INVESTIGATION OF FUEL OXYGENATE ADSORPTION ON CLINOPTILOLITE RICH NATURAL ZEOLITE

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Senem YETGİN

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We approve the thesis of **Senem YETGİN**

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ABSTRACT

INVESTIGATION OF FUEL OXYGENATE ADSORPTION ON CLINOPTILOLITE RICH NATURAL ZEOLITE

The wide use of fuel oxygenates in gasoline as anti-knocking and emission reduction agent have recently led to serious environmental concerns due to their detection in groundwater and surface water. Among the various gasoline additives, methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) are the most frequently used fuel oxygenates worldwide. Due to the physical and chemical properties of fuel oxygenates, the conventional treatment technologies are generally ineffective for their removal from contaminated water. Adsorption is a common process frequently used to remove fuel oxygenates from water. The use of natural zeolites as adsorbent have increased significantly because of their availability and low cost. Clinoptilolite is one of the most abundant zeolites in nature, and Turkey has very large clinoptilolite reserves. In this project the adsorption properties of clinoptilolite rich natural zeolites for use in the removal of MTBE and ETBE from water have been investigated using batch equilibrium and fixed-bed column experiments. The adsorption properties have been compared with those of two activated carbons (i.e., Powdered Activated Carbon (PAC) and Granulated Activated Carbon (GAC)). In addition, bisolute (i.e., benzene and oxygenate) adsorption experiments were also carried out to determine the effectiveness of these adsorbents in the presence of other gasoline hydrocarbons. All the experiments were performed at 25 °C with initial oxygenate and benzene concentrations of 2000 ppb and 400 ppb, respectively.

In batch equilibrium experiments, it has been found that the powdered and granulated activated carbons had higher adsorption capacities for MTBE and ETBE than clinoptilolite. The highest capacity for the amount of MTBE adsorbed per unit mass of adsorbent was achieved using GAC while that of ETBE was obtained using PAC. The presence of benzene decreased the adsorption capacities of GAC and PAC. However, the effect of benzene was not clear and was dependent on the adsorbent loading for clinoptilolite. In fixed-bed column experiments, GAC and clinoptilolite were tested as adsorbents. The column breakthrough curves for clinoptilolite were steep indicating fast adsorption and narrow mass transfer region. For GAC, mass transfer regions were wider due to the relatively flat breakthrough curves. There was no significant effect of benzene on the breakthrough curves for GAC and clinoptilolite.

ÖZET

YAKIT OXYGENATE'LERİN KLİNOPTİLOLİTÇE ZENGİN DOĞAL ZEOLİT ADSORPSİYONUNUN İNCELENMESİ

Benzinde vuruntu önleyici ve emisyon azaltıcı olarak yaygın bir şekilde kullanılan yakıt oxygenate' lerin yeraltı ve yerüstü sularında tespiti, bu kimyasalların kullanımına dair çevresel endişelere neden olmuştur.

Methly *tert* -Buthyl Ether (MTBE) ve Ethly *tert* -Buthyl Ether (ETBE), dünya çapında en çok kullanılan benzin katkı maddeleridir. Geleneksel arıtım teknolojileri, bu maddelerin fiziksel ve kimyasal özellikleri nedeni ile sudan ayrıştırılmasında yetersiz kalmaktadır. Adsorpsiyon, benzin katkı maddelerinin sudan ayrılmasında kullanılan çok yaygın bir yöntemdir. Doğal zeolitler düşük fiyatları ve kolay elde edilebilirlikleri nedeniyle adsorpsiyon yönteminde daha yaygın bir şekilde kullanılmaktadırlar. Klinoptilolit doğada en çok bulunan zeolit türlerinden biridir ve Türkiye zengin klinoptilolit kaynaklarına sahiptir. Bu projede, klinoptilolitçe zengin doğal zeolitin MTBE ve ETBE' yi sudan adsorplama özelliğinin kesikli adsorpsiyon ve sabit yataklı kolon deneyleri ile incelenmesi ve referans olarak seçilen aktif karbonunkilerle karşılaştırılması amaçlanmıştır. Ayrıca, iki çözünenli (benzen ve oksijenli bileşikler) adsorpsiyon deneyleri, bu adsorbentlerin diğer benzin bileşiklerini içerdiğinde gösterdiği etkinliğini belirlemek üzere yapılmıştır. Bütün deneyler 2000 ppb oxygenate ve 400 ppb benzene konsantrasyonunda 25 °C' de gerçekleştirilmiştir.

Denge adsorpsiyon deneylerinde toz (PAC) ve granül (GAC) aktif karbonun adsorpsiyon kapasitelerinin MTBE ve ETBE için klinoptiloliten fazla olduğu tespit edilmiştir. Birim adsorbent başına MTBE adsorpsiyon kapasitesinin GAC için en fazla olduğu bulunmuştur. PAC için ise ETBE adsorpsiyon kapasitesi daha fazladır. GAC ve PAC için adsorpsiyon kapasitelerinin, çözeltinin benzen içermesi durumunda azaldığı gözlemlenmiştir. Ancak, bu etki klinoptilolit için belirgin değildir. Sabit yataklı kolon deneylerinde sadece GAC ve klinoptilolit test edilmiştir. Kolon salıverme eğrileri klinoptilolitin çabuk doygunluğa eriştiğini yani kütle transfer alanının çok dar olduğunu göstermiştir. GAC için kütle transfer bölgesi salınım eğrilerinin genişliği ölçüsünde daha geniştir. Kolon salıverme deneylerinde benzenin, adsorbentlerin adsorpsiyon kapasitelerini değiştirmediği gözlemlenmiştir.

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CHAPTER 1

INTRODUCTION

The significant part of the world energy is obtained from the combustion of fossil fuels (about 86%). The total world energy consumption was 421 quadrillion Btu in 2003, and it is expected to reach 722 quadrillion Btu in 2030 as shown in Figure 1.1 Seventy-one percent increase in world energy consumption is expected over the period of 2003-2030 "(EIA 2006)".
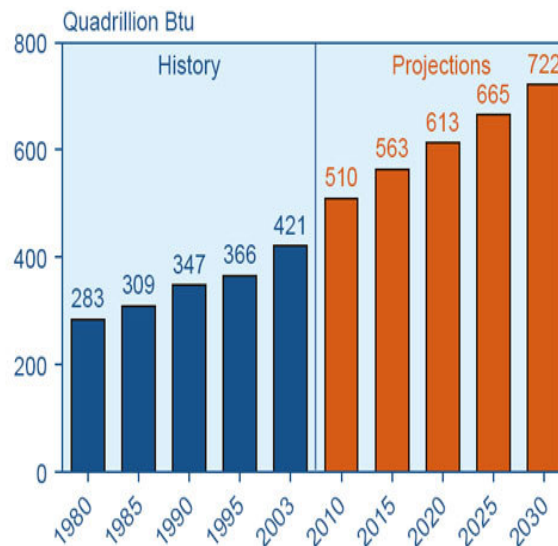
Figure 1.1. World energy consumption
(Source: EIA 2006)

Oil is the dominant energy source, (about 40% of energy consumption is provided by oil) (Figure 1.2), and as shown in Figure 1.3, world-wide oil consumption rises 118 million barrels per day "(EIA 2006)".

The transportation is the major sector for oil demand in the world (about 40% oil is used in transportation), and incomplete combustion of motor–vehicle fuels is the main source of carbon monoxide (CO), which is the main substance having a direct influence on air quality "(National Academy 1996)". Hydrocarbons (HC), nitrogen oxides (NO_X)

and particulate matter (PM) are other substances that are released by combustion engines "(Lenz and Cozzarini 1999)". Consequently, increasing oil consumption in transportation sector is going to affect the air quality in many areas around the world.
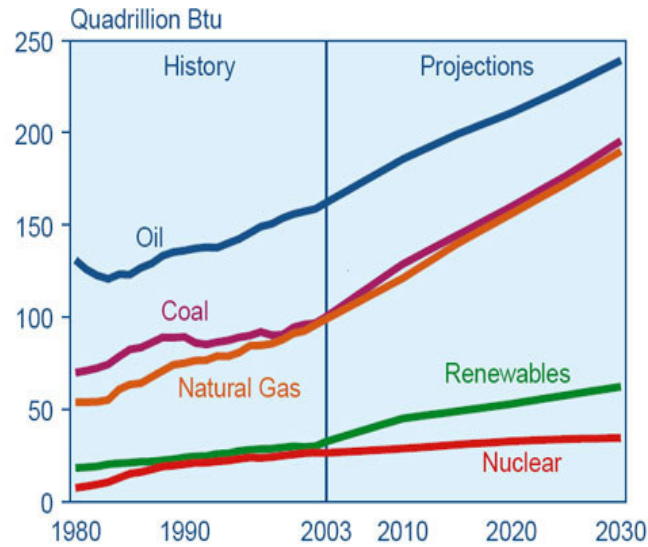
Figure 1.2. World energy consumption by sources

(Source: EIA 2006)

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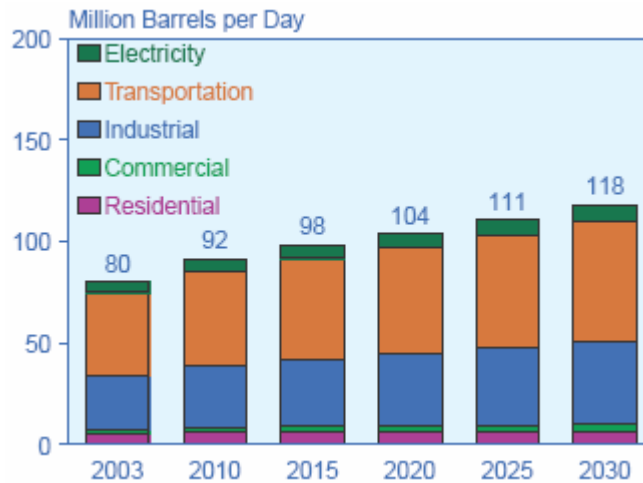
Figure 1.3. World oil consumption by sectors

(Source: EIA 2006)

One of the techniques used to reduce air pollution is the improvement of fuel properties. The lead additives such as tetraalkyllead (TAL), tetraethyllead (TEL) and tetramethyllead (TML) were the most common alkyl-lead compounds employed to

improve fuel properties. These components were used to reduce "knocking" in combustion engines. However, due to the toxicity of lead, its use was phased out and substituted with fuel oxygenates since 1970.

Fuel oxygenates are organic chemicals which contain oxygen in their structure. The most commonly used fuel oxygenates are Methyl Tertiary Butyl Ether (MTBE), Ethyl Tertiary Butyl Ether (ETBE), Ethanol (EtOH), Methanol (MeOH), Tertiary-Amyl Methyl Ether (TAME), Diisopropyl Ether (DIPE) and Tertiary-Butyl Alcohol (TBA). Fuel oxygenates were initially used to increase the burning efficiency and promote complete burning as octane booster in 1970. MTBE was added to about 30% of the gasoline sold in the U.S. "(USEPA 1999a)". During the 1980's, the use of MTBE as octane enhancer increased throughout the country. It was also discovered that MTBE had a number of characteristics that contributed to reducing emissions from gasoline engines "(ADEQ 1999)".

The Clean Air Act Amendments (CAAA) of 1990 has mandated that oxygen must be added to gasoline in areas that do not meet National Ambient Air Quality Standards (NAAQS) for carbon monoxide (CO) and ozone (O_3). The CAA Amendments have initiated two major regulations "(Zogorski et al. 1999)".

• The Oxygenated Fuel Program (OXP): According to this program, gasoline must include 2.7 % oxygen by weight during the cold season.

• Reformulated Gasoline Program (RFG): Suggests that gasoline must contain an average of 2% oxygen by weight in a year.

The CAA Amendments did not specify which oxygenate must be added to gasoline. However, in 1999, 87% of RFG contained MTBE. By the year 1998, MTBE has become the second highest organic chemical produced in the United States "(USEPA 2001)". To meet the required oxygen level of the CAAA, gasoline in OXY areas must contain 15% MTBE by volume during the cold season and RFG areas must contain 11% MTBE by volume year-round. These programs included three phases; Phase I, Phase II, and Phase III.

Phase I regulation started in 1992 in California and became federal law in U.S. in 1995 and lasted throughout 1999. The objective of Phase I regulation was to reduce evaporative hydrocarbon emissions and O_3 level. The Phase I recommended that, 2% oxygen, maximum 1% benzene by volume, no heavy metals and detergents should be

present in fuel. The results of Phase I program showed that VOC and toxic pollutants were cut down to 17.2 and 17%, respectively, and benzene, a known cancer-causing component, reduced to 43% "(USEPA 1999b)". Phase II started in January 1, 2000 for further reduction in hydrocarbons and toxic discharges. Table 1.1 shows the average standard regulations of Phase I and Phase II.

Table 1.1. Reformulated gasoline averaging standards
(Source: EIA 1999)

	RFG Phase I January1995-December 1999			RFG Phase II January 2000		
	Summer Region I	Summer Region II	Winter	Summer Region I	Summer Region I	Winter
Product Quality Standards						
O_2, weight %min	2.1	2.1	2.1	2.1	2.1	2.1
Benzene, Volume %max	0.95	0.95	0.95	0.95	0.95	0.95
Performance Standards (using Phase 2 complex emissions model), percent reduction required:						
Toxic Air Pollutants	18.5 %	17.8 %	17.3 %	21.5 %	21.5 %	21.5 %
VOC	20.8 %	10.5 %	n.a.	29.0 %	27.4 %	n.a.
NO_X	1.4 %	1.6 %	1.7 %	6.8 %	6.8 %	1.5 %

n.a., not applicable

Analysis of fuel data submitted to EPA by industry for compliance purposes shows that emission reductions from the RFG program have been much more than the program requires each year since the program's introduction in 1995 "(USEPA 1999a)". For example, peak ozone concentrations have declined 30% between 1978 and 1997. The average ambient concentration of carbon monoxide in 1997 is 60% lower than it was in 1978; and annual mean nitrogen dioxide concentrations have decreased in urban areas by 25% since 1978 "(EIA 1999)".

Inal and Senkan (2005) have investigated the effects of three different fuel oxygenates (i.e. MTBE, methanol, and ethanol) on species mole fractions in fuel-rich flames of n-heptane/oxygenate/oxygen/argon. It has been found that an increase in oxygen weight percent in fuel blends decreased the concentrations of CO (up to about

4%), small hydrocarbons (up to about 10%), aromatics (up to about 20%) and Polycyclic aromatic hydrocarbons (PAH) species (up to about 40%).

Koshland et al. (1998) have studied the air quality benefits of reformulated gasoline for automotive emissions in California. The experimental studies were clearly addressed the reaction byproducts of MTBE in the presence of other gasoline components for different vehicle technologies. The results demonstrated that the presence of MTBE in reformulated gasoline contributed to improvements in California air quality. However, MTBE and other oxygenates have been found to have no significant effect on exhaust emissions of CO, NOx, benzene, 1,3-butadiene, and VOC from advanced technology vehicles using reformulated fuel. The presence of MTBE in reformulated fuel was associated with an increase in formaldehyde emissions, relative to a non-oxygenated reformulated fuel. Contrarily, in gasoline, it has been reported that, MTBE might be emitted as an unburned hydrocarbon during vehicle use. MTBE was present in the atmosphere and could react with an OH radical to yield tert-butyl formate (TBF) and formaldehyde.

Fernandez and Keller (2000) have studied the cost benefit analysis (CBA) of MTBE and alternative gasoline formulations. In this CBA, they evaluated three gasoline formulations that met California's Phase II Reformulated Gasoline (CaRFG2) requirements: CaRFG2 with MTBE, CaRFG2 with ethanol, and non-oxygenated CaRFG2. It was concluded that, CaRFG2with MTBE had the highest net cost for achieving air quality benefits.

Reuter et al. (1992) carried out the Auto/Oil study. They reported the effect of oxygenated gasoline and Reid Vapor Pressure (RVP) on emissions from twenty 1989 model year vehicles. The test vehicles represented a broad range of engine sizes from 2 to 5.7 liter displacement and had between 10,000-29,000 miles on their odometers. Eleven fuels had been studied including four 3.7 wt % oxygen ethanol fuels, two 2.7 wt % oxygen MTBE fuels, and one 2.7 wt % ETBE fuel. Reuter et al. had found statistically significant reduction in CO, total HC and benzene emission with three fuel oxygenates compared to the non-oxygenated fuels. Contrarily, the NO_X emission increased for all the oxygenates, but the results were statistically significant for only the ethanol fuels, the fuel set with highest oxygen content. The average effect for the complete fuel set was also found to be about (+1.6 ±1) % NO_X per wt % oxygen.

Phase III regulation did not only consider the air pollution but also ground water contamination by fuel oxygenates. Phase III of the reformulated gasoline program tried to phase out the use of MTBE, because, it had potential cancer effects on human body as it was detected in drinking water and groundwater in some areas, due to leaking underground gasoline storage tanks.

MTBE usage as a fuel additive has led to a rise in the reported MTBE groundwater contaminations. In the USA alone, more than 250,000 spillages at filling stations were known as leading to MTBE being introduced into the environment "(Linnemann et al. 2000)". National Water-Quality Assessment (NAWQA) findings indicate that MTBE is the most frequently detected volatile organic compound in ground water underlying urban areas in comparison to agricultural and mixed land-use settings. MTBE was detected in about 14 percent of wells sampled in urban areas. In addition, incidence of MTBE increases in high-use areas. Most of MTBE's high use occurs in Reformulated Gasoline (RFG) areas, where gasoline contains 11-percent MTBE by volume. MTBE has been detected about 4 to 6 times more frequently in the high-use areas than elsewhere "(USGS 2001)". Figure 1.4 shows the commonly detected volatile organic compounds in ground water. It can be seen that oxygenates are the third most commonly detected VOC contaminant in ambient ground water "(USGS 2001)".
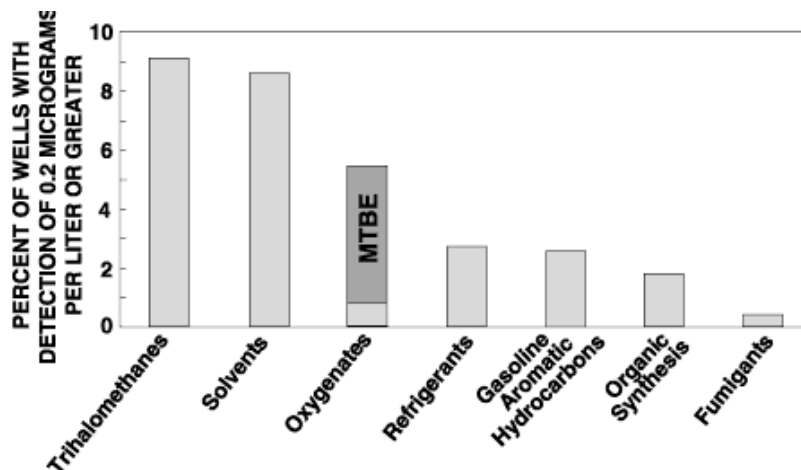
Figure 1.4. Most commonly detected volatile organic component

(Source: USGS 2001)

MTBE has been classified as a possible human carcinogen and its use has been restricted. However, EPA has concluded that the presented data is not adequate to estimate potential health risks of MTBE at low levels in drinking water. Young et al. (1996) have reported MTBE odor thresholds of 13.5 - 45.4 µg/L and taste thresholds of 39-134 µg/L. The possible carcinogenic effects and unpleasant aesthetic issues led to strict EPA guidelines for MTBE in drinking water. In December 1997, the EPA drinking water health advisory for MTBE was 20–40 µg/L "(USEPA 1998)". These limits were arranged to prevent the detection of MTBE by odor or taste and are 20,000 to 100,000 times lower than the exposure levels causing cancer and non-cancer effects in laboratory rats. The California EPA's office of Environmental Health Hazard Assessment set a new MTBE drinking water standard of 14 µg/L as a response to the increased occurrence of MTBE in California drinking water. The most significant development in California was banning the use of MTBE.

MTBE has been completely or partially banned in some states of U.S. As of June 2004, 19 States had passed legislation to completely or partially ban MTBE use in gasoline "(USEPA 2004a)". In 2005, Congress passed the Energy Policy Act that eliminated the oxygen requirement in gasoline as established by the CAAA of 1990. "(USC 2005)". The Energy Policy Act required EPA to take this action by May 5, 200. "(USEPA 2006)".

Detection of fuel oxygenate in ground and surface water, and particularly in public and private drinking water wells, have raised significant concerns about the continued use of MTBE in gasoline. The removal of fuel oxygenates from drinking water sources have become an important issue since fuel oxygenates have negative effects on environment. For this purpose, several water treatment processes have been considered such as adsorption, air stripping, advanced oxidation, membrane separation and biodegradation for their removal from contaminated water. Due to physical and chemical properties of the fuel oxygenates the conventional treatment technologies are generally ineffective. Since MTBE is highly water-soluble, air stripping may not be so effective. Membrane separation is considered too expensive. Ozone and ozone/peroxide might have undesired products. The resistant behaviors of ether compounds make the biodegradation processes ineffective "(Achten 2001)". The most preferable removal process is adsorption due to the low cost.

The objective of this study was to investigate the removal of fuel oxygenates from water using clinoptilolite rich natural zeolite as an adsorbent. In batch (equilibrium) and column (fixed bed) adsorption experiments, the adsorption performance of clinoptilolite was compared with those of two reference adsorbents; granulated activated carbon and powdered activated carbon. In addition, the effectiveness of the adsorbents were also tested in the presence of benzene in bisolute experiments.

The physical and chemical properties of MTBE and ETBE are given in Chapter 2. In Chapter 3, information about the three adsorbents used in this study is presented. The previous studies on the removal of fuel oxygenate and adsorption techniques from water are discussed in Chapter 4. The experimental procedure used and findings of this study are given in Chapter 5 and Chapter 6, respectively. The conclusion is presented in Chapter 7.

CHAPTER 2

FUEL OXYGENATES

Gasoline is a mixture of numerous different hydrocarbons and enhanced with benzene or iso-octane rating, used as fuel in internal combustion engines (WEB_1 2006). Gasoline can be blended in many different combinations, in some cases, alcohols and ethers as oxygenate. Fuel oxygenates are chemicals containing oxygen that can be added to fuels, especially gasoline, to make it burn more efficiently. The addition of oxygenates also improves the gasoline's octane number "(CRS 2006)".

Fuel oxygenates have been used by refineries since the late 1970s. They came into widespread use when leaded gasoline was phased out. Fuel oxygenates, especially MTBE were used as octane enhancer similar to that of lead, but without fouling the catalytic converters with low cost. Fuel oxygenates have also been used to provide cleaner-burning for Reformulated Gasoline (RFG), which as a 1990 CAAA requirement in the nation's most polluted areas since 1995 in U.S.A.

Fuel oxygenates increase octane number and reduce the "knocking". Octane number represents resistance of gasoline to knock and gives a clue on how much the fuel can be compressed. This number is measured by isooctane and heptane content. "0" octane number gives heptane content and "100" octane number gives isooctane content. Isooctane is very resistant to knocking and heptane knocks very easily. For example, 92 octane number means that the gasoline has an octane number, which is similar with 92% isooctane and 8% heptane, rate blended gasoline. At present, three systems of octane rating are used in the United States. Two of these, the Research Octane Number (RON) and Motor Octane Numbers (MON), are determined by burning the gasoline in an engine under different, but specified, conditions. Fuel octane number can be calculated as an average of RON and MON (WEB_2 2006).

$$\text{Octane Number} = \frac{(\text{RON} + \text{MON})}{2} \qquad (2.1)$$

The reduction in knocking and overcoming premature ignition are the octane enhancers' capability. Addition of oxygenate increases this value. Table 2.1. lists some commercial fuel additives and their specific properties to identify their behavior.

Table 2.1. The key properties of the most commonly used fuel oxygenates

Property	RON	MON	Blending octane (R+M)/2	Neat RVP (Psi) 100 F	Blending RVP (Psi) 100 F	Oxygen weight%	Molecular weight
MTBE	117	101	110	7.8	8	18.2	88.15
ETBE	118	101	111	4	4	15.17	102.1
MeOH	129	102	115	2.3	18	34.8	46.06
EtOH	133	105	119	-	40	49.9	32.04

2.1. Methyl Tertiary Butyl Ether (MTBE)

MTBE has been used in the U.S. since 1979, initially as a replacement for lead in gasoline. In 1990, when Clean Air Act (CAA) amendments were passed and the Federal Reformulated Gasoline (RFG) Program was established, MTBE became a standard addition to reformulated gasoline in areas that did not meet air quality standards. MTBE has been credited with drastically increasing the nation's air quality by reducing emissions of volatile organic compounds, CO, and other mobile-source air toxics. Under the CAA, RFG was required to contain 2% oxygen by weight. Most RFG contain MTBE because it easily mixes with gasoline and provides the best emission reductions.

There are three types of MTBE production plants: "(EIA 2000)"

• *Refinery/Petrochemical plants*: Isobutylene, produced as a byproduct in refinery catalytic crackers and in petrochemical ethylene plants, is reacted with methanol to produce MTBE

- *Merchant plants*: Merchant plants isomerize normal butane to isobutane, then dehydrogenate isobutane to isobutylene, and then combine the isobutylene with methanol to produce MTBE

- *TBA plants*: Tertiary butyl alcohol (TBA) is a byproduct of the propylene oxide production process. TBA is reacted with methanol to produce MTBE.

The commercial production of MTBE started in Europe in 1973 and in the USA in 1979. As shown in Figure 2.1. the demand of MTBE in U.S. was higher than any other region in the world. It was reported that total worldwide production capacity was 20.6 million tones in 1994 "(ECOTEC 1997)". MTBE can be manufactured in petroleum refineries and in plants.
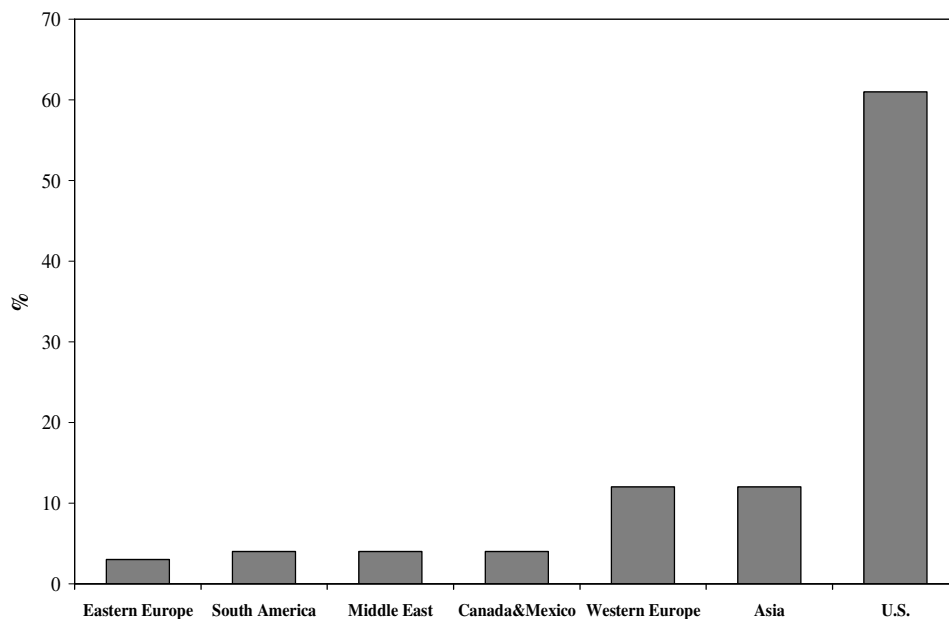
Figure 2.1. Worldwide demand for MTBE in the year 1999.

(Source: Thayer, 2000)

MTBE promotes complete burning of gasoline, and results in the reduction of CO and O_3 levels. MTBE is the most commonly used fuel oxygenate component due to its low cost, and it contributes to the reduction of pollution emissions. According to the report of EPA, the significant reductions of pollutants have been obtained by reformulated gasoline containing 10-15% MTBE (the first phase of the RFG program,

from 1995 through 1999). The reduction of ozone-forming volatile organic compounds and toxics emission was 15%. At the beginning of 1998, NO_X reduction was observed by 1.5%. This was equivalent to taking more than 7 million vehicles off the road. In the year 2000, the second phase of the RFG program was achieved greater benefits for the reduction of VOCs, by 27 %, 22% reduction in toxics, and 7% reduction in oxides of nitrogen emissions, which can initiate smog formation "(USEPA 1997)"

The benzene emissions have decreased by 15–35% using reformulated gasoline compared to the regular gasoline sold in Europe "(Hellen et al. 2002)". The addition of methanol and methyl tert-butyl ether (MTBE) to fuel did not increase acetaldehyde emissions "(CaEPA 1993)".

The high water solubility of MTBE contributes to water contamination by MTBE than any other gasoline component because of its polar nature and hydrophilic structure (Figure 2.2 and Figure 2.3).
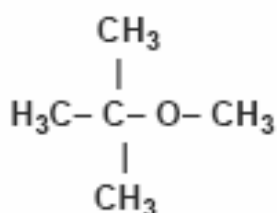
Figure 2.2. Chemical formula of MTBE
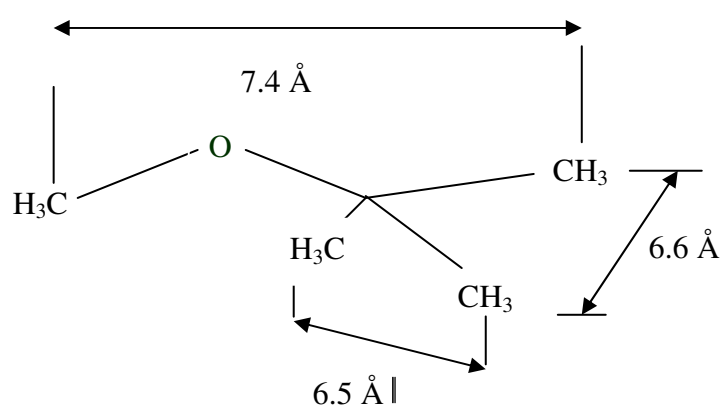
Figure 2.3.   Molecular structures and dimensions for Methyl tertiary-butyl ether ($C_5H_{12}O$) (Source: L.Li et al. 2002)

MTBE, aliphatic ether, is a volatile organic compound (VOC) with a characteristic odor. It is a colorless liquid at room temperature. It is highly flammable and combustible when exposed to heat, flame, or spark. MTBE vapors may form explosive mixtures with air. MTBE is miscible in gasoline and soluble in water, alcohol, and other ethers. It has a molecular weight of 88.15, a vapor pressure of about 245 mmHg at 25 °C, an octane number of 110, and solubility in water of about 50 g/L at 25 °C. These properties have been listed in Table 2.2. It disperses evenly in gasoline and water, and stays suspended without requiring physical mixing. It does not increase the volatility of other gasoline components when it is mixed with gasoline. The log of the octanol-water partition coefficient (log K_{ow}) is reported to range from 0.94 to 1.24, which indicates that there is 10 times more partitioning of MTBE in the lipophilic phase than in the aqueous phase of solvents. In addition, the blood-air, urine-air, saline-air, fat-air and oil-air partition coefficients are reported to be 20, 15.6, 15.3, 142 and 138, respectively. The odor threshold ranges from about 0.32 to 0.47 mg/m^3 (about 90 to 130 ppb) in air and can be as low as 5 ppb (about 0.02 mg/m^3) for some sensitive people. The lowest taste threshold in water is likely to be at or about 2 ppb "(CaEPA 1999)".

Table 2.2. Physical and chemical properties of MTBE

(Source: EFOA, 2000)

Physical State (@ NTP)	Colorless liquid
Boiling point	55.2°C
Melting point	-108.6 °C
Flash point	-30 °C
Water solubility	51 g/L
Auto ignition temperature	425 °C
Flammability limits in air	1.5-8.5 %
Relative density	0,7405 g/ml at 20 °C
Vapor pressure	245 mm of Hg at 25 °C
Refractive index	1.3690 at 20 °C
Color	Colorless
Odor	Air: Strong ethereal odour, threshold 0.18mg/m3 (0.24µg.l-1, 0.05ppm) Water: threshold 95µg.l-1, (0.095ppm)
Taste	Taste Water: threshold 134µg.l-1, (0.134ppm)
Partition coefficient n-octanol/water ($logK_{ow}$)	1.06
Henry's Law constant	65.4 Pa/m^3 mol
Bioaccumulation factor (BCF)	1.6 (estimated from $log_{10}K_{ow}$), 1.5 (measured for fish)

The Henry's law constant of substance specifies the extent to which that substance distributes itself between the gas and aqueous phase. The Henry's constant is particularly a significant parameter for environmental behavior since there is an aqueous and gas phase in all-environmental partition. Figure 2.4. gives the relative solubility and dimensionless Henry's constants for the selected fuel oxygenates "(USEPA 2004b)". The relatively low Henry's constants of oxygenates can result in them being more difficult to remove from contaminated ground water.
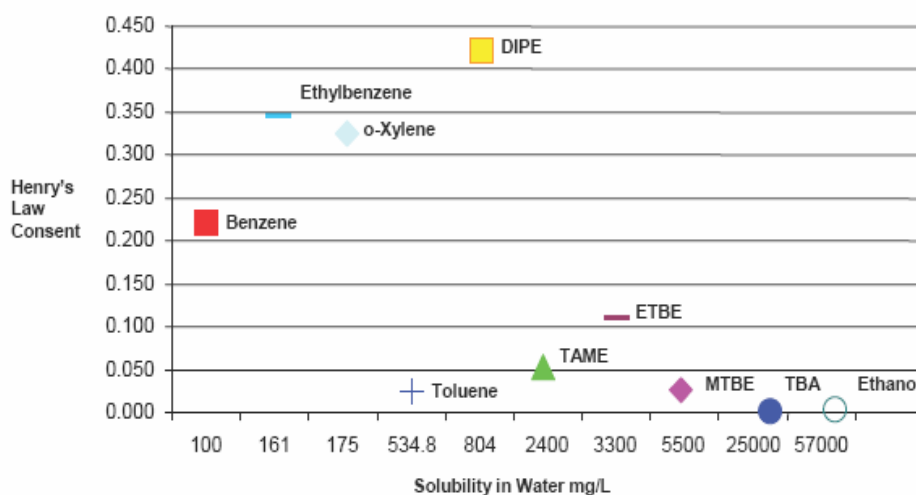
Figure 2.4.   Relative solubility and dimensionless Henry's Law Constants for selected fuel oxygenates (Henry's Law data for MTBE, TBA, and Benzene (Source: USEPA 2004b)

The distribution of MTBE in the soil can also be estimated using the octanol/water coefficient (K_{OW}). The high log K_{OW} value indicates that strong sorption to the soil matrix is not expected. Water solubility of MTBE is the most dominant cause for water contamination. The significant volatility of MTBE is the result of the low boiling temperature of 55 °C and high vapor pressure. The vapor pressure of MTBE is about 3 times higher than that of benzene. According to the Toxics Release Inventory (TRI), releases of MTBE from production sources in the United States amounted to approximately 1.7 million kg in 1996 (EPA), of which about 97% was released to the air and less than 3% was discharged to surface water.

Several studies have been carried out on the toxicity effect of MTBE on animals. Vosahlikova et al. (2006) performed a study to understand MTBE's mutagenicity and environmental toxicity effects by using Microtox1 (*Vibrio fischeri*) toxicity test, Lactuca sativa seed germination test, and Ames bacterial mutagenicity test with *Salmonella typhimurium* strains of TA98, TA100, YG1041, and YG1042,toxicity test. The result of Microtox1 expressed as EC_{50} ,50% reduction of the initial luminescence, was 33 mg (MTBE)/L. Lactuca sativa roots elongation was negative and proved its toxicity for all tested MTBE concentration (0.05, 0.50, and 1.00% v/v). Both Microtox1 test and seeds test proved undoubtedly the MTBE toxicity, while Ames test did not showed genotoxicity of MTBE. Generally no mutagenic response was observed at this

or lower concentrations in any of the four strains used. MTBE contamination can cause symptoms such as, skin and eye burn or irritation. Contact or inhalation with MTBE vapor may cause dizziness or suffocation. In the winter of 1992, it was reported that the inhabitants living in Alaska suffered from severe headaches, dizziness, nausea, after MTBE (15%v/v) was introduced in wintertime-oxygenated gasoline as part of the federal requirements to reduce emissions of CO in Fairbanks and Anchorage "(HHS 1996)".

2.2. Ethyl Tertiary Butyl Ether (ETBE)

ETBE is also a fuel oxygenate that can be blended with gasoline to make it burn more efficiently and thus improve overall air quality. ETBE was first used in 1992, in France. Today, it is widely used and manufactured in most gasoline markets in the Europe "(EFOA 2006)". Mixing ethanol and isobutylene under heat over a catalyst produces ETBE and has a purity of over 98%. The advantage of ETBE is that it eliminates many of the difficulties associated with the use of ethanol such as increased volatility of gasoline and incompatibility with gasoline pipelines. According to available data from European Fuel Oxygenates Association, ETBE also corresponds to biofuels that may provide an advantage in the future to the governments and consumers around the world. The molecular structure of ETBE is given in Figure 2.5.

$$CH_3$$
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O-CH_2-CH_3$$
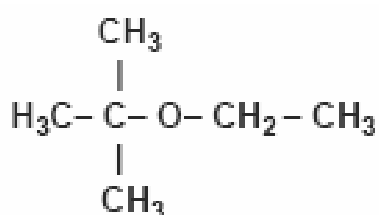
Figure 2.5. Chemical formula of ETBE

Physical and chemical properties of ETBE are listed in Table 2.3. According to this table, ETBE has lower water solubility than MTBE. ETBE is chemically stable under normal conditions of temperature and pressure and has a tendency to be peroxides (auto-oxidize) during storage. ETBE has very low odor and taste thresholds in air and water. In water the thresholds are in the order of 13 and 47 µg/l, respectively. ETBE is

neither a skin nor an eye irritant; however, degreasing of the skin is possible. Animal tests using by ETBE at high doses resulted in liver and kidney effects. However, it is not enough for classifying ETBE as mutagenic, carcinogenic or reproductively toxic.

Table 2.3. Physical and chemical properties of ETBE
(Source: EFOA, 2006)

Physical State (@ NTP)	Colorless, pale yellow, liquid
Boiling point	73.1°C
Melting point	-94°C
Flash point	-19 °C
Water solubility	12 g/L
Auto ignition temperature	310°C
Flammability limits in air	1-6 % (v/v)
Relative density	0.745 g/ml at 20 °C
Vapor pressure	152mm of Hg at25 °C
Refractive index	1.3756 at 20 °C
Odor	Detection: 13 ppb Recognition: 25 ppb
Taste	Detection: 47 ppb Recognition: -
Partition coefficient n-octanol/water ($\log_{10}$)	1.48-1.56
Henry's Law constant	166Pa m^3/ mol
T10	72.8 °C
T50	72.8 °C
T90	73.3 °C
E70 °C	0-30 % vol

Unlike alcohols, ETBE has a non-azeotropic (non-ideal) effect on the vapor pressure of gasoline. Therefore, ETBE blends at near its true vapor pressure and this property makes ETBE ideal for improving the octane number of gasoline, which is significant in maximizing high performance of engines of today's vehicles.

The physical and chemical properties of MTBE and ETBE are shown in Table 2.2. and Table 2.3. Water solubility of MTBE is 51 g/L that is greater than water

solubility ETBE (12 g/L). It means MTBE contaminates water much more than ETBE does. The boiling point of MTBE is lower than ETBE, which has lower vapor pressure, and water solubility. Water solubility of MTBE is greater than ETBE that has lower Henry's Law constant.

CHAPTER 3

ADSORBENTS

3.1. Zeolites

Zeolite is a naturally occurring mineral, in the crystal form, found in volcanic rocks and sedimentary formations of ancient seabeds. Natural zeolite is made of hydrous aluminum silicates of sodium, calcium, potassium or barium. Over 50 types of zeolites are found as occurring naturally in nature and 150 have been synthesized for specific applications. Each of them have a distinctive chemical composition and crystalline structure. "(Anon 2004)". Zeolite is a crystalline, hydrated alumina silicate having a tetrahedral structure; therefore, its pores are fashioned by corner. Structurally, zeolite has the "framework" of aluminosilicate created by infinitely extended three-dimensional network of AlO_4 and SiO_4 tetrahedral structure that form channels and consistent voids that are occupied by cations and water molecules "(Tsitsishvili 1992)".

The metal atoms (classically, silicon or aluminum) are surrounded by four oxygen anions to form an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedral metals are called T-atoms for short (WEB _3 2006).

These minerals have channels and pores in their initial structures, and these pores have water molecules and changeable cations. Water molecules leave a zeolitic structure by heating easily or can be adsorbed again "(Gottardi 1976)".

The zeolitic channels (or pores) are microscopically small, and in fact, have molecular size dimensions so they are often termed "molecular sieves". The size and shape of the channels have unusual effects on the properties of these materials for the adsorption processes, and this property leads to their use in separation processes. Molecules can be separated by using their shape and size effects related to their possible direction in the pore, or by differences in strength of adsorption. Silicon typically exists in a +4 oxidation state, therefore, the silicon-oxygen tetrahedron are electrically neutral. However, in zeolites, aluminum typically exists in the +3 oxidation state so that aluminum-oxygen tetrahedron form centers that is electrically deficient with one

electron. Thus, zeolite frameworks are typically anionic, and charge-compensating cations occupy the pores to maintain electrical neutrality. These cations can participate in ion-exchange processes, and this provides some important properties to zeolites. When charge-compensating cations are "soft" cations such as sodium, zeolites are excellent materials that make water soft, because they can pick up the "hard" magnesium and calcium cations in water leaving behind the soft cations. When the zeolitic cations are protons, the zeolite becomes a strong solid acid. Such solid acids form the foundations of zeolite catalysis applications including the important fluidized bed cat-cracking refinery process. Other types of reactive metal cations can also populate the pores to form catalytic materials with distinctive properties. Thus, zeolites are also commonly used in catalytic operations and catalysis with zeolites is often called "shape-selective catalysis

Zeolite pores consist of different amount of oxygen atoms such as 8, 10 and 12 and are called small, medium and large ring size respectively. They are represented by the empirical formula:

$$M_{x/n} \qquad [\,(AlO_2)_x\,(SiO_2)_y\,]\,. \qquad w\ H_2O$$

exchangeable   anionic framework   sorbate

cations   phase
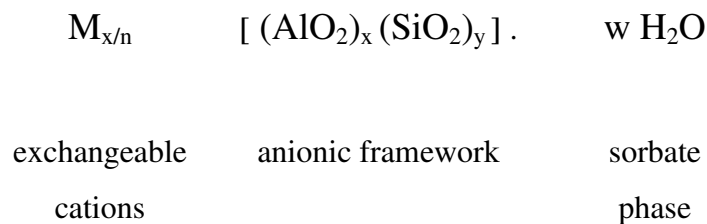
The zeolite structure consists of a pore system with channels in one, two or three dimensions and inner cavities may be present. The diameters of the pores and cavities range from 3 Å to 12 Å, which matches the dimensions of many hydrocarbon molecules and makes it possible for zeolite selectivity for which they are applied as adsorbents and catalysts. The exact diameter of the pore depends on the coordination and the amount of cations and anions present in the ring.

Zeolites have very high water adsorption capacities and are preferred for drying and dehumidification processes. They can also be used as anticake agents and pellet binders for animal feed additive applications. Furthermore, the large surface area is a major advantage for its successful use in capturing contaminants and other substances during purification applications. Zeolites have also been used to adsorb radioactive

substances and mycotoxins; therefore, they are used as toxin binders in food applications.

3.2. Clinoptilolite

Clinoptilolite (Na_6 [$Al_6Si_{30}O_{72}$]. 24H2O), one of the most abundant zeolites in nature, possesses the heulandite (HEU) type framework. High occurrences of clinoptilolite is diged out in many countries, and their interesting properties and varieties of the application have attracted so many areas. The HEU topology contains a ten-member ring channel pore system with eight-member ring cross channels. The higher silica member of this family is identified as clinoptilolite. Clinoptilolite can be classified by Si/Al ratio. If this ratio is between 4-5 bigger than 4, it can be classified as clinoptilolite as shown Table 3.1. Zeolites also can be classified as Clinoptilolite if the criteria of (Na+K) > Ca is available "(Gottardi 1985)". Another important difference between natural heulandite and clinoptilolite is its thermal stability. While clinoptilolite is thermally stable above 500°C, heulandite is stable up to 350 °C because its structure collapses at temperatures higher than 350 °C "(Zhao et al. 1998)"

Table 3.1. Properties of varieties in the heulandite - clinoptilolite series
(Source: Tsitsishvili, 1992)

	Heulandite (high silica)		Clinoptilolite (low Ca silica)	
Si/Al	2.7-3.5	3.5-4.0	4.0-4.5	4.5-5.5
Ca:Na:K	Ca>>Na>K	Ca>Na>>K	Ca>Na$\leq$ K	Ca<Na>< K
Decomposition, °C	350	400	450-550	750
DTA endothermic effects:	200 and 340°C		160°C	-

Clinoptilolite is used in several chemical operations such as; ion exchanger for $NH4^+$, Na^+, K^+, Pb^{2+}, Sr^{2+}, and Cs^+, gas separation such as N_2/CH_4 and O_2/N_2, and removal of SO_2 and NH_3. It has also been applied to wastewater cleaning, agriculture, fertilizers, gas cleaning, gas separation and reducing radioactive wastes due to clinoptilolite's high adsorption capacity and ion exchange ability. For this reason, many

researchers have investigated the synthesis of clinoptilolite for enhance its adsorption efficiency. The structure of clinoptilolite is as shown in the Figure 3.1.

(a)   (b)
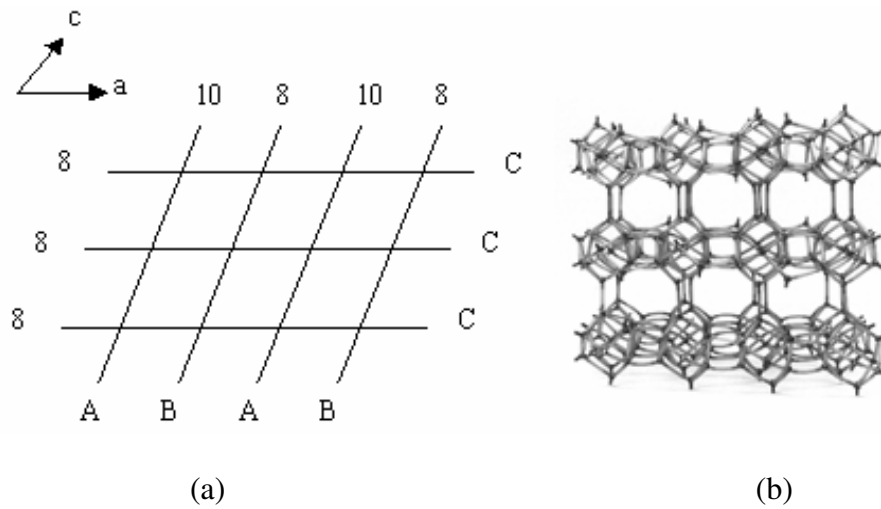
Figure 3.1.   a) Orientation of clinoptilolite channel axis b) Model framework for the structure of Clinoptilolite (Source: Ackley and Yang, 1991)

3.2. Activated Carbon

Carbon materials have been used since 3750 BC by Egyptians and Sumerians Activated carbon (also called activated charcoal) is a type of amorphous carbon prepared by the destruction of organic substances such as wood, vegetables and coconut shells. It is a fine, black powder of largely pure carbon and its large surface area imparts a great adsorptive capacity to this material and is the basis for its industrial and medical uses (WEB_4 2006).

Activated carbon is widely used for the treatment of acute poisoning (overdose) with such substances as acetaminophen, salicylates, barbiturates and tricyclic antidepressants. Activated carbon strongly adsorbs aromatic substances by reducing their absorption from the gastrointestinal tract; however, most inorganic poisons are not significantly adsorbed by activated carbon. Activated carbon is used as a decolorizer in the industry. For example, it is used for sugar refining to produce white sugar in the last stages, and commonly used in air and water filters.

Activated carbon is very favorable in controlling organic chemicals in drinking water. The iodine number is the key test for carbon used primarily for water filtration.

As an ASTM standard, the importance of this number is that it is a good indicator of how well the carbon will adsorb compounds and pollutants from the water. The determination is done by taking a known amount of powdered activated carbon and mixing it into a standard solution of iodine and water. By measuring the remainder of the Iodine in solution, the amount of Iodine adsorbed can be determined. This value is expressed as milligrams of iodine adsorbed per gram of activated carbon. The higher the number, the more chemical contaminants are removed. Some comparative values are shown in Table 3.2.

Table 3.2. Different types of activated arbon and iodine number

Carbon Type	Iodine Number (range)
Lignate	500-650mg/g
Bituminous	850-1100mg/g
Coconut Shell	1000-1500mg/g

Table 3.2. shows that coconut shell has the highest iodine number than Bituminous and Lignate. As a result, it is expected that the adsorption capacity of Coconut Shell should be larger than that of Lignate or Bituminous type activated carbon.

CHAPTER 4

LITERATURE REVIEW

The comprehensive reports about occurrence of gasoline additive MTBE in ground water and urban runoff in the U.S. was the reason that the fuel additives internationally became a subject of discussion in 1990's. MTBE is the most important compound from the group of oxygenates that replace TEL and aromatic hydrocarbons. The results of recent studies have shown that MTBE is a possible carcinogen. Studies concluded some odor and taste problems related with ether contaminants. Because of aesthetic quality problem and possible human carcinogenetic properties of MTBE, it is listed as class C. Therefore, fuel oxygenates should be removed from water. Several studies have shown the formation of tumors in animals' due to at high concentration of MTBE. On the other hand, the International Agency for Research on Cancer (IARC) has concluded that there is limited evidence in experimental animals for carcinogenicity of MTBE and there is not enough evidence in humans.

Ether components can migrate into the environment especially in ground water by numerous sources. Leakage from the underground storage tanks (LUST) is a major source of MTBE migration. It has been reported that underground storage tanks that are not protected against corrosion with cathodic protection and are not designed in double wall with reinforced fiberglass to withstand ground subsidence are very likely to fail and cause massive leaks in the ground "(Nadim et al., 1999)". In addition to this, the contamination also comes from spills, overfilled gas stations, leaking pipelines, spillage from vehicle accident, emissions from marine engines into lakes and reservoirs, and some level from air deposition by unburned fuel oxygenates. Therefore, surface and ground water sources near the gasoline station can easily be contaminated by MTBE.

U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program indicated a frequent detection of low concentrations of MTBE between 1993 and 1998. In the study for ground and surface water, detection of MTBE was related to its usage in gasoline. In ground water, MTBE was detected in 21% samples of the areas (>5% volume in gasoline), generally in either RFG or OXY areas. "(USGS 2000)".

ground water (1993-1998)   surface water (1996-1998)
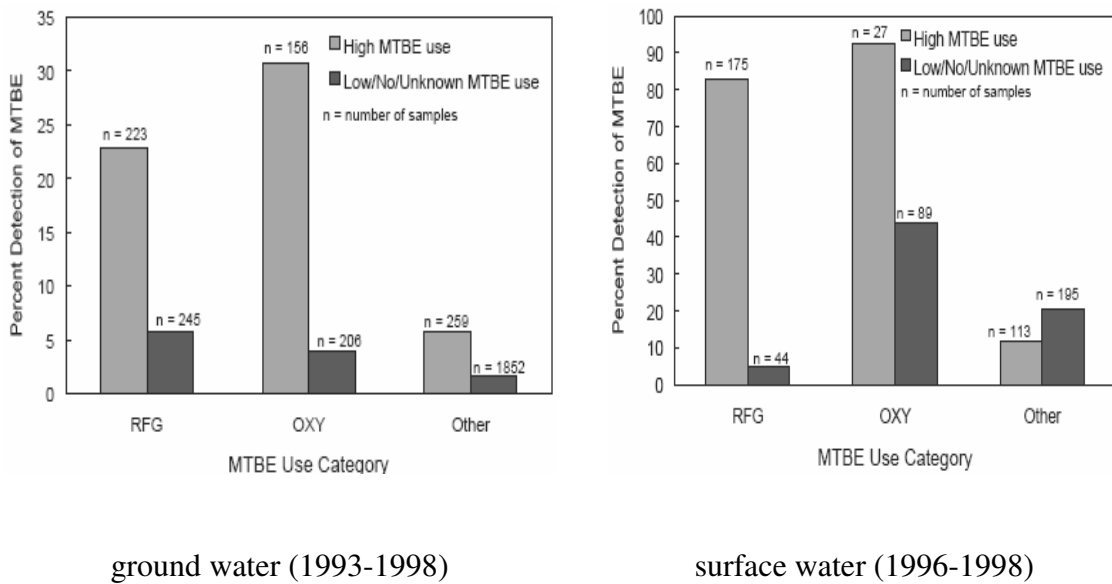
Figure 4.1. Frequency of detection of MTBE in samples of MTBE uses categories.

The use of MTBE, as opposed to another oxygenates, in either RFG or OXY areas resulted in a significant increase in the detection frequency of MTBE in both surface and ground water (Figure 4.1.). In fact, for ground water, the use of MTBE in RFG and OXY areas resulted in an increase in the detection frequency of MTBE of 4 and 8 times, respectively. Even in areas other than those designated as RFG or OXY, the use of MTBE also resulted in a 3-fold increase in the detection frequency of MTBE in ground water. For surface water, the use of MTBE in RFG and OXY areas resulted in an increase in the detection frequency of MTBE of 18 and 2 times, respectively. However, for areas other than RFG or OXY, the frequency of detection of MTBE in surface water was lower for areas that used MTBE compared to areas where either no MTBE was used or its use unknown. This apparent anomaly may be, in part, the result of the uncertainty involved in assigning an MTBE-use category to relatively large geographic areas such as surface water drainage basins that may cross MTBE-use boundaries.

In 1998, a report written by Bureau of Waste Management & Remediation Department of Environmental Protection presented the findings from a study of the occurrence of MTBE and other gasoline components namely benzene, toluene, ethyl benzene and xylene in Maine's drinking water. Water samples obtained from 951 randomly selected household wells and other house hold water supplies (e.g., springs

and lakes) and 793 of the 830 regulated non-transient public water supplies were analyzed "(USEPA 1998)".

Results showed that;

• 15.8% of the 951 sampled wells were contaminated by MTBE

• 1.1% of the sampled waters showed levels of MTBE above the Maine drinking water standard of 35 ppb

• 92.3% either of the sampled waters showed MTBE levels that were not detectable or below 1ppb; and 6.6% were between 1ppb and 35ppb.

In November 1998, the U.S. EPA Administrator appointed a Blue Ribbon Panel to investigate the air quality benefits and water quality concerns associated with oxygenates in gasoline and provides independent advice and recommendations on ways to maintain a quality while protecting water quality.

Recommendations of the Blue Ribbon panel were;

• RFG program has been very powerful on air quality improvements,

• MTBE has more likely to contaminate ground water and surface water than the other components of gasoline,

• MTBE has been found in a number of water supplies nationwide in U.S. above EPA standards and MTBE should be reduced.

• Oxygenates may provide the air quality benefits, and that technological improvements in non-oxygenated fuels has led to fuels that can achieve air quality.

Considering normal conditions, for example, room temperature, MTBE is a volatile, flammable, less biodegradable and colorless liquid that dissolves rather easily in water. Low Henry's constant and low organic partition coefficient shows its hydrophilic nature. It has also high vapor pressure and low boiling point lead to easy evaporation from oxygenated fuel to the atmosphere. ETBE is also a water-soluble component that can be detected in ground water due to its high water solubility, slow biodegradation and low Henry's law constant.

Table 4.1 shows the physical and chemical properties of fuel oxygenates. They tend to be liquid rather than vapor at low temperatures (25 °C), therefore the reason for its ability to contaminate water. Oxygenates are generally more soluble in water and less sorbed on soils than the other major organic compounds in gasoline, namely, benzene, toluene, ethylbenzene, and xylenes (BTEX). Contamination of water or soil inherently should be considered with BTEX.

Table 4.1. Physical and chemical properties of fuel oxygenates

(Source: ITRC, 2005)

Compound Class	Ethers			Alcohols			BTEX
	MTBE	ETBE	TAME	MeOH	EtOH	TBA	Benzene
Molecular weight (g/mol)	88.15	102.18	102.18	32.04	46.07	74. 12	78.11
Boiling point (°C)	55.2	71	85-86	64.6	78.3	82.2	80.1
Density[*] (kg/L)	0.741	0.752	0.77	0.791	0.789	0.786	0.879
Vapor pressure (mm-Hg)[*]	245	152	68.3	121.58	49-56.5	40-42	95.2
Water solubility (g/L)	51	26	2.0	infinite	infinite	infinite	1.8
Henry's constant (atm m^3/mol)	2.399 E-2	1.087 E-1	5.19 E-2	1.08 E-4	2.09 E-4	5.927 E-4	2.219 E-1
Log K_{ow}	1.20	1.74	-	-0.75	-0.31	0.35	2.13

Low Henry's law constant and water solubility support MTBE as water contaminant. MTBE risk assessment reports have showed that contaminated water sources should be treated. Therefore, some restriction acted to reduce. MTBE odor thresholds of 13.5 - 45.4 µg/L and taste thresholds of 39-134 µg/L have been reported. From an engineering point of view, water treatment methods should be efficient and their costs should be lower. The removal of fuel oxygenates from ground water and drinking water has been investigated using separation methods.

Separation methods have been developing by virtue of advancements. Air striping, adsorption, air sparging, pervaporazation, advanced oxidation, membrane separation, adsorption, and other new technologies have been used for remediation of MTBE from the environment. Many technologies that work for remediation gasoline also work for MTBE. Table 4.2 summarizes the remediation technologies that have been used for MTBE.

Table 4.2. Traditional remediation technologies.

(Source: NAVFAC, 2000)

Technology	Applicability for MTBE	Reported field Application	Performance and Comment
Soil vapor extraction	Very applicable	Dozens	MTBE's high vapor pressure make Soil Vapor Extraction
RBCA approach	Fully applicable	Few	Process work fine, but results may be unfavorable for MTBE
Soil extraction	Variable with time	Few	If acted soon after spill can be effective; if acted later, when the MTBE is leached from soil, is ineffective.
Air Sparging	Variable,stillbeing determine	> 12	Field results mixed good to very poor
Bioventing	Not promising so far	3-4	Performance poor; so far control areas show no measurable improvement.
Ground water extraction	Plume control is very poor	Dozens	Pump and treat is great forhydraulic containment, still limited by residual product and hydrogen
	Remediation is good for dissolved phase	Dozens	Better for soluble MTBE than for most compounds.

Furthermore Table 4.3 shows the effectiveness of above ground treatment methods for MTBE impacted water.

Table 4.3. Above ground treatment of MTBE impacted water

(Source: NAVFAC, 2000)

Technology	Theoretical Effectiveness on MTBE	Development Level	Performance and Comments
Air stripping	Good-fair	Field; many good application	Higher air/water ratio needed; air emissions problematic.
Carbon Adsorption	Good in Selected situation	Field; some good application; many poor ones	High Granular active carbon usage (rapid breakthrough possible); virgin coconut GAC best.
Advanced Oxidation Process	Good	Pilot looks promising; field studies starting	Destroys MTBE; high capital cost; byproduct can be problematic
Resin Sorbents	Good	Lab; pilot test starting	Looks promising, especially if TBA is present and of concern; high capital cost.

Adsorption is the most preferable process for water treatment technology. The numerous adsorbents such as granular activated carbon (GAC), macro reticular resin, polymeric resin, high silica zeolites, (Mordenite (MOR), ZSM-5, Y) have been used to treat contaminated ground and drinking water by fuel oxygenates "(Annesini et al.1999, Anderson 2000, Lin et al. 2002, Shih et al. 2003, Hung and Lin 2005)". Copolymers can be designed according to pollutant properties; therefore, they are very applicable to usage in many areas. (Annesini et al.1999). Macroreticular resin adsorbents (e.g. Ambersorb563, Ambersorp 572, Amberlite XAD4, and Polysorb MP-1) have been used in numerous investigations.

Researchers have studied MTBE adsorption from water extensively. They have tried to find better adsorbents. The adsorption experiments have been performed using Batch (equilibrium) and Column (Fixed Bed) adsorption procedures. In batch adsorption, different adsorption models utilized to identify adsorption isotherms such as Langmuir, Freundlich. Column adsorption experiment assists to examine the performance of continuous adsorption operations by breakthrough curves under conditions of different inlet adsorbate concentration, feed flow rates and temperature.

These procedures make it possible for comparing different kinds of adsorbents adsorption capacity while modeling data.

Scott et al. (2000) have tested some promising adsorbents to provide a preliminary screening of the effectiveness of alternative sorbents for treating ground water contaminated with methyl tert-butyl ether (MTBE). Synthetic carbonaceous resin porous graphitic carbon, C18 silicas (octadecyle), and acrylic resin were used to reduce 1mg/L (1ppm) contamination level of MTBE. Activated carbon was also tested for comparison purposes (Filtasorb 400). In addition, competitive adsorption effect was investigated by additional m-xylene. The batch adsorption analyses were carried out. Batch adsorption data were analyzed using Freundlich and Dubinin Astakov adsorption models. Porous graphitic carbon and two synthetic carbonaceous resins have been identified to be more effective for MTBE than active carbon at 1mg/L MTBE concentration. Additional bisolute experiments with m-xylene have indicated that presence of m-xylene had reduced adsorption capacity of adsorbents by depleting the micropore volume available for MTBE.

Lin et al. (2002) have employed commercially available Ambersorb 563. The removal of MTBE was experimentally and theoretically investigated by batch and fixed bed adsorption procedures. MTBE balance between resin and aqueous phase had been sufficiently explained by adsorption isotherms for batch operations, like extended Langmuir, Jossens, or Dubinin-Astakov isotherm. Column adsorption experiments were carried out for different inlet concentrations (10-30-40-50 mg/L) and flow rates (12-10-8-6 ml/min) of MTBE (Figure 4.2.).The experimental data were represented with respect to time, and nonlinear correlations were fitted instead of expected linear correlation. Linear, nonlinear correlations and the breakthrough adsorption capacity of Ambersorb 563 were calculated from following equations 4.1, 4.2, and 4.3. The resin adsorption process has been found to be efficient in removal MTBE from contaminated water relative to GAC.

$$\ln\left(\frac{C}{C_o - C}\right) = k(t - t_1) \tag{4.1}$$

$$\ln\left(\frac{C}{C_o - C}\right) = a_o + a_1 t + a_2 t^2 + a_3 t^3 + ... \tag{4.2}$$

$$\text{Adsorption Capacity} = \frac{FC_b}{M} \int_0^{t_b} \left(1 - \frac{C}{C_o}\right) \partial t \qquad (4.3)$$

In equation 4.1, k represents the rate constant of the adsorption (L/mg h), and F is the feed flow rate (L/h), and M is the mass of adsorbent (g) in equation 4.3.
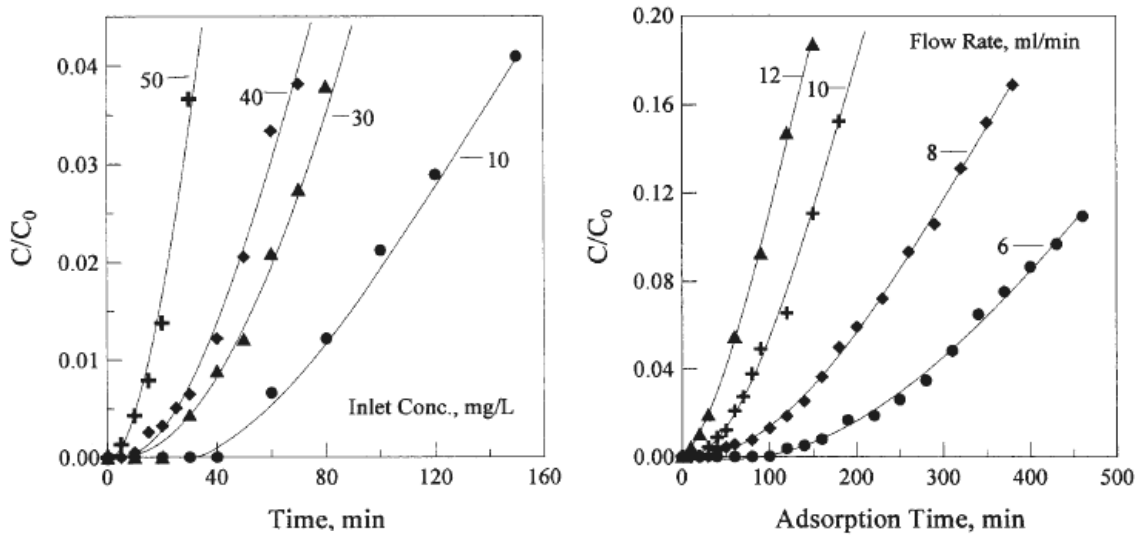
Figure 4.2. Effects of inlet concentration and flow rate in the column adsorption experiment (Source: Lin et al. 2002)

Increasing MTBE concentration decreases the breakthrough time similar with increasing flow rate. In contrary, decreasing inlet MTBE concentration and flow rate has resulted as considerable shifts in the breakthrough curves towards to right. This is expected because of occupied adsorption sites.

The aqueous phase adsorption of methyl-tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) onto an Amberlite resin by batch and column adsorption experiments under different operating conditions (i.e., flow rate, initial concentration, mass of adsorbent) have been investigated by Annesini et al. (1999). The data on bisolute adsorption showed a strong competitive effect between MTBE and TBA. Aqueous phase adsorption of this adsorbent has been found successful for MTBE adsorption than TBA for single solute testing. According to column adsorption data, MTBE adsorbed

faster than TBA. The presence of TBA had reduced MTBE adsorption due to competitive adsorption effect. Non-ideality of the adsorbed can be illustrated by this behavior. Single solute column data showed that column saturated faster for TBA than MTBE when Amberlite resin was used as adsorbent. Although TBA concentration was less than MTBE concentration, breakthrough of TBA controlled the overall process.

Activated Carbon has also been tested for MTBE adsorption studies. It is one of the most favorable adsorbent, due to its large surface area. Gironi et al. (2003) and Shih et al. (2005) have carried out MTBE adsorption studies using activated carbon. Wilhelm et al. (2002) have also used activated carbon to evaluate adsorption capacity for a high concentration of MTBE in Truckee River water. Three types of granulated activated carbon (GAC) and three powdered activated carbon (PAC) have been used in the study. The results of the study are listed in Table 4.4.

Table 4.4. Comparison of selected active carbon
(Source: Wilhelm et al. 2002)

	GAC			PAC		
	Filtrasorb 300	**Hyroderco 4000**	**Picazine**	**Darco**	**Hydrodarco**	**PAC 200**
Based material	Bituminous coal	Lignite	Wood	Hardwood	Lignite	Coal
Activation method	Steam	Steam	_	Chemical	Steam	Steam
Adsorption capacity	Best	<F300[¤]	<F300[¤]	<F300[¤]	<F300[¤]	<F300[¤]

¤ Filtrasob 300

Adsorption capacities of different activated carbons depend on their based materials and activation methods. Wilhelm et al. (2002) used steam activated Bituminous coal based GAC (Filtrasorb 300). Filtrasorb 300 has been identified as the best one. It was concluded that no difference in carbon loading for real contaminated and 18 MΩ cm distilled deionized water (DDW). In addition, the cost analysis of this study reported that total cost of GAC adsorption was cheaper than air stripping method.

Fuel oxygenates adsorption have been tested by Yu et al. (2005) using two bituminous coal activated carbons (i.e. F400 and F600). MTBE, ETBE, TAME, DIPE, TBA, and EtOH sorption were investigated in a batch study. Data were plotted with

linearized forms of Freundlich and Langmuir adsorption isotherms for two common bituminous coal GACs as shown in Figure 4.3 and Figure 4.4, respectively ($R^2>0.97$). No significant adsorption of either TBA or EtOH was observed on these carbons. The relative capacities on both F400 and F600 were DIPE> TAME > ETBE >MTBE >TBA, EtOH.

(a)   (b)
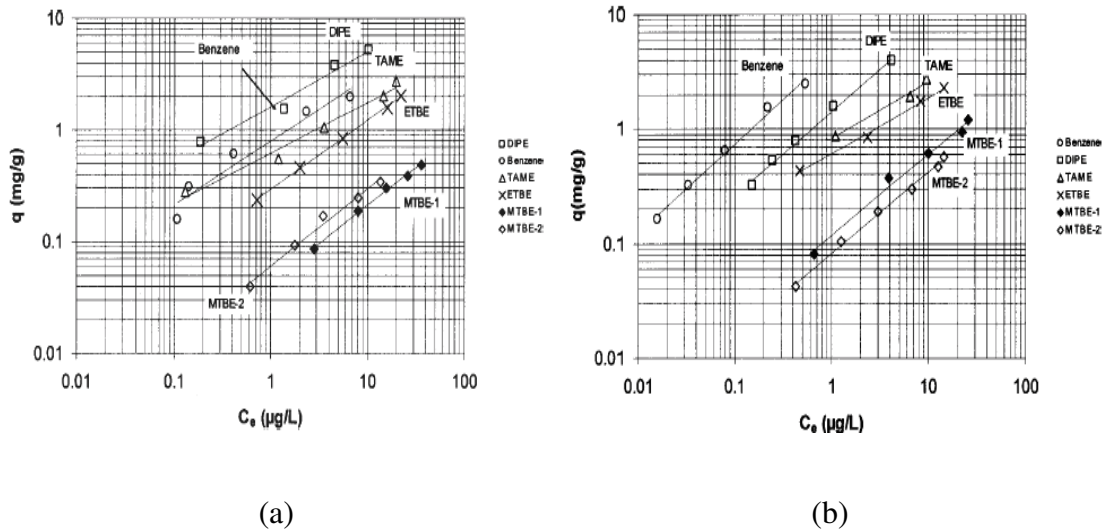
Figure 4.3. Fuel oxygenate Freundlich model isotherms (a) Calgon F400 (b) Calgon 600

Isotherms for F400 and F600 showed that the relative sorption affinity was MTBE< ETBE< TAME < DIPE < Benzene. They concluded that this affinity was consistent with their water solubility values.

(a)   (b)
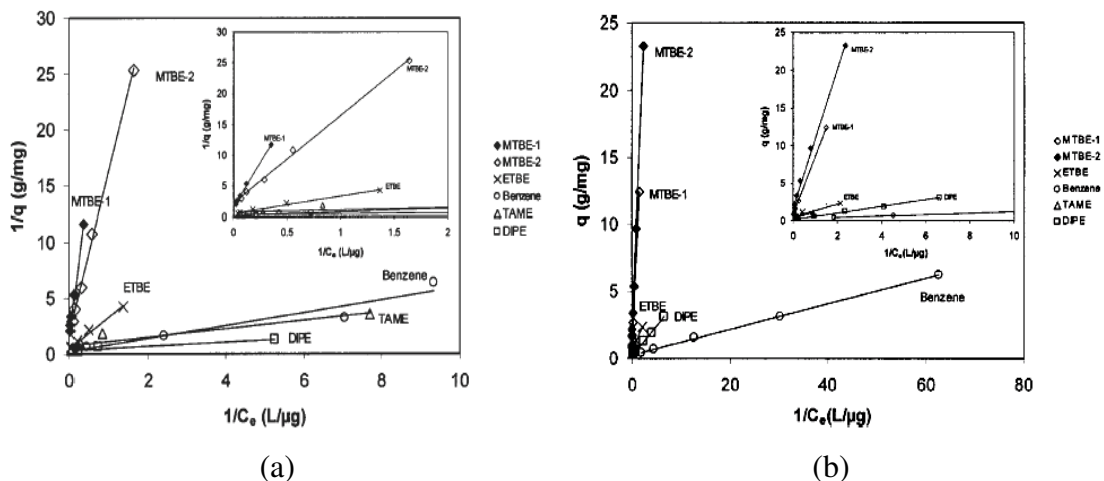
Figure 4.4. Fuel oxygenate Langmuir model isotherms (a) Calgon F400 (b) Calgon 600

Shih et al. (2002) have tested GAC adsorption capacity by using rapid small-scale column tests (RSSCTs). MTBE concentrations ranged from 20 to 2000 µg/L, with or without the presence of tert-butyl alcohol, benzene, toluene, p-xylene (BTX) in two groundwater (South Lake Tahoe Utility District [Lake Tahoe, CA] and Arcadia Well Field [Santa Monica, CA]) and a surface water sources (Lake Perris, CA). The RSSCT's were performed assuming that the intraparticle mass transfer rate was independent of particle size. Figure 4.5 shows the result of breakthrough curves obtained by surface water from Lake Perris with different EBCT (Empty Bed Contact Time).

Figure 4.5. Breakthrough curves for the RSSCTs conducted with water from Lake Perris

CC-602 GAC labeled GAC was found more attractive than PCB-GAC for MTBE adsorption. GAC adsorption performance for the target organics was found reduced by lack of available sites.(by competing chemicals). Therefore, competitive adsorption experiment was concluded that BTX components caused a decreasing GAC adsorption capacity. Significant increase in GAC usage rate was obtained (about 30%). (Figure 4.6.). The GAC performance has found significantly different between EBCT of 10 and 20 min for contaminated Lake Perris (LP), a surface water source with higher TOC content. The lower GAC performance was associated with higher TOC concentration. The lower EBCT was the reason of decreasing column performance.
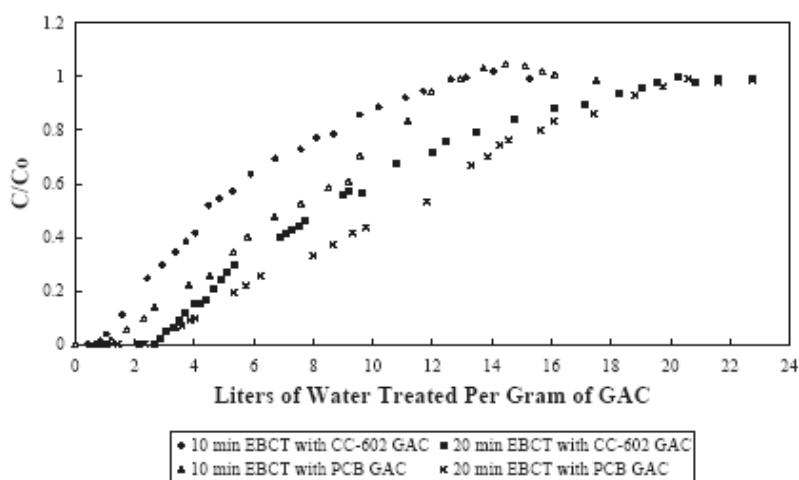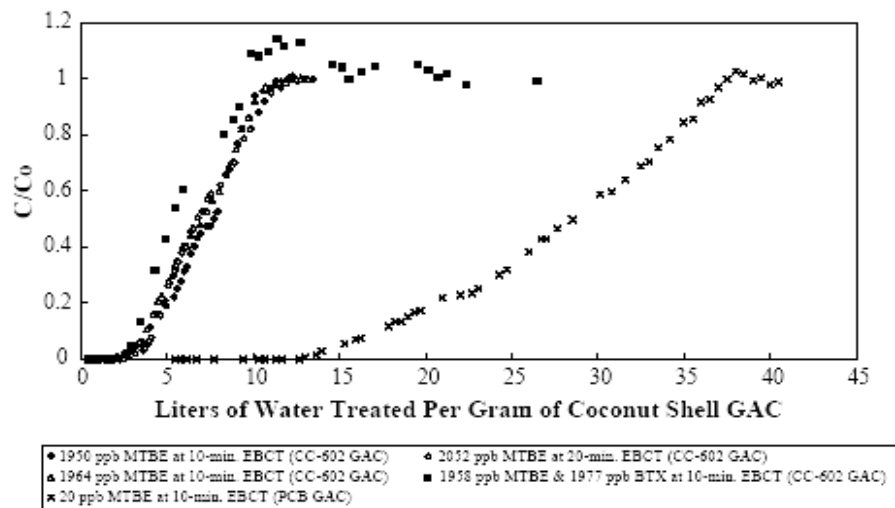

Figure 4.6.   Breakthrough curves of RSSCT conducted with groundwater from South Lake Thaoe

Sutherland et al. (2004) examined the treatment of MTBE, ETBE, TAME, DIPE, and TBA by using air stripping, UV/H_2O_2 and O_3/H_2O_2 advanced oxidation, and GAC adsorption in rapid small-scale column tests (RSSCT). The study has shown that air stripping, carbon adsorption, and advanced oxidation can each be effective at removing MTBE from a variety of groundwater. The results have also showed that competition by other synthetic organic chemicals (SOC) (e.g. benzene, toluene, ethyl benzene, and xylenes) had significant effect on the effective capacity of GAC. Air stripping becomes less efficient at low temperatures, whereas some other processes (e.g., GAC sorption) may become more effective. Activated carbon adsorption provided

the highest treatment costs for all conditions. However, it was concluded that activated carbon adsorption, may have other advantages such as easiness of use. Furthermore using another activated carbon was suggested instead of bituminous coal F400, and F600.

The use of natural zeolites as adsorbent has a great potential due to their availability and low cost. It is known that dehydrated zeolites have excellent adsorption properties, and synthetic zeolites are widely used in drying process as desiccant and gas separation.

Anderson (2000) studied the removal of MTBE from water by high –silica zeolites. Two powder activated carbons, one from Fisher Scientific and one from Barnebey-Cheney, were used as reference sorbent. First, multicomponent batch sorption experiments with aqueous solutions of MTBE, chloroform, and trichloroethylene were conducted with zeolites adsorbents and Barnebey-Cheney activated carbon (AC)

Table 4.5. Properties of zeolites

(Source: Anderson 2000)

Zeolite	Pore size(Å)	SiO_2/Al_2O_3
Mordenite (MOR)	6.5×7.0	200
ZSM-5	5.3×5.6	~1000
Y	7.4	75

Mordenite has found more capable to remove more MTBE from water containing MTBE, chloroform and trichloroethylene than AC and the other two zeolites, ZSM-5 and zeolite Y. These results are shown in Table 4.6.

Table 4.6. Solution concentrations and percent removal after equilibrium of 100 µg/L
solutions with 5 mg of solid phase

	MTBE		CHCl$_3$		TCE	
sorbent	µg/L	% removal	µg/L	% removal	µg/L	% removal
MOR	4.0 ±0.3	96	62.2 ± 5.2	38	23.2 ±4.4	77
ZSM-5	36.6 ±09.4	63	21.9 ±1.2	78	<3	<97
Y	94.9 ±6.1	5	99.6 ±3.9	<1	90.9 ±1.7	9
AC*	48.2 ±3.9	52	43.8 ±2.2d	56	32.2 ±1.6	68

* Barneby –Cheney AC

The study was performed by using 5 mg zeolite powder with 25 ml of a aqueous
solution containing 100 µg/L MTBE equilibrated for at least 15 min. MOR removed
96% of the MTBE. Select zeolites with high SiO$_2$/Al$_2$O$_3$ ratios were effective to remove
MTBE, chloroform, and trichloroethylene (TCE) from water. Pore size and charge
properties have been found the reason for high adsorption. High framework charge Al^{3+}
substitution with Si^{4+} in the crystal lattice shows high cation exchange capacity. Based
on the higher selectivity of mordenite for MTBE, a single-component sorption isotherm
tested up to an aqueous MTBE concentration of 300 µg/L using mordenite and the two
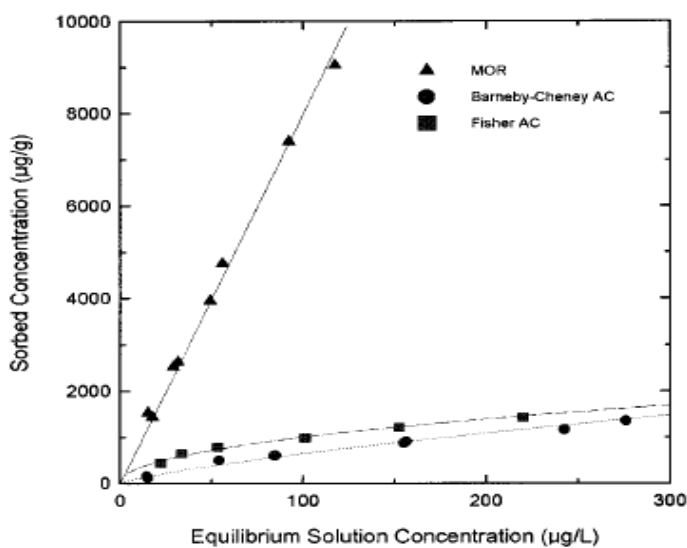activated carbons.

Figure 4.7. MTBE sorption isotherms for high silica mordenite (MOR) and two
activated Carbons

In Figure 4.7., the isotherm shows that MTBE affinity of MOR is higher than two activated carbons. TCE and chloroform molecules have been found less attractive for MOR because of lower van der Walls forces and lower sorption affinity.

Li et al. (2002) studied MTBE adsorption onto synthetic zeolite by batch and column flow systems. It was concluded that the hydrophobicity of the adsorbent was a very important parameter. Si/Al ratio, structure defects, cation present in structure, synthesis condition and post-synthesis treatment were also related with controlling hydrophobicity. Consequently, hydrophobic adsorbents were found more effective to remove both TCE and MTBE from aqueous solution than hydrophilic adsorbents. Adsorption on hydrophilic surfaces results have been found to be consistent with the previous study of Anderson (2000) as shown in Figure 4.8. Adsorption isotherms of these two studies show that the slopes of these isotherms are very similar with each other.
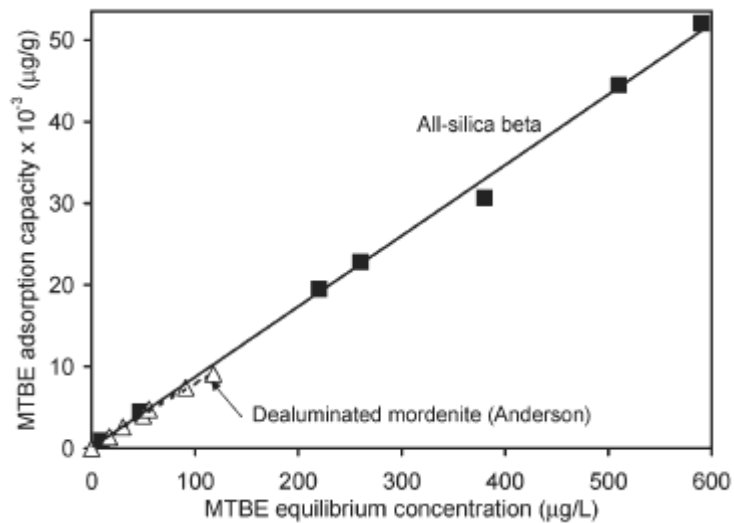
Figure 4.8. Adsorption capacity comparisons with Anderson 2000.

Senatalar et al. (2003) studied liquid phase sorption on hydrophobic molecular sieves over a wide range of concentrations of MTBE in water. The removal of MTBE from water were tested by four high silica zeolites, silicalite-1, mordenite, zeolite beta, and a dealuminated zeolite Y (DAY), and were compared to a granular activated carbon sample as a control. They concluded that at low concentration silicate-1 had the highest

capacity for the removal of MTBE, which was related with the highest Si/Al ratio. (Silicalite-1, Mordenite (CBV 90A), Beta (CP 811E-150 and Zeolite Y (CBV 780) Si/Al ratio were >1000, 90, 150, and 80 respectively)

CHAPTER 5

MATERIALS & METHODS

5.1 Materials

Clinoptilolite rich natural zeolite (Gördes Manisa, Western Anatolia) obtained from Enli Mining was used as adsorbent in this study. For comparison purposes, powdered activated carbon (PAC) and granulated activated carbon (GAC) (steam activated) were used as received. The adsorbents and chemicals used for the adsorption experiments are given in Table 5.1.

Table 5.1. Adsorbent materials and chemicals

Chemicals		Properties of Chemicals
Clinoptilolite	(CLN)	Gördes (150-300 mm particle size)
Granulated Activated Carbon Norit GAC 1240	(GAC)	Fluka
Powdered Activated carbon Norit W35	(PAC)	Fluka
Methyl Tertiary Butyl Ether	(MTBE)	Lab Scan (99, 8%)
Ethyl Tertiary Butyl Ether	(ETBE)	Aldrich (99%)
Benzene		J.T.Baker (99, 7%)
Sodium Chloride	NaCl	Panreac (99,5%)

Sodium chloride was used in headspace analysis to obtain matrix modification as previously described by Oh and Stringfellow (2003). It should be emphasized that NaCl was heated to 550 °C for 5 hours in order to remove the impurities. Some specific properties of activated carbons are shown Table 5.2.

40 ml sampling vials (Environmental Sampling Supply (ESS) certified), were used in batch adsorption experiments with Teflon/Silicone septa screw cap (Cole

Parmer), and 20 ml headspace sampling vials (Agilent) with PTFE/Silicone/PTFE septa were used in concentration analysis.

Table 5.2. Activated carbon properties
(Source: Norit Company)

	GAC	PAC	Units
	Norit GAC 1240	Norit W35	
Iodine Number	1075	800	-
Methylene Blue Adsorption	22	15	g/100 g
Phenol Adsorption (1 mg/l)	45	4	g/100g
Total Surface Area (B.E.T)	1175	875	m^2/g
Apparent Density	480	425	kg/m^3
Effective Size	0.6-0.7 mm	15µm	-
Ash Content	7	10	mass%
pH	alkaline	alkaline	

5.2. Methods

5.2.1. Sample Preparation for Clinoptilolite

Clinoptilolite was used without any chemical modifications. Sieving analyses were performed with different meshes of plate; which were 500-300-150-38µm. Clinoptilolite has been sieved into different particle size; (i.e. 38-150,150-300, and 300-500 µm). Dry sieving and wet sieving analysis were carried out. Deionized water was used in wet sieving procedure to remove the dust and get better size separation.

Clinoptilolite, with particle size in the range 150-300 µm, was used as an adsorbent throughout the study. In order to remove the impurities, samples were first washed with deionized water at 70 °C for 6 h by continuous stirring (100 rpm). Then the samples were dried at 110 °C overnight.

5.2.2. Characterization

The characterizations part of the study included the determination of particle size, surface area, morphology, thermal stability and chemical composition.

Particle size distribution of clinoptilolite was determined by using Micromeritics Sedigraph 5100 to enable adequate suspension of the clinoptilolite. 0.2 g clinoptilolite was mixed with 50 ml 50 % sucrose solution and was shaken for 30 minutes using an ultrasonic shaker.

Specific surface area, pore diameter and pore volume were obtained by using the physical adsorption of nitrogen technique at 77 K using Micromeritics ASAP 2010.

The mineralogical content of the samples was elucidated using X-Ray diffraction analysis by diffractometer (Philips X pert) with CuKα radiation. XRD patterns were collected from 5° to 40°. Scanning electron microscope (SEM) (Philips SFEG 30S) was used for identifying the morphology of the crystalline structure.

Thermal measurements of clinoptilolite were carried out using Thermo Gravimetric Analyzer (TGA–51, Shimadzu) and the Differential Thermal Analyzer (DTA–50, Shimadzu). TGA and DTA analyses gave information about the dehydration, thermal stability properties, water content and types of water within the zeolite structure. 10 mg sample was heated at a heating rate of 10°C/min under 40 ml/min nitrogen stream, up to 1000°C in TGA and DTA analyses. TGA analysis was also used to investigate hydrophobicity.The samples were heated up to 400 °C at a heating rate of 10 °C/min, and were kept at this temperature until constant weight was attained. The hydrophobicity is calculated from the ratio of the weight loss up to 150 °C to the total weight loss "(Giaya et al. 2000)".

Si/Al ratio of the clinoptilolite, the percentage of other elements (Ca, Na, K, Mg, Fe) and their oxide form composition were determined by Inductively Coupled Plasma (ICP) (Varian model Liberty II ICP-AES). Before the ICP analysis, fusion method was used to dissolve zeolite samples. In this method, 0.1 g of zeolite was mixed with 1 g of lithium tetraborate in a platinum crucible. The mixture was then heated to 1000°C and kept at this temperature for 1h. After a rapid cooling, it was dissolved in an aqueous solution of 1.6 M HNO_3.

5.2.3. Theory of Adsorption Modeling

5.2.3.1. Batch Adsorption Modeling

The adsorption isotherm is the relationship that shows the distribution of adsorbate between the adsorbed phase and the solution phase at equilibrium. Adsorption isotherms are essential for the description of how adsorbate concentration interacts with adsorbents and are useful in optimizing their use. Therefore, empirical equations are important for adsorption data interpretation and predictions. The Langmuir and Freundlich, which are the most used models, were used for the evaluation of the experimental results obtained in this study.

Langmuir Model: The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer of adsorbed material and constant temperature. The model is useful when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer forms and no multi-layer adsorption occurs. It also assumes that the surface is homogeneous (Iqbal and Ashiq 2006). The Langmuir equation has the form :

$$q_e = \frac{Q°b\text{C}_e}{1+b\text{C}_e} \tag{5.1}$$

where q_e is the amount adsorbed at equilibrium, C_e is the equilibrium concentration, b and Q^0 are Langmuir coefficients related to the energy of adsorption and the maximum adsorption capacity respectively.

A plot of q_e versus C_e gives the graphical representation of Langmuir isotherm as shown in Figure 5.1.a. Langmuir equation can be described by the linearized form as follows:

$$\frac{1}{q_e} = \frac{1}{Q°} + \frac{1}{bQ°C_e} \tag{5.2}$$

The linear Langmuir plot as shown in Figure 5.1.b. can be obtained by plotting $1/q_e$ versus $1/C_e$. The coefficients Q^o and b can be evaluated from the intercept and slope, respectively.
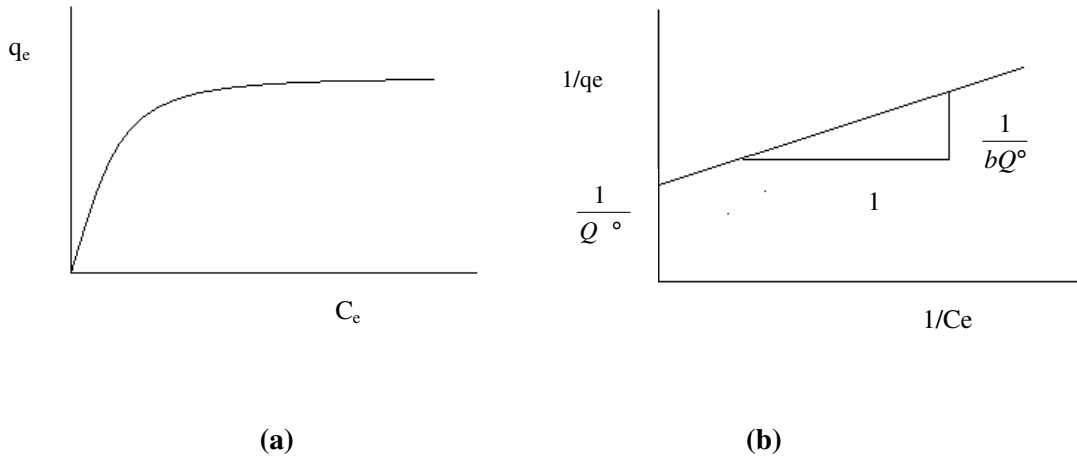

(a) (b)

Figure 5.1. (a) Graphical (b) Linear form of Langmuir isotherm

Freundlich Model: The Freundlich model is an empirical equation, which assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. The model equation is as follows:

$$q_e = K_f C_e^{1/n} \tag{5.3}$$

where q_e is amount adsorbed at equilibrium and C_e is the equilibrium concentration. K_f and n are equilibrium constants (temperature dependent) related to adsorption capacity and intensity, respectively. Graphically, a plot of q_e versus C_e gives the adsorption isotherm, as shown in Figure 5.2.a. The linearized form of Freundlich sorption isotherm is:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5.4}$$

A plot of log q_e versus log C_e gives a linear graph as shown in Figure 5.2.b. The coefficients K_f and n can be calculated from the intercept and slope respectively.
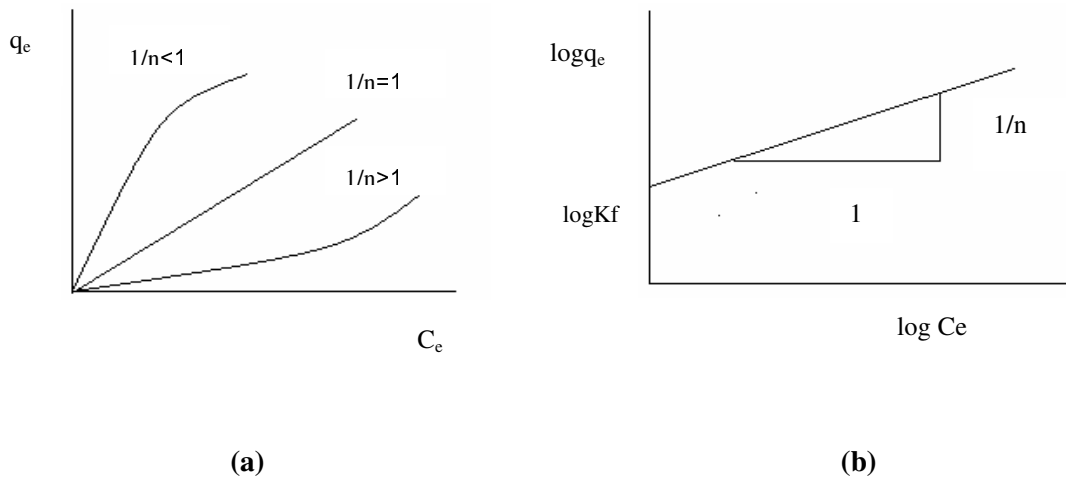
Figure 5.2. (a) Graphical (b) Linear form of Freundlich isotherm

5.2.3.2. Column Adsorption Modeling

Adsorption processes are in many cases associated with adsorption in a column and employs a simple column experiment for the measurement of adsorption isotherms. The adsorbent particles are packed in a column and the fluid containing one or more components of adsorbate flows through the bed.

The experimental data was plotted as breakthrough curves in the form of dimensionless concentration, C/C_o against time, where C and C_o are the outlet and inlet concentrations. The breakthrough curve represents the shape of the adsorbate concentration curve as the solution leaves the bed, and typical concentration profiles for adsorption are shown in Figure 5.3.a. and b. Initially, all the adsorbate is adsorbed in the bed and the solution leaving the bed has an adsorbate concentration of $C= 0$. However, after a certain period of time, the adsorbate begins to appear in the column outlet solution and the concentration increases until it is equal to C_o. At this point, the bed is completely saturated with adsorbate and is called the "saturation point".
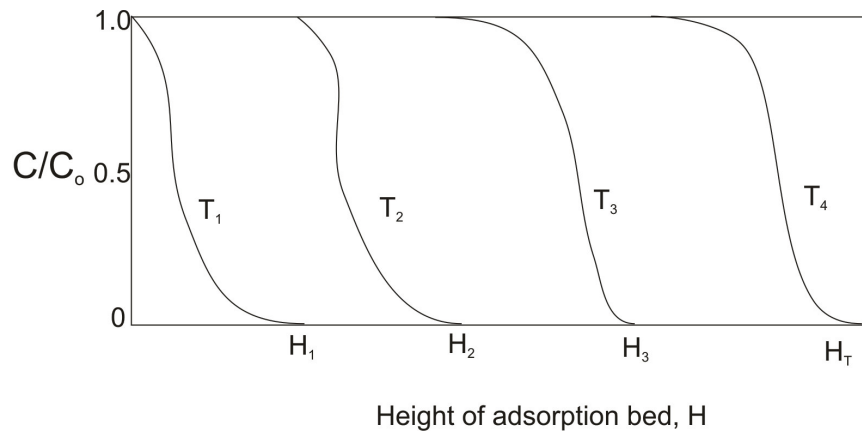
(a)
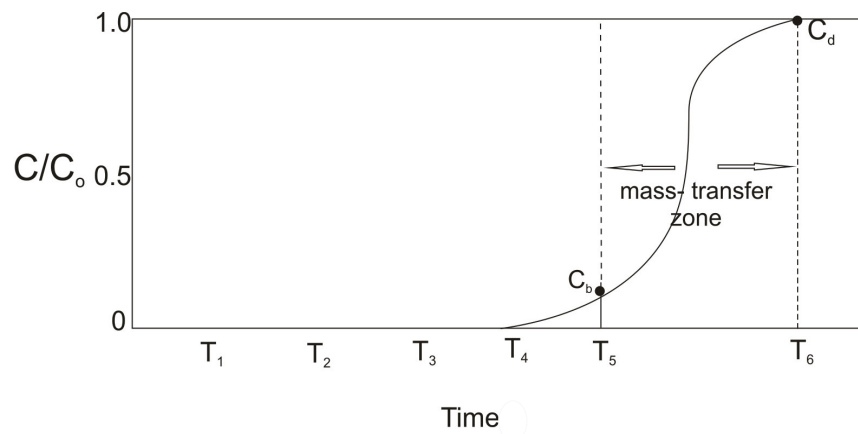
(b)

Figure 5.3. Concentration profiles for adsorption in a fixed bed: (a) profiles at various positions and times in the bed (b) Breakthrough concentration profile in the fluid at outlet of bed

The major part of the adsorption at any time takes place in relatively narrow adsorption or mass –transfer zone. While keeping the solution flow, this mass transfer zone, which is S-shaped, moves down the column. At a given time, T_3 (Figure 5.3.a.) when almost half of the bed is saturated with solute, the outlet concentration is still approximately zero, as shown in Figure 5.3.b, and remains near zero until the mass transfer zone starts to reach the column outlet at time T_4. Then the outlet concentration starts to rise, and at T_5 the outlet concentration has raised to C_b, called the *break point*. After the break-point time is reached, the concentration C rises very rapidly up to point C_d, which is the end of the breakthrough curve. At this point, the bed is considered ineffective. The break-point

concentration represents the maximum that can be discarded and is often taken as 0.01 to 0.05 for C_b/C_o. The value C_d/C_o is taken as the point where C_d is approximately equal to C_o. The mass- transfer- zone width and shape depend on the adsorption isotherm, flow rate, mass-transfer rate to the particles and diffusion in the pores "(Geankoplis, 2003)".

5.2.4. Adsorption Experiments

Adsorption of MTBE and ETBE onto clinoptilolite rich natural zeolite, GAC and PAC were carried out and modeled with two general adsorption procedures; Batch and Column (fixed-bed) adsorption experiments by using the same operation conditions. In addition, bisolute (benzene and ether) adsorption experiments were also carried out to determine the effectiveness of these adsorbents in the presence of other gasoline hydrocarbons. The batch adsorption data were evaluated using the adsorption isotherms, and breakthrough curves were used to describe the column adsorption capacity under continuous flow conditions. All the experiments were performed at 25°C.

Single solute adsorption experiments were performed by using 2000 ppb ether solution, and bisolute adsorption experiments were carried out using the same ether concentration with an addition of 400 ppb benzene into solution. All of the solutions were prepared by using deionized water obtained from a Milli-Q Ultrapure water purification system.

5.2.4.1. Batch Adsorption Experiments

Standard batch adsorption experiments were carried out at room temperature (25°C) in 40 ml VOC vials containing different solid–liquid ratios (0.2, 0.5, 1, 2, 4, 6, 8, and 10 g/L) with pre-determined concentration of ether. The vials were agitated at 100 rpm on a thermostat shaker for 24 h. to reach adsorption equilibrium. Then the equilibrium concentrations of the samples were determined by HS-GC/MS technique.

The equilibration time in batch adsorption was determined by preliminary optimization trials. The sorbent dose was kept constant at 0.2 g for two samples in 40 ml vials. One of the samples was equilibrated for 24 hours, and the other for 72 hours. Sample that was allowed to equilibrate for 72 h did not show much sorption than

samples that equilibrated 24 h. According to this, all adsorption experiments were performed for 24 hours.

5.2.4.2. Column Adsorption Experiments

The experimental setup for column tests consisted of a Pyrex tube of 0.8 cm ID and 20 cm in length. The column was equipped with an external water jacket to keep the operating temperature constant at 25 °C by a constant temperature circulator (PolyScience). During the column adsorption experiments two different adsorbents were used, clinoptilolite and GAC. Stock solution was fed to the top of the column by a peristaltic pump (Masterflex-L/S-model 77390-00 PTFE Tubing Pump) and the flow rate was 10 ml/min for each column adsorption experiment. The column was packed with 1.1 g adsorbent for each run. In order to prevent percolation and the entrainment of solid particles, two 10 mm layers of glass wool were used at the top and bottom of the adsorbing bed. PTFE tubing and fittings were used in the setup. Figure 5.4 shows the experimental setup. The column breakthrough curves were obtained by taking samples from the column exit at different times, and determining the oxygenate concentrations in these samples.
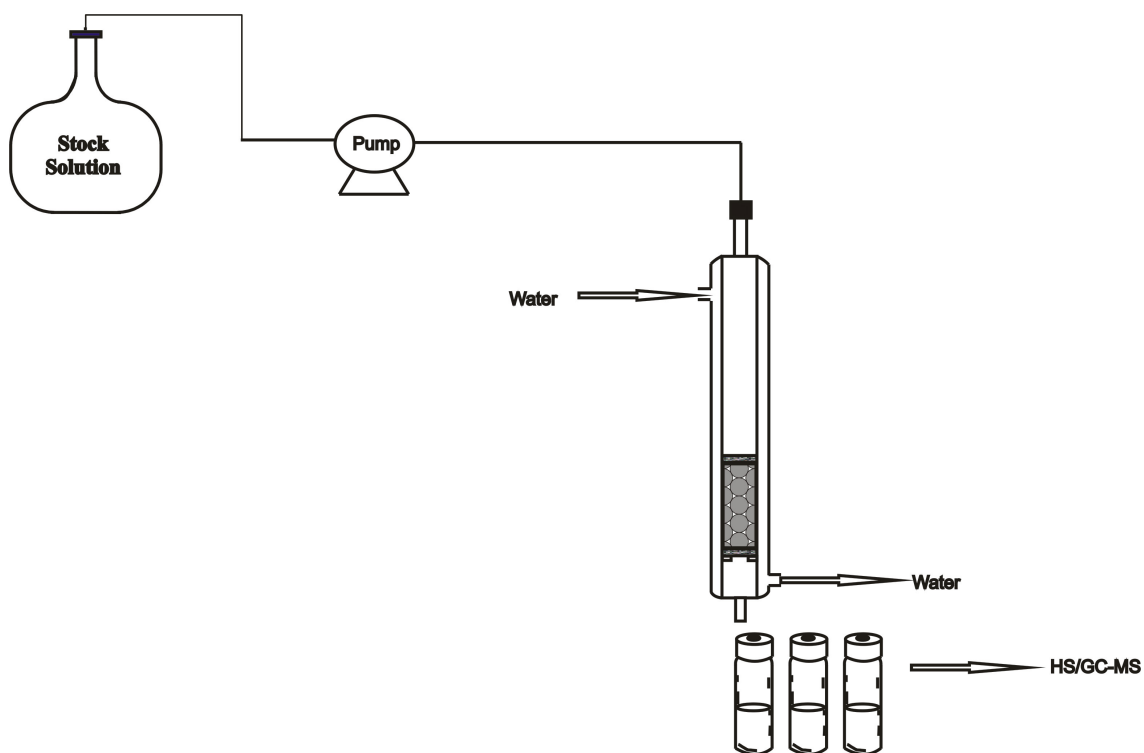

Figure 5.4. Experimental setup for fixed –bed adsorption tests

5.2.5. Analytical Method

Gas Chromatography (GC) is one of the most widely employed techniques to quantify mixtures of organic components. The GC is usually coupled with different types of detectors; Mass Spectrometer (GC/MS) Flame Ionization Detector (FID), Thermal Conductivity Detector (TCD), and Electron Capture Detector (ECD). However, most GC instruments are coupled with a MS detector. The GC separates the compounds from each other, while the mass spectrometer helps to identify them based on their fragmentation pattern (WEB_5 2006).

The GC method is preferable in analyzing volatile organic component (VOC). GC/MS is composed of two major building blocks: the gas chromatogram and the mass spectrometer. The GC part includes a column that can separate the molecules depending on their volatility. The sample containing the mixture of molecules is injected into the GC column and is carried by an inert gas through the instrument, usually helium. The injection port is heated up to 300° C to cause the chemicals to become gases. The molecules take different amount of time (called the retention time) to come out of the gas chromatograph, and this allows the MS downstream to evaluate the molecules separately in order to identify them. The molecules are blasted with electrons, which cause them to break into pieces and turn into positively charged particles called ions. These ions continue through the MS, and they travel through an electromagnetic field that filters the ions based on mass. The mass detector counts the number of ions with specific mass. This information is sent to a computer and a mass spectrum is created. The mass spectrum is a graph of the number of ions with different masses that traveled through the filter (WEB_6 2006).

The most widely used analytical methods of fuel oxygenate analysis are purge and trap, Headspace (HS), Direct Aqueous Injection (DAI) and Solid-Phase Micro Extraction (SPME) combined with GC/MS. The choice of one method or another mainly depends on concentration range "(Pavon et al. 2004)".

The performance of two methods (DAI-GC/MS and HS-GC/MS) were tested before the batch and column experiments. The response of the DAI-GC/MS method for the 0.5 ppm MTBE is given in Figure 5.5., and Figure 5.6 shows the response of the 0.2 ppm MTBE in HS-GC/MS technique. Although the MTBE concentration was lower than that of in DAI-GC/MS technique, the higher response was obtained for HS-GC/MS

method. Therefore, this technique was used for the concentration measurement in this study.
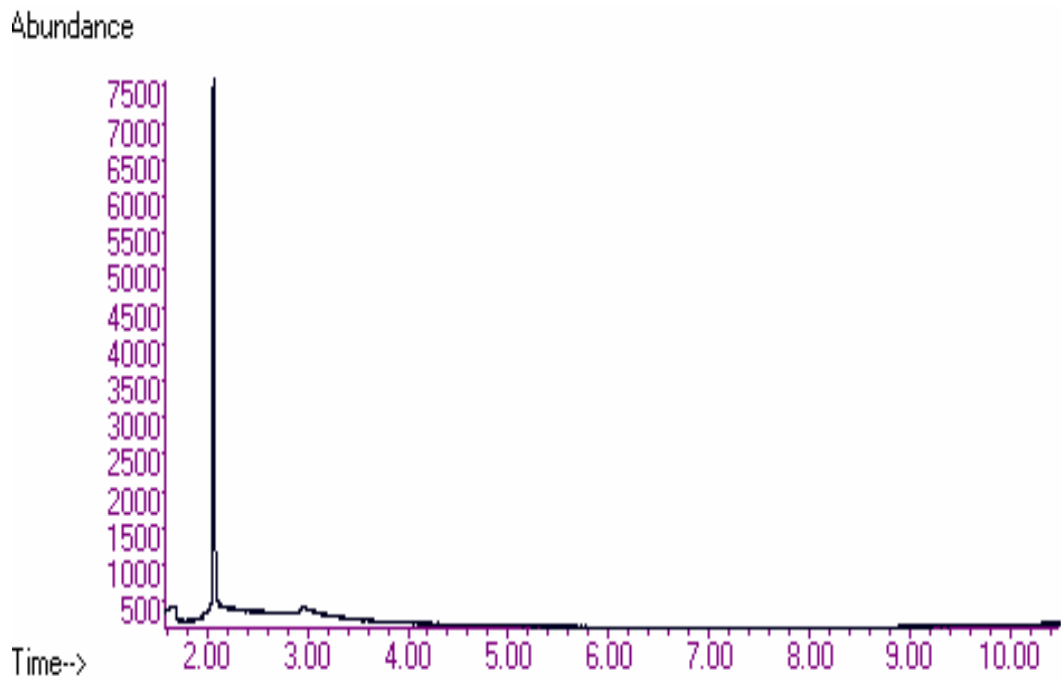

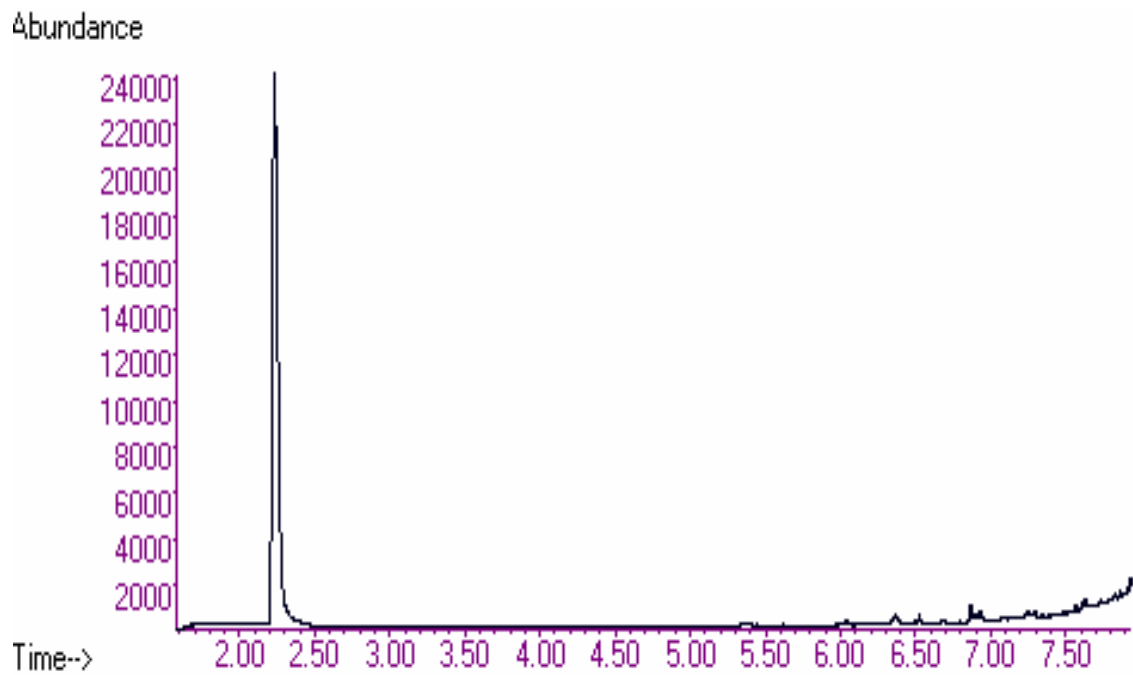Figure 5.5. MTBE analysis at 0.5 ppm concentration by DAI-GC/MS

Figure 5.6. MTBE analysis at 0.2 ppm concentration by HS-GC/MS

Analysis of the chemicals was done using a GC/MS instrument in which the mixture of the organic components is separeted in the column. Different molecules leave the GC column at different times (called the retention time). In the bisolute analysis, the retention time of ether and benzene componnents is different enough to avoid any overlapped or broadened peak. This is needed for the accuracy of the analysis. Figure 5.7 shows that all of the components can be separated in the column.
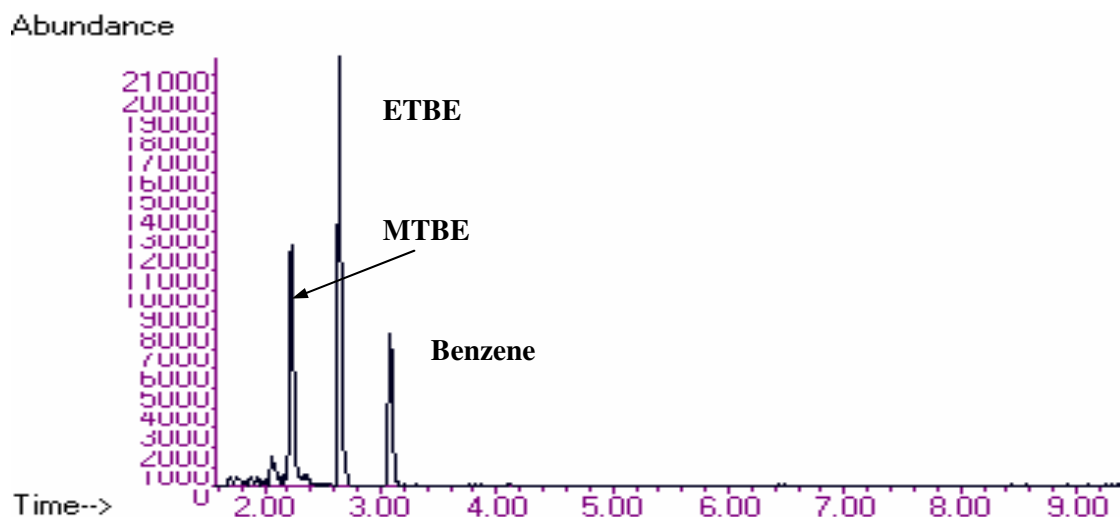

Figure 5.7. HS-GC/MS chromatogram for MTBE, ETBE and benzene

5.2.5.1 Headspace GC/MS Method

The term "headspace" refers to the space above the liquid or solid sample that is measured by headspace technique. Volatile organic compound can be successfully investigated by this method. It is assumed that the vapor in the headspace of the vial is in equilibrium with the same compounds in the liquid or solid sample. Consequently, this analysis procedure made it possible to accurately determine the liquid phase concentration from vapor phase.

The components of even highly diluted samples which are so volatile that they exhibit a suitable high vapor pressure above liquid or solid sample matrix can be introduced into GC column by transfer of a gaseous sample taken from the headspace of sealed sample vials. Only the volatile sample components enter the column for separation and analysis. The transfer of the gaseous sample into the column can be

completed in three different ways (i.e., gas-tight syringe, multiport valve sample loop by-pass technique, balance pressure sampling) "(Gerhard 1990)".

Instrumental analysis was performed by an Agilent 6890 GC, 5890 Mass Spectrometer and Agilent Headspace sampler 7694. The GC column was an Agilent HP-5MS (Capillary 30m×250μm×250μm nominal).

All samples were heated in the headspace oven at 80 °C for 20 min. The sample vial was pressurized with helium for 1.0 min. The loop was filled for 0.2 min and heated to 180 °C after loop fill equilibration time of 0.15 min. Then the sample was transferred to the injection port of the GC, which was kept at 200 °C. The injection time was 1.0 min.

At the injector, the split flow was set at 13.0 ml/min and the ratio of column flow to split was 1:13 (column flow rate was 1.0 ml/min). The column head pressure was maintained at 6.78 psi.

The GC oven was held isothermally at 35 °C for 2 min and the temperature was programmed to 60 °C at a rate of 5 °C/min, then to 250 °C by 40 °C/min so the total GC run time was 11.75 min. The GC cycle time was 40 min.

Fuel oxygenate analysis was done with respect to selected ion monitoring mode (SIM). SIM mode is used for quantitative analysis in which a few characteristic peaks associated with a candidate substance are analyzed. With GC/MS-SIM, the specificity of the mass spectrometric detection system can be tuned by detection with specially selected masses "(Gerhard 1990)". In this study, quantification was performed at the target masses; m=57-73 for MTBE, m=59-87 for ETBE, and m=77-78 for benzene.

5.2.5.2. Calibration and Headspace Sample Preparation

Headspace analysis was achieved using 20 ml headspace vial containing 10 ml of sample and 2 g NaCl, (20% v/v). To avoid vaporization, samples were analyzed within three days.

Five-point calibrations curves of the fuel oxygenate were prepared using MTBE, ETBE, and benzene. Stock solutions were diluted in deionized water to obtain a convenient concentration range. Single and bisolute solutions were prepared. Calibration curves are shown in Figure 5.8. to Figure 5.13. The correlation coefficients (R^2) were greater than 0.917.
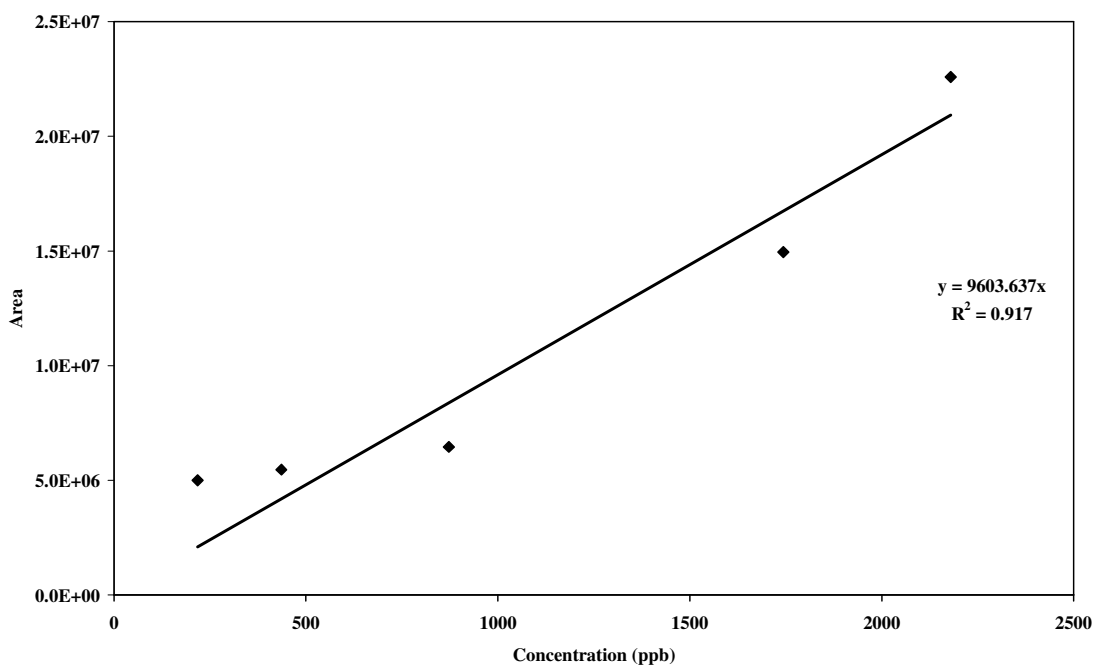
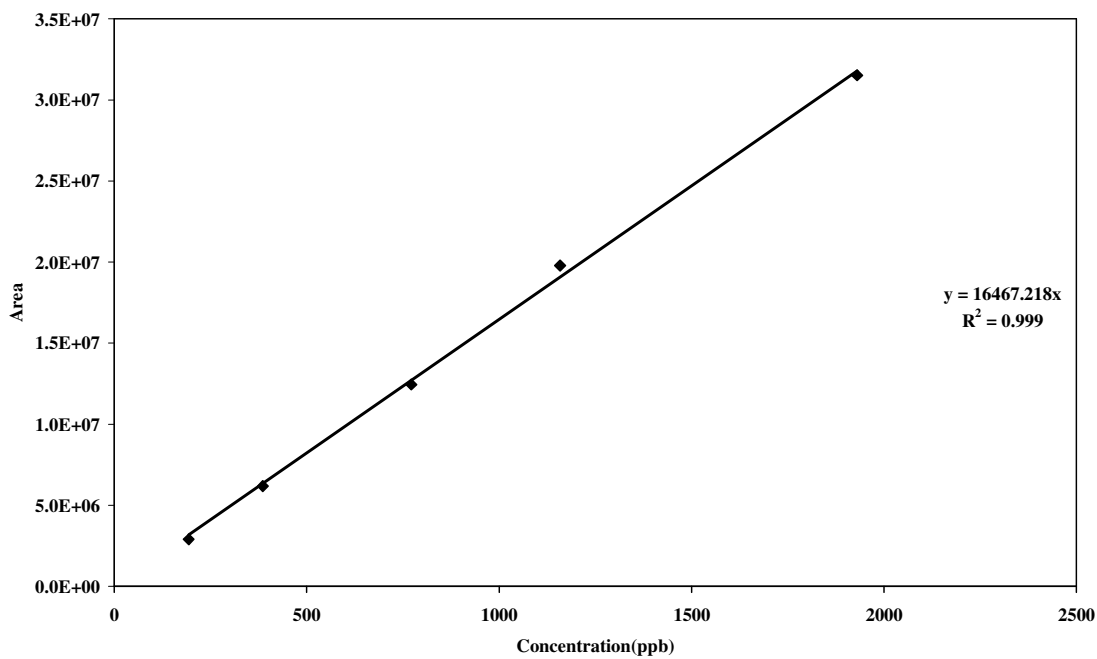Figure 5.8. Single solute MTBE calibration graph

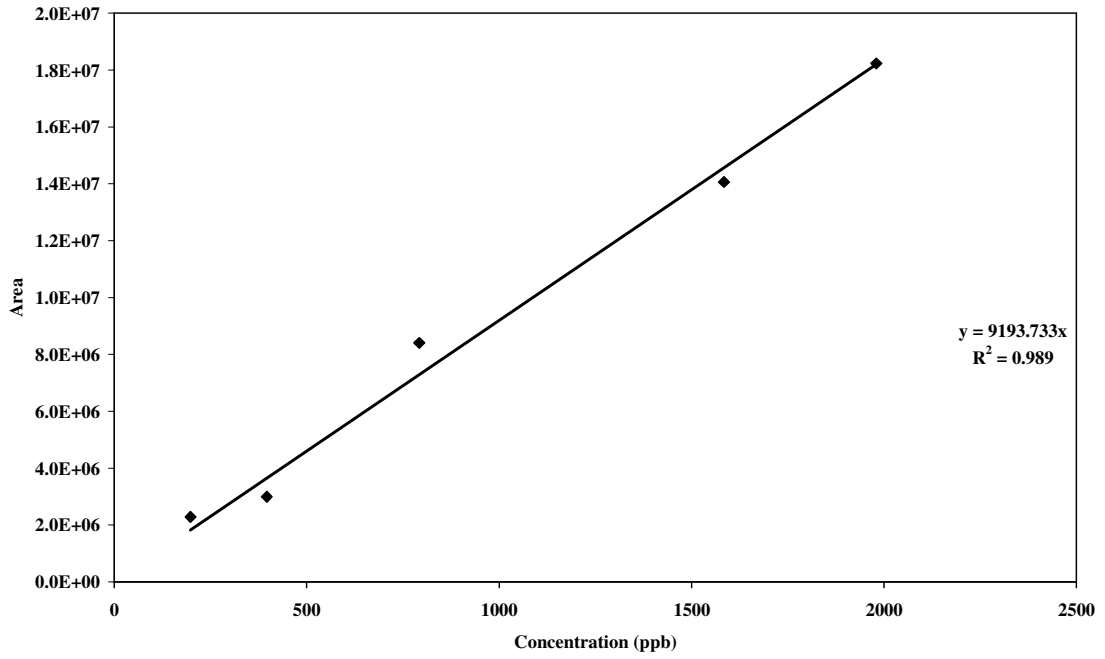Figure 5.9. Single solute ETBE calibration graph
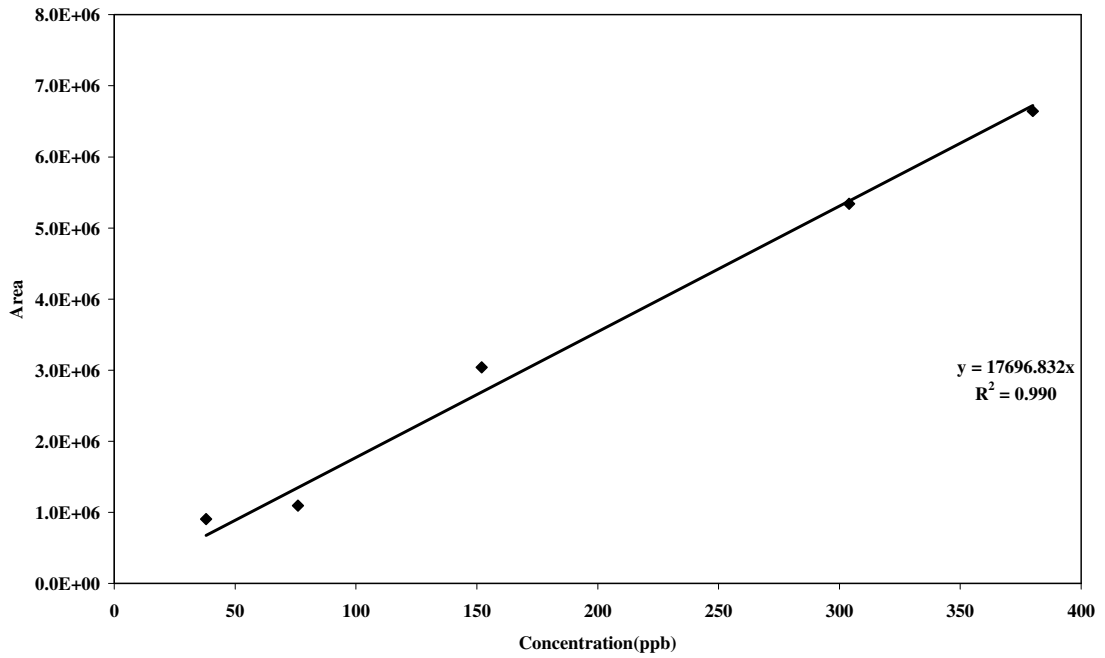
Figure 5.10. Bisolute MTBE calibration graph

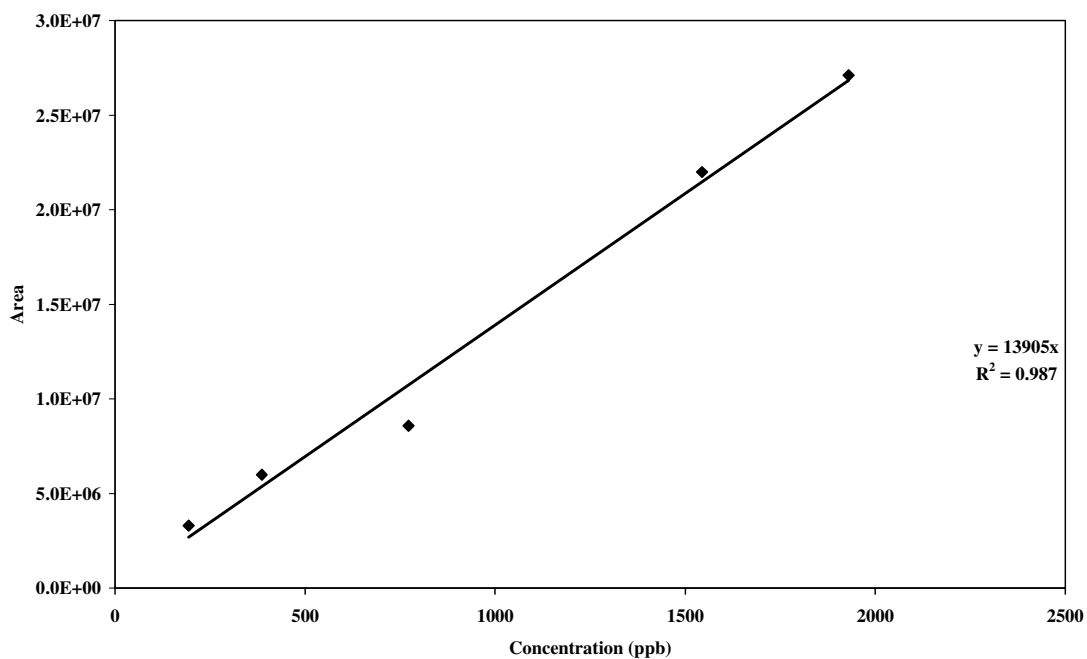Figure 5.11. Bisolute benzene calibration graph (with MTBE)

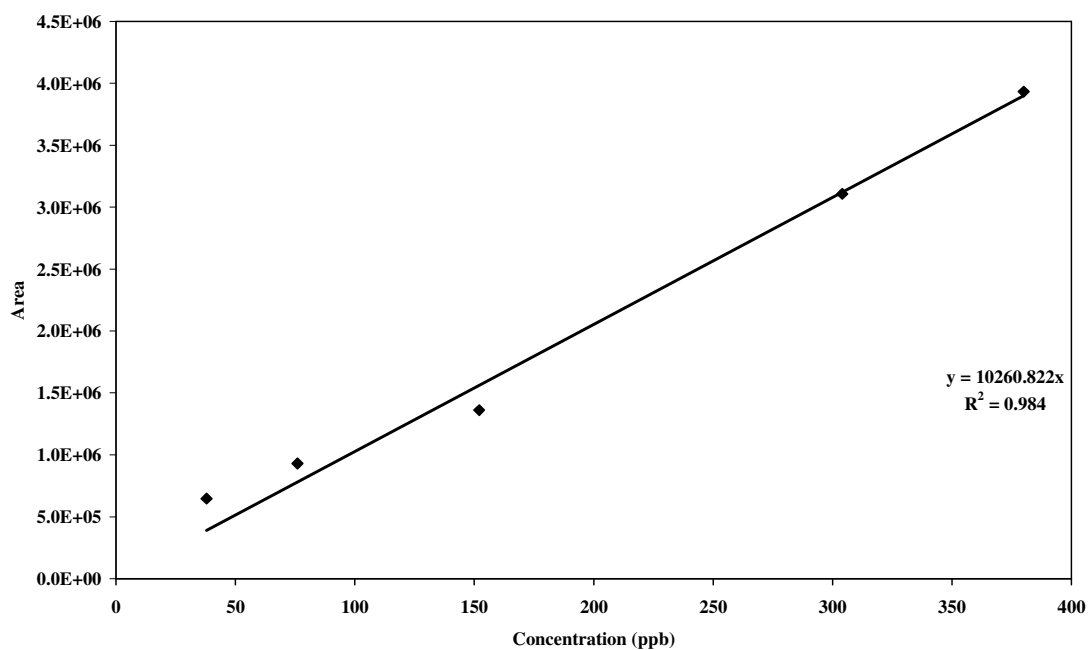Figure 5.12. Bisolute ETBE calibration graph

Figure 5.13. Bisolute benzene calibration graph (with ETBE)

CHAPTER 6

RESULTS & DISCUSSION

6.1. Clinoptilolite Characterization

6.1.1. Particle Size Distribution Measurements

The particle size distribution of clinoptilolite was performed using particle size analyzer (Sedigraph 5100). The experimental data are shown in Figure 6.1.
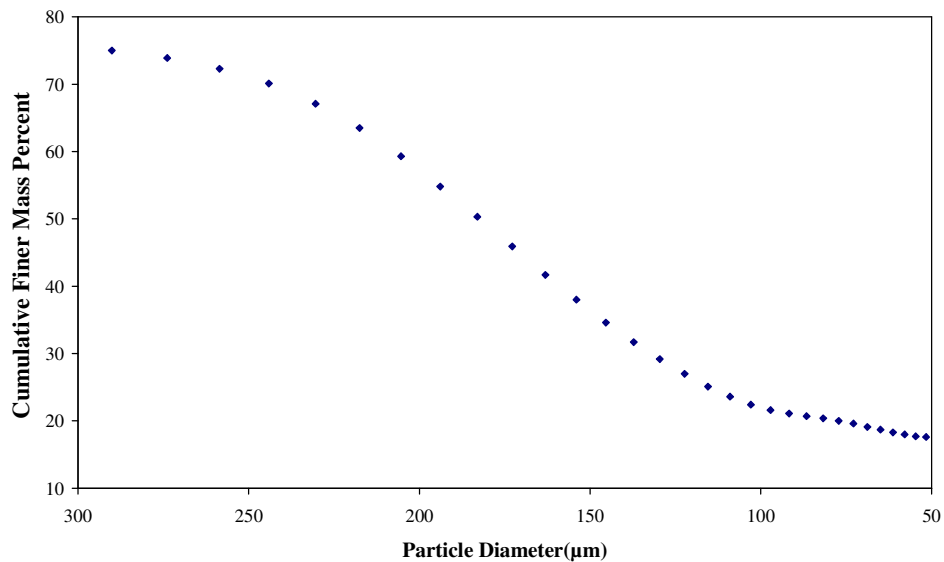

Figure 6.1. Particle size distribution of Clinoptilolite

As shown in Figure 6.1. 75% of the particles by mass were lower than 300 µm in size while 20 % of the particles have a size less than 50 µm. The mean diameter calculated from the size distribution was 179 µm.

6.1.2. Surface Area Analysis

For comparison purpose, BET and Langmuir methods were used in analyzing surface areas, volume, and pore size, and the values obtained for clinoptilolite, GAC and PAC are given in Table 6.1.

Table 6.1. Adsorption and desorption measurements for Clinoptilolite GAC and PAC.

Area	CLI	PAC	GAC
BET Surface Area (m^2/g)	43.4911	569.5249	806.8253
Langmuir Surface Area (m^2/g)	61.2442	847.1812	1217.6318
Micropore Area (m^2/g)	43.2868	579.6829	816.8817
Volume			
Micropore Volume (cm^3/g)	0.05392	0.3386	0.426750
Pore Size			
Average Pore Diameter (4V/A by BET) (Å)	49.5953	23.78	21.1570
H-K Method			
Median Pore Diameter (Å)	10	6	6

The surface area of a porous material is one of the most useful microstructure parameters for defining its properties. According to the values given in Table 6.1., GAC has the largest surface area compared to PAC and clinoptilolite with respect to BET and Langmuir measurements. The BET surface areas of the GAC applied in this study were 806.8 m^2/g. The surface area measurement for adsorption capacity is important. The larger surface area leads to greater adsorption capacity.

Clinoptilolite has the highest median pore diameter, 10 Å. The pore diameter is another important parameter that affects dominantly the diffusion adsorption mechanism.

6.1.3. Morphology and Mineralogy

6.1.3.1. Scanning Electron Microscopy Analysis

The morphology of the clinoptilolite (Figure 6.2) shows the characteristic clinoptilolite crystal structure. Clinoptilolite has the regular platelike crystals structure that is a common morphology of heulandites "(Gottardi 1985)".
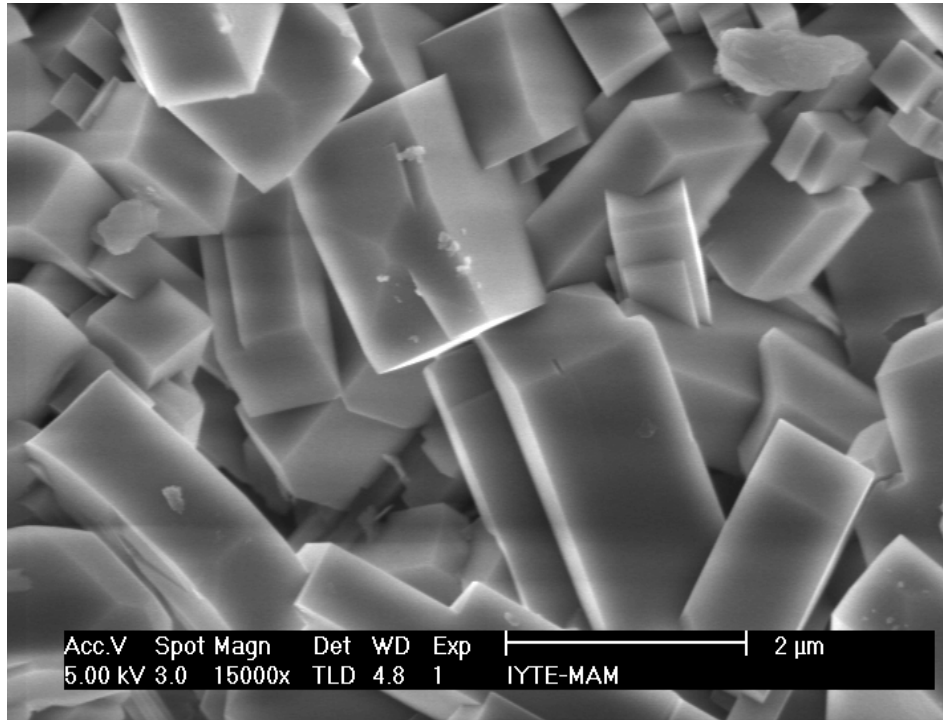
Figure 6.2. SEM micrographs of sedimentary clinoptilolite from Gördes, Manisa
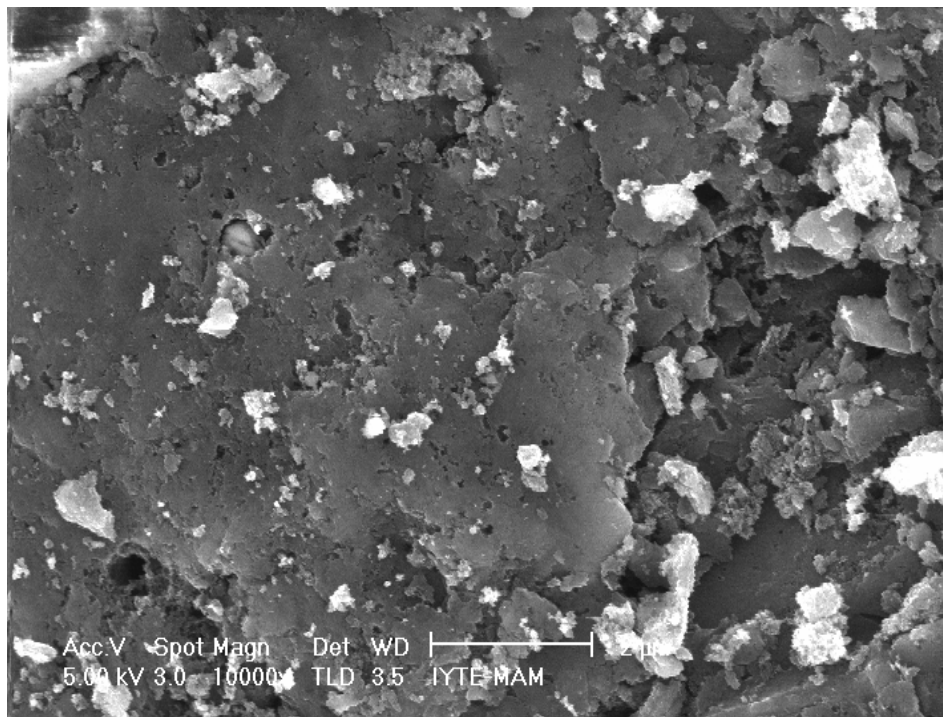
Figure 6.3. SEM micrographs of GAC
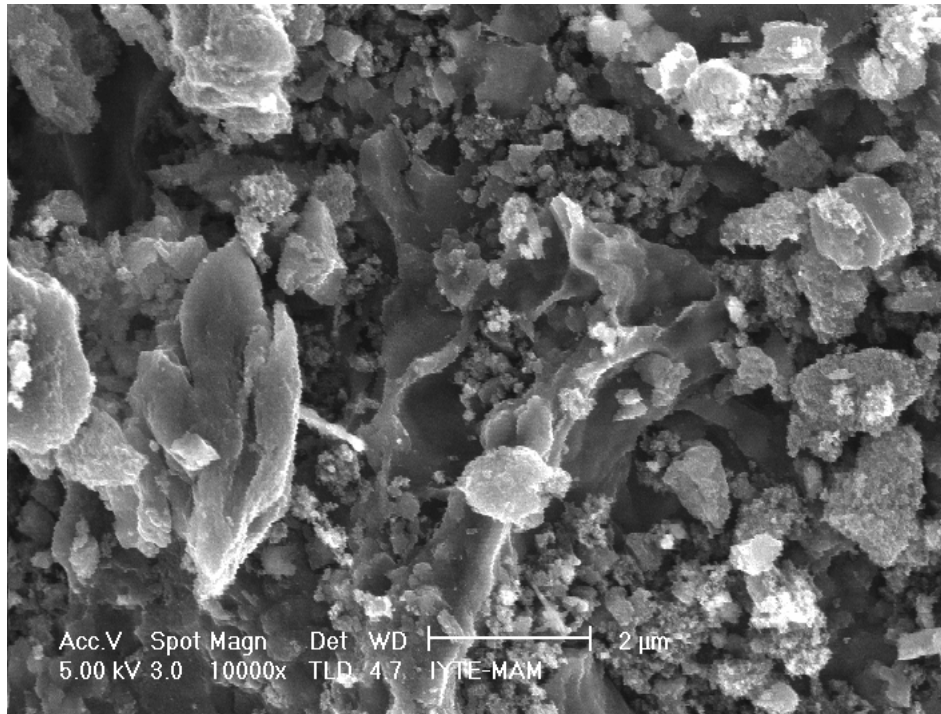
Figure 6.4. SEM micrographs of PAC

Typical SEM micrographs for PAC and GAC are given in Figure 6.3. and Figure 6.4., respectively. The images show that activated carbons have amorphous structure.

6.1.3.2. X-Ray Diffraction Analysis

The X-Ray diffraction (XRD) pattern of clinoptilolite is shown in Figure 6.5. This pattern shows three main characteristic peaks at 2Ө values of 9.77° 22.31° and 29.96° "(Korkuna et al. 2006)". The presence of other peaks arises from some impurities in the clinoptilolite sample.
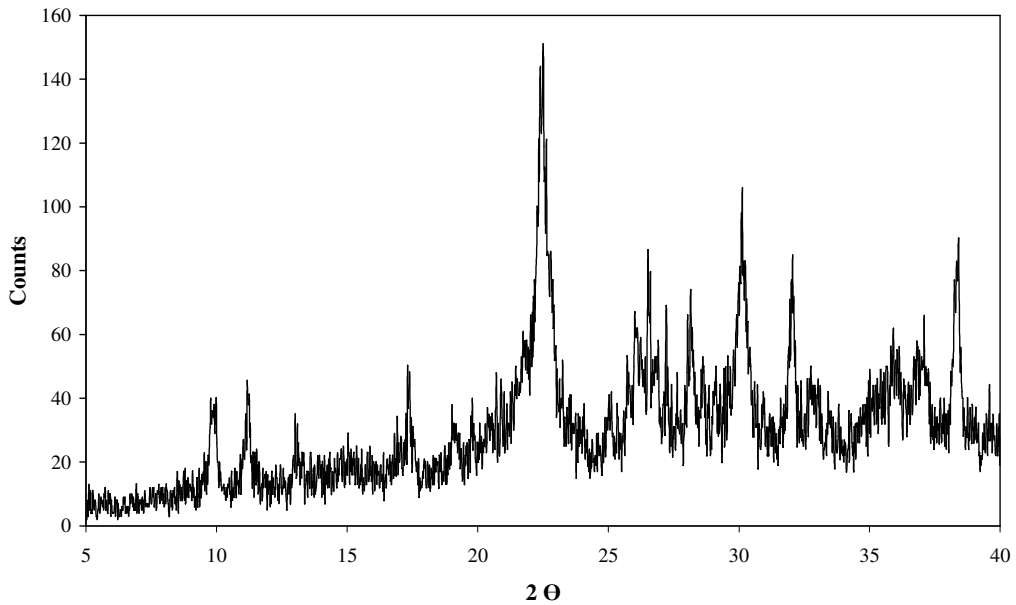
Figure 6.5. XRD diagram of clinoptilolite

6.1.4. Thermal Analysis

6.1.4.1. Thermal Gravimetric Analysis (TGA)

The TGA curve obtained for clinoptilolite is shown in Figure 6.6. The percent weight losses of the clinoptilolite are listed in Table 6.2. These can be related with loss in water content. The water in clinoptilolite was classified into three groups; external water, loosely bound water, and tightly bound water "(Knowlton and White 1981)". The external water is released up to 85°C, and loosely bound water is lost rapidly up to 285°C. After 285°C, the clinoptilolite starts to loose its tightly bound water. The average percent weight losses up to 800°C was calculated as 7.73 %.
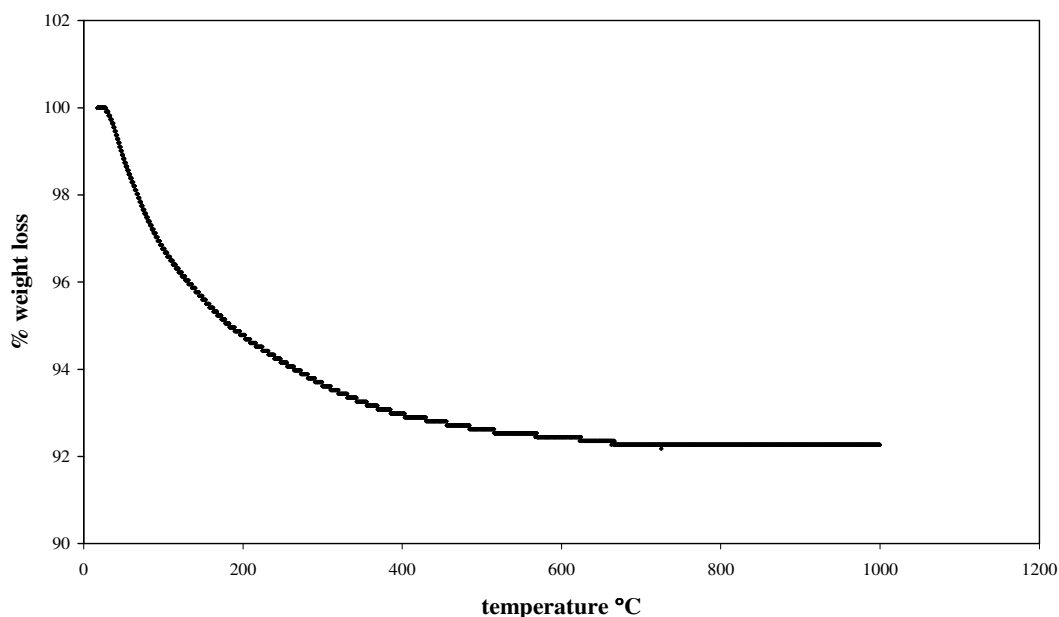
Figure 6.6. TGA curve of clinoptilolite

Table 6.2.   The percent weight losses of external, loosely bound and tightly bound water for Clinoptilolite

Sample	External Water	Loosely Bound Water	Tightly Bound Water		Total
	(< 85°C)	(85°C-285°C)	(285°-500°C)	(>500°)	
CLN	2.7878	3.4173	1.1691	0.3597	7.7339

Senatalar et al (2003) studied hydrophobicity measurement of clinoptilolite by TGA. The sample was heated to 400 °C at a heating rate of 10 °C/min and kept at this temperature till a constant weight was attained.

Hydrophobicities of adsorbent are calculated by equation 6.1. "(Giaya et al. 2000)". In our study, hydrophobicity of the clinoptilolite was calculated from TGA data that was taken using the same procedure. Zeolites are very hydrophilic materials and their hydrophobicity measurement provides information about their behavior in aqueous phase.

$$Hydrophobicity(h) = \frac{\text{Weight Loss up to } 150\,°C}{\text{Total Weight Loss}} \qquad (6.1)$$

The hydrophobicity of the clinoptilolite was found to be 0.646. Senatalar et al. (2003) concluded that hydrophobicity alone was not sufficient to clarify the adsorption behavior. While mordenite had lower hydrophobicity than that of Zeolite Y, it was found that mordenite was more effective in MTBE adsorption.

6.1.4.2. Differential Thermal Analysis (DTA)

The DTA curve of clinoptilolite is shown in Figure 6.7. Two transitions were observed as an endotherm occurring below 100 °C (64.63 °C) and an exotherm occurring at 1071 °C. The endotherm could be related to the dehydration of the sample while the exotherm is related with structural change of clinoptilolite
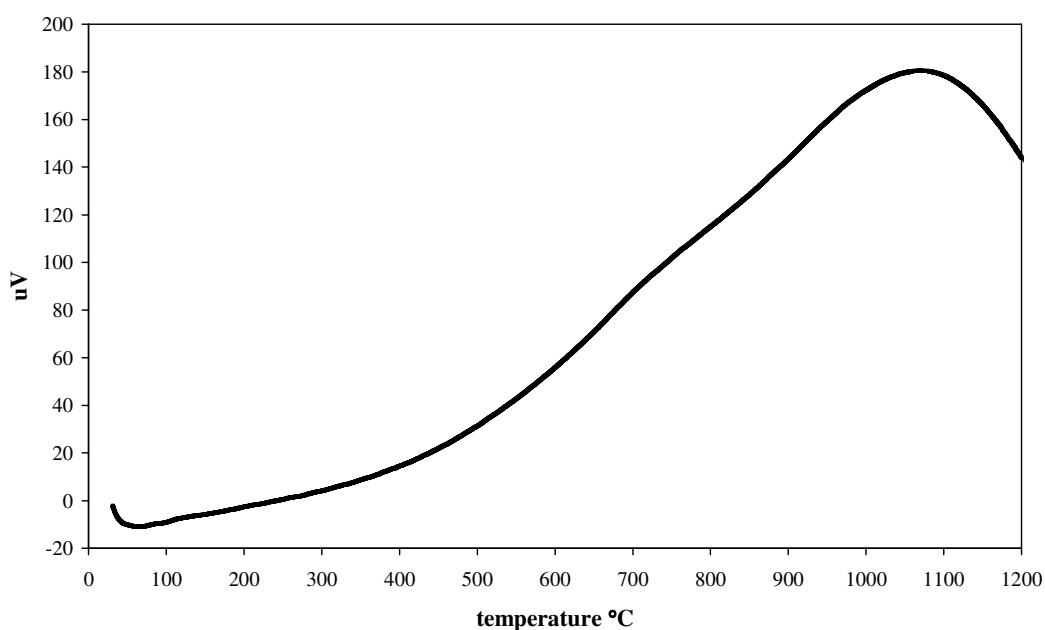

Figure 6.7. DTA curves of original clinoptilolite

6.1.5. Elemental Analysis

The chemical composition of the clinoptilolite sample in oxide form is given in Table 6.3. The ICP results of our sample were compared with the findings of another study performed by Ozaydın et al. (2006). They also used zeolite samples from the same region.

Table 6.3. Chemical composition of two clinoptilolite samples from same origin

Oxide form of elements	Chemical Composition (%) (this study)	Chemical Composition (%) (Ozaydın et al.)
Al_2O_3	13.37	12.4
CaO	2.47	2.54
Fe_2O_3	1.28	1.21
K_2O	6.1	4.46
MgO	1.0	0.83
Na_2O	2.17	0.28
SiO_2	73.57	70.9

Si /Al ratio can be related with thermal stability of clinoptilolite. Thermal stability of zeolites increases with increasing Si/Al ratio. For the clinoptilolite sample used in this study, Si /Al ratio was 4.68 on dry basis. This ratio is in the range of 4.5 - 5.5 reported for the clinoptilolite "(Tsitsishvili 1992)". In addition, the ICP data for clinoptilolite sample was in agreement with the Ca >Na ≤ K order, typical for low (Ca) silica clinoptilolite "(Tsitsishvili 1992)".

6.2. Batch (Equilibrium) Adsorption Experiments

6.2.1. Single Solute Adsorption

The batch adsorption experiments were performed for clinoptilolite, PAC and GAC using the conditions as described in 5.2.4.1. The equilibrium concentration in liquid phase was measured by using HS-GC/MS. The Freundlich and Langmuir adsorption models were used in evaluating the data obtained from the measurements.

The sorption isotherm for clinoptilolite and the two activated carbons (GAC and PAC), are given in Figure 6.8. and Figure 6.9. respectively. The q_e values were plotted against the equilibrium concentrations of MTBE and ETBE, C_e.
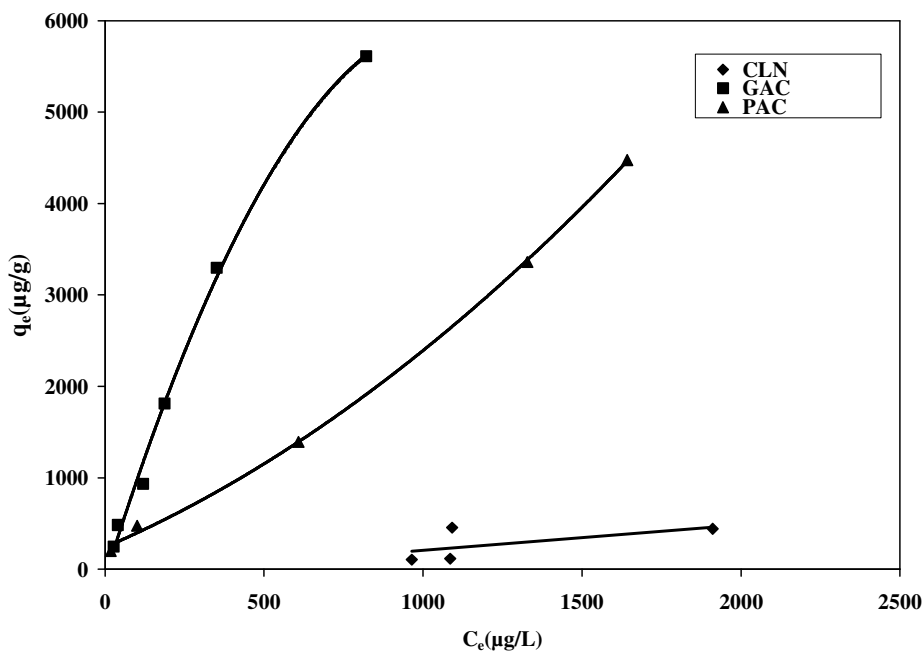
Figure 6.8. Single MTBE adsorption on CLN, GAC and PAC

Single MTBE solution batch experiments were conducted using three different adsorbent materials and the adsorption data obtained were used in plotting the sorption isotherms. According to these isotherms, the highest capacity for MTBE adsorbed per unit mass of adsorbent was obtained in the case of GAC, having a value of approximately 6 000 µg/g. The q_e values.were also higher than the ones corresponding

to PAC and clinoptilolite. Hence, GAC is the most effective for the adsorption of MTBE among the studied adsorbents.
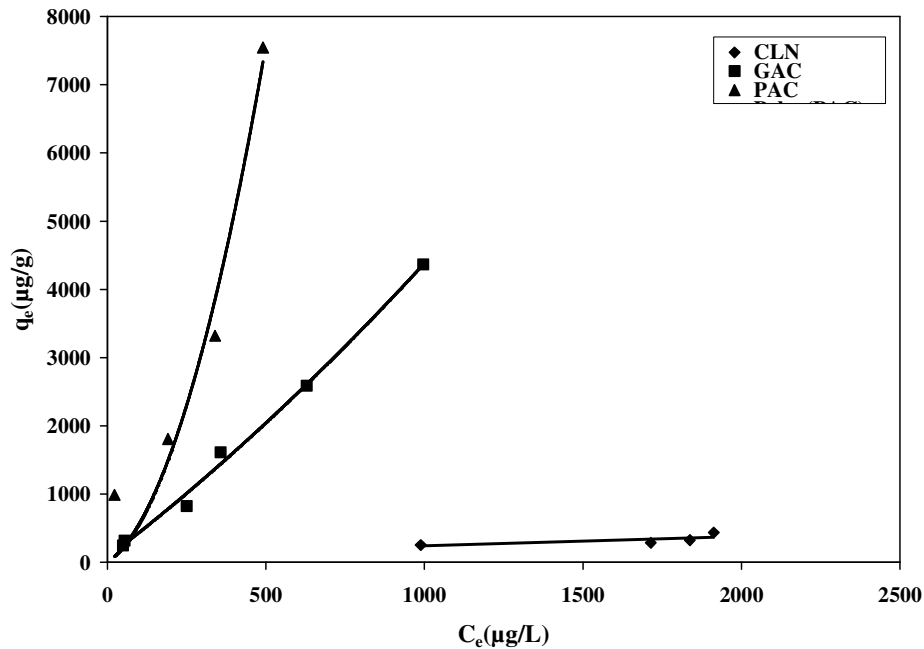
Figure 6.9. Single ETBE adsorption on CLN, GAC and PAC

PAC had higher affinity for ETBE than that of MTBE. In addition, among all adsorbents, PAC showed the highest capacity for ETBE. The q_e value obtained was about 8 000 µg/g, greater than that of GAC, which had a value of 4 500 µg/g.

6.2.1.1. Langmuir and Freundlich Isotherm Models

The data obtained in batch adsorption experiments were fitted to Langmuir and Freundlich models. Langmuir isotherm plots are shown in Figure 6.10. and Figure 6.11. Freundlich plots are given in Figure 6.12 and Figure 6.13 for MTBE and ETBE, respectively.

Figure 6.10. Langmuir plots for single stage MTBE adsorption on CLN, GAC and PAC

Figure 6.11. Langmuir plots for single stage ETBE adsorption on CLN, GAC and PAC

Figure 6.12.Freundlich plots for single stage MTBE adsorption on CLN, GAC and PAC

Figure 6.13 Freundlich plots for single stage ETBE adsorption on CLN, GAC and PAC
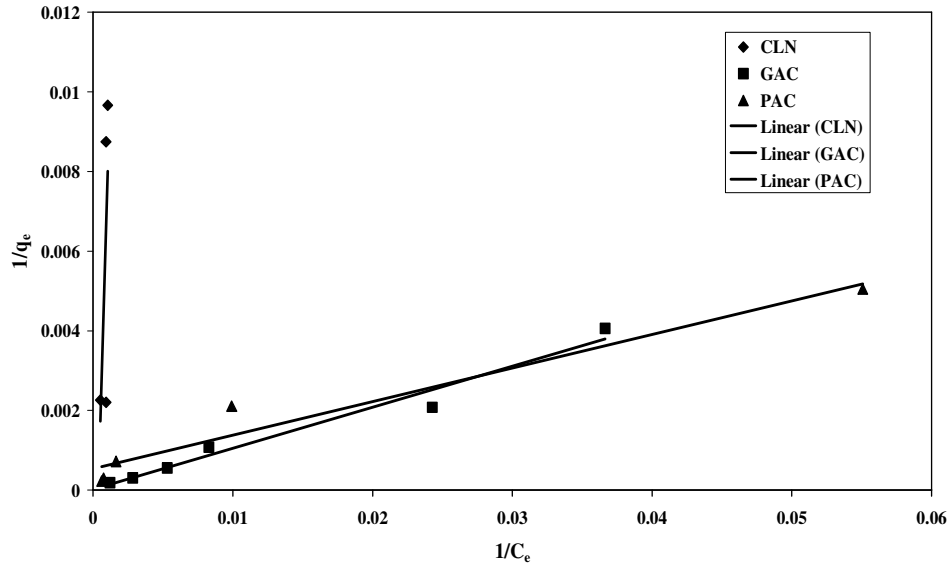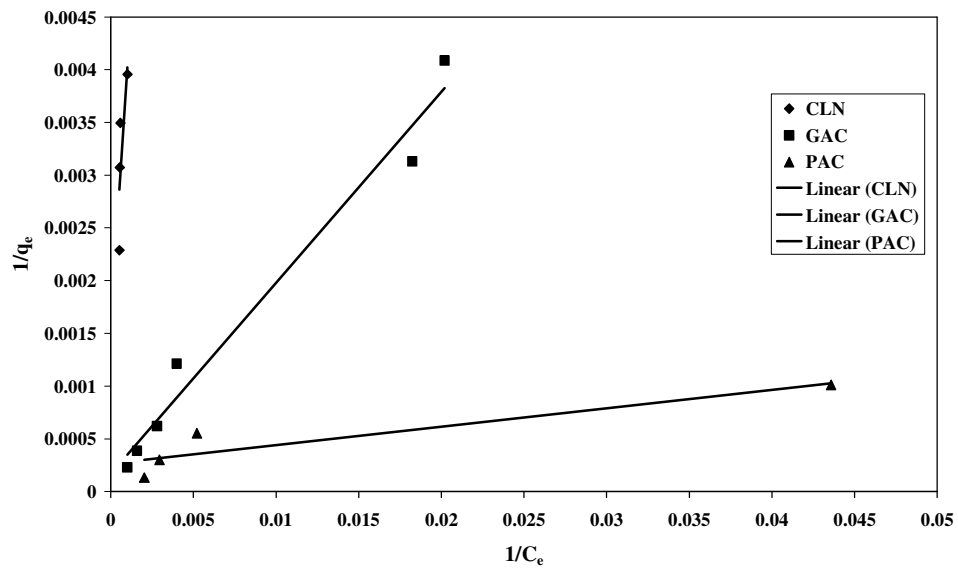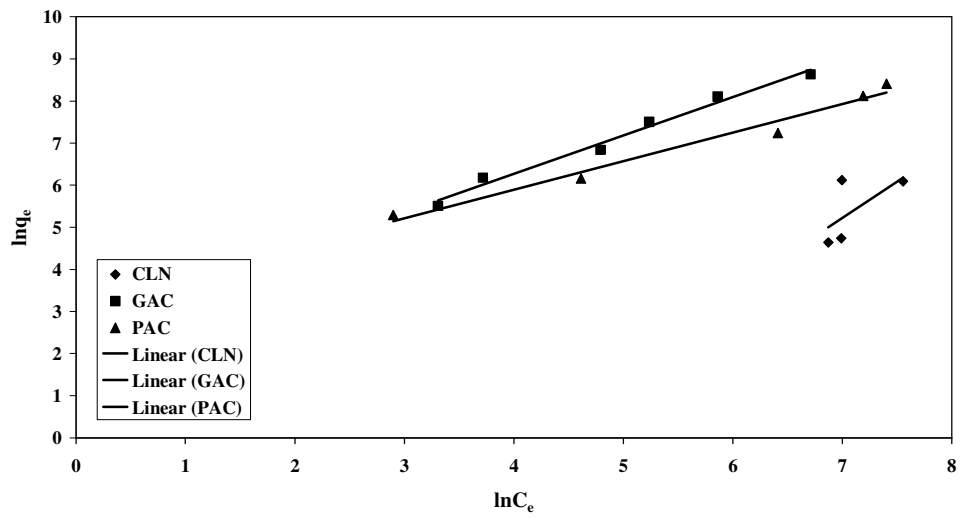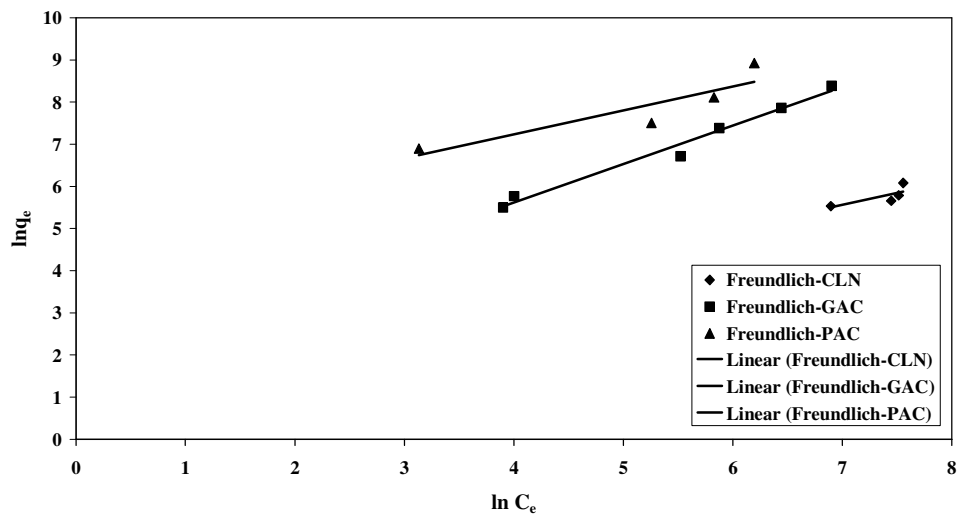
67

Table 6.4.   Parameters of Linear Langmuir and Freundlich Models for Fuel Oxygenate Adsorption Isotherms

Adsorbate	Adsorbent	Langmuir			Freundlich		
		R^2	Q^0	b	R^2	K_f	n
MTBE	**CLN**	0.461	-	-	0.417	927	0.58
	GAC	0.972	50 000	1.9E-4	0.984	13.856	1.098
	PAC	0.953	2 000	0.006	0.975	23.977	1.475
ETBE	**CLN**	0.603	625	6.73E-4	0.567	4.7	1.74
	GAC	0.976	5 000	0.001	0.982	7.10	1.094
	PAC	0.846	3 333	0.01	0.801	143	1.76

Adsorption isotherm constants for MTBE and ETBE on clinoptilolite, GAC, PAC using the Langmuir and Freundlich models are tabulated together with the regression coefficients in Table 6.4. Both models did not properly provide a linear fit of the data for MTBE and ETBE using clinoptilolite as indicated by the poor regression coefficients (≤ 0.60). However, the models provided adequate linear fits for MTBE and ETBE sorption on GAC (R^2=0.972-0.984). These results are consistent with the results obtained by Yu et al. (2005), which showed that the Langmuir and Freundlich models provided proper linear fit of the data for MTBE, ETBE, TAME and DIPE on two common GACs (F400 and F600) .

The Langmuir plots yielded two important parameters: Langmuir monolayer capacity, Q^o, giving the amount of MTBE/ETBE required to occupy all the available sites in unit mass of the adsorbent and the Langmuir equilibrium parameter, b, related to the equilibrium constant. For MTBE, Q^o was found to be 50 000 and 2 000 µg/g for GAC and PAC respectively. Thus, compared to PAC, GAC is more effective for use in the removal of MTBE from water. However, according to the b values, which show the affinity between the adsorbent and adsorbate, PAC had a greater affinity for MTBE adsorption with a value of 0.006. This was also confirmed with the values obtained for ETBE (0.01) which was higher than that of clinoptilolite and GAC.

The magnitude of Freundlich constants, K_f and n for PAC was found to be 23.98 and 1.48, 143 and 1.76 for MTBE and ETBE respectively. The values obtained show that ETBE had a higher adsorption affinity than MTBE. The results indicate that there is

no significant potential for the removal of fuel oxygenate from aqueous solution using clinoptilolite as an adsorbent.

6.2.2. Bisolute Adsorption

The adsorption of MTBE and ETBE in bisolute solutions was investigated using the same adsorbents; clinoptilolite, GAC and PAC. Batch experiments were performed with aqueous solutions containing both MTBE, ETBE, in addition to benzene. Competitive adsorption effects of benzene on the adsorbents were analyzed using adsorption isotherms. The obtained results were shown Figure 6.14 and Figure 6.15.
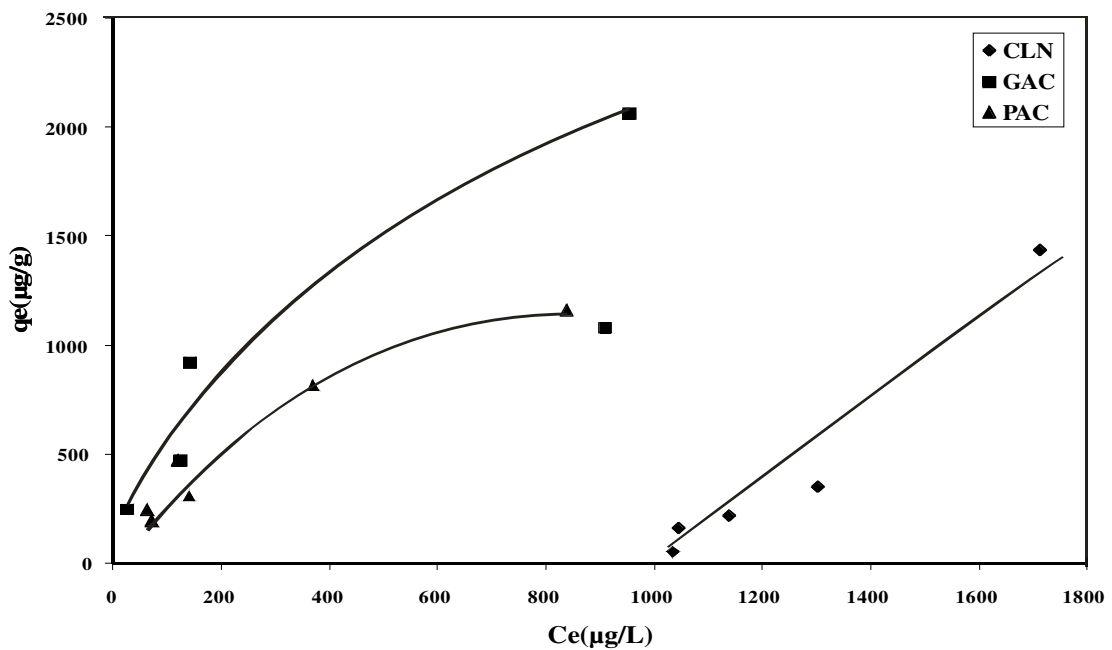

Figure 6.14. Adsorption isotherms of MTBE in the presence of benzene on CLN, GAC and PAC
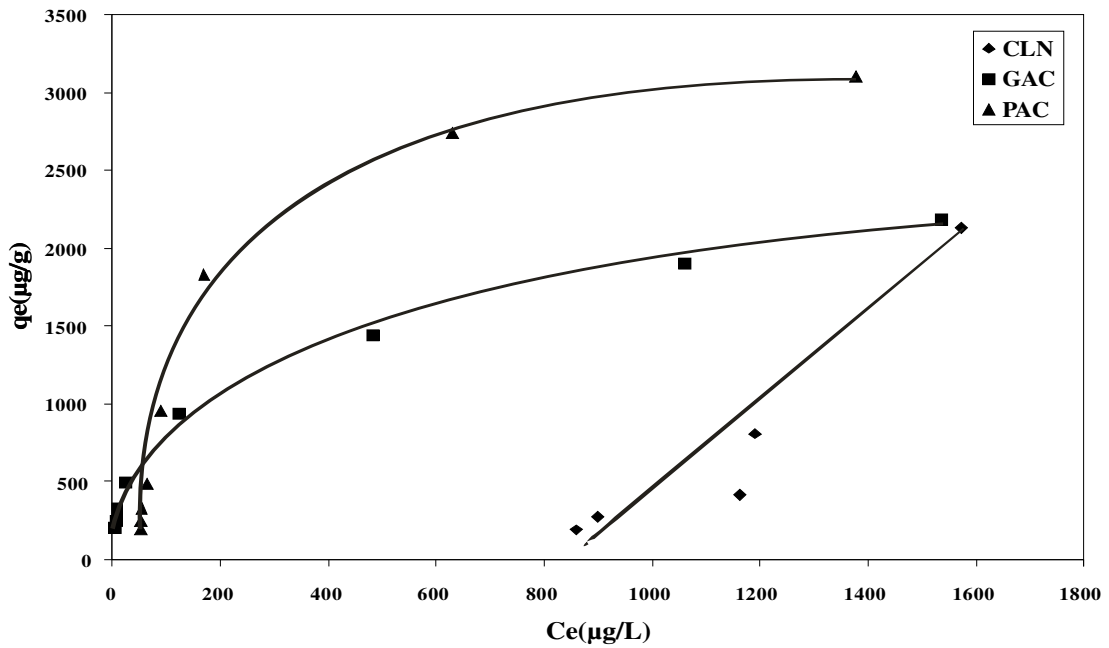
Figure 6.15. Adsorption isotherms of ETBE in the presence of benzene on CLN, GAC and PAC.

From the figures shown above, it can be observed that the presence of benzene decreased the available adsorption sites on GAC and PAC. Considering the single solute MTBE and ETBE adsorption isotherms, the GAC and PAC adsorption capacities for MTBE decreased from 6 000 to 2 000 and 4 500 to 1500 µg/g, respectively. Similar decrease in adsorption capacity was observed for ETBE and these results are consistent with ones reported in literature "(Scott et al. 2000)".

6.3. Column Adsorption

6.3.1. Single Solute Column Adsorption

The kinetic experiment was performed in a fixed bed column by plotted the breakthrough curves. The results of the column adsorption experiments in terms of C/C_o versus time are shown in Figure 6.16 and Figure 6.17 for the same inlet concentration of MTBE and ETBE. A practical application of the breakthrough curve is the determination of the breakthrough time and the saturation time of the column (which means that inlet and exit concentrations are the same, i.e. $C/C_o=1$)

Figure 6.16. Single solute MTBE column breakthrough curves for CLN and GAC
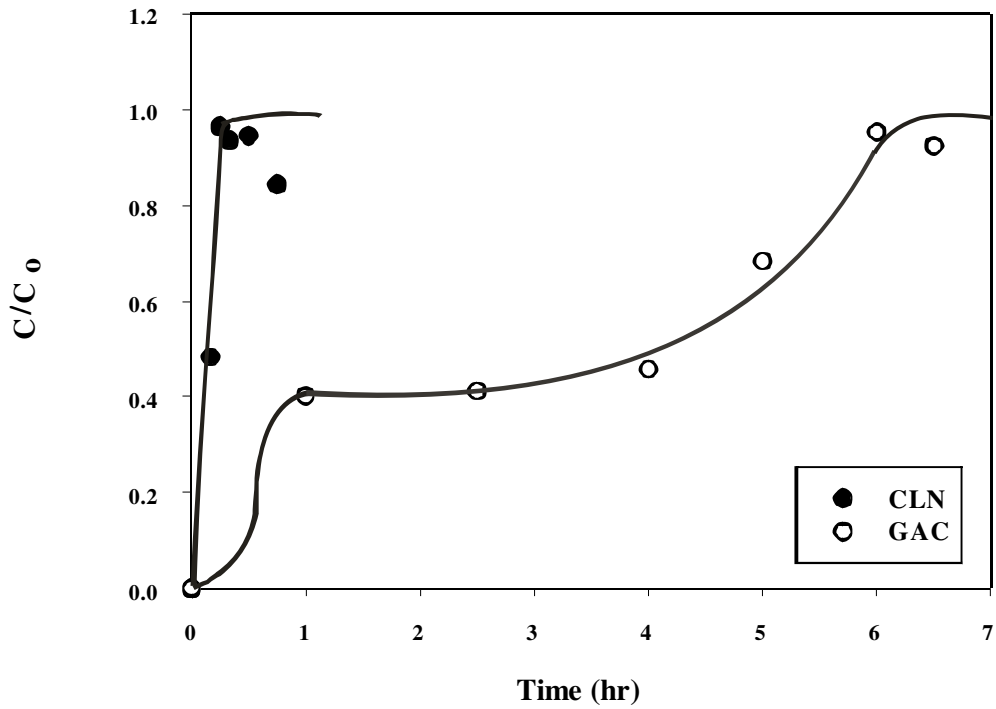
Single MTBE column adsorption experiments show that saturation time occurred at 0.5 hr using clinoptilolite, shorter than that of GAC in which 6-7 hr were required. Clearly, GAC had better adsorption capacity than clinoptilolite because it had a greater mass transfer zone.
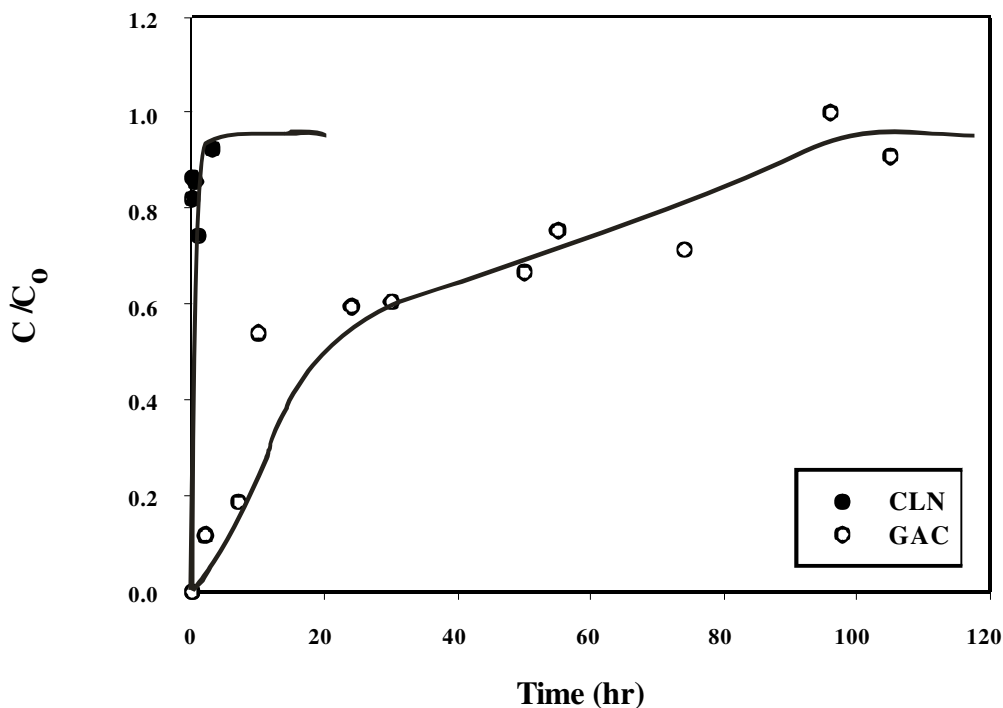
Figure 6.17. Single solute ETBE column breakthrough curves for CLN and GAC

Fixed-bed adsorption runs were also performed for ETBE. Column saturation times for clinoptilolite and GAC were found to be 3 and 100 hr respectively as shown Figure 6.17. Therefore, GAC adsorption capacity for ETBE on continuous adsorption processes was found more effective than clinoptilolite. However, GAC's column mass transfer zone for ETBE was found to be larger than that of MTBE as ETBE's saturation time occurred at approximately 100 hours while that of MTBE occurred in 7 hours. Nevertheless, clinoptilolite adsorption capacity for the continuous system was not effective for the ether components. Clinoptilolite reached its saturation point at 3 and 0.5 hours for ETBE and MTBE respectively.

6.3.2. Bisolute Column Adsorption

6.3.2.1. Clinoptilolite

The column breakthrough curves for clinoptilolite for MTBE and ETBE adsorption in the presence of benzene are shown in Figure 6.18 and Figure 6.19., respectively. The results showed that benzene had no significant effect. This might be

attributed to the fact that benzene molecules are too large to enter the pores of clinoptilolite. Hung and Lin (2006) studied the MTBE adsorption by natural zeolite (mordenite) in the presence of natural organic matter (NOM). They also concluded that there was no significant competition of NOM.
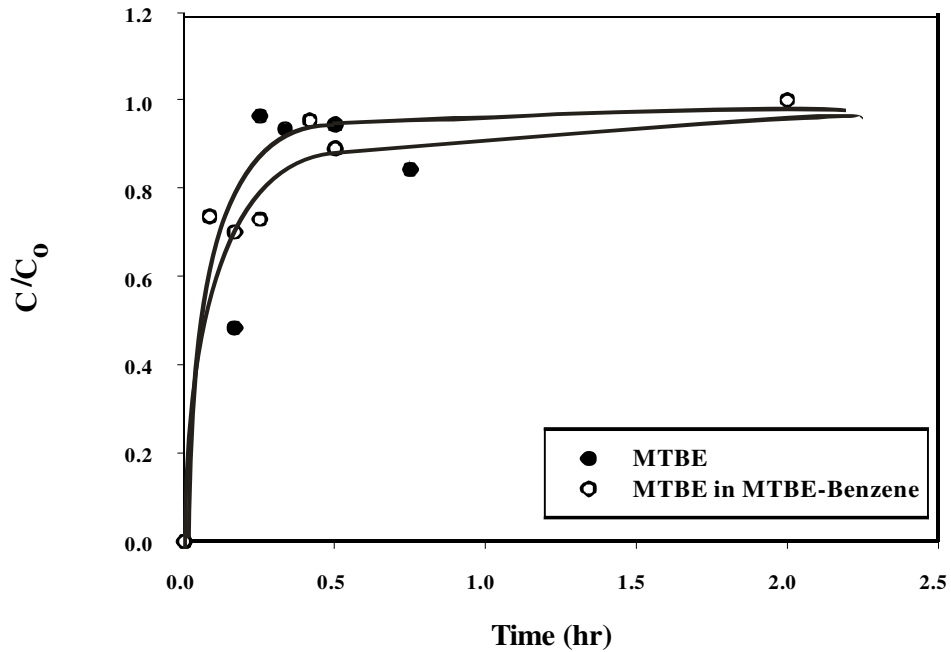

Figure 6.18. Single and bisolute MTBE column breakthrough curves for CLN
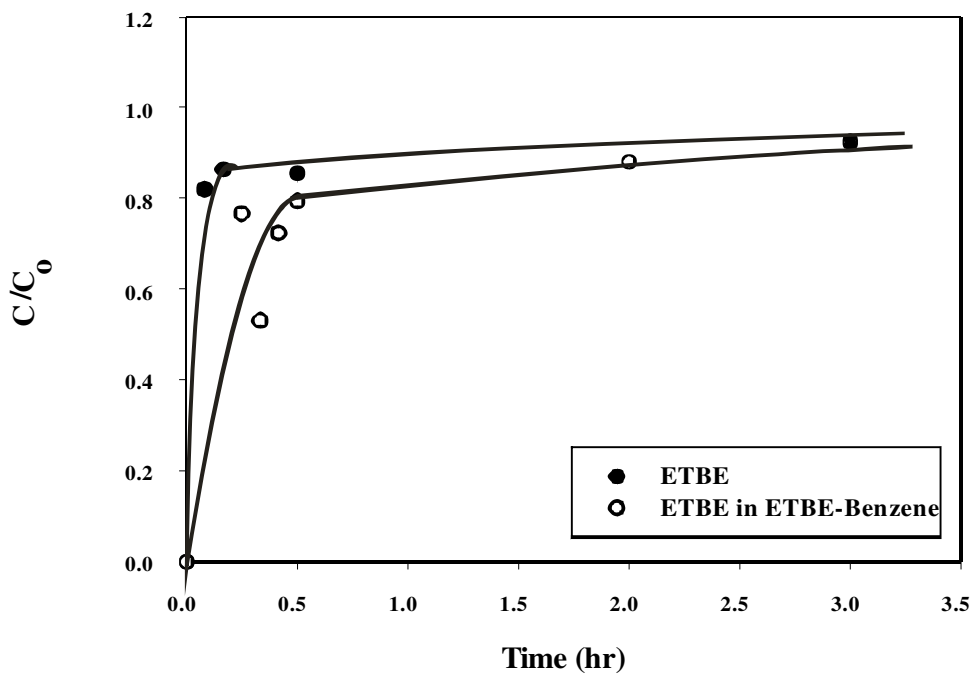
Figure 6.19. Single and bisolute ETBE column breakthrough curves for CLN

6.3.2.2. Granulated Activated Carbon

For the GAC, the presence of benzene had no significant effect on column saturation time as can be seen from the breakthrough curves for single and bisolute MTBE adsorption in Figure 6.20. The saturation time occurred at about the same time for both systems indicating that the presence of benzene did not change GAC adsorption capacity. The GAC adsorption capacities for single and bisolute ETBE are given in Figure 6.21. From these curves, it appears that, the saturation times occurred at about same time. However, the column saturated faster in the presence of the benzene. The differences were small and could be considered statistically insignificant.
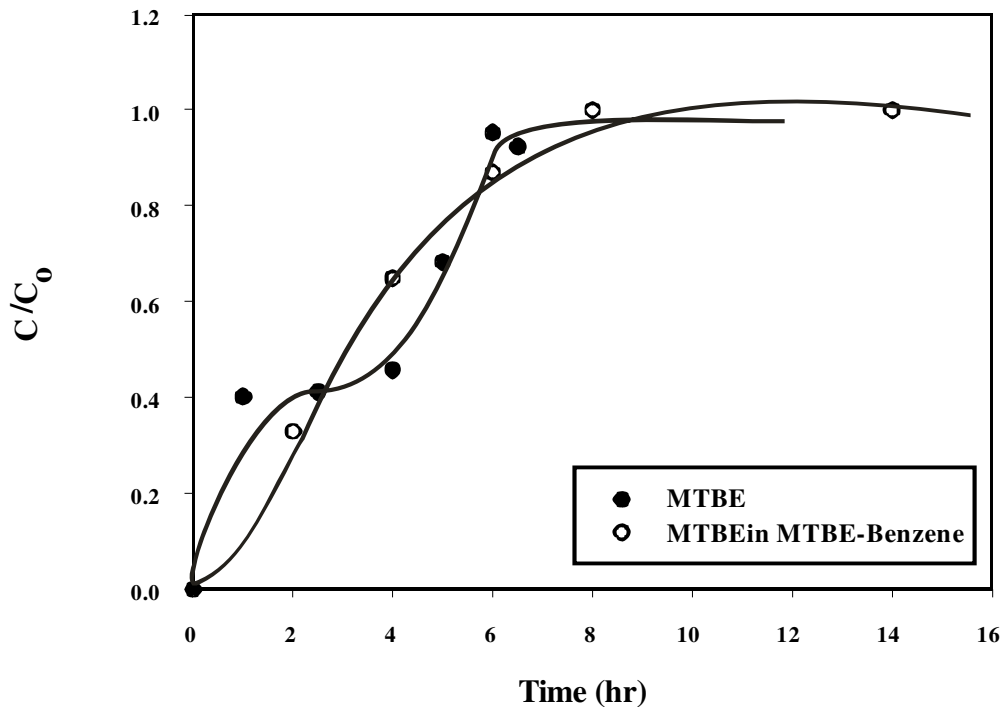
Figure 6.20. Single and bisolute MTBE column breakthrough curves for GAC

Single and bisolute ETBE column breakthrough curves for GAC are shown in Figure.6.21. The column saturated faster in the presence of benzene than single solute ETBE. Single solute saturation occurred within 100 hours. As a result, there is no statistically significant decrease in the adsorption capacity of GAC breakthrough curves to conclude high competitive effect.

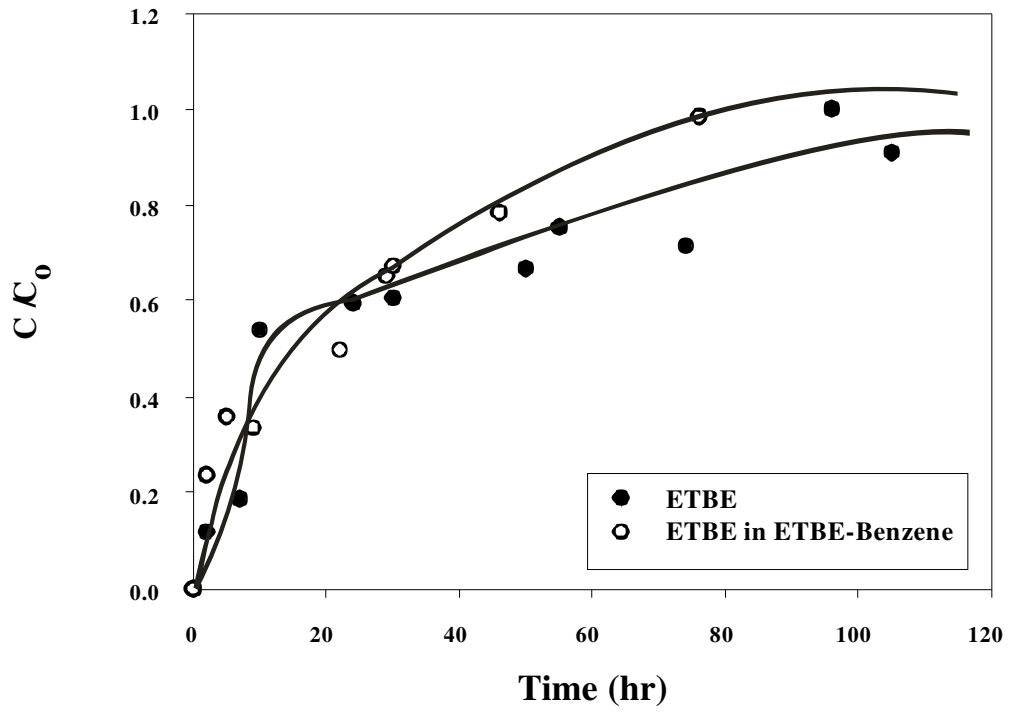Figure 6.21. Single and bisolute ETBE column breakthrough curves for GAC.

CHAPTER 7

CONCLUSION

In this project the adsorption properties of clinoptilolite rich natural zeolites for the removal of MTBE and ETBE from water have been investigated in batch equilibrium and fixed –bed column experiments. The adsorption properties have been compared for two activated carbons (i.e. Powdered Activated Carbon (PAC) and Granulated Activated Carbon (GAC)). Adsorption isotherms were obtained at initial oxygenate and benzene concentrations of 2000 ppb and 400 ppb, respectively.

Clinoptilolite was characterized using elemental and thermal analysis techniques. Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were used to reveal the mineralogy and morphology of clinoptilolite. Inductively Coupled Plasma (ICP) analysis was used to obtain elemental composition of clinoptilolite. According to the results, the adsorbent was dominated by clinoptilolite.

The experimental data were fitted to Langmuir and Freundlich models to elucidate the effectiveness of clinoptilolite, GAC and PAC as adsorbent in the removal of fuel oxygenates from water. The results showed that for clinoptilolite, Langmuir and Freundlich model regression coefficients were very low (R^2 ≤0.6). The results of equilibrium adsorption tests indicate that Langmuir and Freundlich isotherm can adequately describe the MTBE and ETBE equilibrium between the active carbons and the aqueous phases. The results indicate that there is no significant potential for the natural clinoptilolite as an adsorbent material for MTBE and ETBE removal from aqueous solutions. The regression coefficient of the Langmuir and Freundlich models for GAC and PAC are ≥0.97 and ≥0.8 respectively. Therefore in this study, the single solute concentration range sequence of equilibrium sorption affinity were identified for MTBE as GAC > PAC > clinoptilolite. GAC has the highest capacity for MTBE adsorption. The adsorption capacity of ETBE was the highest in the case of PAC, and the sequence was PAC > GAC > clinoptilolite

Bi solute experiments indicate that GAC and PAC sorbents preferentially sorbed the less water-soluble benzene over high water soluble MTBE and ETBE. However, adsorption isotherms, which belong to bisolute experiments, showed that there is no

change in the sequence of the adsorption affinity of GAC and PAC. Effects of benzene were not clear for clinoptilolite.

According to the experimental and modeling observation, benzene may compete with MTBE and ETBE for the adsorption sites within the equilibrium batch tests. The competition effect is substantial for GAC and PAC in deionized water.

Breakthrough curves were drawn for data obtained by column adsorption experiments for clinoptilolite and GAC. GAC was observed as significantly different from clinoptilolite. Clinoptilolite saturated at about 0.5 h for MTBE and 3 h for ETBE. Furthermore, GAC column has saturated at about 7 h for MTBE and 80 h for ETBE. GAC adsorption was found to be more effective than clinoptilolite .Clinoptilolite saturated very fast, and the curves for clinoptilolite were steeper. Therefore, in continuous flow system, using of GAC can be more effective for ETBE adsorption.

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