

**Sorption for Removing Methyl Tertiary Butyl
Ether (MTBE) from Drinking Water**

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ABSTRACT

Methyl tertiary butyl ether (MTBE), the most common oxygenated fuel additive, has been detected in several drinking water supplies in California. MTBE levels as high as 610 $\mu\text{g/L}$ in the groundwater of the City of Santa Monica were reported. An action level of 35 $\mu\text{g/L}$ for drinking water has been established by the California Department of Health Services (CAL-DHS). CAL-DHS has listed MTBE as a carcinogen and will likely establish a secondary drinking water standard of 5 ppb. In addition to the risk associated with human exposure through drinking water, unpleasant taste and odor should not be detected under this new secondary standard.

Removal of MTBE from drinking water can be achieved through several water treatment processes such as air stripping with adsorption of collected material, advanced oxidation, membrane separation, and sorption. Since MTBE is a highly water soluble polar compound, high air to water ratios are required in air stripping process. Consequently, the use of the process may not be economical. Membrane separation is considered too expensive for the use in general water treatment applications. Advanced oxidation processes, such as ozone and ozone/peroxide, are very effective in removing MTBE from drinking water; however, bromate is a by-product of these processes and biodegradable organic carbon is produced and must be removed before drinking water is distributed to prevent the regrowth of bacteria in the water distribution system. The objective of this research is to determine the cost and effectiveness of sorption process as a sole process to remove MTBE from drinking water and as a polishing process after an advanced oxidation method.

Isotherm studies at a moderate MTBE concentration of MTBE 1000 ppb were conducted. Sorbents used in these studies included granular activated carbons (bituminous coal, wood, peat, and coconut), XAD-4 and XAD-8 resins (Amberlite), and XE-572 resin (Ambersorb). Non-traditional sorbents, such as treated and non-treated greensand were also tested. Competitive studies were conducted with humic materials from background Santa Monica well water and tertiary butyl alcohol (TBA) which is a major oxidation by-product.

Based on the results from isotherm studies, the coconut based granular activated carbon (Calgon GRC-22) is the most cost-effective sorbent for removing MTBE from drinking water when the initial concentration of MTBE is 80 ppb or higher. When the initial concentration of MTBE is lower than 80 ppb, the wood based activated carbon is the most cost-effective sorbent. To treat 1000 gallons of water contaminated with 1000 ppb MTBE alone, 0.11 lbs of the coconut based granular activated carbon (GAC) is required and the cost for this amount of the carbon is \$0.14. To treat the water contaminated with 20 ppb MTBE alone with the wood based carbon, the carbon use rate is 0.32 lbs/1,000 gallons and the cost for 0.32 lbs of the wood based carbon is \$0.21. Sorption using the coconut and SA-30 wood based GACs is a reliable alternative for removing MTBE from drinking water. To reduce the cost of MTBE treatment, it is also possible to use the SA-30 wood based GAC sorption as a polishing process for the effluent and/or contaminated air released from air stripping process. The cost of the coconut GAC adsorption to

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treat 1,000 gallons of water contaminated with 20-100 ppb MTBE in the presence of 100 ppb TBA from an advanced oxidation process ranges from \$0.31 to \$0.50 based on the required amount of carbon of 0.25 to 0.40 lbs.

1. INTRODUCTION

Methyl tertiary butyl ether (MTBE) has been used as a gasoline additive in California since 1992 to improve the air quality. MTBE has been added in a concentration as high as 12 percent, to enhance gasoline combustion and reduce tailpipe emissions. During the past few years, MTBE has been detected in groundwater and surface water in a number of urban regions not only in California but throughout the country. A recent study by the United State Geological Survey (USGS) reported MTBE has contaminated at least 14% of the urban drinking water wells (AWCA, 1998). Due to its high water solubility of 42 to 54 g/L at 25 degree C (API, 1993), MTBE is transported more rapidly than other components in gasoline and the sorption of MTBE to soil and aquifer materials is very weak. Although there are several treatment technologies available to remove contaminants from drinking water, none of them have been studied thoroughly for the removal of MTBE.

Groundwater sources of MTBE can come from leaky underground storage tanks (LUST), spills and pipelines leaks. Reservoir sources of MTBE include movement from these sources, air deposition, and unburned and bypassed fuel from motor craft used at the reservoirs. In Southern California, MTBE levels as high as 610 ppb were found in groundwater of the City of Santa Monica. The contamination has resulted in the shut down of drinking water wells in Santa Monica. A concentration of approximately 25 ppb was encountered in Lake Perris (near the surface) which is the raw water source of the Metropolitan Water District (MWD) of Southern California. Tardiff (1996) indicated that people are being exposed to an excess of 100 ppb of MTBE in tap water in some locations because it is present and not being removed by present drinking water processes. State guidelines have established action levels (40-240 ppb) and clean-up levels (12-700 ppb) (Zogorski et al., 1996). The U.S. Environmental Protection Agency (USEPA, 1996) draft drinking water health advisory for MTBE is 70 ppb. According to Dale et al. (1997), the odor threshold number has been determined to be 25 and 70 ppb for flavor and odor at 25 degree C. The odor of MTBE at less than 190 ppb is described as "sweet solvent" by a flavor profile analysis panel (Dale et al., 1997). The California Department of Health Services (CAL-DHS) has set an action level of 35 ppb. Recently, CAL-DHS is considering a primary drinking water standard of 14 ppb. A secondary drinking water standard, which will be set based on taste and odor threshold levels of 5 ppb, has also been proposed by CAL-DHS.

The overall objective of this study is to determine the cost and effectiveness of sorption process for removing MTBE in drinking water to taste and odor threshold levels (< 5 ppb) alone and after advanced oxidation method. Various traditional and non-traditional sorbents, such as granular activated carbons (GACs), XAD resins, and greensand were investigated by bench scale isotherm studies. An initial MTBE concentration of 1,000 ppb was used. The effects of background humic substances in natural water from background Santa Monica well water and the major oxidation by-product, tertiary butyl alcohol (TBA), on the sorption of MTBE were also studied. Cost evaluation of the test results was addressed during the evaluation of this research project. The results from this study can be used to compare with the cost and effectiveness of other

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treatment alternatives, such as air stripping, advance oxidation processes, biofiltration, and hydrophobic membrane, in order to select the most appropriate alternative treatment method(s).

2. BACKGROUND

Two of the most traditional unit operations used at water treatment plants include coagulation with alum or ferric chloride and chlorination. These processes will not be sufficient to remove MTBE. There are several water treatment technologies that can be used for removing MTBE from water.

2.1 Air Stripping

Air stripping can remove more than 99% of MTBE and trichloroethene (TCE) from groundwater (Montgomery Watson, 1996). However, air stripping of MTBE is much less efficient than TCE air stripping. Air stripping of MTBE requires high air to water ratios since the compound is very soluble in water and has low Henry's law constant. Therefore, the economic use of air stripping as a sole process for removing MTBE is questionable. In addition, the process produces contaminated effluent air that may require further treatment.

2.2 Advanced Oxidation Processes (AOP)

During AOPs, ozone (O_3), UV light, hydrogen peroxide (H_2O_2), metal oxides such as titanium dioxide (TiO_2) and Fenton's reagent (iron sulfate and H_2O_2 in an aqueous solution at $pH = 2.5$), and ultrasonic cavitation, or combination of these have been used to react with water to produce hydroxyl radical (OH^*). MTBE would react with hydroxyl radical and form formaldehyde and tertiary butyl alcohol. Karpel Vel Leitner et al. (1994) indicated that effective removal of MTBE (> 80%) from water can be achieved using peroxone (ozone/peroxide) oxidation. The MWD of Southern California plans to implement preoxidation with ozone and peroxone at their Mills Filtration Plant by 2001 and at the Jensen Filtration Plant in 2003. Most recently, MWD has applied a variety of OH^* oxidation processes for water disinfection and taste and odor control of geosmin and methyl isoborneol (MWD, 1991). Liang et al. (1998) have just completed an initial pilot plant study of ozonation and peroxone treatment of MTBE at their ozonation pilot facility under conditions similar to optimum for taste and odor control at an ozone/peroxide ratio of 0.33. Subsequent studies are in progress.

The MWD study evaluated individual parameters of spike level, ozone dose, ozone/peroxide ratio of 0 and 0.33, pH and water quality type. The MWD pilot plant results for two MTBE concentrations (18 to 76 ppb) indicated that peroxone with 4 ppm of ozone and 1.3 ppm of hydrogen peroxide at pH 8.3 could obtain about 80% removal for the State Project and Colorado River waters. Bromate is a by-product of this process. Bromate levels exceeded the 10 ppb maximum contaminant level (MCL) (8 to 141 ppb). At pH 6.5, 20% less removal of MTBE occurred but bromate levels still exceeded the MCL (14 to 96 ppb). Ozonation alone was also effective at longer detention times (Liang et al., 1998). However, bromate concentrations are a critical problem at these doses of ozone and peroxide. Subsequent studies that are in progress indicate that the bromate problem may be solved (Liang, 1998). Thus, AOPs are a viable option with polishing of any MTBE remaining by GAC. GAC will also remove any biodegradable

organic carbon that is produced and also must be removed before drinking water is distributed to prevent the regrowth of bacteria in the water distribution system.

2.3 Membrane processes

MTBE removal by membrane processes has not been widely studied. Nanofiltration (NF) and reverse osmosis (RO) have the potential to remove MTBE from water. The use of membrane processes, especially RO, in general water treatment applications is not cost effective unless other treatment requirements are included.

2.4 Biological treatment

It has been known that MTBE is very resistant to both aerobic and anaerobic biodegradation. Recently, Salanitro et al. (1994) found that MTBE can be degraded both aerobically and anaerobically but only at very high concentrations (~100,000 $\mu\text{g/L}$). In addition, the biodegradation could be achieved by certain species when there were no other easily biodegraded substrates present. These limitations indicate that the biological treatment for removing MTBE from drinking water is not practical since the biodegradation can occur only under highly controlled conditions. In situ bio-oxidation of high levels of MTBE in groundwater sources may be helpful for source water control.

2.5 Sorption

Granular activated carbon (GAC) and powder activated carbon (PAC) have been widely used for control of taste and odor in drinking water (Graese et al. 1987, Lalezary-Craig et al. 1988, Pirbazari et al. 1993). The application of PAC is more flexible and requires less capital costs than those of GAC. However, for a long period of activated carbon application (due to consistent contamination problem), it may be more economical to use GAC (Fiessinger and Richard 1975). A well designed and maintained GAC column can be operated efficiently for several years to remove low to moderate concentrations of contaminant(s) (Graese et al. 1987).

Granular activated carbon (GAC) can be used to remove MTBE drinking water. Montgomery Watson (1996) reported that using activated carbon (type not specified) to remove MTBE is about 21 times more expensive than using activated carbon to remove the same mass of TCE from water. This conclusion is based on a carbon use rate of 4.20 lbs/1000 gallons of water with an initial MTBE concentration of 1,000 $\mu\text{g/L}$. Calgon (1998) found that using a coconut based granular activated carbon (GRC-22), the carbon use rate can be reduced to 0.82 lbs/1000 gallons of water with an initial MTBE concentration of 1,000 $\mu\text{g/L}$ (Table 1 and Figure 1). Calgon (1998) also conducted the isotherm experiments on two bituminous based activated carbons (F-400-HO and F-400) with the same conditions as for the experiment on the coconut based activated carbon. The results, shown in Tables 2 and 3, and Figures 2 and 3, indicate the carbon use rates for treating 1000 ppb MTBE in water of the F-400-HO and F-400 activated carbons are

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2.4 and 3.3 times higher than that of the GRC-22 carbon. This suggests that the type of sorbent used can affect the cost for removing MTBE from drinking water.

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Table 1-Results on adsorption isotherm study using coconut based activated carbon (GRC-22).

Parameters	Carbon (g)	Remaining MTBE		mg Adsorbed (mg)	Loading (mg/g)
		(mg/L)	(mg)		
Carbon Type: GRC-22	Control	1.0300	0.5150	-	-
Sample Volume: 500 mL	0.025	0.6390	0.3195	0.1955	7.82
Agitation Time: 24 hours	0.05	0.3910	0.1955	0.3195	6.39
Temperature: Ambient	0.10	0.2300	0.1150	0.4000	4.00
pH: 6.5	0.25	0.0805	0.0403	0.4748	1.90
Sample Point: Spiked	0.50	0.0259	0.0130	0.5021	1.00
Concentration: 1.03 mg/L	1.0	0.0122	0.0061	0.5089	0.51
	2.5	0.0035	0.0017	0.5132	0.21
	5.0	0.0012	0.0006	0.5144	0.10
	10.0	0.0005	0.0003	0.5148	0.05

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Table 2-Results on adsorption isotherm study using bituminous based activated carbon (F-400-HO).

Parameters	Carbon (g)	Remaining MTBE		mg Adsorbed (mg)	Loading (mg/g)
		(mg/L)	(mg)		
Carbon Type: F-400-HO	Control	1.0300	0.5150	-	-
Sample Volume: 500 mL	0.025	0.8220	0.4110	0.1040	4.16
Agitation Time: 24 hours	0.05	0.6810	0.3405	0.1745	3.49
Temperature: Ambient	0.10	0.4010	0.2005	0.3145	3.15
pH: 6.5	0.25	0.1540	0.0770	0.4380	1.75
Sample Point: Spiked	0.50	0.0567	0.0284	0.4867	0.97
Concentration: 1.03 mg/L	1.0	0.0236	0.0118	0.5032	0.50
	2.5	0.0055	0.0028	0.5123	0.20
	5.0	0.0009	0.0005	0.5146	0.10
	10.0	0.0009	0.0005	0.5146	0.05

Table 3-Results on adsorption isotherm study using bituminous based activated carbon (F-400).

Parameters	Carbon (g)	Remaining MTBE		mg Adsorbed (mg)	Loading (mg/g)
		(mg/L)	(mg)		
Carbon Type: F-400	Control	1.0300	0.5150	-	-
Sample Volume: 500 mL	0.025	0.8900	0.4450	0.0700	2.80
Agitation Time: 24 hours	0.05	0.8380	0.4190	0.0960	1.92
Temperature: Ambient	0.10	0.5110	0.2555	0.2595	2.60
pH: 6.5	0.25	0.2560	0.1280	0.3870	1.55
Sample Point: Spiked	0.50	0.1340	0.0670	0.4480	0.90
Concentration: 1.03 mg/L	1.0	0.0519	0.0260	0.4891	0.49
	2.5	0.0147	0.0074	0.5077	0.20
	5.0	0.0039	0.0020	0.5131	0.10
	10.0	0.0009	0.0005	0.5146	0.05

3. METHODOLOGY

3.1 Materials

3.1.1 Sorbents.

Eight GACs produced from five different raw materials were tested in this study. The details and properties of each GAC are listed in Table 4. To accelerate the adsorption kinetics (time to reach equilibrium), the GACs used in this study were pulverized so that 95% passed a 325 mesh screen (US standard). Zogorsky (1975) and Najm et al. (1990) reported that the adsorption capacity of GAC is not affected by particle size.

Three commercial resins, XAD-4, XAD-8 (Alltech Associates Inc., Deerfield, Illinois), and XE-572 (Supelco Inc., Bellefonte, Pennsylvania) were also experimented. XAD-4 and XAD-8 resins were pretreated to remove residual organics according to the method described in Thurman and Malcolm (1981). In addition, manganese treated and non-manganese treated greensands (Hungerford & Terry, Inc., Clayton, New Jersey) are the two non-traditional sorbents used in this study.

3.1.2 Chemicals.

MTBE (99.6 to 99.8% purity) was purchased from Chem Service Inc., Westchester, Pennsylvania. TBA (99% purity) was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.

3.1.3 Water.

Organic pure water was produced by glass-distilling purified water from a Milli-Q water purification system and passing through a granular activated carbon (F-200, Calgon Carbon Corp., Pittsburgh, Pennsylvania). Water with humic substances (background natural organic matter) was collected from one of the City of Santa Monica water wells that have been shut down due to the contamination of MTBE. Total organic carbon (TOC) and pH of the water are 0.5 ppm and 6.5, respectively. MTBE concentration in the water is below the detection limit of 5 ppb.

3.2 Experimental Design

The experimental design is shown in Table 5. In experiment set no. 1 (only MTBE), all of the sorbents were tested. Based on the results of previous experiment sets, only effective sorbents were tested in experiment set nos. 2, 3, and 4.

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Table 4-Details and properties of GACs.

GAC	Raw Material	Code name used in the experiment	Properties				Manufacturer
			Apparent Density (g/cm ³)	Iodine no. (mg/g)	Tannin no. (g/100 g)	Ash (%)	
F-200	Bituminous coal	Bitu. I	0.55	938	154	5.0	Calgon
Centaur	Bituminous coal	Bitu. II	0.56	800	-	-	Calgon
Norit HD 3000	Lignite	Lignite	0.43	566	259	26.9	Norit
Picabiol	Wood	Wood	0.25	894	182	7.3	Pica, France
Norit Row 0.8S	Peat	Peat	0.39	859	211	5.6	Norit
GRC-22	Coconut	Coconut	-	-	-	-	Calgon
SA-30	Wood	SA-30	0.30	950	-	10	Carbochem
CA-10	Wood	CA-10	0.30	1,000	-	6	Carbochem

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Table 5-Experimental design for isotherm studies.

Sorbent (code name)	Set no. 1	Set no. 2	Set no. 3	Set no. 4
	MTBE (1,000 ppb) in organic pure water	MTBE (1,000 ppb) in Santa Monica water	MTBE (1,000 ppb) + TBA (100 ppb) in organic pure water	MTBE (1,000 ppb) + TBA (100 ppb) in Santa Monica Water
<u>GACs</u>				
Bitu. I	X			
Bitu. II	X			
Lignite	X			
Wood	X			
Peat	X			
Coconut	X	X	X	X
SA-30	X	X	X	
CA-10	X	X		
<u>Resins</u>				
XAD-4	X			
XAD-8	X			
XE-572	X	X	X	X
<u>Greensand</u>				
Treated	X			
Untreated	X			

X = Conducted

3.3 Sample Preparation

For each sorbent tested in the experiment set no. 1 (except for XAD-4 and XAD-8 resins), ten-point isotherm was conducted as described in Table 1 in the background section. A control sample with the same MTBE concentration but without sorbent was also included in each set. Another set of three 1-liter samples with the sorbent dose of 0.025 g was prepared to determine the time to equilibrium. Sorbent dosing was achieved by accurately weighing the desired amounts, then adding directly to the 1-liter amber bottles which were previously filled with 1 liter of water samples. Each sample was hand-shaken until the sorbent was uniformly mixed in water; then 0.1 mL of a stock solution of 10,000 ppm MTBE was added into each bottle to achieve a concentration of 1,000 ppb. For experiment set nos. 3 and 4, 0.1 mL of a stock solution of 1,000 ppm TBA was added into each bottle after the addition of MTBE to achieve a concentration of 100 ppb.

After adding sorbent and spiking MTBE (and TBA for experiment set nos. 3 and 4), the sample bottles were tightly capped, sealed with Teflon tape, and shaken on shakers at a speed of

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approximately 300 rpm. Complete mixing during shaking was insured since there was a headspace of approximately 30 to 50 ml left in each bottle (after adding water sample, sorbent, and MTBE). Control samples were experimented the same way. It was found that there was no significant difference between the initial and final MTBE concentrations (less than 0.5% after the equilibrium was reached). For equilibrium time determination, the equilibrium set of samples was removed from the shaker after 24, 48, and 72, hours, respectively, then 20 mL of each sample were syringe-filtered with 0.7 μm glass fiber filters (Whatman, GF/F) to remove the sorbent. Each sample was either analyzed immediately for MTBE or stored at 4°C in the dark for no longer than 24 hours. Every experiment reached equilibrium within 24 hours; there was no significant difference in MTBE concentration between the equilibrium sample taken after 24 and 48 hours. The isotherm set of samples was removed from the shaker after either 48 or 72 hours. These samples were processed following the same procedure as described above for the equilibrium set. The temperature during the experiment was controlled between 22.5 and 23.0 degree C. The pH during the experiments was also maintained between 6.8 and 7.0 by adding phosphate buffers to a concentration of 0.02 M in each bottle before dosing the sorbent.

For the other experiment sets and XAD-4 and XAD-8 experiments in the experiment set no. 1, the sample preparation procedure is the same as described above except that the data point on the isotherm was reduced to 4 or more points. Also, the weight of XAD-4 and XAD-8 resins used in each bottle was determined by vacuum filtering the total volume of the sample after the experiment and drying at 103 degree C. This is because the resins must be stored under water or a solvent and cannot be dried before use.

3.4 Analytical Methods

MTBE was analyzed according to the EPA Method 524 using a purge and trap unit (LSC-2, Tekmar) followed by a gas chromatograph with flame ionization detector (GC-FID, Hewlette-Packard model 5710). The detection limit was 5 ppb for a sample size of 5 mL. The calibrations were performed for three ranges of MTBE concentration: 5 to 20 ppb, 20 to 100 ppb, and 100 to 2,000 ppb. The coefficient of linear correlation (r) of all three ranges was greater than 0.998. TBA was not analyzed. TOC was analyzed was measured with a Dohrmann Total Organic Carbon Analyzer model DC-80 (Xertex Corporation, Santa Clara, CA) using ultraviolet promoted persulfate oxidation and infrared spectrometry. The analyzer was calibrated daily using 10 mg TOC /L potassium hydrogen phthalate (KHP) standard solution and the multiple point calibration procedure recommended by the manufacturer. The analyzer has a useful range of 0.10 to 20.00 mg/L (limit of quantitation to limit of linearity) and a detection limit of 0.04 mg/L for a sample size of 1 mL. The mean value of three DOC measurements was reported. pH was measured using Orion pH meter model 925.

4. RESULTS AND DISCUSSION

The isotherm data obtained from the experiments were log-transformed to determine the fit between the data and the Freundlich model:

$$Q_e = K_F C_e^{1/n} \quad (1), \text{ or}$$

$$\text{Log } Q_e = \text{Log } K_F + 1/n(\text{Log } C_e) \quad (2)$$

Where Q_e = the equilibrium adsorption capacity (mass of MTBE/mass of sorbent)

K_F = the Freundlich coefficient

$1/n$ = the exponent (constant)

C_e = the equilibrium concentration (mass of MTBE/volume of water).

4.1 Effectiveness of Sorbents in Removing MTBE from Organic Pure Water (described as DI water in Figures in this report)

Figure 4 shows the results of linear regressions of the isotherm data after the log-transformation for all 13 sorbents used in experiment set no. 1 (MTBE in organic pure water). It should be noted that the two points at the two ends of each line are not the data points. The results show that the coconut activated carbon had the highest equilibrium adsorption capacity for MTBE, followed by SA-30, CA-10 activated carbons (both wood based), and XE-572 resin, respectively. The data for these four sorbents also agree with the Freundlich model ($r^2 > 0.95$, data not shown). The regression for the SA-30 activated carbon suggests the carbon is likely to have a better equilibrium adsorption capacity when dealing with an initial MTBE concentration of approximately 350 ppb or higher). The results for rest of the sorbents not only indicate lower equilibrium adsorption capacity but also do not agree strongly with the Freundlich model ($r^2 > 0.17$ to 0.90 , data not shown). Both greensands had very low equilibrium adsorption capacity and their adsorption behaviors could not be described by the Freundlich model ($r^2 > 0.17$ to 0.20 , data not shown). Consequently, it was decided to further investigate only the four effective sorbents (coconut, SA-30, CA-10, and XE-572) in experimental set no. 2 (MTBE in Santa Monica water).

4.2 Effectiveness of Sorbents in Removing MTBE from Santa Monica Water (SMW)

The results of linear regressions of the isotherm data after the log-transformation for 4 sorbents used in experiment set no. 2 are illustrated in Figure 5. The regression lines in Figure 5 clearly indicate that the SA-30 and CA-10 activated carbons were not as effective as the other two sorbents (coconut and XE-572) when there was a competition from humic substances (0.50 ppm as TOC). The interception between the regression lines for the XE-572 resin and coconut activated carbon at an equilibrium concentration of approximately 100 ppb, suggests that the coconut activated carbon is more effective than the XE-572 resin when the initial concentration of MTBE is greater than 100 ppb and humic substances (TOC of 0.5 ppm or higher) are present in the water.

Figures 6 to 9 show the effect of background humic substances in Santa Monica water on the equilibrium adsorption capacity of the four sorbents. Figures 6 to 9 indicate that the equilibrium adsorption capacity of the coconut, SA-30, and CA-10 activated carbons decreased between 0.30

and 0.80 micrograms/g of carbon when there was a competition from humic substances. As shown in Figure 9, the equilibrium adsorption capacity of the XE-572 resin was not affected by the competition from humic substances. The results in Figure 9 also agree the above discussion on Figure 5 that XE-572 is better than the coconut activated carbon for use in removing MTBE from natural waters containing humics when the concentration of MTBE is 100 ppb or lower. This may be because the XE-572 resin is the least hydrophobic among the XE series resins. Since the CA-10 activated carbon did not demonstrate any merits compared to the other three sorbents, the investigation on the CA-10 activated carbon was discontinued. It should be remembered that the SA-30 activated carbon should be further investigated because the carbon tended to be more effective than the coconut carbon at an equilibrium concentration of 350 ppb or higher.

4.3 Efficiency of Sorbents in Removing MTBE from Organic Pure Water Containing TBA

Figure 10 illustrates a comparison of the performances of the coconut and SA-30 activated carbons, and XE-572 resin in removing MTBE from organic pure water when TBA was present at 100 ppb. For this case, the coconut activated carbon had the highest equilibrium adsorption, followed by the XE-572 resin and the SA-30 activated carbon.

Figures 11 to 13 are a similar type of plots as Figures 6, 7, and 9 except that they show how the equilibrium adsorption capacity was affected from the competition from TBA instead of from humics. The results are also very similar; the adsorption capacity of XE-572 was not affected by the competition from TBA while those of the other sorbents decreased when TBA was present. It is also learned from Figures 10 and 11 that although the competition from TBA reduced the equilibrium adsorption capacity of the coconut carbon, the competition effect was not severe and the coconut carbon was still the best sorbent for this case.

4.4 Effectiveness of Sorbents in Removing MTBE from Santa Monica Water Containing TBA

The competition effect of TBA in Santa Monica water on the equilibrium adsorption capacity of the coconut activated carbon and the XE-572 resin is shown in Figures 14 and 15. The SA-30 activated carbon was not studied because the results should be similar to those of the coconut carbon. As expected, there was an additional decrease in the equilibrium adsorption capacity (over the decrease due to humics) of the coconut carbon while the presence of TBA had no effect on the equilibrium adsorption capacity of the XE-572 resin. It should be noted that the higher equilibrium adsorption capacity of the XE-572 resin observed when TBA was present is within the experimental error.

Figure 16, which is a combination of Figure 11 and 14, shows that the presence of humic substances in water had more competition effect than the presence of TBA since the equilibrium adsorption capacity in the presence of TBA in organic pure water was higher than that in the presence of humics. The adsorption capacity for four different cases (four experiment sets) is ranked as: MTBE in organic pure water > MTBE + TBA in organic pure water > MTBE in Santa Monica water > MTBE + TBA in Santa Monica water. Figure 17, which is combination of

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Figure 13 and 15, illustrates that the performance of the XE-572 resin in removing MTBE remained the same even when both humics and TBA were present.

4.5 Cost Analysis for the Use of Sorption in Removing MTBE from Water

Based on the above results and discussion, it is clear that the coconut and SA-30 activated carbons and the XE-572 resin are the three sorbents that should be considered for the removal of MTBE from water. However, it is very difficult to decide which sorbent is the best since none of them performed better than the other two under every condition. Cost of these sorbents should also be considered. The cost analysis was performed according to the information on the costs of sorbents provided by the manufacturers and the carbon use rates which were calculated based on the regression equations of the lines on some of the previously shown Figures. Three assumptions were made:

- 1) The sorbents cannot be regenerated,
- 2) The capital cost (such as construction cost) is neglected, and
- 3) There is no additional cost associated with the replacement of sorbent.

Three different scenarios were considered: a) sorption as a sole process, b) sorption as a polishing process for advanced oxidation process, and c) sorption as a polishing process for air stripping. For sorption as a sole process, the results from experiment set no. 2 (MTBE in Santa Monica water) were used and three different MTBE concentrations were considered: 100 ppb, 500 ppb, and 1,000 ppb. For sorption as a polishing process for advanced oxidation process, the results from experiment set no. 4 (MTBE + TBA in Santa Monica water) were used and two residual MTBE concentrations were considered: 20 ppb and 100 ppb. For the last scenario, sorption as a polishing process for air stripping, the results from experiment set no. 2 (MTBE in Santa Monica water) were used and an MTBE concentration of 20 ppb was considered.

Table 6 shows the results for the cost evaluation of the effective sorbents for different cases. Even the adsorption capacity of the XE-572 resin is not affected by the competitors from TBA and humics, the cost for the use in removing MTBE from water is approximately 90 to 1,000 times more expensive than the cost associated with the other two activated carbons. Between the two carbons, when using sorption as a sole process, the cost for using coconut carbon to remove MTBE from water is less than the cost associated with the SA-30 carbon for all three concentrations. For the case that considers sorption as a polishing process for air stripping, the cost when using the SA-30 carbon is less expensive than the cost when using the coconut carbon. Further mathematical analysis shows that the coconut carbon is best sorbent when the concentration of MTBE is approximately 80 ppb or higher and the SA-10 wood based carbon is best sorbent when the concentration of MTBE is lower than approximately 80 ppb.

5. CONCLUSIONS AND RECOMMENDATIONS

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Isotherm study on thirteen sorbents for the removal of MTBE from water was conducted. These sorbents included 8 types of activated carbon, 3 types of resin, and 2 types of greensand. In the first set of isotherm experiments, all 13 sorbents were tested with 1000 ppb MTBE in organic pure water. Based on the results from this experiment, four sorbents, the coconut, CA-10 (wood based), and SA-10 (wood based) activated carbons and the XE-572 resin, were found to be more effective than the other sorbents in removing MTBE from water. The two types of greensand had very low equilibrium adsorption capacity.

In the second series of experiment, the four effective sorbents were experimented with 1000 ppb MTBE in Santa Monica well water which contained a small amount of humic substances of 0.50 ppm as TOC. The performances of all three activated carbons decreased due to the competition adsorption from background humic substances. The equilibrium adsorption capacity of the XE-572 resin was not affected by the competition from humic substances.

Table 6-Cost evaluation of the effective sorbents for different cases.

Sorbent (code name)	Theoretical sorbent use rate (lb/1000 gals)	Price of sorbent (\$/lb)	Cost for treating 1,000 gallons of contaminated water (\$)
<u>Case 1: Sorption as a sole process</u>			
1.1) 100 ppb MTBE			
Coconut carbon	0.21	1.25	0.26
SA-30 carbon	0.46	0.65	0.30
XE-572 resin	0.19	379.46	72.10
1.2) 500 ppb MTBE			
Coconut carbon	0.13	1.25	0.16
SA-30 carbon	0.64	0.65	0.42
XE-572 resin	0.28	379.46	106.25
1.3) 1,000 ppb MTBE			
Coconut carbon	0.11	1.25	0.14
SA-30 carbon	0.74	0.65	0.48
XE-572 resin	0.33	379.46	125.22
<u>Case 2: Sorption as a polishing process for advanced oxidation process</u>			
2.1) 20 ppb MTBE			
Coconut carbon	0.25	1.25	0.31
XE-572 resin	0.08	379.46	30.36
2.2) 100 ppb MTBE			
Coconut carbon	0.40	1.25	0.50
XE-572 resin	0.14	379.46	53.12

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<u>Case 3: Sorption as a polishing process for air stripping process (20 ppb MTBE)</u>			
Coconut carbon	0.34	1.25	0.43
SA-30 carbon	0.32	0.65	0.21
XE-572 resin	0.13	379.46	49.33

In the third set of experiments, the CA-10 activated carbon was eliminated from the test since it provided the lowest adsorption capacity and was affected by the competition from humic substances. The other three sorbents were studied on the effect of the competition from a major advanced oxidation by-product of MTBE: TBA. TBA was spiked into organic pure water to achieve a concentration of 100 ppb along with 1,000 ppb of MTBE. In the presence of 100 ppb TBA, the performance of the XE-572 resin in removing MTBE remained the same while a decrease in the performances of the other two sorbents was observed. Even with the decrease in the equilibrium adsorption capacity in the presence of 100 ppb TBA, the coconut carbon still had higher equilibrium adsorption capacity than the XE-572 resin.

Only the coconut activated carbon and the XE-572 resin were tested on the effect of simultaneous competitions from humics and 100 ppb TBA. The MTBE adsorption capacity of XE-572 remained the same even when both humics and TBA were present. The coconut carbon had the lowest adsorption capacity among the four cases when both humics and TBA were present.

Based on the results from the cost evaluation, there are four recommendations regarding the use of sorption for removing MTBE from water:

- 1) If only MTBE removal is considered, sorption should not be used as a polishing process for advanced oxidation process(es) since the cost associated with the sorption as a polishing process is more expensive than the cost of using sorption as a sole process. Other reasons such as disinfection and taste and odor removal of geosmin or methylisoborneol must be considered by a water utility and may make AOP/GAC viable.
- 2) Although the adsorption capacity of XE-572 resin was not affected by the competition from both humics and TBA, it is not economical to use the resin for removing MTBE from water since the cost of the resin is prohibitively expensive at present.
- 3) The coconut activated carbon should be used when the concentration of MTBE is 80 ppb or higher.
- 4) The SA-30 wood based activated carbon should be used when the concentration of MTBE is lower than 80 ppb.

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Also, it is recommended that, the two most cost-effective sorbents, the coconut and SA-30 activated carbons, should be studied using a laboratory scale rapid small-scale column test (RSSCT) at two different feed conditions as for experiment set nos. 2 and 4 in the isotherm study. The RSSCT system consists of an MTBE feed tank, a liquid chromatograph (LC), and a purge/trap gas chromatograph (GC). The MTBE feed water is transported by the LC pump through the LC column (packed with sorbent of interest). The product water is either manually or automatically injected into the purge/trap GC for the analysis of MTBE. The RSSCT can simulate the full-scale granular activated carbon column performance and the RSSCT results can be used to scale up the columns as well as to verify the findings of the isotherm study.

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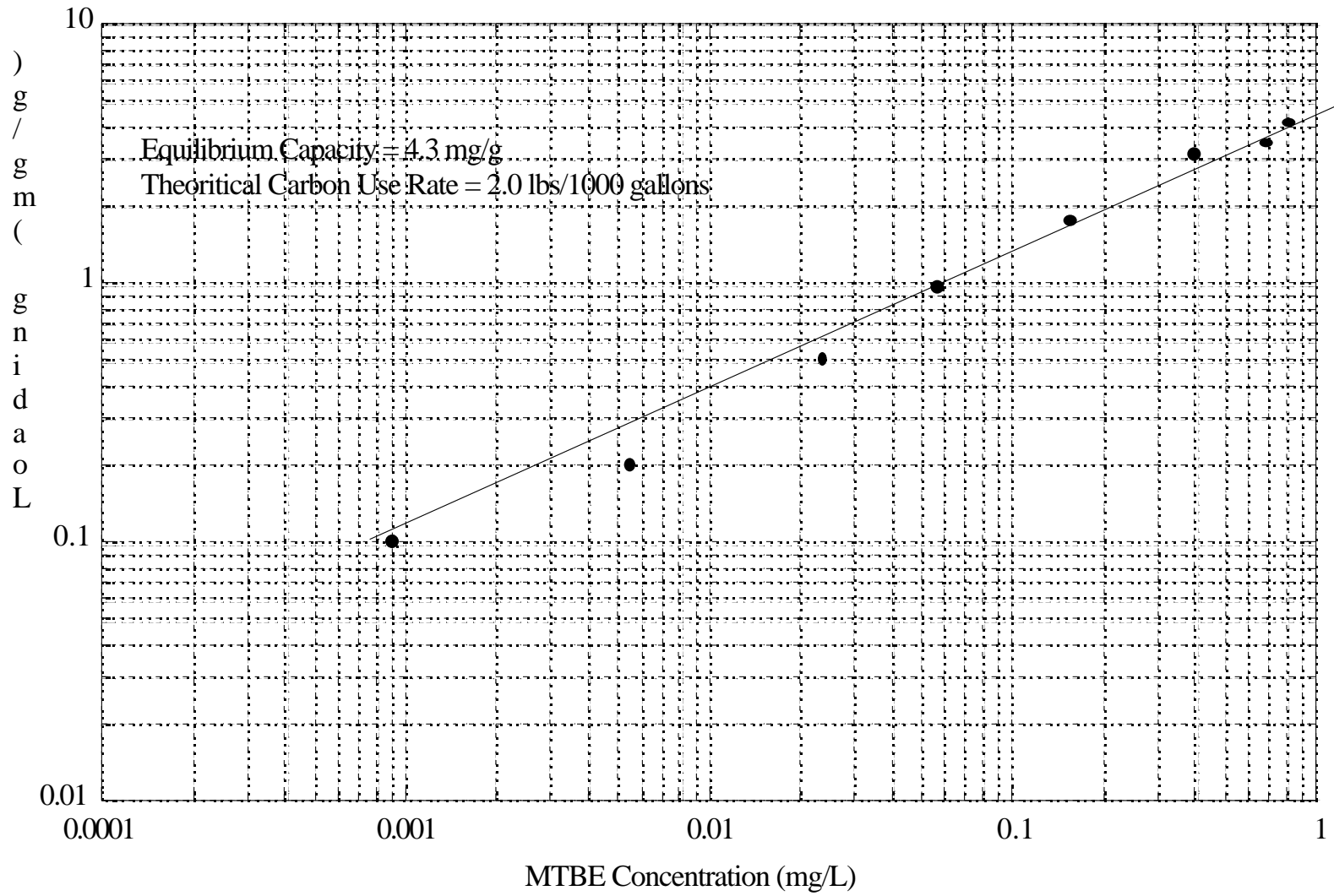


Figure 2-The fit of Freundlich model on the isotherm data when using bituminous based activated carbon (F-400-HO).

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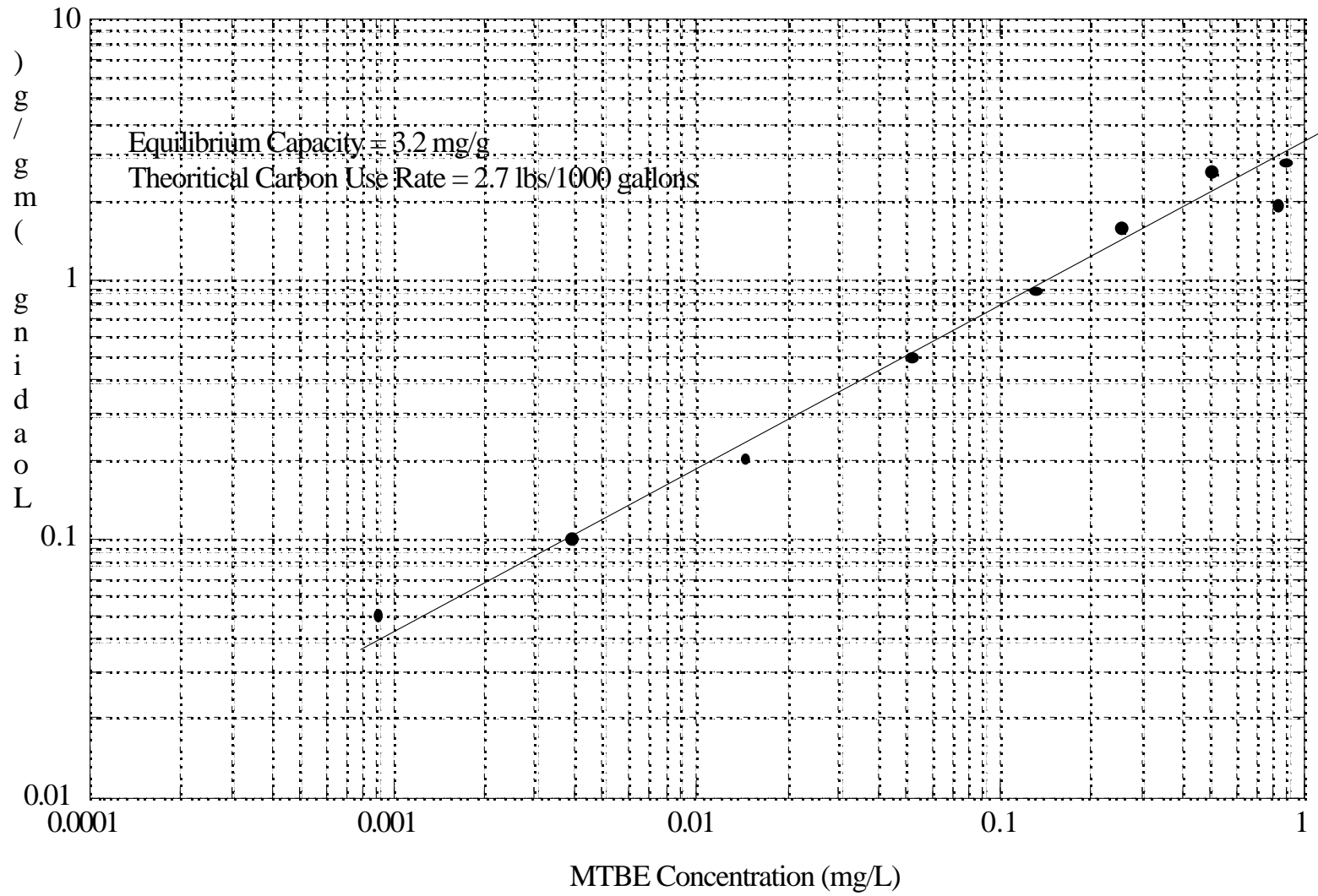


Figure 3-The fit of Freundlich model on the isotherm data when using bituminous based activated carbon (F-400).

Captions for Figures

Figure 1-The fit of Freundlich model on the isotherm data when using coconut based activated carbon (GRC-22).

Figure 2-The fit of Freundlich model on the isotherm data when using bituminous based activated carbon (F-400-HO).

Figure 3-The fit of Freundlich model on the isotherm data when using bituminous based activated carbon (F-400).

Figure 4-Linear regressions of the isotherm data after the log-transformation for sorbents used in experiment set no. 1.

Figure 5-Linear regressions of the isotherm data after the log-transformation for sorbents used in experiment set no. 2.

Figure 6-Effect of background humic substances in Santa Monica water on the adsorption capacity of coconut carbon.

Figure 7-Effect of background humic substances in Santa Monica water on the adsorption capacity of SA-30 carbon.

Figure 8-Effect of background humic substances in Santa Monica water on the adsorption capacity of CA-10 carbon.

Figure 9-Effect of background humic substances in Santa Monica water on the adsorption capacity of XE-572 resin.

Figure 10-Linear regressions of the isotherm data after the log-transformation for sorbents used in experiment set no. 3.

Figure 11-Effect of TBA on the equilibrium adsorption capacity of coconut carbon.

Figure 12-Effect of TBA on the equilibrium adsorption capacity of SA-30 carbon.

Figure 13-Effect of TBA on the equilibrium adsorption capacity of XE-572 resin.

Figure 14-Effect of TBA and background humic substances in Santa Monica water on the adsorption capacity of coconut.

Figure 15-Effect of TBA and background humic substances in Santa Monica water on the adsorption capacity of XE-572 resin.

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Figure 16-Comparison of the adsorption capacity of coconut carbon for all four experiment sets.

Figure 17-Comparison of the adsorption capacity of XE-572 resin for all four experiment sets.