Western Kentucky University
TopSCHOLAR®

Masters Theses & Specialist Projects   Graduate School

8-1-2008

Admicelle-Based Solid Phase Extraction of Phenols Using Dialkylammonium Surfactant in the Hydroxide Form

Kali R. Pickering
Western Kentucky University, kali.pickering@wku.edu

Follow this and additional works at: http://digitalcommons.wku.edu/theses

Part of the Organic Chemistry Commons

Recommended Citation

ADMICELLE-BASED SOLID PHASE EXTRACTION

OF PHENOLS USING DIALKYLAMMONIUM

SURFACTANT IN THE HYDROXIDE FORM

A Thesis Presented to

The Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment of the

Requirements for the Degree

Master of Science

By

Kali R. Pickering

August 2008

ADMICELLE-BASED SOLID PHASE EXTRACTION

OF PHENOLS USING DIALKYLAMMONIUM

SURFACTANT IN THE HYDROXIDE FORM

Date Recommended ___May 2, 2008_____

___ Dr. Eric Conte _____
                            Director of Thesis

___Dr. Stuart Burris _____

___Dr. Chad Snyder _____

_____
Dean, Graduate Studies and Research   Date

ACKNOWLEDGMENT

TABLE OF CONTENTS

ADMICELLE-BASED SOLID PHASE EXTRACTION OF PHENOLS USING

DIALKYLAMMONIUM SURFACTANT IN THE HYDROXIDE FORM

Kali Pickering   August 2008   23 Pages

Directed by: Dr. Eric Conte

Department of Chemistry   Western Kentucky University

A technique for admicelle-based solid phase extraction is presented in which a dialkylammonium surfactant in the hydroxide form is immobilized on silica. By converting dihexadecyldimethylammonium bromide to the hydroxide form, the surfactant is allowed to have the property of a strong base, aiding in the extraction of acidic phenols which are difficult to extract because of their differing polarities. The surfactant-silica admicelle parameters were optimized for the efficient extraction of eight phenols. Adsorbed phenols were eluted from the sorbent using small volumes of methanol. The phenols were preconcentrated from drinking water samples and were determined using high performance liquid chromatography (HPLC) coupled with a photo diode-array detector.

I. INTRODUCTION

A. <u>Background</u>

In chemical analysis, sample preparation is just as important as the latest technology in analytical instrumentation. For example, the pre-concentration of dilute analytes is of great importance when concentrations are lower than the detection limits of a given instrument. This is especially true in environmental samples, where it is also often necessary to separate analytes of interest from a more complex matrix to get a cleaner analysis. Both of these functions can be accomplished by various extraction techniques.

Liquid-liquid extraction (LLE) is one such extraction technique in which an immiscible solvent, usually an organic solvent, is added to the sample matrix. Analyte partitioning occurs between the matrix and the solvent, and then the solvent is removed. Usually several volumes of solvent must be added to achieve a quantitative extraction, thus sample pre-concentration must be accomplished by removing the organic solvent.[1] The excessive use of organic solvents in this technique becomes expensive and also creates a waste stream. LLE has predominantly been replaced by solid phase extraction.

In solid phase extraction (SPE), an aqueous sample is passed through a small volume of a solid stationary phase onto which the analyte of interest is extracted. A small amount of solvent is required to release the analyte from the solid phase. Solid phase extraction has become a leading technology over the past fifty years in the extraction of both organic and inorganic species from aqueous samples. SPE allows for easy concentration of analytes, requires minimal amounts of solvent, and can be

customized to extract either a broad range of analytes or to provide extraction of a specific pollutant or compound class.[2] SPE techniques include normal and reversed phase adsorption, cation and anion exchange, graphitized carbon black, and hemimicelle and admicelle-based extractions.[3]

The use of admicelle-based solid phase extraction procedures continues to increase. In this type of extraction, ionic surfactants are attached to a solid phase of counter charge, typically a metal oxide such as alumina, silica, titanium dioxide, or ferric oxyhydroxides.[4] In hemimicelles, monolayers of surfactants adsorb head down on the oppositely charged surface of the oxide. Admicelles, which have a bilayer structure, occur after the surface is saturated by the adsorbed surfactant, aided by the hydrophobic interaction of their nonpolar chains. These surfaces are versatile because they provide hydrophobic and ionic interactions, both of which can be easily modified due to the large number of commercially available surfactants. These phases have been used to extract analytes such as polyaromatic hydrocarbons (PAH's), linear alkylbenzene sulfonate (LAS) homologs, chlorophenols, estrogens, and ionic substances.[5-9]

B. Phenols

Phenol and its derivatives are found in several industries, including plastics, paper, and pesticides, as both production components and byproducts. Chlorophenols and nitrophenols are used as intermediates in the synthesis of dyes, pigments, phenolic resins, pharmaceuticals, rubber chemicals, photographic chemicals, pesticides, and herbicides. Some are used directly as flea repellents, fungicides, wood preservatives, mold inhibitors, antiseptics, disinfectants, and antigumming agents for gasoline.[10,11]

Presence of phenols in environmental waters is probably most influenced by release from the production plants and chemical firms where they are used as intermediates. Also, mononitrophenols can form from the photodegradation of pesticides, and chlorophenols are produced in chlorination processes.[10,11]

Phenols have an unpleasant effect on the taste and odor of water and fish in which they are present. Some phenols lend an undesirable taste and odor at levels below 1 ppb.[10] Phenols are toxic and are found in the EPA's list of priority pollutants. Acute toxicity levels for 4-chloro-3-methylphenol can occur as low as 30 ppb, while the same for 2,4,6-trichlorophenol can occur at 970 ppb. The EPA's Maximum Contaminant Level Goal (MCLG) for pentachlorophenol is zero. However, an enforceable standard called the Maximum Contaminant Level (MCL) is set at 1 ppb. The EPA believes that even short-term exposure at levels above the MCL can cause damage to the central nervous system. Long-term effects could be damage to the liver and kidneys, adverse reproductive effects, and cancer.[12] It is evident that phenols are of great concern in the monitoring of environmental and drinking waters. Phenols are difficult to extract because of their varying polarities. The structures of eight phenols used in this study and their pK_a values and partitioning coefficients are listed in Figure 1 and Table 1, respectively.
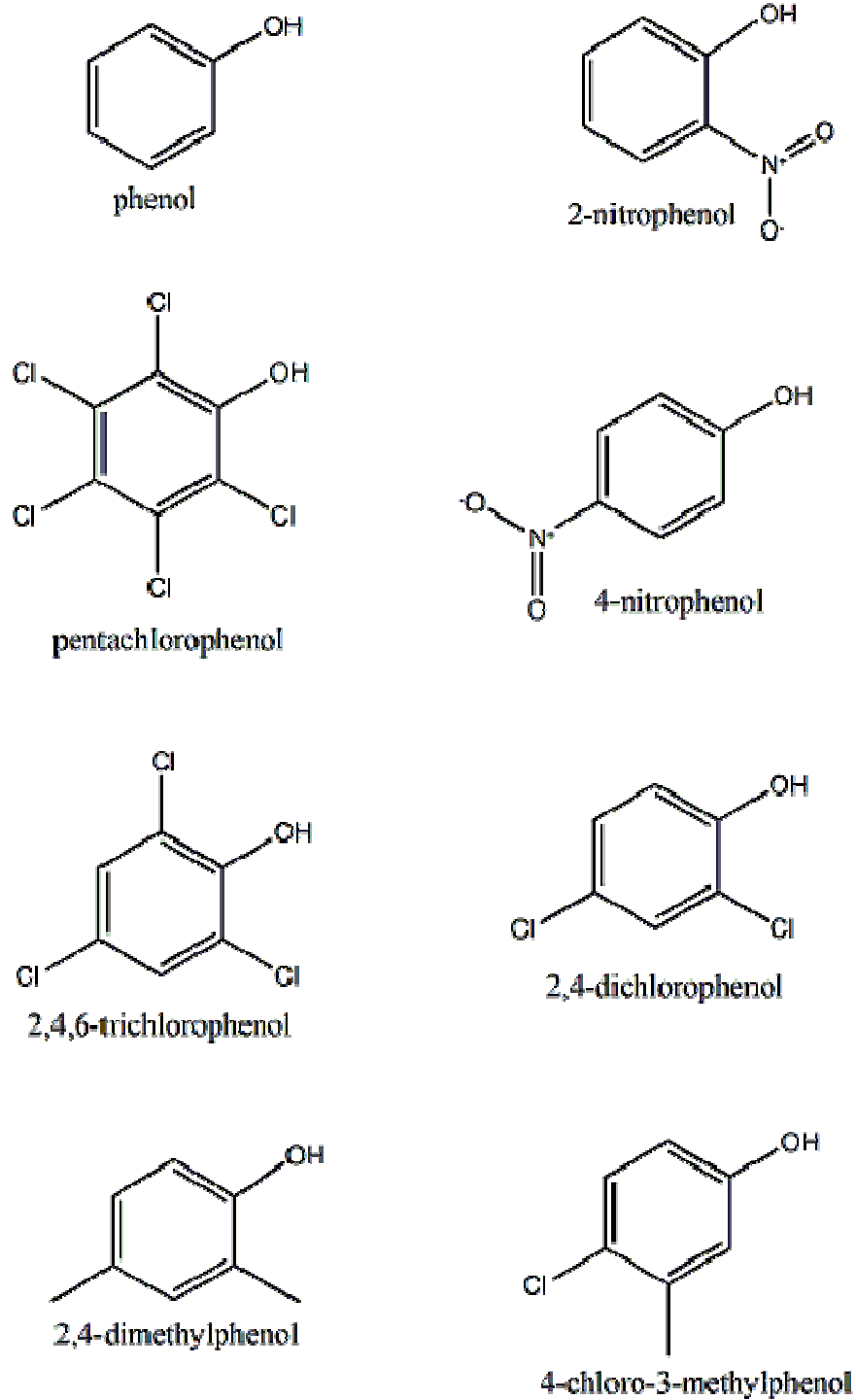
Figure 1. Eight phenols used in this study.

Table 1. pK_a values and partition coefficients in octanol and water (log K_{OW}) for selected phenols.

	pK_a	log K_{OW}
phenol	9.95	1.50
4-nitrophenol	7.15	1.90
2-nitrophenol	7.22	1.78
2,4-dimethylphenol	10.58	2.42
4-chloro-3-methylphenol	9.55	3.10
2,4-dichlorophenol	7.85	3.08
2,4,6-trichlorophenol	6.21	3.69
pentachlorophenol	4.90	5.01

C. Purpose of Study

The current literature on applications of admicelle-based solid phase extraction reports the utilization of surfactants in counter ion forms that are not acidic or basic.[13,14] For example, cetyltrimethylammonium ion can be purchased as the chloride or bromide salt. In these studies, admicelle extractions of analytes are based only on their hydrophobicities. The purpose of this study was to develop the extraction of phenols based on their properties as weak acids by converting surfactants to the hydroxide form in which they have the property of a strong base.

D. Theory and Method

In this work, dialkylammonium surfactants in the bromide form are converted to the hydroxide form through a reaction with Ag_2O (Figure 2). Silver (I) reacts with the

bromide ion on the surfactant to form the AgBr precipitate. The unstable O^{2-} ion pulls H^+ from the solvent to form a hydroxide ion which becomes the counter ion on the surfactant. The hydroxide ion reacts with the H^+ on SiOH to form a water molecule, leaving the positively-charged ammonium group of the surfactant to bind electrostatically to the SiO^- on the silica surface (Figure 3). When a surfactant bilayer is formed, exposed hydroxide ions react with acidic phenols, resulting in phenolate anions as a product. These anions subsequently become the counter ion to the surface-attached surfactant molecules (Figure 4). The surfactant molecules and phenols are released from the silica surface by small volumes of methanol (Figure 5).

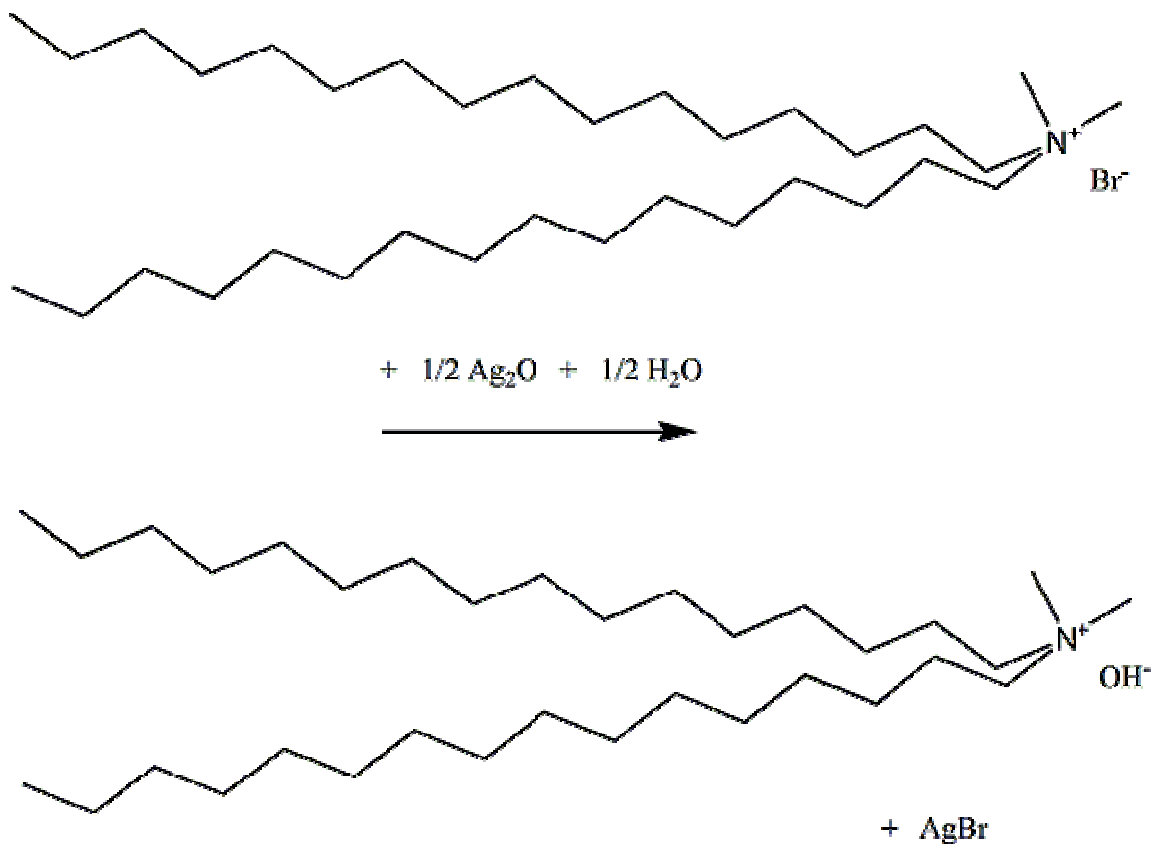**Figure 2.** Bromide counter ion on the surfactant is exchanged for the hydroxide ion.

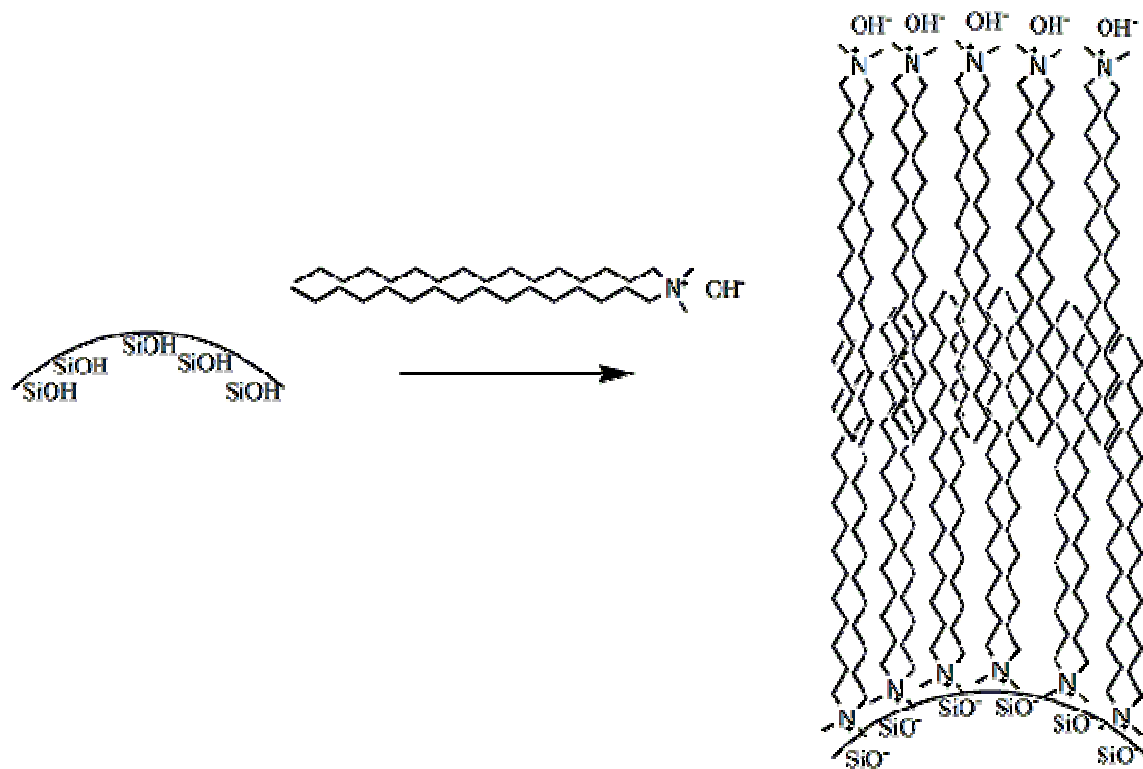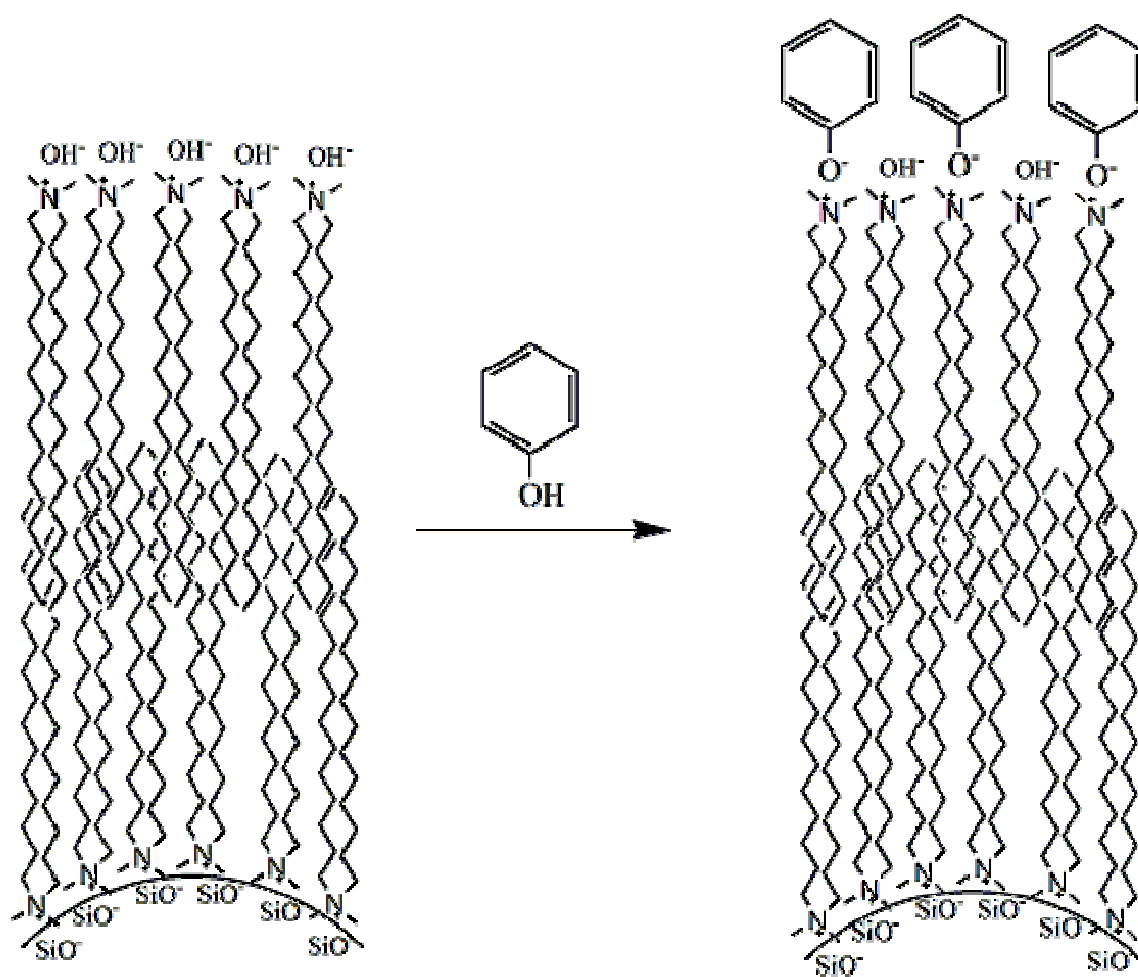**Figure 3.** Surfactant is immobilized on silica surface.

Figure 4. Phenol is adsorbed on sorbent surface due to an acid-base reaction between the acidic hydrogen on phenol and the hydroxide counter ion on the surfactant resulting in electrostatic interactions between the phenolate ions and the exposed ammonium cations.
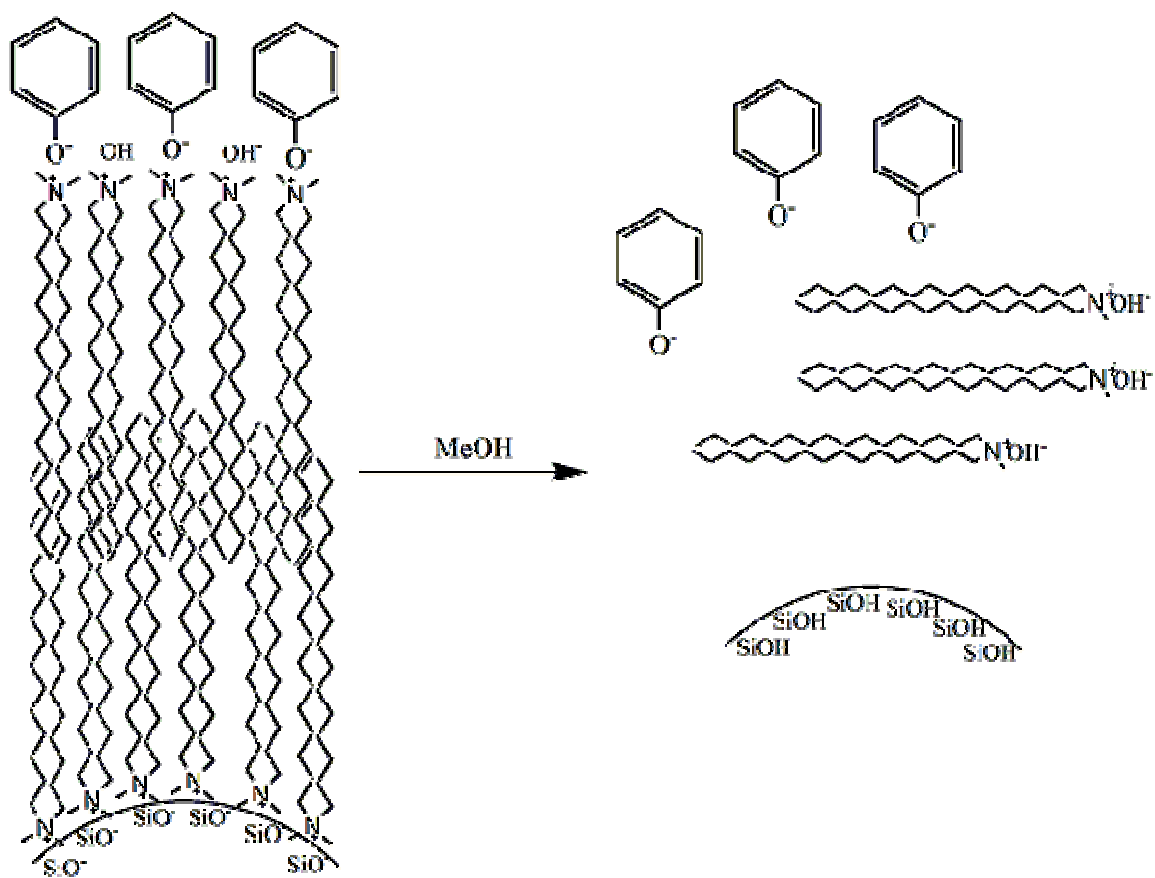
Figure 5. Methanol disrupts the bonds between the surfactant and silica surface.

II. EXPERIMENTAL

A. Chemicals and Materials

      Unmodified silica was purchased from International Sorbent Technology Ltd. (Hengoed Mid Gladm, UK). Dimethyldipalmitylammonium bromide (di-C_{16} dimethylammonium bromide) was purchased from TCI America (Portland, OR, USA). Silver (I) oxide was purchased from Alfa Aesar (Ward Hill, MA, USA). Phenol was purchased from Fisher Scientific. 4-Nitrophenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol were purchased from Aldrich. Calcium chloride dihydrate was purchased from Acros Organics (New Jersey, USA). Methanol (HPLC grade) was purchased from Fisher Scientific.

B. Instrumentation

B.1 TGA

      The surface of the surfactant-immobilized silica was characterized using TGA SSC 5200-H thermogravimetric analysis instrument from Seiko (Chiba, Japan). The analysis temperature was ramped from 100°C to 800°C at a rate of 10°C/min.

B.2 High Performance Liquid Chromatograph (HPLC)

      A Varian High Performance Liquid Chromatograph was used to analyze phenol elution samples. Samples were stored in glass vials and loaded into the Varian Prostar Auto Sampler (Model 410). The HPLC system was fully computer automated. The column was a Varian Microsorb MV C_{18} 100 x 4.6 mm reversed phase column. The detector was a Varian photodiode array (PDA) detector (Model 330). The mobile phase

was programmed on a Varian Reciprocating Pump (Model 9012). The mobile phase was A: 1% formic acid in nanopure water and B: 1% formic acid in acetonitrile. The A:B ratio was set at a gradient of 90:10 to 0:100 in 25 min, and held at 0:100 until 30 min. The flow rate was 1 mL/min. The data collected from the HPLC was used to calculate the percent recoveries of phenols.

B.3 Adjusta-Chrom Chromatography Column

Silica sorbents were housed in a 360 x 1.0 cm I.D. Adjusta-Chrom (Ace Glass, Vineland, NJ, USA) adjustable chromatography column. In order to accommodate the small amount of sorbent, 15 and 30 cm plastic extenders with frits were used.

B.4 Syringe and Syringe Pump

Rinse study solutions were forced through an Adjusta-Chrom column using a KD Scientific (Holliston, MA, USA) Single Syringe Infusion Pump with a glass syringe.

B.5 Sample Delivery System for Phenols

Water samples were placed in a 2 L bulb (5824-15, Ace Glass) that was connected to the Adjusta-Chrom column using a 25 mm adapter (Ace Glass) connected to 1/8" Teflon tubing using a P-621 adapter (Scivex, Oak Harbor, WA). One end of the bulb was attached to the column and the other was connected to air in order to create pressure (8 psi) to send the sample through the column. The air was filtered by a Deltech filter (Model 0202, Tulsa, OK) and the pressure was controlled by a Brooks Pressure Regulator (Model 8601, Hatfield, PA,USA). The sample flow rate was approximately 10 mL/min.

C. Silica Sorbent Preparation

C.1 Surfactant Preparation

Dimethyldipalmitylammonium bromide (0.10 M) was prepared in methanol. Silver oxide was added to the surfactant at a 1:2 mole ratio (0.05 M) to form dimethyldipalmitylammonium hydroxide and silver bromide. Silver bromide was filtered from the solution.

C.2 Surfactant Immobilization on Silica Surface

Initially, 2 mL of unmodified silica were placed in the Adjusta-Chrom column then 5 mL of 0.10 M dimethyldipalmitylammonium hydroxide in methanol was passed through drop-wise.

D. Phenols Extraction

D.1 Sample Adsorption

The Adjusta-Chrom column containing the surfactant-modified sorbent was attached to the 2-L bulb as described in the Instrumentation section. Then a 250-mL water sample was spiked with 100 μL of a stock solution containing 0.20 mg/ml of each of the eight phenols. The sample was put in the bulb and passed through the column.

D.2 Sample Elution

The Adjusta-Chrom column containing the sorbent and captured phenols was attached to the syringe pump where a 2-mL aliquot of methanol was passed through and captured. This step was repeated twice.

E. <u>Sample Analysis</u>

Eluted phenol samples were analyzed by HPLC as described. 100 μL of the

phenols mixture was spiked in 2 mL of methanol for the standard. A chromatogram from

the analysis of a spiked tap water sample is shown in Figure 6. The calibration range,

calibration curve, and detection limit of each of the phenols are shown in Table 2. The

calibration curve was determined by the analysis of five different concentrations of each

phenol on its calibration range. The baseline noise level provided by the instrument was

multiplied times three and plugged into *y* on the calibration curves to find the limit of
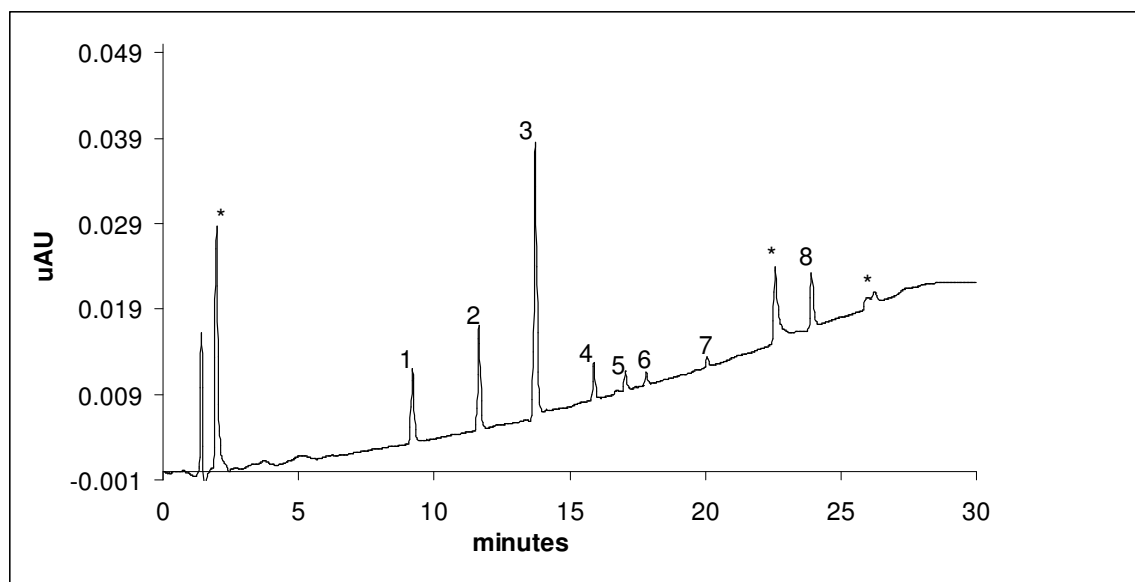
detection of each phenol.

Figure 6. Chromatogram of HPLC separation of eight phenols extracted from a spiked
tap water sample. Peaks with asterisks (*) are background from the tap water sample.
Numbered peaks are phenols: (1) phenol; (2) 4-nitrophenol; (3) 2-nitrophenol; (4) 2,4-
dimethylphenol; (5) 4-chloro-3-methylphenol; (6) 2,4-dichlorophenol; (7) 2,4,6-
trichlorophenol; (8) pentachlorophenol.

Table 2. HPLC calibration data for selected phenols. Detection limits were calculated as three times the baseline noise.

Analyte	Calibration Range (ng/mL)	Calibration Curve	R^2	Detection Limit (ng/mL)
phenol	1.2 – 64.0	y = 12762x + 1391	0.992	0.084
4-nitrophenol	1.2 – 64.0	y = 14074x + 2917	0.990	0.072
2,4-dimethylphenol	1.2 – 64.0	y = 3381x + 845	0.981	0.29
2-nitrophenol	1.2 – 64.0	y = 35964x + 2496	0.953	0.028
4-chloro-3-methylphenol	1.2 – 64.0	y = 3664x - 171	0.970	0.27
2,4-dichlorophenol	2.4 – 64.0	y = 1958x + 220	0.986	0.51
2,4,6-trichlorophenol	2.4 – 64.0	y = 2143x - 826	0.998	0.47
pentachlorophenol	1.2 – 64.0	y = 11746x - 365	0.998	0.086

A. Thermogravimetric Analysis of the Sorbent

TGA was used to analyze the surfactant-silica surface and the surfactant individually. The results in Figure 7 reveal three peaks for the surfactant, the predominant one at 215°C. With the surfactant-silica surface, two broadened nearly symmetrical overlapping peaks appear. This suggests that there are two groups of surfactant in nearly equal amounts on the silica such as in a bilayer arrangement. The peak at the lower temperature is likely to originate from surfactant in the layer interfacing aqueous media, while higher temperatures are required to remove surfactant immobilized to the solid surface.
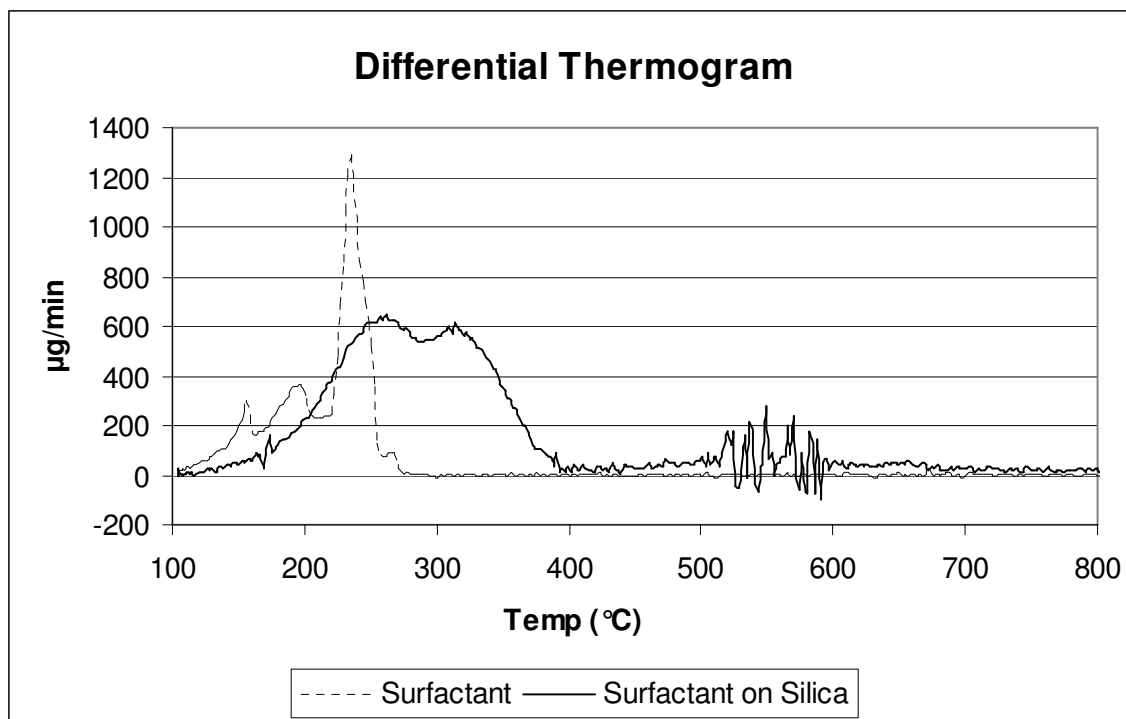

Figure 7. DTG for prepared sorbent and individual surfactant is evidence for admicelle formation on the silica surface.

15

B. Enhancement of Phenol Extraction

Our initial experiments focused on the extraction of the eight phenols using silica modified with the dual-chain surfactant (dihexadecyldimethylammonium) in the bromide form. A 250-mL water sample spiked with 80 ppb of each of the phenols was passed through the sorbent housed in the Adjusta-Chrom column according to the described procedure. As shown in Figure 8, this sorbent was only able to slightly capture 4-nitrophenol, 2-nitrophenol, and pentachlorophenol. The recoveries were very similar to the extraction on unmodified silica. Thus the hydrophobic modification using the surfactant in the bromide form was unable to enhance the extraction of the phenols. When the silica was modified with the hydroxide form of the surfactant, harnessing an acid-base reaction between the phenols and sorbent surface, an obvious improvement in the recovery of all phenols was observed. Quantitative extraction was achieved for all phenols except phenol, which had a recovery of approximately 79%.

Experiments were conducted to test the effect of using a dual chain versus a single chain surfactant. In each case, the chain length was hexadecyl and the surfactant was in the hydroxide form. In Figure 9, the only significant difference is shown in the results for phenol. The recovery for phenol using the dual chain surfactant was greater (approximately 30%) than the single chain surfactant. For this reason the dual chain was used for the rest of the study.

The next parameter optimized was the amount of surfactant loaded onto 1 mL of silica gel. In Figure 10, percent recoveries of the eight phenols were measured after adding 0, 1, 2, 4, and 6 mL of a 0.10M dihexadecyldimethylammonium hydroxide solution in methanol to 1 mL of silica gel in the Adjusta-Chrom column. For most of the

phenols, nearly a quantitative amount of phenols were recovered after adding 1 mL of the surfactant solution. Only phenol and 2,4,6-trichlorophenol have significant improvements in recovery by doubling the amount of surfactant solution to 2 mL. Beyond 2 mL the recoveries for all the phenols were essentially the same.

The amount of silica gel support was further studied. 2 mL of the 0.10M dihexadecyldimethylammonium hydroxide solution was placed on half of the original amount of silica gel (0.5 mL). The results indicated (data not shown) that recoveries of all the phenols were statistically similar. We chose not to explore a further reduction in the amount of silica gel because of the practical limitation of handling fewer amounts with the Adjusta-Chrom column.

Breakthrough studies were conducted by measuring the percent recovery of each phenol with sample volumes of 250, 500, and 1000 mL. 100 μL of the phenol standard was spiked into each of these volumes of DI water. Except for phenol, each of the other seven phenols was quantitatively recovered. The results for phenol, shown in Figure 11, reveal decreasing recovery at higher sample volumes. This is most likely due to the higher polarity of phenol.

Because the surfactant layer is a removable phase, the stability of this phase must be studied by looking at the effect of potentially competing cations in solution. In natural water samples, these ions would be mostly calcium and magnesium. These ions have the potential to prematurely remove the surfactant phase via cation exchange. Hard water samples were prepared by adding calcium chloride dihydrate to water and were passed through the surfactant immobilized sorbents. The eight phenols in three different water hardness levels (250, 500, and 1000 ppm $CaCO_3$) were investigated and the results

presented in Figure 12. The recovery of phenol decreased at higher water hardness

levels, but the other seven phenols were unaffected by water hardness up to 1000 ppm

$CaCO_3$. Within the surfactant phase ionic sites appear to be protected from competing

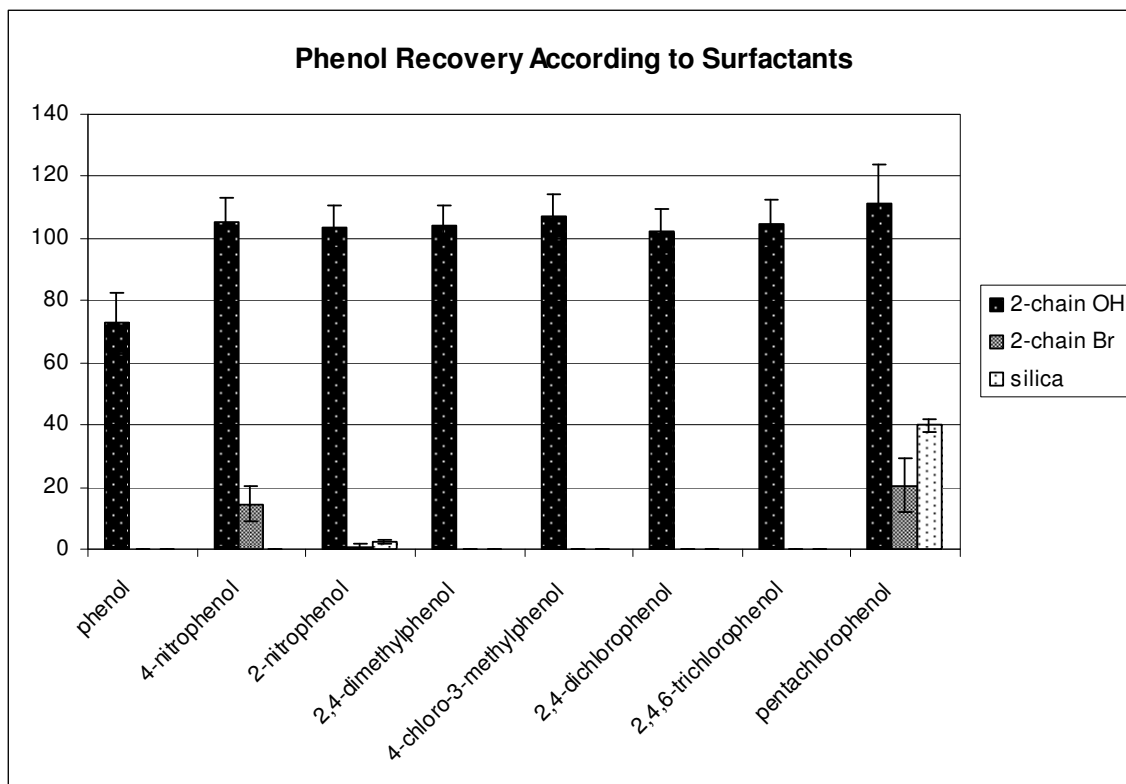counter ions that are found in natural water samples.

Figure 8. Recovery of phenols on three surfaces: dihexadecyldimethylammonium
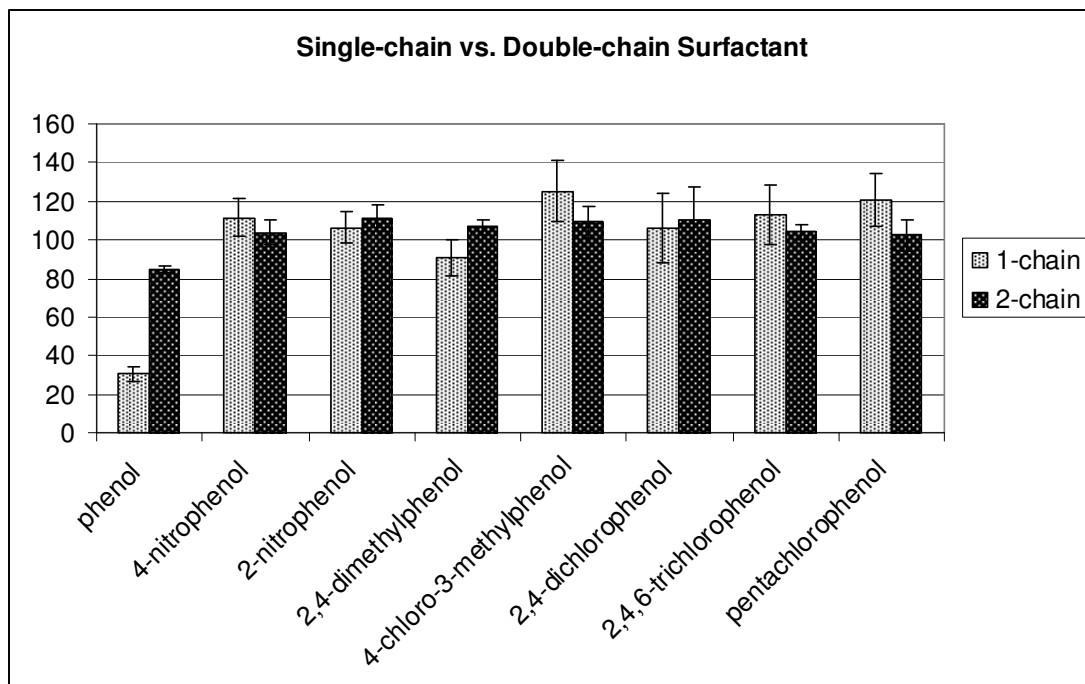hydroxide on silica, dihexadecyldimethylammonium bromide on silica, and plain silica.

Figure 9. Recovery of phenols on surfactant-silica surfaces using two surfactants of C_{16} chain length in the hydroxide form, one with a single chain and another with a double chain configuration.
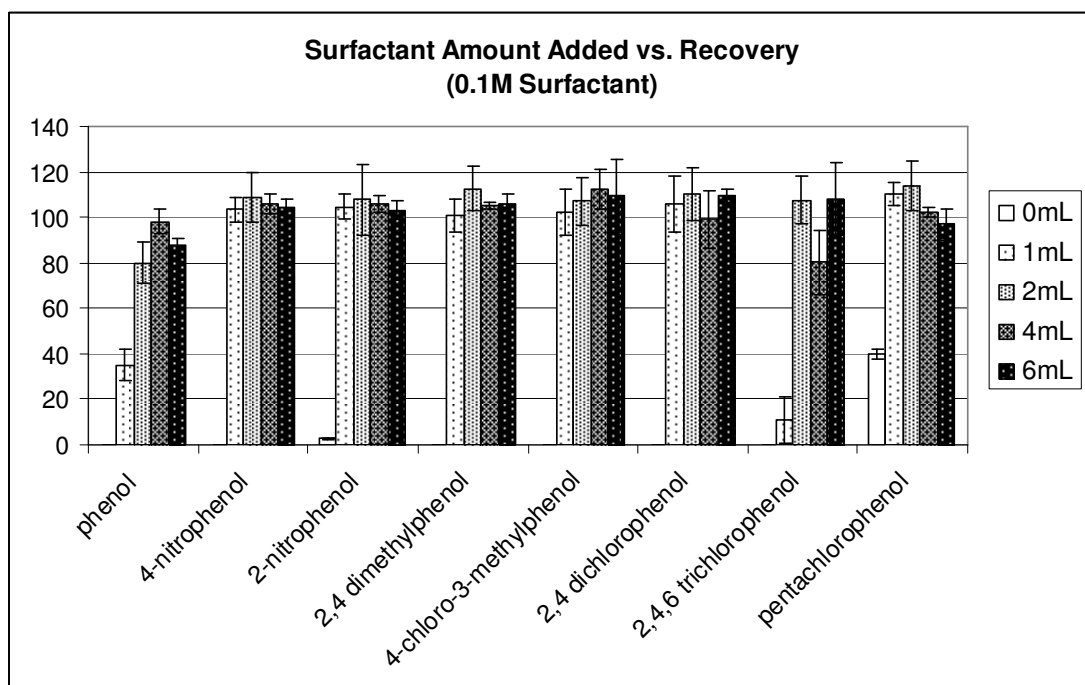

Figure 10. Recovery of phenols according to the amount of 0.1M surfactant used to treat the silica.
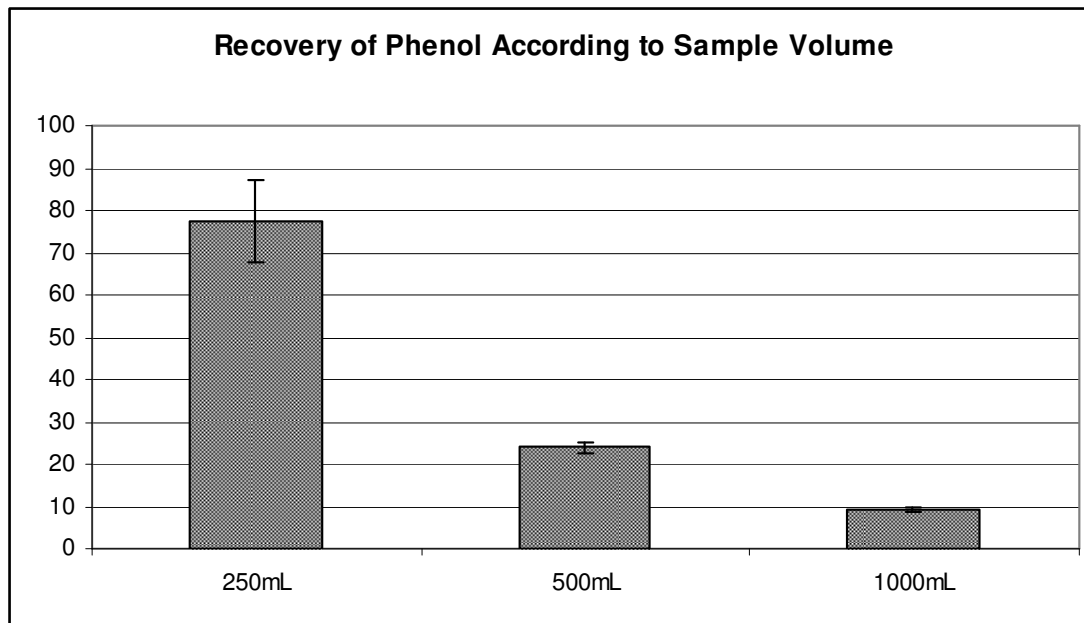
Recovery of Phenol According to Sample Volume

Figure 11. Recovery of phenol decreases when the volume of water passing through the sorbent increases due to its increased polarity.

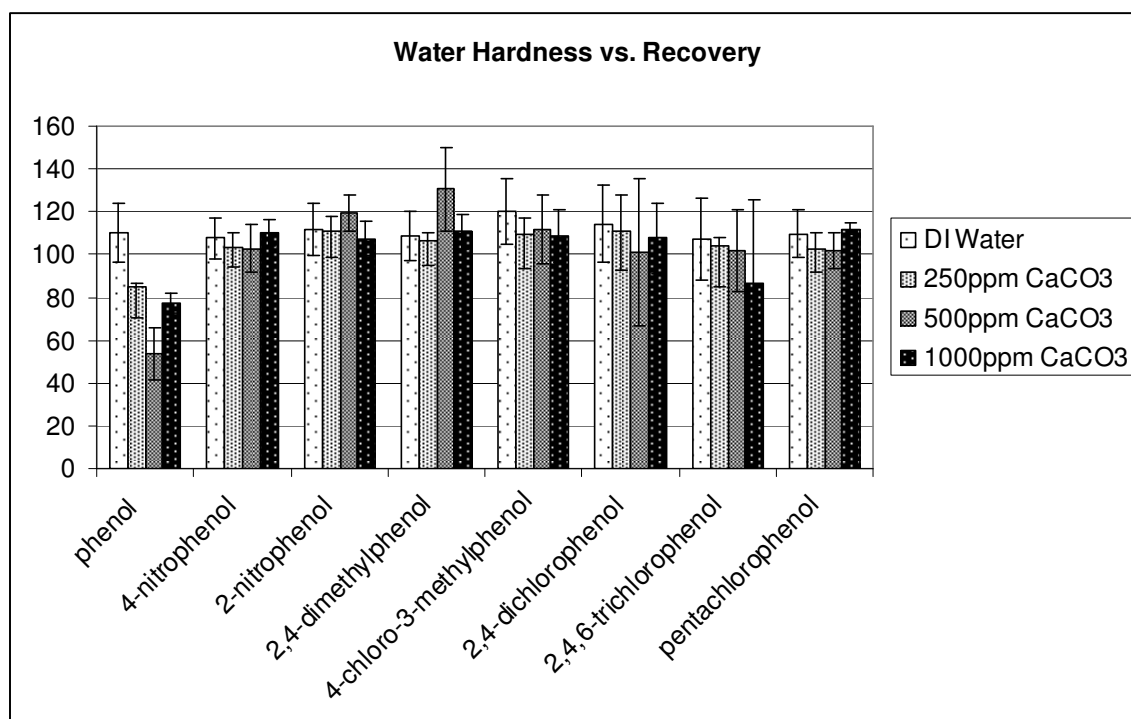**Water Hardness vs. Recovery**

Figure 12. Recovery of phenols in the presence of competing ions (calcium carbonate) in the water sample.

C. Comparison to Anion Exchange Sorbent

A comparison was made between the presented surfactant-bound sorbent and a commercially available anion exchange sorbent using the application of preconcentration of the selected phenols from drinking water. Both sorbents contain hydroxide as the counter ion. As shown in Figure 13, the phenols were recovered better using the surfactant-modified silica than the anion exchange resin. Poorer recoveries with the anion exchange resin can be attributed to either breakthrough or irreversible binding of sorbed phenols. The surfactant-immobilized silica does not suffer these possible setbacks because of two possible reasons. Namely, the removable nature of the phase eliminates potential irreversible binding and the fluid nature of the phase also protects the phenolate ions from being removed prematurely by natural ions in solution.
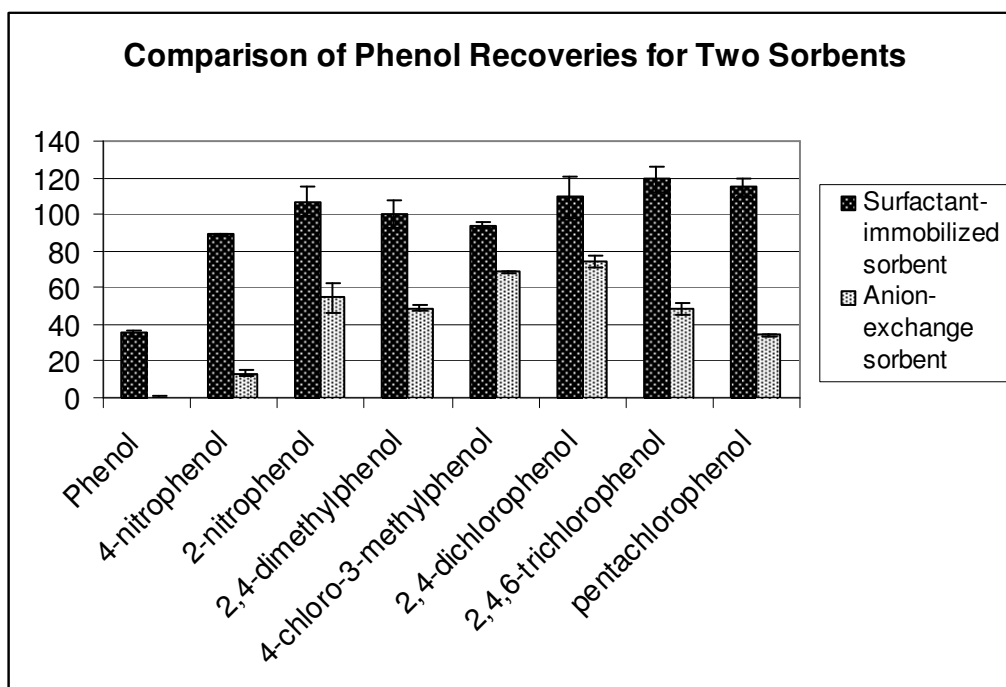

Figure 13. Phenol recoveries on two different sorbents, surfactant-immobilized silica and a commercially available anion-exchange sorbent.

IV. CONCLUSION

An admicelle-based solid phase extraction technique using surfactants with hydroxide counter ions was presented. This technique harnesses an acid-base reaction on the sorbent surface which maximizes the extraction of weak acids, particularly phenols, from aqueous media. Experimental parameters such as the type and amount of surfactant and amount of silica were optimized. A stable solid phase extraction surface was created featuring strong electrostatic interactions on both the silica-surfactant interface and the surfactant-phenol interface that were unaffected by competing ions in solution. Also the hydrophobic nature of the bilayer protected the phenols from competing ions. Dihexadecyldimethylammonium hydroxide admicelles on silica were able to quantitatively extract seven of eight phenols.

V. BIBLIOGRAPHY

1. Hennion, M. C.; Cau-Dit-Coumes, C.; Pichon, V. *J. Chromatogr.* **1998**, *823*, 147.

2. Koester, C. J.; Moulik, A. *Anal. Chem.* **2005**, *77*, 3737-3754.

3. Sarzanini, C.; Bruzzoniti, M. C.; Mentasti, E. *J. Chromatrogr. A* **2000**, *902*, 289-309.

4. Merino, F.; Rubio, S.; Pérez-Bendito, D. *J. Sep. Sci.* **2005**, *28*, 1613-1627.

5. Zhao, Q.; Simmons, J.; Conte, E. D. *J. Chromatogr. A* **2006**, *1132*, 1-7.

6. Lunar, L.; Rubio, S.; Pérez-Bendito, D. *Analyst* **2006**, *131*, 835-841.

7. Saitoh, T.; Kondo, T.; Hiraide, M. *Bulletin Chem. Soc. Japan* **2006**, *79*, 748-750.

8. Garcia-Prieto, A.; Lunar, L.; Rubio, S.; Pérez-Bendito, D. *Analyst* **2006**, *131*, 407-414.

9. Merino, F.; Rubio, S.; Pérez-Bendito, D. *Anal. Chem.* **2004**, *76*, 3878-3886.

10. "Ambient Water Quality Criteria for Chlorinated Phenols." U.S. Environmental Protection Agency, 1980. http://www.epa.gov/waterscience/criteria/library/ ambientwqc/chlorinatedphenols80.pdf. Accessed April 2008.

11. "Ambient Water Quality Criteria for Nitrophenols." U.S. Environmental Protection Agency, 1980. http://www.epa.gov/waterscience/criteria/ library/ambientwqc/nitrophenols80.pdf. Accessed April 2008.

12. "Consumer Fact Sheet on: Pentachlorophenol." U.S. Environmental Protection Agency. http://www.epa.gov/safewater/dwh/c-soc/pentachl.html. Accessed April 2008.

13. Saitoh, T.; Kondo, T.; Hiraide, M. *J. Chromatogr.* **2007**, *1164*, 40-47.

14. Li, J. D.; Cai, Y. Q.; Shi, Y. L.; Mou, S. F.; Jiang, G. B. *J. Chromatogr.* **2007**, *1139*, 178-184.