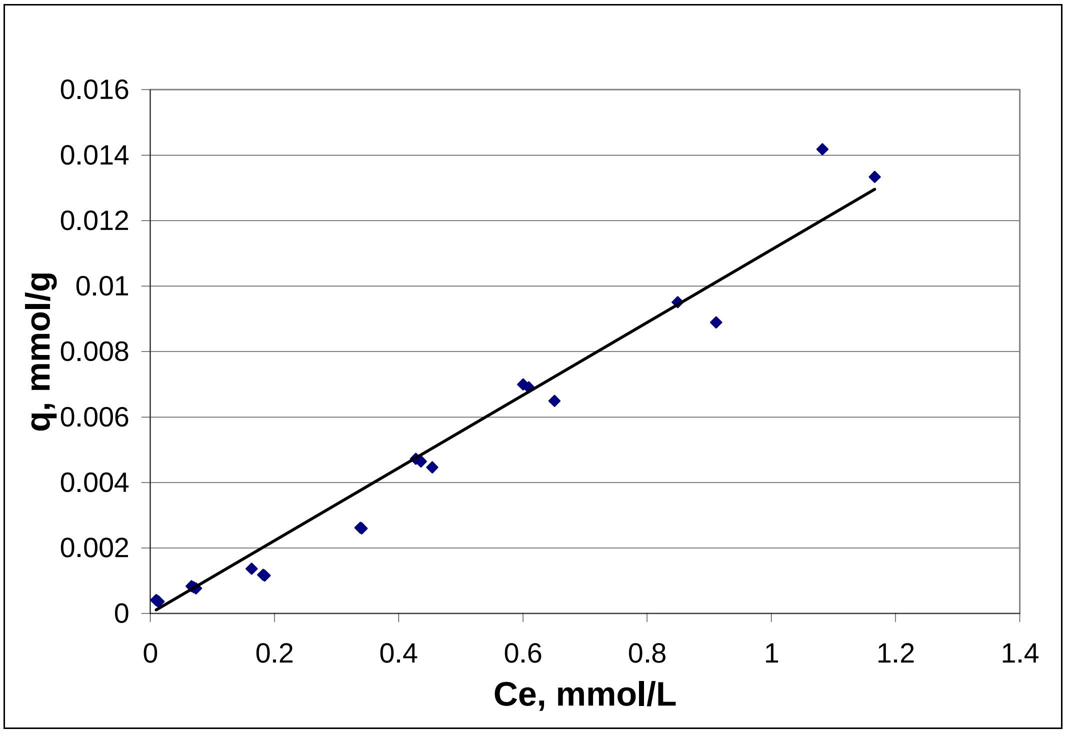

Figure 3.15 – Chromium isotherm in synthetic salt solution at pH 7.2.

Li et al. (1998) studied competitive sorption between chromium and other anions. As sulfate concentrations increased from 0.1 to 10 mM, the Langmuir isotherm describing chromate sorption began to appear more linear. The chromate sorption intensities, b, were 2.4, 1.3, and 0.4 L/mmol for sulfate concentrations of 0.1, 1, and 10 mM, respectively. This data can be related to the results from this research. In this study, sorption in ultrapure water resulted in a chromate sorption intensity of approximately 5.6 L/mmol; this is more than twice that of the sorption intensity of Li's 0.1 mM sulfate experiment. Furthermore, the bicarbonate concentration in the saline water of this study was approximately 50 mM. This is higher than the 10 mM sulfate solution used in Li's experiment, but bicarbonate is a monovalent ion, and would not be expected to compete as effectively as sulfate. Indeed, when carbonate is used to regenerate chromium saturated SMZ, it is less effectiveness at near neutral pHs (where bicarbonate is the dominant species) (Li & Bowman, 2001). Li's chromate Langmuir isotherm in 10 mM sulfate can be approximated at low concentrations as a linear isotherm with a K_D value of 0.006 L/g. This is smaller, but comparable to the K_D of

0.011 L/g observed in this study. More data on the comparative effects of sulfate and carbonate would be needed to fully address the differences in the two data sets.

Both chromate isotherms generated in this study are shown together in Figure 3.16. At low concentrations, chromium has a greater sorptive affinity in ultrapure water than in the synthetic salt solution. As the equilibrium chromium concentration increases, sorption in the saline water background approaches that of the ultrapure water. As the aqueous chromium concentration continues to rise, it can compete more effectively with other ions in solution for adsorption sites. Eventually, the linear isotherm would be expected to level off, as the number of adsorption sites becomes limited (Langmuir isotherm).

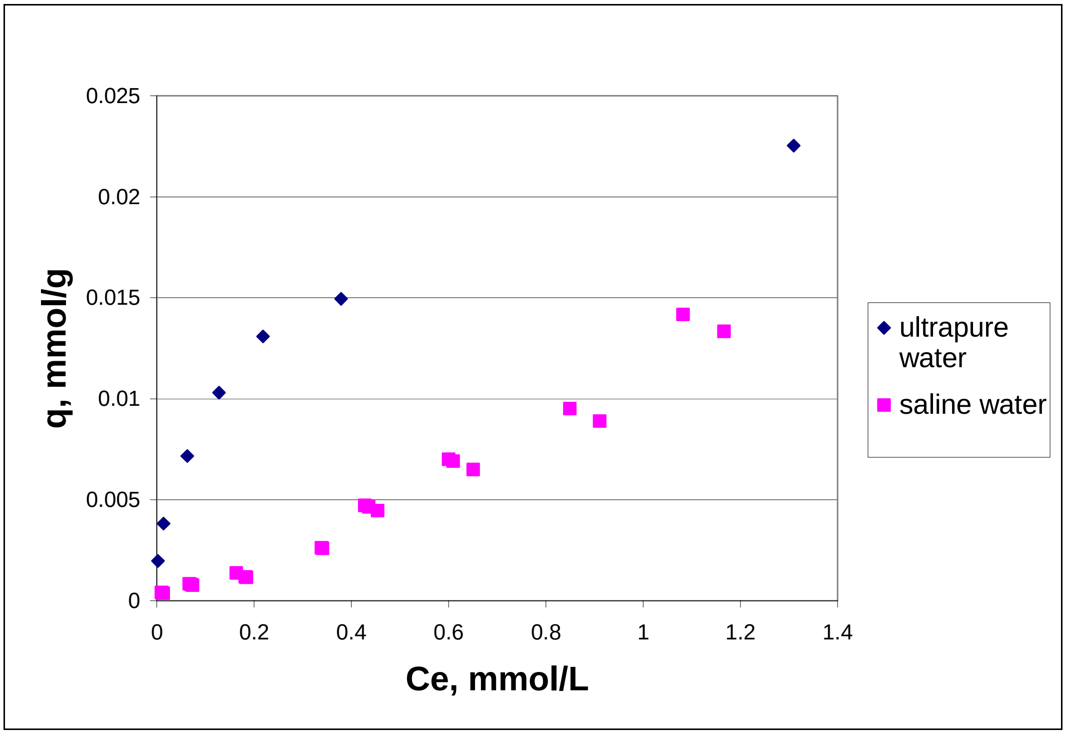

Figure 3.16 – Comparison of chromium isotherms in ultrapure water and salt waters at pH 7.2.

3.3.1.2 Selenium

A selenate isotherm was prepared in Millipore water at pH 7.2 to serve as a control to evaluate the effects the salts present in the saline water on sorption to SMZ. A Langmuir isotherm was fit to the data using non-linear regression and is shown in Figure 3.17 and Equation 3.4. The calculated values for qmaz and b were 0.0193 mmol/g and 3.203 L/mmol, respectively.

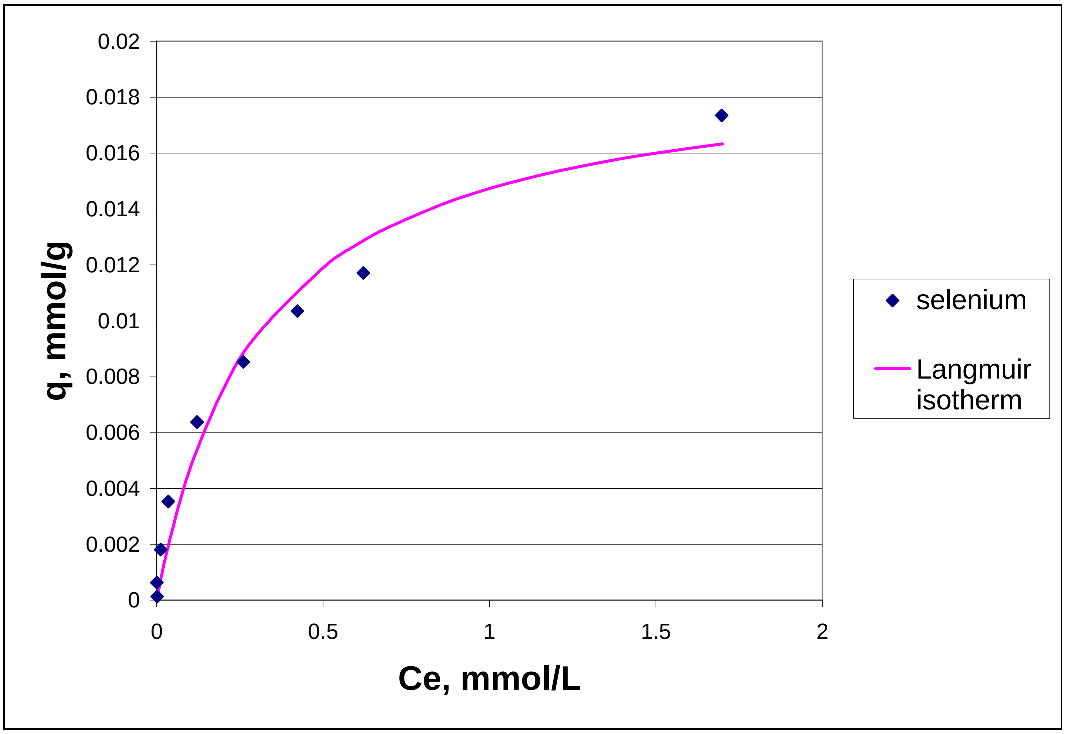

Figure 3.17 – Selenium isotherm in synthetic salt solution at pH 7.2.

A comparison of the sorptive characteristics of chromium and selenium is shown in Figure 3.18. Chromate, with pKa1 = 0.74 and pKa2 = 6.49, is primarily a divalent ion at pH 7.2. Selenate on the other hand is a monovalent ion at pH 7 (pKa1 = 1.7). This higher charge of the chromate appears to have an impact on sorption. This is confirmed by Langmuir isotherms describing chromate and selenate sorption onto HDTMA-modified zeolite published by Haggerty & Bowman (1994). They report sorption capacities for chromate and selenate to be 0.00360 and 0.00225 mmol/g, respectively, onto a surfactant bilayer. The difference in magnitude between these reported values and those obtained in this research could possibly be attributed to the background salinities of the respective solutions. Haggerty & Bowman report that salinities ranging from 5 to 200 mg/L were used in their study, but they do not report which was used for the Langmuir isotherms described above.

This is in contrast to the findings of Li et al. (1998). They indicated that, although unexpected, the monovalent nitrate had a greater affinity for the surfactant bilayer. A similar finding was obtained in this research for chromate sorption.

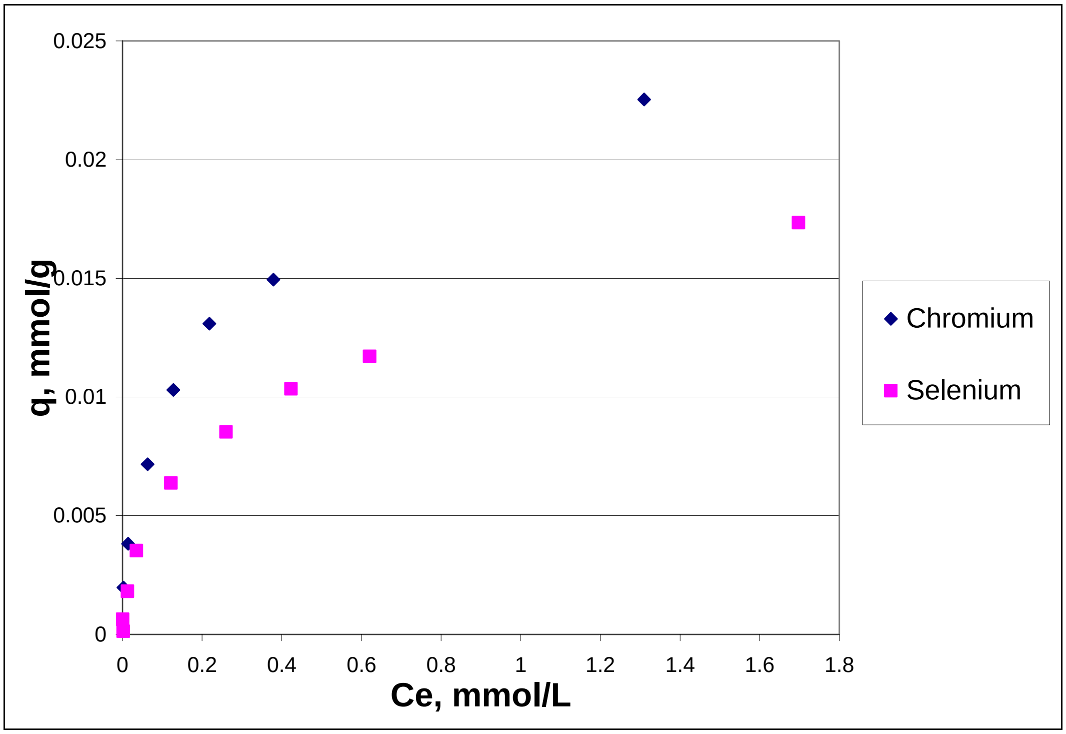

Figure 3.18 – Comparison of chromium and selenium isotherms in Millipore water at pH 7.2.

No selenium sorption was observed when the synthetic salt solution was used as a matrix. This was probably the result of competition from salt ions. This result was similar to that observed for chromium; however, the effect on selenate was more pronounced. Therefore, it is plausible that selenium has a lower affinity for SMZ than other ions in solution. Although nitric acid was used to lower the pH in some samples, and some sulfate was present in the salt solution, the dominant competing anion was probably bicarbonate. This assumption is based upon the fact that there is approximately 500 times more bicarbonate in the salt solution as sulfate, and any nitrate added was minimal in comparison to bicarbonate.

3.3.2 Barium

Barium was used in this study to investigate metal cation sorption, because it was present in the produced water from Wyoming. No published data for barium sorption was found in the literature; however, previous research by the PIs demonstrated that approximately 91% percent of barium was removed from a produced water treated with SMZ.

A barium sorption edge was prepared in the synthetic salt solution. 30 mL of 1.8 mM BaCl2 was added to three grams of SMZ. Eight samples with pHs ranging from 3.5 to 10 were obtained by adding concentrated nitric acid and sodium hydroxide to the samples. Results are shown in Figure 3.19. Barium removal from produced water was hypothesized to occur as an ion exchange process, as the charge balancing calcium, potassium, and sodium ions leave the zeolite surface and enter solution. As shown in Figure 3.19, two regions of sorption are apparent, a pH independent region and a pH dependent region. At low pH, a region of relatively constant Ba removal occurs. This represents the approximate 65% removal at low pH values. The increased removal efficiency at high pH is likely the result of variable charge surfaces present on the zeolite.

Doula et al. (2002) investigated the removal of aqueous copper with zeolite. They attributed the increased removal of copper at high pH to adsorption to surface oxygen sites (≡Si-OH and ≡Al-OH) and bridging oxygen sites (≡Si-OH-Al≡). As solution pH increases, H+ ions desorb from the these oxygen atoms, creating negatively charged adsorption sites. Um and Papelis (2003) confirmed these results with lead sorption onto zeolite. These authors also reported on the ionic strength dependency of cation sorption. At ionic strengths less than 0.1 M, adsorption was essentially complete (100%) from pH 2 to pH 9. When the ionic strength was increased to 1 M, their sorption edge had the same inflection point as shown in Figure 3.19. They concluded that at low ionic strengths, there were enough cation exchange sites to completely remove all lead ions. At high ionic strengths, there are enough competing ions in solution that ion exchange to fixed charge sites can only account for partial lead removal. At pH values greater than 7, the additional sorption is attributed to adsorption to hydroxyl surface sites and surface precipitation.

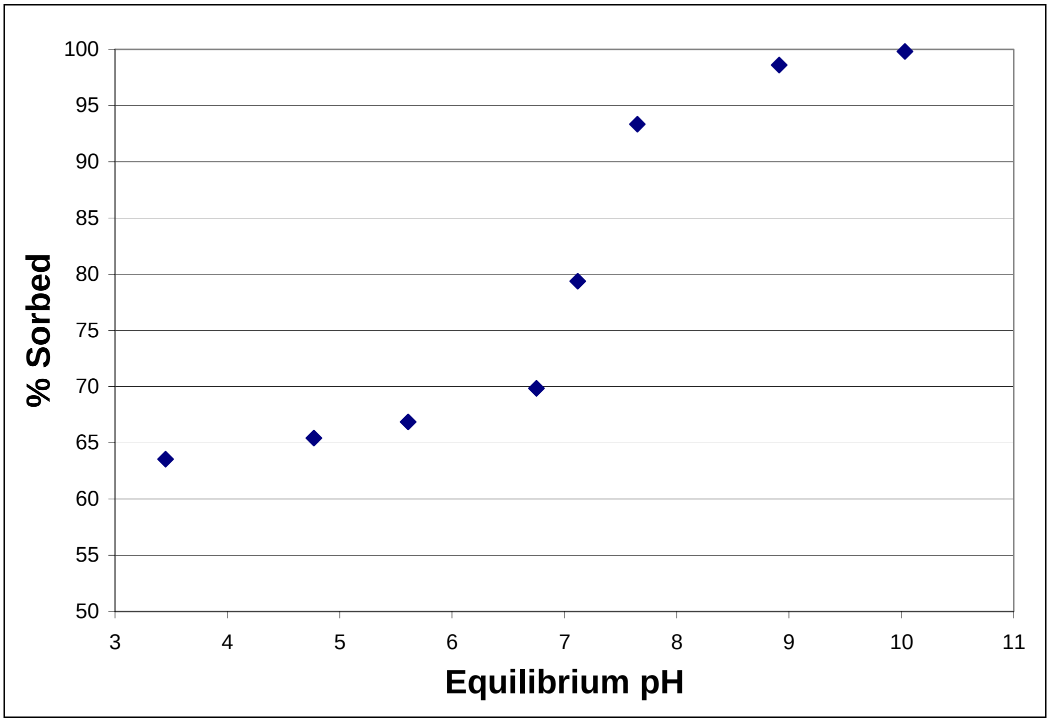

Figure 3.19 – Barium sorption edge in synthetic salt solution.

A barium isotherm describing sorption onto three grams of natural zeolite was prepared by adding varying amount of Ba to 30 mL of synthetic salt solution. pH was held constant at 7.2 with nitric acid and sodium hydroxide. Figure 3.20 shows the experimental data fit to a Langmuir isotherm. The isotherm was fit by non-linear regression of the experimental data with Equation 3.4. The calculated values for qmax and b were 0.0225 mmol/g and 2.909 L/mmol, respectively.

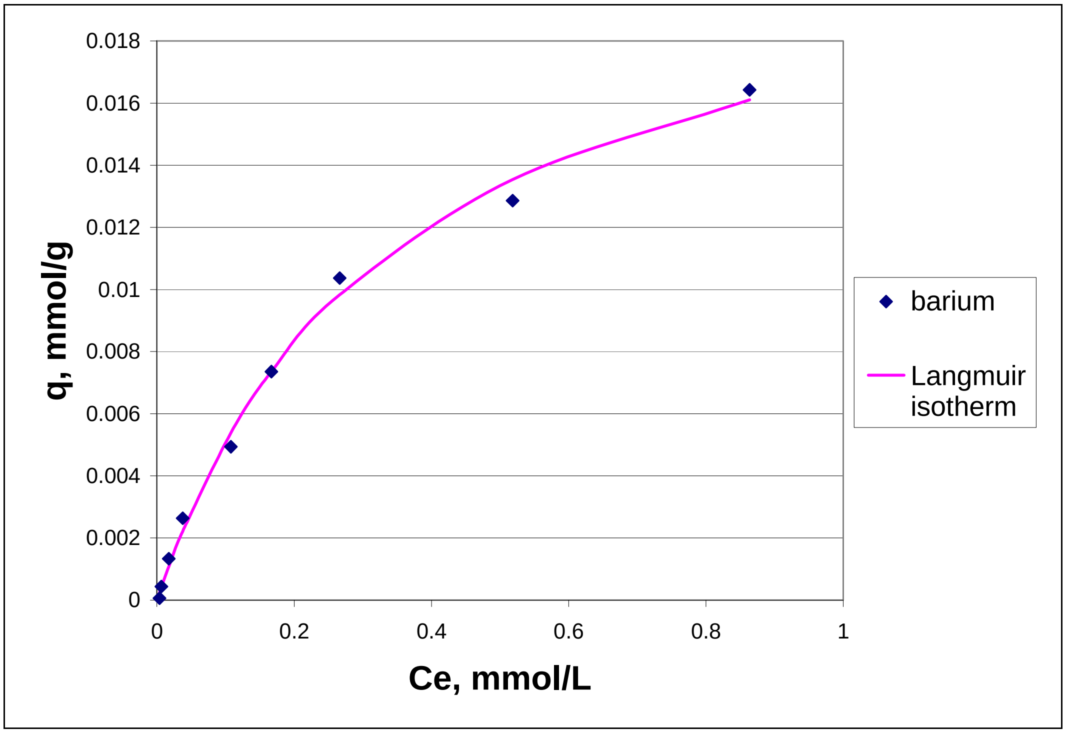

Figure 3.20 – Barium isotherm in synthetic salt solution onto natural zeolite.

A second barium isotherm was prepared with SMZ in a similar procedure. pH was held constant at 7.2. The equilibrium data were fit to a Langmuir isotherm, shown in Figure 3.21 and Equation 4.4 using non-linear regression. The calculated values for qmax and b were 0.0214 mmol/g and 2.28 L/mmol, respectively. A comparison of barium sorption onto natural and modified zeolite is shown in Figure 3.22. The modified zeolite has a slightly lower sorption capacity as indicated by their respective sorptive capacities, although the differences do not appear to be significant. This indicates that the majority of barium sorption occurs onto zeolite's internal exchange sites. This agrees with the amount of internal versus external CEC sites. The external CEC for the zeolite used in this study was approximately 110 meq/kg, while the internal CEC was approximately 800 meq/kg (Bowman et al., 2000). Other metals, such as lanthanum and strontium have exhibited decreased sorption to modified zeolite, while sorption of other metals such as cesium and lead have proven to be unaffected by surfactant modification (Li et al., 2002).

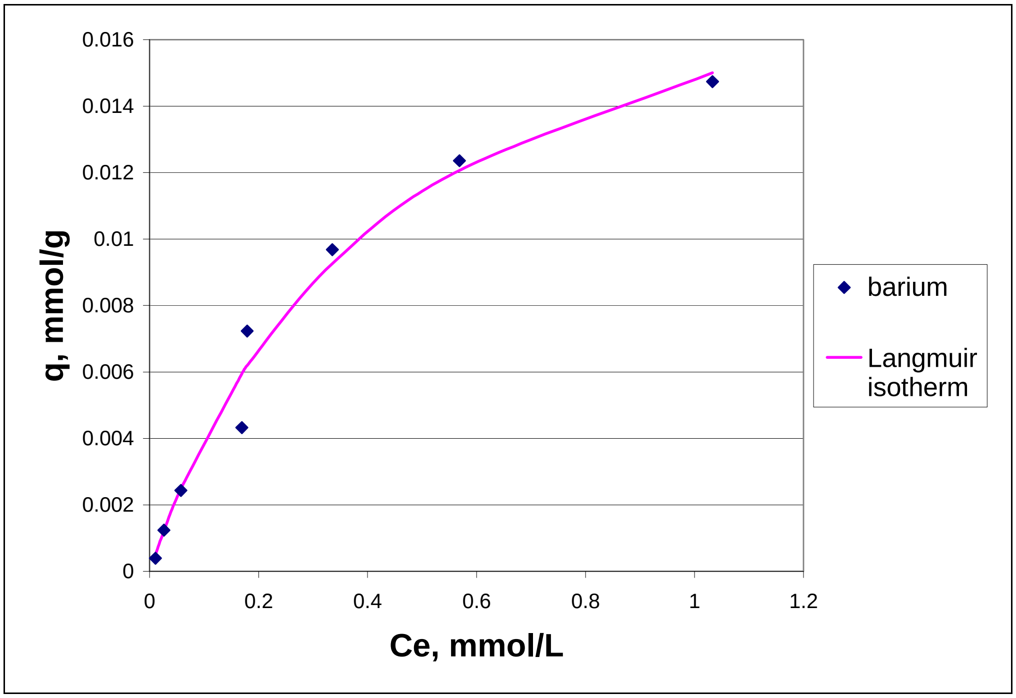

Figure 3.21 – Barium isotherm in synthetic salt solution onto SMZ.

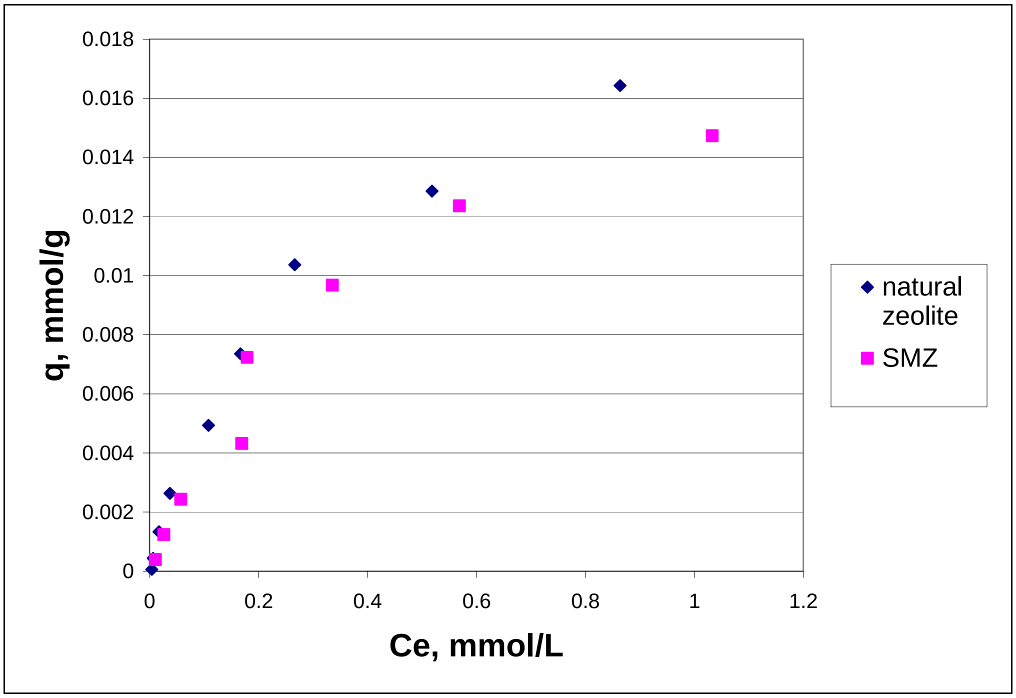

Figure 3.22 – Comparison of barium sorption onto natural and modified zeolite is salt water at pH 7.2.

The reported values of qmax compare well with published data in Li et al. (2002). Sorption capacities ranged from 5 to 54 mmol/g for strontium and cesium, respectively, onto modified zeolite with a surfactant bilayer. The sorption intensities reported in their research (1 to 20 L/mmol) were generally higher than those reported in this research.

3.4 Optimize VPB for the Treatment of Waste Gases Expected from SMZ Regeneration (Lab-Scale)

3.4.1 Continuous Operation

Bioreactor performance stabilized fter adjusting the nutrient supply system on Day 60, and a BTEX removal efficiency of greater than 99% was achieved. Linear BTEX removal profiles were observed across the reactor immediately after the biofilter packing material was mixed on Day 60 (Figure 3.23a). However, as time passed, exponential BTEX removal profiles were observed with the greatest removals observed near the biofilter inlet where the biomass concentrations were the highest (Figures 3.23b and 3.24). Benzene and toluene, in particular, were nearly completed degraded in the first 25 cm of the biofilter column. This type of removal profile is typical of an optimized biofilter system that is not nutrient limited and has not accumulated excess biomass.

After four months of continuous operation treating a 130 ppmv BTEX feed, VOC removal across the biofilter declined slightly although the overall VOC removal remained above 95% (Fig. 3.23c). Xylene removal was found to be the most sensitive to extended operational periods while toluene and ethylbenzene were the least sensitive. Previous research has found that low levels of available nitrogen in the biofilm can greatly reduce xylene degradation in biofilters (Song et al., 2003). Thus, the observed decline in xylene removal may have been due to a nitrogen limitation in the biofilter. However, other research indicates that extensive nitrogen recycling occurs in mature biofilms with up to 50% of the nitrogen requirements of the active biomass being provided by nitrogen

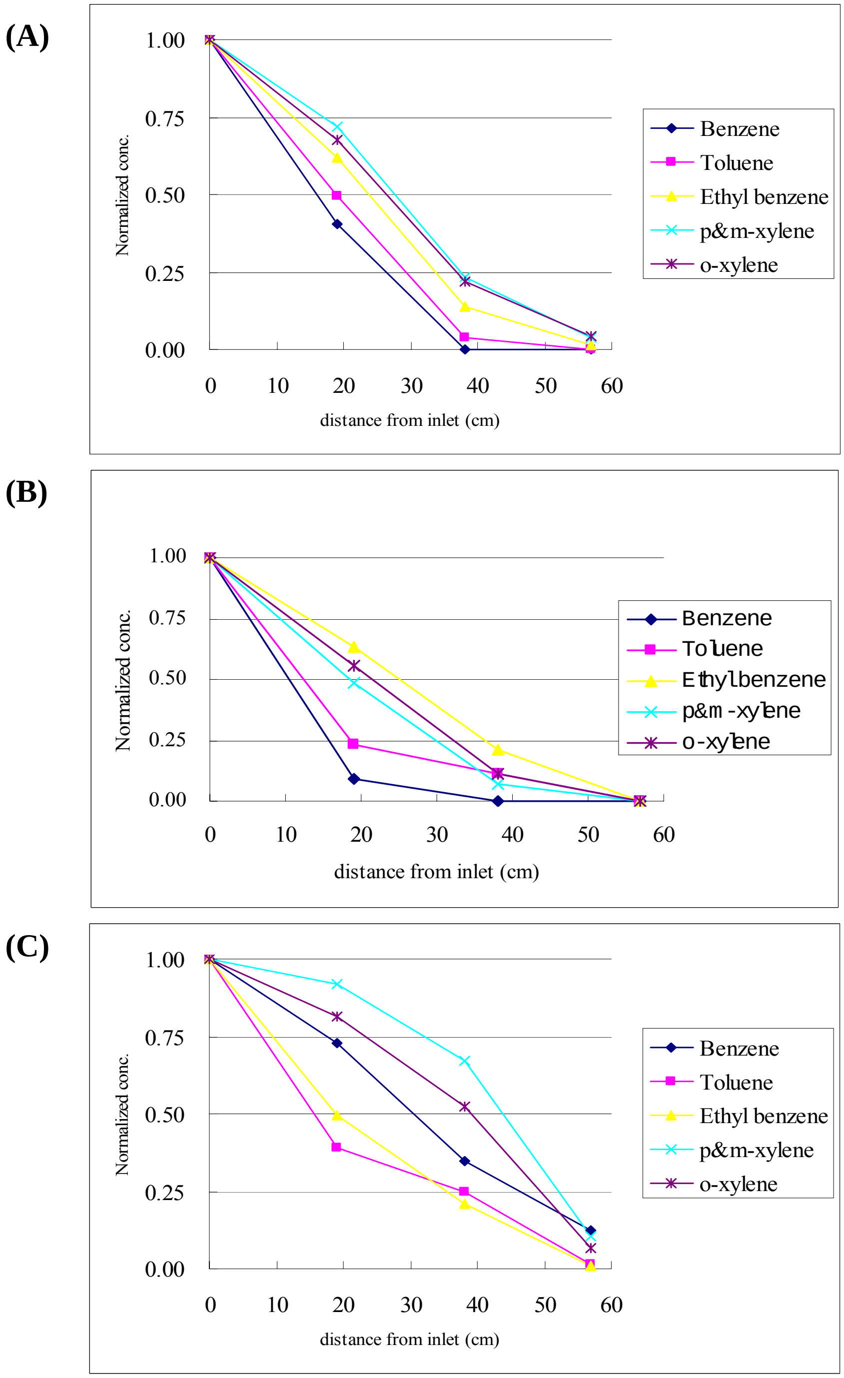

Figure 3.23. – Normalized VOC removal profiles along the biofilter column on days (a): 63, (b): 73, (c): 128 respectively.

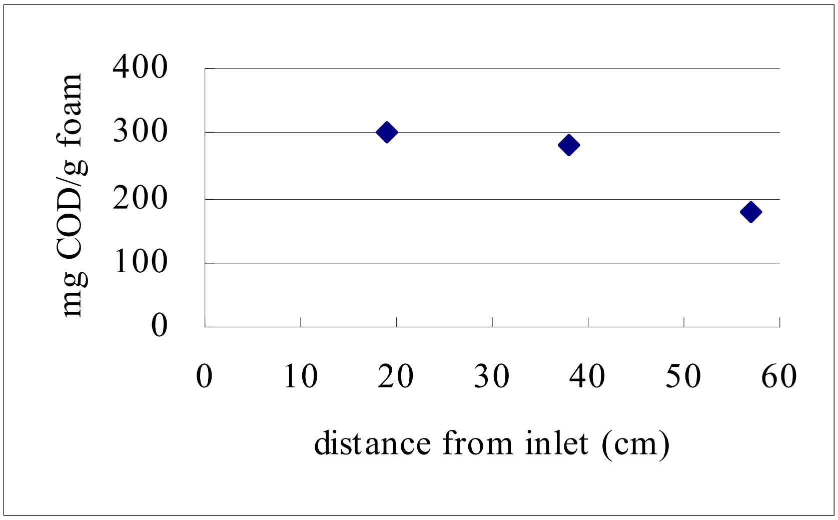

Figure 3.24. – Total biomass accumulation as determined by COD measurements along the bioreactor column on day 88 of operation.

recycled within the biofilm. Since the xylene removal in the experimental biofilter was still quite high after 4 months of operation, this suggests that sufficient nitrogen was available for the xylene-degrading organisms. Nevertheless, the readily available nitrogen in the biofilm (as nitrate and ammonium) should be monitored in biofilters that are operated for extended periods.

3.4.2 Discontinuous Operation

To determine the response of the biofilter to periodic shutdowns, the BTEX feeding to the 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, humidity and nutrient spray were supplied as usual. The recovery of the biofilter following each shutdown test was monitored until the removal efficiency across the biofilter exceeded 95%. Figure 3.25 shows the response of the biofilter after several one day shutdown tests in which the VOC feed to the column was interrupted for a 24 hour period. When the BTEX feed was resumed after each one-day shutdown period, a minimal effect on BTEX removal was observed with the BTEX removal efficiency in the biofilter recovering to pre-shutdown levels within 10 hours. The shutdown had the greatest effect on o-xylene removals which declined to 85% before recovering to 98%. As evident in Figure 3.25, the bioreactor response improved in each subsequent shutdown test as the biomass in the system adapted to the periodic feed cycle.

Figure 3.26 summarizes the response of the biofilter after several 2.8-day shutdown tests which simulated extended weekend shutdown periods. A greater reduction in BTEX removal was observed following the 2.8-day shutdown tests than the 1-day shutdown tests but the system again recovered full BTEX removal efficiency within 10 hours. As in the previous experiments, xylene removal was detrimentally impacted by the 2.8-day shutdown period. Benzene removal was also sensitive to the 2.8-day shutdown period in contrast to the one-day shutdown experiments which showed little effect on benzene removal.

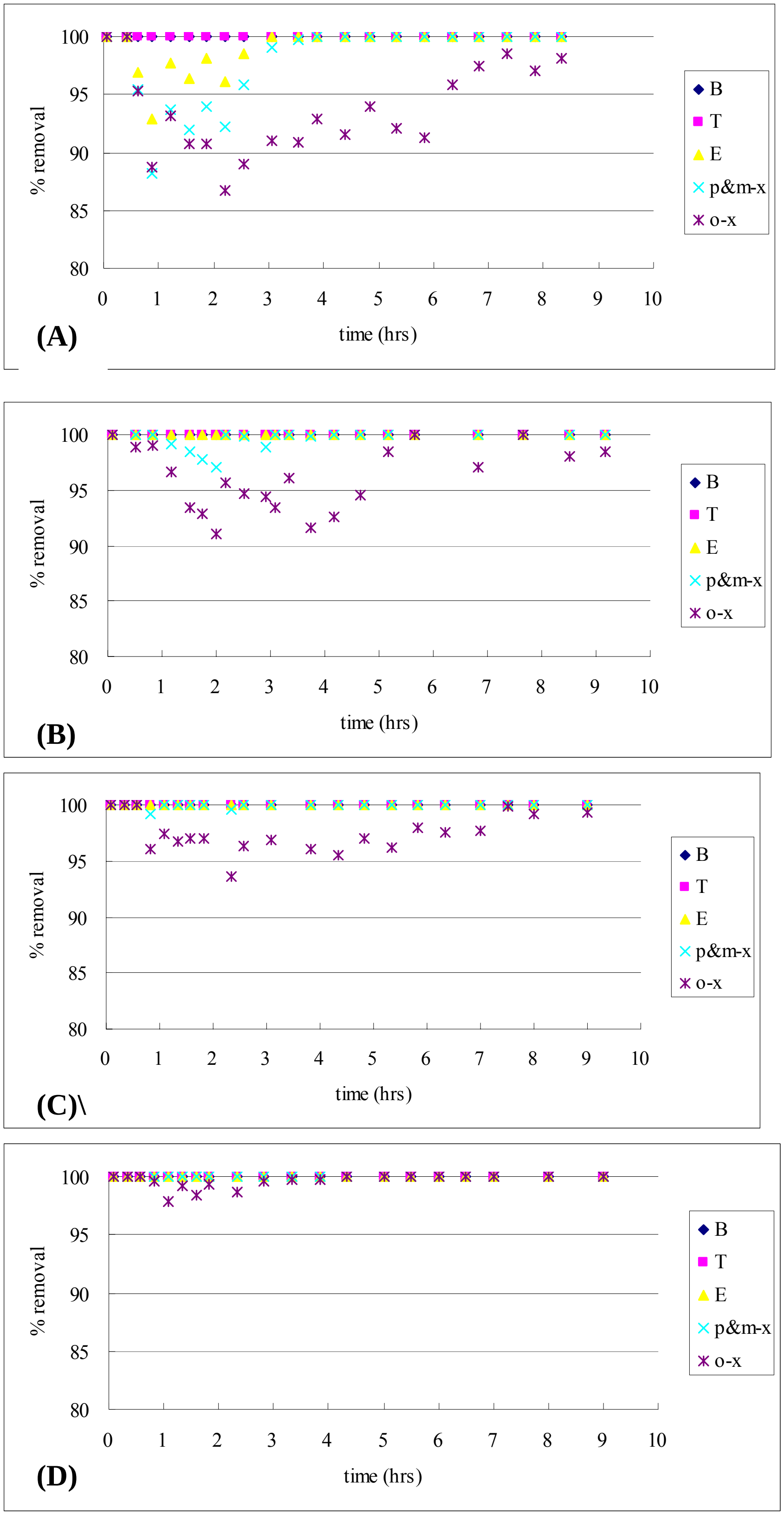

Figure 3.25. – BTEX removal efficiency after a 24 hour shutdown period. (a): 1st shutdown, (b): 2nd shutdown, (c): 3rd shutdown, (d): 4th shutdown.

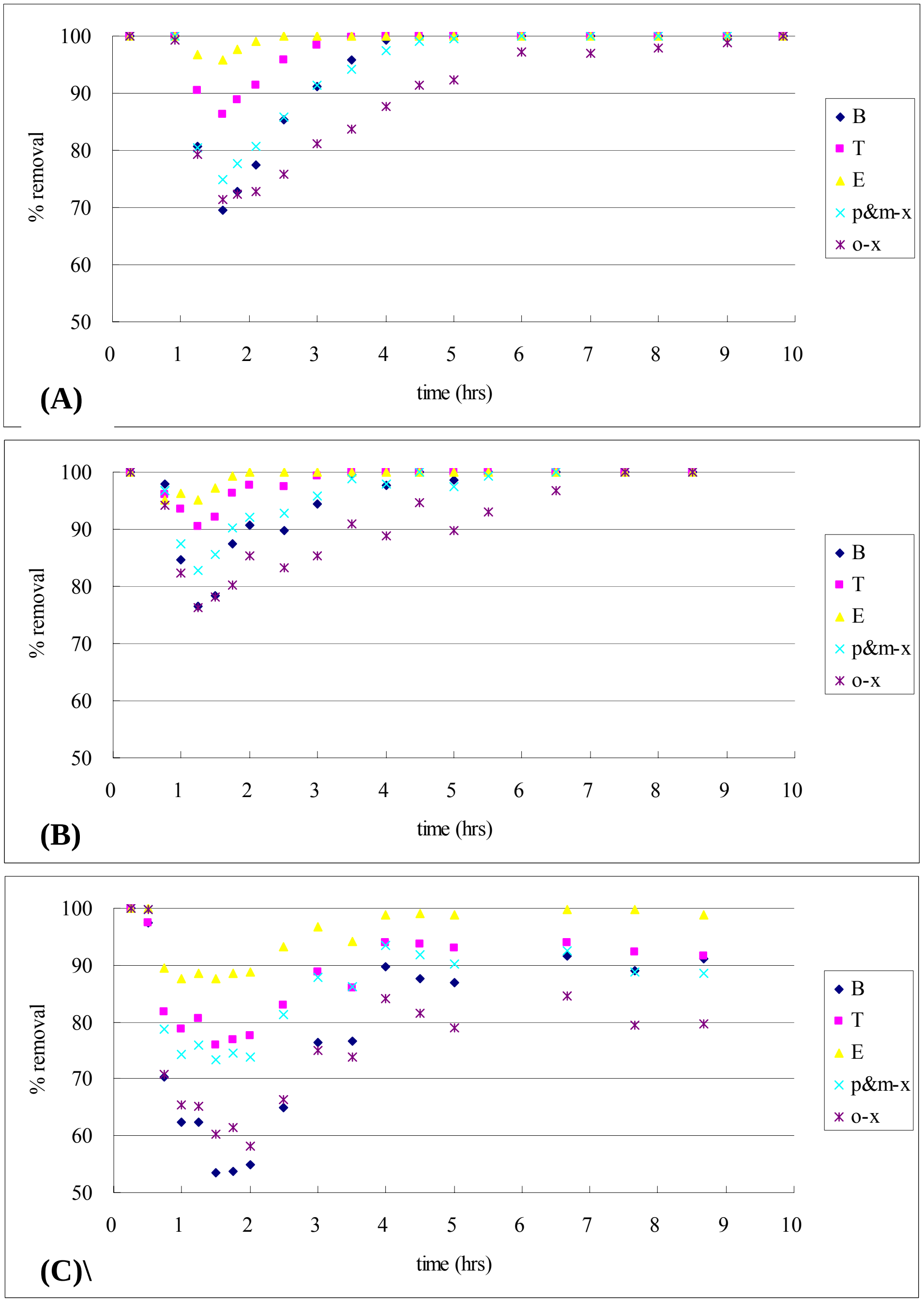

Figure 3.26. – BTEX removal efficiency after 2.8dyas shutdown period. (a): 1st shutdown, (b): 2nd shutdown, (c): 3rd shutdown.

4. Conclusions and Future work

The focus of our work during this report period was to investigate: (1) the interactions between BTEX, volatile organic compounds, metal ions, and SMZ; (2) the efficacy of SMZ treatment of produced water under different solution conditions; and (3) the operating conditions of a lab scale VPB for treatment of the waste gas stream from SMZ regeneration. BTEX sorption was described with linear isotherms. Statistical analysis indicated that a 99.5% confidence level was required to describe isotherms generated in this study as parallel to those reported previously by the PIs. Using these levels of confidence, the effects of pH were determined to be negligible, while high semi-volatile concentrations increased BTEX sorption. Phenol sorption onto SMZ was related to aqueous solubility and octanol/water partitioning coefficients. Although the slopes of these correlations were similar to those developed in the PIs' previous work, the log intercepts were approximately 1-1.5 orders of magnitude greater in this research. Naphthalene sorption could not be precisely measured, but treatment was sufficient to reduce contaminant levels below the EPA's health advisory level.

Metal sorption of chromium could be described by a Langmuir isotherm in ultrapure water, and by a linear isotherm in saline water over the concentration range tested. Selenium sorption was described by a Langmuir isotherm in ultrapure water, but no sorption was observed in the saline water. Barium sorption could be described with Langmuir isotherms; little difference was observed between sorption onto modified and unmodified zeolite. Differences between the sorption of the metal ion and oxyanions could be explained based on ion exchange and surface complexation theory.

The experiments conducted with a lab-scale biofilter packed with foam indicate that this system can achieve high BTEX removal efficiencies once the nutrient delivery system is optimized. The xylene isomers and benzene were found to require the greatest biofilter bed depth for removal indicating that these VOCs would ultimately control the size of the biofilter required for the produced water applicationn. The biofilter recovered rapidly from one day and 2.8-day shutdowns indicating that the system, once established, was resilient to discontinuous feed conditions. This performance stability provides flexibility on the SMZ regeneration process since it does not necessarily have to provide a continuous VOC feed to the downstream biofilter.

Despite the promising results obtained with the foam biofilter, this system requires an external nutrient medium be provided on a regular basis to maintain biofilter performance. Since the SMZ/Biofilter treatment system may be located in very remote locations, it was decided to investigate the performance of a relatively simple biofilter that is packed with a compost-based packing material. This compost material contains its own supply of key nutrients such as nitrogen and thus may be operated for extended periods without an external nutrient supply. A compost-based biofilter system has been constructed and is currently undergoing testing to determine its BTEX removal capacity as well as its ability to handle discontinuous VOC feed conditions. Results collected to date indicate that the compost-based system can achieve BTEX removals of greater than 98% and that the system is also resilient to shutdown and restart conditions.

At this stage of the project, we have completed most of the first two objectives of this study:

Objective 1: Characterize and optimize the SMZ primary and secondary regeneration processes to enable long-term operation of the SMZ process for a wide range of produced water applications (Project Phase 1);

Objective 2: Develop a VPB that is optimized for treating the waste gas streams generated by SMZ regeneration for a variety of produced waters (Project Phase 2).

Therefore, for the next six months, the effort will be to focus on objectives 3, optimize the coupled SMZ/VPB treatment technology both at the laboratory and field scale (Project Phases 3 and 4), as we proposed for this project. We have already assembled necessary equipments and are ready for a field test of the combined SMZ/VPS system this summer. It will be ahead of our proposed schedule for the Phase 4 field test (23-30 month of the project). The results from this preliminary field study, nevertheless, will be adapted to enhance the design of operating parameters for the SMZ/VPS in lab studies.

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