Project Number CHE-RWT-0909

Adsorption of Methyl Tertiary Butyl Ether Using Granular ZSM-5

A Major Qualifying Project Report
Submitted to the Faculty and Staff of
WORCESTER POLYTECHNIC INSTITUTE
for requirements to achieve the
Degree of Bachelor of Science
in Chemical Engineering & Civil Engineering
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Date: April 30, 2009

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Abstract

The goal of this project was to investigate the ability of polycrystalline zeolite ZSM-5 aggregates to remove MTBE from water. Powdered ZSM-5 has shown to adsorb MTBE, but is impractical in flow systems due to very high pressure drops. This report will investigate the adsorption of MTBE using granular ZSM-5. The adsorption of MTBE was measured through the use of batch experiments to create an adsorption isotherm, which was used to assist in the design of a full-scale treatment system.

Acknowledgements

This Major Qualifying Project could not have been completed without the continual support and guidance from professors Robert Thompson and John Bergendahl. Special thanks also goes out to professor Jeanine Plummer, Engin Ayturk, Boquan Li, Pranoti Navare, professor John McDonald, Laila Abu-Lail, Professor Paul Mathisen, and Don Pellegrino.

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Background

About MTBE

Fuel oxygenates are chemicals containing oxygen that are added to fuels, specifically gasoline, to allow them to burn more efficiently. Adding oxygen raises the octane level of gasoline and helps it burn more completely, which reduces harmful atmospheric pollution associated with automobile emissions (U.S. Geological Survey). MTBE (Methyl tertiary butyl ether) has been used in gasoline in the United States at low levels since the late 1970's to replace lead as an octane enhancer. In 1990, Congress passed the Clean Air Act Amendment, which mandated the use of oxygenated gasoline. In order to fulfill these oxygenate requirements, MTBE was used in higher concentrations in some gasoline (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*.

Federal and state regulators have acknowledged that addition of MTBE to gasoline has provided many air quality benefits. EPA has stated that since the reformulated gasoline (RFG) program in 1995, it has resulted in annual reductions of 105,000 tons of smog-producing emissions and at least 24,000 tons of toxic air pollutants such as benzene. According to the EPA, this is equivalent to removing 16 million cars from the road (Meissner & Voll). Despite the benefits of MTBE, there are many tradeoffs that are involved.

MTBE is a volatile, colorless, and flammable liquid that is highly soluble in water, which makes it very difficult to clean up. The high solubility and persistence of MTBE causes it to travel very quickly when released into an aquifer or soil. MTBE was produced in very large quantities, but due to widespread spillage of MTBE-containing gasoline in underground storage tanks, regulatory action was passed under the Toxic Substances Control Act on March 20, 2000 to significantly reduce or eliminate the use of MTBE. Contamination of drinking water aquifers became a very serious concern; the first major incidence was in the city of Santa Monica (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*.

Cases of Contamination

In 1996, two drinking water aquifers in the city of Santa Monica, Charnock and Arcadia, were contaminated with MTBE at levels as high as 610 ppb and 86 ppb respectively. These two aquifers represented 50 percent of the city's drinking water. In response, the city shut down the two aquifers and began purchasing replacement water. This incident was the first major water contamination that brought public attention to the issue of MTBE (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*. Since 1999, MTBE has been phased out as a gasoline additive, because of groundwater contamination (California Enivronmental Protection Agency). Recent state laws have been passed banning MTBE in certain states. California and New York combined to account for 40% of MTBE usage in the United States, and both states banned it in January, 2004. In September of 2005, twenty-five states signed legislation to ban MTBE (Energy Information Administration).

One of the largest cases of MTBE contamination in the United States is in the town of Pascoag, Rhode Island. The Pascoag Water District serves about 5,000 people, and is pumped from one 16" well, drawing 350 GPM from bedrock and aquifers (Allen & Boving, 2006). Following the detection of the MTBE contamination in 2001, residents were notified not to drink the town water and to reduce skin contact. Despite the warning, residents complained about severe headaches, vomiting, wheezing, and blisters. Since then, the drinking water supply in Pascoag has been shut down and the residents have been without their own drinking water source. Currently, Pascoag is receiving water from a local district at a cost of more than $1,000,000 a year. The town cannot sustain this financial burden, and there has been strong political pressure building to reactivate the Pascoag well (Allen & Boving, 2006).

Current Methods of Removal

The main risk of MTBE is that it gives water an unpleasant taste at even low concentrations, which can easily turn large quantities of groundwater unsuitable for drinking (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*. The EPA concluded that at low levels, there is not enough adequate data to quantify health risks. However, data supports MTBE to be a potential carcinogen at high levels of exposure (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*.

The estimated cost of removal of groundwater and soil contamination at the national level ranges from $1-3 billion (SIGMA). There are several current methods of treating MTBE from water; however they are all very expensive.

1. Air Stripping is a process in which contaminated water is passed through a column filled with packing material while upward-flowing air removes the chemicals in the water. Generally, the resulting vapors should not be released directly into the air and should be treated appropriately. MTBE does not easily separate from water into the vapor phase, which often necessitates high air-to-water ratios (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*. .
2. Advanced oxidation uses combinations of ultraviolet light, chemical oxidants, and catalysts to transform the contaminants. Oxidation methods have been proven to oxidize

wide ranges of organic chemicals, including MTBE (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*.

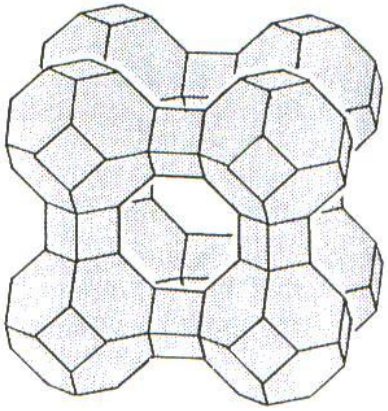
3. Granular activated carbon (GAC) pumps contaminated water through a bed of activated carbon to remove organic compounds. Since MTBE does not adsorb well on organics such as carbon, large volumes of the contaminated water must be passed repeatedly through several GAC columns in order for the MTBE to be effectively removed (Environmental Protection Agency, *Methyl Tertiary Butyl Ether)*.

There are processes and methods that are being tested to treat MTBE and other contaminants from water. One of the methods currently being tested is using zeolites to treat MTBE from contaminated water using adsorption into nanoporous adsorbents.

About Zeolites

Zeolites, or molecular sieves, are micro-porous crystalline structures which mostly contain silicon and aluminum (British Zeolite Association, *What Are Zeolites?*). Currently, there are around 102 known zeolites, 45 of which are naturally occurring. The natural zeolites are rarely used for commercial applications, mainly because there are usually contaminant minerals within them. Natural zeolites were made when volcanic rocks and ash layers went through a low-grade metamorphism and some others were created by changes in heat and pressure (Mineral Gallery, *The Zeolite Group)*.

The framework of zeolites at the molecular level consists of either a silicon or aluminum at the center of four oxygen atoms in tetrahedral coordination. These small structures then attach at the corners and can make many different shapes with different channels within them. Figure 1 shows an example of the structure of a zeolite.



Source: www.chemistrv.ohio-state.edu

Figure 1: Structure of Zeolite A Unit Cell

The diameter of the channels determines what will be able to pass through the zeolite structures. Due to this, zeolites are useful in adsorption because they only allow certain sized molecules inside (British Zeolite Association, *What Are Zeolites?*).

There are numerous ways to synthesize zeolites. Hydrothermal synthesis of zeolites is used in aqueous solutions in closed systems that are typically at high temperatures and high pressures (Cejka, Bekkum, & Schuth, 2007). The other process is solvothermal, which is a versatile low temperature route. This allows polar solvents to be used at conditions above their boiling temperatures. It also causes the solubility of the reactants to increase, which allows for the low temperatures (Chippindale, Darlow, Powell, & Vaquiero, 2004). Additionally, the effect of the solvents depends on viscosity; the higher viscosity of the solvents reduces mass transfer and creates larger crystals. This was used on high silica zeolites, therefore resulting in larger sizes of crystals produced through this process of zeolite synthesis (Cejka, Bekkum, & Schuth, 2007).

Related Works

One of the zeolites found to adsorb MTBE better then activated carbon was silicalite, or Al-free ZSM-5 (Erdem-Şenatalar, et al., 2004). This synthesized zeolite was created by the Mobil Oil Company (Chitnisa, Degnan, & Schipper, 2000). Figure 2 shows a picture of ZSM-5 structure containing silicon and oxygen atoms, where the red balls represent oxygen and the white balls represent silicon (Whittingham).

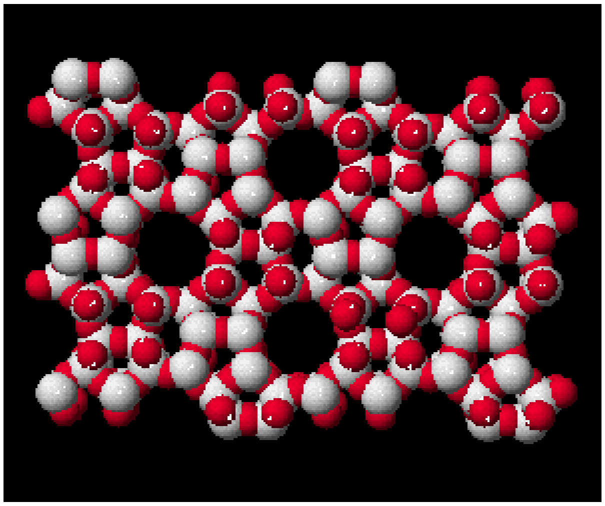


Figure 2: ZSM-5 Silicalite

ZSM-5 is a high silica, hydrophobic zeolite (Butland, et al., 2008). Hydrophobic signifies that the molecule is non-polar, and therefore is attracted to other non-polar molecules or solvents; with this separation of non-polar and polar mixtures can occur (ISCID). Knowing this, the concept of using the ZSM-5 zeolite for the adsorption of MTBE scientifically makes sense.

Michael Anderson from the University of California conducted a study on the *Removal of MTBE and Other Organic Contaminants from water by Sorption to high Silica zeolites*. In the study, three high silica zeolites, including ZSM-5 and activated carbon, were used in batch adsorption tests to determine the overall efficiencies. The solutions contained 100 μg/L of

MTBE and 5 mg of zeolite or activated carbon. The results ultimately showed that the high silica zeolites performed better then the activated carbon, which are commonly used for adsorption of contaminants. Additionally, ZSM-5 was not the most efficient media in this study, but mordenite was able to reduce the concentration of MTBE from 100 to 4 μg/L. The study also concluded that the pore structure of ZSM-5 was too small for the MTBE to fit in neatly (Anderson, 2000). Arjan Giaya authored a Ph.D dissertation at Worcester Polytechnic Institute and repeated the previous experiments at higher concentrations of MTBE. The data obtained in these experiments contradicted the results of Anderson's study.

Ayşe Erdem-Şenatalar, John A. Bergendahl, Arjan Giaya, and Robert W. Thompson conducted experiments of *Adsorption of Methyl Tertiary Butyl Ether on Hydrophobic Molecular Sieves.* This study used the same materials that Anderson used in the previous with the activated carbon, ZSM-5, and dealuminated zeolite Y (DAY). The results of these experiments were that at low concentrations the ZSM-5 adsorbed more MTBE than the other media. In high concentrations the DAY was the preferred zeolite, but it gave poor results at low concentrations while ZSM-5 still gave appealing values at high concentrations. The results of these data compared to the results by Anderson in the above work were very different. One of the large differences was a waiting period of 24 hours to reach equilibrium while the Giaya experiment only used 8 hrs. The Giaya experiment showed that DAY was preferred with higher concentrations and that at low concentrations it was very inefficient. The ZSM-5 was nearly equally efficient as activated carbon in adsorbing TCE, but was slightly more effective at adsorbing MTBE (Erdem-Şenatalar, et al., 2004). Figure 22 in Appendix 5 shows the graph of aqueous MTBE adsorption isotherm used in this study. This study showed that ZSM-5 did have potential and showed values that would be desirable in the MTBE adsorption process.

In a M.S thesis, Tricia Butland used batch and fixed bed experiments to determine the best zeolite for Tertiary Butyl Alcohol (TBA) adsorption.

Table 1: Zeolite Properties and Sources

Powdered Sample	$\frac{SiO_2}{Al_2O_3}$	**Company Name**	**Lot #**	**Cation Form**
Zeolite Beta	150	Zeolyst	1822-75	H+
Zeolite Mordenite	90	Zeolyst	1822-60-30	H+
Zeolite-Y	80	Zeolyst	78001N00257	H+
ZSM-5/Silicalite	>1000	Grace Davison	5-8888-0702	---
Granular Sample	$\frac{SiO_2}{Al_2O_3}$	**Company Name**	**Lot #**	**Micropore Area (m^2/g)**
Zeolite Beta	35	Engelhard	L6598-48-1	266
Zeolite Mordenite	50	Engelhard	05001C-BWC2-06	304.3
Molsiv HISIV 1000 (High silica faujasite)	< 6.5	UOP	2006003165	247.1
Molsiv HISIV 3000 (High silica faujasite)	< 10	UOP	2002001440	230.5
Zeolite-Y	---	Engelhard	20275-45-1	73.4
Zeolite-Y	---	Engelhard	20275-45-2	58.7
ZSM-5	280	Zeolyst	CBV28014	141.8

Table 1 shows the seven granular zeolite forms that were tested, and HiSiv 3000 and ZSM-5 were found to be the most efficient. For the time trials, the samples were prepared to create 1 mg/L samples. Two sets of ZSM-5 and HiSiv 3000 zeolites (one lower mass of zeolite, one higher mass) were baked in an oven at 350 ^{o}C for 12 hours (in order to clean out the pores). The sample vials were then placed in a rotisserie for 48 hours at 15 rpm. At designated times – 0, 6, 12, 24, and 48 hours – the vials were removed and centrifuged for separation at 3000 rpm for 10 minutes. In order to test the equilibrium capacities, the samples were again prepared with 99% TBA with water in concentrations of 0.1, 1, and 10 mg/L. These would be used to determine the best TBA adsorbents. For isotherm samples, they were again prepared in 99% TBA and water solutions in concentrations between 0-150 mg/L. The zeolites were baked in an oven at 300° C for 12 hours. A certain mass would be chosen for each zeolite and recorded, then added to each vial. The vials were then placed on a shaker table for 48 hours at 5 rpm and after 48 hours, were removed and placed in the centrifuge for separation (Butland, et al., 2008).

For fixed bed experiments, the zeolites were added into a column attached to a pump to control the feed flow rate. The feed would flow through the column, through a flow adapter, through the packed bed, and finally the liquid would leave the column into a waste container. Samples were taken at the exit of the column at specific time intervals (Butland, et al., 2008).

Batch experimentation with several different zeolites determined that the contact time necessary for complete adsorption is 48 hours which can be seen in Figure 3

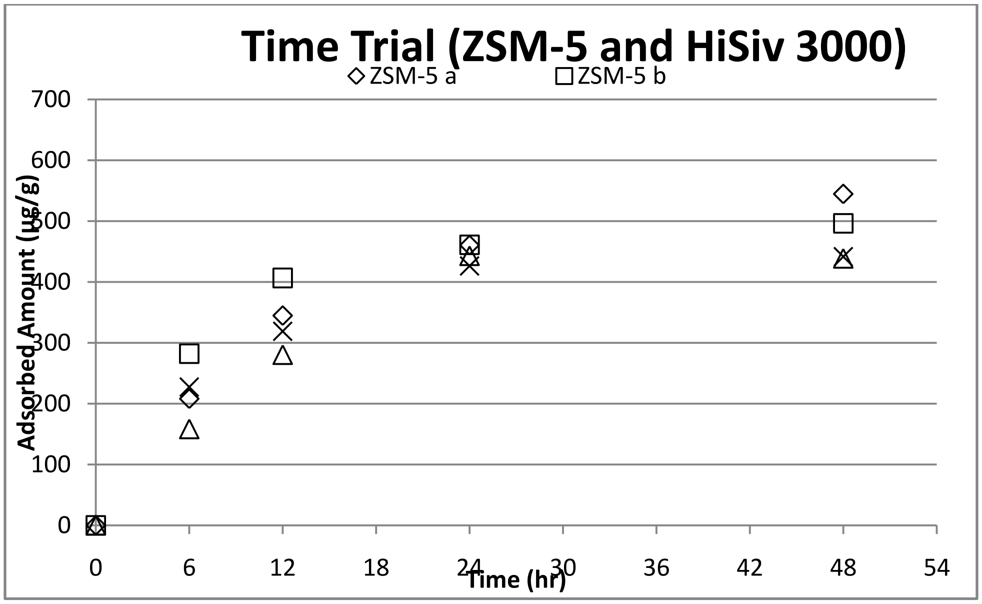


Figure 3: Time Trial Data

Of the seven zeolites tested ZSM-5 and HiSIV 3000 adsorbed more in the 48-hour period than the other zeolites (Butland, et al., 2008). In the column experiments, each column's equivalent adsorption capacity was determined and showed that adsorption in the columns were 10 times less than in the batch experiments. This was thought to be due to the contact time (48 hours) needed to complete adsorption and a very slow mass transfer process occurring in the zeolite pores (Butland, et al., 2008). These results point out that equilibrium adsorption capacity may not administrate the behavior of fixed bed absorbers if mass transfer is limited significantly (Butland, et al., 2008).

Project Goals

From the understanding of the experiments described above, the experiments for this report were developed. The procedure for batch adsorption used in the most recent experiments was conducted with the ZSM-5 zeolite. In the previous experiment, a clay binder was added to the granular form of the ZSM-5 before it was shaped into pellets. The clay binders were possibly affecting the efficiency of the ZSM-5 adsorbing MTBE because of pore blockage. The granular ZSM-5, called polycrystalline zeolite aggregates, were synthesized so that to create ZSM-5 without the clay binder.

Methodology

Analysis of ZSM-5 Sample

In a previous MQP, it was conjectured that Derek Pszybysz made granular ZSM-5 zeolites, but he did not accurately record x-ray diffraction data on the samples. In a subsequent study, Bradford Carleen repeated the experiments and was able to provide more samples as the previous set of zeolites was limited in amount. Because such little information was known about these zeolites, analyses were conducted to determine three things: whether the samples created were truly ZSM-5, whether the samples had thorough crystalline structures, and whether the samples were calcined or uncalcined. For reference in this report, the ZSM-5 pellets from run 4 that were made by Derek will be referred to as the "old sample," while the ZSM-5 pellets that were synthesized by Brad will be referred to as the "new sample."

Powder X-Ray Defraction (XRD)

The powder x-ray diffraction was used to determine if the samples of pellets were actually synthesized correctly. A pellet was taken from run 4 of the day 8 vial from the old samples; the pellet was ground to powder using a mortar and pestle. The powder was then placed onto a glass slide and placed into the machine. The computer then gave the analysis. The new sample that Brad had made also used this machine, but we did not do the analysis since he provided the XRD results.

Scanning Electron Microscope (SEM)

The scanning electron microscope was used to take images of the samples to show if the crystalline structures were uniform throughout the pellet. To prepare the sample for the SEM the sample is first placed on a special stand that is coated with carbon paint so that the sample is secure and the vacuum used in the machine will not be able to displace the sample. The sample was then coated with a thin layer of gold by a machine called a sputter coater. This was done to help reduce the effects of the electrons so that the image would be clear. The sample was placed in the SEM and the pictures were then taken at different places to show that the crystalline structure was uniform. This was done twice – the first was a sample that was found to already be broken from run 4 of the old sample, and the second was a whole pellet from the new sample that was broken before being placed into the machine. This was done to show the difference between a sample that could have been broken during synthesis and a sample that was clearly not broken during synthesis.

Thermal Gravimetric Analysis (TGA)

The TGA was used to determine if the old sample had been calcined or not. The machine is designed to increase the temperature of the sample and measure the weight loss, because as the temperature rises certain components volatilize or burn off. The sample being analyzed was from run 4 of the day 8 of the old samples; this was assumed to be the stage of the synthesis where the samples would most likely have been calcined. To be analyzed in the TGA, the sample needed to be in a powder form. This was done by using a mortar and pestle to grind the pellet. There were also two other samples that were used as controls: sample ZSM-5 powders that were calcined and uncalcined. The tray that the sample was to be placed in was put over a

Bunsen burner to burn off any other samples that were used in other experiments. The sample was put into the tray and then placed into the TGA machine. The TGA was set to be in the range of 0-500° C. During the experiment there was to be a drop off at two significant sections. The first was at 100° C, where water boils off and is removed from the mass, and the second at around 250-300° C where the organic template would theoretically burn off. It was found that there was a 15% weight reduction, signifying that the old sample was uncalcined. Therefore, the new sample was used for our batch experiments, because they were calcined by Bradford Carleen after the synthesis.

COD Calibration Curve

In a previous study, Michelle Slack used ultraviolet & visual spectroscopy for analysis. Chemical Oxygen Demand (COD) tests were used to measure the concentrations of MTBE in the samples. The COD test is used to indirectly measure the amount of organic compounds in water. A strong chemical oxidant is used along with acid and heat to oxidize the organics. It measures the amount of oxidant consumed in the breakdown of the organic matter, which indirectly gives the amount of MTBE in the sample (Droste, 1996). The procedure for the COD test is in Appendix 4. A calibration curve was created in order to read the concentrations of MTBE; her calibration curve is located in Appendix 1. A standard solution of MTBE and water was made for analysis. The objective was to create a calibration curve using our standard solution that matched with Slack's curve. Four standard solutions were used: 0, 50, 175, and 275 mg/L of MTBE in water. When creating calibration curves, one or two concentrations are not enough information, and more than four concentrations will require unnecessary work to obtain the same information that only four concentration points would show. The calculations for this can be seen in Appendix 3.

The calculated volumes of MTBE were added to a 42 mL vial and then filled with E-pure water to dilute the MTBE and achieve the specified stock concentration. The vials were placed in a rotisserie to be mixed for 24 hours. Afterwards, the vials were removed for COD analysis.

Time Trials

The time trials were conducted to determine how long it took samples to reach equilibrium, where the zeolite reaches saturation. The chosen concentration was 275 mg/L of MTBE, because it was towards the top of the COD equilibrium curve so that when the samples were analyzed the results would appear on the COD equilibrium curve. The time trials tested the overall adsorption of four different samples: powder calcined ZSM-5, powder uncalcined ZSM-5, an old sample, and a new sample. The process for preparing the vials was the same as during the COD equilibrium curve; however in this experiment zeolites were added to the vials. The weight of each pellet used for this experiment was recorded using a bench scale.

The time intervals used for this experiment were 0, 6, 12, 24, 48 and 72 hours. The intervals of 12 and 72 hours were only used for the new sample since more detail was desired for this sample and the other samples were used for comparative reasons. To be more efficient with the experiments, the zeolite and solutions were combined prior to being put in the rotisserie. The samples were placed in the rotisserie in the order of 72, 48, 24, and then 6 hours was the last vial to put in the rotisserie. This was done so that after 72 hours, all the vials were ready for COD analysis.

To determine the concentration of the amount adsorbed in each sample Equation 1 was used.

Equation 1: Amount of MTBE adsorbed

$$q_e(\frac{mg}{g}) = \frac{(C_{io} - C_e) * V}{m_{zeolite}}$$

In Equation 1, C_{io} is the initial concentration of the sample, C_e is the concentration of the sample after adsorption, $m_{zeolite}$ is the mass of the zeolite, and V is the volume of the vial (0.042 L). The q_e values and time intervals were graphed and are shown in the Results section. In order to determine the weight should be used for the granular samples, old pellets were weighed and the average was taken. The weight used for the granular samples was ≈0.01907g. Raw data can be found in Appendix 2.

Adsorption Isotherm

The adsorption isotherm was used to determine over a range of concentrations how much the ZSM-5 pellet could adsorb at equilibrium. The range of concentrations was 25-300 mg/L of MTBE in water. Calculations were done to determine how much stock sample was used for each concentration, which can be seen in Appendix 2. The calculated amount of MTBE was added to a 42 mL vial and filled with E-pure water. A new ZSM-5 pellet was added after being weighed and recorded. A total of 12 samples were placed into the rotisserie to mix for 72 hours. Afterwards, the samples were taken out for COD analysis. Equation 1 was used to determine the amount of MTBE that was adsorbed. The q_e values and time intervals were graphed and are shown in the Results section.

Results & Discussion

Analysis of Samples

Powder X-Ray Defraction

The run 4 old sample was analyzed by powder diffraction in order to determine whether or not the sample had been calcined and, what phase the sample was in. The results can be seen below in Figure 4.

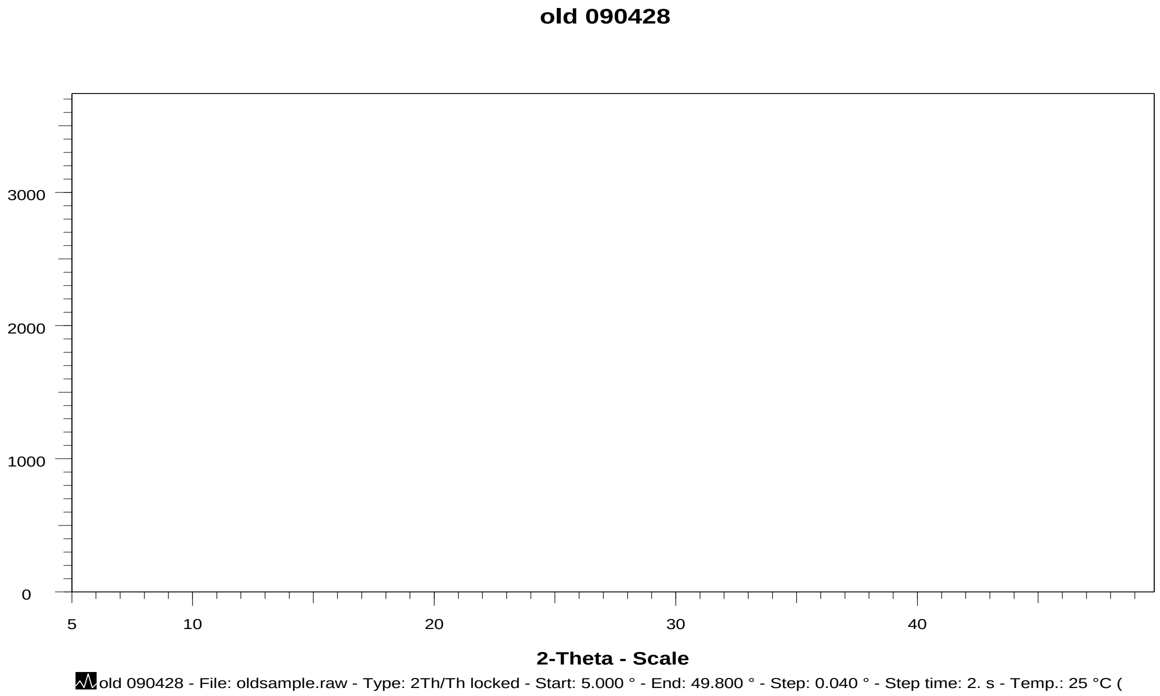


Figure 4: XRD Results of Old Sample

To verify whether the results showed a calcined or uncalcined ZSM-5, a reference was used from which can be seen in Appendix 5. In comparing the results, this test verified that all samples from run 4 of the old sample after day 8 were calcined ZSM-5.

The new sample was also tested using the powder diffraction by Brad Carleen. The results he provided can be seen in Figure 5.

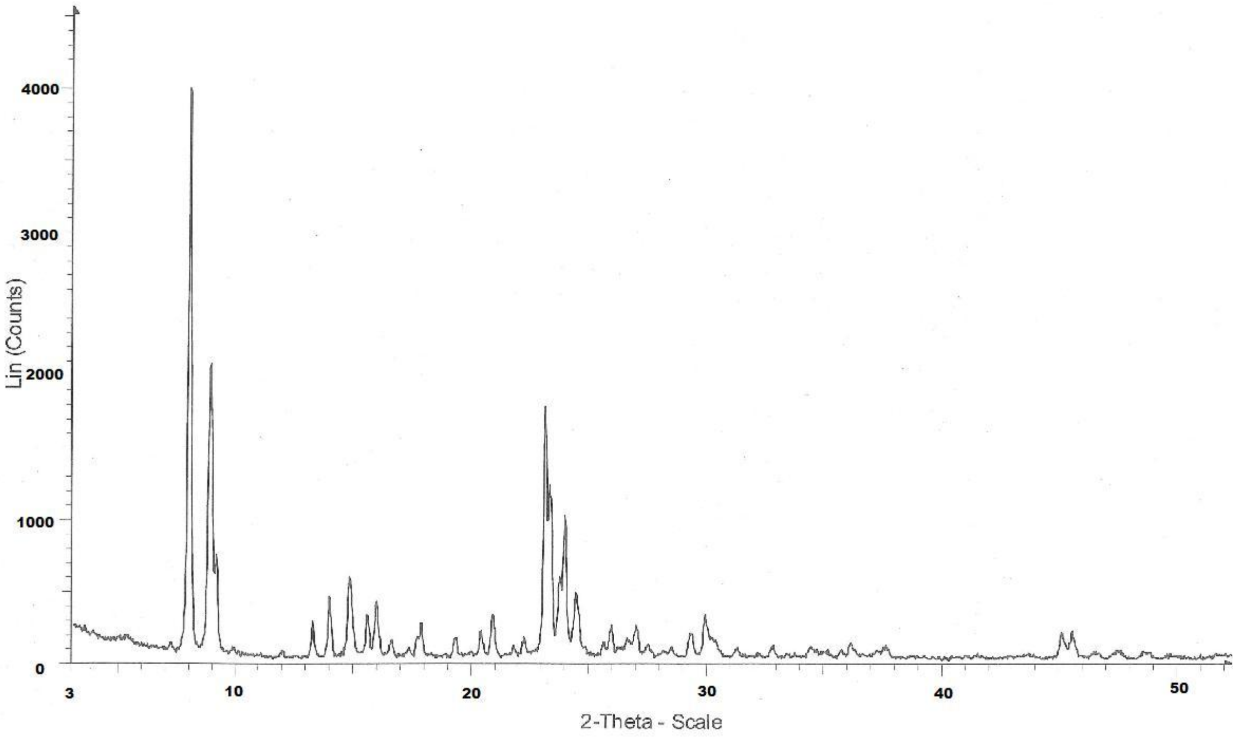


Figure 5: XRD Patterns for Calcined Zeolite

Comparing the patterns shown in Figure 5 to the Figure 21 in Appendix 5, a theoretical ZSM-5 XRD, showed that the samples had similar graphs and verified that the new sample had been calcined.

Scanning Electron Microscope (SEM)

The use of the scanning electron microscope (SEM) was to show if the crystallization of the samples made were uniform during synthesis. Figure 6 shows the old sample that was photographed in the SEM. This piece was broken when it was found so it cannot be proven whether it was broken after or during synthesis.

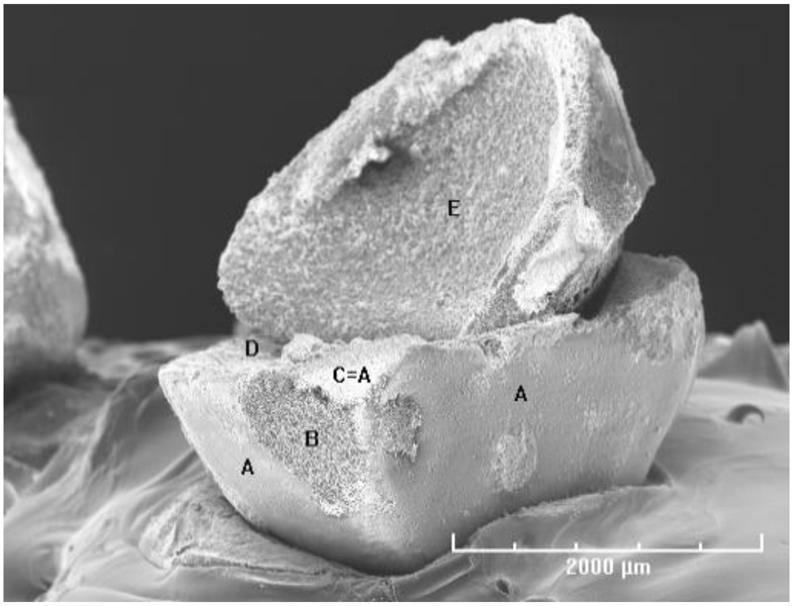


Figure 6: SEM – Full View of Old Sample

Figure 6 shows that there are a few different surfaces that were viewed. The surfaces labeled A and C were the outer surfaces of the synthesized silicon bead. The surface B was where it appeared to be a broken area of the sphere with rough edges. Surfaces D and E were areas that were part of the broken piece and were located towards the center of the sphere. Figure 7 shows a zoomed-in image of what surfaces A and C.

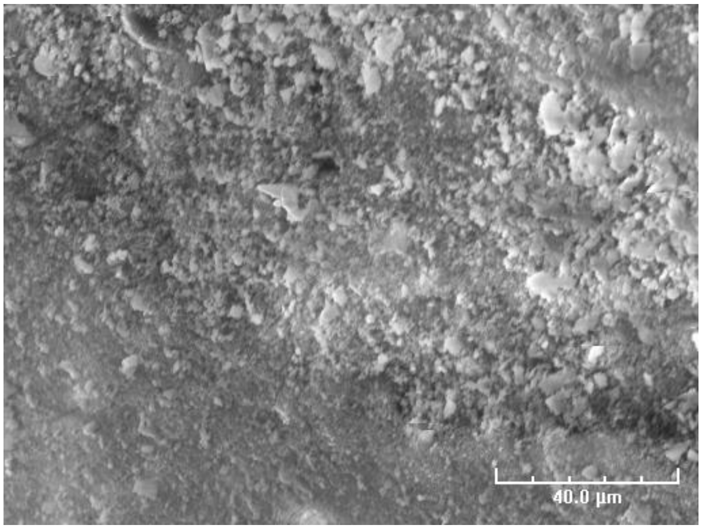


Figure 7: SEM – Surfaces A and C

Figure 7 shows that the surface has no crystallization occurring at the outer surfaces and appears to be very smooth. Figures 8, 9, and 10 show zoomed-in images of surfaces B, D, and E of the old sample.

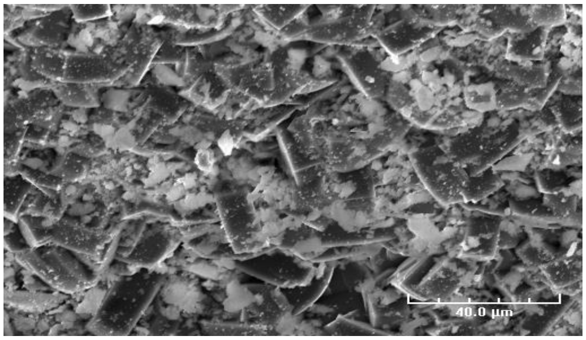


Figure 8: Surface B of Old Sample

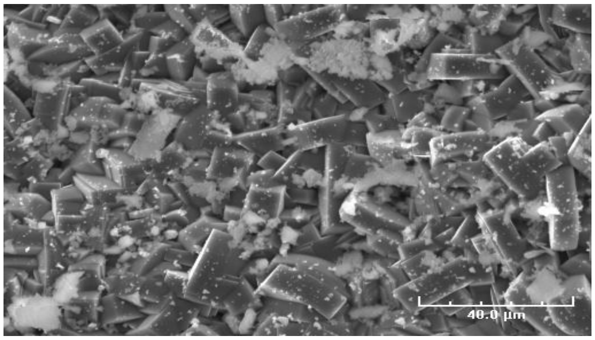


Figure 9: Surface D of Old Sample

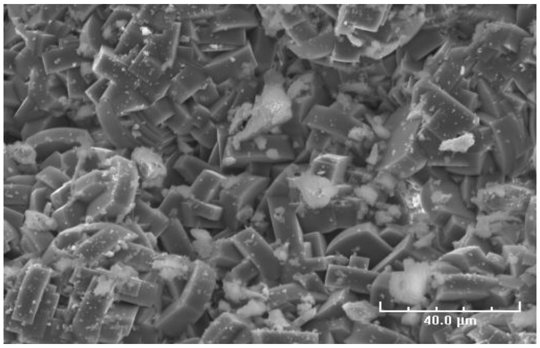


Figure 10: SEM – Surface E of Old Sample

These images clearly show that there has been crystallization on the sample. The crystals have been exposed to the environment as well as being placed in a vial for a long period of time. Therefore, there are a lot of extra matter that appears in the picture that are not crystals and may not have been created during the synthesis. A new sample may or may not have this extra matter and may have given better images of the crystallization. The scale for the crystals is at 40 µm; the crystals appear to have a width of around 5 µm and a length of 25-30 µm. Since it was unclear as to whether or not the old sample was broken during synthesis or after synthesis, another sample was analyzed using the SEM. A pellet from the new samples of ZSM-5 was taken and cut with a razor blade. Figure 11 shows a full view of the new sample that was photographed in the SEM.

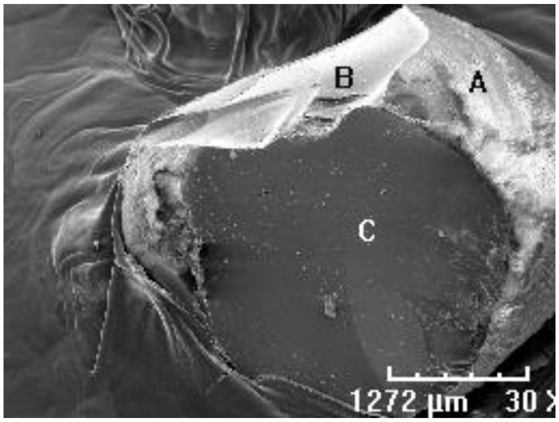


Figure 11: Full View of New Sample

Figure 11 shows that the three locations that were photographed. Surface A is the outer surface. Surfaces B and C are both surfaces that were cut before being placed in the SEM. Figure 12 shows the surface of location A.

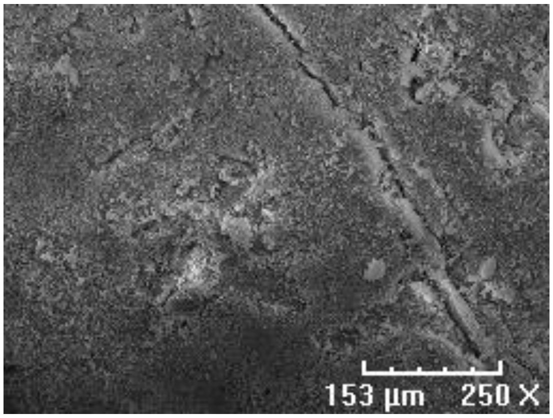


Figure 12: SEM – Surface A of New Sample

Two observations can be made from Figure 12. First it is clear that the outer surface is very smooth. Second, a crack on the outer surface was noticed. This could mean that during the synthesis, there was a coating on the outer surface of the silicon bead that cracked when the depth of the coating reached its maximum. Figures 13 and 14 show the surfaces of B and C where the pellet was cut.

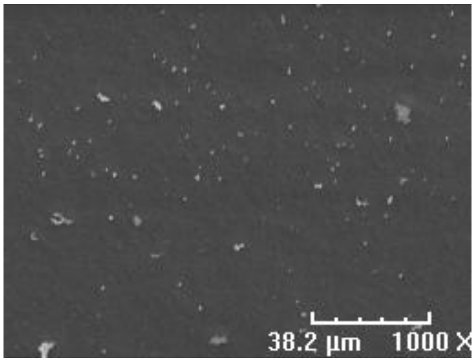


Figure 13: SEM –Surface B of New Sample

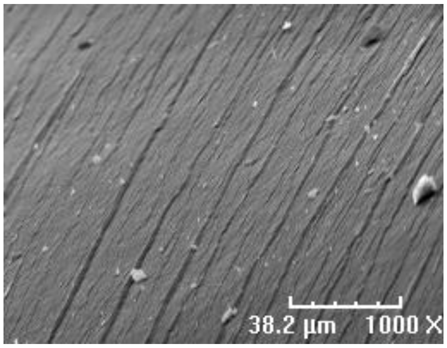


Figure 14: SEM – Surface C of New Sample

Figures 13 and 14 show that there was no crystallization inside a completely spherical pellet. Surface B was a piece that had cracked off when using the razor blade to cut the bead, and surface C was the surface after the razor blade thoroughly cut through the pellet.

Overall, a few observations can be made from the images that were taken off the old sample and the new sample. The old sample was clearly a piece that was broken during synthesis since the new sample that was a complete sphere had no crystallization at all. One of the explanations for this could be that the silicon beads had such smooth surfaces that there was nowhere for the crystals to grow. The images of the new sample showed that the surface had just started to get rough and develop cracks. If the synthesis was allowed a longer period of time then there may have been some crystallization on the surface. Additionally, the old sample showed that a broken piece of zeolite or a piece that was broken during synthesis created a rough surface that was perfect for crystallization. Further research would be required to fully answer these questions. The analysis for this part of the report focused on crystallization, and the samples that were used in later experiments for the project focused on whole pellets that did not have crystallization on them. The pellets that were used that were not crystalline might not be as efficient as pellets that had crystallization. This could be researched with more experiments.

Thermal Gravimetric Analysis (TGA)

Figure 15 shows the results for the TGA testing that were used to determine whether or not the samples were calcined or uncalcined.

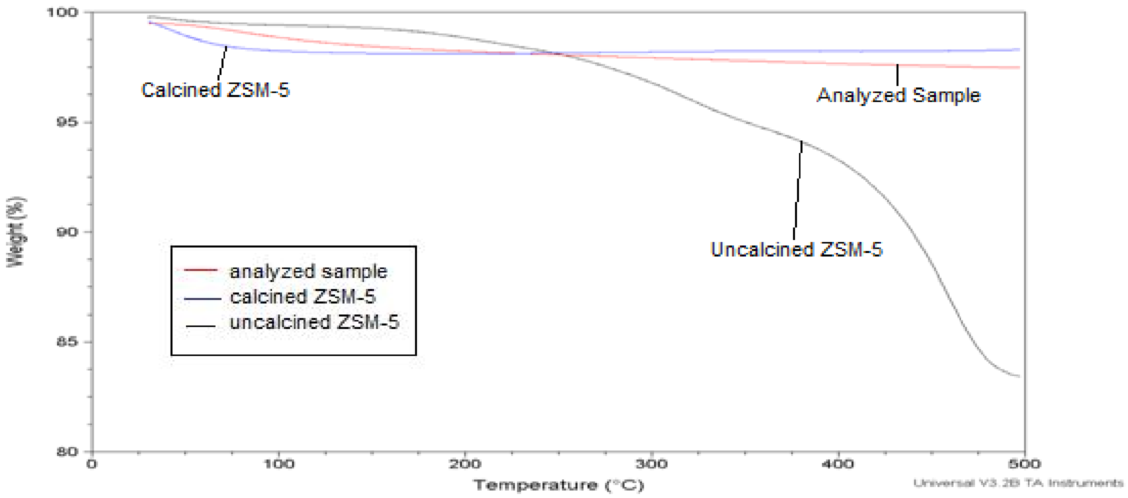


Figure 15: TGA Results of Old ZSM-5 Pellet

The red line, or the line in the middle at 100ºC, is the sample that was being analyzed, which was the run 4 day 8 vial from the old samples. The blue line, or the lowest line at 100ºC, was the new sample that was experimented with, and the black line, or the top line at 100ºC, was a sample of uncalcined ZSM-5. As Figure 15 shows, the uncalcined ZSM-5 had about a 15% weight drop where the organic template had been burned off, verifying that the sample was uncalcined. The old sample showed no weight decrease in the 250-500 ºC temperature range. Using these as controls for a calcined and uncalcined sample, it was concluded that the ZSM-5 sample to be used for the experiments was indeed calcined.

Experimental Results

COD Calibration Curve

In order to interpret the data from our experiments, a calibration curve was used for chemical oxygen demand. Figure 16 shows a calibration curve of various concentrations that were used for our calibration curve as well as a curve from Michele Slack's report. (Slack, 2004).

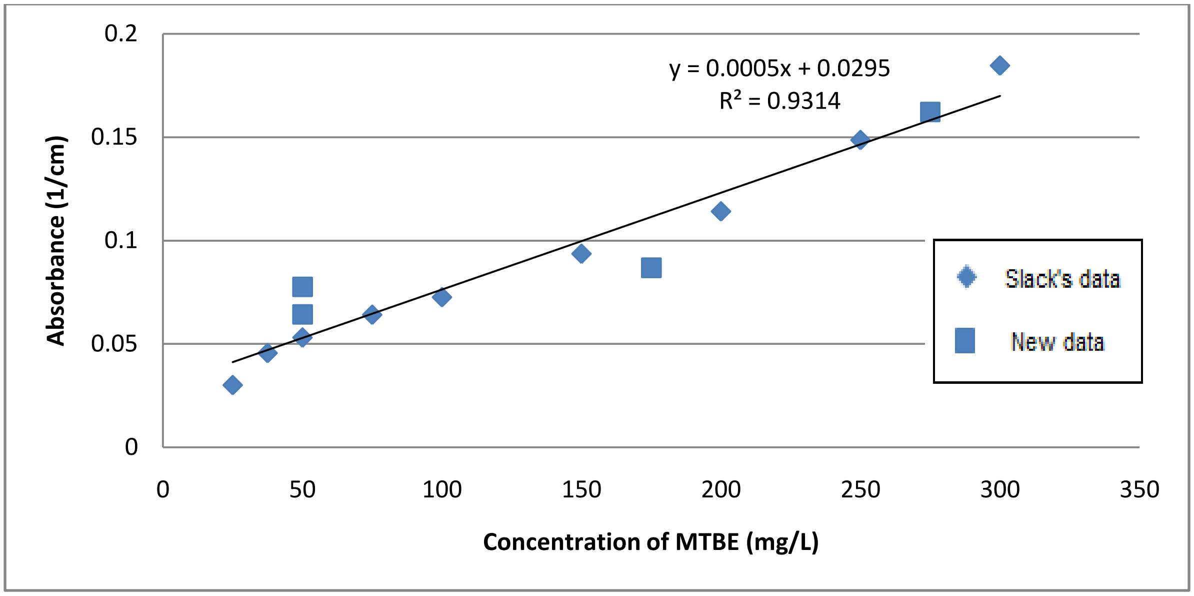


Figure 16: COD Calibration Curve with Combined Data Points

There were three specific concentrations that were tested for this project to verify that Slack's curve was accurate to use for following experiments, which can be seen along with the old results in Appendix 1 and 2. The results show that the data points retrieved in this experiment fell on the same line as the Slack's COD calibration curve. This concluded that the COD calibration curve that was previously made by Michele Slack could be used for analyzing the data in the following experiments.

Time Trial

Figure 17 shows the results of the time trials with the four samples of ZSM-5: old sample, new sample, uncalcined powder, and calcined powder.

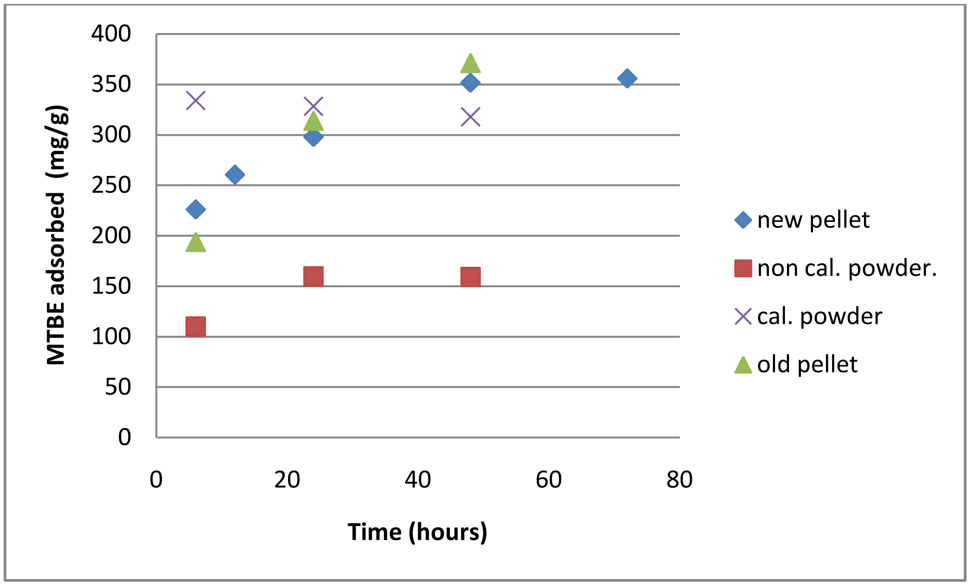


Figure 17: Time Trials for ZSM-5 Samples

Figure 17 compares the efficiency of the different samples of ZSM-5. The y-axis shows the q_e (amount adsorbed in mg/g) from the calculations done with Equation 1. The uncalcined powdered ZSM-5 adsorded significantly less then the other samples. This occured because the uncalcined samples had an organic template occupying pore volumne and could not adsorb as much MTBE. Additionally, it reached equilibrium between 24-48 hours. The calcined powdered ZSM-5 was able to adsorb more then both the ZSM-5 pellets initially, but it had reached equlibrium almost instantly. The mass transfer process is quite rapid in powders compared to the aggregates. This may or may not be efficient, as that would result in zeolites that would have to be regenerated frequently and a comparison of cost for regeneration would have to be done to make conclusions. The new and old ZSM-5 pellets follow roughly the same trend and reach equlibrium between 48-72 hours. For experiemntal purposes, 72 hours was considered the time for saturation. A table with all of the details to the time trials can be seen in Appendix 2.

Adsorption Isotherm

Figure 18 shows the equlibrium curve, where a range of concentrations were used with a single new ZSM-5 pellet using a 72 hour equilibirum time.

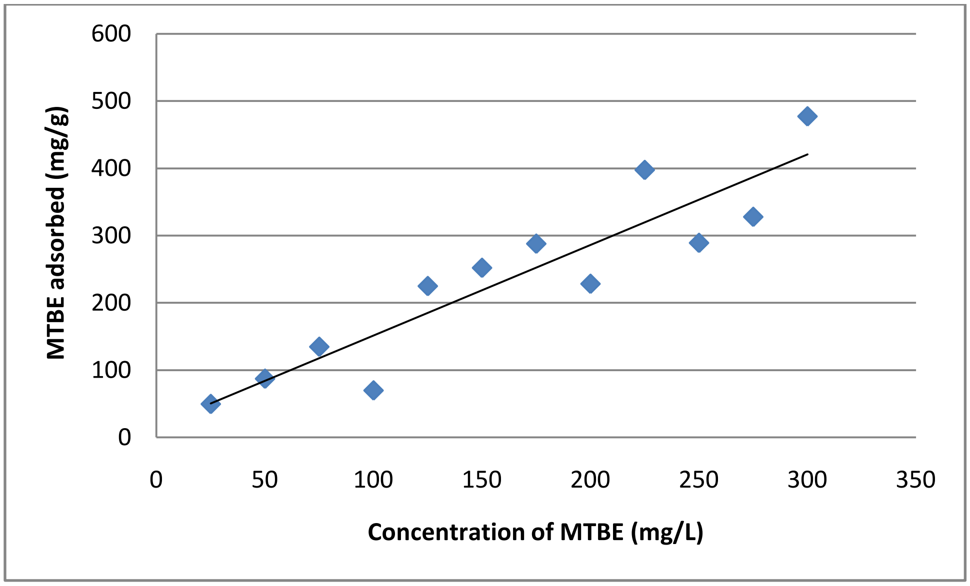


Figure 18: Adsorption Isotherm of MTBE After 72 hours

Figure 18 gives the concentration between 0 and 350 mg/L of MTBE and how much MTBE can be adsorbed when the zeolites reach equilibrium. The first six data points had ending concentrations so low that they were not on the COD calibration curve that was used. The equation of the line was extended to determine the ending concentrations of MTBE. The calculations can be seen in Appendix 2 and 3. The adsorption isotherm in Figure 18 was comparable to prior data done on MTBE adsorption using ZSM-5 in Figure 19.

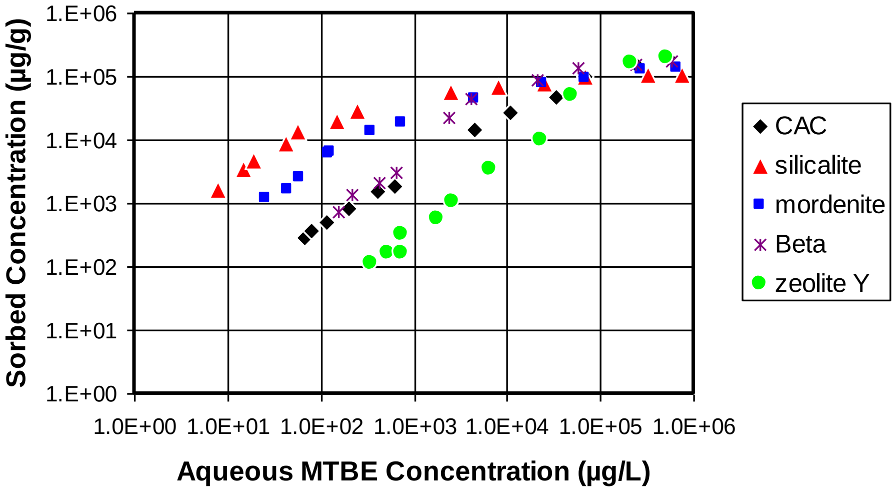


Figure 19: Ayşe Erdem-Senatalar Adsorption Isotherm

(Bergendahl, Erdem-Şenatalar, Giaya, & Thompson, 2004)

The comparison shows that the granular ZSM-5 that was used for the experiemnts in this report were more efficent at higher concentrations and were very similar at lower concentrations. The data between the two the units in Figure 19 had to be divided by 1000 to be in the same units as Figure 18. From Figure 18, the highest concentration of MTBE was 300 mg/L and was able to adsorb about 490 mg/g. Using Figure 19 for the same concentration the zeolite was able to adsorb about 100 mg/g. Additionally, looking at the other concentrations from 50-300 mg/L of MTBE the ZSM-5 sample used in this report was able to adsorb more then Ayşe's from Figure 19. From Figure 18, the lowest concentration of MTBE was about 25 mg/L and was able to adsorb about 50 mg/g. Using the same concentration from Figure 19 the zeolite was able to adsorb about 90 mg/g. There was no data for concentrations lower than 25 mg/L but by extending the equation of the line in Figure 18 it compares to the lower concentrations seen in Figure 19. This shows that at the lower concentrations the ZSM-5 used in this report did not adsorb as much MTBE as the ZSM-5 shown from Ayşe's data in Figure 19.

Design of Treatment System

The contamination scenario at Pascoag, Rhode Island was used as the basis for the design aspect of this project. Although the contamination at Pascoag is currently being treated, the plume is so large that much of the water supply is still contaminated. Current contamination levels of MTBE were found to reach a maximum of 15,000 µg/L in the bedrock aquifer (Allen & Boving, 2006). For comparison, the Rhode Island drinking limit for MTBE is 40µg/L.

In 2004, the Rhode Island Department of Environmental Management installed a treatment system that includes submersible pumps, air strippers, liquid and vapor phase granular activated carbon and is designed to handle a flow of 100 gallons per minute (Rhode Island Department of Environmental Management, 2005). This design parameter was used as the pumping rate through the system. A total of three columns were used in series, where two columns would be operating and would be offline for regeneration or maintenance. Figure 19 shows a piping schematic of this system.

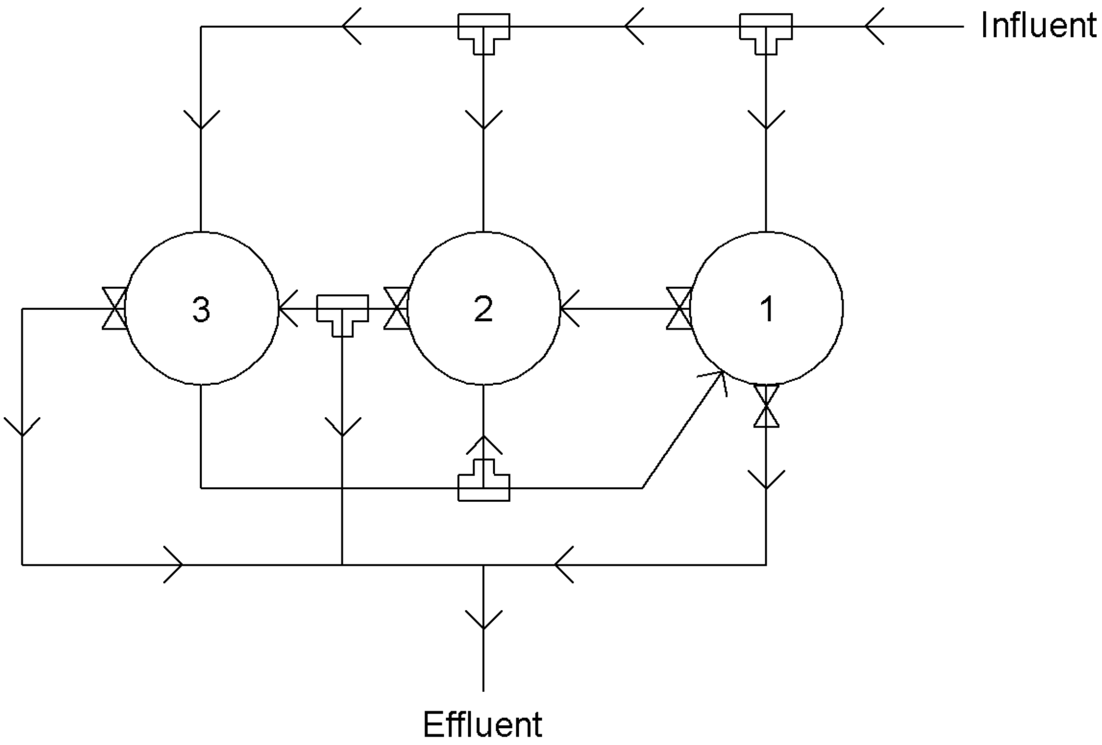


Figure 20: Design Schematic

This system was designed so that the effluent from a column would be able to feed into any other column in the case that one is offline. The influent contaminated groundwater is pumped in at a rate of 100 gallons per minute with a concentration of 15 ppm. Using the adsorption isotherm developed in the methodology, the adsorbed amount (in mg MTBE per g of zeolite) was found using Equation 2, where y is the q_e (mg/g adsorbed) and x is the effluent concentration in mg/L.

Equation 2: Equation from adsorption isotherm

$$y = 1.3376x + 18.088$$

Because the adsorption isotherm represents equilibrium, the effluent concentration will equal the influent concentration when the column is fully saturated. Knowing this, the adsorbed amount at equilibrium was found to be 38.06 mg/g.

The volume of one column was found to be 1200 gallons in order to hold 1000 gallons of zeolites. The volume of zeolites was calculated by using the flow of 100 gallons per minute and an empty bed contact time of 10 minutes. This contact time was used to increase the volume in the reactor and maintain a feasible runtime before regeneration was necessary. A height of approximately 14 feet and a diameter of 11 feet were determined using Equation 3.

Equation 3: Equation for Diameter

$$\boldsymbol{D(ft) = \sqrt{\frac{4 * V_{zeolites}(ft^3)}{\pi * h(ft)}}}$$

The bulk density of the zeolites was measured to be 971 kg/m^3. Using Equation 4, the volume of contaminated water that can be treated before regeneration was found to be 9,340,636 L.

Equation 4: Bed Life Design Equation

$$q_e(\frac{g}{g}) * V_{zeolites}\ (L) * \rho_{zeolites}\ (\frac{kg}{m^3}) = C_0(\frac{mg}{L}) * V_{fluid}\ (L)$$

In Equation 4, q_e is the amount adsorbed in units of g/g. Using the calculated volume of treated contaminated water and the flow rate, the time before the column is completely saturated was determined to be approximately 17 days. It would be recommended to hire a worker to measure the effluent concentrations of the reactors every 2 days. When the effluent concentration reaches the same level as the influent concentration, the column has reached saturation and is to be turned offline for regeneration. The gate valve will be turned off so that the influent feed will bypass this reactor.

The entire system has a velocity of 5 feet per second, with a 3 inch pipe. The total amount of piping was estimated to be about 220 feet. Previous system designs involving 3 columns in series estimated the usage of about 200 feet of piping (Hart, 2003). The amount of piping would cover influent and effluent feed, and all of the piping that connects the columns as shown in the design schematic, Figure 19. A cost analysis of the system was completed and compiled in Table 2.

Table 2: Cost Analysis of System Design

Material	Cost	Quantity	Total Cost	Brand
Centrifugal Pump	$2,777	1	$2,777	Warren-Rupp
CPVC Pipe	$3.50	220	$770.00	
Gate Valve	$268	12	$3,216	Nibco
3-Way Valve	$125	3	$375	Kohler
*Reaction Column	$20,000	3	$60,000	Tigg Corp.
*Zeolites	$4,860	3	$14,580	
			Total:	$81,718

*These prices are estimates

In order to determine the specifications of the pump, the total head loss of the pump was necessary. The head loss in the column was calculated using Equation 5:

Equation 5: Head Loss to Pump

$$H_P(ft) = \frac{P}{\gamma} = 115\ ft$$

Then, the head in the column due to the filtering media (zeolites) was calculated using the Kozeny Equation, shown in Equation 6 (Droste, 1996).

Equation 6: Kozeny Equation

$$h = \frac{k\mu(1-\varepsilon)^2}{g\rho\varepsilon^2}\left(\frac{A}{V}\right)^2 v$$

The porosity of granular activated carbon (0.70) was used because information on the porosity of granular ZSM-5 was not available (Clements & Haarhoff, 2006). The head loss due to the zeolites was found to be 1.16 x 10^{-4} feet. This value can be taken to be essentially zero. The total head loss to the pump was calculated by summing the head loss from the tank and the head loss from the zeolites and was used as 115 feet.

Using Equation 6, the power required for the pump was calculated assuming 75% efficiency.

Equation 6: Power for Pump

$$Power = \frac{\gamma * Q * H_P}{33{,}000} * 75\% = 2.2\ HP$$

With the given design parameters, the Warren-Rupp centrifugal pump was chosen for this system.

Although the amount of piping necessary may fluctuate, the overall price of piping is miniscule compared to the cost of other items. Gate valves were used to so that the feed water could bypass columns in regeneration, and 3-way valves were used at 3-way intersections shown in the schematic. Zeolite ZSM-5 was found to sell at approximately $2.3 per pound. Using the measured bulk density of the zeolites, one column would require about 2140 pounds of zeolites. This sums to approximately $5,000 of zeolites for one column. The price range for a 1200 gallon adsorber was quoted as $10,000 to $20,000 by a representative from TIGG Corporation. The higher price was taken for purposes of cost estimating. This price was multiplied by three because the system requires 3 columns in series. Excluding the cost of labor and maintenance, the total cost to install this treatment system was estimated to be roughly $82,000.

Design Recommendations and Conclusions

Zeolite ZSM-5 could be an effective method of treating MTBE from water. The cost is relatively low to design a system. One column would have to be regenerated every 17 days, thus it is recommended to check the effluent concentrations every 2 days. The granular form of ZSM-5 would be more effective in a reaction column than the powdered form, as the powder zeolite would be impractical. ZSM-5 could potentially be more efficient and cost-effective than granular activated carbon. Although activated carbon is cheaper by the pound than zeolites, when granular activated carbon is regenerated it loses about 5-15% of its carbon mass per cycle (U.S. Army Corp of Engineers, 2001). Therefore, activated carbon can only be used so many times before it loses its efficiency.

In order to more quantitatively compare the effectiveness of ZSM-5 and granular activated carbon on MTBE, further research is recommended on these two processes including research and cost analysis of regeneration processes. Further research may show that ZSM-5 is a more cost effective method because it does not lose efficiency as much as activated carbon. It is also noted that further research should be done using column experiments. The tests that were used in this report involved batch experiments. Analysis of adsorption tests using bench-scale column reactors may prove useful in comparing the adsorption effectiveness of ZSM-5 and granular activated carbon in fixed bed treatment systems.

References

Environmental Protection Agency. (n.d.). *Methyl Tertiary Butyl Ether*. Retrieved 23 September, 2008, from http://www.epa.gov/mtbe/faq.htm

Allen, J., & Boving, T. (2006). *MTBE Drinking Water Contamination in Pascoag, RI: A Tracer Test for Investigating the Fate and Transport of Contaminants in a Fracture Rock Aquifer.* Kingston.

Anderson, M. A. (2000). Removal of MTBE and other Organic Contaminants From Water by Sorption to High Silica Zeolites. *Environmental Science & Technology* , 725-727.

Bergendahl, J., Erdem-Şenatalar, A., Giaya, A., & Thompson, R. (2004). *Adorption of MTBE on Hydrophobic Molecular Sieves.* Environmental Engineering Science.

British Zeolite Association. (n.d.). *What Are Zeolites?* Retrieved October 15, 2008, from British Zeolite Association: www.bza.org/zeolites.html

Butland, T. D., Abu-Lail, L., & Thompson, R. (2008). *Removal of Tertiary Butyl Alcohol from Water by Adsorption on Zeolites.*

California Enivronmental Protection Agency. (n.d.). *2000-10-03 Cleaner-Burning Gasoline Without MTBE*. Retrieved October 15, 2008, from California Air Resources Board: http://www.arb.ca.gov/fuels/gasoline/cbgmtbe.htm

California EPA. (n.d.). *California Air Resources Board*. Retrieved October 15, 2008, from California Environmental Protection Agency: http://www.arb.ca.gov/fuels/gasoline/cbgmtbe.htm

Cejka, J., Bekkum, H. V., & Schuth, F. (2007). Introduction to Zeolite Molecular Sieves. *Elsevier* .

Chippindale, A. M., Darlow, D. P., Powell, A. V., & Vaquiero, P. (2004). Solvothermal Synthesis of Novel Antimony Sulphides Containing [Sb4S7]2− Units. *Solid State Ionics* , 601-605.

Chitnisa, G., Degnan, T., & Schipper, P. (2000). *History of ZSM-5 fluid catalytic cracking additive development at Mobil.* Elsevier Science.

Clements, M., & Haarhoff, J. (2006). *Practical experiences with granular activated carbon (GAC) at the Rietvlei Water Treatment Plant.*

Droste, R. L. (1996). *Theory and Practice of Water and Wastewater Treatment.* John Wiley & Sons, Inc.

Energy Information Administration. (n.d.). *Satus and Impact of State MTBE Bans*. Retrieved October 16, 2008, from http://www.eia.doe.gov/oiaf/servicerpt/mtbeban/table1.html

Hart, C. L. (2003). *MTBE Removal with Zero-Valent Iron and Hydrogen Peroxide.* Worcester.

ISCID. (n.d.). *Hydrophobic*. Retrieved October 14, 2008, from International Society of Complexity, Information, and Design: http://www.iscid.org/encyclopedia/Hydrophobic

Meissner, M., & Voll, A. (n.d.). *What is MTBE?* Retrieved October 15, 2008, from MTBE Litigation Info: http://www.mtbelitigationinfo.com/external/?fuseaction=external.docview&cid=942&documentID=72925

Ohio State University. (n.d.). Retrieved December 2008, from Department of Chemistry: http://www.chemistry.ohio-state.edu/~woodward/ch754/zeoliteA.gif

Rhode Island Department of Environmental Management. (2005). *Pascoag Water District Fact Sheet.* Providence.

SIGMA. (n.d.). *Weekly Report*. Retrieved October 15, 2008, from Society of Independent Gasoline Marketers of America: http://www.sigma.org/wr/reports/05/050523.html

Slack, M. L. (2004). *Chemical Oxidation of Water-Borne Contaminants in a Membrane-Isolated Domain.* Worcester.

The Zeolite Group. (n.d.). Retrieved April 2009, from Mineral Gallery: http://www.galleries.com/minerals/Silicate/ZEOLITES.htm

U.S. Army Corp of Engineers. (2001). *Engineering and Design Adsorption Design Guide.*

U.S. Geological Survey. (n.d.). *The Atmosphere - A Potential Source of MTBE to Ground Water*. Retrieved October 3, 2008, from United States Geological Survey: http://toxics.usgs.gov/highlights/mtbe.html

Whittingham, S. (n.d.). *Synthesis of Zeolite*. Retrieved 2009, from Binghamton University: http://materials.binghamton.edu/labs/zeolite/zeolite.html

Appendix

Appendix 1: Figures

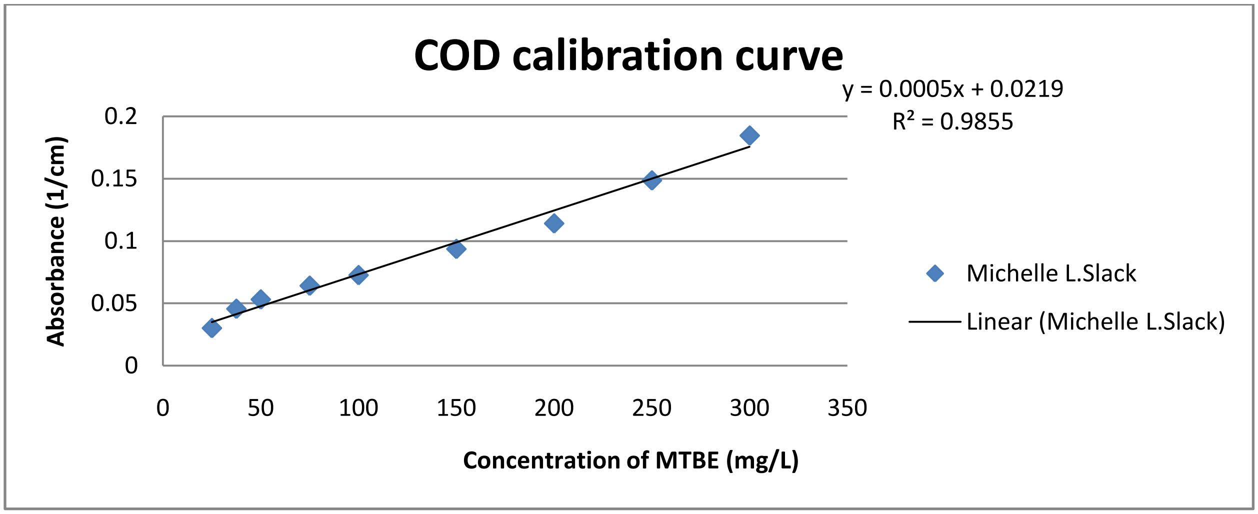


Figure 21: Michelle Slack's COD calibration curve

(Slack, 2004)

Appendix 2: Tables

Table 3: COD All Calibration Curve Data

MTBE concentration (mg/L)	M. Slack Absorbance	New Sample Absorbance
300	0.1845	
275		0.1622
250	0.1485	
200	0.114	
175		0.0868
150	0.0935	
100	0.0725	
75	0.064	
50	0.053	0.0643
37.5	0.0455	
25	0.03	

Table 4: Weights of Pellets for Time Trial

Old Sample	Weight(g)
1	0.0119
2	0.0308
3	0.0165
4	0.0313
5	0.0106
6	0.0133
Average:	0.01907

Table 5: Raw Data from Time Trial Calculations

Time (hours)	Sample	Abs. (1/cm)	End Conc. (mg/L)	Weight of Zeolite (g)	Conc. Difference (mg/L)	q(mg/g)
72	New	0.0649	76	0.0235	199	355.6596
48	Old	0.0942	138	0.0155	137	371.2258
48	Powdered Uncalcined	0.1246	203	0.019	72	159.1579
48	Powdered Calcined	0.0898	129	0.0193	146	317.7202
48	New	0.1008	152	0.0147	123	351.4286
24	Old	0.0848	118	0.021	157	314
24	New	0.0957	141	0.0189	134	297.7778
24	Powdered Uncalcined	0.1239	202	0.0192	73	159.6875
24	Powdered Calcined	0.0881	125	0.0192	150	328.125
12	New	0.0819	112	0.0263	163	260.3042
6	Old	0.0903	130	0.0314	145	193.949
6	New	0.0812	111	0.0305	164	225.8361
6	Powdered Uncalcined	0.1349	225	0.0191	50	109.9476
6	Powdered Calcined	0.0858	120	0.0195	155	333.8462

Table 6: Summary of Calculations for Amounts Used in Solutions for the Adsorption Isotherm Samples

New Sample	Conc. MTBE (mg/L)	From Stock (μL)	Rounded (μL)	Other stocks (μL)	Rounded (μL)
1	300	2518.8	2520		
2	275	2308.9	2310		
3	250	2099.0	2100		
4	225	1889.1	1890		
5	200	1679.2	1680		
6	175	1469.3	1470		
7	150	1259.4	1260		
8	125	1049.5	1050		
9	100			42042.04204	42040
10	75			31531.53153	31530
11	50			21021.02102	21020
12	25			10510.51051	10510

Table 7: Raw Data from Adsorption Isotherm Calculations

New Sample	Abs. (1/cm)	Start Conc. (mg/L)	End Conc. (mg/L)	Weight (g)	Conc. Difference (mg/L)	q (mg/g)
1	0.0684	300	83	0.0191	217	477.1728
2	0.0649	275	76	0.0255	199	327.7647
3	0.0616	250	69	0.0263	181	289.0494
4	0.0522	225	49	0.0186	176	397.4194
5	0.0441	200	31	0.0311	169	228.2315
6	0.043	175	28	0.0245	147	252
7	0.0365	150	15	0.0197	135	287.8173
8	0.0316	125	4	0.0226	121	224.8673
9	0.0578	100	60	0.0241	40	69.7095
10	0.0282	75	0	0.0234	75	134.6154
11	0.025	50	0	0.0241	50	87.1369
12	0.0186	25	0	0.0212	25	49.5283

Appendix 3: Calculations for Solutions

For 5000 mg/L of MTBE:

$$\frac{5000\ mg}{L} * \frac{1g}{1000\ mg} * \frac{1mL}{0.74\ g} = \frac{6.76mL}{L}$$

In the solution we put 6.76 mL of 100% MTBE and added E-pure water to an Erlenmeyer flask to achieve a total volume of 1 L. This stock solution was a diluted solution that would be used for the experiments.

Calculations for concentrations of **50,175, and 275 mg/L of MTBE**

$$\frac{175\ mg}{L\ MTBE} * \frac{1g}{1000mg} * \frac{1mL}{0.74g} = \frac{0.236\ mL}{L\ MTBE} * 0.042\ L = 0.00993mL$$

$$X = 0.00993mL * \frac{L}{6.76mL}$$

$$X = 0.001469L = 1469\mu L$$

Rounded to 1470 μL

$$\frac{275mg}{L\ MTBE} * \frac{1g}{1000mg} * \frac{1mL}{0.74g} = \frac{0.372\ mL}{L\ MTBE} * 0.042\ L = 0.0156mL$$

$$X = 0.0156mL * \frac{L}{6.76mL}$$

$$X = 0.002307L = 2307\ \mu L$$

Rounded to 2310 μL

For solutions of 100 and less, specific calculations need to be done as to make sure there was enough MTBE to be traced. The calculations were for double the amount of MTBE for half the volume.

For **50 ppm in a 42 mL vial,** a concentration was **100 ppm in 21mL** was used.

The stock solution was calculated by:

$$\frac{100mg}{L} * \frac{1g}{1000mg} * \frac{1mL}{0.74g} = \frac{0.135mL}{L}$$

$$\frac{100\ mg}{L\ MTBE} * \frac{1g}{1000mg} * \frac{1mL}{0.74g} = \frac{0.135\ mL}{L\ MTBE} * 0.021\ L = 0.002838mL$$

$$X = 0.002838mL * \frac{L}{0.135mL}$$

$$X = 0.021021L = 21{,}021\mu L$$

The amounts obtained were the amounts used that were taken from the stock solution for specific concentrations.

Appendix 4: Chemical Oxygen Demand Procedure

For the purposes of this report, COD vials of low range (5-150 mg/L) were used.

1. COD heater block was preheated 20 min before use and set at 150˚ C.
2. Label COD vials accordingly.
3. 2.5 mL of sample were carefully added down the side of the COD vial.
4. Cap and invert the vial for mixing.
5. Place in COD heater block for 2 hours.
6. Remove vial from heater block and allow cooling to room temperature.
7. Allow any suspended precipitate to settle.
8. For Low Range Reagent (5-150 mg/L)
    a. Set spectrophotometer to 600 nm
    b. Zero the absorbance reading with E-pure water
9. Measure and record the absorbance value for each vial.

Appendix 5: Reference Images

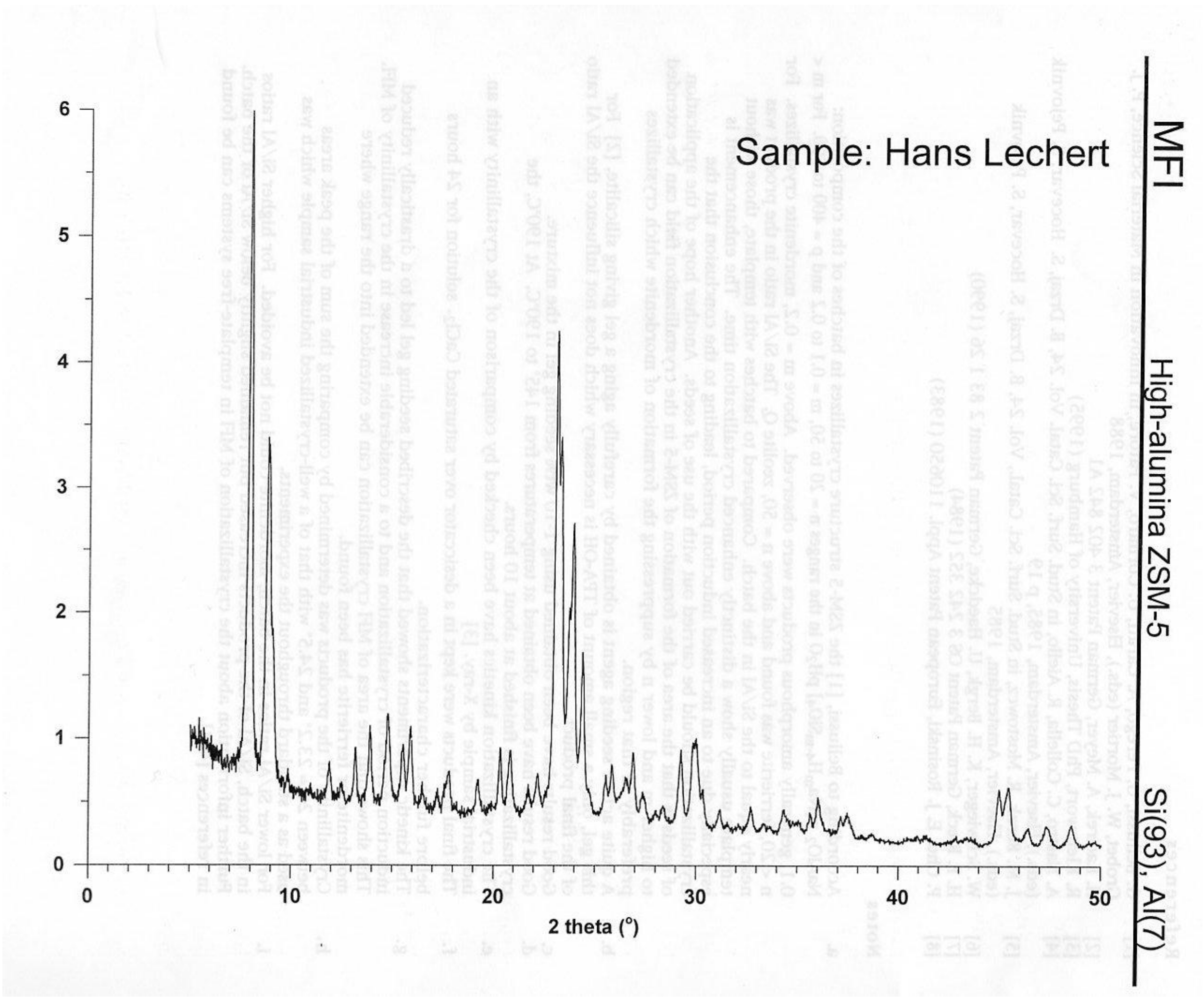


Figure 22: Theoretical XRD for Calcined ZSM-5