

**SORPTION OF CHROMATE AND LEAD  
ONTO SURFACE-MODIFIED ZEOLITES**

by

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### Abstract

Surface-modified zeolites were investigated regarding their ability to sorb cationic and anionic metals. Two distinct clinoptilolite-dominated zeolites were used for this research. The natural zeolites were surface-modified with five different quaternary ammonium cations. These quaternary ammonium cations were tetramethylammonium (TMA), tetraethylammonium (TEA), benzyltriethylammonium (BTEA), dibenzyltrimethylammonium (DBDMA), and hexadecyltrimethylammonium (HDTMA). Batch studies were performed to evaluate the effect of the surface-modification upon the sorption of the cationic and anionic metals. Testing to an aqueous concentration of 10,000 mg/L, no sorption differences could be noted between the un-modified and the surface-modified zeolite for the metal lead. The sorption of the aqueous anionic metal chromate onto un-modified zeolites was very small while the surface-modified zeolite's sorption was significantly increased.

The mechanism responsible for the sorption of chromate was investigated. Three mechanisms were hypothesized for chromate sorption. These mechanisms were reduction of chromate, reorientation of excess quaternary ammonium cation on the zeolite's surface, and partitioning of chromate into the established organic layer upon the zeolite's surface. Testing showed all three hypothesis incorrect. A new hypothesis suggested that the quaternary ammonium cation was becoming permanently bonded to the zeolite's surface, thereby neutralizing the outer surface charge. Non-specific forces would then be able to bond the chromate to the zeolite's surface.

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**I.**

**INTRODUCTION**



Awareness of environmental problems in the past few years has increased. Contamination of the groundwater has become a global problem of enormous proportions. When contamination of groundwater is found, it is very likely that the cause of the contamination is not just a single contaminant, but more likely, multiple contaminants. A very good example is the problem of leaking underground storage tanks. Leaded gasolines not only contain benzene, toluene, ethylbenzenes, and xylenes, but also contain tetraethyl lead as an antiknocking compound (Rutter and Robins, 1983). Lead poisoning can be a very serious problem affecting the kidneys, heart, central nervous system, and interfering with hemoglobin production (Rutter and Robins, 1983). Another example of multiple contaminants is the presence of chromates in groundwater with other contaminants such as nickel (Langard, 1983). Chromate is anionic in nature and very mobile in groundwater. Small quantities of chromium are considered essential to life, but large quantities can cause cancer and ulcers (Langard, 1983).

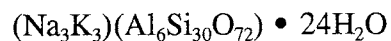
The removal of neutral organic groundwater contaminants such as benzene have been possible through the use of activated carbon. While this technique is very effective, it is also very expensive when large quantities need to be removed from solution. It is also well known that activated carbon is not effective at removing ions such as lead or chromate from solution as it contains no surface charge.

The use of surface-modified clays have been found to be very effective at removal of certain petroleum contaminants such as benzene, toluene, and xylene (BTX) (Cadena, 1989; Alther et al., 1990; Boyd et al., 1988). Unmodified clays also have the natural ability to sorb cations such as lead through cation exchange. The surface-modified clay,

however, would not be suitable for use in such applications as column filters or infiltration pads where permeability is important. The amount of contaminated water capable of passing through a surface-modified clay column, for example, is extremely limited and therefore unsatisfactory in its overall capacity to remediate the problem of inorganic and organic contamination in water. Surface-modified clays are however very useful in the stopping of both inorganic and organic contaminants when used as a containment wall (Cadena, 1989).

Natural zeolites have an extremely high cation exchange capacity (CEC). When crushed, they have a very high permeability comparable to most sands, which make them a perfect choice for use in places where surface-modified clays are limited due to permeability. Zeolites are crystalline, hydrated alumino-silicates of alkali and alkali-earth cations that possess infinite three-dimensional crystalline structures. This structure produces void volumes of 20 to 50 percent and internal surface areas of several hundred thousand square meters per kilogram. The most effective cation exchangers known are zeolites with CECs of 200 to 300  $\text{cmol}_c \text{ kg}^{-1}$ , two to three times that of most smectites and vermiculites (Ming and Mumpton, 1989).

The zeolite of interest used in this study was clinoptilolite, the most abundant of the sedimentary zeolites, with a unit cell formula of:



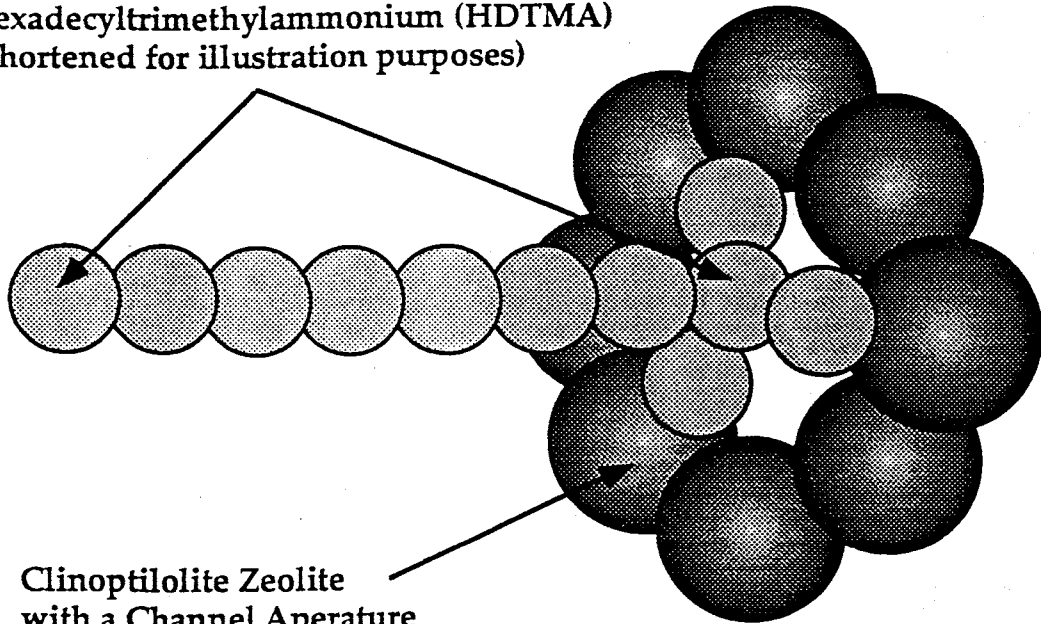
The void volume of this ideal clinoptilolite has been determined to be 34% with a CEC of 220  $\text{cmol}_c \text{ kg}^{-1}$ . This CEC and void volume were determined from the unit-cell formula, density, and unit-cell parameters (Ming and Mumpton, 1989).

Zeolites, due to this three-dimensional structure, have the ability to screen out those molecules which are too large to enter the channel openings. Hence, zeolites are capable of "molecular sieving". Although H<sub>2</sub>O and several inorganic cations are able to move about freely through much of the framework of the zeolite, the channels leading into the simple polyhedral cages are too small for all but the smallest molecules to pass. Clinoptilolite has calculated channel openings of 0.41 x 0.47, 0.44 x 0.72, and 0.40 x 0.55 (nm) corresponding to the a, b, and c planes respectively (Ming and Mumpton, 1989). Figure 1.1 represents the concept of "molecular sieving" of zeolite. Due to its extreme complexity of three-dimensional structure, the dark spheres in figure 1.1 only represent the clinoptilolite zeolite in general and do not correspond to any actual part of the zeolite structure.

Huddleston (1990) cites that at least 28 different organic cations have been studied for their surface-modifying characteristics to clay materials, mainly smectites. The main focus of surface-modifying clay was the determination of the sorption effects these clays had upon organic molecules, mainly BTXs, and chlorinated hydrocarbons. No study was found which evaluated the effect on sorption of inorganics caused by the surface-modifying process.

Surface-modifying zeolites is a relatively new idea. Its potentials are poorly understood when compared with surface-modified clays. A literature search revealed six references which deal with the surface-modification of zeolites. These references are Goa et al. (1990), Huddleston (1990), Huddleston and Bowman (1990), Barrer (1978), Barrer et al. (1967), and Chen (1976). Huddleston's research focused upon the

Hexadecyltrimethylammonium (HDTMA)  
(Shortened for illustration purposes)



Clinoptilolite Zeolite  
with a Channel Aperature  
Opening of 0.41 nm X 0.47 nm

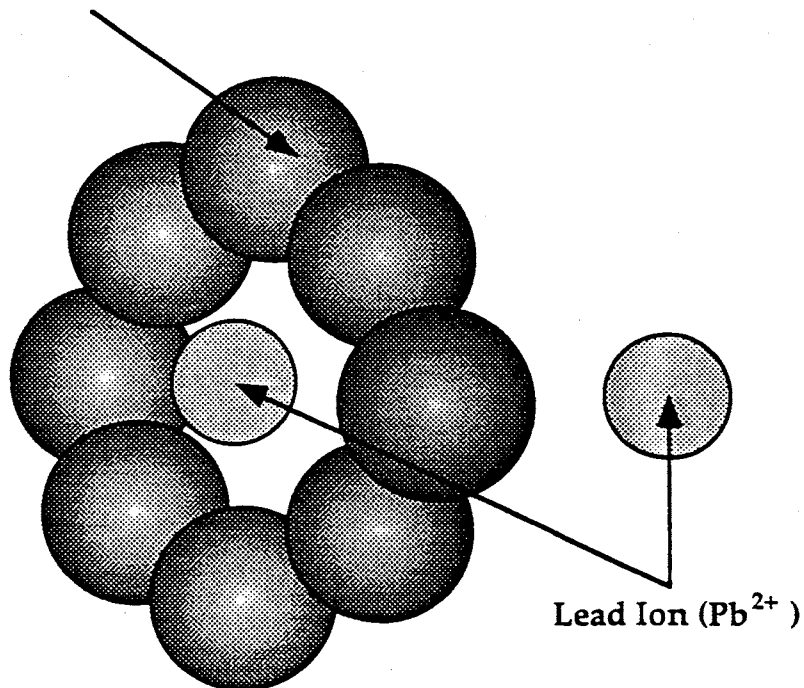


Figure 1.1 Conceptual Model of Molecular Sieving. Due to its three-dimensional complexity, the darker spheres only represent the simplified structure of clinoptilolite.

capability of surface-modifying the zeolites, the stability of the surface-modification, and the sorptive characteristics of the surface-modified zeolite for organics. This project is a continuation of Huddleston's research.

The project under which this study is funded is evaluating the sorptive properties of natural and surface-modified zeolites for organic and inorganic contaminants. The main objective of this particular study was to evaluate the effect upon inorganic sorption caused by surface-modification of natural zeolites with quaternary ammonium cations. Lead and chromate were chosen as the contaminants due to their cationic and anionic natures, and because both are highly toxic at low levels when in drinking water.

The specific objectives of this research were to:

1. Evaluate the sorption of lead and chromate on natural and surface-modified zeolites.
2. Determine the physical and chemical variability among different zeolites, mainly CEC, clay content, and sorptive properties.
3. Determine the effect of solution chemistry on the sorption of chromate.
4. Determine the mechanism which is responsible for the chromate sorption onto surface-modified zeolites.

## **II.**

### **MATERIALS & METHODS**

## Materials

### Zeolites

Two distinct clinoptilolite-dominated zeolites were used for this research project. The first zeolite was supplied by Zeotech division of Leonard Minerals (Albuquerque, New Mexico) from their mine in Tilden, Texas. This zeolite will be referred to as the Tilden zeolite. The second zeolite was supplied by the St. Cloud Mining Company (Truth or Consequences, New Mexico) from their mine located in Winston, New Mexico. This zeolite will be referred to as the St. Cloud zeolite. Both zeolites were sieved to a gradation of grain sizes ranging from 0.2 - 2.0 mm.

### Surface-Modifying Agents

When surface-modification of zeolites was first studied, quaternary ammonium cations (QACs) were chosen due to their ability to effectively establish an organic layer upon the outer surface of the zeolite. QACs are large organic molecules which are positively charged. The QACs used were: tetramethylammonium (TMA), hexadecyltrimethylammonium (HDTMA), tetraethylammonium (TEA), dibenzyl dimethylammonium (DBDMA), and benzyltriethylammonium (BTEA). All chemicals were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin). Selection criteria for the QAC were:

1. No double or triple bonds (except benzene ring).
2. A charge of 1+ when in solution.
3. A high carbon content and molecular weight.

Biological degradation of the QAC was of concern, therefore the criterion of no double

or triple bonds present, except for the benzene ring, was established. Figures 2.1 and 2.2 represent the QACs used in this project. Table 2.1 presents the properties of the QACs used in this project.

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**Table 2.1 Quaternary Ammonium Properties**

Cation	Molecular Formula	Molecular Weight
TMA	C <sub>4</sub> H <sub>12</sub> NCl	109.60
TEA	C <sub>8</sub> H <sub>20</sub> NCl	165.71
BTEA	C <sub>13</sub> H <sub>22</sub> NCl	227.78
DBDMA	C <sub>16</sub> H <sub>20</sub> NCl	261.45
HDTMA	C <sub>19</sub> H <sub>42</sub> NCl	320.01

### **Inorganic Contaminants**

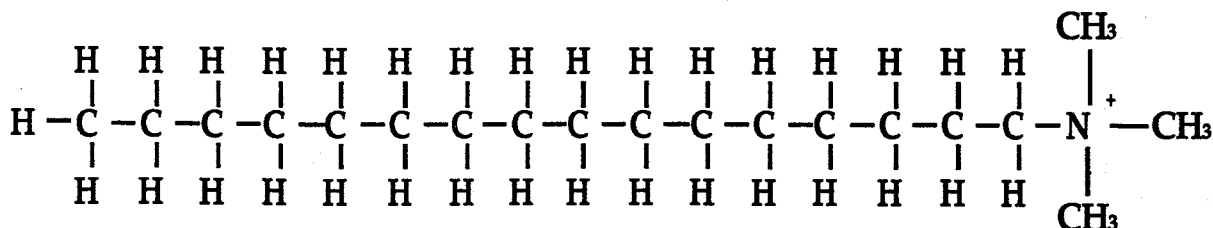
It was decided that both an anionic and cationic metal should be tested for removal by surface-modified zeolite. The cationic metal used in this research was lead in the form of lead nitrate, Pb(NO<sub>3</sub>)<sub>2</sub>, purchased from Aldrich Chemical Company.

The anionic metal used in this research was chromate. Potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), purchased from Aldrich Chemical Company, was chosen as the source of chromate in solution.

The inorganic contaminants were dissolved in a solution of 0.01 M calcium chloride (CaCl<sub>2</sub>) to a concentration of 10,000 milligrams per liter (mg/L). The 0.01 M CaCl<sub>2</sub> electrolyte was originally used to prevent dispersion of the clay present in the Tilden zeolite. Dilutions using 0.01 M CaCl<sub>2</sub> were performed as needed to produce other required concentrations.



# HDTMA



# BTEA

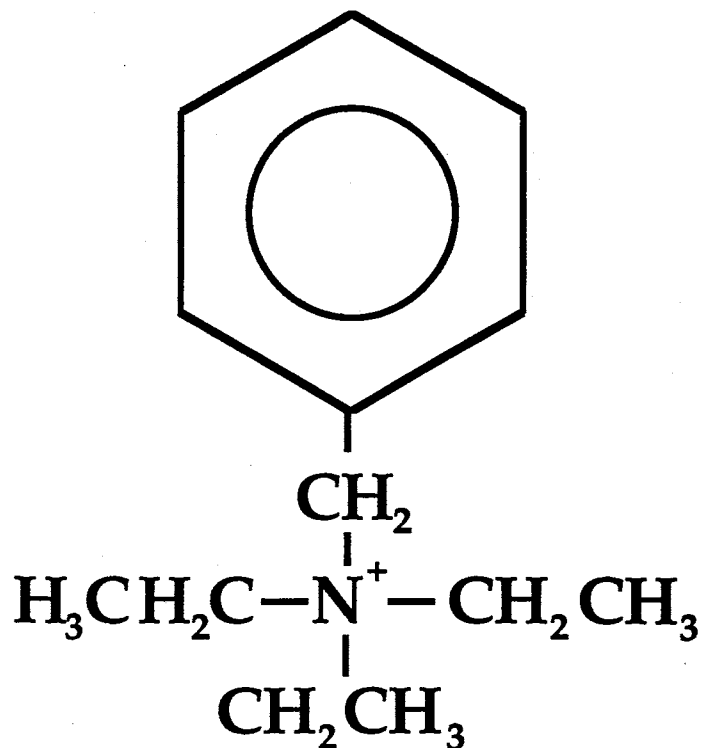


Figure 2.1 Representation of BTEA & HDTMA

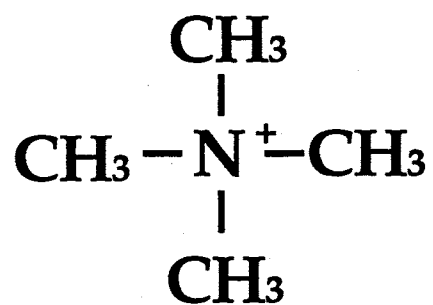
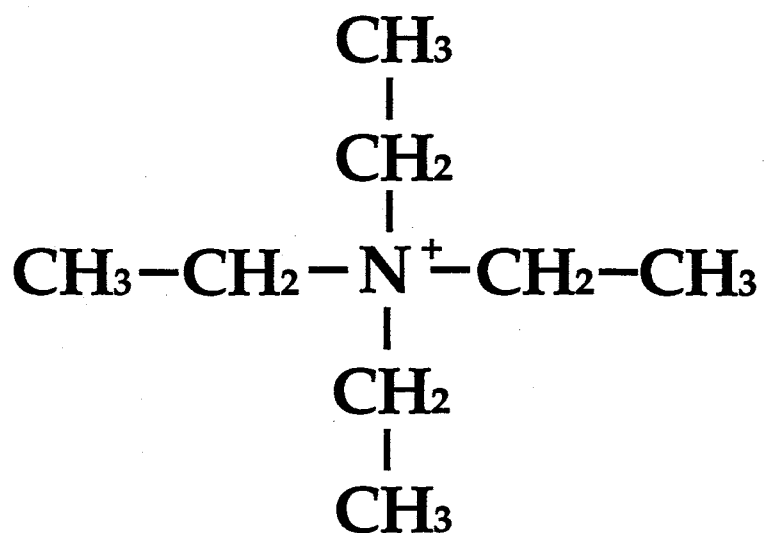
**TMA****TEA**

Figure 2.2 Representation of TMA &amp; TEA

## Methods

### Characterization of Zeolites

Prior to this research, the characterization of the Tilden zeolite had been conducted by Huddleston (1990). The Tilden zeolite had been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the cation exchange capacity (CEC) was determined. The St. Cloud zeolite was also characterized by XRD and the CEC determined. Results of the SEM for the Tilden zeolite did not show distinct clinoptilolite. The St. Cloud zeolite was not analyzed by SEM. The XRD for the Tilden zeolite was conducted by the New Mexico Bureau of Mines (Socorro, New Mexico), and the XRD for the St. Cloud zeolite was conducted by Gold Hill Geological Research (Albuquerque, New Mexico) and later confirmed by New Mexico Bureau of Mines. The SEM conducted on the Tilden zeolite was done at New Mexico Institute of Mining and Technology Metals and Metallurgy Department.

The CECs of the Tilden and St. Cloud zeolites were determined using both the Rhoades (1982) and the Ming and Dixon (1987) methods. The Rhoades method determines total CEC of the zeolite while the Ming and Dixon method determines both the internal and external CECs of the zeolite. The Rhoades method was employed to check the accuracy of the Ming and Dixon method. The summation of both the internal and external CEC should equal the total CEC determined by the Rhoades method. The Rhoades method determines the total CEC by forcing all exchangeable cations present to be replaced by sodium cations. These ions are then replaced by ammonium cations. The amount of sodium in solution can then be determined, which was assumed equivalent

to the total CEC of the zeolite. The Ming and Dixon method again saturates all exchangeable sites with sodium, but tert-butyl ammonium was added to the system which replaces the sodium on the external surface of the zeolite. The amount of sodium displaced was assumed equivalent to the external CEC as the tert-butyl ammonium was too large to enter the internal exchange sites. Ammonium was once again added to displace the internal sodium ions. The zeolite has a higher affinity for tert-butyl ammonium and it was not removed from the external surfaces by the ammonium ion. The amount of sodium displaced internally was assumed equivalent to the internal CEC.

#### **Surface-Modification of Zeolite**

The procedure used for surface-modification of the zeolite was developed by Huddleston (1990). Through continued use and experimentation, a slightly modified procedure was developed:

- a) All zeolites were washed in an 0.1 M acetic acid bath, buffered to a pH of 5 by 0.1 M sodium acetate, for 72 hours. The acid was replaced every 24 hours.
- b) The zeolite was rinsed and dried on a Buchner funnel.
- c) 6.66 grams of zeolite was weighed and placed in a 50 mL test tube where 20 mL of the QAC in solution was added.
- d) The test tube was shaken for 24 hours.
- e) The test tube was centrifuged and all excess solution was removed.
- f) 20 mL of deionized water was placed in the test tube, shaken for 10 minutes, centrifuged and removed. This procedure was repeated a total of 3 times.
- g) The zeolite was removed from the test tube and placed in a Buchner funnel where it was rinsed again and allowed to dry.

The amount of QAC used in solution in part c was determined by the external CEC of the zeolite used. Excess amounts of QAC versus the external CEC were allowed.

### **Quantification of Inorganic Sorption to Modified Zeolites**

Batch sorption studies were the focus of this research. These studies helped in quantifying the extent of the inorganic contaminant sorption onto the surface-modified zeolite. For comparison, and to evaluate the effectiveness of the sorption of the modified zeolites, natural (un-modified) zeolites were included in the sorption studies.

The following batch sorption procedure was created and followed:

- a) A dry sample of 2.50 grams of surface-modified zeolite was weighed and placed in a 50-mL test tube.
- b) 10 mL of contaminant solution was placed in the test tube.
- c) The test tube was mechanically shaken for 24 hours.
- d) The test tube was centrifuged to yield a clear supernatant solution.
- e) The supernatant solution was decanted and analyzed.

A duplicate for each concentration for both modified and unmodified zeolites was prepared, along with a tube blank (zeolite-less) of the same solution concentration for analysis and comparison. A contaminant blank (0 mg/L + zeolite) was also included in all batch studies to check for background levels. All blanks were treated equally throughout the batch studies.

The amount of inorganic contaminant used in the batch studies ranged from 0 - 10,000 mg/L. This large range was used in hopes of showing the overall effectiveness of the zeolite. It was later decided to look also at a smaller range of 0 - 10 mg/L. This smaller range was more realistic for actual contaminated water, easier to obtain more reproducible results and was considerably easier to analyze.

This project initially began using Tilden zeolite. With the introduction of the St. Cloud zeolite, the Tilden zeolite was set aside due to the unknown effects that the clay which it contained might produce in our studies. All batch studies performed to calculate the mechanism responsible for chromate sorption and solution chemistry used the St. Cloud zeolite.

An Instrumentation Laboratory (Worcester, MA) Video 12 AA/AE Spectrophotometer was used for the analysis of the chromate and lead. Atomic adsorption (AA) spectrophotometer standards were prepared using 0.01 M CaCl<sub>2</sub> for both lead and chromium based upon the detection range defined by the wavelength used. The following table gives the settings used for the analysis by AA:

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**Table 2.2 Spectrophotometer Settings**

Contaminant (metal)	Wavelength (nm)	Current (mA)	Bandwidth (nm)	Voltage	Detection Range ( $\mu\text{g}/\text{mL}$ )
Chromium	357.9	4.0	1.0	500	1 - 8
Lead	283.3	5.0	0.5	510	1 - 10

The linear range for chromium, as supplied by Instrument Laboratory, at the given wavelength, was 1 - 5  $\mu\text{g}/\text{mL}$ , while lead's linear range was 1 - 10  $\mu\text{g}/\text{mL}$ .

In the analysis, samples of the same concentration were analyzed together. Between each concentration, the AA spectrophotometer was re-zeroed with deionized water to lessen the chance of cross-contamination. The difference between the tube blank concentration and the concentration of the spent supernatant from the modified zeolite

was assumed to be the amount of the chromium or lead removed from solution. The amount of removed metal was then converted into mass removed per kilogram of zeolite. The amount of removed metal was then plotted against the concentration of metal remaining in solution, resulting in an isotherm.

Although many different isotherm shapes are possible and have been observed, the most common of isotherm shapes for aqueous solutions are the linear, Langmuir, and Freundlich types (Bohn et al., 1985). This research only utilizes the linear and the Freundlich types of isotherms.

The linear isotherm is often seen with sorption of low-solubility organic compounds and low solute concentrations. The isotherm is described by the equation:

$$S = K_d C$$

where:

$S$  = Mass of solute sorbed to substrate, [mg/kg]

$K_d$  = Distribution coefficient, [L/kg]

$C$  = Equilibrium solution concentration, [mg/L]

A plot of  $C$  vs.  $S$  will yield a straight line of the slope  $K_d$  when sorption can be described as linear. The linear isotherm implies the sorbent has infinite capacity to retain dissolved species.

The Freundlich isotherm is described by the equation:

$$S = K_f C^N$$

or in the linearized form:

$$\log S = N \log C + \log K_f$$

Where in addition to previously defined variables,

$N$  = Empirical constant, [-]

$K_f$  = Freundlich constant

The Freundlich equation implies that an infinite number of sorption sites are available, and that energy of sorption decreases logarithmically as surface coverage increases.

### Effects of Solution Chemistry

The sorption of the inorganics to the surface-modified zeolites should behave in a predictable manner. Variations in electrolyte levels should produce variations in chromate sorption due to changes of ionic strength in solution (chromate activity). If only the ionic strength of the solution was being altered, the activity of the chromate can be taken into account by replotting the solution concentration times the activity versus the solute mass sorbed. This plot should produce a distribution coefficient ( $K_d$ ) identical for any concentration of electrolyte in solution. If the results are not identical, a competitive effect or complexation of the chromate with the electrolyte could be assumed to be occurring.

The standard electrolyte concentration used throughout these experiments was 0.01 M  $\text{CaCl}_2$ . Two electrolyte solutions of 1.0 M and 0.0001 M  $\text{CaCl}_2$  were generated and used to dilute the chromate's original concentration of 10,000 mg/L to appropriate concentrations of 1, 3, 5, 7, and 10 mg/L. Isotherms were then prepared.

The geochemical speciation program MINTEQA2 was used to calculate the activity coefficient for chromate using the extended Debye-Huckel equation. MINTEQA2 was also used to look for the possibility of complexation between the electrolyte and chromate in



solution. The activity coefficients of chromate were calculated individually for 1, 3, 5, 7, and 10 mg/L chromate concentrations in the 0.0001 M  $\text{CaCl}_2$  solution. The change in chromate concentration at a low electrolyte concentration would vary the ionic strength of the solution enough to shift the activity coefficient of chromate significantly. The 0.01 M  $\text{CaCl}_2$  solution had a high enough ionic strength that variations of the chromate in solution would cause only minor variations in chromate activity. Therefore, the chromate activity coefficient was calculated at 10 mg/L in the 0.01 M  $\text{CaCl}_2$  solution. Calculating the activity coefficient for chromate in the 1.0 M  $\text{CaCl}_2$  solution proved to be difficult. The Debye-Huckle and the Davies equations are only valid to calculate activity coefficients to ionic strengths of 0.01 M and 0.05 M respectively. This problem will be addressed in the results section.

### **Determination of Chromate Sorption Mechanism**

#### **Tail Interaction**

The surface of the zeolite is capable of accepting only a finite amount of surface-modifying agent at which time the external CEC becomes satisfied. When more surface-modifying agent is added than the external CEC, the hydrophobic tails of the large cations in solution may sorb to the hydrophobic ends of the cations already bound to the zeolite surface. When this occurs, with large organic cations, it is termed amphipathic sorption (Black, 1969). For this paper, the term amphipathic sorption will be referred to as "tail interaction". An amphipathic molecule is one both having a polar and nonpolar functional group. In our case, the nonpolar group is the long organic chain (Figure 2.1) of the QAC. In amphipathic sorption, the long organic chain tends to orient

itself towards the mineral surface thereby allowing the polar group to orient itself outward toward solution. It was proposed that this tail interaction was accounting for some unknown amount of chromium removal from solution. To test this possibility, St. Cloud zeolite was surface-modified to satisfy 25, 50, 75 and 100 percent of the known external CEC. The 25, 50 and 75 percent samples were assumed not to be capable of tail interaction as all available surface-modifying agent would bond to the surface of the zeolite. The results of batch tests performed upon these samples would tell us if any tail interaction was present in the 100 percent satisfied CEC samples.

### **Reduction of Chromium (VI) to Chromium (III)**

A proposed mechanism for the sorbed chromate from solution was the reduction of chromate ( $\text{CrO}_4^{2-}$ ), which is in the form  $\text{Cr}^{6+}$ , to chromium (III). Chromium (III) is a cation ( $\text{Cr}^{3+}$ ), and can therefore readily sorb to the negatively charged zeolite surface. Proving that reduction of chromate was or was not the mechanism responsible for chromate removal from solution became difficult. Spectrophotometry was our only reasonable means of distinguishing between chromium (III) and chromium (VI). Experiments using the spectrophotometer proved to be inaccurate and unreliable. Atomic adsorption spectrophotometry reads total chromium in solution and does not differentiate between the species of chromium present. Therefore, detection of chromium (III) alone in our chromate solution was not possible. Another method needed to be found. It was hypothesized that if the chromate ion was being reduced to the chromium (III) cation, then there should be little or no reversal of the sorption due to strong electrostatic interaction between the negatively charged zeolite and the positively charged chromium

(III). This hypothesis was supported in part by experiments conducted by Bowman et al. (1981) whereby desorption of nickel ( $2^+$ ) from natural soils was found to be extremely difficult. A desorption batch study was then conducted to test this hypothesis.

The procedure for a desorption isotherm followed Bowman et al. (1981). The amount of time required for the chromate sorbed by the zeolite to desorb back into solution needed to be determined. The first step in determining a desorption equilibration time was performing a standard sorption batch study for St. Cloud zeolite and 5 mg/L chromate solution concentration with 8 sets of duplicates. When the standard 24 hour equilibration (sorption) time was complete, 5 mL of the spent supernatant solution was decanted and replaced by 5 mL of 0.01 M  $\text{CaCl}_2$  solution in the tube set. Each set of test tubes was given a specific time duration after which the supernatant solution was analyzed. These times were 0.5, 1, 2, 4, 8, 12, 24, and 48 hours. This procedure identified the time at which the chromate in solution equilibrated with the chromate on the zeolite's surface.

The procedure used for the desorption batch study was almost identical to the equilibration time test described above except that only one set of duplicates was needed, and at the end of the equilibration time, the solution was removed, analyzed, and replaced with 0.01 M  $\text{CaCl}_2$  solution. This procedure was repeated until a trend was established.

**Partitioning with Organics**

Another hypothesis for the sorption of chromate was that the chromate partitions into the organic layer generated by the surface-modification of the zeolite. To prove or disprove this hypothesis, hexadecane was used as an organic solvent into which the chromate (also in solution) could partition. 100 mL of hexadecane and 100 mL of 5 mg/L chromate solution were added together in a 500 mL flask and shaken for a 12-hour period. The solution was then allowed to stand undisturbed for an additional 12 hours to separate. The spent aqueous chromate solution was then analyzed and compared to the original solution.

**III.**  
**RESULTS**

## **Zeolite Characterization**

### **XRD Results**

The Tilden zeolite has a mineralogy of approximately 60% clinoptilolite, 20% montmorillonite, 15% amorphous material, and the remainder carbonates and other materials (Huddleston, 1990). The St. Cloud zeolite has a mineralogy of 84% clinoptilolite, 12% volcanic glass, 3% feldspar, and 1% hematite (Gold Hill Geologic Research, Albuquerque, New Mexico). The XRD of the St. Cloud zeolite was for a composite sample collected in the field. Personal inspection of the zeolite deposit (1991) showed variation in the color which was explained by the St. Cloud staff geologist as variations of impurities within the zeolite. Certain areas of the deposit are believed to be upwards of 95 percent pure zeolite, while the zeolite on the outer edge of the deposit is believed to be approximately 75-80 percent pure (B. Bockish, 1991, personal communication).

### **CEC Results**

The Tilden zeolite CEC was determined by Huddleston (1990). Huddleston characterized the Tilden zeolite as having an external CEC of 30 me/100g and an internal CEC of 30 me/100g. Using the same Tilden zeolite sample, I determined an internal CEC of 37 me/100g and an external CEC of 26 me/100g. Reasons for the variations of the CEC determination were not fully understood, but the overall difference between the two analyses was minor. Huddleston (1990) discussed CEC determinations made by other workers on the same Tilden zeolite and noted a very wide range of results. This large variation was attributed to changes in mineralogy of the zeolite. Our sample tested

however, was of the same subsample and therefore mineralogy differences cannot be credited to the variations in determined CEC values. Because the variation was small, laboratory error was deemed responsible.

The CEC of the St. Cloud zeolite was determined on two separate occasions. The first determination of CEC for the St. Cloud zeolite by the Rhoades (1982) method showed a total CEC of 84 me/100g. The Ming and Dixon (1987) method showed an internal CEC of 52 me/100g and an external CEC of 25 me/100g. The second determination of CEC for the same St. Cloud sample by the Rhoades (1982) method showed a total CEC of 76 me/100g. The Ming and Dixon (1987) method established an internal CEC of 53 me/100g and an external CEC of 21 me/100g. The small variations of CEC between analyses are once again believed due to laboratory error. The agreement between the Rhoades (1982) method and the Ming and Dixon (1987) method was very good.

The Ming and Dixon (1987) method of CEC determination requires the use of tert-butyl ammonium chloride (TBAC) in the external CEC analysis. The TBAC cannot be purchased commercially. The TBAC needs to be synthesized prior to the actual CEC determination. On average, TBAC requires at least 5 hours to produce regardless of the quantity. To avoid TBAC synthesis, we decided to substitute TBAC with commercially available HDTMA. External CEC was then determined by using HDTMA in place of TBAC within the Ming and Dixon (1987) procedure. The results of the test (Table 3.2) showed that the replacement of TBAC with HDTMA had little effect upon the external CEC. Overall, the difference between external CEC determinations was less than six percent.

**Table 3.1 External CEC Determination with HDTMA**

Sample	TBAC me/100g	Std. Dev.	HDTMA me/100g	Std. Dev.	% Difference
Tilden	26.10	1.75	26.27	0.57	0.65
St. Cloud	20.51	0.43	21.60	1.30	5.3

### Quantification of Inorganic Sorption to Modified Zeolites

Surface stability experiments on Tilden zeolite were conducted by Huddleston (1990) to test if the QACs were exchangeable or stable. The only QAC tested that was used in this research was HDTMA. The HDTMA-treated zeolite was deemed stable over time. Testing with pH variations, electrolyte variations and competing QACs showed that on average 99+ % of the HDTMA remains upon the surface of the zeolite. Recent testing with St. Cloud zeolite (G. Haggerty, 1992, personal communication) and HDTMA also showed the same trends of stability as seen with the Tilden zeolite.

### Lead Sorption

Zeolite's natural ability to sorb cations has been mentioned by Assenov et al. (1988), Guangsheng et al. (1988), Gradev et al. (1988), and Pesci-Donath and Nagy (1988). Research has been conducted in the sorption of lead by natural zeolites by Semmens and Sayforth (1976) and Assenov et al. (1988). Both research groups showed that natural clinoptilolite was very useful in lead removal. Sorption studies were conducted in this research on the natural zeolites ability to sorb the lead cation. Results of these studies



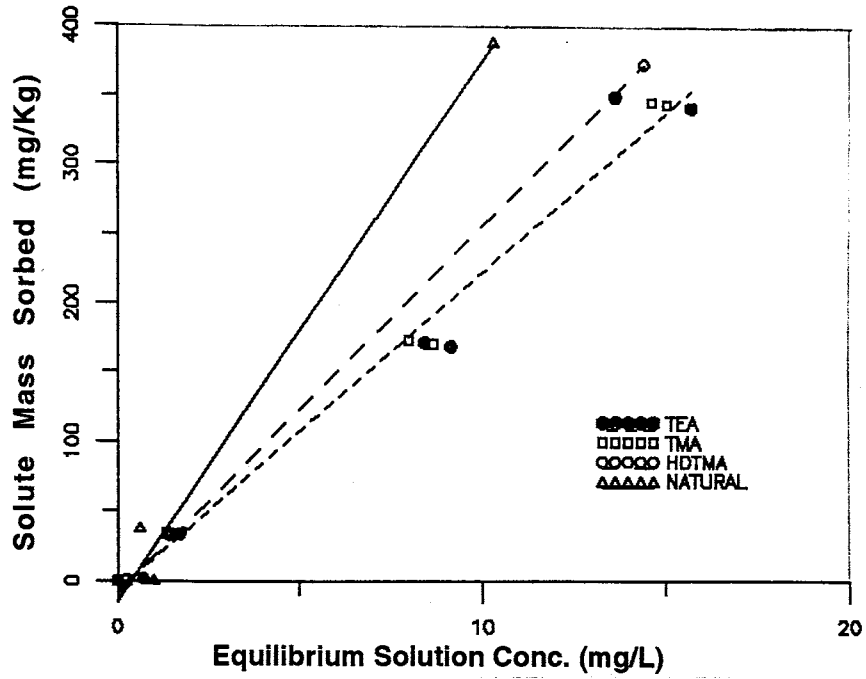


Figure 3.1A Lead Linear Isotherm (0-100) with HDTMA, TEA, TMA, and Nautral Tilden Zeolite.

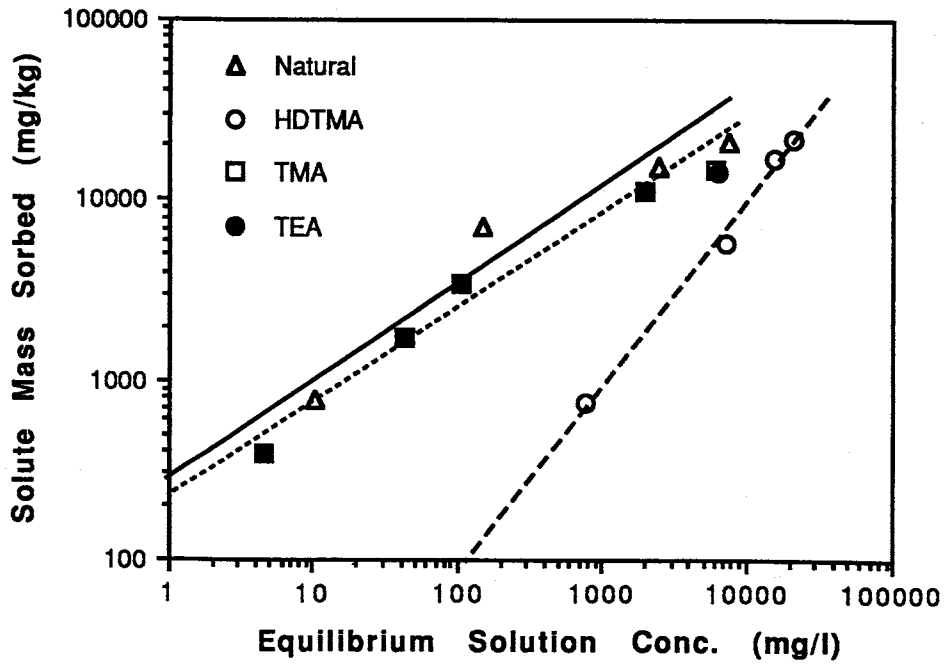


Figure 3.1B Lead Freundlich Isotherm (100-10,000) with HDTMA, TMA, TEA, and Natural Tilden Zeolite

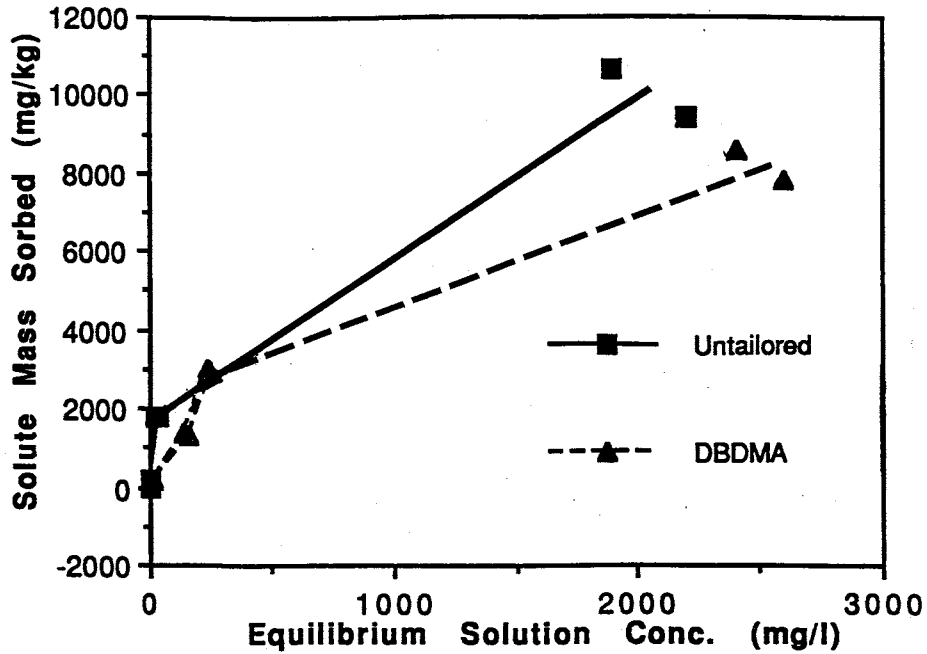


Figure 3.2. Lead Isotherm using DBDMA and Natural Tilden Zeolite

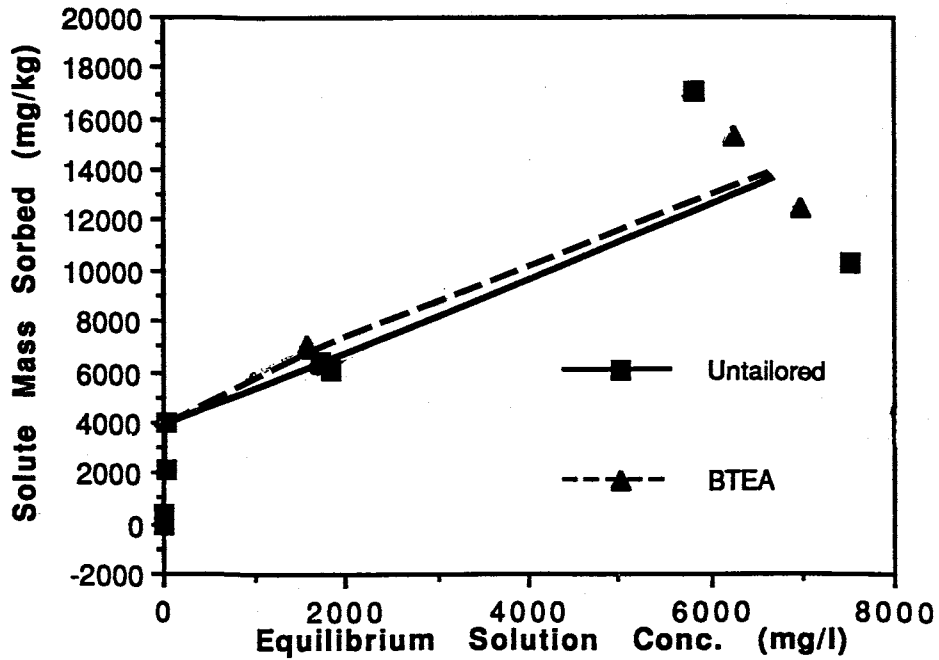


Figure 3.3. Lead Isotherm using BTEA and Natural Tilden Zeolite

were used only as a reference for the changes imposed by the surface-modifications of the zeolite.

The Tilden zeolite was surface-modified with HDTMA, TMA, TEA, DBDMA, and BTEA quaternary ammonium cations. Figures 3.1 - 3.3 show no reduction in sorption of the lead cation as compared to the natural, unmodified, Tilden zeolite. The overall sorption behavior was linear in the lower concentration ranges (0-100 mg/L) as seen in figure 3.1A. The overall sorption in the upper concentration ranges (100-10,000 mg/L), as seen in figure 3.1B, behaved in a Freundlich manner. Please note that in figures 3.1A and 3.1B, the symbol for TMA and TEA are superimposed upon each other. Figure 3.2 and 3.3 also show this same dual trend as established in 3.1A and 3.1B.

#### **Chromate Sorption with Tilden Zeolite**

Batch studies for chromate were initially performed on natural, TMA, and HDTMA surface-modified zeolites. There was a slight adsorption of chromate by the natural zeolite. The mechanism responsible for this slight sorption is unknown at this time. There was also a slight sorption of the chromate onto TMA-modified zeolite (Figure 3.4A), but this could be caused by the same unknown mechanism responsible for natural zeolite's slight sorption of the chromate. The HDTMA-modified zeolite showed a remarkable affinity for the chromate (Figure 3.4A). This was unexpected. The sorption of the chromate at high concentrations (10-10,000 mg/L) showed a Freundlich behavior (Figure 3.4B).

The experiment was rerun. A second batch study was performed with natural,

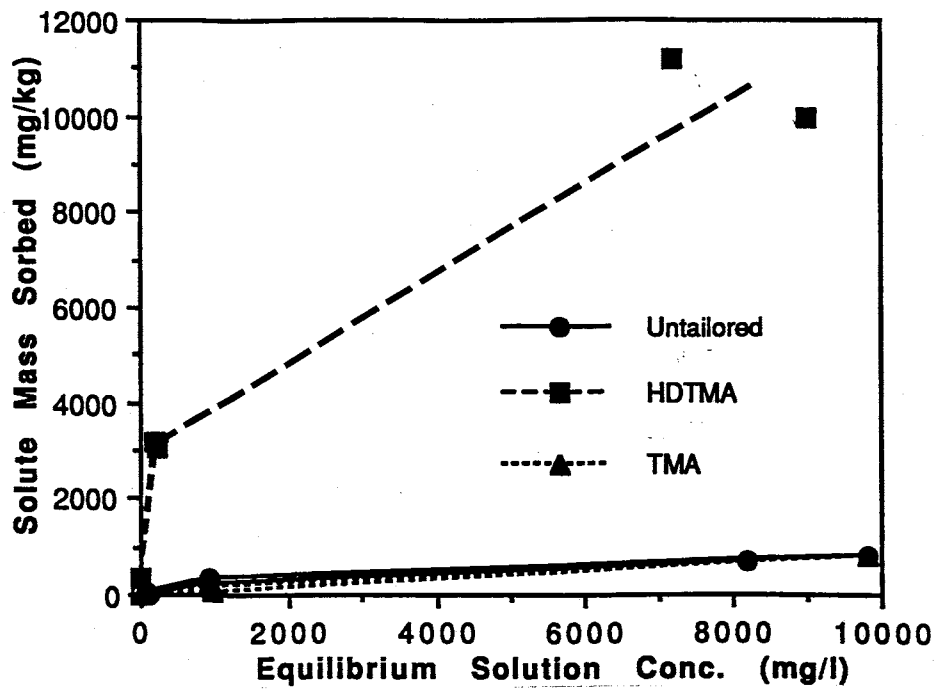


Figure 3.4A Chromate Isotherm using Tilden Zeolite in Natural, TMA-, and HDTMA-Modified form.

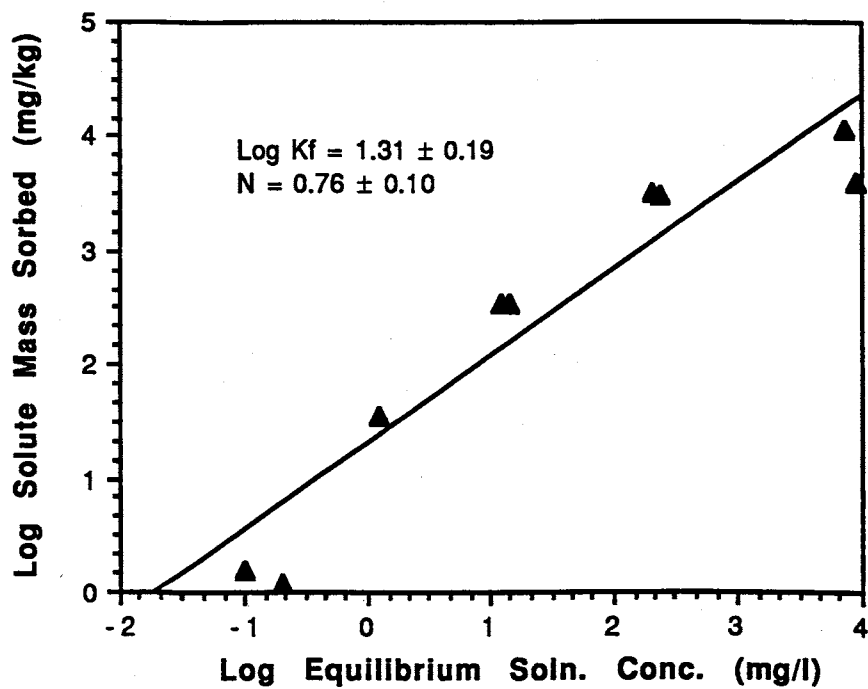


Figure 3.4B Freundlich Isotherm of Chromate Sorption onto HDTMA-Modified Tilden Zeolite (#1)

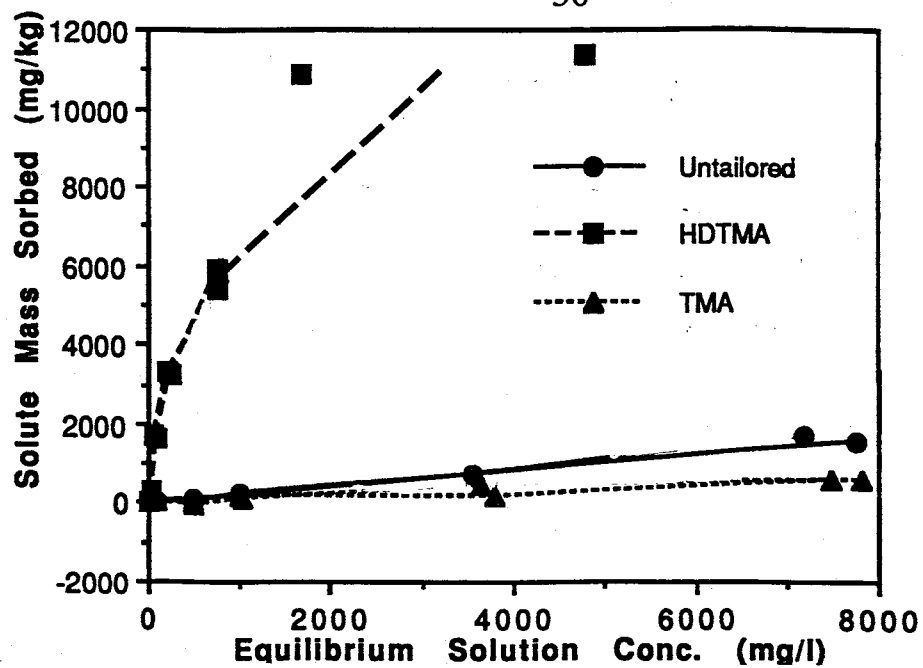


Figure 3.5A Chromate Isotherm using Tilden Zeolite in Natural, TMA-, and HDTMA-Modified forms #2.

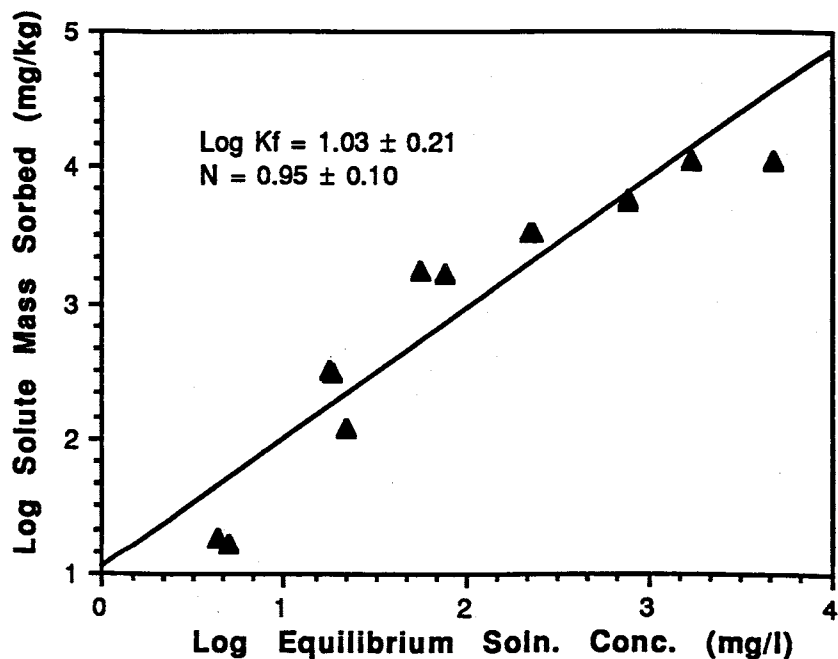


Figure 3.5B Freundlich Isotherm of Chromate Sorption onto HDTMA-Modified Tilden Zeolite (#2).

TMA, and HDTMA-modified zeolites (Figures 3.5A and 3.5B). The  $\log K_f$  value for the first HDTMA batch study was  $1.31 \pm 0.19$ , while the second batch study for HDTMA had a  $\log K_f$  value of  $1.03 \pm 0.22$ . Within the 95% confidence intervals, these two  $K_f$  values agree and therefore statistically represent the same results. Figures 3.4A, 3.4B, 3.5A, and 3.5B show this. These results confirmed that the chromate was being removed by the HDTMA-modified zeolite.

To further test for chromate sorption, additional zeolites were surface-modified with different QACs using the same methods for selection as described in section II. Figure 3.6 shows the isotherm for DBDMA-modified zeolite and chromate. Again, the DBDMA-modified zeolite showed an increased affinity for the chromate as compared to the natural, unmodified zeolite. A problem arose when the manufacturers of DBDMA (Aldrich Chemical Co.) discontinued its production. It was decided to discontinue pursuit of DBDMA as a surface-modifier of zeolites. BTEA was used to modify Tilden zeolite in hope that a pattern could be determined as to what types of QACs enhance chromate sorption. The isotherm for BTEA-modified zeolite and chromate is shown in figure 3.7. BTEA-modification did not enhance chromate sorption compared to natural zeolite.

TEA-modified zeolite was available through another research project, and therefore a batch study was conducted using chromate. The isotherm with TEA-modified Tilden zeolite can be seen in figure 3.8. The TEA-modified zeolite produced no discernible enhancement of chromate compared to the natural zeolite.

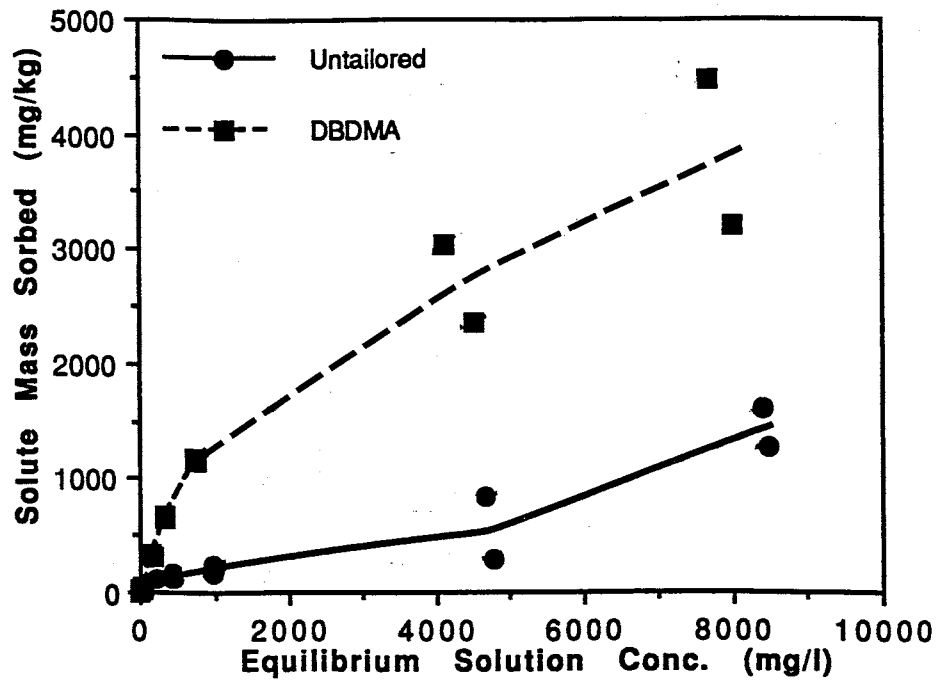


Figure 3.6. Chromate Isotherm using Tilden Zeolite in Natural, and DBDMA Modified Form.

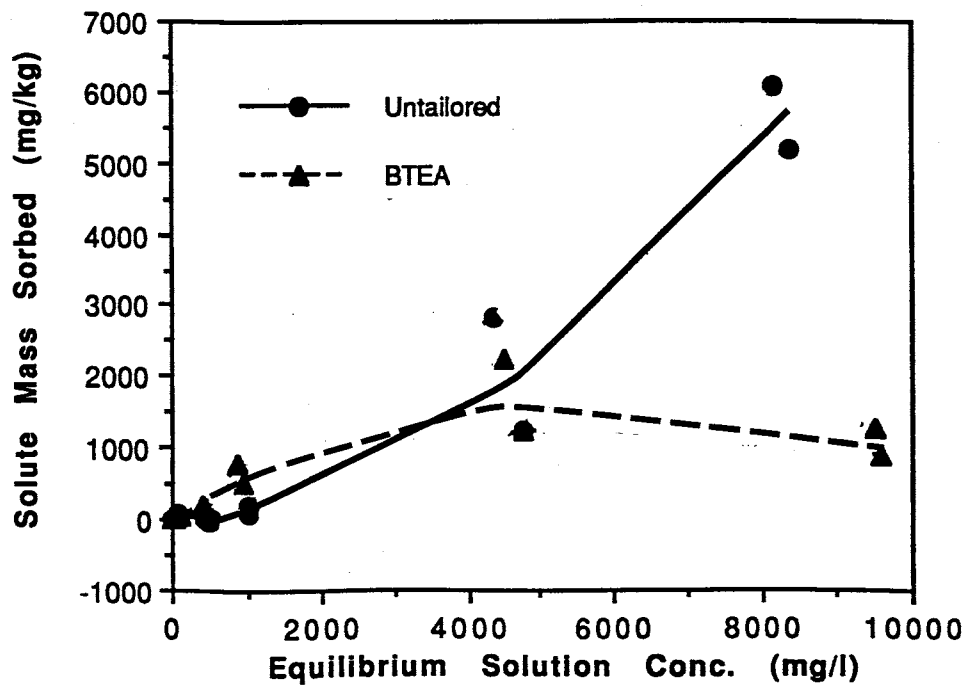


Figure 3.7. Chromate Isotherm using Tilden Zeolite in Natural, and BTEA Modified Form.

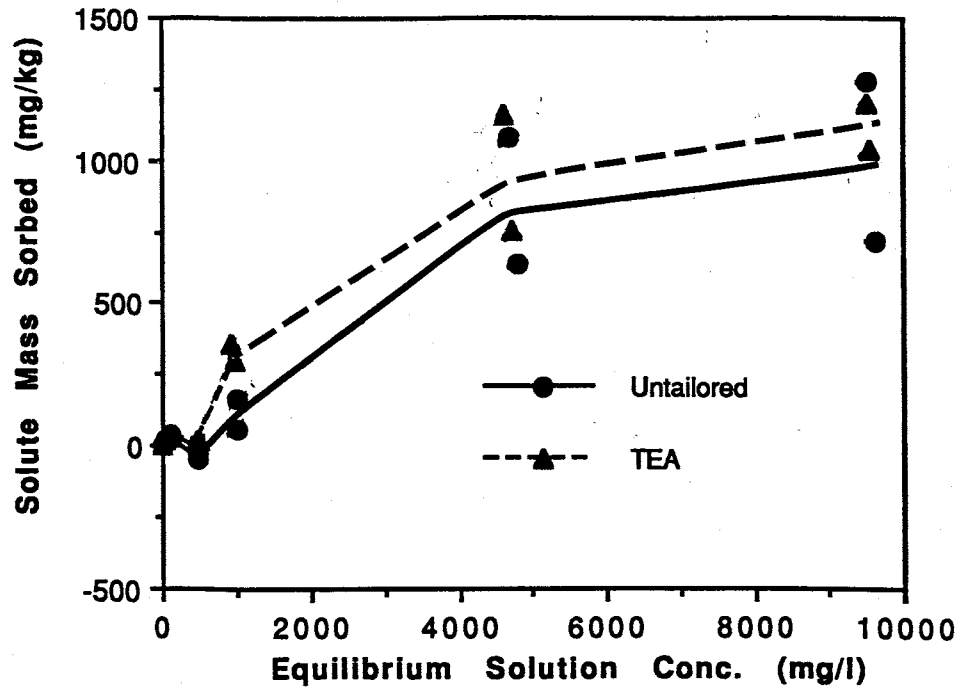


Figure 3.8. Chromate Isotherm using Tilden Zeolite in Natural and TEA Modified Form



### **Chromate Sorption with St. Cloud Zeolite**

The St. Cloud zeolite was introduced to the project due to its 85% purity of clinoptilolite and absence of clay. It was felt that the St. Cloud zeolite should produce results that more clearly represent the actual sorption characteristics of natural clinoptilolite. The St. Cloud zeolite was surface-modified with HDTMA and a batch study was performed. The isotherm for St. Cloud zeolite is shown in figure 3.9. For comparison reasons, the Tilden HDTMA-zeolite was similarly subjected to the same batch study parameters and conditions as the St. Cloud zeolite. The affinity for chromate sorption is stronger with the St. Cloud zeolite than with the Tilden zeolite (Figure 3.10). In figure 3.10, the St. Cloud isotherm is the same isotherm from 3.9. The HDTMA-modified Tilden zeolite has an isotherm with a  $K_d$  of 4.3 while the St. Cloud HDTMA-zeolite isotherm has a  $K_d$  of 19.4 (Figure 3.10). Reasons for the sorption of the chromate to the surface-modified zeolite are investigated in the following sections.

### **Effects of Solution Chemistry**

Figure 3.11 shows the isotherms resulting from electrolyte level variation. Noted from this figure is the change in  $K_d$  values associated with the change in electrolyte concentration. In order to determine whether the sorption results were influenced by the ionic strength of solution and/or complexation, thereby causing the chromate activity to change, a second graph was generated plotting the solute mass sorbed versus the activity of chromate. The results can be seen in figure 3.12. Figure 3.12 is based upon the activity coefficients given in table 3.3 calculated by MINTEQ and approximated by Pitzer (1979). The activity of chromate in the 1.0 M  $\text{CaCl}_2$  solution is an estimation by Pitzer (1979)

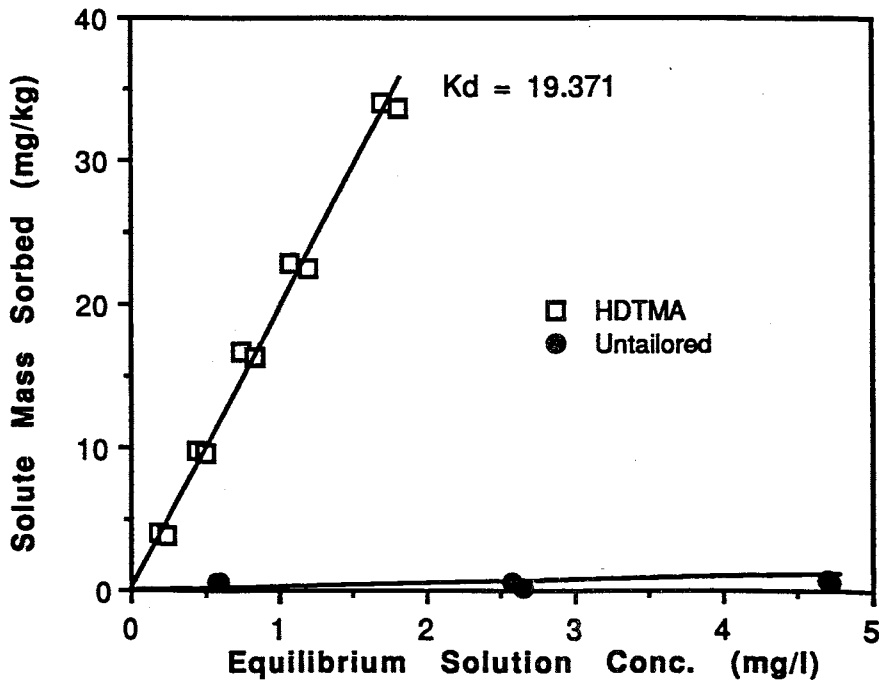


Figure 3.9 Chromate Isotherm using St. Cloud Zeolite in Natural and HDTMA Modified Forms

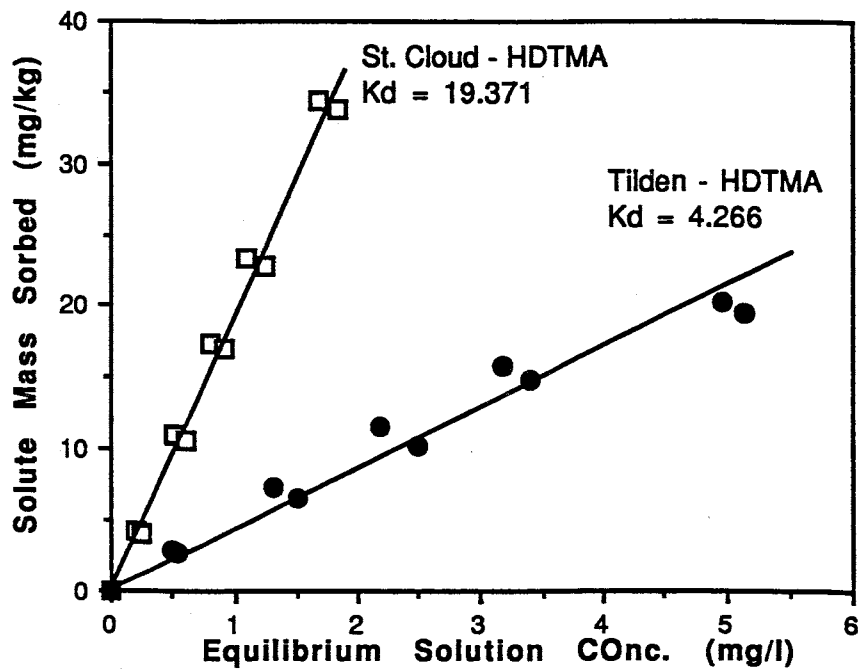


Figure 3.10 Comparison of St. Cloud and Tilden HDTMA-Modified Zeolites.

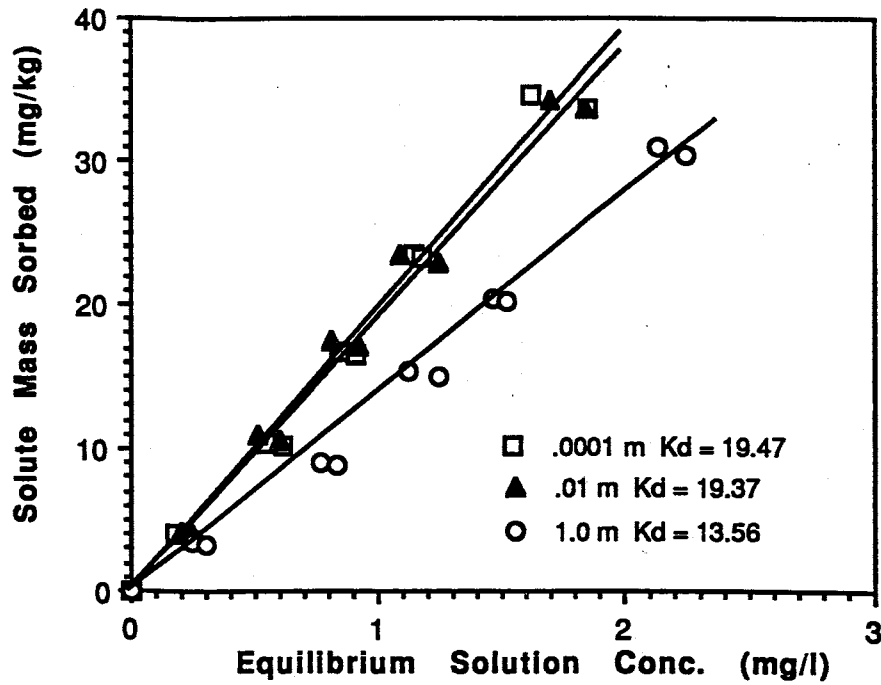


Figure 3.11. Effects Caused by Variations in Solution Chemistry On HDTMA-Modified, St. Cloud Zeolite

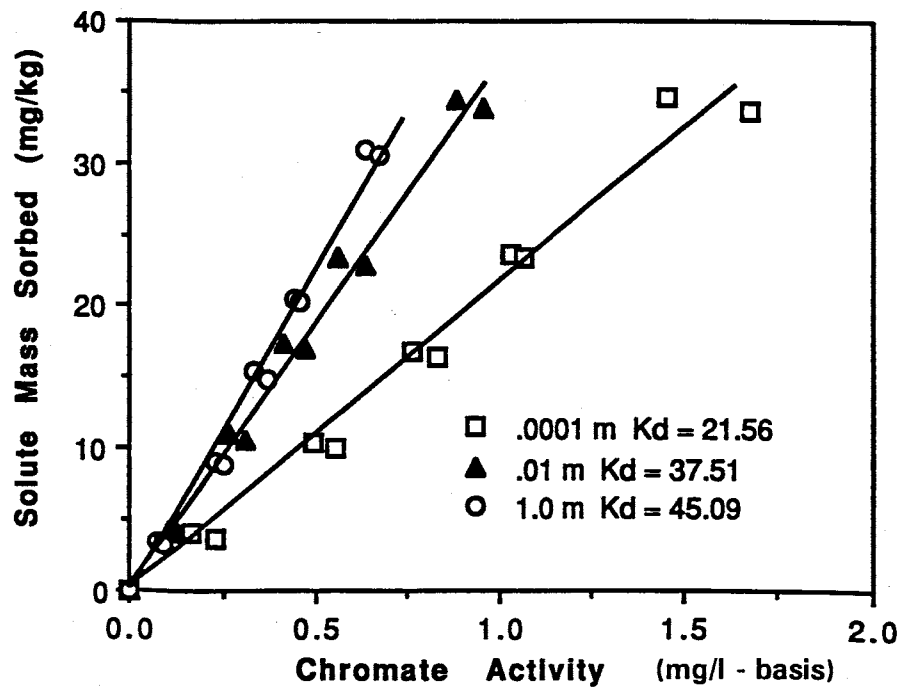


Figure 3.12. Variations in Solution Chemistry Considering Changes in Ionic Strengths and Chromate Activity.

which uses an ion interaction approach for calculating activity coefficients in electrolyte solutions. The activity of chromate is calculated by multiplying the chromate concentration by the activity coefficient.

The results from MINTEQ showed that no significant amounts of complexation occurred at any concentration.

---

**Table 3.2 Activity Coefficients of Chromate**

CaCl <sub>2</sub> Con- centration	Chromate Con- centration	Activity Coefficient	Source
0.0001 M	1 mg/L	0.921006	MINTEQ
0.0001 M	3 mg/L	0.915363	MINTEQ
0.0001 M	5 mg/L	0.910065	MINTEQ
0.0001 M	7 mg/L	0.905197	MINTEQ
0.0001 M	10 mg/L	0.898434	MINTEQ
0.01 M	10 mg/L	0.516363	MINTEQ
1.0 M	10 mg/L	0.300	Pitzer (1979)

### Determination of Chromate Sorption Mechanism

#### Tail Interaction

Without tail interaction, chromate sorption should be directly related to QAC loading of the external CEC. The 25%-CEC surface-modified zeolite's results should give us enough information to predict the outcome of the 50%, 75%, and 100%-CEC surface-modified zeolites. Results of the varying %-CEC sorption tests are found in table 3.3.

**Table 3.3 Results of Varied %-CEC Sorption Studies**

Amount Modified	Experimental $K_d$ [L/kg]	95% Confidence Interval	Predicted $K_d$ [L/kg] from 25% CEC Exper.
25% CEC	4.38	$\pm 0.67$	-----
50% CEC	10.68	$\pm 2.21$	7.42 - 10.10
75% CEC	16.03	$\pm 2.51$	11.13 - 15.15
100% CEC	19.37	$\pm 1.48$	14.84 - 20.20

Analysis of sorption isotherm data presented in Table 3.3 indicates that chromate sorption is directly related to QAC loading. The 25%-CEC zeolite has an experimental  $K_d$  value ranging from 3.71 to 5.05 L/kg within its 95% confidence interval. Using a  $K_d$  value of 5 L/kg for 25%-CEC zeolite, we would predict that the  $K_d$  value of 50%-CEC would be 10 L/kg. As seen from Table 3.3, this value is within the 95% confidence interval obtained experimentally. Again, using the  $K_d$  of 5 L/kg for 25%-CEC zeolite we would predict a  $K_d$  of 15 L/kg for 75%-CEC zeolite and 20 L/kg for 100%-CEC zeolite. These values are within the 95% confidence intervals of the experimentally obtained  $K_d$  values. Figure 3.13 presents the experimentally obtained isotherms defined in Table 3.3. Because the predicted values agree with those values experimentally obtained, we must conclude that tail interaction is not responsible for the sorption of chromate from solution.

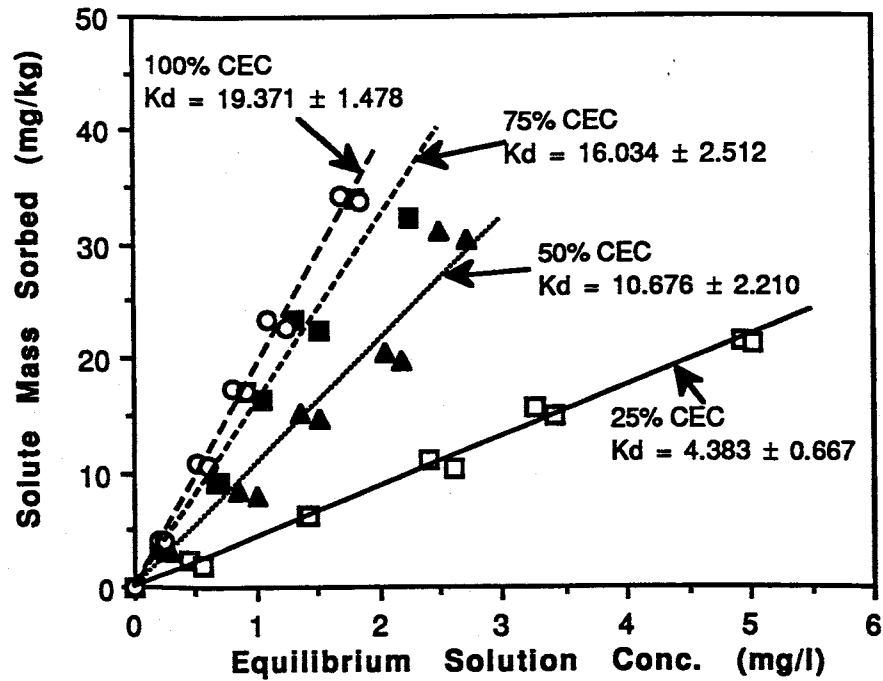


Figure 3.13 Experimentally Obtained Chromate Isotherms of St. Cloud Zeolite with Different HDTMA Loadings.

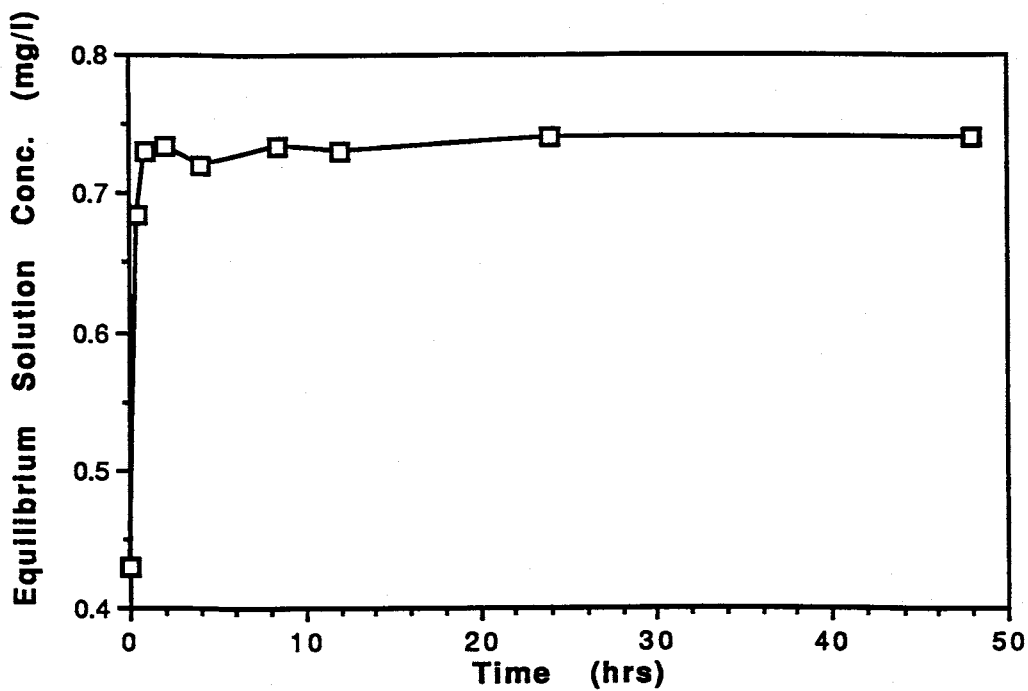


Figure 3.14 Equilibrium Desorption Time Scale Test (Mean) Using HDTMA-St. Cloud Zeolite and 5 mg/L Chromate Solution.

### **Reduction of Chromium (VI) to Chromium (III)**

Figure 3.14 shows the length of time required for the chromate on the surface of the modified zeolite to re-equilibrate with the chromate in solution. As noted from the graph, a time of two hours was chosen as the amount of time used for reequilibration in the desorption batch study.

Figure 3.15 through 3.17 show the individual desorption batch studies performed. The figures do show that chromium is being removed from the zeolite surface. The desorption of chromium from the zeolite suggests that most of the chromium (VI) is not being reduced to chromium (III). If this was the case, the chromium (III) would be extremely hard to remove from the zeolite due to electrostatic attractions. This has been shown by Bowman et al. (1981) when nickel ( $2^+$ ) was not desorbed from natural soils tested.

The possibility of the chromate entering the internal structure of the zeolite was considered as a means for the chromate removal, but the re-equilibration time of only two hours is likely too short a time for the chromate to exit the internal structure of the zeolite.

### **Partitioning with Organics**

The tailoring of the zeolite causes an increase of organic matter present on the outer surface of the zeolite. This was seen and noted by Huddleston (1990). Huddleston found the organic carbon content of unmodified Tilden zeolite at 0.16%. The HDTMA-modified Tilden zeolite had an increased organic carbon content of 6.33% (by weight). Because the HDTMA is not capable of entering the internal structure of the zeolite, all of the increased organic carbon must be on the external surface of the zeolite. This increased external organic layer was a possible means by which the chromate could be Figure 3.15 Desorption

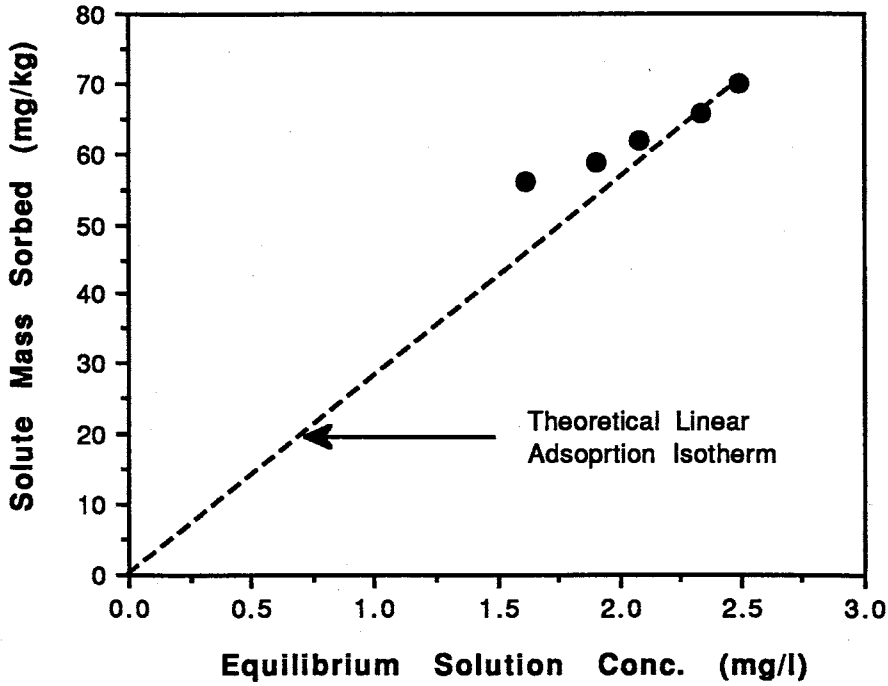


Figure 3.15 Desorption Isotherm with St. Cloud Zeolite; Test Tube A

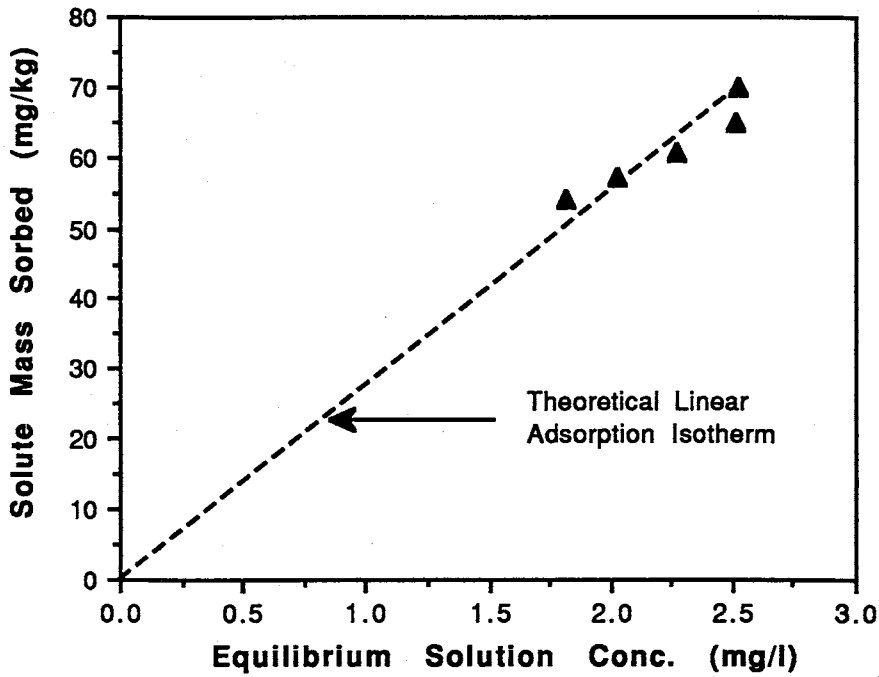


Figure 3.16 Desorption Isotherm with St. Cloud Zeolite; Test Tube B



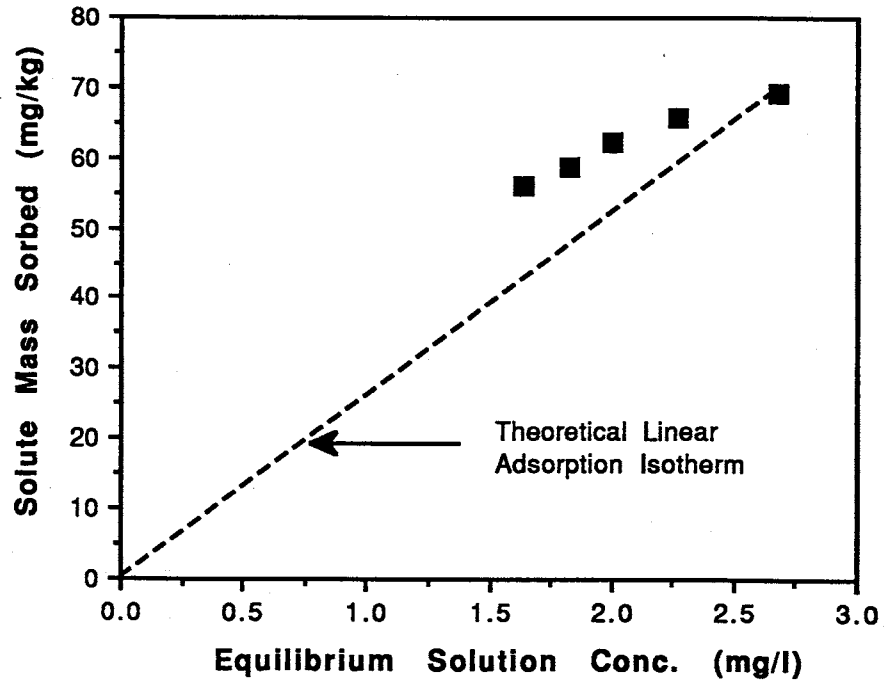


Figure 3.17 Desorption Isotherm with St. Cloud Zeolite; Test Tube C

removed. The results of the experiment containing both hexadecane and aqueous chromate showed that after a 24 hour period, 93.2% of the aqueous chromate remained. Bartlett and Kimble (1976), and Bartlett and James (1983) did state that chromate can be reduced if in contact with soil organic matter. However, the time scales noted for this reaction was roughly in months or years of prolonged contact, not one day in which our experiments show a loss of aqueous chromate. The results of our experiment show that aqueous chromate does not partition into established organic layers.

**IV.**  
**DISCUSSION**

## Surface-Modified Zeolite's Adsorptive Characteristics

Natural zeolites have a strong attraction for cations such as lead, while anions, like chromate, are strongly repulsed. Research by Mercer and Ames (1976) showed natural zeolite's ability to remove ammonium ions from solution. Gradev et al. (1988) showed that natural zeolites can efficiently remove silver from solution. Guangsheng et al. (1988) showed natural zeolite's ability for removing copper from solution. Assenov et al. (1988) also showed that natural zeolites can easily remove other cations such as cobalt and strontium from solution. Figures 3.1 through 3.3 show that cation ( $Pb^{2+}$ ) sorption by zeolite was not affected by surface modification. What became of interest to this project was the enhanced capability of the HDTMA-modified zeolite to remove or sorb the anion chromate from solution. Figures 3.4 through 3.10 show that natural zeolites absorb less than 5 percent of the anionic metal chromate from solution while the surface modified zeolite adsorbs 50 - 85 percent of chromate from solution, depending upon the zeolite.

The mechanism responsible for the sorption of the lead cation was believed to be electrostatic attraction from the internal surfaces of the zeolite. The hypothesis was that the lead ion is small enough to enter the internal structure of the zeolite. Clinoptilolite has calculated channel openings of  $0.41 \times 0.47$ ,  $0.44 \times 0.72$ , and  $0.40 \times 0.55$  nm corresponding to the a, b, and c planes respectively (Ming and Mumpton, 1989). The approximate hydrated radius of lead ( $Pb^{2+}$ ) at  $25^\circ C$  is  $4.2 \text{ \AA}$  (Dean, 1985). The lead ion was small enough to enter into the zeolite structure through the b plane channel opening during our batch tests. Testing to prove that the lead ion was actually entering the zeolite's internal structure has not been performed.

The mechanism responsible for chromate sorption will be discussed in the following paragraphs.

### **Effects of Solution Chemistry**

The high background electrolyte concentration affected the amount of chromate sorbed onto the HDTMA-modified St. Cloud zeolite. Through increased electrolyte levels, the ionic strength of the solution was changed, and therefore the activity of the chromate was changed. Reduction of chromate activity was a possible reason for the reduced sorption noted in the batch study (figure 3.11). When results of the batch study were replotted using the activity of the chromate in solution, the final graph (figure 3.12) showed the opposite trend. This means that the stronger ionic strength solution had the highest sorption of chromate even though the solution had the lowest activity of chromate. Reasons for this are not fully understood.

### **Chromate Sorption Mechanism**

The chromate sorption mechanism, in the beginning, was attributed to three possible causes. These were tail interaction, reduction of chromium (VI) to chromium (III), and organic partitioning. Results of experiments performed throughout this project have led to rejection of these three potential mechanisms. It was also theorized from the beginning that chromate, having only a hydrated radius of 4 Å (Dean, 1985), could enter the internal structure of the zeolite, but due to its negative charge it would be repulsed by the zeolite's net negative surface charge. What then is the mechanism? At this time, the mechanism is not known, but an additional hypothesis has been formulated. The proposed hypothesis suggests that the organic cations used to surface-modify the zeolite are becoming permanently

bonded to the zeolite's surface, thereby causing the zeolite's net negative surface charge to become neutral. Chromate was therefore capable of bonding to the external surface of the zeolite by non-specific forces such as van der Waals forces. The following paragraphs explain the theories involved with this hypothesis.

It is very important to note that the DBDMA-modified Tilden zeolite was capable of chromate removal from solution, but not in as significant amounts as the HDTMA-modified Tilden zeolite. If you refer back to table 2.1, you will notice that HDTMA and DBDMA are the two largest quaternary ammonium cations tested. As discussed in section II, Huddleston (1990) conducted experiments concerning the stability of the quaternary ammonium cation HDTMA on the external surface of the Tilden zeolite. Other researchers have also noted the permanent bonding of a large organic cation to surface-modified clays. Hayes, et al. (1978) measured the sorption enthalpy of large pyridinium compounds to sodium montmorillonite. They found exothermic sorption in all cases. Therefore, the large organic cations are favored to sorb thermodynamically, but the desorption of these large cations would not be favored unless energy was added to the system. It is reasonable to assume that other large organic cations would behave in a similar manner. Once sorbed, the organic cations may be held onto the mineral surface by other forces such as hydrogen bonding, van der Waals forces, and ion-dipole forces, depending upon the molecule (Boyd et al. 1988).

Solution entropy also contributes to the "irreversible" sorption of the large organic compounds. Sorption of a large molecular cation displaces several water molecules from the mineral's surface. This causes an increase in the solution entropy (Boyd et al., 1988).

When the large hydrophobic cation is in solution, water molecules are rigidly structured around the molecular ion (Hamaker and Thompson, 1972). When the molecular ion becomes associated with the mineral surface, the solution water molecules are able to become loosely structured, whereby hydrogen bonding and loose hydration shells can form around the inorganic ions present. This increases the solution entropy. With a decrease in enthalpy and an increase in entropy, the permanent bonding of the large cation to the mineral surface is favored.

The current hypothesis for chromate adsorption suggests that the external surface of the zeolite has essentially become neutral in charge, allowing the chromate to approach the zeolite surface without electrostatic repulsion. Non-specific forces are capable of binding the chromate to the zeolite surface. This hypothesis is not refuted by the desorption isotherms, effects of solution chemistry competition by chloride, and the variation of CEC surface-modification tests performed. However, rigorous proof of this mechanism requires further investigation.

**V.**

**SUMMARY & CONCLUSIONS**



### Summary

Clinoptilolite dominated zeolites from two different sources were surface-modified to observe the effect upon sorption of metals. Five different types of quaternary ammonium cations were used in the surface-modification of the zeolites. The inorganic contaminants lead and chromate were tested for their removal by the surface-modified zeolite. The mechanism for the removal of chromate was investigated.

The effect of surface-modification upon cationic lead sorption was minimal for both zeolites. Some scatter was seen in the data but can be attributed to laboratory error.

Natural clinoptilolite has almost no ability to sorb chromate from solution. With the surface-modification by HDTMA, the zeolites obtained the ability to sorb chromate from solution. Both the Tilden and the St. Cloud zeolite showed a strong affinity for the chromate, with the St. Cloud zeolite having the stronger affinity.

The mechanism for the chromate sorption by HDTMA-modified zeolites was of interest. Tail interaction, reduction of the chromate, and the possibility of chromate partitioning into the established surface organic layer were all tested and refuted as possible causes for the chromate sorption. Only the larger cations HDTMA and DBDMA were capable of enhancing chromate sorption. The stability upon the surface of the zeolite has only been tested for HDTMA. Literature shows that such large cations are thermodynamically favored to become permanently bonded to the zeolite's surface instead of exchanging with other cations in solution. Because of this permanence, the cations essentially neutralize the net negative external surface charge of the zeolite, thereby allowing the chromate to come in contact with the outer surface. Once in contact with the surface, non-specific

forces such as van der Waals forces may be strong enough to bond the chromate. The desorption study, competition of chloride with chromate for sorption, and varied CEC surface-modification batch studies tend to support this theory.

### **Conclusions**

Interpretation of the results led to several conclusions. In summary, these were:

- ▶ Surface modification of the zeolites did not reduce the zeolite's ability to adsorb cationic metals such as lead.
- ▶ The lead ion is small enough to enter the internal structure of the zeolite and bond to the internal surface.
- ▶ Natural clinoptilolite had little capability to sorb chromate, but surface-modified zeolites were very effective at removing chromate from solution.
- ▶ The modified St. Cloud zeolite was capable of removing chromate more efficiently from solution than the modified Tilden zeolite.
- ▶ The mechanism responsible for the surface-modified zeolite's ability to remove chromate from solution is yet to be fully discovered.
- ▶ Current theory suggests that the chromate is being bonded to the zeolite through van der Waals forces. No experiments to date refute this hypothesis.

### **Suggestions for Future Work**

The results of this project indicate that the surface-modified zeolites are unaffected in terms of cation removal from solution, but also have gained the ability to sorb the anionic metal chromate. Testing should continue into the surface-modified zeolite's capability

to sorb chromate, but should also focus on whether the modified zeolite is capable of sorbing other anionic metals as well. The theory of whether van der Waals interactions can explain chromate removal should also be explored.

The surface-modified zeolites have the potential applications as amendments to clay containment slurry walls built to immobilize organic and inorganic contaminant releases. Continued study into these areas are merited.

In addition, the large particle size of zeolites make them perfect candidate for use in column studies. The actual applicability in the field of surface-modified zeolites relies upon these studies. As always, more research can be conducted through introduction of new quaternary ammonium cations to the zeolites already under study. It would also be very relevant to obtain other clinoptilolite zeolites and test their sorptive abilities. In summary, there are many aspects of this type of research yet to be studied which promise greater discoveries in the years yet to come.

**VI.**  
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**APPENDIX A: Abbreviations**



AA: Atomic Adsorption Spectrophotometry

BTEA: Benzyltriethylammonium

BTX: Benzene, Toluene, and Xylene

CEC: Cation Exchange Capacity

DBDMA: Dibenzyl dimethylammonium

HDTMA: Hexadecyltrimethylammonium (Cetyltrimethylammonium)

QAC: Quaternary Ammonium Cation

SEM: Scanning Electron Microscopy

TEA: Tetraethylammonium

TMA: Tetramethylammonium

TBAC: Tert-butylammonium Chloride

XRD: X-ray Diffraction Spectroscopy

## **APPENDIX B: Sorption Isotherm Data**

Abbreviations:

TB: Test Blank (zeolite-less)

1A: Original Concentration of 1 ppm, Test Tube A

Pb: Lead

**Sorption of Pb onto Untailored Zeolites**

**Type of Zeolite: Tilden**

**Mass of Zeolite : 2.5 grams**

**Figure 3.1**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.1	1	1.1	
1A	1	1	1	0.4
1B	0.8	1	0.8	1.2
TB	10.1	1	10.1	
10A	0.6	1	0.6	38
10B	1.4	1	1.4	34.8
TB	10.7	10	107	
100A	1.03	10	10.3	386.8
100B	1.03	10	10.3	386.8
TB	10.47	100	1047	
1000A	1.473	100	147.3	3598.8
1000B	1.473	100	147.3	3598.8
TB	4.398	1000	4398	
5000A	2.503	1000	2503	7580
5000B	2.429	1000	2429	7876
TB	10	1000	10000	
10000A	7.41	1000	7410	10360
10000B	7.33	1000	7330	10680

**Sorption of Pb onto HDTMA Zeolites****Type of Zeolite: Tilden****Mass of Zeolite : 2.5 grams****Figure 3.1**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.1	1	1.1	
1A	0.7	1	0.7	1.6
1B	0.7	1	0.7	1.6
TB	10.1	1	10.1	
10A	1.7	1	1.7	33.6
10B	1.7	1	1.7	33.6
TB	10.7	10	107	
100A	1.44	10	14.4	370.4
100B	1.44	10	14.4	370.4
TB	10.47	100	1047	
1000A	3.17	100	317	2920
1000B	3.17	100	317	2920
TB	4.398	1000	4398	
5000A	2.296	1000	2296	8408
5000B	0.879	1000	879	14076
TB	10	1000	10000	
10000A	7.27	1000	7270	10920
10000B	N/A	1000	N/A	N/A

**Sorption of Pb onto TMA Zeolites**

**Type of Zeolite: Tilden**

**Mass of Zeolite : 2.5 grams**

**Figure 3.1**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0.007	1	0.007	
0A	0.18	1	0.18	-0.692
0B	0.245	1	0.245	-0.952
TB	4.891	2	9.782	
10A	0.677	2	1.354	33.712
10B	0.699	2	1.398	33.536
TB	5.107	10	51.07	
50A	2.471	5	7.99	172.32
50B	2.622	5	8.64	169.72
TB	5.021	20	100.42	
100A	0.461	10	14.61	343.24
100B	0.504	10	15.04	341.52
TB	4.783	100	478.3	
500A	0.85	50	42.5	1743.2
500B	0.893	50	44.65	1734.6
TB	3.897	250	974.25	
1000A	1.066	100	106.6	3470.6
1000B	1.153	100	115.3	3435.8
TB	4.868	1000	10000	
5000A	2.015	1000	2015	11412
5000B	2.041	1000	2041	11308
TB	3.935	2500	9837.5	
10000A	2.456	2500	6140	14790
10000B	2.56	2500	6400	13750

**Sorption of Pb onto TEA Zeolites**

**Type of Zeolite: Tilden**

**Mass of Zeolite : 2.5 grams**

**Figure 3.1**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0.007	1	0.007	
0A	0.223	1	0.223	-0.864
0B	0.245	1	0.245	-0.952
TB	4.891	2	9.782	
10A	0.72	2	1.44	33.368
10B	0.742	2	1.484	33.192
TB	5.107	10	51.07	
50A	1.682	5	8.41	170.64
50B	1.824	5	9.12	167.8
TB	5.021	20	100.42	
100A	1.571	10	15.71	338.84
100B	1.362	10	13.62	347.2
TB	4.783	100	478.3	
500A	0.85	50	42.5	1743.2
500B	0.85	50	44.65	1743.2
TB	3.897	250	974.25	
1000A	1.066	100	106.6	3470.6
1000B	1.131	100	113.1	3444.6
TB	4.868	1000	10000	
5000A	2.015	1000	2015	11412
5000B	2.015	1000	2015	11412
TB	3.935	2500	9837.5	
10000A	2.482	2500	6205	14530
10000B	2.611	2500	6527.5	13240

**Sorption of Pb onto Untailored Zeolites****Type of Zeolite: Tilden****Mass of Zeolite : 2.5 grams****Figure 3.2**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0.107	1	0.107	-0.428
0B	0.046	1	0.046	-0.184
TB	6.45	2	12.9	
10A	0.22	1	0.22	50.72
10B	0.36	1	0.36	50.16
TB	4.83	10	48.3	
50A	0.41	10	4.1	176.8
50B	0.41	10	4.1	176.8
TB	N/A	20	N/A	
100A	N/A	10	N/A	N/A
100B	N/A	10	N/A	N/A
TB	4.8	100	480	
500A	0.34	100	34	1784
500B	0.25	100	25	1820
TB	4.56	1000	4560	
5000A	2.2	1000	2200	9440
5000B	1.9	1000	1900	10640
TB	N/A	2500	N/A	
10000A	N/A	2500	N/A	N/A
10000B	N/A	2500	N/A	N/A



**Sorption of Pb onto DBDMA Zeolites****Type of Zeolite: Tilden****Mass of Zeolite : 2.5 grams****Figure 3.2**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0.199	1	0.199	-0.796
0B	0.26	1	0.26	-1.04
TB	6.45	2	12.9	
10A	1.98	1	1.98	43.68
10B	1.93	1	1.93	43.88
TB	4.83	10	48.3	
50A	0.96	10	9.6	154.8
50B	1.008	10	10.08	152.88
TB	N/A	20	N/A	
100A	N/A	10	N/A	N/A
100B	N/A	10	N/A	N/A
TB	4.8	100	480	
500A	1.4	100	140	1360
500B	1.6	100	160	1280
TB	4.9	200	980	
1000A	1.2	200	240	2960
1000B	1.25	200	250	2920
TB	4.56	1000	4560	
5000A	-	1000	N/A	N/A
5000B	-	1000	N/A	N/A
TB	N/A	2500	N/A	
10000A	N/A	2500	N/A	N/A
10000B	N/A	2500	N/A	N/A

**Sorption of Pb onto Untailored Zeolites****Type of Zeolite: Tilden****Mass of Zeolite : 2.5 grams****Figure 3.3**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0.11	1	0.11	
0A	0.11	1	0.11	0
0B	0.13	1	0.13	-0.08
TB	10.64	1	10.64	
10A	0.32	1	0.32	41.28
10B	0.25	1	0.25	41.56
TB	5.37	10	53.7	
50A	0.15	10	1.5	208.8
50B	0.19	10	1.9	207.2
TB	10.34	10	103.4	
100A	0.22	10	2.2	404.8
100B	0.21	10	2.1	405.2
TB	5.6	100	560	
500A	0.22	100	22	2152
500B	0.25	100	25	2140
TB	5.14	200	1028	
1000A	0.15	200	30	3992
1000B	0.15	200	30	3992
TB	3.33	1000	3330	
5000A	1.82	1000	1820	6040
5000B	1.72	1000	1720	6440
TB	5.05	2000	10100	
10000A	2.92	2000	5840	17040
10000B	3.76	2000	7520	10320

**Sorption of Chromate onto HDTMA Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.4**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed $\mu\text{g/kg}$
TB	0	1	0	
CB1	0	1	0	0
CB2	0	1	0	0
TB	0.5	1	0.5	
CB3	0.2	1	0.2	1.2
CB4	0.1	1	0.1	1.6
				0
TB	5	2	10	
CB5	0.6	2	1.2	35.2
CB6	0.6	2	1.2	35.2
				0
TB	5	20	100	
CB7	0.6	20	12	352
CB8	0.7	20	14	344
				0
TB	5	200	1000	
CB9	1.2	200	240	3040
CB10	1	200	200	3200
				0
TB	5	2000	10000	
CB11	4.5	2000	9000	4000
CB12	3.6	2000	7200	11200

**Sorption of Chromate onto TMA Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.4**

Sample ID	Dilute Equil.	Dilution Factor	Equilibrium	Solute Mass
	Concentration		Soln Conc.	Sorbed
	mg/L		mg/L	µg/kg
TB	0	1	0	
CC1	0	1	0	0
CC2	0	1	0	0
TB	0.5	1	0.5	
CC3	0.3	1	0.3	0.8
CC4	0.1	1	0.1	1.6
TB	5	2	10	
CC5	2.8	2	5.6	17.6
CC6	4	2	8	8
TB	5	20	100	
CC7	4.3	20	86	56
CC8	4.5	20	90	40
TB	5	200	1000	
CC9	4.8	200	960	160
CC10	4.9	200	980	80
TB	5	2000	10000	
CC11	4.9	2000	9800	800
CC12	4.9	2000	9800	800

**Sorption of Chromate onto Untailored Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.5**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed mg/kg
TB	0	0	0	
DA1	0	0	0	0
DA2	0	0	0	0
TB	4.5	2	9	
DA11	3.46	2	6.92	8.32
DA12	3.43	2	6.86	8.56
TB	5.184	10	51.84	
DA3	4.032	10	40.32	46.08
DA4	4.012	10	40.12	46.88
TB	1.91	50	95.5	
DA5	1.708	50	85.4	40.4
DA6	1.708	50	85.4	40.4
TB	4.908	100	490.8	
DA7	4.687	100	468.7	88.4
DA8	4.819	100	481.9	35.6
TB	4.2	250	1050	
DA9	4.027	250	1006.75	173
DA10	3.96	250	990	240
TB	3.74	1000	3740	
DA13	3.55	1000	3550	760
DA14	3.55	1000	3550	760
TB	3.049	2500	7622.5	
DA15	2.88	2500	7200	1690
DA16	3.104	2500	7760	-550

**Sorption of Chromate onto HDTMA Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.5**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed mg/kg
TB	0			
DB1	0	0	0	0
DB2	0	0	0	0
TB	4.5	2	9	
DB11	2.42	2	4.84	16.64
DB12	2.16	2	4.32	18.72
TB	5.184	10	51.84	
DB3b	5.436	4	21.744	120.384
DB4b	5.392	4	21.568	121.088
TB	1.91	50	95.5	
DB5b	4.379	4	17.516	311.936
DB6b	4.517	4	18.068	309.728
TB	4.908	100	490.8	
DB7d	3.071	25	76.775	1656.1
DB8d	2.189	25	54.725	1744.3
TB	4.2	250	1050	
DB9	2.289	100	228.9	3284.4
DB10	2.2	100	220	3320
TB	3.74	1000	3740	
DB13b	4.533	500	2266.5	5894
DB14b	4.753	500	2376.5	5454
TB	3.049	2500	7622.5	
DB15	4.898	1000	4898	10898
DB16	4.788	1000	4788	11338

**Sorption of Chromate onto TMA Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.5**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed mg/kg
TB	0	0		
DC1	0	0		0
DC2	0	0		0
TB	4.5	2	9	
DC11	3.6	2	7.2	7.2
DC12	3.38	2	6.76	8.96
TB	5.184	10	51.84	
DC3	4.113	10	41.13	42.84
DC4	4.153	10	41.53	41.24
TB	1.91	50	95.5	
DC5	1.627	50	81.35	56.6
DC6	1.708	50	85.4	40.4
TB	4.908	100	490.8	
DC7	4.93	100	493	-8.8
DC8	4.84	100	484	27.2
TB	4.2	250	1050	
DC9	4.071	250	1017.75	129
DC10	4	250	1000	200
TB	3.74	1000	3740	
DC13	3.628	1000	3628	448
DC14	3.79	1000	3790	-200
TB	3.049	2500	7622.5	
DC15	3.132	2500	7830	-830
DC16	2.99	2500	7475	590

**Sorption of Chromate onto Untailored Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.6**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed mg/kg
TB	0	0		
DA1	0	0		0
DA2	0	0		0
TB	4.996	2	9.992	
DA3	2.1	2	4.2	23.168
DA4	2.1	2	4.2	23.168
TB	4.9	10	49	
DA5	4.85	10	48.5	2
DA6	4.3	10	43	24
TB	5	50	250	
DA7	4.4	50	220	120
DA8	4.4	50	220	120
TB	4.9	100	490	
DA9	4.5	100	450	160
DA10	4.6	100	460	120
TB	5.1	200	1020	
DA11	4.8	200	960	240
DA12	4.9	200	980	160
TB	4.86	1000	4860	
DA13	4.65	1000	4650	840
DA14	4.79	1000	4790	280
TB	4.4	2000	8800	
DA15	4.24	2000	8480	1280
DA16	4.2	2000	8400	1600



**Sorption of Chromate onto DBDMA Zeolites****Type of Zeolite : Tilden****Mass of zeolite : 2.5 grams****Figure 3.6**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln Conc. mg/L	Solute Mass Sorbed mg/kg
TB	0	0		
DE1	0	0		0
DE2	0	0		0
TB	5	2	10	
DE3	1.469	2	2.938	28.248
DE4	1.296	2	2.592	29.632
TB	4.9	10	49	
DE5	4.3	10	43	24
DE6	3.9	10	39	40
TB	5	50	250	
DE7	3.3	50	165	340
DE8	3.4	50	170	320
TB	4.9	100	490	
DE9	3.27	100	327	652
DE10	3.24	100	324	664
TB	5.1	200	1020	
DE11	3.62	200	724	1184
DE12	3.67	200	734	1144
TB	4.86	1000	4860	
DE13	4.1	1000	4100	3040
DE14	4.5	1000	4500	1440
TB	4.4	2000	8800	
DE15	3.84	2000	7680	4480
DE16	4	2000	8000	3200

**Sorption of Chromate onto Untailored Zeolites****Type of Zeolite : Tilden****Mass of Zeolite : 2.5 grams****Figure 3.7**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	10.5	1	10.5	
10A	6	2	12	-6
10B	6.5	2	13	-10
TB	5.43	10	54.3	
50A	5.19	10	51.9	9.6
50B	5.29	10	52.9	5.6
TB	5.3	20	106	
100A	1.75	50	87.5	74
100B	1.87	50	93.5	50
TB	4.65	100	465	
500A	4.77	100	477	-48
500B	4.61	100	461	16
TB	10.43	100	1043	
1000A	5.1	200	1020	92
1000B	4.95	200	990	212
TB	5.06	1000	5060	
5000A	4.75	1000	4750	1240
5000B	4.35	1000	4350	2840
TB	4.83	2000	9660	
10000A	4.07	2000	8140	6080
10000B	4.18	2000	8360	5200

**Sorption of Chromate onto BTEA Zeolites****Type of Zeolite : Tilden****Mass of Zeolite : 2.5 grams****Figure 3.7**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	10.5	1	10.5	
10A	5.57	2	11.14	-2.56
10B	5.79	2	11.58	-4.32
TB	5.43	10	54.3	
50A	10.1	5	50.5	15.2
50B	10.5	5	52.5	7.2
TB	5.3	20	106	
100A	4.85	20	97	36
100B	4.92	20	98.4	30.4
TB	4.65	100	465	
500A	2.1	200	420	180
500B	2.21	200	442	92
TB	10.43	100	1043	
1000A	1.84	500	920	492
1000B	1.7	500	850	772
TB	5.06	1000	5060	
5000A	1.8	2500	4500	2240
5000B	1.9	2500	4750	1240
TB	4.91	2000	9820	
10000A	1.9	5000	9500	1280
10000B	1.92	5000	9600	880

**Sorption of Chromate onto Untailored Zeolites****Type of Zeolite : Tilden****Mass of Zeolite : 2.5 grams****Figure 3.8**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0.1	1	0.1	
0A	0.08	1	0.08	0.08
0B	0.09	1	0.09	0.04
TB	10.41	1	10.41	
10A	5.07	2	10.14	1.08
10B	5.21	2	10.42	-0.04
TB	5.6	10	56	
50A	5.16	10	51.6	17.6
50B	5.25	10	52.5	14
TB	5.28	20	105.6	
100A	4.91	20	98.2	29.6
100B	4.79	20	95.8	39.2
TB	4.71	100	471	
500A	4.82	100	482	-44
500B	4.73	100	473	-8
TB	10.35	100	1035	
1000A	5.1	200	1020	60
1000B	4.97	200	994	164
TB	2.48	2000	4960	
5000A	4.69	1000	4690	1080
5000B	4.8	1000	4800	640
TB	4.91	2000	9820	
10000A	4.75	2000	9500	1280
10000B	4.82	2000	9640	720

**Sorption of Chromate onto TEA Zeolites****Type of Zeolite : Tilden****Mass of Zeolite : 2.5 grams****Figure 3.8**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0.1	1	0.1	
0A	0.09	1	0.09	0.04
0B	0.1	1	0.1	0
TB	10.41	1	10.41	
10A	5.05	2	10.1	1.24
10B	5.25	2	10.5	-0.36
TB	5.6	10	56	
50A	5.09	10	50.9	20.4
50B	5.15	10	51.5	18
TB	5.28	20	105.6	
100A	4.92	20	98.4	28.8
100B	4.82	20	96.4	36.8
TB	4.71	100	471	
500A	4.65	100	465	24
500B	4.71	100	471	0
TB	10.35	100	1035	
1000A	4.8	200	960	300
1000B	4.73	200	946	356
TB	2.45	2000	4900	
5000A	4.61	1000	4610	1160
5000B	4.71	1000	4710	760
TB	4.91	2000	9820	
10000A	4.76	2000	9520	1200
10000B	4.78	2000	9560	1040

**Sorption of Chromate onto HDTMA Zeolites****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.9**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.24	1	1.24	
1A	0.24	1	0.24	4
1B	0.2	1	0.2	4.16
TB	3.25	1	3.25	
3B	0.51	1	0.51	10.96
3A	0.6	1	0.6	10.6
TB	5.18	1	5.18	
5B	0.92	1	0.92	17.04
5A	0.81	1	0.81	17.48
TB	3.47	2	6.94	
7A	1.09	1	1.09	23.4
7B	1.24	1	1.24	22.8
TB	5.14	2	10.28	
10B	1.7	1	1.7	34.32
10A	1.85	1	1.85	33.72

**Sorption of Chromate onto HDTMA Zeolites**

**Type of Zeolite: Tilden**

**Mass of Zeolite : 2.5 grams**

**Figure 3.10**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.13	1	1.13	
1A	0.51	1	0.51	2.48
1B	0.53	1	0.53	2.40
TB	2.87	1	2.87	
3A	1.32	1	1.32	6.20
3B	1.49	1	1.49	5.52
TB	4.87	1	4.87	
5A	2.50	1	2.5	10.00
5B	2.24	1	2.24	10.52
TB	3.54	2	7.08	
7A	3.13	1	3.13	15.8
7B	3.43	1	3.43	14.6
TB	5.12	2	10.24	
10A	4.96	1	4.96	21.12
10B	5.11	1	5.11	20.52

**Sorption of Chromate onto HDTMA Zeolites (0.0001m CaCl<sub>2</sub>)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.11**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.18	1	1.18	
1A	0.25	1	0.25	3.72
1B	0.18	1	0.18	4
TB	3.14	1	3.14	
3B	0.54	1	0.54	10.4
3A	0.61	1	0.61	10.12
TB	5.04	1	5.04	
5B	0.91	1	0.91	16.52
5A	0.84	1	0.84	16.8
TB	3.51	2	7.02	
7A	1.14	1	1.14	23.52
7B	1.18	1	1.18	23.36
TB	5.13	2	10.26	
10B	1.62	1	1.62	34.56
10A	1.86	1	1.86	33.6



**Sorption of Chromate onto HDTMA Zeolites (0.01m CaCl<sub>2</sub>)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.11**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.24	1	1.24	
1A	0.24	1	0.24	4
1B	0.2	1	0.2	4.16
TB	3.25	1	3.25	
3B	0.51	1	0.51	10.96
3A	0.6	1	0.6	10.6
TB	5.18	1	5.18	
5B	0.92	1	0.92	17.04
5A	0.81	1	0.81	17.48
TB	3.47	2	6.94	
7A	1.09	1	1.09	23.4
7B	1.24	1	1.24	22.8
TB	5.14	2	10.28	
10B	1.7	1	1.7	34.32
10A	1.85	1	1.85	33.72

**Sorption of Chromate onto HDTMA Zeolites (1.0m CaCl<sub>2</sub>)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.11**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.1	1	1.1	
1A	0.3	1	0.3	3.2
1B	0.24	1	0.24	3.44
TB	3.04	1	3.04	
3B	0.77	1	0.77	9.08
3A	0.83	1	0.83	8.84
TB	4.97	1	4.97	
5B	1.12	1	1.12	15.4
5A	1.24	1	1.24	14.92
TB	3.29	2	6.58	
7A	1.47	1	1.47	20.44
7B	1.52	1	1.52	20.24
TB	4.93	2	9.86	
10B	2.13	1	2.13	30.92
10A	2.24	1	2.24	30.48

**Sorption of Chromate onto HDTMA Zeolites (100% CE****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.13**

Sample ID	Dilute Equil. Concentration mg/L	Dilution Factor	Equilibrium Soln. Conc. mg/L	Solute Mass Sorbed mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.24	1	1.24	
1A	0.24	1	0.24	4
1B	0.2	1	0.2	4.16
TB	3.25	1	3.25	
3B	0.51	1	0.51	10.96
3A	0.6	1	0.6	10.6
TB	5.18	1	5.18	
5B	0.92	1	0.92	17.04
5A	0.81	1	0.81	17.48
TB	3.47	2	6.94	
7A	1.09	1	1.09	23.4
7B	1.24	1	1.24	22.8
TB	5.14	2	10.28	
10B	1.7	1	1.7	34.32
10A	1.85	1	1.85	33.72

**Sorption of Chromate onto HDTMA Zeolites (75% CEC)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.13**

<b>Sample ID</b>	<b>Dilute Equil. Concentration mg/L</b>	<b>Dilution Factor</b>	<b>Equilibrium Soln. Conc. mg/L</b>	<b>Solute Mass Sorbed mg/Kg</b>
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.07	1	1.07	
1A	0.21	1	0.21	3.44
1B	0.25	1	0.25	3.28
TB	2.97	1	2.97	
3B	0.68	1	0.68	9.16
3A	0.7	1	0.7	9.08
TB	5.18	1	5.18	
5B	1.05	1	1.05	16.52
5A	0.91	1	0.91	17.08
TB	3.58	2	7.16	
7A	1.52	1	1.52	22.56
7B	1.31	1	1.31	23.4
TB	5.16	2	10.32	
10B	1.81	1	1.81	34.04
10A	2.25	1	2.25	32.28

**Sorption of Chromate onto HDTMA Zeolites (50% CEC)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.13**

<b>Sample ID</b>	<b>Dilute Equil. Concentration</b> mg/L	<b>Dilution Factor</b>	<b>Equilibrium Soln. Conc.</b> mg/L	<b>Solute Mass Sorbed</b> mg/Kg
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.07	1	1.07	
1A	0.24	1	0.24	3.32
1B	0.29	1	0.29	3.12
TB	2.97	1	2.97	
3B	1	1	1	7.88
3A	0.84	1	0.84	8.52
TB	5.18	1	5.18	
5B	1.35	1	1.35	15.32
5A	1.52	1	1.52	14.64
TB	3.58	2	7.16	
7A	2.19	1	2.19	19.88
7B	2.05	1	2.05	20.44
TB	5.16	2	10.32	
10B	2.5	1	2.5	31.28
10A	2.73	1	2.73	30.36

**Sorption of Chromate onto HDTMA Zeolites (25% CEC)****Type of Zeolite: St. Cloud****Mass of Zeolite : 2.5 grams****Figure 3.13**

<b>Sample ID</b>	<b>Dilute Equil. Concentration mg/L</b>	<b>Dilution Factor</b>	<b>Equilibrium Soln. Conc. mg/L</b>	<b>Solute Mass Sorbed mg/Kg</b>
TB	0	1	0	
0A	0	1	0	0
0B	0	1	0	0
TB	1.07	1	1.07	
1A	0.45	1	0.45	2.48
1B	0.56	1	0.56	2.04
TB	2.97	1	2.97	
3B	1.4	1	1.4	6.28
3A	1.43	1	1.43	6.16
TB	5.18	1	5.18	
5B	2.6	1	2.6	10.32
5A	2.4	1	2.4	11.12
TB	3.58	2	7.16	
7A	3.25	1	3.25	15.64
7B	3.41	1	3.41	15
TB	5.16	2	10.32	
10B	5.01	1	5.01	21.24
10A	4.92	1	4.92	21.6

**Desorption of Chromate from HDTMA Zeolite****Zeolite: St. Cloud****Solution Conc.: 20 ppm****Figures 3.15, 3.16, & 3.17**

<b>Sample Number</b>	<b>Soln. Conc. (ppm)</b>	<b>Mass Removed (<math>\mu\text{g}</math>)</b>	<b>Solute Mass Sorbed (<math>\mu\text{g}</math>)</b>	<b>Solute Mass Sorbed (mg/kg)</b>
0a	2.49	175.10	175.10	70.04
1a	2.34	10.95	164.15	65.66
2a	2.08	9.10	155.05	62.02
3a	1.90	8.60	146.45	58.58
4a	1.62	6.70	139.75	55.90
0b	2.52	174.80	174.80	69.92
1b	2.51	12.50	162.30	64.92
2b	2.27	10.15	152.15	60.86
3b	2.03	8.95	143.20	57.28
4b	1.81	7.95	135.25	54.10
0c	2.68	173.20	173.20	69.28
1c	2.27	9.30	163.90	65.56
2c	2.00	8.65	155.25	62.10
3c	1.83	8.30	146.95	58.78
4c	1.64	7.25	139.70	55.88
0 avg	2.56	174.37	174.37	69.75
1 avg	2.37	10.92	163.45	65.38
2 avg	2.12	9.30	154.15	61.66
3 avg	1.92	8.62	145.53	58.21
4 avg	1.69	7.30	138.23	55.29

Where 1a =&gt; Test tube A at time interval #1