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## SORPTION OF ORGANICS TO SURFACE-ALTERED ZEOLITES

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### INTRODUCTION

Over 41 naturally occurring zeolites have been discovered (Newsam 1986). This mineral group is characterized by high cation exchange capacities (CECs) and a cage-like structure allowing for a molecular sieving effect. The CEC is separated into external and internal sites. Small cations including many metals can enter into the internal structure of the mineral, which allows for enhanced sorption of these compounds. In contrast, the internal sites are typically unavailable to large organic cations such as quaternary amines. Untreated zeolites have low organic carbon contents (<1%) and although they are capable of sorbing metals, they do not favor sorption of organic compounds prior to modification.

Previous work (Huddleston 1990) showed that zeolite modified with hexadecyltrimethylammonium (HDTMA) had an enhanced ability to sorb non-polar chlorinated solvents from aqueous solution. In addition, Huddleston (1990) also showed that the

ion exchange process through which HDTMA is bonded to the zeolite is essentially permanent. The modified surface greatly increases the organic carbon content, which has been seen to enhance the sorption of non-polar organic compounds (Chiou 1989). In effect, the modification process creates an organic coating over the surface of the zeolite, which allows partitioning of the organic molecules into the organic coating. Thus, it seems likely that the same material could remove the gasoline components benzene, toluene, and xylene (BTX) from contaminated waters.

The objectives of this research project were to:

- characterize sorption of BTX to HDTMA-altered zeolite
- determine the magnitude of competition effects among multiple sorbates in solution
- compare the experimental results with literature values for sorption of BTX on other materials

## METHODS AND MATERIALS

The zeolite used for these experiments was supplied by the Zeotech Division of Leonard Minerals from their mine in Tilden, Texas. The mineralogical composition of the material, determined by X-Ray Diffraction (XRD), was approximately 60% clinoptilolite, 20% smectite, 15% amorphous material, and 5% carbonates. The external CEC of the Tilden sample, determined by Huddleston (1990) using the procedure of Ming and Dixon (1987), was approximately 30 milliequivalents/100 g.

The modifying agent, HDTMA, was chosen for its demonstrated success in similar experiments with clay minerals and its commercial availability. The surface of the zeolite was modified with HDTMA using the procedure outlined in Huddleston (1990). It was previously determined that once modified, the surface of the zeolite is stable (Huddleston 1990).

The sorption experiments were performed as batch isotherms, using a 0.005 M CaCl<sub>2</sub> solution as the aqueous phase. Solutions containing concentrations of 10, 50, 100, 150 and 250 mg/l of each chemical were injected into 15-ml crimp-top vials containing 2.5 g of the surface-modified zeolite. In the case of p-xylene, the maximum aqueous concentration obtained was 198 mg/l which is the aqueous solubility of the chemical. The zeolite-solution mixtures were placed on a shaker for 24 hours in order to reach equilibrium. After equilibration, approximately 2 ml from each vial was withdrawn using a Hamilton gas-tight syringe and placed in gas chromatography (GC) crimp-top vials. Appropriate blanks prepared both with and without zeolite were prepared in a similar manner. The samples were analyzed with a Hewlett Packard 5890A GC using an FID detector. From this data, the amount of chemical sorbed and the equilibrium concentration of the solution were obtained.

The sorption of each compound was first determined individually, with no other sorbates present. This procedure was used to maximize the sorption of the chemical to the HDTMA-modified surface. After quantifying individual sorption, pairs of sorbates were used to determine if there was any competition among chemicals for sorption sites.

## RESULTS AND DISCUSSION

Figure 1 illustrates the increased sorption capability of HDTMA-treated zeolite for benzene

compared to the untreated or natural zeolite. As seen in this plot, the sorption of benzene is increased over 20-fold by the surface alteration. Using the same data as an example, Figure 2 illustrates that the sorption of organic chemicals onto altered surfaces can be quantified as a linear process. The sorption affinity is characterized by the distribution coefficient,  $K_d$  (L/kg), which is the slope of the line obtained from a plot of the chemical sorbed (mg/kg) versus the compound concentration in solution at equilibrium (mg/l). The greater the slope of the line, the greater the chemical's sorption.



Figure 1. Sorption of benzene to treated versus untreated zeolite.

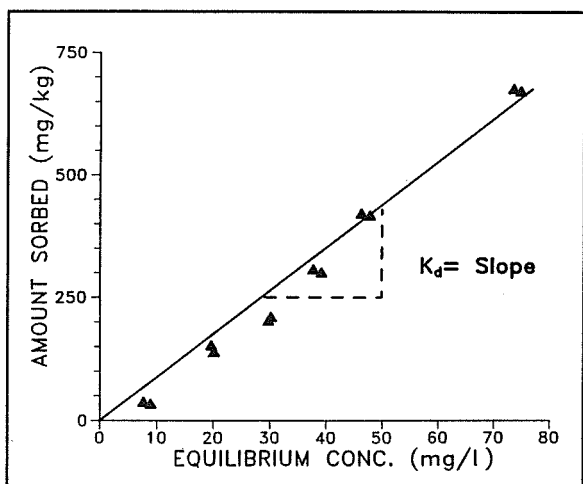


Figure 2. Determination of distribution coefficient ( $K_d$ ) from sorption isotherm.

Figure 3 shows the results obtained for three separate benzene experiments; sorption of benzene

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alone, sorption of benzene while in solution with equal concentrations of toluene, and sorption of benzene with an equal concentration of p-xylene. Figure 3 clearly indicates that neither the presence of toluene nor the presence of p-xylene has any marked influence on the sorption of benzene. Indeed, the converse relation also holds true for these chemicals; the presence of benzene has little or no effect on the sorption of either toluene or p-xylene (data not presented). This lack of competition for sorption sites is indicated by the experimental  $K_d$  values obtained for each experiment. As shown in Table 1, the  $K_d$  values of the multiple sorbates do not differ greatly from the  $K_d$  values obtained from the individual isotherm experiments. Thus, in this case, the sorption of any particular organic in aqueous solution is not influenced by the presence of other components.

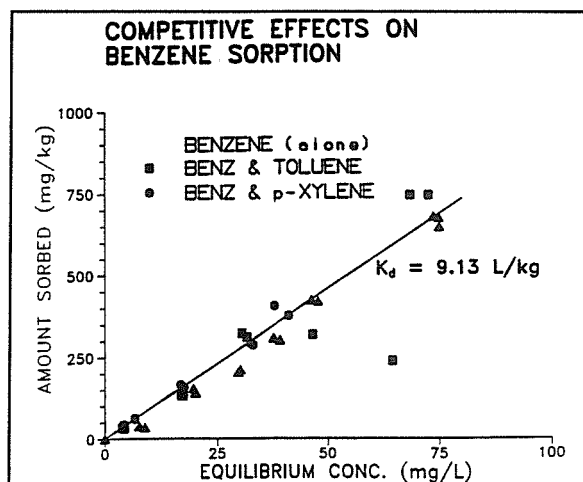


Figure 3. Sorption of benzene to HDTMA-zeolite individually and with multiple sorbates.

Table 1. Summary of competition experiments

Chemical	$K_d$ (l/kg)
Benzene (alone)	8.59
Benzene with Toluene	8.44
Benzene with p-Xylene	9.40
Toluene (alone)	19.2
Toluene with Benzene	19.1
p-Xylene (alone)	70.4
p-Xylene with Benzene	56.6

To validate the methodology and the experimental results, a comparison of experimental  $K_d$  values for these chemicals with values obtained in the literature was necessary. However, literature values for these chemicals are scarce, so the relationship between the distribution coefficient and the organic carbon distribution coefficient ( $K_{oc}$ ) was used to provide this comparison. The relationship between the two is as follows (Dragun 1988):

$$K_{oc} = \frac{K_d}{f_{oc}}$$

where:  $f_{oc}$  = mass fraction organic carbon

The literature values for  $K_{oc}$  were calculated by means of the octanol-water coefficient ( $K_{ow}$ ), shown as equation 6.20 in Dragun (1988). Table 2 shows the comparison of  $\log K_{oc}$  values obtained from literature  $K_{ow}$  values and those calculated from the experiment based on an organic carbon content of 6.4% for HDTMA-modified zeolite (Huddleston 1990). Evaluation of Table 2 demonstrates that the experimental data agrees well with literature values, which infers that the observed sorption is an ideal partitioning process. The lack of competition among sorbates also supports this conclusion (Chiou 1989).

Table 2. Comparison of experimental  $K_{oc}$  values with literature values.

	Lit. $\log K_{oc}$	Exp. $\log K_{oc}$
Benzene	2.02	2.14
Toluene	2.43	2.48
p-Xylene	2.76	3.00

As previously seen, from a theoretical standpoint the sorption of organics to surface-altered zeolites shows great promise for the research and academic community. But of what value does this information provide to the consulting or perhaps regulatory community? Figures 4 and 5 illustrate practical uses for these surface-modified minerals. One possible use would be to incorporate modified zeolites into pump-and-treat systems as shown in Figure 4 for remediation of contaminated groundwater. The zeolites could be used as packed col-

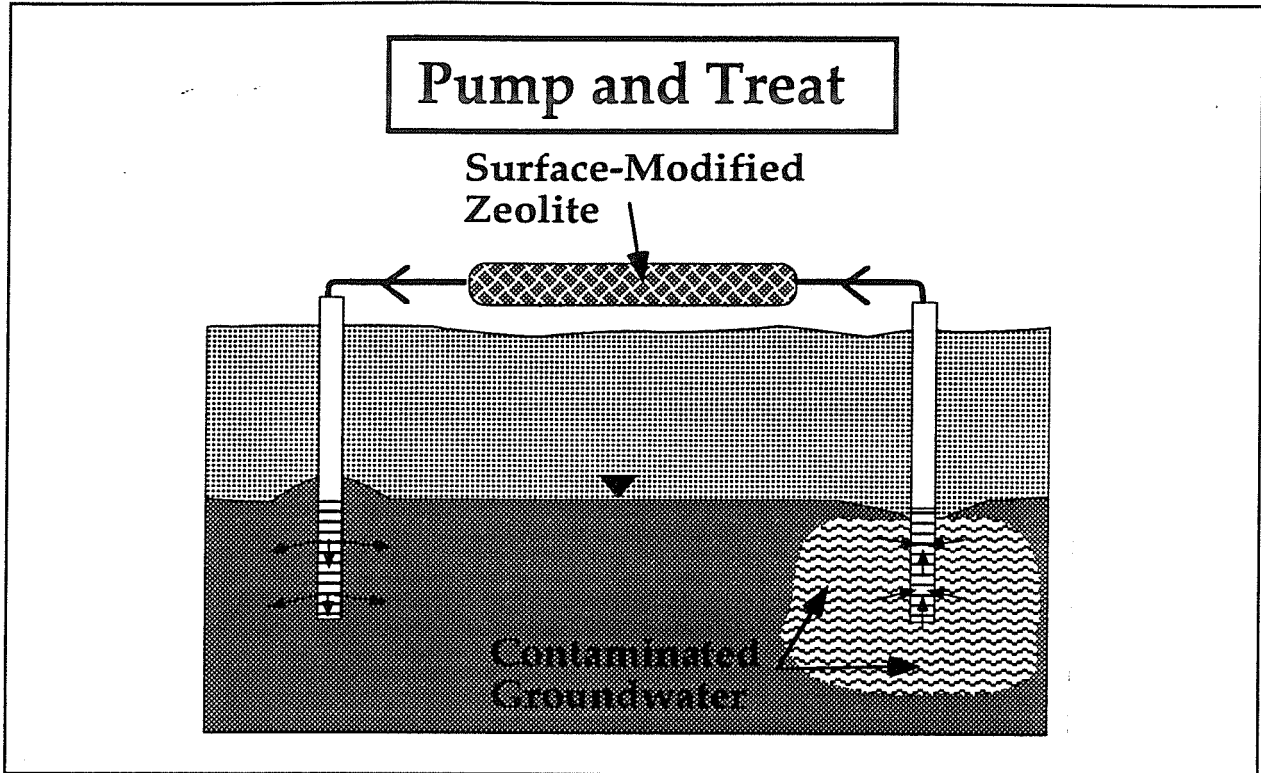


Figure 4. Possible practical use of surface-altered zeolite in a pump and treat groundwater system.

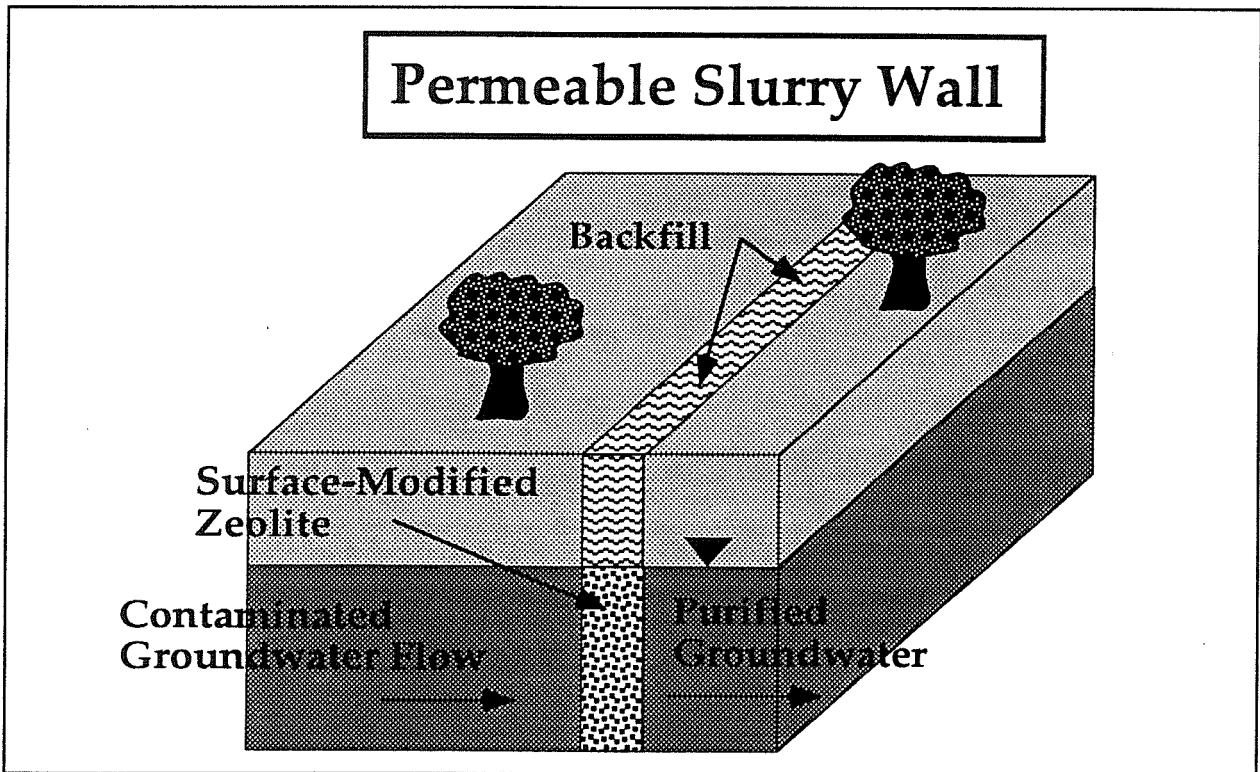


Figure 5. Potential use of surface-altered zeolite as a permeable slurry wall.

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umns through which the contaminated water flows before being re-injected into the aquifer. Another use for the zeolites is as part of a land application spray system that introduces contaminated water to a bed of surface-modified zeolite for the purpose of providing purified recharge to the aquifer. Yet another application might be in the form of a permeable slurry wall as shown in Figure 5. Contaminated groundwater could be diverted to the slurry wall whereby the organic compounds (or metals) would be sorbed to the surface. This process would also allow the contaminants to be concentrated in a smaller area, perhaps enhancing the use of additional remediation techniques, such as bioremediation. Of course in all these applications, the zeolite surface would have to be regenerated, much like activated carbon or other ion-exchange materials are now. Further study of these materials will be necessary in order for these applications to be implemented. However, the availability of zeolites and the demand for additional environmental remediation techniques make zeolites a viable option for the future.

### ACKNOWLEDGEMENTS

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