Removal of Hydrocarbons From Wastewaters

By

Gülsan KOLTUKSUZ

A Dissertation Submitted to the
Graduate School in Partial Fulfillment
of the Requirements for the Degree of

MASTER OF SCIENCE

Department: Environmental Engineering
Major: Environmental Engineering
(Environmental Pollution and Control)

İzmir Institute of Technology
İzmir, Turkey

February, 2002

We approve the thesis of **Gülsan KOLTUKSUZ**

Date of Signature

... **01.02.2002**
Prof. Dr. A. Semra ÜLKÜ
Supervisor
Department of Chemical Engineering

... **01.02.2002**
Asst. Prof. Dr. Hürriyet POLAT
Co-Supervisor
Department of Chemistry

... **01.02.2002**
Prof. Dr. Devrim BALKÖSE
Department of Chemical Engineering

... **01.02.2002**
Asst. Prof. Dr. S. Fehime ÖZKAN
Department of Chemical Engineering

... **01.02.2002**
Asst. Prof. Dr. Sacide ALSOY
Department of Chemical Engineering

... **01.02.2002**
Asst. Prof. Dr. Selahattin YILMAZ
Head of Interdisciplinary
Environmental Engineering Program

ACKNOWLEDGMENTS

I would like to express my grateful thanks to Prof. Dr. Semra Ülkü and Asst. Prof. Dr. Hürriyet Polat for their help, guidance and encouragement during this project.

I also would like to thank to Dr .Ülkü Günaslan, Sevim Okumuş, Nükhet Akkaya and to the laboratory technicians of PETKIM for their valuable comments and helps in ‘Gas Chromatography’ analysis.

I am also grateful to my special friend Müşerref Türkmen and to all my friends in the Engineering Faculty for their sincere friendships during our thesis studies.

Special thanks are to all research assistants and technicians from ‘Faculty of Science’ in IYTE for their helps and friendships.

I would like to thank especially to my family for their support and to my husband Ümit for his patience, understanding, encouragement and help. He encouraged me in all stages in this study. I owe a special dept to him.

ABSTRACT

Wastewater of chemical industries and petrochemical spills are the main sources of hydrocarbon pollution. Benzene, toluene and o- xylene are generally found in petrochemical spills which effect the all livings in the environment because of its toxicity.

This thesis was an investigation of benzene, toluene and o- xylene (nonpolar aromatics) adsorption on clinoptilolite rich natural zeolite and surfactant modified zeolite. The aim of surfactant modification was to make highly polar zeolite surface hydrophobic and thereby remove the hydrophobic benzene, toluene and o- xylene molecules from the aqueous phase with the help of hydrophobic attraction forces. Cationic surfactants Dodecyl Amine (DA), Tetramethylammonium (TMA^+) and an anionic surfactant Sodium Dodecyl Sulfate (SDS) were used for surface modification.

The degree of surface hydrophobicity was examined by calculating the change in Gibbs free energy ($\Delta G = \gamma_{WA} (\cos\theta - 1)$) of the zeolite-water system by using the contact angle and surface tension measurement results in the presence and absence of surface modification. For natural zeolite the mean contact angle (θ_m) value was found 7.76^o. Modification by DA and TMA^+ increased θ_m from 7.76^o to 51.13^o and 29.37^o respectively at a concentration of 1×10^{-3} M. In case of SDS, at the pH value of 4, there was only a slight increase from $7.76\ ^o$ to $18.03\ ^o$ at a concentration of 1×10^{-4} M. Effect of these surfactants on interfacial tension at air water interface was also different from eachother. DA decreased the surface tension from 72.8 to 37 dynes/cm while TMA+ did not bring any change. This part of the study showed that the presence of surfactant makes zeolite surface more hydrophobic.

In adsorption studies, natural zeolite removed ≈ 20% of hydrocarbons from water. Except toluene, there was an optimum time that the removal was high. Presence of surfactant was able to increase this percent up to ≈ 40% under some conditions depending on the surfactant and hydrocarbon type and concentration. The highest benzene adsorption was obtained with TMA^+ modified zeolite. The sequence was benzene > toluene > o-xylene. In case of DA modified zeolite, on the other hand, o-xylene was adsorbed more than the other hydrocarbons. The removal follows the order o- xylene > toluene > benzene in this case.

ÖZ

Hidrokarbon kirliliğinin başlıca kaynaklarını kimya sanayileri atıksuları ve denizlere dökülen petrokimya atıkları oluşturmaktadır. Benzen, toluen ve o-ksilen genellikle denizlerde görülen petrokimya atıklarında bulunur ve çevrede bulunan tüm canlıları zehirlilikleri nedeniyle etkilemektedir.

Bu tez kapsamında benzen, toluen ve o-ksilen’ in (nonpolar aromatikler) klinoptilolitçe zengin doğal zeolit ve yüzey aktif madde ile modifiye edilmiş zeolit üzerine adsorbsiyonu incelenmiştir. Yüzey aktif madde modifikasyonunun amacı, polaritesi yüksek olan zeolitin yüzeyini hidrofobik yapmak ve bu sayede hidrofobik olan benzen, toluen ve o-ksilen moleküllerinin hidrofobik çekim yardımıyla sıvı fazdan ayırmaktır. Yüzey modifikasyonu için katyonik olan dodesil amin (DA) ve tetrametilamonyum (TMA$^+$) yüzey aktif maddeleri ve anyonik bir yüzey aktif madde olan sodyum dodesil sülfat (SDS) kullanılmıştır.

Yüzey modifikasyonunun olması ve olmaması durumuna göre zeolit-su sistemi için kontakt açısı ve yüzey gerilimi ölçümleri sonuçlarına göre Gibbs serbest enerji ($\Delta G = \gamma_{WA} (\cos\theta - 1)$) değerleri hesaplanmıştır. Klinoptilolitçe zengin doğal zeolit için ortalama kontakt açısı (θ_m) 7.76^o bulunmuştur. 1×10^{-3} M DA ve TMA$^+$ modifikasyonu, θ_m değerini sırasıyla 7.76^o ‘ dan 51.13^o ’ e ve 29.37^o ‘ ye yükseltmiştir. 1×10^{-4} M SDS (pH=4) durumunda ise 7.76 ^{o} ‘ dan 18.03 ^{o} ‘ e az miktarda yükselme gerçekleşmiştir. Bu yüzey aktif maddelerin hava-su ara yüzeyindeki etkileri birbirlerinden farklıdır. DA yüzey gerilimini 72.8’den 37 dyne/cm ‘ye indirmiştir ki böyle bir etkiyi TMA$^+$ yaratmamıştır. Çalışmanın bu bölümünde yüzey aktif madde varlığında zeolit yüzeyinin daha hidrofobik olduğu gösterilmiştir.

Adsorbsiyon çalışmalarında doğal zeolit hidrokarbonları sudan %20 civarında ayırmıştır. Toluen hariç, ayırımın yüksek olması için optimum bir zaman vardır. Yüzey aktif madde varlığında bu yüzde yüzey aktif madde ve hidrokarbon tipine ve konsantrasyonuna bağlı bazı koşullar altında yaklaşık %40 ‘a yükselmiştir. En yüksek benzen adsorbsiyonu TMA$^+$ ile modifiye edilmiş zeolit ile elde edilmiştir. Sıralama benzen > toluen > o-ksilen şeklindedir. DA ile modifiye edilmiş zeolit durumunda ise, o- ksilen diğer hidrokarbonlara göre daha fazla adsorblanmıştır. Ayırım o- ksilen > toluen > benzen sıralaması düzenindedir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

1.1. Statement of the Problem

The increase of the population and the continuously development of industries in the world cause many environmental problems. Millions of liters of water are needed every day worldwide for different purposes in our life. Despite our dependence on water, we use it as a dumping ground for all sorts of waste, and do very little to protect the water supplies we have.

Hydrocarbon (HC) pollution in our world cause serious environmental problems. Petrol, crude oil, gasoline, diesel, jet fuel, some solvents and gas contain several types of HC’s. Petroleum is a mixture that contains hydrocarbons up to 90 atoms of carbon in the molecule. Crude oil contains about 98% hydrocarbons, which are aliphatic, aromatic, and heterocyclic hydrocarbons. The chemical processing of crude oil (cracking, reforming, polymerization, alkylation, etc.) forms many derivative products (organic acids, esters, alcohols, aldehydes, phenols, mercaptans, aliphatic and aromatic amines, glycols, furfural, acetone) that may be found in petrochemical wastewaters. The most important pollution of HCs are petrochemical spills caused by ships and boats which are very dangerous for aquatic life and humans. They generally form a layer on the surface of water, which can spread rapidly. The most important problem is that it prevents the oxygen transfer from the atmosphere to water. Up to now many seabirds are killed and many livings in the aquatic ecosystem are destroyed because of these spills. HC’s react with nitrogen oxides in sunlight and produce a number of harmful compounds called photochemical oxidants. These include peroxacetyl nitrate(PAN) and ozone, both of which are dangerous for humans and cause plant damage. Ozone also causes acid rain and the greenhouse effect (Dojlido J.R., 1993).

One of the greatest ecological disasters in history happened during the Gulf War. The environmental attack came in two parts: The release of oil into the Gulf, and the burning of Kuwait's oil wells. There was a release of a huge amount of oil into the Gulf. The range was estimated as 0.5 million to 11 million barrels, and the average was about 6 million barrels. The oil formed a slick 30 miles long and 8 miles wide. The slick is thought to have killed between 15,000 and 30,000 birds. The problem was not just the huge amount of oil in the Gulf, but also the nature of the Gulf itself. This inland sea is 35m deep, and has only a narrow connection to the Indian Ocean through the Straits of Hormuz, which means that it takes between three and five and a half years for all the water in the Gulf to be changed, so there was no hope of the oil dispersion.

The burning of Kuwait's oil wells caused serious air pollution problems. It is estimated that about 67 million tones of oil were burned in total, which produced about 2.1 million tones of soot and 2 million tones of sulphur, one of the main causes of acid rain. Fortunately, the soot particles did not go any higher than 5,000 meters, which meant that they were washed down with the rain. If the soot had got above the rainclouds, it would have remained up there, with severe consequences to the world's climate. The World Health Organization estimated that death rates in Kuwait raise because of associated breathing difficulties and skin problems.

At 1979 the HC pollution in Mediterranean Sea was between 0,5 - 1 million tons. This big amount came from shore discharges and open sea discharges. In addition there are more than 60 petroleum refineries on the coasts of the Mediterranean Sea. The petrol refineries were the most important sources of petroleum HC pollution and the amount was estimated as 20.000 tons a year.

Along Edremit and Aliağa bays there are many industrial activities, which pollute Aegean Sea. Ayvalık has many olive oil production factories. Aliağa has a petrochemical and a refinery complex. The tankers, which are carrying petroleum to the refinery in Aliağa are HC pollution sources because of their leakages and washing water.

Izmir Bay is the Centrum of the Aegean shores. It has a population of nearly 3 million and has many industries. It is very active in transportation. Many of the industries are discharging their wastewater to the Izmir bay without any treatment. Therefore the pollution is excessively large. Some industries discharge their wastewater to Melez, Manda, Arap streams and Gediz River. These streams bring a huge amount of pollutants to the Izmir Bay (Çağlar B.B., 1995).

These days Izmir has an efficient treatment plant and day by day a decrease in the pollution of the Izmir Bay is detected. The industries are forced to treat their wastewater before discharging their wastewater.

1.2. Sources of Hydrocarbon Pollution

The hydrocarbon pollution comes to our environment during producing, transporting, refining and marketing fuel every time. Therefore petroleum industries must be very careful because of the serious effects of hydrocarbons to the livings. Everyone know that several hydrocarbons are important for live but there are risk in taking them from the Earth, such as in drilling wells, storing fuel for future use and transporting it from place to place. In addition hydrocarbons seep to the surface of our earth along fault lines and cracks in rocks. As a result contamination of water is unavoidable. In Figure 1 the sources of hydrocarbon pollution are shown as a summary .

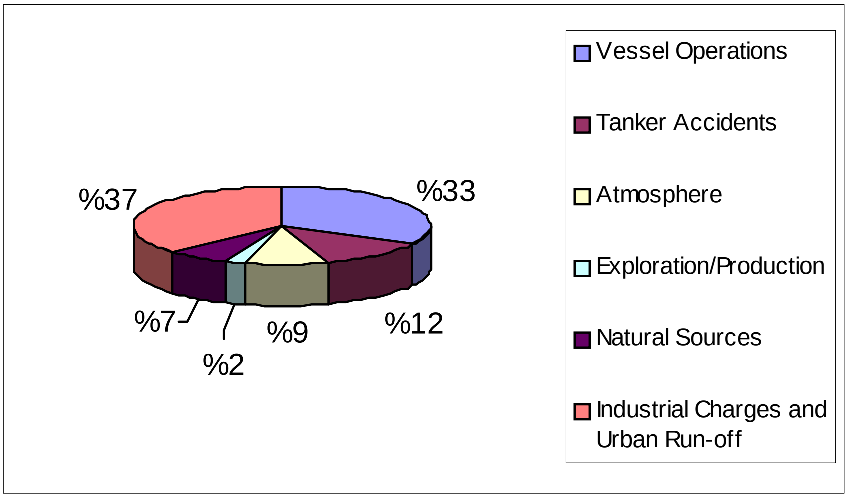


Figure 1. Sources of Hydrocarbon Pollution

Road traffic is another source of HC pollution that comes from vehicle exhaust and spillages from traffic accidents.

Hydrocarbons are used in many ways in our live such as fuel (for transportation and factories), electricity generation, machinery, asphalt, heating, wax (crayons, candels, medicines, ink, plastics, fertilizers, pesticides, paints and varnishes.

1. 3. Removal Techniques of Hydrocarbon Pollution

Hydrocarbon pollution in our world is a serious problem for the ecosystem. Therefore some techniques are applied to remove hydrocarbons from water. There are three ways to clean up hydrocarbons especially from groundwater, which are known as “Chemical Dispersion”, “Natural Dispersion”, and “Collection”.

-Chemical Dispersion

The most important problem with hydrocarbon slicks is the floating on the surface of the water. They also stick together. In order to solve this problem some chemicals have been developed to spray on the oil spread. This way can break the slick apart.

After the dispersant has been applied the slick breaks into some droplets, which dilutes into the water without causing any major problems (Figure 2). However, these dispersants can not be used on viscous oils, which includes some crude oils and all heavy fuel oils. In addition most crude oils that can be dispersed change their characteristics in a few hours in cold water, and can no longer be dispersed. This means that any dispersant response must be fast. For the viscous oil pollution dispersant-spraying aeroplanes and helicopters are generally used.

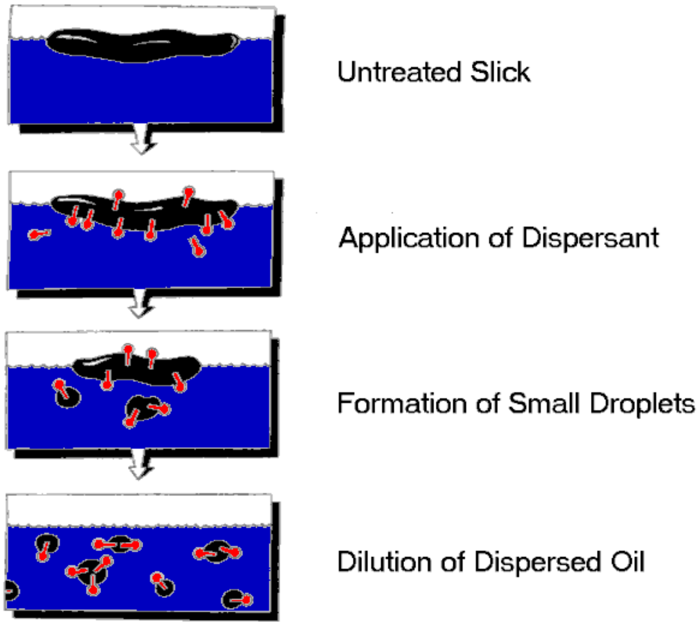


Figure 2. Determination of the Chemical Dispersion Technique

American scientists have developed new types of oil dispersants that are actually living organisms. These organisms are using oil as their feed. The genetically engineered organisms have been very successful in laboratory tests.

Although the less toxicity of modern dispersants, they are still a pollutant. Before the use of dispersants it must be decided whether they may cause more environmental damage than the spill would if it was left untreated. Whether dispersants should be used or not depends on the depth of the water, how strong the currents are, and what lives in the water.

-Natural Dispersion

Certain weather conditions help oil slicks to disperse and break down naturally. High wind and waves prevented the application of clean-up techniques. Oil slicks are mostly dispersed by natural dispersion even when other clean-up methods are used. It is estimated that only around 8 percent of the oil spilled was recovered in the Exxon Valdez spill despite the huge sums spent on the clean-up. The rest was dispersed by the fierce Arctic storms of the region.

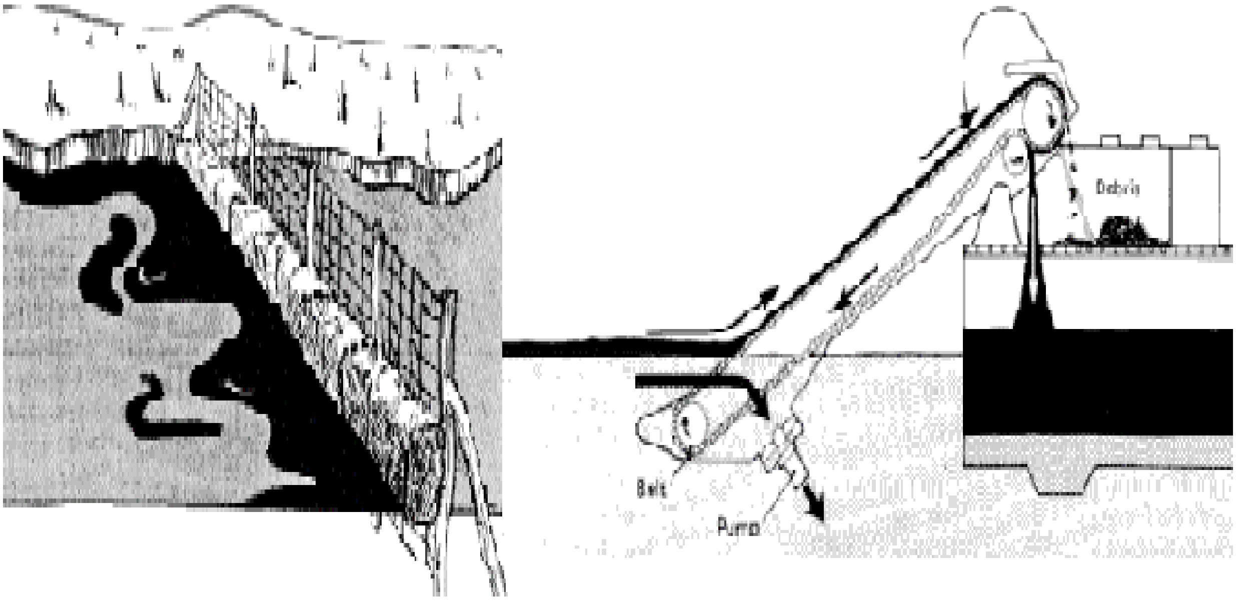
-Collection

Collection is the best way to clean up an oil slick. Not only is the oil completely removed from the environment (unlike chemical and natural dispersion techniques), but it can also be used again.

There are two ways to collect spilled oil, which are known as booms and skimmers. Booms (Figure 3) do the first step of collecting the spilled oil, which come in two types: The boom on the left is inflatable, with a chain along the bottom to keep it the right way up. The boom on the right uses solid floats. Inflatable booms are easier to store and they take up much less space. However they are not resistant to damage. Booms can be obtained from locally available materials, such as fences and bales of hay.

Figure 3. Booms as the First Collection Step

After booms, which are used as the first collection step, skimmers or sorbents are used as the second step of collecting oil slicks.



(a) (b)

Figure 4. (a)Suction Skimmers, (b) Adhesion Skimmers

Skimmers (Figure 4) can be grouped in two types: suction and adhesion. Suction skimmers (Figure 4a) operate like giant hoovers and suck the oil off the water. However, these suck up lots of water as well. Often more than 90 percent of the liquid collected is water. Adhesion skimmers (Figure 4b) sweep a material through the spill. The oil sticks to the material. and is carried away from the spill. The oil is then squeezed out of the material.

Sorbents are materials, which can absorb oil. These materials can be either natural, such as straw, grasses, coconut husks, wood chips, or synthetic, such as polypropylene. They can be used in a variety of shapes, such as sheets. Large volumes of oil can not be collected by sorbents. Therefore sorbents should be used in the final stages of cleaning when only small parts of oil are left. There are ships that integrate these methods to make a complete oil collection system. This system was used to clean up oil slicks after the Gulf War. A ship lays inflatable booms around a section of the slick, and then sucks the oil off the water using vacuum pumps as shown in Fig.4.b. The mixture of oil and water sucked in is separated, and the water is pumped back out into the sea. The oil is kept in storage tanks on the ship, from where it can be off-loaded to a tanker or a refinery.

Hydrocarbon bioremediation is an alternative and efficient way to remove hydrocarbons biologically. A company in U.S.A discovered a formula for hydrocarbon bioremediation in which naturally occurring communities of aerobic and microaerophilic microorganisms, that have been selected from worldwide soil and water sources, have been used. These communities of microbes have the ability to effectively recycle a wide range of compounds and hydrocarbons by converting them into non-toxic components. The microorganism mixture is composed of single cells ranging in size from 1 to 10 microns. They have reported that Archibacteria, which is selected from the natural environment for their collective ability to degrade hydrocarbon molecules, is very effective.

This Formula is packaged in powder. The microorganisms are blended with nutrients and dried into an inert base. The importance is that powder is a living mechanism. Therefore it must be very careful because caustics, high concentrations of chlorine, high temperatures, some solvents, and chemicals can destroy it. The microorganism mixture is very effective by removing aromatics, benzene, biphenyl, branched hydrocarbons, crude oil, diesel fuels, fuel oils, gasoline, heating oils, jet fuels, marine fuels, motor oils, toluene and xylene pollutants.

Organic compounds can be removed also by unit processes such as reverse osmosis, ion exchange, air stripping, adsorption, oxidation and coagulation. Reverse osmosis is a growing research area for organic compound removal but its application is expensive. Polar and ionized organic compounds (phenols, amines) that are highly soluble can be removed by ion exchange. Air stripping eliminates volatile organics, which have low solubility and molecular weight. Adsorption is recommended especially for the removal of pesticides and polynuclear aromatic hydrocarbons. Oxidation and/or coagulation are suitable for degrading and precipitating high molecular weight humic and fulvic acid. In general oxidation and coagulation are applied as a first stage process prior to ion exchange, air stripping and adsorption for the removal of a wide range of organic pollutants from water (Montgomery, M.J., 1985).

1. 4. The Scope of the Study

The scope of this project was to investigate the adsorption of benzene, toluene and o-xylene from water on natural zeolite and surfactant-modified zeolite. Zeolite was modified with a small-chain surfactant tetramethylammonium (TMA^+) and a long-chain surfactant dodecyl amine (DA) to increase the adsorption capability of non-polar aromatic hydrocarbons. The sorption results for natural zeolite and surfactant-modified zeolite were compared.

The hydrophobicity of surfactant-modified zeolite was investigated by contact angle measurements. Zeolite was modified with tetramethylammonium (TMA^+) , dodecyl amine (DA) and sodium dodecyl sulfate (SDS) (pH=4) for these measurements. Surface tension measurements of the surfactant solutions were performed to find the most favorable case.

CHAPTER 2

HYDROCARBON ADSORPTION ON ZEOLITES

2.1. Hydrocarbons

Hydrocarbons are compounds which contain only carbon and hydrogen. They are divided into two groups: saturated and unsaturated hydrocarbons.

2.1.1. Saturated Hydrocarbons

Saturated hydrocarbons are known as alkanes (paraffins). Alkanes contain only single carbon- carbon bonds. Carbon chains for alkanes can take different forms: unbranched (normal alkanes or *n*-alkanes), branched or rings (cyclic alkanes). Alkanes melting points and boiling points respectively change between (–187.7^{o}C) – (36.8 ^{o} C) and (-161.7 ^{o} C)- (343 ^{o} C). They are insoluble in water and their densities are lower than one.

Petroleum and crude oil mostly contain alkanes. Crude oil is a viscous, dark mixture in which alkanes and aromatic hydrocarbons takes place. They can be separated by fractional distillation. It is also known that petroleum is the principal source of carbon, from which the organic starting materials for some products (plastics, pharmaceuticals) are made.

Natural gas is another alkane source which is mostly methane. Some anaerobic bacteria can produce methane by decaying organic matter.

Fuel is the greatest use of alkanes in recent years. In the United States 38% of motor fuels, 34%of fuel oils and 6% for aviation fuels have been consumed in the last years.

2.1.2. Unsaturated Hydrocarbons

Alkenes and Alkynes are unsaturated hydrocarbons because of their double and triple bonds. Therefore they have fewer hydrogens than alkanes. All groups surrounding each carbon should lie in one plane with bond angle of about 120^{o} for alkenes. In addition each carbon have approximately trigonal geometry with H-C-H bond angles of 117°. Alkynes are structurally linear.

Alkenes (olefins) and alkynes have nearly the same physical properties as alkanes. They are less dense than water and also insoluble in water.

Alkenes are considered as petroleum product but they are not obtained from oil wells. They are produced synthetically from saturated hydrocarbons by a process called cracking. Large saturated hydrocarbons are cracked into smaller unsaturated hydrocarbons by cracking. Ethylene is the most important organic compound produced synthetically by chemical industries and can also be obtained from petroleum. It is the starting material for many industrially important organic compounds. Ethylene is used for the production of polyethylene, polystyrene, antifreeze, fibers and solvents.

Alkynes are mostly produced by thermal cracking. Ethylene is cracked to acetylene and H_2 at temperatures above 1200°C. Acetylene is very soluble in acetone.

2.1.3. Aromatic Hydrocarbons

Benzene is known as the simplest aromatic hydrocarbon. The structure of benzene shows two types of carbon-carbon bonds: single and double bonds. Benzene is a clear, colourless liquid with a characteristic, aromatic hydrocarbon odour and is highly flammable. It is extremely flammable both in liquid and gas phase. Its vapour is heavier than air and may spread long distances. In liquid phase it can spread quickly float on water and may travel to distant locations. At high temperatures benzene can form toxic gases.

Benzene occurs naturally in crude oil, natural gas and in some groundwaters. It is also manufactured from crude oil and is present in crude oil vapours. The main use of benzene is as starting material for the manufacture of chemicals such as cyclohexane, ethyl benzene, phenol and maleic anhydride. It was formerly used as a solvent, but in most cases safer substances have now replaced this use. Benzene can contain small amounts of toluene and xylene. In addition toluene and o-xylene are derivatives of benzene. Petrol contains 2 to 3 % benzene in the United Kingdom. Small amounts of it are produced when some organic substances burn incompletely, for example, it is found in cigarette smoke and vehicle exhausts. It is produced as a by-product during the manufacture of coke from coal (Canadian Center for Occupational Health and Safety Report, 1997-2000).

Toluene is an organic liquid with a sweet and benzene-like odor. It is mostly used for the production of benzene and urethane.

Toluene may be found in some public or private drinking water supplies. It is released into the atmosphere from the volatilization of petroleum fuels, toluene-based solvents and thinners and from motor vehicle exhaust. It is also released in wastewaters or by spills on land during the storage, transport and disposal of fuels and oils. According to EPA's Toxic Chemical Release Inventory, toluene releases to land and water totalled over 4 million lbs., primarily from petroleum refining industries between 1987 to 1993. The largest releases directly to water occurred in Connecticut and West Virginia.

Xylenes are known as three different isomers, which are m-xylene, o-xylene, p-xylene. They are clear liquids with a sweet odor. Xylenes are generally used as a solvent that is much safer than benzene. They are used as a part of BTX component (benzene-toluene-xylene) in gasoline. Xylene mixtures are used to produce phthalate plasticizers, polyester fiber, film and fabricated items. (Canadian Center for Occupational Health and Safety Report, 1997-2000; Loudon G.M., 1984; Cadena F. *et al*,1995).

The most important water pollution increases from spills of hydrocarbon fuels and solvents. Gasoline, diesel, and aircraft fuels generally spill from rail or tank cars or from pipeline leaks. Leakage from underground storage tanks is another source of hydrocarbon spill. On the other hand hydrocarbon waste streams come from some industries which are using organic solvents in large quantities as a part of manufacturing process. Benzene, toluene and o-xylenes are mostly found in petrochemical spills (in crude oil, gasoline, diesel, and jet fuel spills) (Harwell J.H. *et al*, 1999; Cadena F. *et al*, 1995).

2.1.4. Health Effects

2.1.4.1. Benzene

Benzene is harmful if inhaled or swallowed and is a central nervous system depressant. The vapour may cause headache, nausea, dizziness, drowsiness and confusion. Benzene may cause blood and bone marrow effects. It evaporates easily, and most people can just detect its distinctive smell at concentration between 2.5 and 5 parts per million (ppm) in air. It can cause skin and eye irritation. It is also an aspiration hazard because swallowing or vomiting of the liquid may result in aspiration into the lungs. Benzene is considered a cancer hazard and can cause cancer at levels above maximum contaminant level (MCL). It may cause genetic damage as a mutagenic above MCL.

Autopsy of a youth who died while inhalation benzene indicated that benzene was distributed to the urine, stomach, bile, liver, kidney, abdominal fat, and brain. According to some searches benzene can also effect the fetus and placenta. In addition it was detected in liver and in the bone marrow.

Lethal oral doses of benzene are estimated to be 10 mL in humans, nonlethal oral doses of benzene can impact the nervous, hematological, and immunological systems. Ingested benzene produces symptoms of neurotoxicity at acute doses of 2 ml for humans. A four week exposure of mice to >=8 mg of benzene/kg/day in the drinking water induced the synthesis and catabolism of monoamine neurotransmitters and produced dose related decreases in red-blood cell parameters and lymphocyte numbers.

Exposure of the general population to benzene may occur in residential areas near chemical manufacturing sites; exposure has also been associated with the ingestion of contaminated food and drinking water, cigarette smoking, and pumping gas. Estimated daily intake values for 70-kg adults was investigated in average 2.86 g/kg/day for drinking water, 7.8 g/kg/day for smoking 20 cigarettes/day, and 2.76 g/kg/day for exposure to emissions from nearby chemical manufacturing plants.

The acute toxicity of benzene inhalation depends on the concentration of benzene and duration of exposure. It effects directly the central nervous system. Symptoms may range from mild manifestations such as headache and light-headedness (50-250 ppm) to more severe effects that include convulsions, respiratory paralysis, and death (20,000 ppm, 5-10 minutes) (Daugherty, M.L., 1992).

According to EPA the Maximum Contaminant Level (MCL) must be 5 parts per billion (ppb) (Table 1) because EPA believes that this low value requires a removing process if it occurs in drinking water.

2.1.4.2. Toluene

Toluene causes minor nervous system disorders such as fatigue, nausea, weakness, confusion if the levels are above MCL and it occurs in very short periods of time. These effects are known as short-term effects. More serious problems consist if a lifetime exposure at levels above the MCL occurs that is known as long-term effects. These health effects are spasms, tremors, and impairment of speech, hearing, vision, memory, coordination; liver and kidney damage. No certain evidence is reported to state if toluene has the potential to cause cancer from lifetime exposures in drinking water.

2.1.4.3. Xylene

Xylenes cause disturbances of cognitive abilities, balance, and coordination when people are exposed to it at levels above the MCL for relatively short periods of time. They cause also damage to the central nervous system, liver and kidneys if the exposure occurs during a lifetime above the MCL.

Table 1.Current Drinking Water Standards

Organic Chemicals	**MCLG[1] (mg/L)[2]**	**MCL[1] (mg/L)[2]**	**Potential Health Effects From Ingestion of Water**	**Sources of Contaminant in Drinking Water**
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Toluene	1	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Xylenes (total)	10	10	Nervous system damage	Discharge from petroleum factories; discharge from chemical factories

[1] **Maximum Contaminant Level (MCL)** - The highest level of a contaminant that is allowed in drinking water. MCLs are enforceable standards.

Maximum Contaminant Level Goal (MCLG) - The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.

[2] Units are in milligrams per liter (mg/l). Milligrams per liter are equivalent to parts per million.

In Table 1 a summary of the health effects of benzene, toluene and xylenes are shown according to the "National Primary Drinking Water Regulations" (NPDWRs or primary standards) which are legally enforceable standards. These standards protect public health by limiting the levels of contaminants in drinking water.

2.2. Zeolites

The development of "*Zeolites*" increases in many ways and its use raise in many scientific areas. Especially in inorganic and organic chemistry, physical chemistry, colloid chemistry, biochemistry, mineralogy, geology, surface chemistry, oceanography, crystallography, catalysis and in all types of chemical engineering processes like separation and recovery of gases, liquids and ions, catalysis and ion exchange. Nowadays 50 types of natural zeolites and more than 120 synthetic zeolites have been reported in literature (Breck D.W., 1974; Vasant E.F., 1990).

Zeolites are porous, crystalline, hydrated aluminosilicates of group I and group II elements (Na, K, Mg, Ca, Sr, Ba) from natural and synthetic sources. Their frameworks enclose regular networks of interconnected channels and cavities which contain cations and water molecules. The main unit of zeolites is a tetrahedron of four oxygen atoms surrounding a silicon or aluminum atom. The SiO_4 and AlO_4 tetrahedra is arranged so that each oxygen atom is shared between two tetrahedra. The aluminum atom has one less positive charge than silicon. Therefore the framework is negatively charged (Dyer A., 1978; Barros M.A.S.D *et al*, 1997).

Natural Zeolites are natural volcanic minerals with several characteristics and are found in massive deposits in many regions of the world. Clinoptilolite is the most abundant natural zeolite of the heulandite group. The uses of these materials are based on their physicochemical properties (Rivera A., *et al* 2000). Clinoptilolite is thermal resistant up to 750 ^{o}C. The Si/Al ratio various between 4.25 and 5.25.Their ion exchange property is very important especially for radioactive waste treatment, heavy metal and ammonia removal from wastewater (Barros M.A.S.D *et al*, 1997; Breck D.W., 1974).Ames used clinoptilolite to remove Cs and Sr from radioactive wastwater. (Akdeniz Y., 1999.)

Zeolites (natural and synthetic) have strong affinity for water. Therefore they are mostly used as drying agents (Chen N.Y., 1976). They are used in gas purification systems. It was reported that zeolites are used as cation exchange filter for the removal of gold from wash and wastewater in gold processing industries. In addition zeolites are used as soil conditioner and for odour control (Akdeniz Y., 1999).

2.3. Adsorption of Hydrocarbons on Zeolites

Many scientists investigated the adsorption properties of hydrocarbons on zeolites. Generally synthetic zeolites were used for hydrocarbon adsorption.

The thermodynamics and kinetics of gas phase adsorption of organic molecules by zeolites had been investigated using aliphatic and aromatic hydrocarbons (Pope C. G., 1986, Hill and Seddon, 1991). Breck and Sons (1974) reported that the pore characteristics of zeolite structure can be obtained by sorption of organic molecules. Zeolite X and zeolite Y selectively adsorb sugars and sugar alcohols from aqueous solution was reported in a study (Franklin K.R. *et al* , 1988). Other studies on liquid phase adsorption in silicalite were the adsorption of alcohols, phenols, cresols, benzyl alcohols and liquid-hydrocarbons (Milestone and Bibby,1981; Narita E. *et at*,1985; Ma and Lin, 1985). It was reported that the adsorption from aqueous solution depends not only on the pore structure but also on the competition between the organic adsorbate and water for the adsorption site (Shu H. *et al*, 1997).

Papaioannou *et al* (1997) studied the adsorption of benzene, cyclohexane, methylcyclopentane and cyclohexane on faujasite zeolites in columns. The used zeolite type was NaX, $Ni_{20}X$, NaY and $Ni_{14}Y$. $Ni_{20}X$ and $Ni_{14}Y$ zeolites were prepared from NaX and NaY by ion exchange. The analyses were carried out by GSC (Gas-solid chromatography). In the chromatography column 2 g zeolite sample with a diameter of 0.3-0.5 mm was placed and dehydrated by He stream with a flow rate of 24ml/min. Dehydration was first at 723 K for 4 h and then at 673 K for 10 h. $Ni_{20}X$ and $Ni_{14}Y$ zeolites were reduced by H_2 with a flow rate of 58 ml/min for 2 h at 673 K. Maximum 10μl pulses of benzene, cyclohexane, cyclohexene and methylcyclopentane were injected into the column at 673 or 573 K. Helyum was used as carrier gas with a flow rate of 24 ml/min.

In this study the adsorption isotherms were obtained and was fitted to the Langmuir equation as follows:

$$a = \frac{G \times b \times P}{(1 + b \times P)}$$

where G is the maximum adsorption capacity, b the adsorption constant and P partial pressure. At the beginning of the isotherm it was found that $b \times P << 1$. Therefore the Langmuir equation is close to the Henry equation;

$$a = G \times b \times P = K \times P$$

where $G \times b$ is equal to K which is known as the Henry constant. K gives an information about the adsorbate-adsorbent interaction. If K increases the adsorption gets stronger.

At 673K it was found that the maximum adsorption capacities *G* are in this sequence: G(Na zeolites)>G(Ni zeolites)>G(reduced Ni zeolites). For reduced Ni zeolites G was greater at 573K than at 673K. The decrease of G at 573K gave the result that there is a decrease of the available adsorption sites with temperature. According to the Langmuir model the saturation adsorption capacity is temperature dependent.

Then they showed that the adsorption of benzene, cyclohexene, cyclohexane, and methylcyclopentane on Na, Ni and reduced Ni zeolites occurs chemically (chemisorption) at 673K and 573K. The maximum adsorption capacity *G* sequence for NaX, $Ni_{20}X$, and reduced $Ni_{20}X$ zeolites was benzene>cyclohexene>cyclohexane ≈ methylcyclopentane at 673 K. This sequence was same for NaY,$Ni_{14}Y$ and reduced $Ni_{14}Y$ at 673 K. In addition they found that benzene, cyclohexane and methylcyclopentane are more adsorbed on NaX than on $Ni_{20}X$ and reduced $Ni_{20}X$. They reported also that the strong adsorption of benzene could be because of the special interaction between π electrons of the benzene ring and Na^+ adsorption sites. Cyclohexene (polar molecule) is more strongly adsorbed on Na^+ ions than cyclohexane or methylcyclopentane.

Borovkow *et al* (1978) studied also the adsorption of benzene on NaX, $Ni_{20}X$, NaY and $Ni_{14}Y$ and they reported that the micropores are channels between the supercages in these zeolites. As many as 4 benzene molecules are adsorbed per supercages and the diffusion between neighboring supercages were not prevented.

Choudary and Srinivasan (1986) reported that benzene interacts more strongly with Na^+ ions than with protons in the zeolite structure. That's the result that benzene is a weak base and the interaction with protons is weaker compared with that of the π benzene ring electrons with Na^+ ions. If temperature increases, the interaction of benzene with protons is negligible. Especially when the temperature is above the critical temperature of benzene (562K), no physical adsorption occurs.

Gündüz (1992) searched also about benzene adsorption on NaX and NaY zeolite. In this study the liquid phase adsorption of Benzene on NaX and NaY zeolite at 21°C was investigated. It was shown that the micropore volume is important for the determination of the adsorption capacity. According to this study benzene is a suitable adsorbate for the determination of surface area. In this study zeolite was firstly activated in an oven. The activation temperature was chosen from the literature as 350°C. For the analyses gas chromatography was used. The results showed that the benzene adsorption isotherms are Type I. It was reported that benzene is adsorbed selectively on NaY type zeolite.

According to this study, a benzene molecule can be adsorbed on the surface in two ways. If the benzene molecule is in the horizontal form the occupied area of the benzene molecule is 40Ǻ. On the other hand if the benzene molecule is in the vertical form the area is 25 Ǻ. This difference is because of the л-electrons of benzene molecules. Kacirek *et al* (1980) investigated the benzene adsorption on NaX, NaY and NaHY between 423-623K and found that the adsorption of benzene fits the Langmuir model.

The adsorption of n-Hexane/n-Olefin mixtures from liquid solution was investigated on NaX zeolites (Herden H. *et al*, 1981). Three milliliters of n-hexane/n-olefin solution of known composition was added to about 1 g activated zeolite (20hr at 673 K, 0.01 Pa pressure). This system was stirred at 293 K. After 48 hr the equilibrium composition was reached. The solution was analyzed by GC (Gas Chromatography). They reported that olefins are adsorbed selectively in the large cavity of NaX zeolite because of their greater specific interaction energy.

Ching and Ruthven (1989) investigated the sorption and diffusion of amino acids (glycine, lysine, alanine, phenylalanine) in KX zeolite crystals. X and Y type zeolites (7.5-8.0 Å) are useful and size selective. The analyses were done by a liquid chromatography. The column was packed with KX zeolite crystals with the mean size of 50μm. Large unaggregated zeolite crystals were used to increase the intracrystalline resistance and to omit macropore diffusion resistance. The results showed that the adsorption of alanine and lysine is independent of temperature, but a little dependence was shown for the adsorption of glysine. They reported that the adsorption of phenylalanine was not significant probably because of kinetic limitations. According to the experimental results the sequence of diffusivities was glycine> alanine> lysine. This sequence is also valid for the molecular size of the molecules. The sequence of diffusional activation energies E was glycine<alanine<lysine probably because of the molecular size of these molecules.

The effect of moisture on the adsorption of p-xylene, o-xylene, ethylbenzene and mesitylene was investigated (Yan T.Y., 1988). ZSM-5 type zeolite and was used in this study. The adsorption of hydrocarbons by ZSM-5 depends on its Al content or SiO_2/Al_2O_3 ratio. The moisture content has no effect on hydrocarbon adsorption of ZSM-5 with low Al content (or high SiO_2/Al_2O_3 ratio). This is because of hydrophobicity of ZSM-5. It was reported that the presence of moisture for high-silica ZSM-5 increases the relative adsorption of o-xylene to p-xylene. For low-silica ZSM-5 it was interesting because the moisture content lowers the p-xylene and total hydrocarbon adsorption without effecting the adsorption of ethylbenzene and o-xylene. This result showed that hydrocarbons prefer different types of sites in the zeolite cavities. Pope (1986) reported that sorption capacities for benzene, toluene and p-xylene was similar both on silicalite and ZSM-5.

2.4. Modification of Zeolites for Hydrocarbon Adsorption

Many modification techniques were applied to improve zeolites for several purposes. Modification techniques are (1) Ion exchange process, (2) Preadsorption of polar molecules, (3) Zeolitic framework modification: i) Pore size modification by crystallographic changes, ii) Internal and external modification of the zeolite structure (silanation, disilanation, boranation, implanation of boron-nitrogen compounds, modification by inorganic acids and their salts), iii) External surface modification (Vasant E.F., 1990).

In recent years modification of zeolite has been used to change the physical-chemical properties of natural zeolites for different purposes. In the literature mostly acid treatment (dealuminization) was used as a modification technique to make the zeolite surface hydrophobic.

Chen (1976) investigated the hydrophobic properties of zeolites by acid treatment with HCl. In this study changes in the sorption for cyclohexane were measured. Two methods were used for dealuminization of two samples of synthetic mordenite (zeolon): (1) Acid extraction by refluxing in 2N HCl solution, (2) Repeated alternate treatments, with the HCl solution for 4hr and followed by treating with 1 atm of steam at 538° C for 2 hr. The sorption measurements were done gravimetically at 25° C with a quartz spring. Adsorption isotherm for Si/Al ratio of 47 of dealuminized mordenite sample shows type II (S-shaped) isotherm for cyclohexane.

During the dealuminization aluminum was removed from the structure of synthetic zeolon. Therefore the affinity of zeolon for cyclohexane was increased. The aluminum removal of 30% showed an increase of 15% in cyclohexane sorption capacity. Cyclohexane sorption capacity had a maximum value at Si/Al ratio between 10 and 20 and decreased to a constant value above a Si/Al ratio of 40.

As the aluminum was removed from the zeolite hydrocarbon molecules continued to fill the pores at low P/P_0's, but water molecules were no longer filling the pores of the zeolite samples with high Si/Al ratio. The acid treated zeolon with Si/Al>80 adsorbed little or no water molecules at these relative pressures. As a result it was reported that *“highly siliceous zeolites are hydrophobic”* .

It was reported by Choudhary and Srinivasan (1986) was reported that diffusion of a compound in the zeolite depends on the chemical environment of the diffusing compound and on Si/Al ratio, degree of cation exchange and pretreatment conditions of zeolites. Benzene sorption and diffusion by H-ZSM-5 was investigated in this study. It was reported that the sorption isotherms are nonlinear at low $P/P_{0.}$ At 523 K it was shown that the sorption of benzene increases with decrease in the Si/Al ratio. In contrast, the diffusion of benzene increases with the increase in the Si/Al ratio at the same temperature. It was observed that the increase of the degree of H^+ -exchange from 0.51 to 0.99 in H-ZSM-5 decreases the sorption and increases the diffusion of benzene. The H^+-exchanged H-ZSM-5 samples were obtained by exchanging them with 1 M sodium nitrate solution repeatedly at 353K. Effective channel diameter might be reduced as H^+ is replaced by Na^+. The increase in the Na^+ content showed that benzene interacts more strongly with Na^+ ions than with H^+ ions.

The effect of deammoniation temperature showed that the sorption of benzene decreases due to the dehydroxylation occuring during deammoniation at high temperature (1223 K). However, the diffusion of benzene increases with deammoniation at high temperature. It was reported that deammoniation at high temperature causes a certain amount of dealumination of the zeolite. The sorption of benzene in H-ZSM-5 decreased with steam treatment because of the decrease in the acidity of the zeolite, but the diffusion increased. They showed that diffusion increases because of dealumination and the decrease in the acidity of the zeolite during steam treatment like for deammoniation. They also reported that a small change in the acidity of the zeolite can cause a change in the effective channel diameter.

Post et al. (1984) reported that the diffusion of 2,2-dimethyl butane decreases with the increase of Al-content in H-ZSM-5 at 373K. They obtained a decrease in the diffusivity with the increase in the Al-content of the zeolite.

Orthophosphoric acid was also used for acid treatment. Natural zeolite was treated with 4 M H_3PO_4 solution at 373K for 5,10,20 and 40 minutes. The treatment with H_3PO_4 reduced the Fe and Al contents without framework destruction (Pozas C.*et al*, 1996).

2.4.1. External Surface Modification of Zeolites

External surface modification becomes important if nonpolar molecules are adsorbing on charged surfaces. In this case organic cations (surfactants) are very important to modify charged surfaces into hydrophobic surfaces. External surface modification controls the pore-opening without affecting the internal pore system of zeolite. Modifying agents with larger molecular size than the zeolite pores are used so that they can not enter the poresand interact only with the external surface.

There are several methods for this type of modification. It was reported that $Si(OCH_3)_4$ causes a reaction with the hydroxyl groups on the H-Zeolite type and covers the external surface of the zeholite after a serie of reactions. Another way is the usage of methyl-chlorosilanes to form silica-polymers at the zeolite external surface. Disilane is also used as modifying agent at high temperature (Vasant E.F., 1990).

Surfactants (surface-active agents) are the most versatile products of the chemical industry. They are used in many areas such as environmental engineering, food science, mineral science, biotechnology, detergent industry, agricultural activities and printing. When a surfactant is present at low concentration in a system, it has the property of adsorbing onto surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. Interface is explained as a boundary between any two immiscible phases, surface means an interface where one phase is a gas (usually air). Surfactants are usually used to decrease the interfacial free energy. The interfacial free energy is the minimum amount of work required to create that interface.

Surfactants have a characteristic molecular structure consisting of two structural groups: hydrophilic group, hydrophobic group (Figure 5).

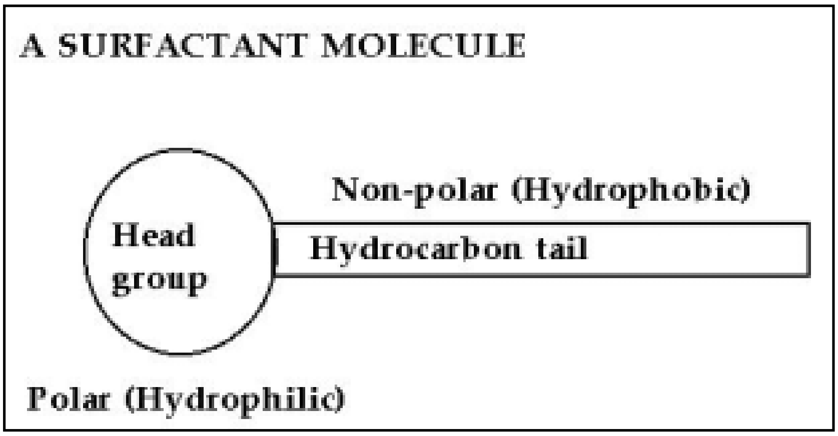


Figure 5. Parts of a Surfactant Molecule

The hydrophobic group is usually a hydrocarbon chain and the hydrophilic group is an ionic or highly polar group. The classification of surfactants depends strongly on the nature of the hydrophilic group: (1) Anionic; surface active portion has negative charge (alkylbenzene sulfonate), (2) Cationic; surface active portion has positive charge (quaternary ammonium chloride), (3) Zwitterionic; positive and negative charges present together in the surface active portion (sulfobetaine), (4) Nonionic; surface active portion has no ionic charge (polyoxyethylenated alkylphenol).

Naturally available surfaces are generally negatively charged like clinoptilolite rich natural zeolite and silica. The positively charged cationic surfactant will be adsorbed onto the surface because of electrostatic attraction and its hydrophobic group is oriented away from the surface (Rosen M.J., 1989).

Cadena and Cazares (1995) used clinoptilolite-rich zeolitic tuffs for the sorption of benzene, toluene, o-xylene (BTX) from aqueous solution after surfactant modification. The zeolitic tuffs were taken from different locations which are CH (Crisman Hill, Oregon), TL (Tilden,Texas), WN (Winston, New Mexico), and BW (Bowie, Arizona). They used four different surfactants, which are summarized in Table 2. TMA^+ has the smallest molecular structure. $HDTMA^+$, $EHDDMA^+$ and CP^+ are long-chain alkyl groups.

Table 2. Physicochemical Properties of the Surfactants

Abbreviation	**Molecular Name**	**Chemical Formula**	**Used form**	**M.W. (g/mole)**	**Solubility (g/liter)**
TMA^+	Tetramethylammonium	$C_4H_{12}N^+$	Cl salt	74	56
$HDTMA^+$	Hexadecyltrimethylammonium	$C_{19}H_{42}N^+$	Br salt	284	100
$EHDDMA^+$	Ethylhexadecyldimethylammonium	$C_{20}H_{44}N^+$	Br salt	298	100
CP^+	Cetylpyridinium	$C_{21}H_{38}N^+$	Cl salt	304	>100

According to the characterization studies the external surface areas were found as 200.1m^2/g for BW, 56.8 for TL, 55.4 for CH and 14.9 for WN.

In Table 3 the linear sorption coefficient K values are shown for the untreated and treated samples obtained for benzene, toluene, o-xylene (BTX) removal.

Table 3. K values for BTX removal

Surfactant	Zeolite	o-Xylene	Toluene	Benzene
None	CH	1.2	1.2	1.0
	TL	0.0	2.5	0.2
	WN	0.0	0.2	0.6
	BW	0.0	0.6	0.8
TMA^+	CH	3.9	6.9	63.0
	TL	1.8	4.5	34.6
	WN	0.3	0.7	1.3
	BW	0.0	0.6	0.8
$EHDDMA^+$	CH	38.3	24.9	11.5
	TL	72.8	37.9	13.0
CP^+	CH	50.5	26.3	11.9
	TL	73.3	23.7	15.7
$HDTMA^+$	CH	94.8	27.5	14.2
	TL	73.9	35.4	1.8

The results showed that TMA^+ was the most effective surfactant for benzene sorption from water. It was effective especially for CH and TL zeolites. It was interesting that no significant sorption occurs for the untreated zeolites. The removal sequence of pollutants was benzene>toluene>o-xylene for all the samples modified with TMA^+. The TMA^+ cations attach onto the exchange site so that the charge of the cation is very close to the exchange site on the surface of the solid. It was reported that the benzene molecule fits well in the spaces created between TMA^+ groups.

The removal sequence of BTX was o-xylene>toluene>benzene for the zeolitic tuffs treated with long-chain surfactants. The long-chain surfactants are larger than the structural channels in zeolitic tuffs. Therefore the modification should occur on the most accessible outer sites of the samples. The reached maximum K values are shown in Table 3.

Cazares (1992) reported in another study that the amount of pollutant sorbed on zeolitic tuffs is a linear function of the amount of long-chain surfactant on the surface of the tuff. These zeolitic tuffs induced an effective environment for partition of non-polar organic compounds such as benzene, toluene, o-xylene. This result was also valid for clays modified with long-chain surfactants.

BTX removal by clays treated with TMA^+ was reported in the literature (Cadena F. *et al*, 1990; Cadena and Cazares 1990). The TMA^+ modified clay showed an efficient removal of benzene from water selectively over closely related compounds.

Zhang *et al* (1993) reported the stability of the $HDTMA^+$ sorption on montmorillonite. The sorption of $HDTMA^+$ was due to cation exchange effect, length of the tail group and van der Waals forces between the tail and the surface. This result showed that $HDTMA^+$ sorption on clinoptilolite is a function of cation exchange, van der Waals forces and hydrophobic forces that are acting together.

Shu H. *et al* (1997) reported that surfactant loaded pillared clay can adsorb phenol and chlorophenols from aqueous solution. However it was not a good method for use as a practical adsorbent. They obtained a high capacity for phenols by using hydrophobic silicate with a high Si/Al ratio. At the Si/Al ratio of 563 the capacity reached to the maximum. In addition silicalites was not found as good adsorbents for large molecules which can not access their internal pore structure. Dealuminated zeolite beta was observed to be an efficient adsorbent because of its large pore structure .

Valsaraj K.T. *et al* (1998) reported that there is an increase in adsorbed phenanthrene with increasing surfactant surface concentration of alumina. They used sodium dodecyl sulfate (anionic surfactant) to modify the alumina. According to the results it was shown that the modification is pH dependent. The maximum adsorption capacity of alumina for sodium dodecyl sulfate was obtained at the pH value of 3.9 where alumina surface is positive. The adsorption of phenanthrene increases linearly with increasing sodium dodecyl sulfate concentration.

2.5. Comparison of the Method Used in this Project with other Methods to Remove Hydrocarbons

Activated carbon has a wide usage in the area of environmental engineering especially for the removal of organic contaminants. It is also used as an adsorbent in the chemical industry because of its high adsorption capacity. However the use of activated carbon has some disadvantages. It is a relatively expensive adsorbent and has high regeneration and attrition costs. It will be economical only when it can be easily regenerated or disposed of the spent carbon. There are some examples of recovery technologies which are high temperature desorption, solvent extraction and microbial degradation. Sometimes the regeneration cost can be 80% of the operating cost. Therefore an economical way is needed for the removal of organic pollutants.

In order to solve the environmental problem of hydrocarbon pollution the treatment process must be effective and economical. Turkey is a very rich country of natural zeolites. They are widely available and have low cost. Therefore they are very suitable for environmental remediation.

CHAPTER 3

MATERIALS AND METHOD

3.1. Materials

3.1.1. Zeolite

In this study clinoptilolite rich natural zeolite was taken from Gördes, West Anatolian. Zeolite samples were prepared to obtain representative samples (Table 4) by mixing three different particle sizes.

Table 4. Particle Size Ranges of Natural Zeolite

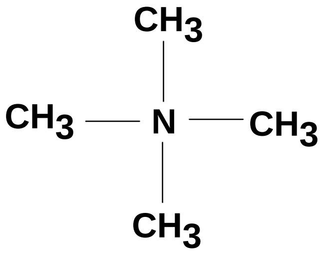
Zeolite	Size (mm)
Clinoptilolite- Rich Natural Zeolite Gördes II	0-0.7
	0.7-1.8
	1.8-3.5

The samples were washed three times with deionized water at 100°C for 1 hour to remove impurities and were allowed to settle down overnight. After the liquid phase was separated from the solid phase, zeolite samples were dried in two steps which were drying at 100°C in an oven for 1 hour and drying at 160 ° C at nearly 500 mmHg in a vacuum oven for 30 minutes.

3.1.2. Surfactants

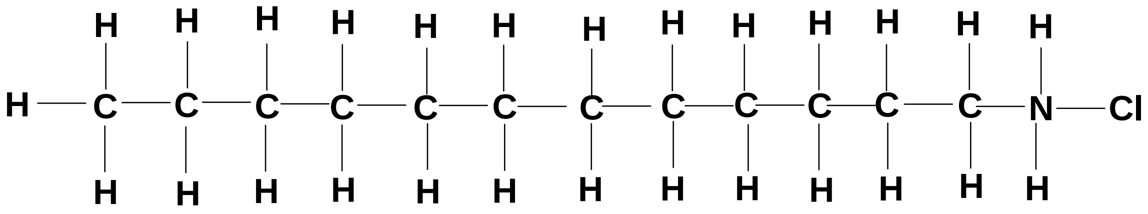
In order to modify clinoptilolite rich natural zeolite for hydrocarbon adsorption three different surfactants were used. The cationic surfactants were *dodecyl amine* (DA) with a molecular weight of 185.4 g/mole and a density of 0.81g/ml (Sigma Chemical Company) and *tetramethylammonium* (TMA^+) as Cl salt with a molecular weight of 109.60 g/mole and 97% purity (Aldrich Chemical Company). Structural formulas of the surfactants (DA and TMA^+) used in the adsorption studies are given in Figure 6. The used anionic surfactant was *sodium dodecyl sulfate* (SDS) as Na salt (Sigma Chemical

Company) with a molecular weight of 288.4 g/mole and approximately 99% purity. Sodium dodecyl sulfate (SDS) was only used for contact angle measurement experiments at the pH value of 4. Used acid and base solutions were 0.1M HNO_3 (Merck, 65%) and 0.1M NaOH (Carla Erba, 99.5-100.5%) for the adjustment of pH in case of SDS. Properties of the surfactants are given in Table 5.



$(CH_3)_4N$

TMA^+



$H(CH_2)_{12}NH_2Cl$

DA

Figure 6. Structural Formulas of the Surfactants Used for Adsorption Studies

Table 5. Properties of the Surfactants

Molecular Name	**Chemical Formula**	**Molecular weight (g/mole)**	**Critical Micelle Concentration(CMC) (M)**
Dodecyl Amine (DA)	$C_{12}H_{27}N$	185.4	1.31×10^{-2} *(a)*
Tetramethylammonium (TMA$^+$)	$C_4H_{12}N$	109.6	-
Sodium Dodecyl Sulfate(SDS)	$C_{12}H_{25}O_4SNa$	288.4	8.2×10^{-3} *(b)*

(a)Hunter R.J., "Foundations of Colloid Sciences", Volume I , Oxford Science Publications, New York, 1986.

(b) Gecol H., et al , "Use of Surfactants to remove Water based Inks from Plastic Films", Colloid and Surfaces A: Physicochemical and Engineering Aspects, 189, 55-64, 2001.

3.1.3. Hydrocarbons

In this study benzene, toluene and o-xylene were used as aromatic hydrocarbons. Benzene (C_6H_6) was obtained from Riedel-de Haën Chemical Company(99.5% purity). Extra pure toluene (C_7H_8) was provided by Merck. The third used hydrocarbon was o-xylene from Acros Chemical Company (99% purity). The physical and chemical properties of benzene, toluene and o-xylene are given in Table 6. The structural formulas of these hydrocarbons are shown in Figure 7.

Table 6. Physical and Chemical Properties of the Hydrocarbons

Molecular Name	**Chemical Formula**	**Molecular weight (g/mole)**	**Melting Point, °C**	**Boiling Point, °C**	**Density, g/ml**	**Solubility, (g/l)**
Benzene	C_6H_6	78	5.5	80.1	0.8786	1.78
Toluene	C_7H_8	92	-95	110.6	0.8669	0.52
o-Xylene	C_8H_{10}	106	-25.5	144.4	0.8802	0.15

(* Unit of Dimensions = Å, t= thickness)

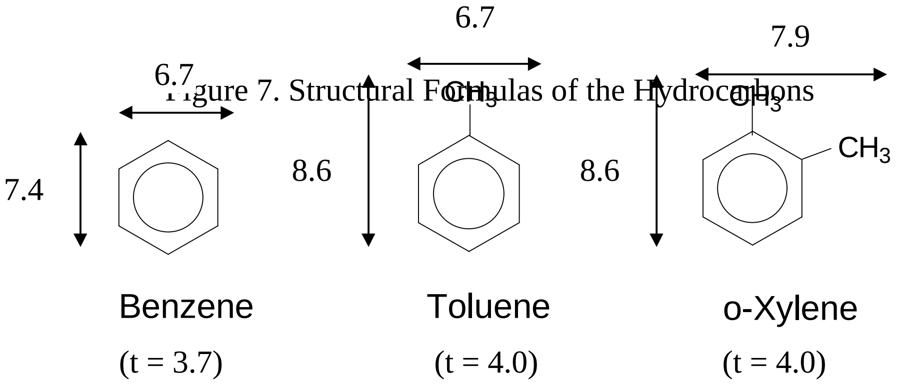


Figure 7. Structural Formulas of the Hydrocarbons

3.1.4. Water

The water used to prepare chemical solutions was deionized water which was additionally passed through Barnstead Easypure UV- compact ultrapure water system (@ 18.3Ωohm). Chromic acid was used to clean the glassware during the experiments. Deionized water was only used to remove chromic acid from the glassware.

3.2. Method

3.2.1. Characterization of Natural Zeolite

- **Particle Size Analyses**

Particle size measurements give an idea about the particle size ranges of the clinoptilolite rich natural zeolite samples. For these measurements three washed clinoptilolite samples of 100 g were placed into a ball mil (Retsch S1000) and were grinded for 10, 30, 60 minutes at 50 rpm. In addition unwashed samples were grinded and sieved to determine the differences in their characterization. Each sample was sieved with stainless steel sieves for 20 min at amplitude of 90. The amount of zeolite on each sieve was used to calculate the particle size distributions and the mean particle sizes for washed samples were calculated for 10 minutes, 30 minutes and 60 minutes ball milling time respectively.

- **Surface Area Analyses**

The adsorption and desorption properties of washed and unwashed samples were investigated using a volumetric adsorption system (Micromeritics, ASAP 2010). The degass process was performed at 300 ^{o}C with 50^{o}C increments. After the degass process the samples in the analysis bath were cooled to 77K. Nitrogen was used as an adsorptive for the analysis.

Micromeritics, ASAP 2010 measures the molar quantity of gas n (of standard volume V_a , or general quantity q) adsorbed or desorbed at a constant temperature T by an initially clean solid surface as a function of gas pressure P. The gas volume adsorbed at each pressure, which is expressed as relative pressure (P/P_o), defines adsorption isotherm.

- **Thermogravimetric Analyses (TGA)**

Thermal behaviour of washed and unwashed clinoptilolite rich natural zeolite samples was performed using Shimadzu TGA-51 thermobalance. Before the TGA washed and unwashed samples were placed for 10 days in a desiccator containing NH_4Cl to provide constant relative humidity. Nitrogen flowrate of 40 ml/min and 10^{o}C/min heating up to 1000^{o}C were employed. During the heating process weight loss percentages were obtained from TGA curves.

3.2.2. Modification of Zeolite Surface

3.2.2.1. Contact Angle Measurements

Contact angle measurements give an idea about the hydrophobicity of a solid surface. The contact angle can be defined as the angle formed between the solid surface and a tangent drawn to the liquid surface at the point of contact with the solid (MacRitchie F., 1990). The third phase is generally air. Contact angle measurements give information about the interaction between solid, liquid and gas phases.

In this study a piece of zeolite was perfectly polished. It was placed in different surfactant solutions, which are summarized in Table 7, for an hour. This process was applied to see in which case the zeolite surface is more hydrophobic. Then it was dried naturally. Deionized water droplets were let on the zeolite surface by a microsyringe which is defined as the sessile drop technique (Figure 8). Thirty contact angle measurements were done for each surfactant concentration. A contact angle measuring system Krüss-G10 was used for these measurements. To represent the distribution of the contact angles on zeolite surface frequency distribution plots were used. The mean contact angles and the standard deviations were calculated by using the formulas below:

Mean of the Contact Angles:

$$\frac{1}{n}\sqrt{\sum_{i=1}^{n} x_i} \qquad ; \qquad -\infty < x < +\infty$$

Standard Deviation of the Contact Angles:

$$\frac{1}{n}\sqrt{\sum_{i=1}^{n} (x_i - x_m)^2} \ ; \qquad -\infty < x < +\infty$$

Table 7. Surfactant Concentrations used for Contact Angle Measurements

Surfactant	Concentration (M)
Dodecyl Amine	1×10^{-5} 1×10^{-4} 1×10^{-3}
Tetramethylammonium	1×10^{-5} 1×10^{-4} 1×10^{-3}
Sodium dodecyl sulfate (pH =4)	1×10^{-5} 1×10^{-4}

	1×10^{-3}

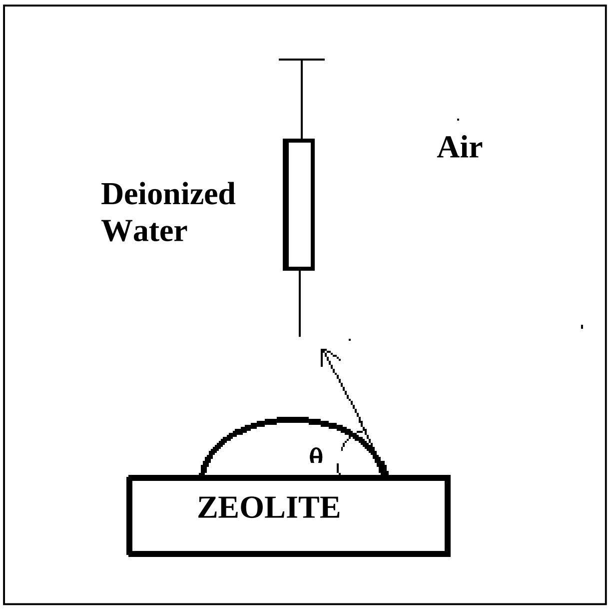


Figure 8. Sessile Drop Technique

3.2.2.2.Surface Tension Measurements

Surface tension measurements were performed with a Krüss Digital Tensiometer K 10ST using the ring method. Before the measurements the ring was cleaned by cotacting it with flame. When the ring is brought into contact with the surfactant solution, the liquid phase jumps to the ring and pulls it into the liquid. The force caused by this wetting is measured by pulling the ring up to the level of the liquid surface. This measured force is “surface tension”. Surface tension was measured for the concentrations of DA and TMA^+ given in Table 7. The aim of this study was to explain the relation of contact angle and surface tension.

3.2.3. Adsorption Studies

The adsorption of benzene, toluene, o-xylene on clinoptilolite rich natural zeolite and surfactant modified zeolite was investigated as kinetic batch studies at room temperature. The experimental procedure is shown in Figure 9. The effects of physical and chemical parameters were investigated (Table 8).

The sealed head space bottles containing 10 ml of a hydrocarbon solution and a certain percentage of zeolite were placed on a shaker (IKA-KS501 digital shaker). Solid % means the amount of zeolite (gram) in 10 ml of HC solution. To obtain kinetic results samples were taken at different time periods between 0.5 and 16 minutes. Preparing the solutions in different bottles prevented the changes in HC concentration / zeolite ratio.

The modification of zeolite was applied in two steps: (1) Water addition to zeolite, (2) Addition of the surfactant and shaking for 5 minutes. Then the bottles were sealed in order to prevent volatilization of the HC's. Finally the hydrocarbon was injected into the solution. After HC injection kinetic samples were taken and analyzed.

It is known that surfactants are efficient at low concentrations for modification. Therefore 1×10^{-6} M surfactant concentration was additionally used for the modification of zeolite with DA and TMA^+.

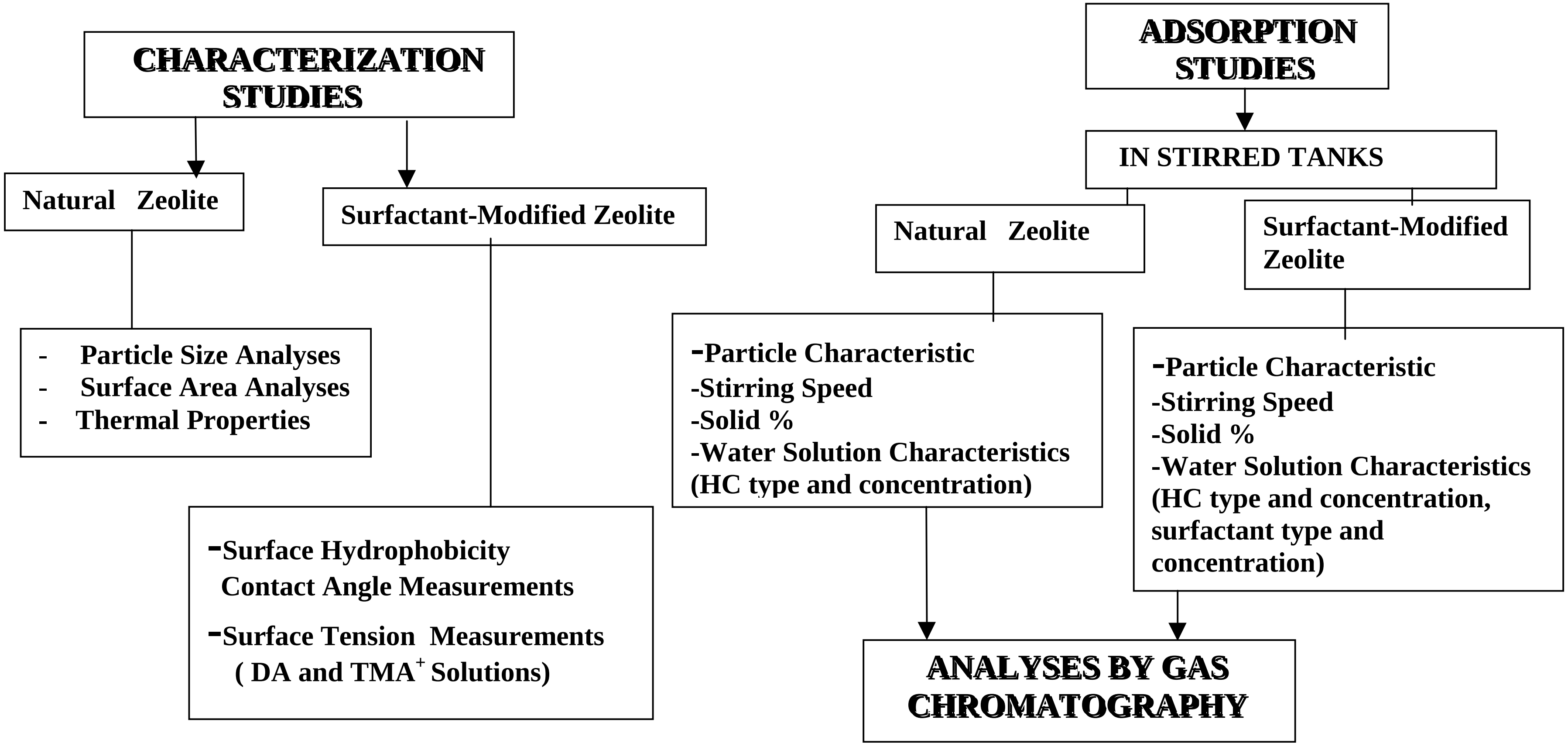


Figure 9. Experimental Procedure

Table 8. Physical and Chemical Parameters

Mean Particle Size(μm)	87
Clinoptilolite Rich Natural Zeolite (%)	1.5
Molarity (M)	
Benzene	0.02
Toluene	0.005
o- Xylene	0.001
Surfactant Concentration (M)	
Dodecyl Amine	1×10^{-6} 1×10^{-5} 1×10^{-4} 1×10^{-3}
Tetramethylammonium	1×10^{-6} 1×10^{-5} 1×10^{-4} 1×10^{-3}
Shaking Speed (rpm)	600

The samples were analyzed using a Hewlett Packard 5890 gas chromatography. SUPEROX II (60metal, 0.32mm ID fused silica capillary column) column was used. Dynamic head space sampling method was used for the analyses of the HC’s. The conditions for the gas chromatography are summarized in Table 9.

Table 9. Analyses Conditions of the Gas Chromatography

Carrier gas	N_2
Carrier gas flowrate	0.98ml/min
Detector	Flame ionization detector
Detector temperature	250^{o}C
Column temperature	70^{o}C
Flowrate of H_2	30ml/min
Flowrate of air	275ml/min
Temperature of injection port	230 ^{o}C
Split ratio	102:1
HEAD SPACE	
Bath temperature	80 ^{o}C
Loop temperature	90 ^{o}C
Bottle volume	20ml
Sample volume	10ml

The head space sampling method is based on the principle that the volatile hydrocarbons in water are in thermodynamic equilibrium with the vapor phase in a closed container, so that the vapor pressure of organic compounds is constant if their concentration in water is constant at a given temperature (Figure 10) (Grant D.W., 1996; Bruner F., 1993).

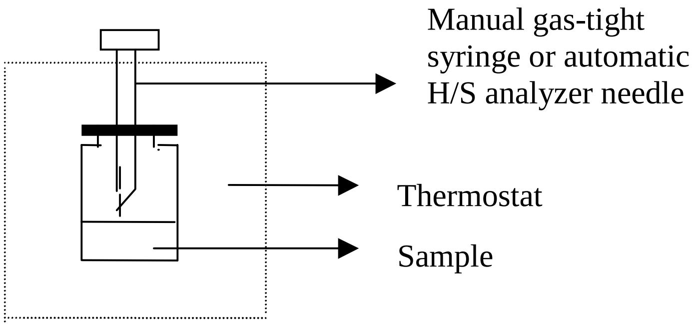


Figure 10. Dynamic Head Space Sampling Method

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Characterization of Natural Zeolite

Particle Size Analyses

The particle size distributions (Figure 11) were obtained for washed clinoptilolite rich natural zeolite samples of different ball milling times. The mean particle sizes of the washed samples were calculated as 122 µm, 87µm and 68 µm for 10 minutes, 30 minutes and 60 minutes of ball milling time respectively. The adsorption studies were carried out using the particle size of 87 µm.

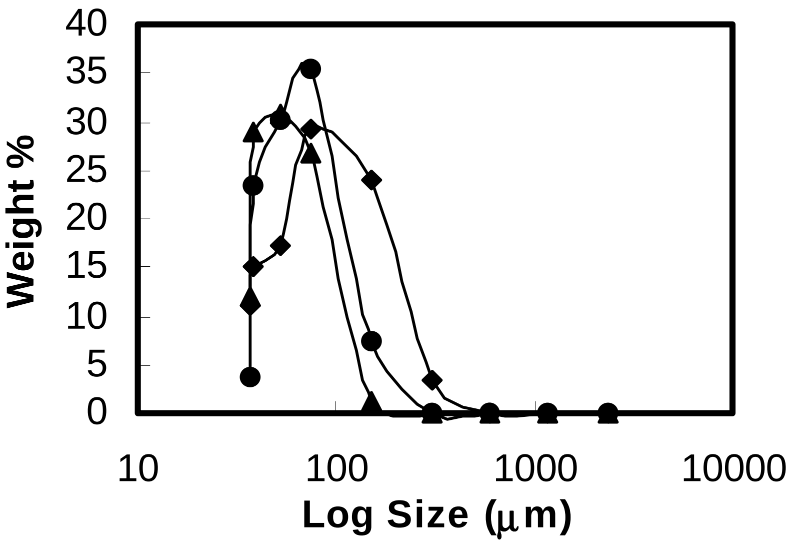


Figure 11. Particle Size Distributions of Washed Zeolite Samples

◆— 122µm , ●— 87µm , —▶68µm

Surface Area Analyses

The adsorption-desorption isotherms of washed and unwashed clinoptilolite rich zeolite samples for N_2 adsorption are given in Figure 12. Type II/b isotherm was obtained for N_2 adsorption both on washed and unwashed zeolite at 77 K. This isotherm type defines aggregates of plate-like particles that are non-rigid slit-shaped pores (Sing K. *et al*, 1999).

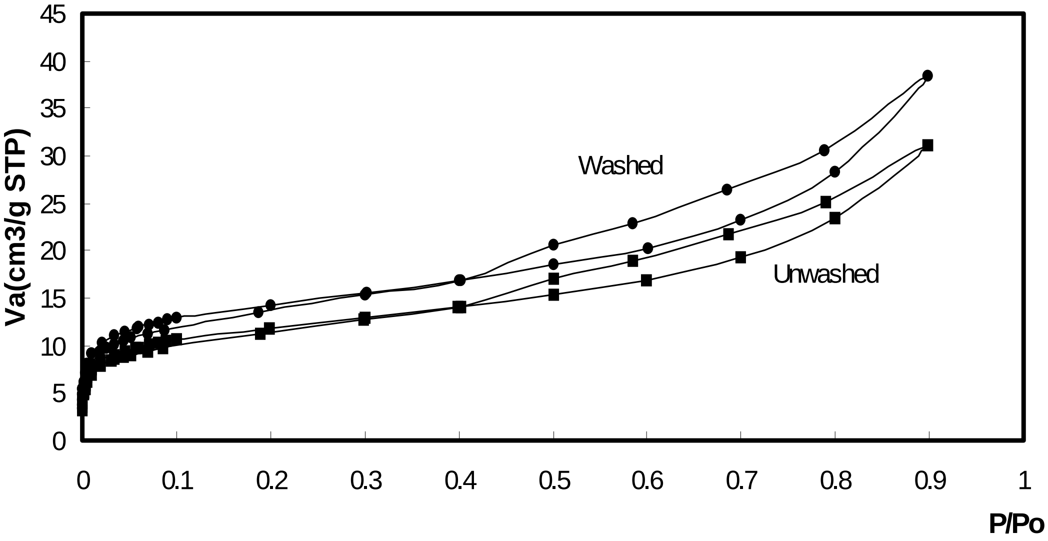


Figure 12. N_2 Adsorption-Desorption Curves for Washed and Unwashed Zeolite Samples

The surface areas of the samples were obtained using different methods for N_2 adsorption. The surface area of the washed sample is greater than the unwashed sample because of the washing process. The impurities in the structure of zeolite are removed during washing. The results are given in Table 10 for washed and unwashed samples.

Table 10. Summary of the Surface Area Measurements for Washed and Unwashed Zeolite

Method	Unwashed	Washed
Single Point Surface Area	39.4965m^2/g (at P/P_o= 0.30115340)	47.5020 m^2/g (at P/P_o =0.30131214)
BET Surface Area	39.7262 m^2/g	47.7157 m^2/g
Langmuir Surface Area	48.7935 m^2/g	59.1449 m^2/g
BJH Adsorption Cumulative Surface Area of Pores (17-3000Å)	23.9472 m^2/g	28.7157 m^2/g
BJH Desorption Cumulative Surface Area of Pores (17-3000Å)	31.9184 m^2/g	39.4446 m^2/g
Dubinin-Astakhov Micropore Surface Area	25.224354 m^2/g	64.584351 m^2/g

Thermogravimetric Analyses (TGA)

TGA curves (Appendix A) give the weight losses for washed and unwashed clinoptilolite rich natural zeolite samples. The smooth and continuous TGA curves show that no structural deformation occurred when they were heated up to 1000^{o}C. According to Knowlton G.D. *et al* (1981) the % weight losses of ‘external water’, ‘loosely bound water’ and ‘tightly bound water’ for unwashed and washed zeolite samples of different particle sizes are given in Table 11 .

Table 11. % Weight losses of the Zeolite Samples

Sample	External Water <85 °C	Loosely Bound Water 85-275 °C	Tightly Bound Water >275 °C	Total Weight Loss
Unwashed (122 µm)	3.33	4.16	2.35	9.84
Unwashed (87 µm)	4.06	4.06	2.20	10.32
Unwashed (68 µm)	3.44	4.11	2.69	10.24
Washed (122 µm)	2.64	3.99	2.80	9.43
Washed (87 µm)	3.23	3.93	2.13	9.29
Washed (68 µm)	3.08	4.1	2.42	9.6

Generally it is expected that the % weight losses for washed samples are greater than for unwashed samples. However in this study the total weight loss for unwashed samples were found greater than those for washed samples. These results may be because of the operational conditions during thermogravimetric analysis.

Narin G. (2001) calculated the %weight losses as 10.535 for unwashed and as 10.878 for washed zeolite samples up to 800°C. On the other hand Akdeniz Y. (1999) obtained 13.90% weight loss for original zeolite up to 1000 °C heating. In both of the studies Gördes II zeolite samples were used as it was for this study. It can be concluded that these %weight loss percentage differences may be due to the differences in water content which depends on the amount and type of the extra-framework cations for the same region samples (Narin G.,2001). This means that every sample taken from the same region can give different results.

Although an increase in the % weight loss with the decrease in the particle size was an expected result in this study % weight loss has no relationship with the particle size changes.

4.2. Modification of Zeolite Surface

Hydrophobicity of clinoptilolite rich natural zeolite surface without any treatment was determined by using the contact angle measurements according to the method given in Chapter 3. The mean contact angle (θ_m) was found to be 7.76° in this case. The distribution of angles were also obtained. The standard deviation was found to be 0.2041. The results for zeolite without any treatment are important to determine the effect of surfactant modification.

4.2.1. Contact Angle Studies

4.2.1.1. Treatment of Zeolite by Tetramethylammonium (TMA^+)

Zeolite surface was treated with a cationic surfactant TMA^+ according to the method given in Chapter 3. In this part of the study pH of the solution was around 8 and expected to provide negatively charged zeolite surface. The effect of TMA^+ was found to be a function of concentration. The results are given in Figure 13 together with no treatment case. The mean contact angle value increased from 7.76° to 29.37° at a TMA^+ concentration of 1×10^{-3} M. The standard deviation values were found to be 0.3575, 0.3812,0.3267 for 1×10^{-5} M, 1×10^{-4} M, 1×10^{-3} M TMA^+ treatment respectively. This is the indication of an increase in the hydrophobicity of zeolite surface.

4.2.1.2. Treatment of Zeolite by Dodecyl Amine (DA)

Dodecyl Amine is another cationic surfactant with a higher molecular weight compared to TMA^+. The results are presented in Figure 14 as a function of DA concentration. DA concentration changed from 1×10^{-5} M to 1×10^{-3} M and increased the contact angle. The mean contact angle changed from 7.76° to 51.13 ° at a DA concentration of 1×10^{-3} M. The standard deviations were found to be 0.33, 0.3592, 0.3595 for 1×10^{-5} M, 1×10^{-4} M, 1×10^{-3} M DA treatment respectively. This is the evidence of more hydrophobic surface compared both to unmodified surface and TMA^+ modified surface. It seems that DA makes surface more hydrophobic. The higher concentration (1×10^{-2} M) was also tested. The highest mean value (65.23^o) was obtained for this concentration but it is not used here since the viscosity of the solution also increased.

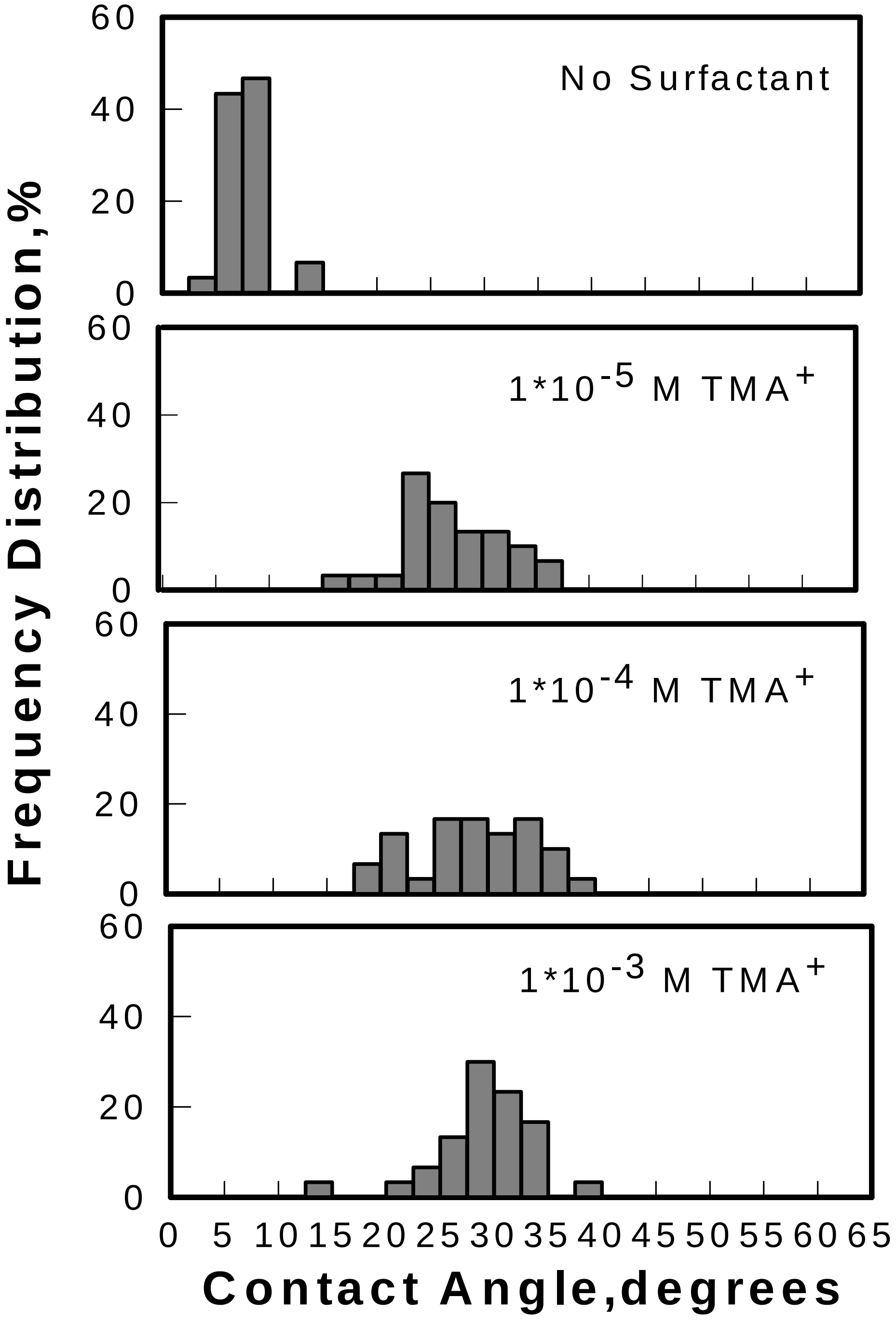


Figure 13. Contact Angle Distributions of Zeolite Sample Modified by TMA$^+$ as a Function of TMA$^+$ Concentration

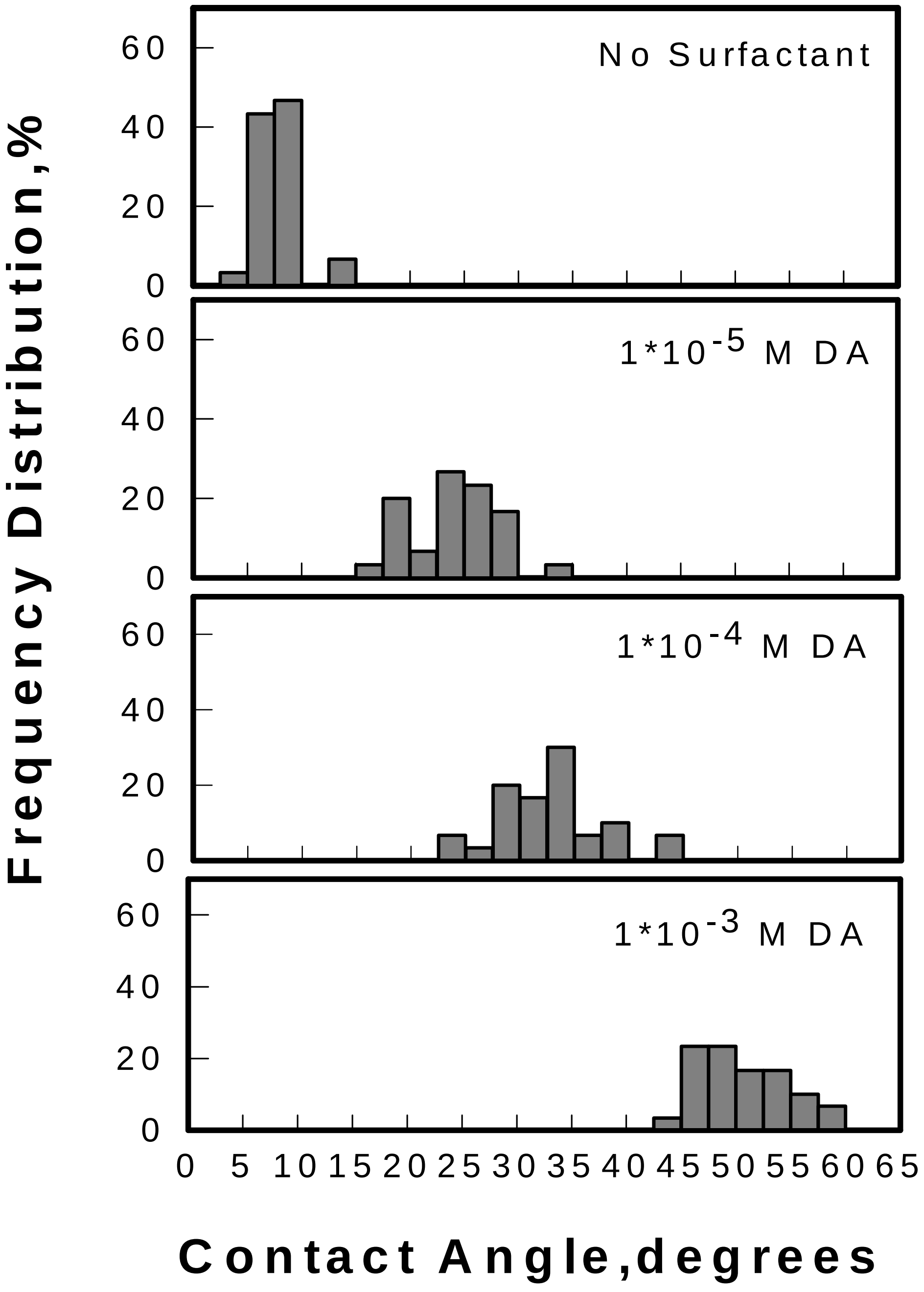


Figure 14 . Contact Angle Distributions of Zeolite Sample Modified by DA as a Function of DA Concentration

4.2.1.3. Treatment of Zeolite by Sodium Dodecyl Sulfate (SDS)

Sodium dodecyl sulfate (SDS) is an anionic surfactant which carries negative charge in natural form. Therefore pH of the solution was adjusted to 4 in order to change the charge of zeolite surface to positive. The results are given in Figure 15. According to the results it was found that an anionic surfactant adsorption on the surface is not sufficient to change the surface hydrophobicity. The contact angle values obtained were lower than the those obtained with TMA^+ and DA. The mean contact angle values were 16.73°,16.87° and 18.03 ° for 1×10^{-3}M, 1×10^{-5} M and 1×10^{-4}M respectively. The maximum mean contact angle value was obtained at 1×10^{-4} M SDS concentration in contrast to TMA^+ and DA. The standard deviations were found to be 0.4186, 0.3514, 0.4142 for 1×10^{-5} M, 1×10^{-4} M, 1×10^{-3} M SDS treatment respectively.

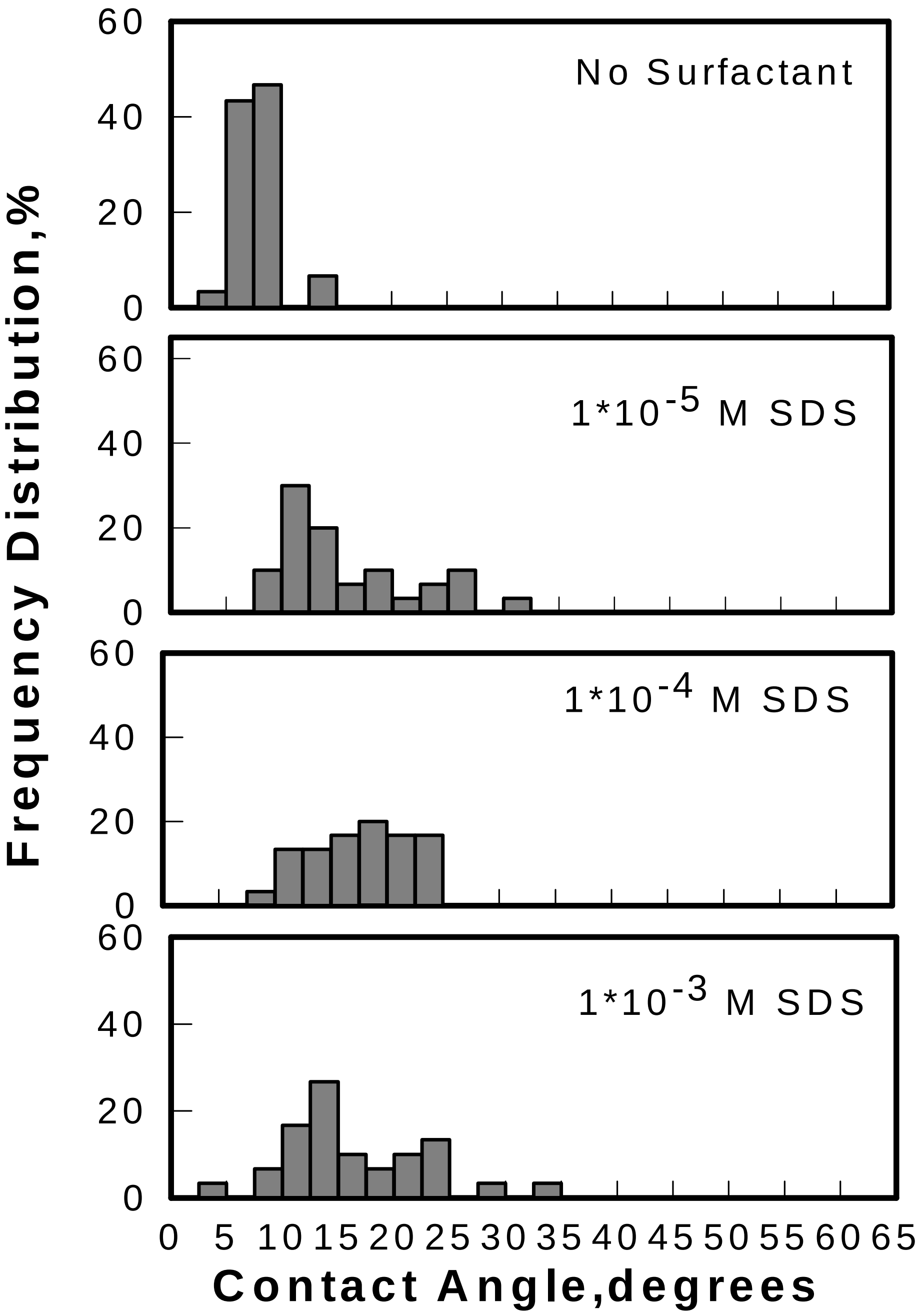
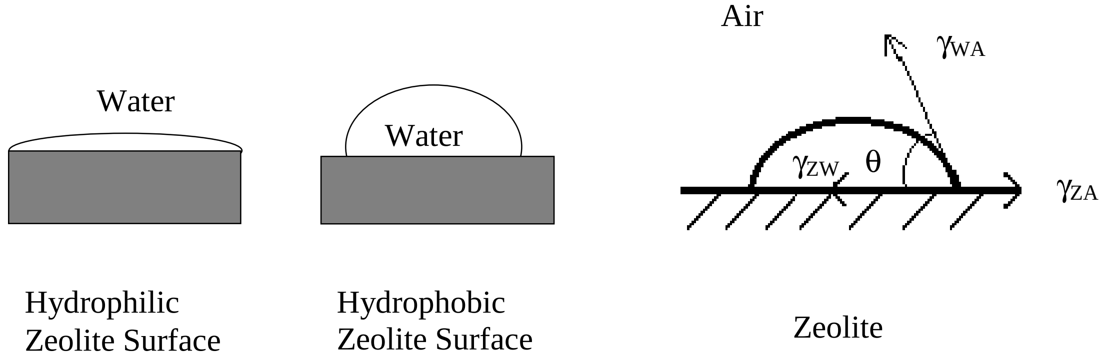


Figure 15. Contact Angle Distributions of Zeolite Sample Modified by SDS (pH=4) as a Function of SDS Concentration

4.2.2. Surface Tension Studies: Calculation of Gibbs Free Energy

The contact angle measurement results of TMA^+ and DA showed that these cationic surfactants make zeolite surface hydrophobic. Surface tension measurements showed also these results. Gibbs free energy changes of the systems were investigated by these measurements. The Gibbs free energy analyses the system in terms of combine effect of surface tension and contact angle in making surface more hydrophobic. That is the change in the Gibbs free energy of the zeolite system gives an idea about the water affinity of zeolite surface in terms of surface tension and contact angle change (Figure 16).



$$\gamma_{ZA} = \gamma_{ZW} + \gamma_{WA} \cos \theta$$

(Young's Equation)

For this system ΔG (Gibbs free energy) could be written as

$$\Delta G = \gamma_{ZA} - \gamma_{ZW} - \gamma_{WA}$$

If Young's equation is inserted into the equation above, ΔG is obtained as

$$\Delta G = \gamma_{WA} (\cos \theta - 1)$$

Figure 16. Derivation of ΔG for Zeolite-Water-Air System

So, ΔG will change with a change in both γ_{WA} and θ. Increasing θ by itself does not mean that surface will have less affinity to water. That is, surface will be more hydrophobic. ΔG values are calculated for different γ_{WA} and θ values and tabulated both for TMA^+ and DA in Table 12.

Table 12. ΔG Values for TMA^+ and DA

	TMA^+			**DA**		
Surfactant Concentration (M)	**ΔG** (dyne/cm)	**γ_{WA}** (dyne/cm)	**θ** (degrees)	**ΔG** (dyne/cm)	**γ_{WA}** (dyne/cm)	**θ** (degrees)
1×10^{-5} M	-8.18	72.4	27.5	-6.24	70.3	24.33
1×10^{-4} M	-9.11	72.2	29.1	-7.09	44.1	32.93
1×10^{-3} M	-9.29	72.3	29.37	-13.78	37	51.13
No Surfactant	ΔG= -0.66		γ_{WA}= 72.8		θ= 7.76	

As it is seen from the table, ΔG becomes more negative in the presence of surfactants. It was only –0.66 without any treatment and became –13.78 in the case of 1×10^{-3} M DA. This means that this is the most favourable condition among these to make zeolite surface more hydrophobic.

The mean contact angle values are given in Figure 17 for the three surfactants used for contact angle measurements as a summary. It is seen that cationic ones are much better than the anionic one. DA was found to be the most effective surfactant to increase contact angle at a concentration of 1×10^{-3} M. Based on the results the concentration of 1×10^{-3} M DA and TMA^+ was chosen to use in this study for surface modification. However their effect was similar at low concentrations.

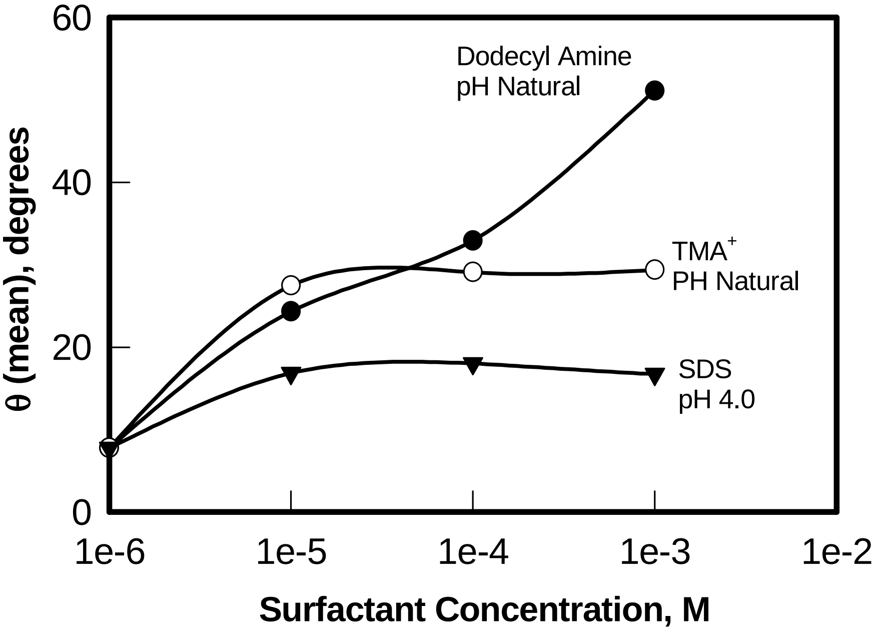


Figure 17 . Effect of DA, TMA^+, SDS (pH=4) treatment on the Mean Contact Angle (θm) of Zeolite as a Function of Surfactant Concentration

The possible mechanism for the adsorption of surfactant molecules on zeolite surface is given in Figure 18a-b schematically. At low concentrations (below CMC) cationic surfactant molecules are dispersed in the solution and the positively charged hydrophilic part can easily bind to the negatively charged zeolite surface because of electrostatic attraction (Figure 18-a). The hydrophobic groups are directed away from the zeolite surface and thereby a hydrophobic zeolite surface is obtained. The used hydrocarbons in this study (benzene, toluene, o-xylene) are hydrophobic molecules and expected to come together with the hydrophobic zeolite surface by hydrophobic attraction.

At high concentrations (higher than the CMC) on the other hand surfactant molecules aggregates and form micelles (Figure 18-b). The hydrophobic groups are directed to the interior of the micelles and the hydrophilic groups are directed to the solution. In this case hydrophobic zeolite surface can not be obtained. As a result, surfactants (below CMC) are expected to be more effective to make zeolite surface hydrophobic. Therefore DA and TMA^+ concentrations lower than 1×10^{-3} M should be used during the adsorption studies for the modification of zeolite.

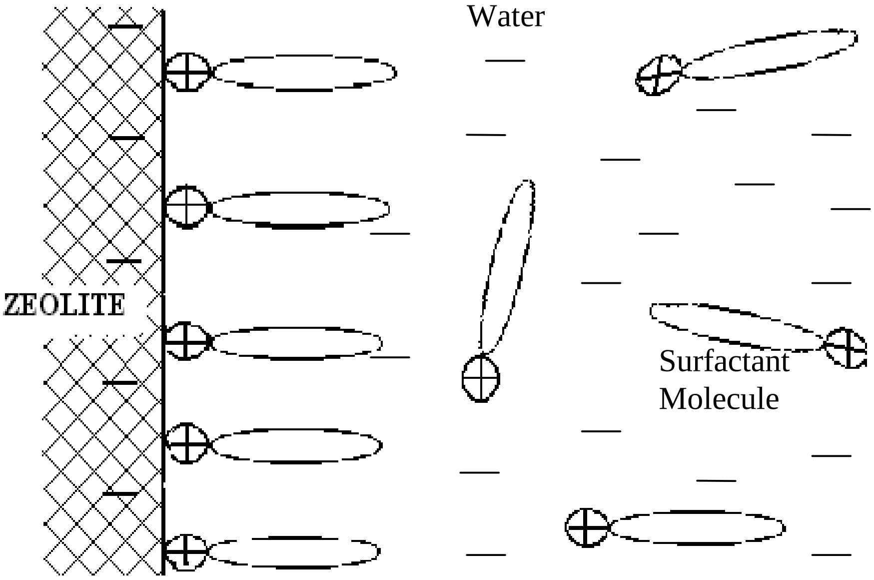


Figure 18(a). Surfactant Molecules at Low Concentrations in Zeolite / Water System

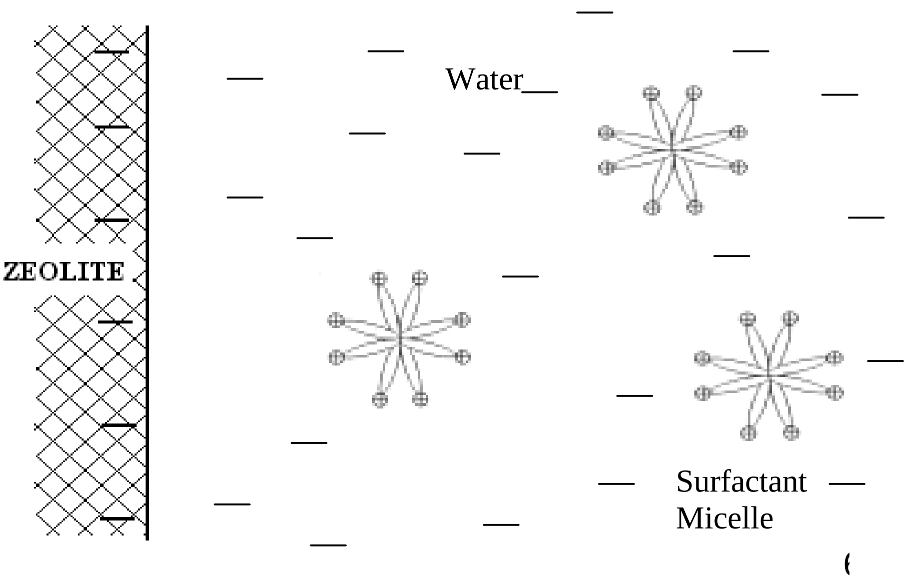


Figure 18(b). Surfactant Molecules at High Concentrations in Zeolite / Water System

4.3. Adsorption Studies

4.3.1. Kinetics of Hydrocarbon Adsorption on Natural Zeolite

Adsorption of benzene, toluene and o-xylene was investigated on natural zeolite as a function of time according to the experimental method given in Chapter 3. The results are presented and discussed in the following paragraphs in detail.

4.3.1.1. Benzene

Adsorption of benzene on natural zeolite was given in Figure 19 as gr benzene / gr zeolite, in Figure 20 as removal % and in Figure 21 as final concentration change in solution as a function of time. As it is seen from the figures, the shaking times less than 10 minutes are important for the adsorption of benzene. Therefore the adsorption up to 16 minutes was studied separately and given in Figures 19,20,21 as insert figures.

According to Figure 19, 0.026 gram of benzene was adsorbed by one gram of zeolite. The maximum removal % of benzene was found to be around 24.7 for 8 minutes. The insert figures up to 16 minutes show that the benzene removal was the highest around 2 minutes (Figure 20). This removal decreased with increasing time. This might be due to the desorption of benzene under these conditions with the increasing time. Figure 21 also gives the minimum benzene concentration in solution as 1113 ppm.

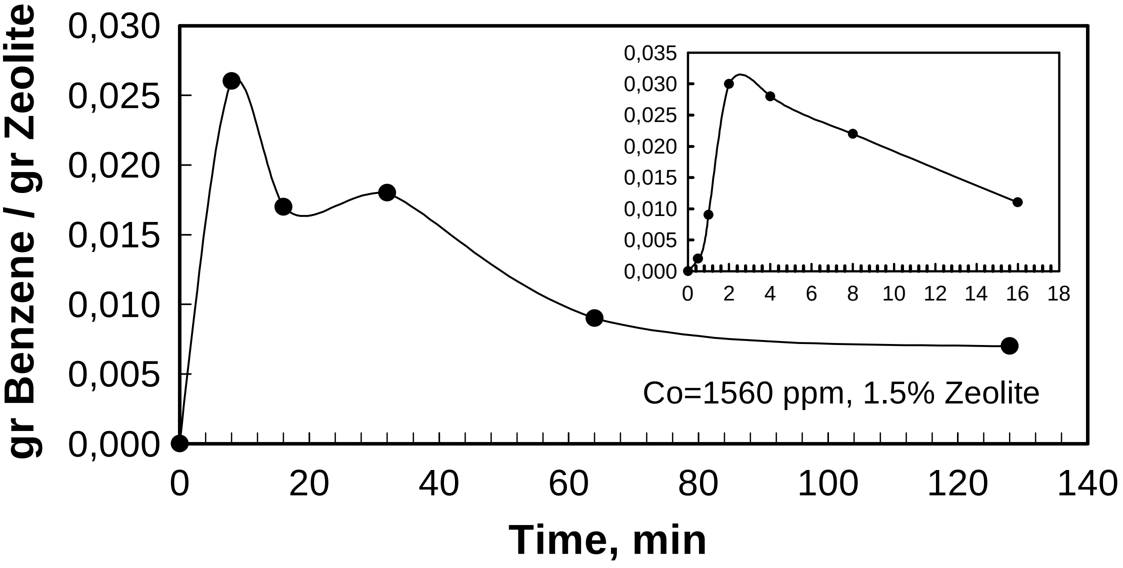


Figure 19. Adsorption of Benzene on Natural Zeolite

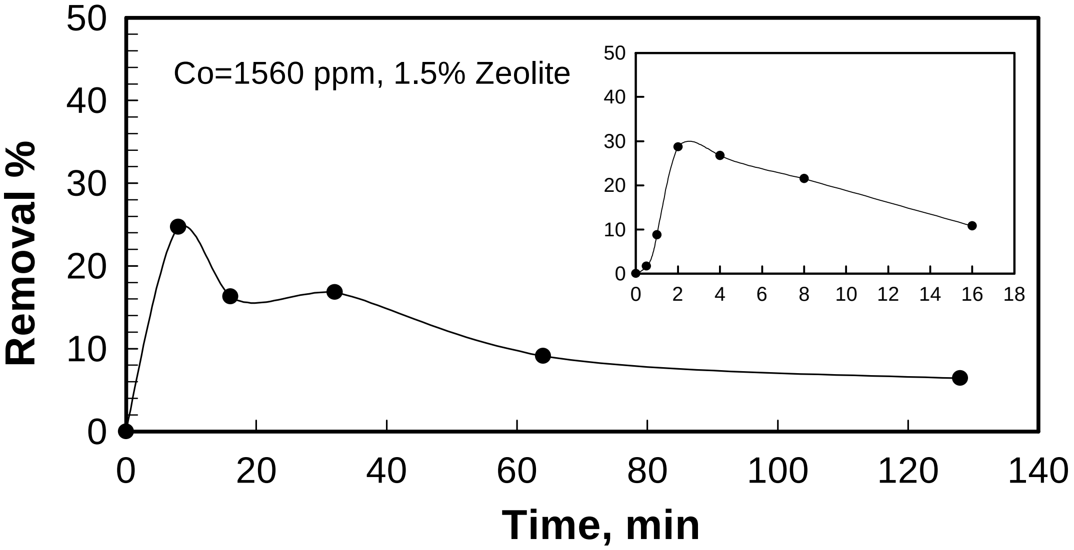


Figure 20. Benzene Removal % on Natural Zeolite

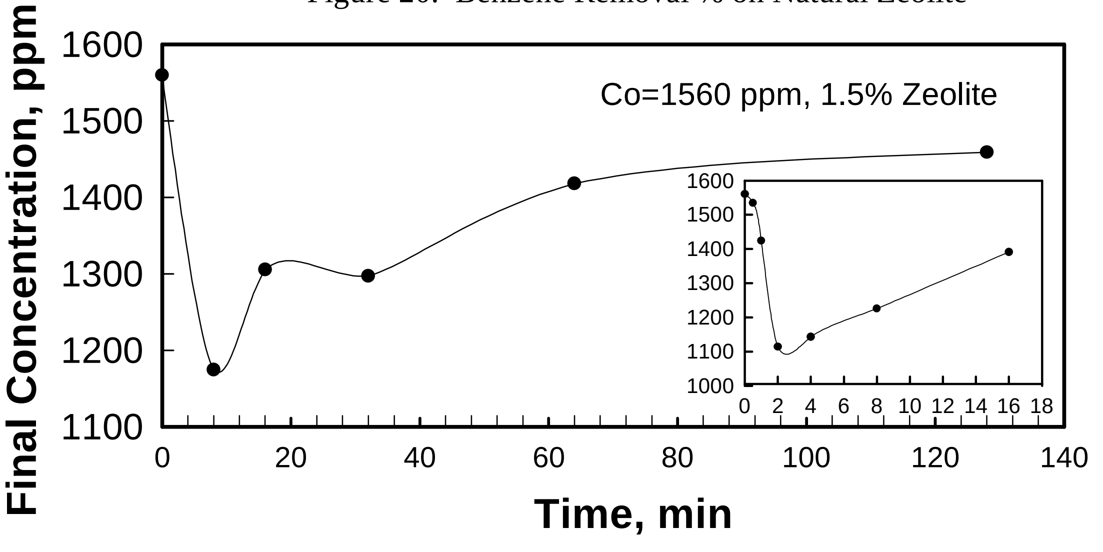


Figure 21. Change of Benzene Concentration in the Solutions

4.3.1.2. Toluene

Adsorption of toluene on natural zeolite was shown in Figures 22,23,24 as gr toluene/gr zeolite, removal % and final concentration change in the solutions respectively. Toluene removal was lower than the removal of benzene by natural zeolites.

As it is seen from Figure 22, 0.0063 gram of toluene was adsorbed by per gram of zeolite after 16 minutes of conditioning. In other words the removal % was around 20.43. Toluene removal started to increase after 4 minutes and the highest value was reached at 8 minutes. After 8 minutes this value did not change with further increase in time (Figure 23). This might be a result of the more complex structure of toluene compared to benzene. This difference in their behaviour could be due to their structure. Toluene’s structure is more complex than that of benzene and toluene has relatively lower solubility (0.52 g / lt).

4.3.1.3. o- Xylene

Adsorption of o-xylene on natural zeolite was shown as gram o-xylene per gram of zeolite in Figure 25, as removal % in Figure 26 and as final concentration change in the solutions in Figure 27 as a function of time. According to the results the minimum removal was obtained for this hydrocarbon compared to the other hydrocarbons. This might be due to the most complex structure of o-xylene compared to the others and the lowest solubility in water (0.15 g/lt).

As shown in Figure 25, 0.0012 gram o-xylene was adsorbed by per gram of zeolite. Consequently the highest removal % was 17 around 2 minutes (Figure 26). After 2 minutes the removal decreased with increasing time. This might be also a result of desorption.

In general the adsorption studies on natural zeolite showed that the removal was in this sequence: benzene > toluene > o-xylene. The adsorption of benzene was more easier because of its simpler structure and its higher solubility in water (1.78g/lt) (Cadena F., Cazares E., 1993).

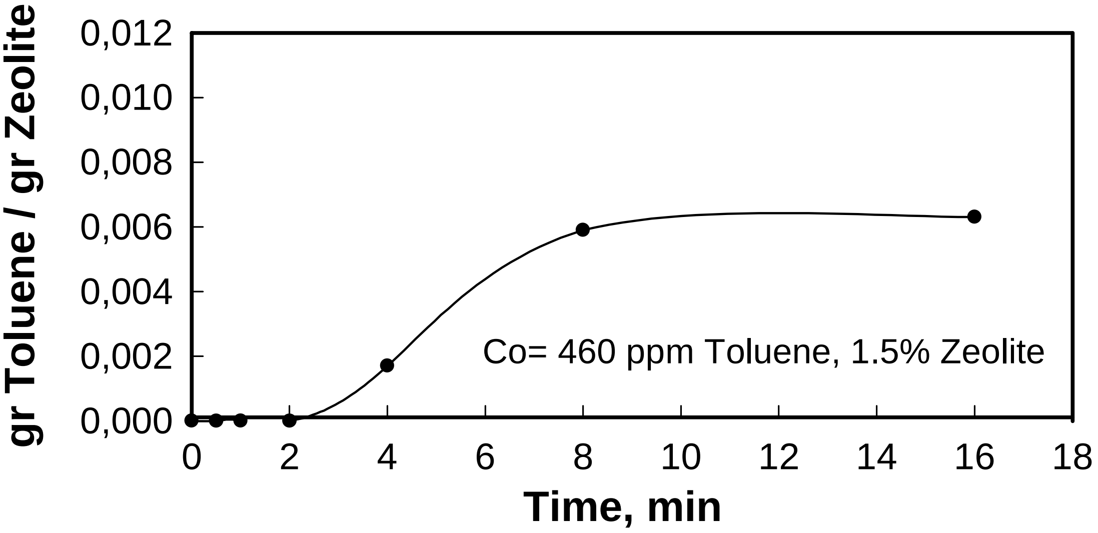


Figure 22. Adsorption of Toluene on Natural Zeolite

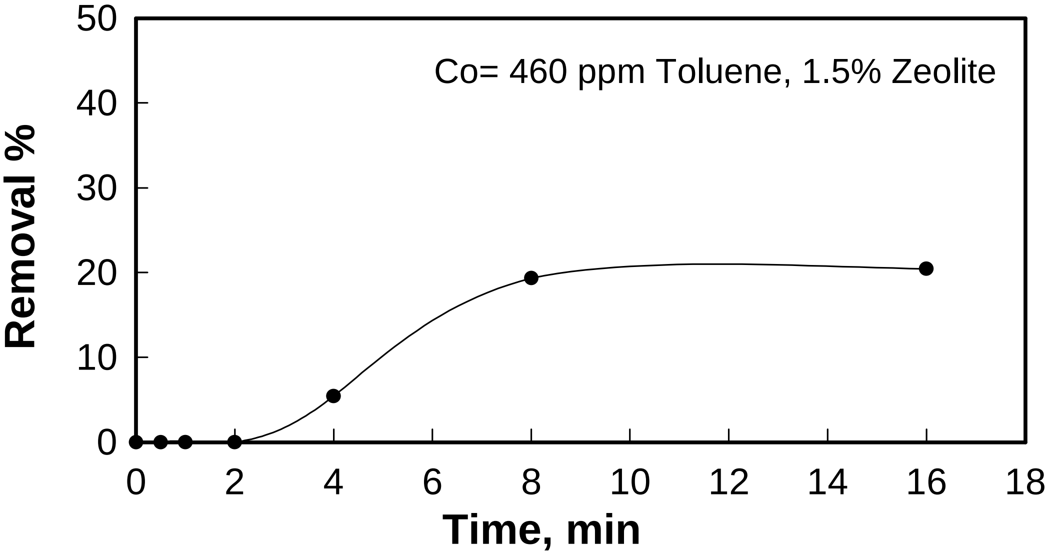


Figure 23.Toluene Removal % on Natural Zeolite

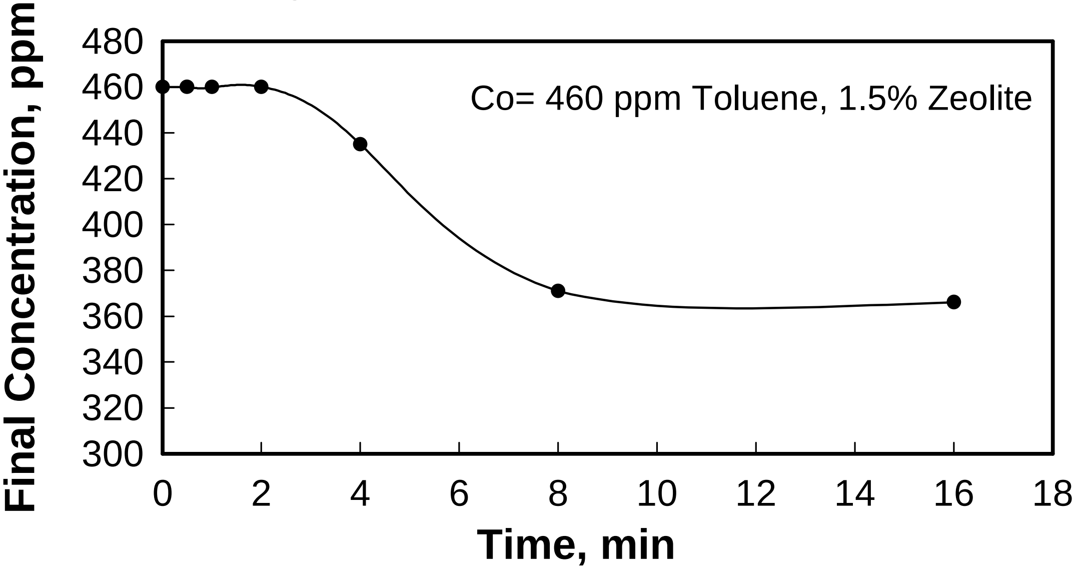


Figure 24.Change of Toluene Concentration in the Solutions

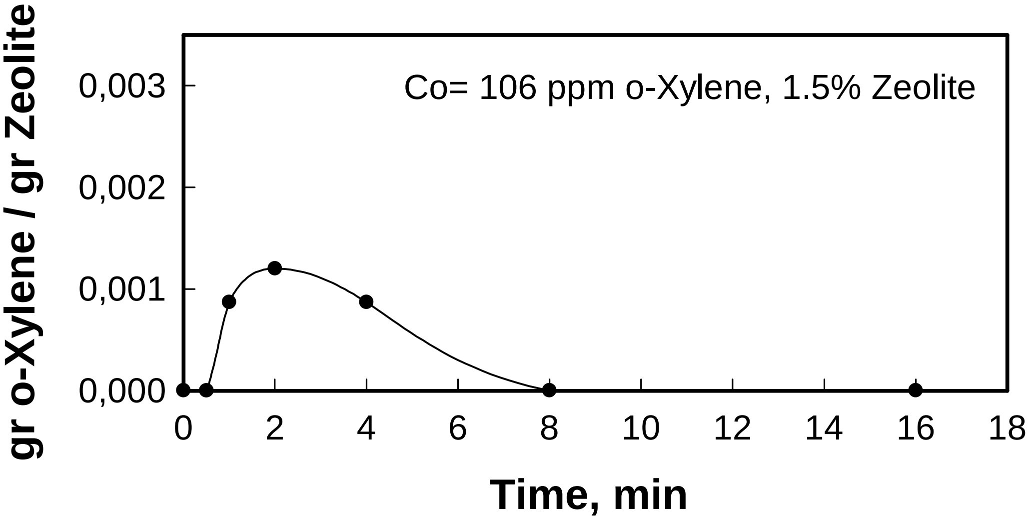


Figure 25. Adsorption of o-Xylene on Natural Zeolite

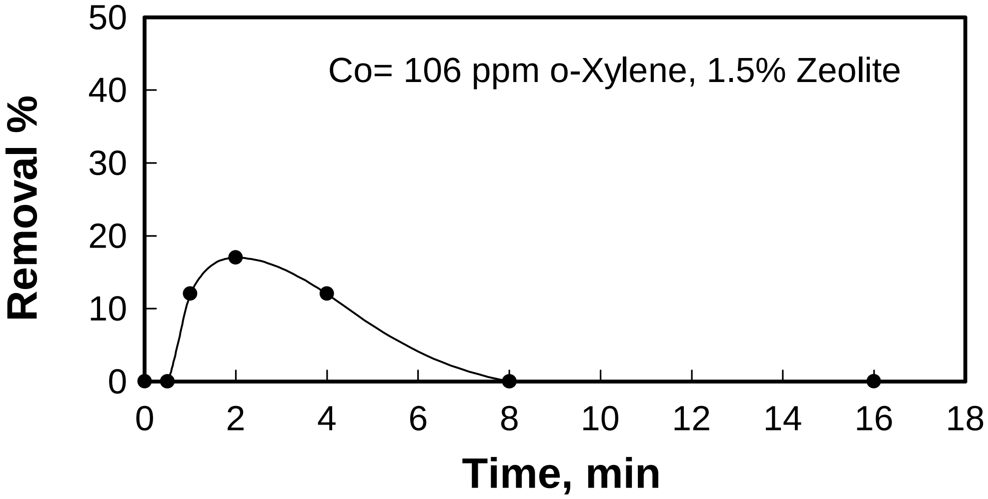


Figure 26. o-Xylene Removal % on Natural Zeolite

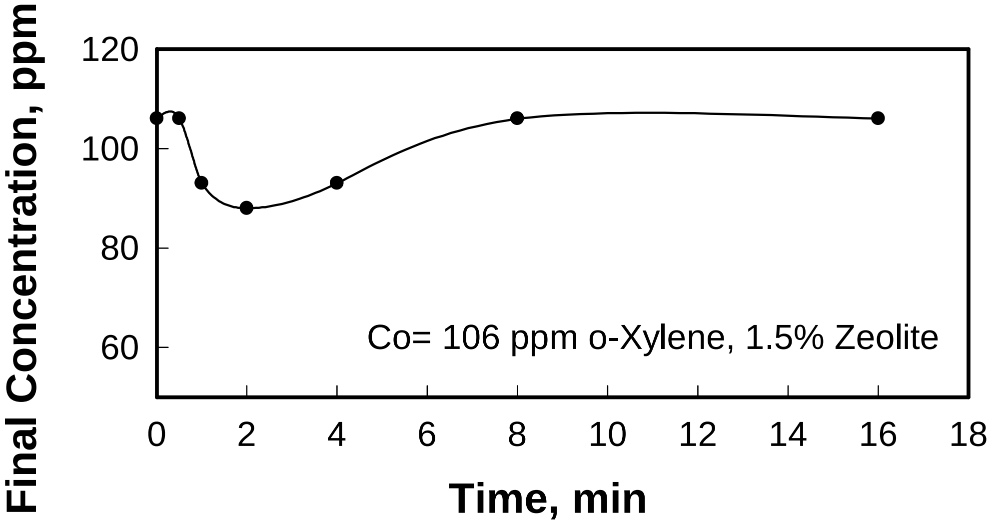


Figure 27.Change of o-Xylene Concentration in the Solutions

As a result, hydrocarbons are adsorbed on zeolite surface in this study. The adsorption mechanism of this system is as follows:

The adsorption of these nonpolar aromatic compounds is physically. This means that these aromatic rings can bind to the surface only by induced dipole-dipole interaction which is a type of Van der Waals forces. This type of interaction takes generally place between nonpolar-polar systems.

In addition because of the π - electrons of the nonpolar aromatic compounds, there may exist an interaction between the π - electrons and the cations (for example Na^+) of clinoptilolite rich natural zeolite (Chapter 2.3). The same mechanism may also occur between the hydrogens of the aromatic compounds and the oxygens on the zeolite surface (Figure 28).

Because of the smaller and simpler structure of benzene, it could also be adsorbed by the mesopores of natural zeolite.

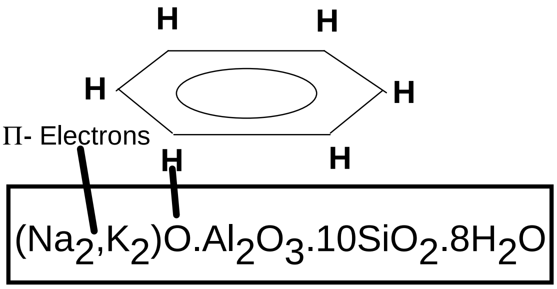


Figure 28. Interactions Of Nonpolar Organic Molecules On Zeolite Surface

4.3.2. Kinetics of Hydrocarbon Adsorption on Surfactant Modified Zeolite

The aim of the use of surfactants was to increase the hydrophobicity of zeolite surface and therefore increase the adsorption capacity of benzene, toluene and o-xylene, which are hydrophobic in nature. The results, which show how the surfactants DA and TMA^+ make zeolite surface hydrophobic, were presented in previous paragraphs (Section 4.2). As explained before the hydrophobic attraction forces between hydrophobic parts of the surfactants and hydrocarbons observed the removal of these hydrocarbons.

4.3.2.1. Benzene Adsorption on DA and TMA^+ Modified Zeolite

The adsorption of benzene on zeolite surface was investigated in the presence of a cationic surfactant, DA. The results are presented in Figure 29, 30 and 31 as a function of DA concentration. Although a significant change in contact angle values of zeolite surface in the presence of this surfactant, this effect could not be observed in case of adsorption studies. There was only a slight increase in the adsorbed amount. The kinetics of adsorption, on the other hand, did not change significantly in the presence of this surfactant. This might be explained as follows.

As it was discussed in the previous paragraphs benzene could be adsorbed by the mesopores. However, in the presence of surfactant, especially in the presence of DA which is a long chain surfactant, may plug these pores and decrease the adsorption in this way.Therefore increasing adsorption due to surface modification may be decreased. In the case of small chain surfactant TMA^+, removal increased and additionally benzene desorption is prevented in the presence of TMA^+.

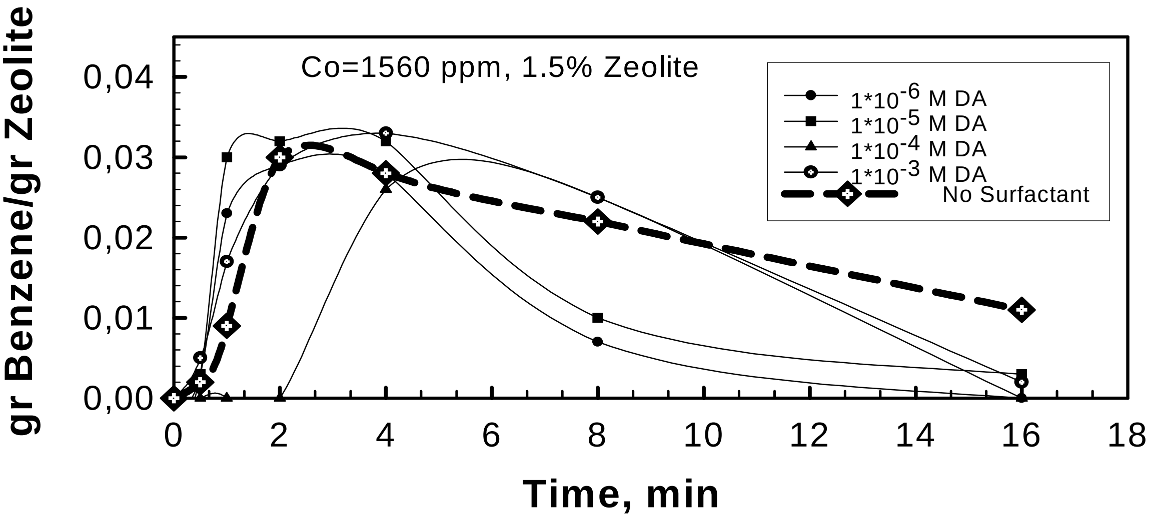


Figure 29.Effect of DA Concentration on the Adsorption of Benzene on DA modified Zeolite

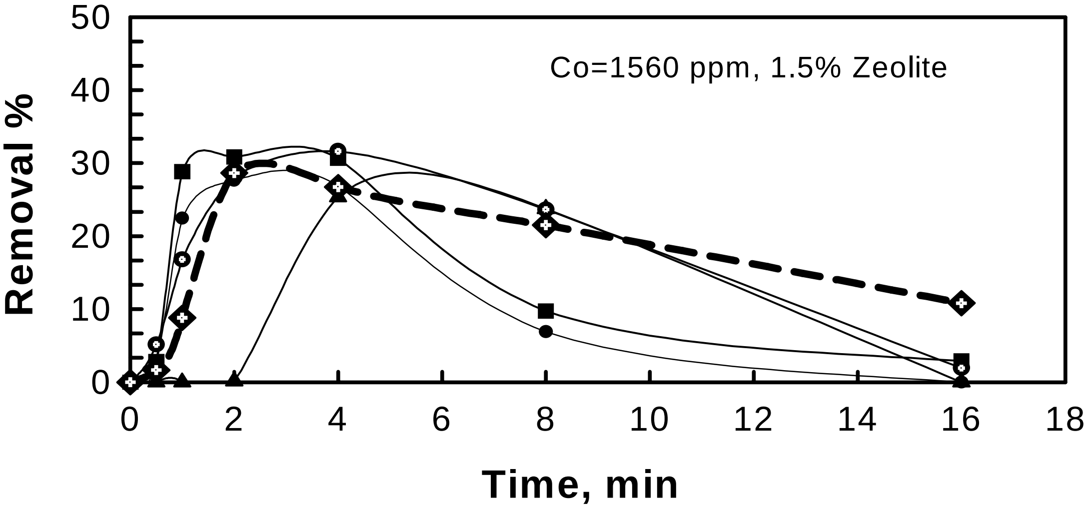


Figure 30.Effect of DA Concentration on the Removal % of Benzene on DA modified Zeolite

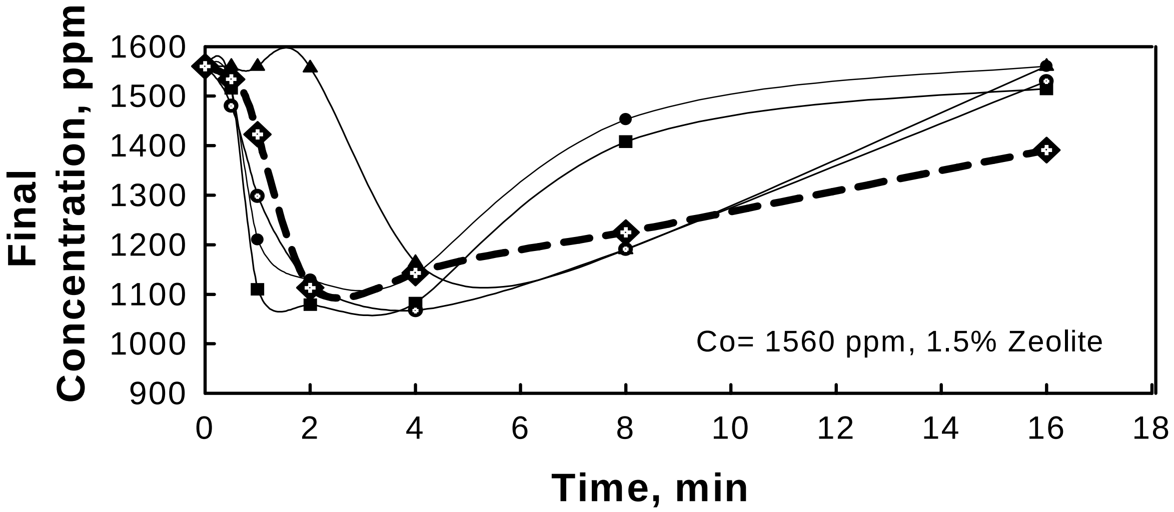


Figure 31. Effect of DA Concentration on the Final Benzene Concentration in the Solutions

The adsorption of benzene on the modified zeolite surface was also investigated in the presence of TMA^+ as a modifier. The results are given in Figures 32,33,34 as a function of TMA^+ concentration. It is seen from the figures that the amount of benzene adsorbed was the same with the unmodified zeolite up to 2 minutes of conditioning time. After 2 minutes, the amount of adsorbed benzene decreased from 0.03 g/g of zeolite to 0.01 g/g of zeolite in case of unmodified surface during the 16 minutes conditioning time. However this amount increased to 0.04 g/g of zeolite during this time in case of TMA^+ modified surface. The results also show that there are no significant changes as a function of TMA^+ concentration. Although the best contact angle results were obtained in case of 1×10^{-3} M TMA^+ concentration, this could not be seen in adsorption results.

As a conclusion, TMA^+ modification affected the benzene adsorption at longer times probably due to the preventing the desorption of benzene with time. The amount adsorbed was only 0.03 g/g of zeolite in case of unmodified surface after 16 minutes while it was around 0.04 g/g of for TMA^+ modified surface. Therefore this surfactant is more effective than DA for benzene adsorption. Cadena and Cazares (1993) also found that TMA^+ modification was more effective than the others for the adsorption of benzene. They reported that the spaces created between TMA^+ groups on zeolite are suitable regions for the planar benzene molecules.

4.3.2.2. Toluene Adsorption on DA and TMA^+ Modified Zeolite

The effect of DA and TMA^+ concentration on toluene adsorption on zeolite is given in Figures 35-40. There was not much difference between the results of DA and TMA^+. The kinetics of adsorption is effected by surfactant at certain concentrations and within 2 minutes the amount of adsorbed toluene reached the amount that was obtained after 8,10 minutes of conditioning in case of unmodified surface. However the amount adsorbed after 16 minutes did not change significantly.

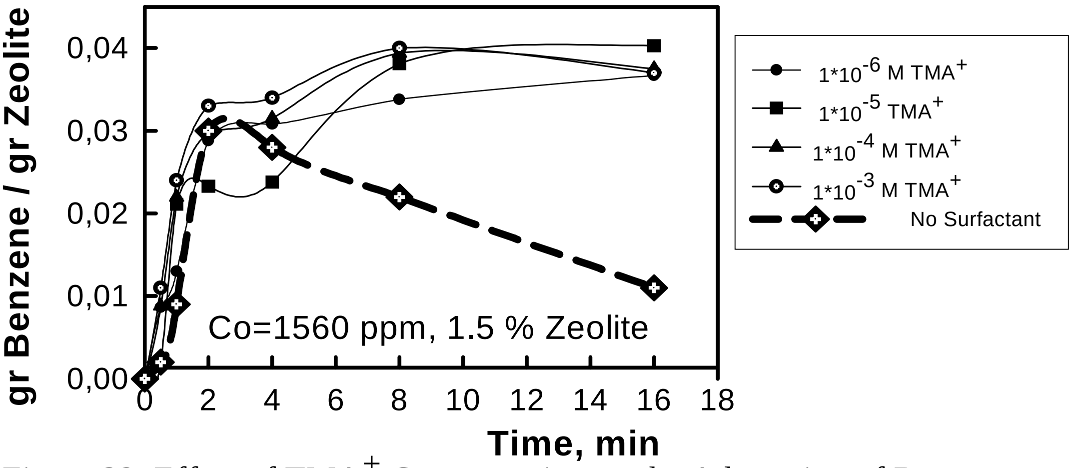


Figure 32. Effect of TMA$^+$ Concentration on the Adsorption of Benzene on TMA$^+$ Modified Zeolite

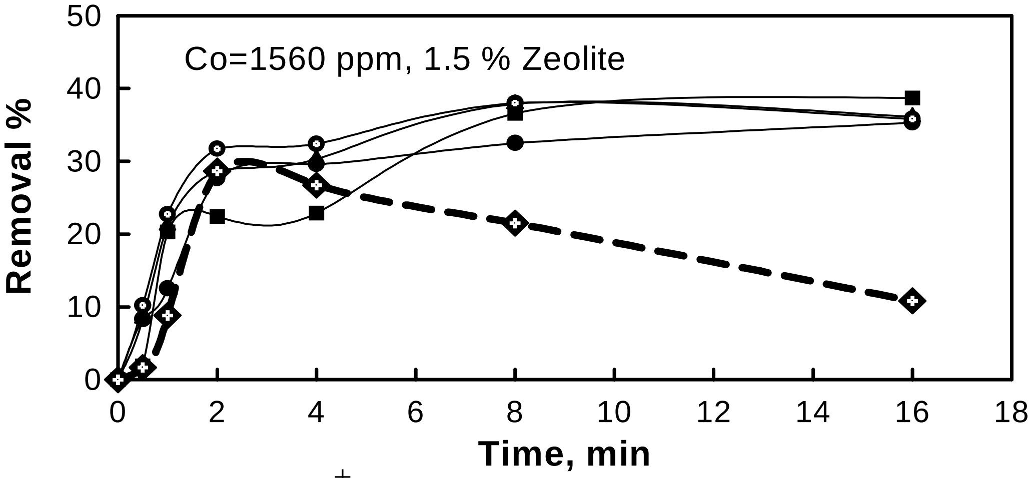


Figure 33. Effect of TMA$^+$ Concentration on the Removal % of Benzene on TMA$^+$ Modified Zeolite

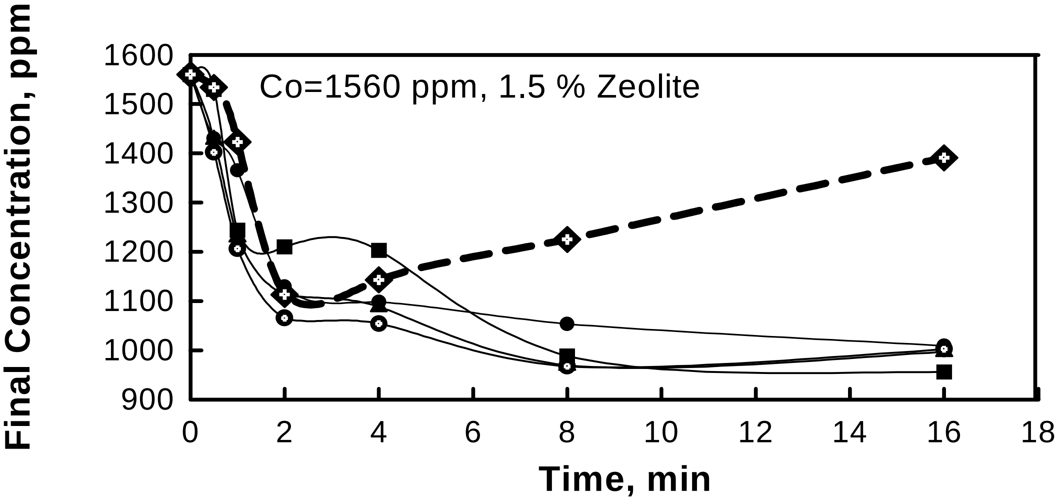


Figure 34. Effect of TMA$^+$ Concentration on the Change of Benzene Concentration in the Solutions

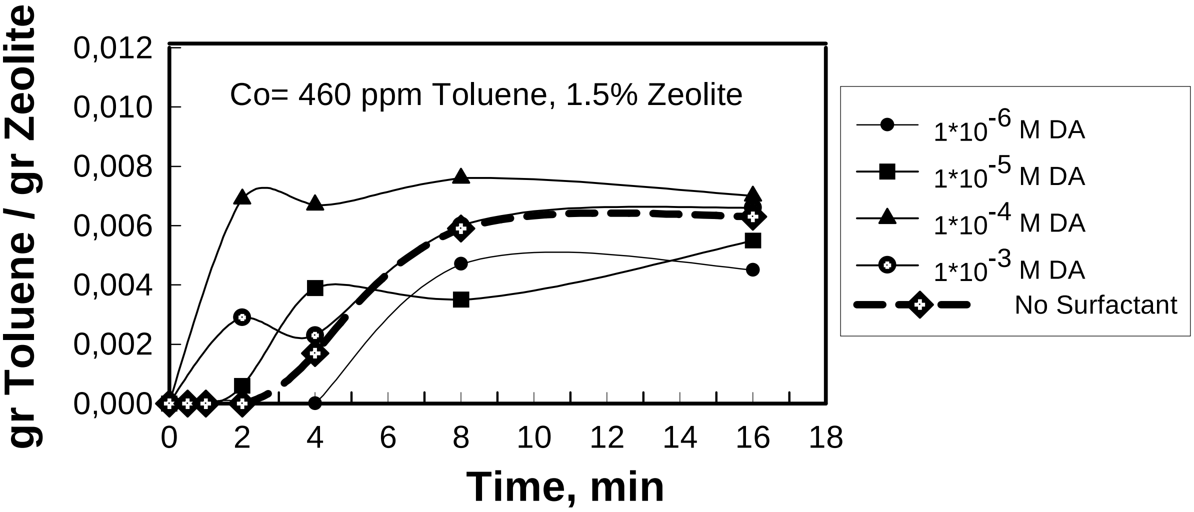


Figure 35. Effect of DA Concentration on the Adsorption of Toluene on DA Modified Zeolite

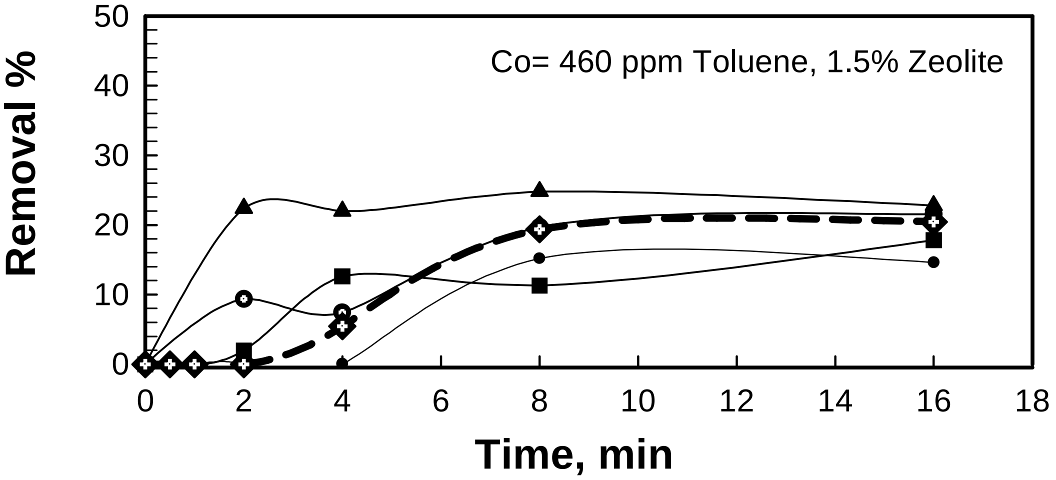


Figure 36. Effect of DA Concentration on the Removal % of Toluene on DA Modified Zeolite

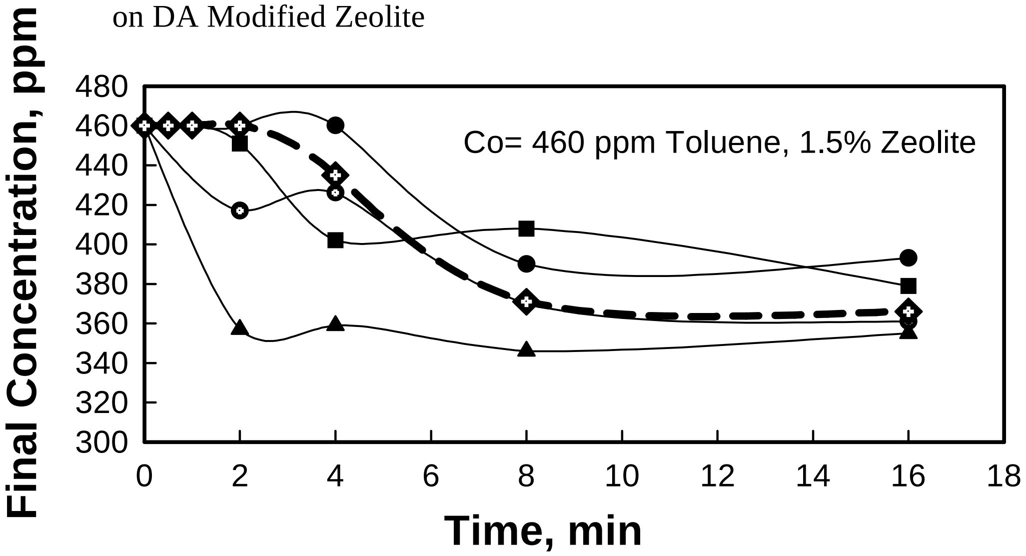


Figure 37. Effect of DA Concentration on the Change of Toluene Concentration in the Solutions

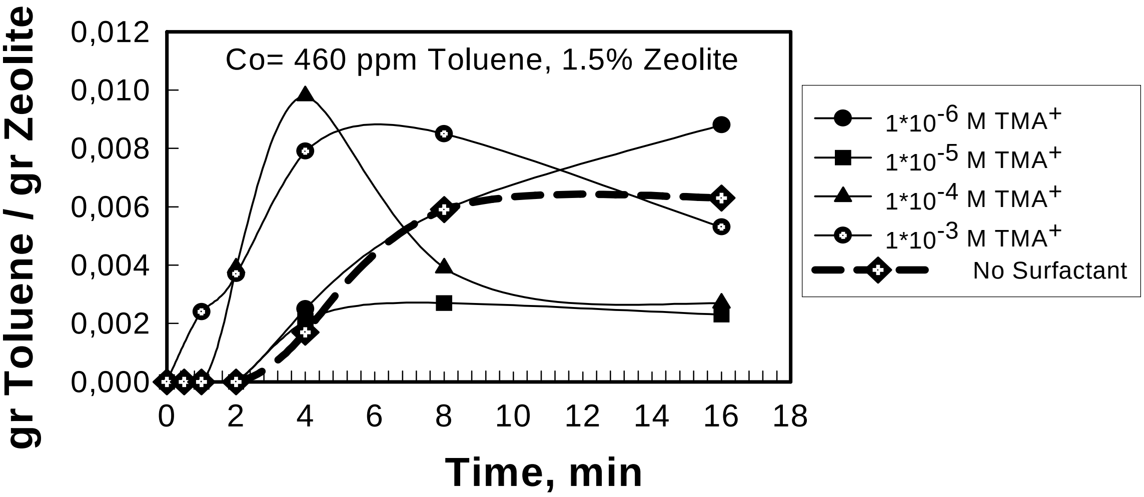


Figure 38. Effect of TMA$^+$ Concentration on the Adsorption of Toluene on TMA$^+$ Modified Zeolite

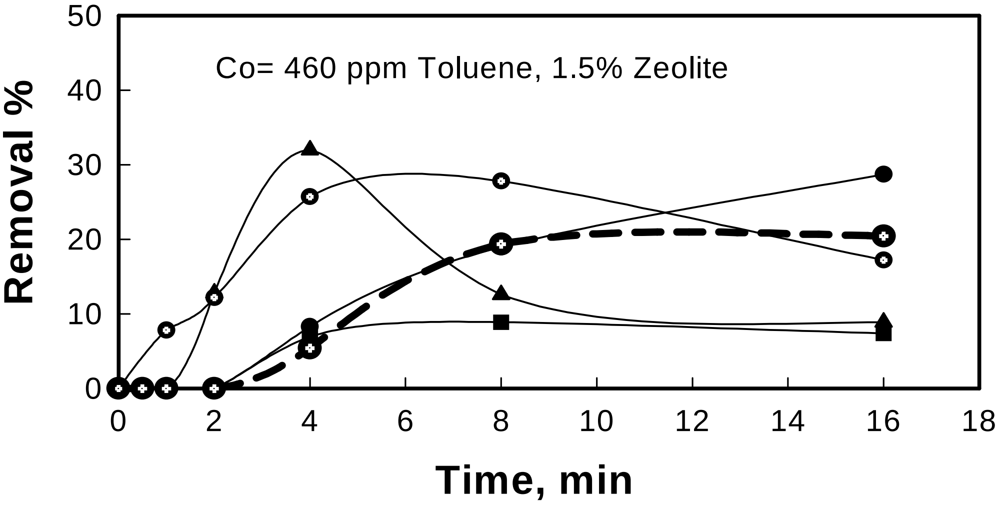


Figure 39. Effect of TMA$^+$ Concentration on theRemoval % of Toluene on TMA$^+$ Modified Zeolite

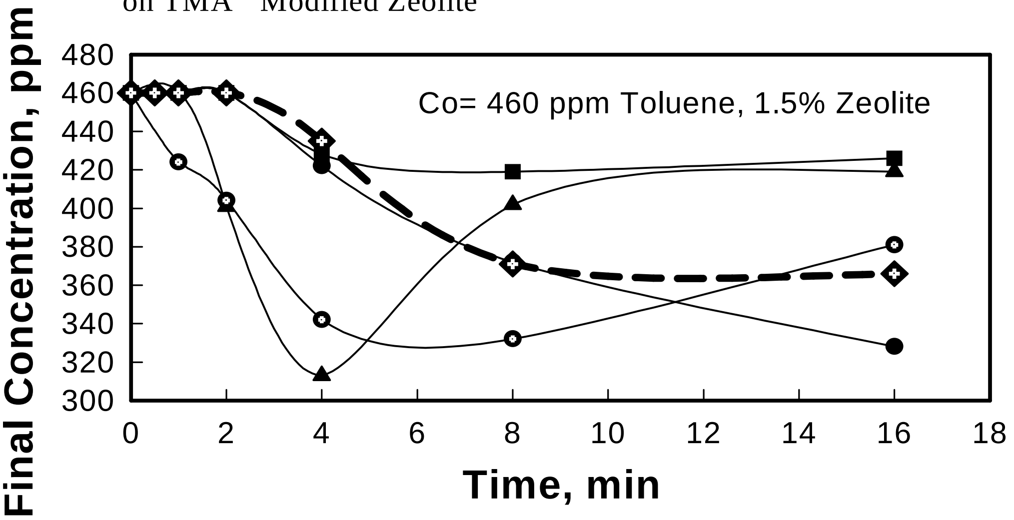


Figure 40. Effect of TMA$^+$ Concentration on the Change of Toluene Concentration in the Solutions

4.3.2.3. o-Xylene Adsorption on DA and TMA^+ Modified Zeolite

Similarly, the effect of DA and TMA^+ on o-xylene adsorption on zeolite was also studied as a function of these surfactant concentrations. The results are given in Figure 41-46. It is seen that o- xylene adsorption with a bigger molecule is affected more than that of the other hydrocarbons. Both the kinetics and the amount adsorbed after 16 minutes of conditioning were changed as a function of surfactant concentration.

DA delayed the adsorption of o- xylene and started after 2 minutes instead of 0.5 minute in case of unmodified surface. After 2 minutes, adsorption started to increase and reached a maximum value around 4 minutes and therefore removal increased from 17% to 35% under these conditions. A nonlinear effect of surfactant concentration can be observed here. The best result is obtained at a lower concentration as 1×10^{-6} M DA. The effectiveness seems to decrease with increasing concentration. However, 1×10^{-3} M showed a very different result, adsorption started after 4 minutes of conditioning and increased with increasing time. After 16 minutes the adsorbed amount was still increasing (Figure 41). This part of the study requires more research to explain this behaviour. In case of no surfactant, o- xylene adsorption reached to a maximum value at 2 minutes. After 2 minutes the decrease of o-xylene adsorption was most probably due to desorption and reached to zero after 8 minutes. In the presence of surfactants, however, there was still adsorption after 16 minutes of conditioning time. The results of TMA^+ were very similar except the beginning of the adsorption in case of DA modified surface. It started as soon as the conditioning has started (as it was also for unmodified zeolite).

The removal sequence for DA modified zeolite was o-xylene>toluene> benzene. This sequence was also obtained by Cadena and Cazares(1993).They reported that this mechanism is related to the solubility and the carbon number of the hydrocarbon. If solubility decreases and if the carbon number increases, as it is for o-xylene, the adsorption increases on long-chain surfactant modified clinoptilolite rich natural zeolite. Therefore o-xylene was favored and toluene was easier to adsorb than benzene. Cadena and Cazares (1993) reported alsothat the removal on TMA^+ follows this trend: benzene> toluene>o-xylene. The same result was obtained in this study.

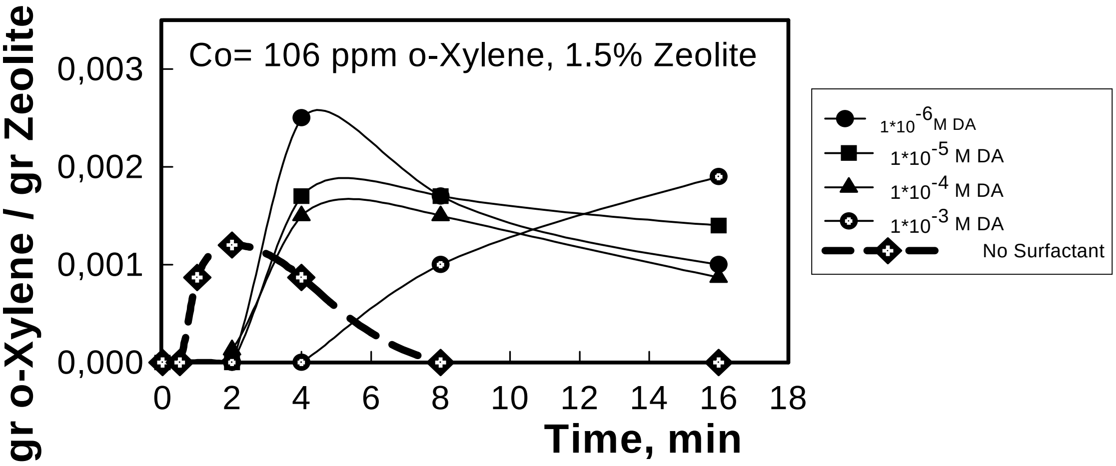


Figure 41. Effect of DA Concentration on the Adsorption of o-Xylene on DA Modified Zeolite

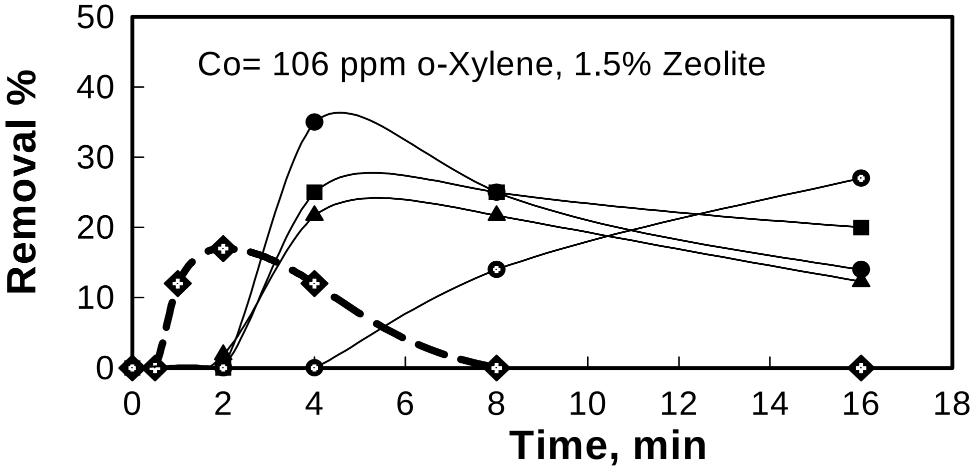


Figure 42. Effect of DA Concentration on the Removal % of o-Xylene on DA Modified Zeolite

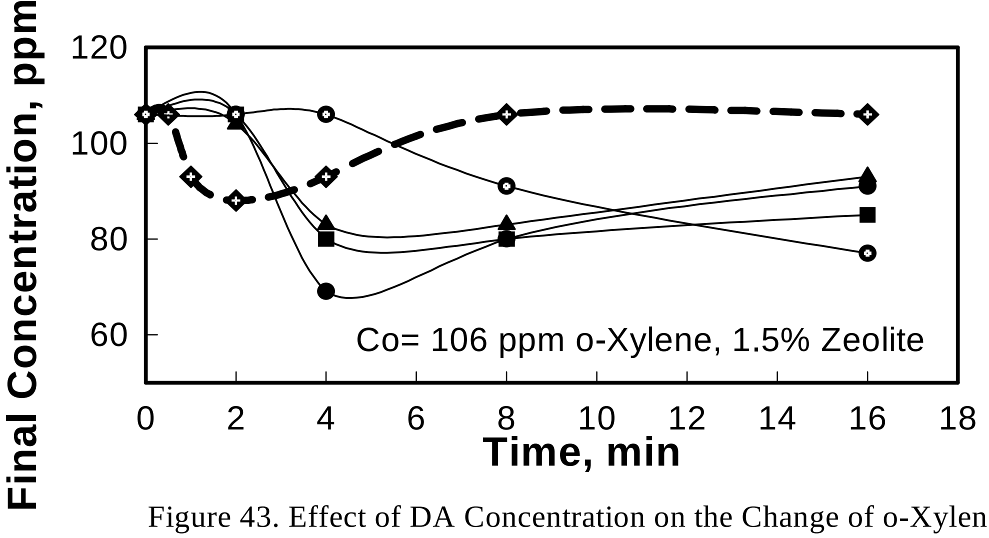


Figure 43. Effect of DA Concentration on the Change of o-Xylene Concentration in the Solutions

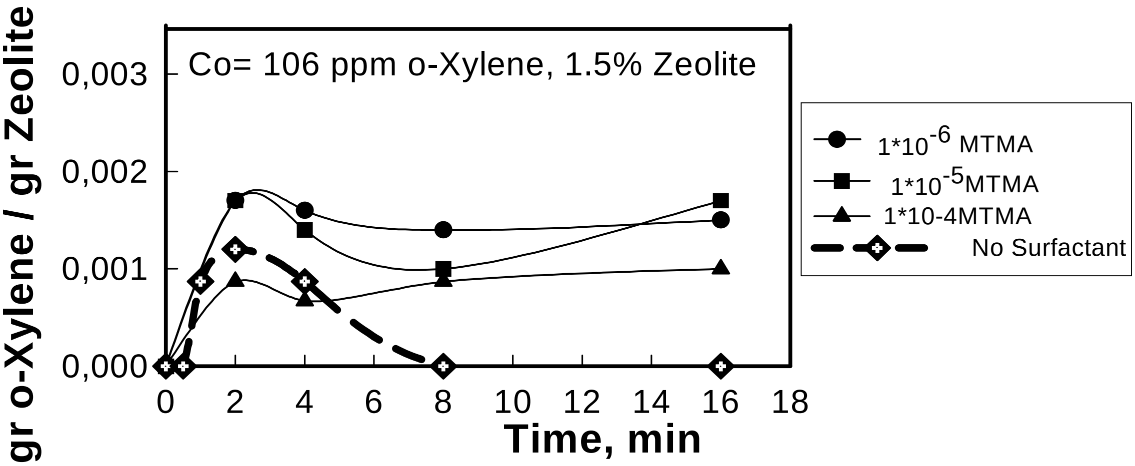


Figure 44. Effect of TMA$^+$ Concentration on the Adsorption of o-Xylene on TMA$^+$ Modified Zeolite

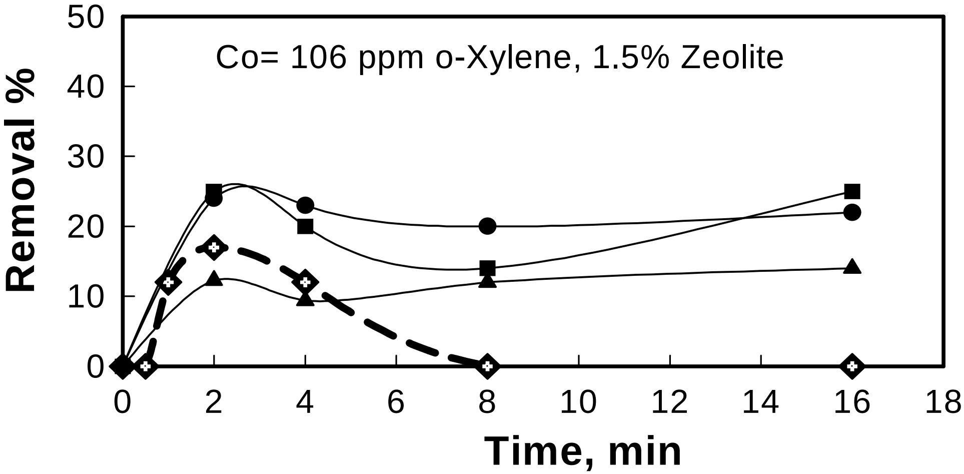


Figure 45. Effect of TMA$^+$Concentration on the Removal % of o-Xylene on TMA$^+$ Modified Zeolite

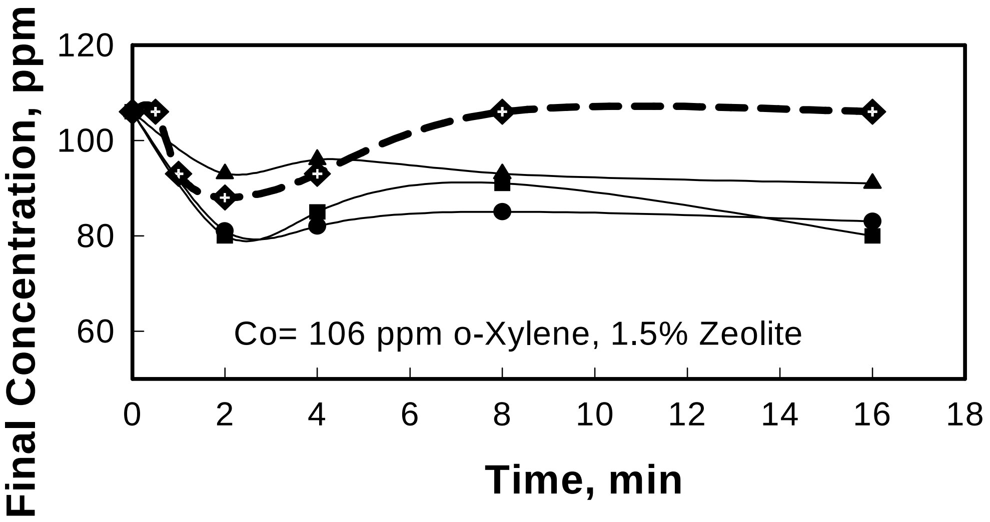


Figure 46. Effect of TMA$^+$ Concentration on the Change of o-Xylene Concentration in the Solutions

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

In this study, the removal of benzene, toluene and o-xylene by clinoptilolite rich natural zeolite from simulated waste water was studied. For this purpose adsorption studies were conducted to determine the amount removed from water. In some cases, a high energy-polar zeolite surface was made more hydrophobic using cationic surfactants as dodecyl amine (DA), tetramethylammonium (TMA+) and an anionic surfactant as sodium dodecyl sulfate (SDS). pH of the zeolite-water suspension were adjusted such that surface was positive when the anionic surfactant was used. For this purpose contact angle and surface tension measurements were conducted and the free energy change of the system was calculated to investigate the hydrophobic degree of the zeolite surface. The results of these studies have shown that the removal of hydrocarbons from contaminated water by this type of zeolite is marginal. This could however be improved by surface modification under some conditions as surfactant type, concentration, hydrocarbon type and the treatment time. The following specific conclusions were obtained:

The contact angle and surface tension measurements have shown that surface could be more hydrophobic in the presence of surfactants. DA was found to be more effective compared to others and increased the mean contact angle degree from 7.76^o to 51.13^o at a concentration of 1×10^{-3} M. In case of the other cationic surfactant, TMA^+, the mean contact angle was only 29.37^o at this concentration. By using these values the calculated free energy change of the system has shown that surface has more affinity to the hydrocarbon type organic structures after modification in the presence of surfactants compared to the unmodified surface.

Surfactant effect on the hydrophobicity however was a function of its type and concentration.

The kinetic adsorption studies with unmodified natural zeolite surface showed a time dependent removal of hydrocarbons from water. The time and the amount of the maximum removal changed as a function of hydrocarbon type. It was 2 minutes and 28.6% for benzene, 16 minutes and 20% for toluene and 2 minutes and 17% for o-xylene respectively. Except toluene, there was an optimum time that the removal was high. This is most probably due to the desorption of these type of hydrocarbons from surface after a certain time.

The kinetic adsorption studies with surfactant modified zeolite surface showed an improvement in the removal of hydrocarbons depending on the hydrocarbon and surfactant type and concentration. In case of benzene, surface modification did not bring any significant change for DA. TMA^+ modification, however, decreased the desorption at longer times significantly. Therefore the removal increased to about 30-40%. In case of toluene, surfactant effect was at short times. While there is no adsorption up to 5 minutes without surfactant this value increased about 30% percent in case of both the surfactants, DA and TMA^+. In case of o-xylene, on the other hand, this effect was on the decreasing desorption at longer times. Therefore an increase in the removal of hydrocarbons from water is about 30%.

According to these conclusions some further studies are needed. The mechanism of desorption was not clearly understood. During this study higher removal was expected on modified zeolite. Therefore some experiments are needed to obtain further increases by modification. Hexadecyltrimethylammonium ($HDTMA^+$), which is a cationic surfactant, should also be used. This surfactant is recently used for the modification of negatively charged surfaces.

REFERENCES

Akdeniz Y.," Cation Exchange in Zeolites, Structure Modification by Using a Microwave", MSc. Thesis, Izmir, September 1999.

Barros M.A.S.D, Machado N.R.C.F, Alves F.V., Sousa-Agular E.F., “Ion Exchange Mechanism of Cr^{+3} on Naturally Occurring Clinoptilolite”, Brazilian Journal of Chemical Engineering, 14, No.3, pp. 233-241, September 1997.

Borovkow V.Yu., Keith-Hall W., Kazansky V.B., J.Catal.,51, 437, 1978.

Breck D.W., "Zeolites Molecular Sieves-Structrue, Chemistry, and Use", John Wiley&Sons, Canada, 1974.

Bruner F., “Gas Chromatographic Environmental Analysis”, VCH, USA, 1993.

Cadena F., Cazares E., “Regenerative properties of spent tailored soils”, New Mexico Water Resources Res. Inst., Tech. Completion Rept.345690, p. 38, 1990.

Cadena F., Cazares E., “Sorption of Benzene, Toluene, and o-Xylene from Aqueous Solution on Surfaces of Zeolitic Tuffs Modified with Organic Cations”, Natural Zeolites’93, Ming D.W. and Mumpton F.A., eds., pp.309-324. Int.Comm.Natural Zeolites, Brockport, New York 14420,1993.

Cadena F., Garcia R., Peters R.W., “Adsorption of benzene from aqueous solutions by bentonite treated with quarternary amines”, Env. Prog., 9, 245-253, 1990.

Canadian Centre for Occupational Health and Safety Report, Canada, 1997-2000.

Cazares E., “Removal of single-ring aromatics by tailored zeolites” , Ph.D. Dissertation, New Mexico State University, Las Crucas, New Mexico, p.135, 1992.

Chen N.Y., “Hydrophobic Properties of Zeolites”, The Journal of Physical Chemistry, Vol.80, No.1, 1976.

Ching C.B., Ruthven D.M., ”Sorption and Diffusion of Some Amino Acids in KX Zeolite Crystals”, The Chemical Engineering Journal, 40, pp. B1-B5, 1989.

Choudhary V.R.,.Srinivasan K.R., “Sorption and Diffusion of Benzene in H-ZSM-5: Effect of Si/Al Ratio, Degree of Cation Exchange and Pretreatment Conditions”, Journal of Catalysis, 102, pp.328-337, 1986.

Çağlar B.B., “Ege Denizi Kıyılarındaki Sediment ve Organizmada Petrol Hidrokarbonlarının Dağılımı”, MSc Thesis, Izmir, 1995.

Daugherty, M.L.,M.S., Chemical Hazard Evaluation and Communication Group, Biomedical and Environmental Information Analysis Section, Health and Safety Research, September,1992.

Dojlido J.R., Best G.A., ”Chemistry of Water and Water Pollution”, Ellis Horwood Ltd., Great Britain, 1993.

Dyer A., “Separation of Closely Related Systems by Molecular Sieve Zeolites”, Separation Science and Technology, 13(6), pp.501-516, 1978.

Franklin K.R., Hunt R.R., Williams C.D., “Sorption of butan-1-ol from aqueous solution by silica molecular sieves, Zeolites 8, 432-435, 1988.

Grant D.W., “Capillary Gas Chromatography”, John Wiley&Sons, England, 1996.

Gündüz G., ″Benzene Adsorption on a NaX and NaY Zeolite″, Journal of Engineering and Environmental Science, pp.325-329, 1992.

Harwell J.H., Sabatini D.A., Knox R.C., “Surfactants for Ground Water Remediation”, Colloid and Surfaces, A: Physicochemical and Engineering Aspects, 151, pp.255-268, 1999.

Herden H., Einicke W.D., Schöllner R., ”Adsorption of n-Hexane/n-Olefin Mixtures by NaX Zeolites from Liquid Solution”, Journal of Colloid and Interface Science, Vol.79, No.1, pp.280-283, January 1981.

Hill S.G., Seddon D., Comparison of the sorption of benzene in ZSM-5, silicalite-1, and silicalite-2, Zeolite 11, 699-704,1991.

Kacirek H., Schweitzer W., Wittern K.P., “NMR investigations of mobility mechanism of benzene molecules in the cavities of faujasite type zeolites and connections with catalytical and sorption properties of these substances”, The Proceedings of the Conference on the Properties and Applications of Zeolite, April 1979; London, Towsend R.P. (editor), The Chemical Society, 164-175, 1980.

Knowlton G.D., White T.R, “Thermal Study of Types of Water Associated with Clinoptilolite”, Clays and Clay Minerals, Vol.29, No.5, 403-411, 1981.

Loudon G.M., “Organic Chemistry”, Addison-Wesley Publishing Company, Canada, July 1984.

Ma Y.H., Lin Y.S., Adsorption of liquid hydrocarbon, AIChE Symp. Ser. 81, 39,1985.

Milestone N.B., Bibby D.M., “Concentration of alcohol on silicalite”, J.Chem.Technol. Biotechnol., 31, 732-736, 1981.

Montgomery, M.J., ”Water Treatment Principles and Design”, John Wiley and Sons, U.S.A, 1985.

Narin G., “ A Chromatographic Study of CO Adsorption in Clinoptilolite”, MSc. Thesis, Izmir, January 2001.

Narita E., Horiguchi N., Okabe T., “Adsorption of phenol benzyl alcohol from aqueous solution by silicalite, Chem.lett., xxx, 787, 1985.

Papaioannou Chr., Petroutsos G., Gunsser W., “Examination of the Adsorption of Hydrocarbons at Low Coverage on Faujasite Zeolites”, Solid State Ionics, 101-103, pp.799-805, 1997.

Pope C.G., “ Sorption of Benzene, Toluene, and p-Xylene on Silicate and H-ZSM-5”, J.of Phys.Chem., 90, pp.835-837, 1986.

Post M.F.M., Van Amstel J., Kouwenhoven H.W., “Proc. 6th Int. Zeolite Conf., Reno, July 10-15, 1983” (Olson D. and Bisio A., Eds.), p.517, Butterworths, London, 1984.

Pozas C., Kolodziejski W., Roque-Malherbe R., “Modification of Clinoptilolite by Leaching with Orthophosphoric Acid”, Microporous Materials, 5,pp. 325-331, 1996.

Rivera A., Rodriguez-Fuentes G., Altshuler E., “Time Evolution of a Natural Clinoptilolite in Aqueous Medium: Conductivity and pH Experiments”, Microporous and Mesoporous Materials, 40, pp.173-179, 2000.

Rosen M.J.,” Surfactants and Interfacial Phenomena ”, John Wiley & Sons, Canada, 1989.

Shu H., Danyum L., Scala A.A., Ma Y.H., “Adsorption of Small Organic Pollutants from Aqueous Streams by Aluminosilicate-Based Microporous Materials”, Separation and Purification Technology, 11, pp.27-36, 1997.

Sing K., Rouquerol F., Rouquerol J., "Adsorption by Powders & Porous Solids Principles, Methodology and Applications", Academic Press, London, 1999.

Valsaraj K.T., Jain P.M., Kommalapati R.R., Smith J.S., "Reusable Adsorbents for Dilute Solution Separation. 1. Adsorption of Phenanthrene on Surfactant-Modified Alumina", Separation and Purification Technology, 13, pp.137-145, 1998.

Vasant E.F., "Pore Size Engineering in Zeolites", John Wiley & Sons Ltd, England, 1990.

Yan T.Y., "Effects of Moisture in Separation of C_8 Aromatics using Medium-pore Zeolites", Ind.Eng. Chem.Res., 27, pp.1665-1668, 1988.

Zhang Z.Z., Sparks D.L., Scrivner N.C., "Sorption and desorption of quarternary amine cations on clays", Environ. Sci. Technol., 27, p.1625-1631,1993.