WORCESTER POLYTECHNIC INSTITUTE

Molecular Dynamics Simulations of Diffusion through Zeolites

A Major Qualifying Project

Ariel Hyman

Chemical Engineering Class of 2012

Abstract

The purpose of this paper was to investigate the diffusion rates of water contaminants through zeolites. These water contaminants are a threat to the natural environment and are causing a wide range of health concerns in humans and animals. The contaminants impact the negative effects differently, depending on exposure amount, exposure time, amount of different contaminants, etc. Three water contaminants, phenol, benzene, and toluene, were researched and modeled using molecular dynamics. The removal of water contaminants is very important in keeping the environment and population healthy. Zeolites are known to be able to remove water contaminants from water. Silicalite, an all silicon zeolite, was modeled as the zeolite. Simulations were run with each contaminant inside silicalite. Diffusion rates were calculated for the three contaminants, and we found benzene had a diffusion rate of 1.8228 10^{-9} m^2/sec, phenol had a rate of 1.15 10^{-9} m^2/sec and toluene had a rate of 5.9204E-02 10^{-9} m^2/sec.

Table of Contents

List of Figures

List of Tables

1 Background

1.1 Problems of Water Contamination

Studies have shown that there is a dramatic effect that water contamination has on humans, animals, and the environment. Contaminants are released into the environment and transferred in multiple ways. Pollutants come to the natural water resources from the effluents of a variety of chemical industries such as cool refineries, phenol manufacturing, pharmaceuticals, and industries of resin paint, dying, textile wood, petrochemical, pump mills, etc. (Gad and Saad). The natural water resources are where aquatic organisms live and where humans get their drinking water from, including the use of water wells. Since the human population is continuing to grow each year, the demand for Earth's limited supply of freshwater is also growing. Protecting these freshwater resources is one of the most essential environmental issues of the century (Kolpin, Furlong and Meyer).

Pollutants are threatening the natural environment and the health of human and animals. Some of the health issues that are arising are cancer, abnormal physiological processes and reproductive impairment, and the development of antibiotic-resistant bacteria. The National Reconnaissance (Kolpin, Furlong and Meyer) demonstrated the amounts of different water pollutants putting humans and the environment at risk. It was shown that many of these compounds are entering the environment, dispersing, and then persisting to a greater extent than anticipated. Wastewater treatment processes are not taking into consideration the removal of household chemicals, pharmaceuticals, and other consumables as well as biogenic hormones that are released directly into the environment. However, there are a number of compounds that wastewater treatment processes are trying to remove. These organic wastewater contaminants are associated with human, industrial, and agricultural wastewaters and include antibiotics, prescription drugs, nonprescription drugs, steroids, hormones, personal care products, products of oil use and combustion, and other widely used chemicals. The study took samples of multiple streams in the United States; however, it should not be considered representative of all the streams in the United States because some streams at higher risk of contamination were chosen purposely. After sampling, it was found that 80% of the total measured concentration was contributed by detergent metabolites, plasticizers, and steroids. Also, 75% of the sampled streams were found to have more than one organic wastewater contaminant identified. It is also suggested that a study should be done on the toxicity of compounds when they are combined. Select chemical combinations can exhibit additive toxic effects, even when the compounds have different modes of action (Kolpin, Furlong and Meyer).

A 2004 study (Stackelberg, Furlong and Meyer) (put reference here) was performed similarly to the 2002 Reconnaissance, and focused on the potential for organic wastewater contaminants to survive a conventional treatment process. They found the presence of pharmaceutically active compounds such as lipid-regulating drugs, analgesics, antibiotics, antiseptics, hormones, and chemotherapy and beta-blocking heart drugs in wastewaters, streams, and group-water resources. These compounds were found more frequently in streams that receive agricultural, domestic, and/or industrial wastewater effluent. Most of the problems arising from the lack of contaminants treated during treatment processes are due to the large number of compounds present, the inability to determine all of the compounds, and the lack of toxicity information and drinking-water standards for many of these compounds. The occurrence of many of these compounds in drinking water is unregulated and most of them have not even been monitored for in the Nation's source- and potable- water supplies. Seven of the tested compounds were found in each sample of stream water and raw-water supplies. Several other compounds were frequently detected in the samples. This indicates that these compounds are resisting removal through conventional wastewater treatment processes. It was concluded that the inconsistency in concentrations of compounds, such as bisphenol-A, is at least partly due to a reduction in concentration along the treatment process. Other compounds detected frequently in samples of stream water and raw-water supplies, such as phenol, were not detected in samples of the finished treated water. This indicated that concentrations of these compounds were effectively reduced to levels less than detection limits or that the compounds were transformed to other compounds through the conventional wastewater treatment processes. Once results were obtained, the study demonstrated the detection of organic wastewater contaminants such as prescription and nonprescription drugs and their metabolites, fragrances, flame retardants, plasticizers, disinfectants, personal care products, detergent metabolites, products of oil use and combustion, and other used chemicals in streams which flow contains effluent. Some contaminants are surviving treatment processes and are occurring in water supplies. In order for the amount of concern to decrease, regulation of these contaminants in drinking water needs to be further developed (Stackelberg, Furlong and Meyer).

It is important to find the concentrations of contaminants that begin to cause effects on the environment, both through a short-time period and through chronic exposure. It is also very important, as suggested by the two studies mentioned, that mixtures of contaminants are studied as well. There are a limited number of sorbent materials used to extract these contaminants from the water (Edmiston and Underwood). By studying different sorbent materials, we can get a better understanding of what ones can remove these contaminants to make sure there is no harm done. Some of the contaminants we will refer to are methyl tertiary butyl ether, estrone, and bisphenol-A, while the main one we will focus on is phenol. We will then look into methods of removing the contaminants from water, such as air stripping, oxidation, microbial, and most profoundly, adsorption using zeolites.

1.2 Water Contaminants

This section will discuss the three different water contaminants, phenol, toluene, and benzene. It will refer to basic information of each contaminant, attempts to remove the contaminant from water, and the importance of removal from water.

1.2.1 Benzene

Benzene is an organic aromatic chemical compound. It is colorless, highly flammable, sweet smelling, and a liquid at room temperature. It made of 6 carbon atoms in a ring with 1 hydrogen atom attached to each carbon atom. To account for all of the carbon and hydrogen bonds, alternating double carbon bonds must exist. Each carbon-carbon bond is a length of 140 pm. Benzene is produced by catalytic reforming, toluene hydrodealkylation, toluene disproportionation, and stem cracking (Benzene).

Benzene's main use is the production of other chemicals. Over 80% is consumed for producing ethylbenzene, cumene, and cyclohexane. Ethylbenzene is used to make polymers and plasters, cumene is used for resins and adhesives, and cyclohexane is used in the manufacturing of Nylon. Benzene is also used to make rubbers, lubricants, dyes, detergents, drugs, explosives, and pesticides. Another main use of benzene is as a component of gasoline. It is useful because it increases the octane rating and reduces knocking (Benzene).

There are multiple ways to be exposed to benzene. Outdoor air contains levels of benzene from tobacco smoke, gas stations, motor vehicle exhaust, and industrial emissions. Indoor air contains more levels of benzene than outdoor air from the use of glues, paints, furniture wax, and detergents. Benzene can leak from underground storage tanks or from waste sites, which is hazardous to well water. This exposure can lead to health issues. Some immediate signs of exposure to benzene include drowsiness, dizziness, irregular heartbeat, headaches, tremors, unconsciousness, and at very high levels even death. If benzene enters the body through food or drinks, signs may include vomiting, dizziness, convulsions, and irregular heartbeat. Exposure to the skin can damage and irritate tissues. If exposed to benzene to longer periods of time, more severe symptoms will occur. Long term benzene exposure can cause harmful effects on the bone marrow and can causes a decrease in red blood cells, which leads to anemia. Excessive bleeding may occur, damaging the immune system. If woman are exposed, irregular menstrual periods and a decrease in the size of ovaries have been found (Facts About Benzene). Benzene is also known to cause cancer, mainly leukemia and cancers of blood cells. Leukemia has been found to be higher in studies of workers exposed to high levels of benzene from occupations in the chemical industry, the shoemaking industry, and the oil refining industry. Studies have also known links to acute lymphocytic leukemia in children and to chronic lymphocytic leukemia and other blood related cancers in adults (Benzene).

1.2.2 Phenol

Phenol is an organic, white crystalline solid compound. Even though it is pure as a solid, it is mostly used in the liquid form. It dissolves very well in water (Habeck). The molecule is structured with a phenyl bonded to a hydroxyl group. It is mildly acidic (pKa=9.95), but can cause burns. Its main use is to convert into plastics or other materials. It is also required for building polycarbonates, epoxites, Bakelite, nylon, detergents, and a wide variety of drugs, aspirins, herbicides, and pharmaceuticals. Its byproducts are also used in cosmetics like sunscreens, hair dyes, and skin lightening preparations. Phenol can be produced by many routes, including the partial oxidation of cumene, hydrolysis of chlorobenzene, oxidation of benzene with nitrous oxide, and oxidation of toluene. Condensation between phenol and acetone will produce bisphenol-A (refer to Section 1.2.3) (Phenol).

Small releases of phenol are usually removed from the air in less than one day, and from soil in two to five days. However, it stays in water for over nine days. These time estimates will increase if more phenol is released at one given time, or if a continuous amount is released over time. In the environment, phenol is usually found in surface waters, wastewater sites, and surrounding air from when it was released from an industry or from commercial products (Habeck).

Phenol can be exposed through a number of different pathways. Since it is present in many consumer products, it can be exposed by being swallowed, rubbed on, or added to various body parts. Some of these products include ointments, ear and nose drops, cold sore lotions, mouthwashes, toothache drops, throat lozenges, and antiseptic lotions. It has also been found in everyday drinking water, air, automobile exhaust, tobacco smoke, marijuana smoke, and certain foods. Even though all of these methods of exposure can be found harmful, usually they are at low levels and usually over short time periods. If one works in a contaminated area, one may even be exposed simply by inhaling air. There could also be exposure over long periods of time, as well, if one lives near contaminated water sources. Studies have shown that phenol will usually enter and exit the body in urine within 24 hours of exposure (Habeck).

Serious health effects of phenol, as most other harmful chemicals, increase with the level and length of exposure. Small exposures in drinking water can lead to diarrhea and mouth sores (Habeck). If large amounts of phenol are inhaled it can cause lung edema, kidney damage, harmful effects on the central nervous system and heart, dysrhythmia, seizures, and coma. With contact, phenol can damage one’s eyes, skin, and respiratory tract. If contact is repetitive, it can cause dermatitis, or second and third degree burns. There is no evidence stating the phenol can cause cancer to humans (Phenol), but it has caused cancer in mice when exposed to their skin. There is not a lot of information as to what would happen to exposure on human reproduction and on a developing fetus. Tested animals gave birth to offspring with low birth weights and birth defects. Phenol can also be used for positive effects when used for specific medical reasons. It kills germs in mouthwash, relieves pain in sore-throat medications, reduces nerve disorder pain, and removes warts and other skin disorders (Habeck).

A study was done to see how phenol affects physiological parameters of *Oreochromis niloticus,* a large type of fish native to Africa, Egypt, and Israel. Different concentrations of phenol were tested on these fish over a 16 week period. Results showed that phenol is a highly toxic pollutant to fish even under sublethal doses. It induces genotoxic, carcinogenic, immunotoxic, hematological and physiological effects and has a high bioaccumulation rate along the food chain. Cholesterol and total lipids in serum of the fish increased with increasing phenol concentrations. There was a substantial increase of micronuclei production, a decrease in appetite (decreasing the amount of protein intake), and a decrease in growth rate directly proportional to the phenol concentrations and the time of exposure. It was also found that phenol accumulated in the fish muscles, gills, and liver. It was concluded that phenol has caused a lot of harmful effects to fish and to the public's health, and treatment methods should be investigated (Gad and Saad).

1.2.3 Toluene

Toluene is a clear, sweet-smelling, water-insoluble liquid used as an industrial feedstock and as a solvent. The structure of toluene consists of a benzene ring, with an external CH_3 bond. This structure makes it about 25 times more reactive than benzene in most reactions. Naturally, toluene occurs at low levels in crude oil, and is usually formed from the production of gasoline, in an ethylene cracker, or making coke from coal (Toluene).

Toluene is a very useful solvent. It is used in paint thinners, silicone sealants, many chemical reactants, rubber, printing ink, glues, liquors, leather tanners, cements, and disinfectants. One of the most common uses of toluene is as an octane booster in gasoline fuels. Toluene was used because it will eat through the standard rubber fuel lines. This breaks down fuel pumps and causes more problems on the automobile's cylinder. Similar issues are present in alcohol fuels (Toluene).

The abuse of toluene can lead to many health issues. The major exposures are from common household products indoors, printers at the workplace, and automobile emissions. Some immediate effects of being exposed to too much toluene are fatigue, headaches, nausea, and cardiac arrhythmia. If ingestion occurs, symptoms like a swollen liver, congestion and hemorrhage of the lungs, tubular kidney necrosis and even death can occur. If exposed to toluene in a regular basis, more serious health issues arise, such as depression, tremors, impaired speech, hearing, and vision, irritation of the upper respiratory tract, difficulty to sleep, reproductive anomalies, and cancer (Toluene Hazard Summary). Deliberate toluene abuse has become widespread among children and adolescents. It is easily available and inexpensive. Due to the hazards of toluene, the Occupational Safety and Health Administration (OSHA) has set a Permissible Exposure Limit at 200 ppm. Most health issues arise around 500 ppm (Toluene Toxicity).

1.3 Methods of Removing Water Contaminants

The removal of water contaminants is very important in keeping the environment and population healthy. Depending on the type of contaminant, different removal techniques can be considered. The main objectives of drinking water treatments are “to produce high quality water that is safe for human consumption, has aesthetic appeal, conforms to state and federal standards, and is economical in production” (Kvech and Tull). Some of the techniques we will cover in this section include air stripping, advanced oxidation processes, removal of microbial contamination, and adsorption. A more in-depth analysis will be done on adsorption methods.

1.3.1 Air Stripping

Air stripping is a technique of removing volatile organic compounds (VOCs) from water into air. It is a chemical engineering technology used to purify groundwater and wastewater that contains VOCs. The process usually occurs inside a packed tower or tray tower, also called an air stripper. The packing material usually is made of plastic, steel, or ceramic (A Citizen's Guide to Air Stripping). It operates with countercurrent flow of water and air (Air Stripping). A basic air stripper can vary in height and diameter, depending on the chemical concentration of the contaminated water. The tower is built with a spray nozzle at the top, which releases groundwater that has been pumped to the surface over the column’s packing. As the water is released, air goes up through the column, causing the VOCs to evaporate. The amount of volatilization, or the process of transfer of a chemical from the aqueous phase to the gas phase, is maximized by the packing increasing the surface area of the polluted water exposed to air. A low-profile air stripper has numerous packing trays that are horizontal. Water goes over the trays to maximize air-water contact and to minimize vertical space, making it a good alternative for groundwater treatment. The tower may also work together with an air heater to improve the removal efficiency and air emission (Air Stripping). A visual representation of an air stripper can be seen in Figure 1 (Typical Air Stripping System).

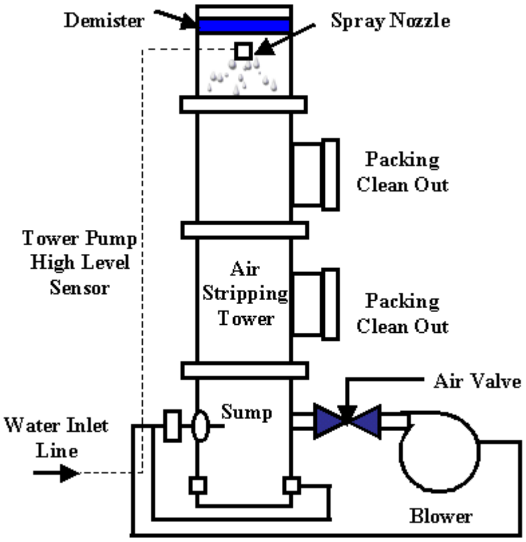

Figure 1 Sketch of Air Stripper (Typical Air Stripping System)

One major limitation of air stripping is that contaminants are just transferred from one phase to another. It does not do anything to eliminate the contaminant. This causes problems when the air stripper releases the contaminants into the air, which means careful evaluation of each contaminant must take place. Most towers will have some sort of treatment before the chemical is released into the air. Because of the hazardous nature of the compounds being stripped, the air that exits the air stripper may require a secondary technique to clean pollutant emissions. Some techniques commonly used are carbon adsorption and catalytic oxidation (Air Stripping). Another limitation of air stripping is that it can only work with water contaminants with a Henry's Law constant greater than 0.01. Henry's Law constant is a measurement of the extent to which a chemical separates between water and air. A higher Henry's Law constant means that a compound is more likely to volatize (Air Stripping). This is a safe technique to consider. The contaminated water is contained throughout the stripping process and the clean water can be returned to the site. It works best on water with contaminants that can evaporate easily, unlike metals, PCBs, or other chemicals that do not evaporate (A Citizen's Guide to Air Stripping). This technique is good for compounds with benzene, toluene, ethylbenzene, and xylene from gasoline, and ammonia (Air Stripping). When the air stripper is properly designed, it can remove 99% of contaminants, and it is easily maintained and easily cleaned (A Citizen's Guide to Air Stripping).

1.3.2 Advanced Oxidation Processes

Advanced oxidation processes are the procedures designed to remove organic and inorganic materials in wastewater by oxidation (Advanced oxidation process). Oxidation is defined as "a common form of chemical reaction which is the combining of oxygen with various elements and compounds" (Oxidation). Four reagents of oxidation are ozone, hydrogen peroxide, oxygen, and air (Advanced oxidation process). Oxidation with a combination of UV irradiation can target specific contaminants in water by direct radiation with the oxidizers, UV photolysis, and through UV light with ozone and/or hydrogen peroxide. The final products of oxidation should be carbon dioxide, water, and salts, meaning they undergo mineralization. The process can be carried out in batch or continuous flows. A wide range of organic and explosive contaminants are able to be oxidized, including petroleum hydrocarbons and chlorinated hydrocarbons, which are used as industrial solvents and cleaners. Easily oxidized organic compounds are destroyed rapidly in the oxidation process (Advanced Oxidation Processes). It is also useful for biologically toxic or non-degradable materials like aromatics, pesticides, petroleum constituents, and VOCs in wastewater (Advanced oxidation process). A sketch of this process can be found in Figure 2 below.

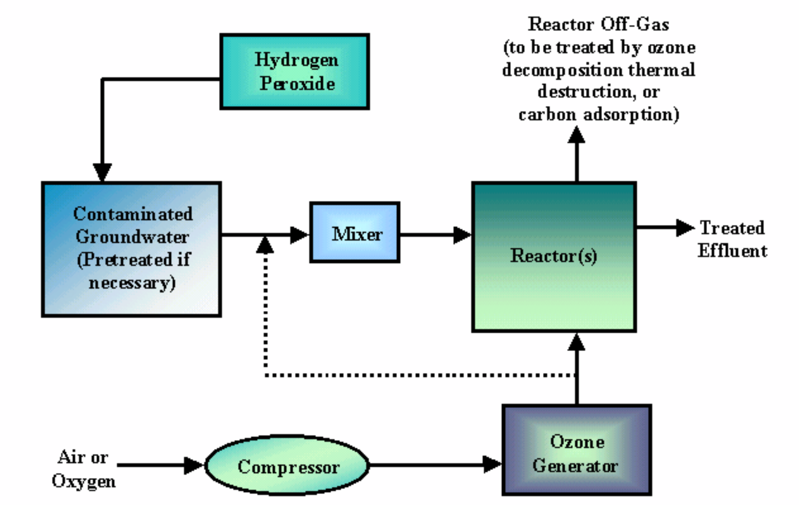

Figure 2 Advanced Oxidation Process (Advanced Oxidation Processes)

An advantage of oxidation, compared to air stripping and adsorption, is that it destructs the contaminants rather than extracting them and changing its phase (Advanced Oxidation Processes). It also has rapid reaction rates, small footprint, and potential to reduce toxicity by complete mineralization. An oxidation processes does not concentrate waste for further treatment, produce materials that require further treatment, or create sludge. It can also treat multiple organic contaminants at one time because of its non-selective pathways (Air and Water Treatment- Advanced Oxidation Processes).

There are limitations to using oxidation, however. The first is the aqueous stream must have good transmission of UV light, and should contain almost no heavy metal ions, insoluble gas, or grease. This process is also more expensive than other techniques because of energy requirements, and it is more difficult to maintain and clean (Advanced Oxidation Processes). Another limitation is that complex chemistry may occur for each separate contaminant (Air and Water Treatment- Advanced Oxidation Processes).

1.3.3 Microbial Contamination

Microbial contamination is the contamination of water resources by pathogenic, or disease-causing, microorganisms that cause a serious threat to human health. Microorganisms are microscopic bacteria, viruses, protozoa, etc. When contaminants are ingested through drinking water, diseases such as cholera, typhoid, hepatitis, and infectious gastrointestinal diseases may arise. Some symptoms may include fever, fatigue, weight loss, vomiting, abdominal cramping, diarrhea, stomachaches, and in severe cases, death. The population that is most at risk is infants, young children, older persons, and immune-compromised individuals such as those with HIV/AIDS and those undergoing chemotherapy (What You Need to Know about Microbial Contamination).

Multiple steps must be used to protect wastewater resources from microbial contamination. If treated before entering the water supply, it is easier to completely eliminate the contaminants. One major source of this contamination is failing sewage disposal systems. This includes waste treatment systems, pump stations, and malfunctioning cesspools, septic tanks, and leachfields. To prepare sewage disposal systems, it is important to use proper planning within the watershed, constantly inspect septic systems, and promote public education on caring for a septic system. Another source of contamination is agriculture due to animal waste in barnyards, storage areas, dairy farms, pastures, etc. Flood waters are also a major threat for health in outdoor areas, such as ball fields, playgrounds, and residential yards. To identify the amount of risks after a flood, it is necessary to identify potential contamination sources, determine factors that may influence microbial concentration and survival, determine the potential effect on the population, and consider the intended use for previously flooded areas. A study done after

Hurricane Katrina showed that microbial contaminants were increased as well as illnesses during the flooding event (Guidance on Microbial Contamination in Previously Flooded Outdoor Areas).

In order to treat microbial contaminants, processes such as water treatment coagulation and filtration must take place. Bacteria and viruses have proven to be removed from water by these treatments, but protozoa are resilient. In these cases, one might need to consider ozonation or UV disinfection (What You Need to Know about Microbial Contamination).

1.3.4 Adsorption

Adsorption is defined as the accumulation or concentration of molecules of a gas or liquid on a surface in contact with the gas or liquid, resulting in a relatively high concentration of the gas or solution at the surface (Adsorption). The process creates a film of the molecules or atoms being accumulated, called the adsorbate, on top of the surface of the adsorbent. Sorption refers to both processes of adsorption and absorption, which is when a fluid permeates or is dissolved by a liquid or solid. Different chemicals are adsorbed in different ways, mainly dependent on specific details of the chemical involved in the process. Adsorption is used in numerous natural physical, biological, and chemical systems. It also has a wide variety of uses, such as activated charcoal, synthetic resins, tunable nonporous carbon, and water purification (Adsorption). In this section is discussed how adsorption for water purification works for different chemicals. Adsorption of activated carbon and different zeolites, such as silicalite, dealuminated zeolite Y, mordenite, and zeolite beta, will be reviewed.

1.3.4.1 Activated Carbon

Activated carbon (AC) is often used in adsorption to purify drinking water. It is easily produced from multiple materials, such as coal, wood, and coco-nut shells. It depends on the material's surface size, preferably large, and how porous they are. If a material has larger pores, AC can function longer at a given time (Activated Carbon Adsorption). The material can then undergo physical reactivation, such as carbonization, oxidation, or a combination of the two, or chemical activation, which is when the material is saturated with an acid, strong, base or salt before carbonization (Activated carbon). When it is exposed to other oxidizing substances like chemicals and gas, it is then "activated" (Activated Carbon Adsorption). A representation of what AC looks like can be seen in Figure 3.

Figure 3 Activated Carbon (Activated carbon)

When activated carbon is activated, it can have a surface area in excess of 500 m^2. When taking a closer look under an electron microscope, as shown in Figure 4, you can see the individual particles displaying numerous kinds of porosity. There are areas where flat surfaces of material run parallel to each other. The micropores provide the necessary conditions for adsorption processes, since it can interact with many surfaces at the same time. AC binds materials using van der Waals force or London dispersion force. It does not bind well to chemicals that include alcohols, glycols, strong acids and bases, and metals and most inorganics (Activated carbon).

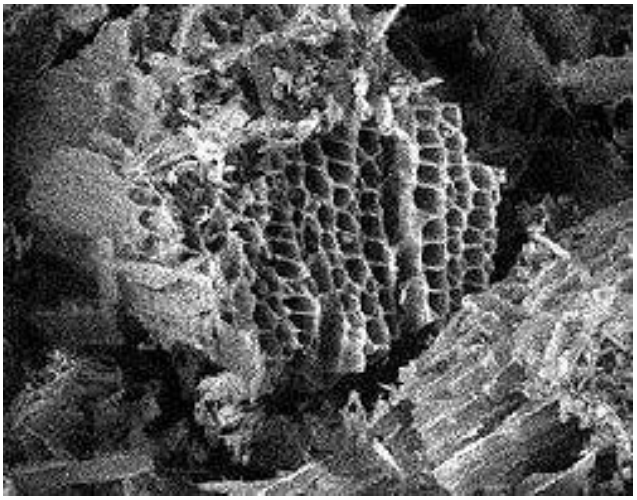

Figure 4 Activated carbon under an electron microscope (Activated carbon)

Activated carbon is categorized by different properties. They are complex products, so it is difficult to categorize them based on behavior, surface characteristics, and preparation methods, however, some broad categorizing can be made based on physical characteristics. The first type of AC is powdered activated carbon, or PAC. PACs are made as powders or fine granules less than 1.0 mm in size. They are present in a large surface to volume ration with a small diffusion distance. It is generally added directly to other process units, for example, raw water intakes, rapid mix basins, clarifiers, and gravity filters. The next type of AC is granular activated carbon, or GAC. GAC has a larger particle size compared to PAC and presents a smaller external surface. GACs are preferred for all adsorption processes because their diffusion rate is faster. GACs are typically used for water treatment, deodorization and separation of components of flow systems. Another type of AC is extruded activated carbon (EAC), which is the combination of PAC with a binder fused together and extruded into a cylindrical shape AC block. EAC is used for gas phase applications due to their low pressure drop, high mechanical strength and low dust content. Bead activated carbon, BAC, is supplied in diameters from 0.35 to 0.88 mm. It also has a low pressure drop, high mechanical strength, and low dust content, but with a smaller grain size as EAC. It is used mainly in fluidized bed applications, such as water filtration. There are other forms of AC that use different techniques to help water treatment (Activated carbon).

When activated carbon is used to remove water contaminants, it is necessary to determine its “breakpoint,” or the time when it will no longer be an adsorbent and needs to be replaced. The process of purifying water occurs in stages. The first is the contaminating substances adhering to the surface of the carbon. The second step occurs as the substances move into the large pores. Lastly, they are adsorbed onto the inner surface of the carbon (Activated Carbon Adsorption).

Like most processes, there are times when activated carbon is not effectively able to adsorb a particular contaminant. Even though AC works well in numerous applications, it suffers from a lack of reversibility, uncertainty when determining whether capacity has been reached, and an inability to remove highly polar organic species (Edmiston and Underwood). When a study was performed on the adsorption of MTBE in GAC, it was found that the removal was less effective than for less water-soluble compounds, requiring more carbon per mass of contaminant removed. Since MTBE has a high aqueous solubility, it simply does not have a great affinity for GAC (Erdem-Senatalar, Bergendahl and Giaya).

1.3.4.2 Zeolites

Zeolites are microporous, aluminosilicate materials used as adsorbents. There are over 190 different zeolite frameworks identified, and over 40 naturally occurring frameworks known. The microporous structure of the zeolite can accommodate many cations, or positively charged ions. Natural zeolites can crystallize in post-depositional environments over extremely long periods of time. However, natural zeolites are often contaminated by other minerals, metals, or other zeolites. This excludes most natural zeolites from adsorption and commercial applications. Zeolites are the aluminosilicate part of microporous solids referred to as *molecular sieves*. This refers to the material's ability to sort molecules based on a size exclusion process. The dimensions of channels in a zeolite control the maximum size of the molecular or ionic species it wishes to adsorb. The ring size of the aperture refers to a closed loop built from coordinated silicon or aluminum atoms. The rings are commonly found unsymmetrical because of strain from bonding between units. This makes the pores in zeolites not perfectly cylindrical (Zeolite). Zeolite pores, however, do have a definite structure that may affect sorption processes (Erdem-Senatalar, Bergendahl and Giaya).

They are often used for water purification or as catalysts. They are also commonly used in the production of laundry detergents, in medicines, and in agriculture. In chemical terms, they are used to separate molecules of certain sizes and shapes and as traps for molecules. In the petrochemical industry, synthetic zeolites are used as catalysts. They confine molecules in small areas to change their structure through reactivity. In the nuclear industry, zeolites are used in advanced reprocessing methods. The microporous aspect of zeolites allows them to capture some ions while allowing others to pass through. This allows many fission products to be removed from nuclear waste and trapped permanently. Zeolites are also used in heating and refrigeration as solar thermal collectors and for adsorption refrigeration. Other uses include detergents, construction, gemstones, vacuum pumping, nutritional supplements, soil treatment, fish aquariums, and cat litter (Zeolite).

1.3.4.2.1 Silicalite

Silicalite is the all-silica correspondent of the synthetic zeolite catalyst ZSM-5. This implies that cations that would normally be present in the channels that compensate for the extra charge from Al/Si substitutions are not present (Demontis, Stara and Suffritti, Behavior of Water in the Hydrophobic Zeolite Silicalite at Different Temperatures. A Molecular Dynamics Study). Silicalite has a density of 1.8 g/cm^3 and a specific pore volume of 0.19 cm^3/g. Silicalite is a member of the family of pentasil zeolites due to the framework built up from five-membered rings. A unit cell is composed of 96 SiO_2 units and contains straight channels and zigzag channels. It demonstrates a reversible phase transition at 340 K. Above this temperature silicalite belongs to the orthorhombic symmetry group, while below the temperature it belongs to the monoclinic symmetry group (Framework Type MFI). Silicalite demonstrates a hydrophobic quality, meaning the water-water interactions are stronger than the interactions between water molecules with the zeolite framework. When looking at internal surfaces of other zeolites, there may be cations or polar groups that water molecules adsorb to more strongly than to the all-silica surfaces (Demontis, Stara and Suffritti, Behavior of Water in the Hydrophobic Zeolite Silicalite at Different Temperatures. A Molecular Dynamics Study).

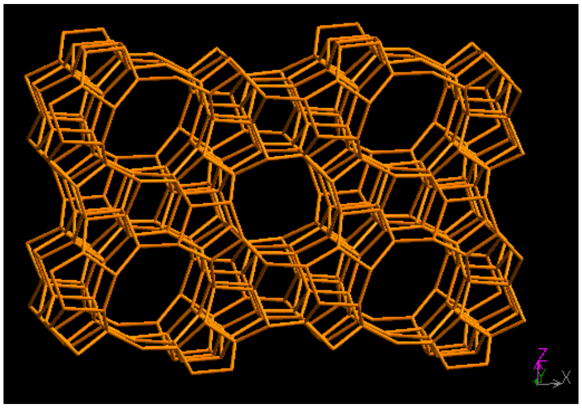

Figure 5 Silicalite Structure (Framework Type MFI)

There are defects found in real silicalite frameworks. One is that aluminum T-atoms or silanol groups can appear if a Si-O-Si bridge is broken. This causes the self diffusion coefficients and the adsorption capacities of the zeolite to be different than for pure silicalite. When aluminum atoms are present, countercations exist to keep the system neutral, the self diffusion coefficients are lowered because of clusters of water around the cations, and the sorption capacities are raised because countercations are present. Another defect of silicalite is that hydrogen bonds can be broken relatively easily, even at low temperatures. Hydrogen bonds stabilize silicalite, so the decrease of these bonds between water molecules makes the diffusion process easy. This would also cause a low value for the diffusion activation energy for silicalite compared to bulk liquid water. (Fleys, Thompson and MacDonald).

In several experimental studies, like the one done by Yazaydin and Thompson, of silicalite, the chemical was accepted as a hydrophobic material because of the adsorption of organics from water. The hydrophobicity is attached to the ≡Si-O-Si≡ bonds. There were a few defects found in these studies. Firstly, structure defects allow amounts of water to be adsorbed. Secondly, the presence of extraframework cations account for the non-neutrality of the framework because of aluminum sites substituting the missing silicon atoms. The last defect is the presence of Si-OH groups. These are caused when broken Si-O bonds are attacked by water molecules. This can occur on the external surface of silicalite or within the zeolite lattice where a silicon atom is missing. These Si-OH groups are formed per each missing silicon atom, creating a structure referred to as silanol nests. Defect-free silicalite is claimed to only adsorb a small amount of water. When silanol nests are added, it increases the amount of water adsorbed. The addition of silanol nests raises the amount of water adsorbed significantly (Yazaydin and Thompson).

A study was done to see how MTBE is adsorbed from water using silicalite, and compared it to the adsorption with AC, dealuminated zeolite Y and mordenite. Silicalite-1 had the highest capacity to adsorb MTBE from contaminated water. However, it was predicted that it would have a hard time adsorbing MTBE because the pores are slightly smaller than the MTBE molecules. In order for silicalite to adsorb MTBE, MTBE must deform slightly. There can also be defects in the silicalite crystalline structure that allow it to accommodate molecules that are larger than their pore dimensions. Another explanation could be that natural vibrations in the crystal lattice allow penetration of the MTBE molecule into the pores (Erdem-Senatalar, Bergendahl and Giaya).

1.3.4.2.2 Dealuminated Zeolite Y

Dealuminated zeolite Y (DAY) has a framework composed of sodalite units interconnected through double six-membered ring oxygen bridges. The units form supercages that connect with cages around it through four tetrahedral twelve-membered rings, with a diameter of 7.5 Å. Its pore volume is 0.38 cm^3/g and it has a high symmetry, causing difficulty to distinguish between cages and windows. The structure of DAY can be seen in Figure 6 (DAY).

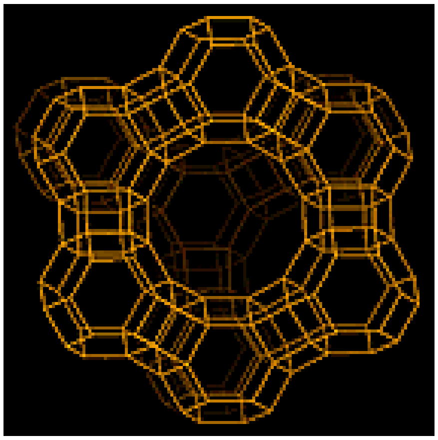

Figure 6 Dealuminated Zeolite Y Structure (DAY)

The perfect dealuminated zeolite Y structure would have no defects and no aluminum atoms present. The presence of aluminum atoms causes a modification in adsorption capacities, for reasons previously noted for silicalite. The activation energy for diffusion was determined to be a lower value because of the confinement in the structure (Fleys, Thompson and MacDonald). This influences the thermodynamics of the system and the geometries of hydrogen bonds. The hydrogen bond strength decreases as temperature decreases, as well as the average number of hydrogen bonds per water molecule. When comparing the DAY pore system to bulk liquid water, the number of hydrogen bonds per water molecule is lower in the DAY pore system. The hydrogen bonds cause stabilization between water molecules, which is also lower in the DAY pore system than in bulk liquid water, leading to a lower diffusion activation energy. When higher temperatures are used, water molecules are found to be more energetic, which allows the translational and rotational barriers for diffusion to be overcome more easily. Also with high temperatures, there is a decrease in the number of stable hydrogen bonds (Fleys, Thompson and MacDonald).

The same study by Yazaydin and Thompson mentioned in the silicalite section included a comparison of the adsorption of MTBE with activated carbon, silicalite, dealuminated zeolite Y, and mordenite. The larger pores in DAY did not perform well at low concentrations of MTBE or trichloroethylene. However, the sorbed quantity did exceed the capacity of the other sorbents at high concentrations due to its larger pore volume. Also at low concentrations of MTBE, DAY was significantly inferior to the other tested zeolites. This can be due to the same problem as silicalite, where MTBE molecules are slightly too large to fit in well inside the DAY pores. Again, it adsorbed effectively when high concentrations of MTBE were used (Erdem-Senatalar, Bergendahl and Giaya).

1.3.4.2.3 Mordenite

Mordenite is one of the most commonly found zeolites. It crystallizes in the form of fibrous aggregates, masses, and vertically striated prismatic crystals. The formed crystals are long, thin, and delicate. It is usually found to be colorless, or a faint white, yellow, or pink. The structure of mordenite contains chains of five-membered rings of linked silicate and aluminate tetrahedra. The high ratio of silicon to aluminum atoms makes it harder to be attacked by acids (Mordenite). It is known that some synthetic mordenite can accept cations or molecules larger than 4.5 Å, unlike natural mordenite. A representation of the structure of mordenite can be seen in Figure 7. Since mordenite can be found in the crystalline nature, fiborous mordenite minerals should be carefully examined and handled. It should be used with caution with exposure to humans and animals limited, specifically during mining, processing, handling, and utilizing the minerals (Mordenite Datasheet).

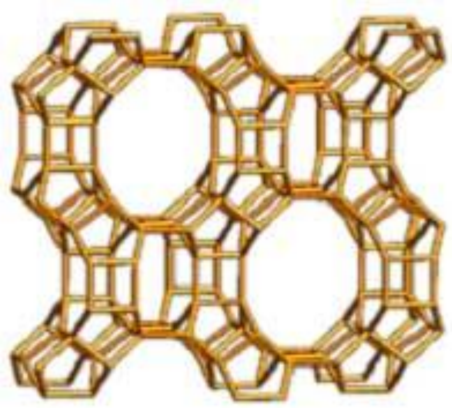

Figure 7 Structure of Mordenite (Mordenite X-TEX-Z-200)

Mordenite is the most commonly found zeolite in volcanic deposits and lava flows. It crystallizes over a range of physical conditions, as a replacement of volcanic gas or pre-existing zeolite phases, from the surface temperatures of lakes in arid climates. They are present in hydrologically closed systems, hydrologically open systems, and marine sediments from arc-source terrains (Mordenite Datasheet). Mordenite is commonly used as a catalyst in the petrochemical industry for isomerization of alkanes and aromatics (Mordenite). It is also used in generic applications in agriculture and the building industry as stone. It can be used in gas separation processes for the production of high-grade oxygen from air by pressure-swing operating generators (Mordenite Datasheet).

A study (Erdem-Senatalar, Bergendahl and Giaya) was done to look into how mordenite could remove MTBE from water. At high concentration levels, it was able to remove about eight to twelve times more MTBE from the contaminated water than AC. It was also found that the larger pores in mordenite, compared to silicalite and dealuminated zeolite Y, are more conductive for accepting MTBE molecules at high concentration levels. At low concentrations, mordenite performed very poorly at adsorbing traces of MTBE from water.

1.3.4.2.4 Zeolite Beta

Zeolite beta has a very complex structure. It consists of the growth of the two structures Polymorphs A and B. They grow as sheets, alternating randomly between the two structures. Both of the polymorph structures have a three dimensional network of 12-ring pores (Zeolite Beta). Polymorph A represents an uninterrupted sequence of stacking, while Polymorph B has an alternating stacking sequence. Since the tertiary building unit has no preference for mode of connection, both occur almost equally in zeolite beta. This causes a random extent of interplanar stacking. Faulting can occur when terminated by hydroxyl groups. This does not cause a big effect on the pore volume, but it changes the tortuosity of the pore connectivity (Newsam, Treacy and Koetsier). A representation of the zeolite beta structure can be found in Figure 8.

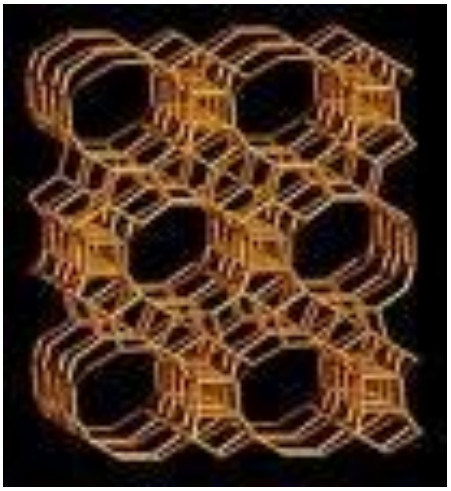

Figure 8 Structure of Zeolite Beta (Production of rice husk ash to zeolite beta)

1.4 Diffusion and Diffusion Rates

Diffusion is defined as the spread of particles through random motion from regions of higher concentration to regions of lower concentration. The diffusion equation is as follows

$$\frac{\partial \phi(\mathbf{r},t)}{\partial t} = \nabla \cdot \left[D(\phi,\mathbf{r}) \, \nabla \phi(\mathbf{r},t) \right],$$

where $\phi(\mathbf{r}, t)$ is the density of the diffusing material at location **r** and time *t* and $D(\phi, \mathbf{r})$ is the collective diffusion coefficient for density ϕ at location **r**; and ∇ represents the vector differential operator del. It is caused by the movement and spreading of particles. The force driving diffusion is generated by the presence of a concentration, or energy difference (Diffusion). A diffusion rate is the number of randomly moving molecules that pass through a unit area per second. Diffusion rates are fastest when a large concentration difference exists on either side of the unit area. Diffusion rates increase with temperature, and decrease with increasing pressure, molecular weight, and molecular size (Definition of Diffusion Rate (Rate of Diffusion)).

2 Methodology

The first part of this project was to model the three water contaminants; phenol, benzene, and toluene. In order to do so, the geometry for each molecule was initially set by using the program Argus Lab. This program inserts each element and bond found in a specific molecule. Once a representation was made, it created a geometry output file. This file was then used in DL_FIELD, which is the program that helps create the files, CONFIG, CONTROL, and FIELD. The CONTROL file determined mainly the number of steps used for each simulation. The larger the number of steps, the longer the simulation ran. Each simulation was given a long enough time to get accurate results from the OUTPUT file. These three files were then used in the DL_POLY program. This is the program that runs the desired simulation and generates necessary output files needed to illustrate each simulation. Once each molecule successfully ran, VMD was used to see exactly what happens to each molecule in the given space and time from the CONTROL file. Specific illustrations can be found in the Results and Discussion section.

The second part of the project was to model the zeolite, silicalite. This was done by using the International Zeolite Association website, where dimensions of the molecule were used (International Zeolite Association). These dimensions were used to create a CONFIG file for the simulation. FIELD and CONTROL files were written, allowing a simulation to run using DL_POLY. Again, VMD was used to show exactly what happens to the molecule in the given space and time from the CONTROL file. Specific illustrations can be found in the Results and Discussion section.

The final part of the project was to model phenol, toluene, and benzene within silicalite. A CONFIG file was written using the known dimensions from each individual simulation. FIELD and CONTROL files were also written, allowing a simulation to run using DL_POLY. Once each of the simulations ran, VMD was used to show the illustration of what occurs in each mixture. The given OUTPUT file was used to give specific diffusion rates of each compound. These diffusion rates were then compared to each other to get a better understanding of how silicalite can be used to remove contaminants from water.

3 Results and Discussion

As mentioned in the methodology, the first part of the project required models of the three water contaminants. Figure 9 is the model of Benzene, taken from the VMD program. The green molecules and bonds represent the carbon ring. Each carbon is bonded to a hydrogen atom, shown as the white molecules. The ring includes three double bonds, separated by a single bond. Even though the program does not show the double bonds in the model, Argus Lab assumed double bonds were present and calculations were given respectfully.

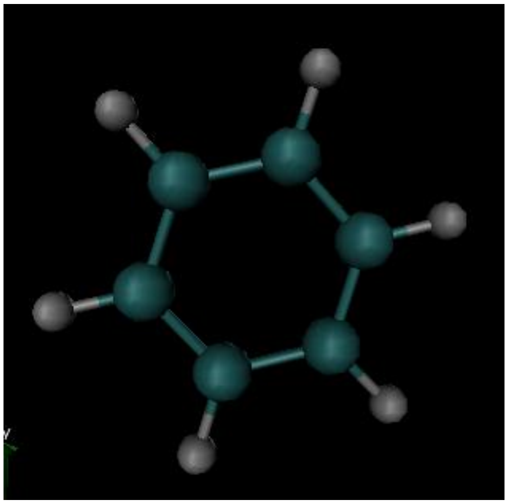

Figure 9 Model of Benzene

Figure 10 is the model of phenol. Again, the green molecules represent the carbon ring. It also has alternating double carbon bonds. The major difference between the benzene molecule and the phenol molecule is the OH bond. One of the carbons is bonded to an oxygen atom, which is bonded to a hydrogen atom.

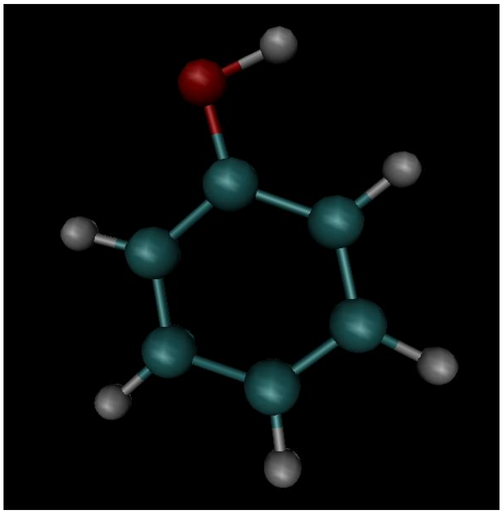

Figure 10 Model of Phenol

Lastly, Figure 11 is a model of toluene. Toluene consists of the benzene ring with a CH_3 side group.

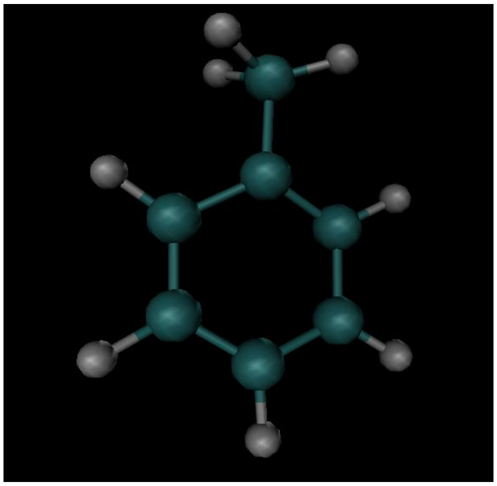

Figure 11 Model of Toluene

Figures 12, 13, and 14 are all models of silicalite, shown at different angles. It is a complex structure with large visible pores.

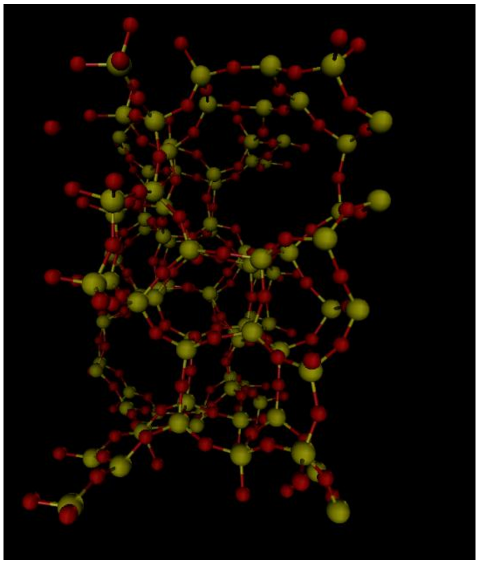

Figure 12 Model of Silicalite viewed along X-axis

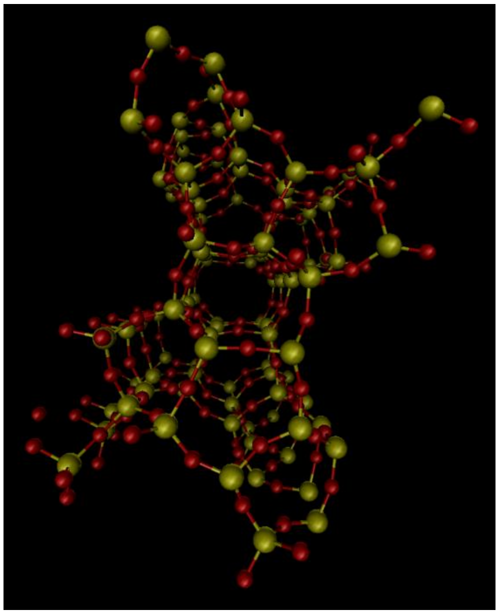

Figure 13 Model of Silicalite viewed along Y-axis

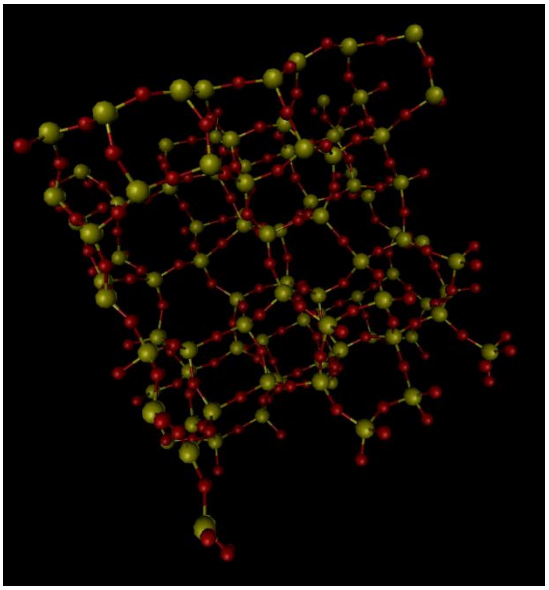

Figure 14 Model of Silicalite viewed along Z-axis

The last section of the project was to determine diffusion rates of each of the contaminants in silicalite. The first model, shown in Figure 15, represents benzene inside silicalite. Benzene rests inside one of silicalite's large pores. As the simulation ran, benzene moved around, but stayed within the pore. Table 1 shows the diffusion rates given from the simulation's output file. The rates for OZ and Si can be neglected because they do not move during the simulation. The diffusion rate is given by the CA atom (the aromatic carbon atom of benzene) as well as the HP atoms (hydrogen atoms of benzene). During simulation, the carbon bonds continue to bend and move around in its structure while interacting with silicalite, which is why emphasis is put on the carbon diffusion rates. The final diffusion rate for benzene in the silicalite is 1.8338 x 10^{-9} m^2/sec.

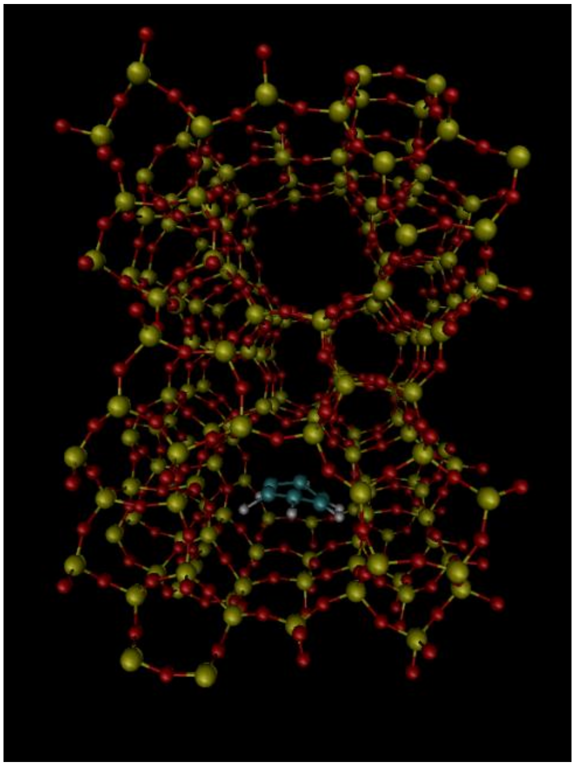

Figure 15 Model of Silicalite and Benzene together

Table 1 Diffusion Coefficients for Silicalite and Benzene

Atom	Diffusion Rate (10^{-9} m^2/sec)
OZ	4.8194E-02
Si	3.1995E-02
CA	1.8228E+00
HP	2.1751E+00

Figure 16 represents phenol inside silicalite. Phenol again rests inside one of silicalite's large pores. As the simulation ran phenol showed vibrations inside the specific pore. Table 2 shows the diffusion rates given from the simulation's output file. The rates for OZ and Si can be neglected again because they do not move during the simulation. The diffusion rate is given by the CA atom as well as other atoms in phenol (HP, or the aromatic hydrogens, O, and H attached to O). During the simulation, the carbon bonds continue to bend and move around in its structure while interacting with silicalite. The final diffusion rate for the phenol in silicalite is 1.15 x 10^{-9} m^2/sec.

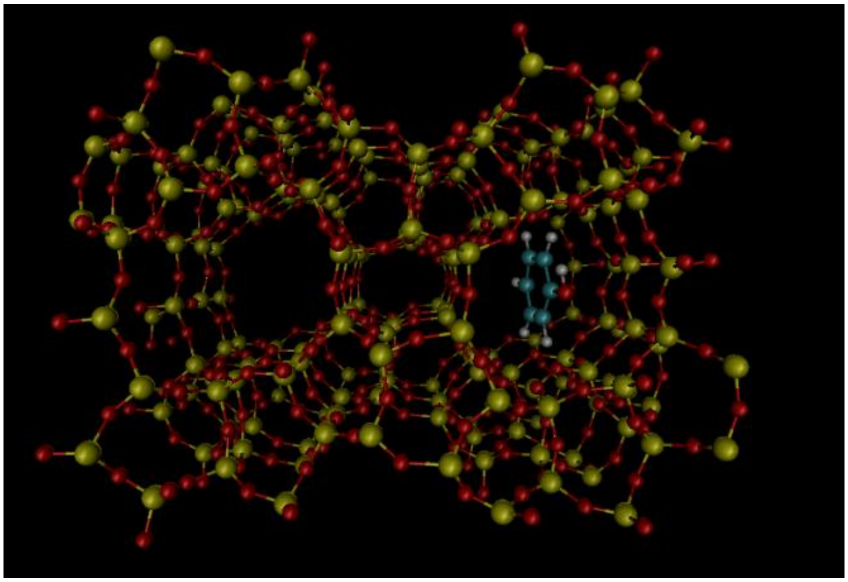

Figure 16 Model of Silicalite and Phenol

Table 2 Diffusion Coefficients for Silicalite and Phenol

Atom	Diffusion Rate (10^{-9} m^2/sec)
OZ	1.7750E-01
Si	1.3451E-01
CA	1.1500E+00
OH1	5.2425E+00
H	5.3019E+00
HP	4.9238E+00

Figure 17 is the final model representing toluene inside silicalite. Toluene was placed inside a similar large pore of silicalite. Throughout the simulation, toluene showed minimal vibrations inside the pore. Table 3 shows that the diffusion rate is 0.0592 10^{-9} m^2/sec. This very low number shows that toluene does not diffuse in silicalite very well.

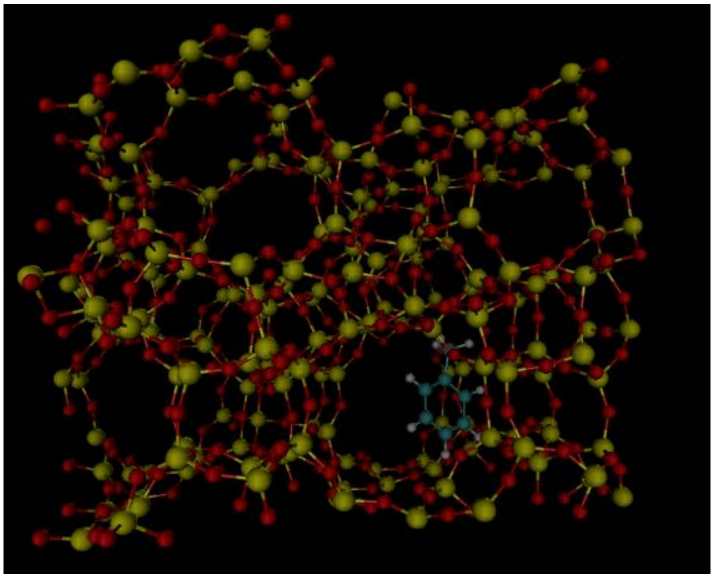

Figure 17 Model of Silicalite and Toluene

Table 3 Diffusion Coefficients for Silicalite and Toluene

Atom	Diffusion Rate (10^{-9} m^2/sec)
OZ	9.2534E-05
Si	0.0000E+00
CT3	0.0000E+00
HA	0.0000E+00
CA	5.9204E-02
HP	2.0311E-01

4 Conclusions

When comparing all three molecule simulations, it is safe to say that benzene would diffuse the best in the zeolite silicalite, followed by phenol then toluene. Table 4 shows the final diffusion rates together.

Table 4 Comparison of Diffusion Rates

Molecule	Diffusion Rate (10^{-9} m^2/sec)
Benzene	1.8228E+00
Phenol	1.1500E+00
Toluene	5.9204E-02

It was shown that the least complex molecule, benzene, was able to move around more within the silicalite pore. This is needed to allow the contaminant to diffuse in the zeolite. When a molecule is unable to move around within the zeolite, it has less of a chance or no chance to diffuse. Phenol's C-O bond is strongly polarized towards oxygen due to electronegativity. The bond lengths for this bond are around 143 picometers. This is an added length to the benzene ring, again, making it harder for the molecule to move inside the silicalite pore. Plus phenol can form hydrogen bonds between OH group and O in silicalite. Toluene's C-C bond is longer than the C-O. It is around 154 picometers. This long addition to the benzene ring makes it nearly impossible for toluene to diffuse in silicalite.

It was concluded that silicalite would be a good molecule to use for diffusion of some water contaminants. Further research should study silicalite with more contaminants to see if it is a good molecule to use for more abundant contaminants. If silicalite is proved to only remove a small amount of water-borne contaminants, more zeolites should be studied to see if any can remove a larger percentage from water.

5 Works Cited

2012. <http://www.iza-online.org/>.

A Citizen's Guide to Air Stripping. December 2001. 19 October 2011. <http://clu-in.org/download/citizens/airstripping.pdf>.

Activated carbon. 11 October 2011. 20 October 2011. <http://en.wikipedia.org/wiki/Activated_carbon>.

Activated Carbon Adsorption. n.d. 20 October 2011. <http://www.theactivatedcarbon.com/page/activated-carbon-adsorption/>.

Adsorption. 2005. 19 October 2011. <http://www.biology-online.org/dictionary/Adsorption>.

Adsorption. 14 October 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Adsorption>.

Advanced oxidation process. 9 October 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Advanced_oxidation_process>.

Advanced Oxidation Processes. n.d. 19 October 2011. <http://www.frtr.gov/matrix2/section4/4-45.html>.

Air and Water Treatment- Advanced Oxidation Processes. n.d. 19 October 2011. <http://www.spartanwatertreatment.com/about-spartan.html>.

Air Stripping. 12 May 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Air_stripping>.

Air Stripping. n.d. 19 October 2011. <http://www.cpeo.org/techtree/ttdescript/airstr.htm>.

Allen, Michael P. "Introduction to Molecular Dynamics Simulation." 2004.

Benzene. 15 March 2012. <http://en.wikipedia.org/wiki/Benzene#cite_note-31>.

Benzene. 5 November 2010. <http://www.cancer.org/Cancer/CancerCauses/OtherCarcinogens/IntheWorkplace/benzene>.

Bisphenol A. 12 October 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Bisphenol_A>.

Bisphenol-A. 2011. 19 October 2011. <http://www.ewg.org/chemindex/chemicals/bisphenolA>.

DAY. n.d. 18 October 2011. <http://www.iza-structure.org/databases>.

Definition of Diffusion Rate (Rate of Diffusion). 2012. <http://dictionary.babylon.com/diffusion_rate_(rate_of_diffusion)/>.

Demontis, Pierfranco, et al. "Dynamical Properties of Confined Water Nanoclusters: Simulation Study of Hydrated Zeolite NaA: Structural and Vibrational Properties." *American Chemical Society NANO* 2.8 (2008): 1603-1614.

Demontis, Pierfranco, Giovanna Stara and Giuseppe B. Suffritti. "Behavior of Water in the Hydrophobic Zeolite Silicalite at Different Temperatures. A Molecular Dynamics Study." *J. Phys. Chem. B* 107 (2003): 4426-4436.

Diffusion. 6 March 2012. <http://en.wikipedia.org/wiki/Diffusion>.

Edmiston, Paul L. and Laura A. Underwood. "Absorption of dissolved organic species from water using organically modified silica that swells." *Separation and Purification Technology 66* (2009): 532-540.

Erdem-Senatalar, Ayse, et al. "Adsorption of Methyl Tertiary Butyl Ether on Hydrophobic Molecular Sieves." *Environmental Engineering Science* 21 (2004): 722-729.

Estrone. 7 September 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Estrone>.

Facts About Benzene. 22 February 2006. <http://www.bt.cdc.gov/agent/benzene/basics/facts.asp>.

Farhadian, Nafiseh, et al. "Molecular Dynamics Simulation of Water and Ions in Nanopores of Lysozyme Protein Crystal." *International Journal of Chemical Reactor Engineering* 9.A23 (2011): 1-22.

Fleys, Matthieu, Robert W. Thompson and John C. MacDonald. "Comparison of the Behavior of Water in Silicalite and Dealuminated Zeolite Y at Different Temperatures by Molecular Dynamic Simulations." *J. Phys. Chem. B* 108 (2004): 12197-12203.

Framework Type MFI. 2008. 18 October 2011. <http://izasc.ethz.ch/fmi/xsl/IZA-SC/ftc_fw.xsl?-db=Atlas_main&-lay=web&STC=MFI&-find>.

Gad, Nahed S. and Amal S. Saad. "Effect of Environmental Pollution by Phenol on Some Physiological Parameters of Oreochromis niloticus." *Global Veterinaria* 2.6 (2008): 312-319.

Guidance on Microbial Contamination in Previously Flooded Outdoor Areas. 8 April 2011. 19 October 2011. <http://www.cdc.gov/nceh/ehs/Publications/Guidance_Flooding.htm>.

Habeck, Michael. *Phenol*. 2010. 19 October 2011. <http://www.eco-usa.net/toxics/chemicals/phenol.shtml>.

Kim, Yong-Ho, et al. "Selective adsorption of bisphenol A by organic-inorganic hybrid mesoporous silicas." *Microporous and Mesoporous Materials* 138 (2011): 184-190.

Kolpin, Dana W., et al. "Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance." *Environmental Science and Technology* 36.6 (2002): 1202-1211.

Kvech, Steve and Erika Tull. *Activated Carbon*. 1997. 20 October 2011. <http://www.cee.vt.edu/ewr/environmental/teach/wtprimer/carbon/sketcarb.html>.

Methyl Tertiary Butyl Ether. 24 November 2007. 19 October 2011. <http://www.epa.gov/mtbe/faq.htm>.

Molecular Dynamics. 26 October 2011. 31 October 2011. <http://en.wikipedia.org/wiki/Molecular_dynamics>.

Mordenite. 7 August 2011. 20 October 2011. <http://en.wikipedia.org/wiki/Mordenite>.

Mordenite Datasheet. 7 July 2011. 20 October 2011. <http://www.iza-online.org/natural/Datasheets/Mordenite/mordenite.html>.

Mordenite X-TEX-Z-200. 2011. 20 October 2011. <http://www.xextex.com/products/xtexz200.htm>.

Newsam, J. M., et al. "Structural characterization of zeolite beta." *Proceedings of the Royal Society of London* 1988: 375-405.

Oxidation. 2002. 19 October 2011. <http://metals.about.com/library/bldef-Oxidation.htm>.

Phenol. 18 October 2011. 19 October 2011. <http://en.wikipedia.org/wiki/Phenol>.

Production of rice husk ash to zeolite beta. 24 January 2009. 20 October 2011. <http://nanoall.blogspot.com/2009/01/production-of-rice-husk-ash-to-zeolite.html>.

Stackelberg, Paul E., et al. "Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant." *Science of the Total Environment* 329 (2004): 99-113.

Todd, D. Billy. "Introduction to Molecular Dynamics." n.d. *Centre for Molecular Simulation.* 31 October 2011. <http://www.swin.edu.au/ict/research/cms/documents/mod7.pdf>.

Toluene. 9 4 2012. <http://en.wikipedia.org/wiki/Toluene>.

Toluene Hazard Summary. 6 11 2007. <http://www.epa.gov/ttn/atw/hlthef/toluene.html>.

Toluene Toxicity. 2012. <http://emedicine.medscape.com/article/818939-overview#a0101>.

Typical Air Stripping System. n.d. 19 October 2011. <http://www.frtr.gov/matrix2/section4/D01-4-46.gif>.

Update on Bisphenol A for Use in Food Content Applications. 22 March 2010. 19 October 2011. <http://www.fda.gov/NewsEvents/PublicHealthFocus/ucm197739.htm#background>.

Wen, Huajing, John A. Bergendahl and Robert W. Thompson. "Removal of Estrone from Water by Adsorption on Zeolites with Regeneration by Direct UV Photolysis." *Environmental Engineering Science* 26.2 (2009): 319-326.

What You Need to Know about Microbial Contamination. n.d. 19 October 2011. <http://www.mass.gov/dep/water/drinking/microb.htm>.

Yazaydin, A. Ozgur and Robert W. Thompson. "Molecular Simulation of the Adsorption of MTBE in Silicalite, Mordenite, and Zeolite Beta." *J. Phys. Chem. B* 110 (2006): 14458-14462.

Yazaydin, Ozgur A. and Robert W. Thompson. "Molecular simulation of water adsorption in silicalite: Effect of silanol groups and different cations." *Microporous and Mesoporous Materials* 123 (2009): 1690176.

Zenker, Matthew J., Robert C. Borden and Robert W. Thompson. "Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments." *Environmental Engineering Science* 20.5 (2003): 423-432.

Zeolite. 20 October 2011. 20 October 2011. <http://en.wikipedia.org/wiki/Zeolite>.

Zeolite Beta. n.d. 20 October 2011. <http://www.personal.utulsa.edu/~geoffrey-price/zeolite/beta.htm>.