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BENCH-SCALE STUDY OF AQUEOUS MTBE DEGRADATION BY COMBINED ADVANCED OXIDATION AND BIOLOGICAL PROCESSES

by

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ABSTRACT

Bench-Scale Study of Aqueous MTBE Degradation by Combined Advanced Oxidation and Biological Processes

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The oxidation of methyl *tert*-butyl ether (MTBE) by advanced oxidation processes in conjunction with biological treatment is investigated. First, the degradation of MTBE by UV/H_2O_2 and UV/TiO_2 is studied. It is found that the optimum molar ratio of H_2O_2/MTBE is about 14 while the optimum concentration of TiO_2 is 1.5 g/L. In addition, it is observed that a combined process of UV/H_2O_2 and UV/TiO_2 does not have any advantages over each of these processes alone. In the second phase, biodegradability of MTBE by aerobic microorganisms is evaluated in three different approaches including BOD_U assessment, removal of MTBE by non-acclimated, and acclimated microorganisms. . It is shown that the acclimatization of microorganisms enhances the rate of biodegradation of MTBE. Finally, it is observed that the rate of bioreaction is not improved after a photochemical pre-treatment. It is also found that using the integration of photochemical and biological treatment reduces the total residence time.

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I would like to dedicate this thesis to my husband, Tondar, and my daughters, Taraneh and Bahar, for their patience and supports and rendering enjoyable my time during the accomplishment of this study.

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NOMENCLATURE

AC: Activated Carbon

AOP: Advanced Oxidation Process

a : Ratio of relative volumetric reactor cost of the AOP versus the biological process

BOD: Biological Oxygen Demand, mg/L

C: Concentration, mg/L

CB: conduction band

COD: Chemical Oxygen Demand, mg/L

DO: Dissolved Oxygen, mg/L

DOC: Dissolved Organic Carbon, mg C/L

e^-: electron

EPA: Environmental Protection Agency

GAC: Granular Activated Carbon

GC: Gas Chromatography

h : Planck's constant, 6.62×10^{-27} erg sec

h^+: hole

IDEA: Intermittently Decanted Extended Aeration

k: Kinetic constant

MLVSS: Mixed Liquor Volatile Suspended Solid, mg/L

NPDOC: Non-Purgeable Dissolved Organic Carbon

r: rate

R: molar ratio of H_2O_2 / MTBE

RE: Removal Efficiency

RFG: Reformulated Gasoline

S : substrate concentration, mass/ volume

SBR: Sequential Batch Reactor

T: TiO_2

t: residence time, min

TBA: *tert*-butyl alcohol

TBF: *tert*-butyl formate

TOC: Total Organic Carbon, mg C/L

TSS: Total Suspended Solid, mg/L

VB: valance band

X :concentration of microorganism, mass/volume

Y :maximum yield coefficient, mg/mg

Greek Letters

η : Efficiency

ν : frequency of UV radiation

μ : specific bacterial growth rate, $time^{-1}$

Subscripts

0: initial

B: biological reactor

C: chemical reactor

g: bacterial growth

m: maximum

S: substrate

t: residence time

T: *tert*-butyl formate

U: ultimate

CHAPTER 1

INTRODUCTION

Today one of the most important global issues is water because of its limited and valuable sources in the world. For many years, suspension materials were separated mechanically and dissolved pollutants were biologically treated. However, the global growth of the population, the rapid industrial development, and human activities over the last centuries have resulted in more environmental problems.

The most used treatment process for the removal of organic substances from water and wastewater is the biological oxidation. This old method of treatment is not able to satisfy the requirements of acceptable treated water and wastewater. The complexity and the development of industries in recent years have resulted in new pollutants in wastewater, which cannot be degraded easily by only biological treatment methods. These are effluents from different industries that are mostly toxic and not biodegradable. On the other hand, the cheapness and the availability of biological treatment are its main advantages.

Activated sludge is a widely accepted method of decreasing dissolved organic materials in wastewater when these substances are biodegradable. If they are resistant to biodegradation or the high reaction rate is a matter of importance, advanced oxidation or chemical processes are applied. Two important methods that are used for the removal of

contaminants are phase transfer and oxidation. Different methods of phase transfer are adsorption on granular activated carbon, extraction, and air stripping. These methods only lead pollutants from one phase to another, therefore, they are becoming unpopular. Advanced oxidation processes (AOPs) are suitable substitute for phase transfer methods for the removal of contaminants from wastewater, but compared with physical and biological treatments, these methods are expensive. Over the two past decades, the interest of exploitation of photooxidation processes for water and wastewater treatment has grown rapidly and chemical oxidation of dissolved pollutants is significantly being considered. In order to enhance the efficiency of the degradation of contaminants, many attempts have been performed to combine different advanced oxidation processes with biological treatment because integration of chemical and biological processes may result in a more cost-effective method of treatment. The application of both chemical and biological treatments needs optimization of the dose of chemicals as well as residence time in each process.

In this study, methyl *tert*-butyl ether (MTBE) was chosen as model compound since it has been used in gasoline increasingly and its application has raised many safety concerns. Low level of MTBE makes drinking water unusable because of its taste and odour. Available data support that MTBE is a potential human carcinogen at high doses (EPA, 2003). One of the goals of this study was to investigate the feasibility of photodegradation of MTBE by means of UV/H_2O_2, UV/TiO_2, and their combination along with the evaluation of the efficiency of each process. The optimum amount of H_2O_2 and TiO_2 was determined, the rate of MTBE decomposition was examined and rate

constants were estimated. Another objective was to assess the biodegradation of MTBE. First the toxicity of MTBE and its by-products of photooxidation were investigated. Then the biodegradation of MTBE was examined by three approaches, measurement of ultimate BOD for different concentrations of MTBE, degradation of MTBE by non-acclimated activated sludge, and the degradation of MTBE by acclimated activated sludge. In the next step, the effect of photocatalysis on the biodegradability of MTBE was studied. Finally, the retention time in each chemical and biological reactor in an integrated process was optimized and a cost-efficiency method of treatment was proposed.

CHAPTER 2

LITERATURE REVIEW

2.1. MTBE: History and its Effect On The Environment

Methyl tertiary butyl ether (MTBE) is a chemical compound, which is formed by reaction between methanol and isobutylene he presence of an acidic catalyst (Trotta and Miracca, 1997; Jacobs et al., 2001):

$$(CH_3)_2CCH_2 + CH_3OH \rightarrow CH_3OC(CH_3)_3 \qquad (2.1)$$

Since 1979, MTBE has replaced the lead to enhance octane number in gasoline. Additives (alcohols and ethers) enter more oxygen to gasoline, which increase the combustion efficiency (Uhler et al., 2001). For its oxygen content, MTBE can be added to gasoline up to 15% (v) to reduce the emission of CO in inter-combustion engines (Jacobs et al., 2001). In 1980's, the production of MTBE was increased in US and it was in the list of top 50 chemicals produced there (Uhler et al., 2001). Since 1992, MTBE was added to gasoline at higher concentrations to accomplish the oxygenate necessities, set by Congress in the 1990 Clean Air Amendments. MTBE production in the U.S.A. was over 200,000 barrels per day in 1999 (EPA, 2003). Its production is economical and easy. Without separating from gasoline, MTBE can be blend simply and transferred through existing pipelines, therefore, most of the refineries prefer MTBE because of its economic reasons (Squillace et al., 1997).

MTBE enters groundwater and soil by leaking aboveground and underground storage fuel tanks, pipelines, refuelling spills, automobile accidents damaging the fuel tank, disposal of old gasoline, marine engines, storm water runoff, and precipitation mixed with MTBE in the air. Its high solubility causes MTBE to transfer to water more than other gasoline compounds (EPA, 2003). In the early and mid 1990's, a low amount of MTBE was reported in groundwater (Uhler et al., 2001). U.S. Geological survey has announced that MTBE is the second detected chemical in shallow ambient groundwater (Squillace et al., 1997). Some events have increased concerns about the healthiness of MTBE. In 1996, Santa Monica city, U.S.A., shut down two wellfields supplying drinking water because of the contamination of MTBE at a level as high as 610 and 86 ppb (EPA, 2003). In 1992, EPA considered Draft Health Advisory for MTBE equal to 20-200 μg/L in drinking water, which was changed to 20-40 μg/L in 1997. In 1999, the amount of 13 μg/L as health advisory action level was confirmed by the state of California (Uhler et al., 2001).

There are many debates about MTBE. Some believe that MTBE has caused clean-burning fuels production and some suppose that MTBE results in diseases. The air quality office of U.S. EPA supported MTBE as an automobile emission reducing agent (Jacobs et al., 2001). The current data indicate a low level of MTBE and in limited number of detections, higher levels of contamination in surface and groundwater were observed. Almost 1% of detections are higher than 20 μg/L. Higher concentrations more than 20 μg/L of MTBE in water supply have been observed where reformulated gasoline (RFG)

is sold (EPA, 2003). The concentration of 200 mg/L MTBE in groundwater has been reported. In California, MTBE concentration of surface water, where recreational boats were working, was reported as 12 mg/L (Jacobs et al., 2001).

2.1.1. Properties of MTBE

Physical and chemical properties of MTBE are listed in Table 2.1.

Table 2.1. Physical and chemical properties of MTBE.

Molecular Weight	88.14 g/mol
Boiling Point	53.6°C
Vapor pressure	254 mm Hg @ 20°C
Freezing Point	-108.6°C
Density	0.741 g/ml @ 20°C
Solubility in Water	4.8% @ 20°C
Henry's law constant	5.87×10^{-4} atm-m^3/mole @ 25°C

MTBE is ether with structure formula of $CH_3OC(CH_3)_3$ (Figure 2.1). CH_3-O-C bond is the representative of ether molecule and CH_3-C-CH_3 bond is the propane. In standard pressure and temperature, MTBE is a colourless, flammable, and volatile liquid (Jacobs et al., 2000). Molecular weight of MTBE is 88.14 g/mol. Usually hydrocarbons with molecular weight of less than 150 g/mol are completely volatile and have low melting and boiling points with high vapour pressure. MTBE melts at –109°C and boils at 53.6-55.2°C. MTBE tends to move downwards because it is adsorbed by soil easily, so it

reaches to groundwater relatively quickly. MTBE solubility in water at standard pressure and temperature is 4.8%, which is relatively high (Jacobs et al, 2000). Henry's law defines the partitioning of a contaminant between aqueous and vapour phases. Henry's law constant for a compound is the ratio of partial pressure of compound in vapour phase to compound concentration in aqueous phase in a specific temperature. To estimate the tendency for volatility from water to air, the value of Henry's law constant is more suitable than either vapour pressure or water solubility. It has been shown that compounds with Henry's law constants equal or more than 5×10^{-2} atm-m^3/mole are very volatile from water and compounds with lower values tend to remain in aqueous phase or if the contaminated gas is in contact with water, they tend to transfer to aqueous phase (Sequillace et al., 1997). According to this classification, the Henry's law constant for MTBE shows that it would partition significantly with water.

Although MTBE is less toxic than other components of gasoline, its low amount in water produces odour and taste problems. Some studies on animal exposure have shown that MTBE is carcinogenic (An et al., 2002). Water contaminated with MTBE is not consumable by human beings because of its unpleasant odour and taste. Although MTBE is considered as a potential health risk, there are little evidence or no evidence that MTBE causes cancer in human. Fortunately taste and odour of MTBE in water at low levels are detectable by human (Jacobs et al., 2001).

Since MTBE dissolves easily in water and does not cling to soil, its movement in the ground is faster and farther than other components of gasoline and, therefore, more likely

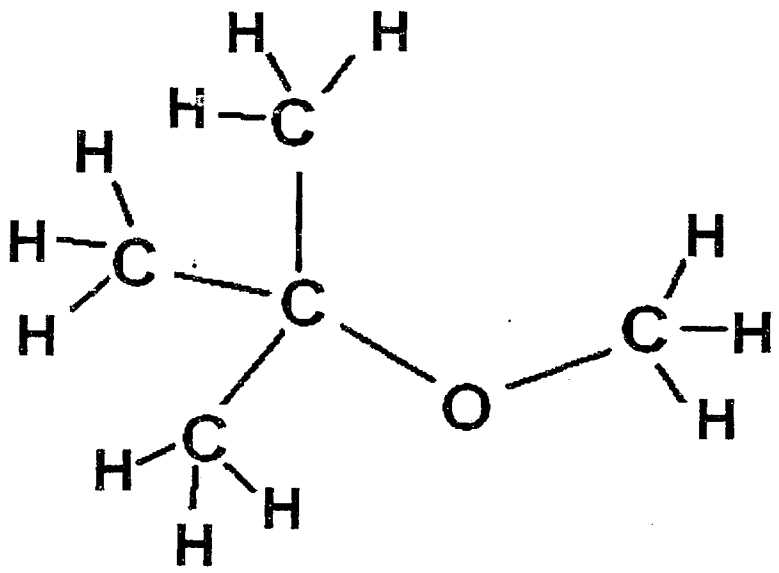

Figure 2.1. Molecular structure of MTBE.

to contaminate drinking water (EPA, 2003).

Degradation of a compound in groundwater is its natural tendency to decrease its concentration during the time by chemical processes. These processes include either live organism activity like bacteria or non-biological processes. Because of its chemical and physical characteristics, removal of MTBE from groundwater is expensive, time-consuming, and difficult (Jacobs et al., 2001). Ethers are compounds that are known resistant to biodegradation based on the presence of their ether bond (Fayolle et al., 2003). The presence of t-butyl group in its molecular structure makes MTBE to be more defiant to natural biodegradation than other components of gasoline. Two bio-recalcitrant functional groups in MTBE structure, ether link and branched structure, make MTBE resistant to biodegradation and have a low biomass yield (Fortin et al., 2001). Some authors classified MTBE as a recalcitrant compound, which is probably the result of special behaviour of carbon atom or/and ether structure (Jacobs et al., 2001).

Removal of MTBE from groundwater is very difficult because of its relatively high solubility and its resistance to biodegradation. Air stripping is a process in which contaminated water passes through a packed column and upward flowing air removes the chemical compounds. Oxygen atom in the molecular structure of MTBE provides hydrogen bonding between MTBE and water. The required energy for breaking this bond indicates why MTBE tends to remain in aqueous phase and not to transfer to vapour phase by air stripping. MTBE does not readily transfer from water to air and often needs high ratio of air to water usually >200/1 for 95% removal (Safarzadeh-Amiri, 2001).

Vapours should not release directly in air and, therefore, need to be treated (Jacobs et al., 2001). In treatment by granular activated carbon, contaminated water is pumped through a bed of activated carbon. Since MTBE does not attach to carbon well, high volume of contaminated water must pass through the granular activated carbon (GAC) system (EPA, 2003) as a result, it cannot be cost-effective.

Studies on the removal of MTBE from groundwater indicate that:

-Although MTBE can be metabolized by bacteria and produce CO_2, the rate of growth is slow (Jacobs et al., 2001).

-Application of physical methods such as activated carbon or air stripping is 10 times less cost-effective than application of these methods in the removal of hydrocarbons like benzene, toluene, ethylbenzene, and xylene from groundwater (Jacobs et al., 2001).

-Although separation techniques are less expensive than oxidation processes, they only transfer the pollutant from one phase to another and they need an additional treatment step for degradation.

MTBE is a major part of gasoline and is removed with difficulty, so an economical method of treatment should be applied. Since bioremediation is usually applied for decomposition of petroleum hydrocarbons, using a method that can be accompanied with biotreatment is appropriate (Barreto et al., 1995). AOP which applies a suitable combination of UV, chemical oxidants and catalysts can oxidize a wide range of organic compounds. Partial decomposition of MTBE is a way for transition of MTBE to

biodegradable products. Increasing use of MTBE may lead to techniques like chemical oxidation integrated by biological degradation.

2.2. Principles of Advanced Oxidation Processes (AOPs)

Oxidative procedure, which is applied for organic compounds in water, are generally referred to advanced oxidation processes (AOPs) (Legrini et al. 1993). High rate of pollution removal and large range of applicability are two major advantages of these technologies (Stefan et al., 1996). These processes, which are based on the generation of very active and oxidizing free radicals, have received considerable attention because of their high oxidant power (Benitez et al., 2001). In AOPs organic radicals are formed either by photolysis of organic substrate or by reaction with hydroxyl radicals ($^{\bullet}OH$) (Legrini et al., 1993). The rate constant of $^{\bullet}OH$ attack to organic compounds varies from 10^6 to 10^9 M^{-1} s^{-1}. Abstraction of hydrogen atom or addition to double bonds are the most possibility for $^{\bullet}OH$ to oxidize organic substrates (Stefan et al., 1996). The products of oxidation usually are readily degraded and have lower molecular weights. Theoretically, the combination of ultraviolet light with an oxidant such as O_3 and H_2O_2 results in complete mineralization of organics to carbon dioxide and water. For wastewater treatment, UV/O_3 and UV/H_2O_2 are effectively used to degrade organic compounds (Bolduc and Anderson, 1997). Low-pressure mercury arcs wavelength are widely used in water treatment. Unlike medium-pressure lamps, which emit a large number of lines in the range of 200-400 nm, low-pressure lamps have only a single but strong line at 254 nm because the quartz used in their structures absorbs their 185-nm lines (Sonntag et al.,

1993). The couplings of UV light with different oxidants are discussed in the following sections.

2.2.1. UV/Hydrogen Peroxide Process

Single UV radiation may be used for removal of pollutants from water but photochemical properties of some substrates may be such that they cannot absorb light in the specific wavelengths. To enhance the degradation of such compounds, hydrogen peroxide is used along UV process (Sonntag et al., 1[illegible]. Rate of oxidation can be accelerated by addition of H_2O_2 to UV. Hydrogen peroxide can be decomposed to hydroxyl radicals in the presence of UV light and initiate a chain reaction resulting in degradation of organic pollutants (Clarke and Knowles, 1982). $^{\bullet}OH$ is one of the most important oxidants because of its high activity and non-selectivity towards organic compounds (Mitani et al., 2002).

Capability of its oxidation is defined by its potential oxidation (Clarke and Knowles, 1982):

$$^{\bullet}OH + H^{+} + e \rightarrow H_2O \qquad 2.80 \ volts \qquad (2.2)$$

Since H_2O_2 is a strong oxidant (standard potential 1.80 V and 0.87 V at pH 0 and 14, respectively), it can be a suitable option in the treatment of various pollutants (Venkatadri and Peters, 1993). Photolysis of H_2O_2 at wavelength of < 400 nm includes the breakage

of the molecule and formation of two hydroxyl radicals per quantum of radiation absorbed according to the following reaction:

$$H_2O_2 \xrightarrow{h\nu} 2^{\bullet}OH \qquad (2.3)$$

The production of hydroxyl radicals from H_2O_2 needs sufficient energy (48.5 kcal.mole^{-1}) to break the O-O bond. The energy of the short wavelength in UV-C lamps (with wavelengths of 200-280 nm) is adequate for this breakage and leads to the formation of radicals (Clarke and Knowles, 1982). H_2O_2 is photoreactive at wavelength of 185-400 nm. However, in the range of wavelength 200-280 nm, it exhibits the highest yield of hydroxyl radical production.

Higher pH can increase the rate of hydrogen peroxide photolysis. Organic substrate reacts with these hydroxyl radicals to produce an organic radical ($^{\bullet}$RH).

$$^{\bullet}OH + HRH \rightarrow {}^{\bullet}RH + H_2O \qquad (2.4)$$

The reaction between the organic radical and dissolved oxygen produces organic peroxide radical ($RHO_2^{\bullet}$), which entails thermal oxidation reactions. Generation of organic cations, superoxide anions, carbonyl compounds and back reaction to $^{\bullet}$RH and O_2 are the possible subsequent reactions for organic peroxide radicals. And finally, radical-radical recombination must be also taken into account (Legrini et al., 1993).

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad (2.5)$$

Currently, technologies such as air stripping followed by activated carbon adsorption are less applied because they basically transfer contaminants from liquid phase to vapour or solid phase. Instead, the UV/H_2O_2 process can entirely oxidize the contaminants (Venkatadri and Peters, 1993). Advantages of hydrogen peroxide make it a suitable choice as an oxidant in chemical or photochemical water treatment. The main advantages of UV/H_2O_2 process are as follows:

-Hydrogen peroxide is a commercially available oxidant, which has minimal capital investment.

-It is thermally stable and infinitely soluble in water.

-Each molecule of H_2O_2 produces two hydroxyl radicals; therefore, this oxidant is cost-effective source of hydroxyl radicals.

The weak points of the process include the absorption of $^{\bullet}OH$ radicals by H_2O_2 and removal of these radicals by bicarbonates. Because of unfavourable reactions of $^{\bullet}OH$ with H_2O_2 and bicarbonates, H_2O_2 and pH should be optimized (Sonntag et al., 1993).

One suggested pathway for MTBE degradation by hydroxyl radicals is cited by Chang and Young, 2000:

$$^{\bullet}OH + (CH_3)_3COCH_3 \rightarrow H_2O + (CH_3)_3COCH_2^{\bullet} \quad (2.6)$$

$$(CH_3)_3COCH_2^{\bullet} + O_2 \rightarrow (CH_3)_3COCH_2OO^{\bullet} \quad (2.7)$$

$$(CH_3)_3COCH_2OO^{\bullet} + (CH_3)_3COCH_3 \rightarrow (CH_3)_3COCH_2OOH + (CH_3)_3COCH_2^{\bullet} \quad (2.8)$$

$$(CH_3)_3COCH_2OOH \rightarrow (CH_3)_3COCHO + H_2O \quad (2.9)$$

2.2.2. Photocatalysis

. Photocatalysis is referred to the application of UV-light to excite a semiconductor such as TiO_2 to catalyze the redox reaction with organic substrates in water (Bolduc and Anderson, 1997). TiO_2 is stable, insoluble, non-toxic, resistant to corrosion, and reusable (Aceituno et al., 2002). In a semiconductor, the energy difference between the highest valence band and the lowest conduction band is called band-gap. Thermal or photonic excitations can build a bridge and transfer electron from valance bad to conduction band. When TiO_2 is illuminated with photons ($h\nu$) of energy equal to or greater than its band-gap, electrons from the valance band (VB) migrate to its conduction band (CB). The result of this process is the creation of photoholes (h^+) in the valence band and free photoelectrons (e^-) in the conduction band (Herrmann, 1999). Since the required energy to overcome the band-gap is 3.2 eV, only UV lights with wavelength of 380 nm or less have the energy higher than the band-gap energy and can promote the electrons from valance band to conduction band (Dionysiou et al., 2000). The following reactions take place in a semiconductor photocatalytic process (Venkatadri and Peters, 1993):

$$TiO_2 \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \qquad (2.10)$$

Where $h\nu, e^-_{CB}$ and h^+_{VB} are UV radiation, conduction-band electrons and valance-band holes, respectively.

In an aqueous media, OH^-, H^+ and water are bound to TiO_2. Production of hydroxyl radicals ($^{\bullet}OH$) occurs when the holes are trapped by adsorbed hydroxide ions and the molecular water (Bolduc and Anderson, 1997; Venkatadri and Peters, 1993).

$$h^+_{VB} + OH^-(surface) \rightarrow {}^{\bullet}OH \qquad (2.11)$$

$$h^+_{VB} + H_2O(adsorbed) \rightarrow {}^{\bullet}OH + H^+ \qquad (2.12)$$

In the reductive part of the reaction, oxidants such as oxygen scavenge the electrons and produce superoxide radicals ($O_2^{\bullet -}$). Oxygen molecule in water is an electron scavenger, as a result, its existence is essential to trap electrons and prevent recombination of the holes with electrons.

$$e^-_{CB} + O_2 \ (adsorbed) \rightarrow O_2^{\bullet -} \qquad (2.13)$$

Contaminates may also be attacked by $O_2^{\bullet -}$. Other radicals such as hydroperoxide radicals ($HO_2^{\bullet}$) are also produced (Dionysiou et al., 2000). Another source of hydroxyl radicals can be hydrogen peroxide, which is formed from superoxide ion. When the first

excitation reaction occurs, the holes and electrons may recombine and produce heat, which causes the photoefficiency of the photocatalytic process reduce.

$$e^{-}_{CB} + h^{+}_{VB} \rightarrow heat \qquad (2.14)$$

The advantage of UV/TiO_2 process is its ability to completely mineralize wide range of contaminants to CO_2 (Venkatadri and Peters, 1993). Moreover, it is stable in water in the entire range of pH. TiO_2 is inexpensive and no additive is required. This process has the possibility of combination with other degradation methods such as biological treatment (Herrmann, 1999). Its disadvantages are the high operating cost as well as its low quantum yield (≤ 0.05) (Bolduc and Anderson, 1997).

A photocatalytic mechanism for MTBE was suggested by Barreto et al. (Barreto et al., 1995). The first step is the abstraction of an α-hydrogen by $^{\bullet}OH$ and formation an organic radical leading to reaction with O_2 and formation of peroxy radical. This radical abstracts an α-hydrogen from MTBE molecule and forms an HperMTBE. Under acidic conditions the cleavage of O-O bond in HperMTBE produces *tert*-butyl formate (TBF).

$$(CH_3)_3COCH_3 + O_2 \xrightarrow{TiO_2,h\nu} (CH_3)_3CO(CH_2)OOH \qquad (2.15)$$

$$(CH_3)_3CO(CH_2)OOH \xrightarrow{H^+/H_2O} (CH_3)_3CO(\dot{C}O)H + H_2O \qquad (2.16)$$

Formation of *tert*-butyl alcohol (TBA) and formic acid occurs in next step:

$$(CH_3)_3CO(CO)H \xrightarrow{H^+/H_2O} H(CO)OH + (CH_3)_3COH \qquad (2.17)$$

while formic acid can be photocatalytically oxidized to CO_2, in the presence of hydrogen peroxide, TBA transforms to alkenes, which can be oxidized easily (Barreto et al., 1995).

2.2.3. Ozone/UV Process

Ozone (O_3) may be used either directly with organic compounds or in combination with H_2O_2, which increases the oxidative capability by production of hydroxyl radicals. Organic compounds which are resistant to ozonation can be degraded by photolytic ozonation. At present, the combination of UV and O_3 process seems to be the most commonly applied AOPs. Homolysis of O_3 by UV light and production of $^{\bullet}OH$ radicals by the reaction of $O(^1D)$ with water are two steps in Ozone/UV process as follows (Legrini et al., 1993):

$$O_3 \xrightarrow{h\nu<310\ nm} O_2 + O(^1D) \qquad (2.18)$$

$$O(^1D) + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad (2.19)$$

Dissolved ozone can be photolized and produce hydrogen peroxide:

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 + O_2 \qquad (2.20)$$

$H_2O_2/O_3/UV$ system has been also applied for water and wastewater treatment. Mechanisms of generating hydroxyl radicals are different and in some cases are superior as shown in the following reactions:

$$H_2O_2 + H_2O \leftrightarrow H_3O^+ + HO_2^- \qquad (2.21)$$

$$O_3 + H_2O_2 \rightarrow O_2 + {}^{\bullet}OH + HO_2^{\bullet} (very\ \ slow) \qquad (2.22)$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet-} + O_2 \qquad (2.23)$$

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \qquad (2.24)$$

$$O_3^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + HO^- + O_2 \qquad (2.25)$$

$^{\bullet}$OH radicals start oxidative degradation of organic compounds (Legrini *et al.*, 1993).

The following reactions for $^{\bullet}$OH attack to MTBE in O_3/H_2O_2 process, which has the same profile as UV/H_2O_2 but with production of different ratio of TBA/TBF, has been suggested (Safarzadeh-Amiri, 2001; Stefan et al., 2000):

$$(CH_3)_3COCH_3 + {}^{\bullet}OH \rightarrow (CH_3)_3COCH_2{}^{\bullet} \quad or \quad {}^{\bullet}CH_2(CH_3)_2COCH_3 + H_2O \qquad (2.26)$$

$$(CH_3)_3COCH_2{}^{\bullet} \; or \; {}^{\bullet}CH_2(CH_3)_2COCH_3 + O_2/O_3 \xrightarrow{-H_2O_2/-H_2O} products \qquad (2.27)$$

Stefan et al. (2000) considered different pathways for above reactions that resulted in many different products, which are suggested in their study.

2.2.4. Fenton's Reagent

Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron. This process produces hydroxyl radicals as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2.28)$$

Hydroxyl radicals can attack the organic compounds and degrade them. The optimum pH range for Fenton's reagent is 2-4 (Venkatadri and Peters, 1993). Colured organic compounds that have interference with UV light in UV/H_2O_2 process can be degraded effectivcly by Fenton's reagent.

The activity of Fenton's reagent can be enhanced by UV radiation. This is the result of increased concentration of hydroxyl radicals, which occurs by regeneration of Fe^{2+} through photolysis of Fe^{+3} complexes (Andreozzi et al., 1999):

$$Fe(OH)^{2+} \xrightarrow{hv>300\ nm} Fe^{2+} + {}^{\bullet}OH \qquad (2.29)$$

In some cases irradiated reactions are reported 1.5-2.7 times faster than Fe^{3+}/H_2O_2. Iron and H_2O_2 concentrations, and pH value are important factors in Fenton and photo-Fenton reactions (Venkatadri and Peters, 1993).

Since the oxidation of MTBE by Fenton's reagent is mediated by the formation of $^{\bullet}OH$, the same mechanism as of the other AOPs is suggested for the formation of TBA and TBF with this catalytic reaction (Xu et al., 2004).

2.2.5. Vacuum Ultraviolet (VUV) Process

When air (oxygen) absorbs radiation, the vacuum ultraviolet is a suitable choice in photooxidation. In this process, spectroscopic work at shorter wavelengths can only be performed in vacuum or in non-absorbing gases. In VUV process, H_2O can be photolized to generate hydroxyl radicals, which can attack the organic substrate as following reaction:

$$H_2O \xrightarrow{172\ nm} \frac{1}{2}H_2 + {}^{\bullet}OH \qquad (2.30)$$

This process is very simple and no chemicals are added. Its application is limited in low concentrations of contaminants. Xe excimer lamps can be applied for water photolysis (Legrini et al., 1993).

2.3. Biological Treatment of Organics in Water

Microorganisms have important role in water and wastewater treatment. The foundation of biological treatment is the relation between wastewater and microorganisms because they can use organic compounds in wastewater as their nutrients. Environmental conditions such as presence of oxygen, mineral nutrients, pH, and temperature should be suitable for the growth of microorganisms to speed up the decomposition of wastes. The main purpose of most biological treatments is to decrease the organic loads in wastewater. Generally, biological treatments are divided in two groups: aerobic processes, in which microorganisms need oxygen for growth, and anaerobic processes, in which living organisms do their metabolisms in the absence of oxygen (Metcalf and Eddy, 1991). The activated sludge is known as the most acceptable technology to remove biodegradable dissolved organic matters from wastewater. In activated sludge, wastewater is introduced into a suspended aerobic bacterial culture in a tank for several hours to use organic matters in wastewater as substrate and remove them by synthesis of new bacterial cells. Main units of activated sludge processes are biological reactor equipped with aerator, clarifier, and recycle pumps for recycling of the activated sludge (Reynolds and Richards, 1996). A mechanical or diffused aeration system supplies oxygen to provide aerobic condition as well as well-mixed liquor in the tank. Microorganisms consume the organic pollutants and convert them to water and carbon dioxide while high amount of microbes are synthesized. In the next step, the mixture is led to a settling tank. In the settling tank, living organisms, which usually have density higher than water, settle down and subsequently are separated from the treated

wastewater. A portion of the activated sludge is returned to the treatment tank to remain the desired concentration of microorganisms in the reactor (Metcalf and Eddy, 1991).

Biological reactors vary by geometry and hydraulic regime. Sequential Batch Reactors (SBR) is a single batch reactor with timed control sequence used for the removal of undesirable components from wastewater. An SBR can be a simulation of any conventional activated sludge process (EPA, 1999). Unit processes of SBR are the same as the conventional activated sludge systems, but unlike these systems in which the processes are carried out simultaneously in separate tanks, the functions of SBR are carried out in a sequence of time in the same tank, therefore, SBR is a time-oriented system. It operates based on fill-and-draw strategy. In a period of time, influent enters the reactor containing acclimated biomass. The reactions complete in this batch reactor, the mixed liquor settles and clarified supernatant is removed from the reactor (Irvine et al., 1989). In the SBR, there is no need for separate primary and secondary clarifiers. A typical SBR includes five discrete time periods: fill, react, settle, draw and idle.

In the fill period, the influent is added to the biomass, remained from previous cycle. This period is typically terminated when the desired volume of tank is filled. Different strategies for fill period include static fill (no mixing-no aeration), mixed fill (mixing-no aeration) and aerated fill (mixing-aeration).

During the react period, biological reactions initiated in fill period are completed. Low dissolved oxygen and high dissolved oxygen are conditions that can be provided by

mixed react and aerated react, respectively. Duration can range from 0 to more than 50% of the total cycle.

Quiescent settlement of solids takes place during settle period. The period should last for the time to ensure that sludge remains under the level of withdrawal and does not rise.

Discharge of treated effluent to the predetermined level takes place in draw period. The time in draw period typically ranges from 5% to more than 30% of the total cycle time.

The period between draw and fill periods in the next cycle is called idle, which can include sludge waste, if necessary. Excess biomass is usually wasted to maintain the ratio of substrate in influent to biomass constant (Irvine and Ketchum, 1989) so the need for recycling activated sludge is eliminated. To achieve specific treatment purposes, some modifications may be made in the performances and times with each step. To meet the desired effluent quality, the number of cycles per day can be varied.

2.4. Combination of Advanced Oxidation Processes and Biological Treatment

Effluents from different industries are mostly not biodegradable and sometimes resistant to conventional methods of treatment. Although AOPs are usually effective for mineralization of resistant organic compounds in water and wastewater, their energy consumption is higher than that of biological processes. Advanced oxidation processes

are expensive technologies with high capital and operating costs while these costs in biological processes are 5-20 and 3-10 times lower (Marco et al., 1997). Conventional biological treatment methods, such as activated sludge, are less expensive and less successful in destruction of resistant compounds. Potential applications for two-step treatments rather than single processes are suggested. Recalcitrant compounds are wastewater contaminates that can benefit from integrated processes. Pre-treatment of toxic or resistant organic compounds by AOPs may lead to improve their biodegradability and result in the production of intermediates, which can be consumed more easily by microorganisms, so further mineralization by AOPs is not economically justified. Partial oxidation of persistent compounds can be substituted for total oxidation with much less costs in biological treatment. Combination of chemical and biological processes is a successful system, which is less expensive method for treatment of resistant compounds, and therefore, is a good option for complete degradation of organic compounds. A successful biological treatment will remove the remaining organic matter. This combination of chemical and biological processes seems to be most recommendable for the treatment of resistant pollutants in water and wastewater.

2.5. Examples of Applications of Different AOPs for Degradation of Organic Compounds

Previous studies on the removal of organic compounds from water and wastewater by AOPs have considered different aspects. The removal of azo-reactive dyes from textile wastewater by applying UV in the presence of H_2O_2 was studied (Georgiou et al., 2002). Experimental results showed that without H_2O_2, no colour removal occurred, but

addition of even a small amount of H_2O_2 resulted in a complete destruction of colour in all cases. In the presence of H_2O_2, 90% removal of intermediates (containing aromatic rings) and more than 80% removal of TOC were observed. Obtained results demonstrated that during the degradation, dye solution became acidic (pH = 3-3.5). The increasing chemical oxygen demand (COD) at the beginning of irradiation was the result of dye molecules destruction to simpler and less resisted compounds.

In another study, aniline, p-toluidine and 2,4-xylidine were chosen as model compounds to investigate the photooxidation of aromatic compounds in both forms of slurry and immobilized TiO_2 (Preis et al., 2002). The experimental results showed that:

-Increasing in pH between 7-11 resulted in increase reaction rate.

-Higher concentration of pollutants resulted in decrease photooxidation efficiency.

-The activity of TiO_2 was lower in immobilized form than that in slurry one.

Ince (1999) studied the kinetics of dyeing stuff degradation by AOPs. The obtained results showed an increase in the degradation with increasing H_2O_2 up to the approximately ratio of 14 H_2O_2/dye. Above this value, inhibition of degradation was observed. This inhibition can be explained by the competition of UV absorbance by dye and H_2O_2. A first order kinetic was assumed for the degradation and a model was defined based on the competitive inhibition. Proposed model predicted the same ratio as the optimum dose of H_2O_2.

Degradation of several strongly coloured compounds (methylen blue, Rhodamine B, methyl orange and salicylic acid) was studied in presence of TiO_2 in a flat bed reactor illuminated by sunlight and a medium-pressure mercury lamp (Matthews, 1991). The results showed that TiO_2 and UV light had essential roles in the degradation of the coloured compounds. In the absence of the photocatalyst, even in the presence of H_2O_2 the photodegradation was only 40% greater than that of the removal rate by dark reaction with TiO_2. The presence of TiO_2 resulted in 5 times faster removal rate while the presence of H_2O_2 resulted in 2.5 times faster rate. It was observed that generally an increase of flow rate resulted in an increase of removal rate and also a decrease of initial concentration resulted in an increase of apparent rate constant. For each experiment, the degradation by sunlight was greater than that by artificial light, due to greater avoidable energy for catalyst activation.

Hofstadlert and Bauer (1994) studied the degradation of 4-chlorophenol (4-CP) by UV/TiO_2 immobilized on fused-silica glass fibres. The results showed that between 10-60°C the rate of decomposition of 4-CP was increased linearly. Use of light with shorter wavelength (280-320 nm) resulted in higher oxidation rate of 4-CP but not of TOC, which meant higher resistant against oxidation to CO_2 by products than that of 4-CP. The results for both immobilized and suspended TiO_2 were the same. Degradation rate was increased by H_2O_2 addition, but for TOC, the rates were equal. Decreasing pH from 5.8 to 3.5 enhanced the degradation of 4-CP and TOC.

2.6. Previous Studies on MTBE Degradation

The potential for removal of MTBE by AOPs has been the subject of only limited research. To date, only a few studies have been conducted for investigation of the effects of AOPs on MTBE degradation.

With considering environmental concerns about MTBE, Stefan et al. (2000) studied aqueous solution of MTBE and its products resulting from its degradation by UV/H_2O_2 (Stefan et al., 2000). They suggested the details of the mechanism of a pseudo first-order reaction resulting in complete mineralization of all initial organic compounds or organics produced during the treatment process. The by-products of the irradiation were detected and quantified. The generation of *tert*-butyl formate (TBF), 2-methoxy-2-methyl propionaldehyde (MMP), formaldehyde, acetone, *tert*-butyl alcohol (TBA), methyl acetate, hydroxy-iso-butyraldehyde, hydroxyacetone, pyruvaldehyde, hydroxy-iso-butyric acid, formic acid, pyruvic acid, acetic acid and oxalic acid was confirmed.

The possibility of the application of UV/H_2O_2 as a method of treatment for waters polluted by MTBE to quantify the kinetics of MTBE degradation and the kinetics of the formation and destruction of the by-products was studied (Chang and Young, 2000). For the reaction with hydroxyl radicals, a second-order rate constant of 3.9×10^9 $M^{-1}s^{-1}$ for MTBE and 1.2×10^9 $M^{-1}s^{-1}$ for TBF as a by-product of MTBE degradation by UV/H_2O_2 was studied.

The removal of MTBE by O_3 and O_3/H_2O_2, in which the production of $^{\bullet}OH$ was the driving force, was studied (Mitani et al., 2002). The kinetics of MTBE oxidation and its intermediates were studied. In a range of 21-45°C the second-order rate constant for reaction of MTBE with O_3 and of MTBE with $^{\bullet}OH$, resulted in the O_3/H_2O_2 process, was measured to be 1.4×10^{18} exp (-95.4/RT) and 8.0×10^{9} exp(-4.6/RT) M^{-1} s^{-1}, respectively. It was indicated that in a continuously stirred tank reactor (CSTR), the addition of H_2O_2 to O_3 resulted in an increase of the rate and degree of MTBE degradation. t-butyl formate (TBF), t-butyl alcohol (TBA), methyl acetate, and acetone were determined as products of the reactions of O_3 and O_3/H_2O_2 with MTBE.

Kinetics and oxidation efficiency of MTBE by O_3/H_2O_2 was examined (Safarzadeh-Amiri, 2001). That study was performed in two phases including MTBE concentrations greater and lower than 10 mg/L. Ozone mass transfer was a limiting factor in the rate of oxidation of MTBE, specially in the first phase. Depending on the ozone gas flow rate, the pseudo-first-order reaction rate constant varied from 2.0×10^{-3} to 5.4×10^{-3} s^{-1}. In his study, an efficiency index for comparison of MTBE oxidation in different water was defined.

The feasibility of photocatalytic process for the mineralization of MTBE was investigated and a first-order reaction constant for its degradation in the presence of UV light in TiO_2 slurry was suggested (Barreto et al., 1995). The by-products of the reaction were identified and the reaction scheme in which MTBE was changed to harmless compounds was proposed. The primary by-products were t-butyl formate (TBF) and t-

butyl-alcohol (TBA), which readily but with lower rate were degraded. While the pseudo first-order rate constant for photocatalysis of MTBE was 1.2×10^{-3} s^{-1}, these constants for TBF and TBA were 1.93×10^{-4} and 2.34×10^{-4} s^{-1}, respectively.

2.7. Previous Studies on the Combination of Advanced Oxidation and Biological Processes

The possibility of combination of photochemical and biological treatment has been studied by many researchers and its beneficial effects were reported (Bankian Tabrizi and Mehrvar, 2004). Some of these studies are summarized here:

Experiments were performed to compare the treatment of domestic wastewater by activated sludge and by combined chemical-biological processes (Beltran et al., 1999a). The biological pre-treatment partially removed the compounds in wastewater and reduced the competition for ozonation in the next step. The performance of biological step could control the efficiency of the chemical step. After a biological treatment, a post-ozonation process improved the reduction of dissolved organic matters. The ozonation changed the structure of chemicals and resulted in the formation of more biodegradable products and, therefore, increased the ratio of BOD/COD, which meant the improvement of biodegradability in the system. This effluent could be easily treated in natural water systems. They also reversed the sequence of oxidation and observed that pre-ozonation could improve the biodegradation expressed as BOD/COD ratio and remove recalcitrant organics by changing the molecular structure of oxygenated products that were more readily to biodegradable (Beltran et al., 1999b). While single activated sludge resulted in

80% and 47% removal of BOD and chemical oxygen demand (COD), combined system could have 88% and 66% removal of BOD and COD, respectively. From the results of these two studies, it was concluded that combined processes were more effective than single biological or chemical treatment and the best sequence was found to be the ozonation followed by biological treatment.

To minimize the use of expensive chemical oxidants, experiments were performed in a cycle of consecutive biological and ozonation process (Karrer et al., 1997). After ozonation, an increase of BOD in biologically pre-treated wastewater was observed. To have as much as possible work for biotreatment, it was suggested that ozonation process to be stopped at the highest level of BOD and leave the removal of biodegradable compounds to biotreatment. The new oxidation step would be started afterward. It was observed that the consumption of ozone in an exclusive ozonation was more than combined treatment and it was concluded that although there would be a few oxidation products, which react with ozone and were biodegradable, majority of ozonation products had very slow reaction with ozone.

The effectiveness of different AOPs for decomposition of THMs was studied (Ito et al., 1998). It was suggested that the highest degradation rate in $O_3/H_2O_2/UV$ was the result of higher generation rate of hydroxyl radicals compared to H_2O_2/UV and H_2O_2/O_3 processes. While single ozonation increased the biodegradability, it was not effective on mineralization. On the other hand, AOPs enhanced both mineralization and

biodegradability. Further AOPs resulted in a complete degradation of biodegradable compounds.

A study was conducted for the comparison of the application of various AOPs before biodegradation of a textile wastewater (Ledakowicz and Gonera, 1999). The results showed that O_3/UV or O_3/UV/H_2O_2 could be the most advisable process. The pre-treatment textile wastewater showed less inhibitory on microbial growth in further biological step than non-treated one. Meanwhile, the concentration of H_2O_2 was determined, which did not have any detrimental effect on microorganisms.

The development of an advanced treatment process for textile dye wastewater was reported (Li and Zhao, 1999). Dye wastewater was treated by an intermittently decanted extended aeration (IDEA) reactor for biological treatment, passed through a sand filter to polish residual biomass and suspended solid and then followed toward TiO_2 photocatalytic reactor for complete decolourisation and high COD removal. Both the batch and continuous modes in the photoreactor were studied. The results after biological treatment showed 92.3% and 73.3% BOD removal in reactive dye and acid dye, respectively. But only 44.7% and 68.1% of COD removal were reported. In the batch mode, the concentration of TiO_2 in the photoreactor was 1-10 g/L while the concentration of TiO_2 increased; the time for required decolourisation was decreased. The colour was removed completely in a shorter period of time than what was required for COD reduction. In the continuous mode, increasing the flow rate resulted in decreasing COD and colour removal. The reaction efficiency in batch operation was higher than that in

continuous mode. The treated wastewater in this reactor could satisfy the requirements of the water suitable for reusing in textile dye processes.

The removal of three different commercial dyes in a combined photoreactor system was investigated (Li and Zhao, 1997). The pollutants were initially treated in an IDEA followed by a photocatalytic reactor. A re-circulating batch plate-type photocatalytic reactor was used and TiO_2 was immobilized on the natural zeolite. Experiments were conducted in 4 phases include biological reactor alone, photocatalytic reactor alone, photobioreactor without re-circulation, and by photobioreactor with re-circulation. In the first phase, the treatment of all kinds of dyeing wastewater used in the experiment was not achieved. The second phase showed complete COD removal in wastewater samples (over 90%), but in a very long period of time (200-250 hours). The results in photobioreactor system without re-circulation demonstrated that the amount of TiO_2 on zeolite and light intensity affected the rate of decolourisation significantly. In comparison to the second phase, the time of the reaction was shortened to 20% in the third phase. In this case, BOD was increased while COD was decreased, which indicated the existence of some simpler organic compounds

Experiments were performed to investigate the effects of UV radiation, UV/H_2O_2, Fe^{+2}/H_2O_2 (Fenton reaction), and $UV/Fe^{+2}/H_2O_2$ (photo-Fenton reaction) on the treatment of wastewater from olive industry (Benitez et al., 2001). Production of hydroxyl radical, which occurred through UV/H_2O_2, Fenton and photo-Fenton reactions, enhanced the degradation rate in comparison to single UV reaction. An anaerobic digestion for this

wastewater was also studied and the constant values of a modified Monod model were estimated. It was observed that pre-treatment of wastewater from olive industry by chemical processes improved the rate of digestion in the following anaerobic stage.

Since MTBE is known as a recalcitrant compound, no study has been found about the application of a combined system for its removal, but recent studies have shown that different bacterial cultures have the capability of MTBE degradation.

The possibility of MTBE degradation by using a BC-1 culture was examined (Salanitro et al., 1994). This mixed bacterial culture, which was derived from an industrial chemical biotreater, could degrade MTBE up to 200 mg/L. In a continuous cell recycle unit, low rate of microorganisms growth was observed. In batch removal experiments, MTBE was degraded much faster and produced TBA. The rate of TBA degradation was lower than that of MTBE and the highest rate was when all MTBE was consumed. Generally, this study showed that MTBE could be biodegraded in high extent by BC-1 but growth rate and cellular yield were low. The low rate could be the result of limiting intermediates or MTBE activity as a metabolic inhibitor.

A metabolism for biodegradation of MTBE by mycobacterium austroafricanum IFP 2012 in which the intermediates were identified was suggested (Fayolle et al., 2003). The growth of this bacteria included a long lag phase corresponding to the conversion for MTBE to TBA and a rapid growth on produced TBA. The effect of the competition between MTBE and TBA for the same enzymatic activity was examined and it was

concluded that the competition was not the reason of MTBE slow degradation, but probably the TBA hydrolysis was inhibitor in MTBE biodegradation.

The potential of MTBE for biodegradation was examined (Kane et al., 2001). For this purpose, microcosms containing aquifer sediment and ground water from leaking underground storage tanks were used. In the best case, after a 4-day lag period, 4.5 mg/L MTBE was biodegraded within 15 days and 43-54% of it was converted to CO_2. PM1 was the responsible bacteria strain for this process. The effects of water soluble components of gasoline on MTBE degradation were investigated and it was observed that the presence of dissolved compounds did not necessarily decrease the degradation of MTBE and TBA.

Strain IFP 2007, which was isolated from a sampled activated sludge of a wastewater treatment plant, was used in a study (Hernandez et al., 2001). This study compared the consumption of MTBE as a source of carbon in presence and absence of other carbon sources such as ethanol and it was shown that while sole MTBE was not consumed, it had a cometabolic degradation with ethanol.

The possibility of biodegradation of MTBE and TBA by bed-sediment microbial communities was also studied (Bradley et al., 1999). It was observed that these microorganisms were capable to convert 73% MTBE and 84% TBA to CO_2 in a mixed aerobic/anaerobic conditions. Under completely anaerobic conditions, no mineralization was observed.

The consumption of MTBE as a sole carbon source by pure bacterial cultures isolated from activated sludge was investigated (Mo et al., 1997). After the first week of incubation on 200 ppm MTBE, 8% of MTBE was converted to CO_2 and after 2 weeks 28% degradation was observed. The initial fast degradation rate was followed by a slower rate. The applied bacteria strain could also grow on TBF. The presence of other organic compounds such as TBF and TBA decreased the bacterial growth on MTBE. When MTBE was consumed as a sole carbon source, the low growth rate led the researchers to conclude that MTBE was a poor energy source. In their study, greater capability of mixed culture than that of pure culture for degradation of MTBE was observed.

The feasibility of several propane-oxidizing bacteria was tested for growth on MTBE (Steffan et al., 1997). After growth on propane, the strain was able to mineralize more than 60% of MTBE with 20 mg/L initial concentration in less than 30 hours. The pathway of degradation was proposed and TBA as a first measurable degradation product of MTBE was determined. Production of TBA led to the presence of formaldehyde, which was further oxidized to formate and CO_2.

The possibility of MTBE biodegradation in the presence of alkanes was studied (Garnier et al., 1999). For this purpose, the metabolization kinetics of MTBE by a bacteria strain, isolated from soil consortium, in the presence of pentane as a source of carbon and energy was studied. With conducted experiments, the parameters of suggested model for this biodegradation was identified. The maximum growth rate and specific

degradation rate of pentane was about 0.19 h^{-1} and 105 mg h^{-1} $g_{dry\ biomass}$. This study indicated that MTBE could be cometabolized in the presence of pentane, but no degradation was observed in its absence. In the presence of pentane, in the first 30 hours, only pentane was degraded and MTBE concentration did not change. Between 30 and 50 hours the maximum MTBE degradation was occurred. After 60 hours, pentane was completely consumed and MTBE degradation rate became low. Overall, 20% mineralization of MTBE was observed during this time. Investigation on the effect of various amounts of pentane showed that the increase of this carbon source could result in the increase of MTBE degradation, so for MTBE degradation a model was suggested in which the main parameters were initial concentrations of pentane and of MTBE. Up to 900 mg/L MTBE had no inhibitory effect on bacteria growth.

The bioremediation potential of MTBE was investigated by using aerobic microcosm of Borden aquifer materials (Schirmer et al., 1999). A psuedo first-order reaction for MTBE degradation was considered and its constant rate was found to be 0.0012 day^{-1}. It was concluded that MTBE was quite rare to be selected as a primary substrate. Although it can be biodegraded by natural microbial populations at Borden, the rate of the degradation of MTBE was much slower than that of usual gasoline contaminants.

The capability of a microbial consortium cultivated in a liquid system, which was originated from MTBE-contaminated sites and enriched in biotrickling filters was investigated (Fortin et al., 2001). It was found that biodegradation of MTBE in concentrations, as much as 100 mg/L or less, followed a zero-order reaction with rate

constant of 2.8 $mgL^{-1}.h^{-1}$. The specific activity and the biomass yield for this culture were 7-52 $mg_{MTBE}\ g^{-1}_{dw}\ h^{-1}$ and 0.11 $g_{dw}\ g^{-1}_{MTBE}$, respectively. During 80 hours, 79% of MTBE converted to CO_2. The possibility of production of more biomass by supplementing the culture with diethyl ether as an alternative carbon source was studied. MTBE was only biodegraded after complete consumption of diethyl ether and an increase of biomass concentration equal to 0.1-0.6 $g_{dw}\ g^{-1}$ was observed, which probably was not the result of primary MTBE degraders. Comparison between energy wasted during bacterial growth on MTBE and that of TBA suggested that large energy expenditure was related to the breakage of ether bond in MTBE, but still losses of energy occurred after the initial step of MTBE degradation to TBA.

CHAPTER 3

EXPERIMENTAL WORK

3.1. Photochemical Treatment

3.1.1. Photochemical Experimental Set-up

Figure 3.1 shows the photoreactor used for all photochemical experiments. A total volume of 3 L deionized water was used in the batch photoreactor in each experiment. The reactor was immersed in a cylindrical PVC container with a volume of 7 L. The water in the container was fed by tap water continuously to keep the temperature of the solution constant within 15-20°C. This container was also used as a shield to prevent the transmission of light from the reactor. Two different Philips UV lamps with wavelength 365 nm (PL-S 9W/10) or 254 nm (PL-S 9W TUV) were used. In each experiment, a lamp, located on a support, was immersed into the solution at the centre of the reactor. Hydrogen peroxide and/or TiO_2 were added to the aqueous solution. A magnetic stirrer bar was used to mix and unify the solution and to avoid any mass transfer limitation.

3.1.2. Chemical Degradation Experiments

In order to explain the role of H_2O_2, TiO_2, and UV light in the oxidation of MTBE, a series of experiments were conducted. A typical degradation experiment included 3 L test solution containing MTBE and deionized water in the presence and absence of H_2O_2 and/or TiO_2. The MTBE concentration was used at 2-30 mg/L. The influence of TiO_2 and H_2O_2 concentrations on the degradation of MTBE were studied. Powdered TiO_2 and/or

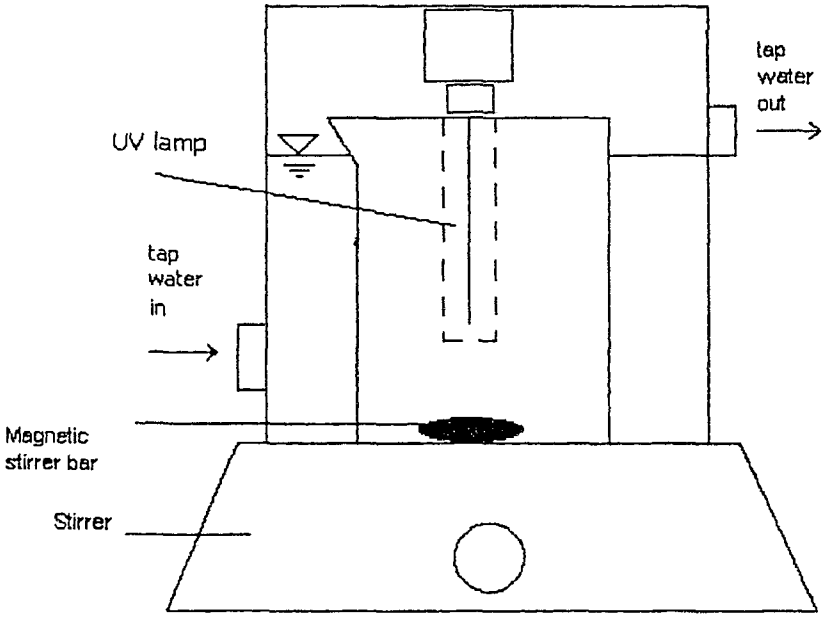

Figure 3.1. Experimental Set-up for the photochemical treatment of MTBE.

50% H_2O_2 solution were then added and stirred with a Teflon-coated magnetic bar under light and the temperature was kept constant at 15-20°C during the reaction time. The mixing system also provided sufficient oxygen for the reactions. Samples were withdrawn at time intervals of 1 h and immediately analyzed. Samples from photocatalytic reactions were centrifuged by an ADAMS centrifuge for 30 minutes and supernatant was used for gas chromatography (GC) analyses.

The parameter that was measured to control the degradation rate of MTBE under different conditions included MTBE residue (Appendix B). In addition, biological oxygen demand (BOD) and chemical oxygen demand (COD) were estimated. Temperature and pH were also other monitored parameters. Each experiment was conducted in three separate runs and the average of obtained results for the same intervals of time reaction were shown. Commonly, the value of $\frac{SD}{\sqrt{n}}$, in which SD is the standard deviation and n is the number of samples, was used as the value of error bars or standard error of the mean. Between +1 and –1 standard error was the range in which there was 68% probability that the true mean value was measured. For more strong probability, the limits were extended to +2 and –2 times the standard error and, therefore, provided 95% confidence. Since the numbers of samples were 3, the standard errors with 95% confidence are:

$$\pm 2 \times \frac{SD}{\sqrt{3}} \approx SD$$

Therefore, the error bars in graphs are equal to standard deviations. Because of different analytical and sampling errors, different values of error bars were observed.

3.2. Biological Treatment

3.2.1. Biodegradability of MTBE and Intermediates

To assess the biodegradability of MTBE and its intermediates, a series of BOD tests were conducted. BOD laboratory tests utilize living organisms to determine the effect of conditions to which organisms are exposed. The performance of these tests was under controlled environmental conditions and duration (Section 3.5.7). In these tests, oxygen consumption of polyseed microorganisms in the presence of MTBE and intermediates was performed. The greater dissolved oxygen consumption corresponded to more microbial growth and activity.

3.2.2. Study of Biological Treatment

Knowledge of the rate of bioreactions is a requirement for the design of biological degradation. A study was conducted in aerobic processes to provide rate constants. Batch reactors were set to perform the biodegradation of MTBE in three different approaches:

Experiment 1 was used to test the ultimate BOD for MTBE in water.

Experiment 2 was used to examine the possibility of a mixed culture for MTBE biodegradation.

Experiment 3 was used for a survey, investigating the potential for acclimation of a mixed culture to degrade MTBE.

3.2.2.1. Biological Experimental Set-Up for Determination of Ultimate BOD

The procedure for ultimate BOD (BOD_U) test was the same as BOD_5 (Section 3.5.7), except it had some specific requirements and differences in applications which is explained as follows:

BOD bottles containing MTBE concentrations of 5, 10, 30, and 50 mg/L along with polyseed solution (Section 3.5.7.1) and dilution water, as described in BOD_5 tests (Section 3.5.7), were prepared and placed in an incubator at 20°C, dissolved oxygen (DO) was monitored frequently to ensure that low dissolved oxygen or anaerobic condition did not dominate. Whenever DO concentration was less than 2 mg/L, the sample was reaerated by bubbling with air and the concentration of DO after aeration became the initial DO for next reading. DO measurement was extended until consumption of DO in a week became 1-2% below the total consumption (Standard Methods for the Examination of Water and Wastewater, 1998).

3.2.2.2. Biological Experimental Set-Up for Biodegradation of MTBE by Mixed Culture

Biodegradation of MTBE by mixed culture was carried out in a 1500 ml flask. Microorganisms obtained from activated sludge unit of municipal wastewater treatment plant of North Toronto, located in the Don Valley, were added with 480 mg/L concentration of mixed liquor volatile suspended solid (MLVSS) (Section 3.5.8) into the flask containing 30 mg/L solution of MTBE. 0.5 ml of each Phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride were used as nutrients in amounts to be consistent with the ratio of BOD: N: P equal to 100: 5: 1 (Eckenfelder,

2000). To avoid the lack of nutrients, the same amounts (0.5 ml of each solution) were added weekly. The flask was sealed with cotton ball and incubated in a New Brunswick scientific C25KC shaker incubator at 20°C and shaking at 150 rpm. Another flask operating in the same conditions and containing the same mixed solution except sludge was considered as blank to quantify the disappearance of MTBE by volatilization. During 30 days of experiment, less than 5% of initial MTBE disappeared in this blank flask, which was not remarkable. At various times, samples of the culture were filtered for substrate determination and further analysis.

The characteristics of wastewater were monitored by measuring DO, pH, COD, and MTBE concentration. Because of the very low biomass yield of MTBE, the increase of MLVSS during bacterial growth compared to the initial MLVSS was very negligible and could not be measured with present analytical balance in the laboratory, therefore, this parameter could not be monitored. In addition, small volume of reactor was a limiting factor for measuring BOD_5 in this process because for each BOD_5 test, more than 200 ml of solution was necessary, so this parameter was not monitored as well. The aeration was controlled by DO, which was in the range of 6.5 to 7.7 mg/L

3.2.2.3. Biological Experimental Set-up for Biodegradation of MTBE by Acclimated Microorganisms

To acclimate the microorganisms, obtained from activated sludge unit of municipal wastewater treatment plant of North Toronto, a 7-L sequential batch reactor (SBR) was used and operated at room temperature, which was 25 ± 1°C (Figure 3.2). The operation

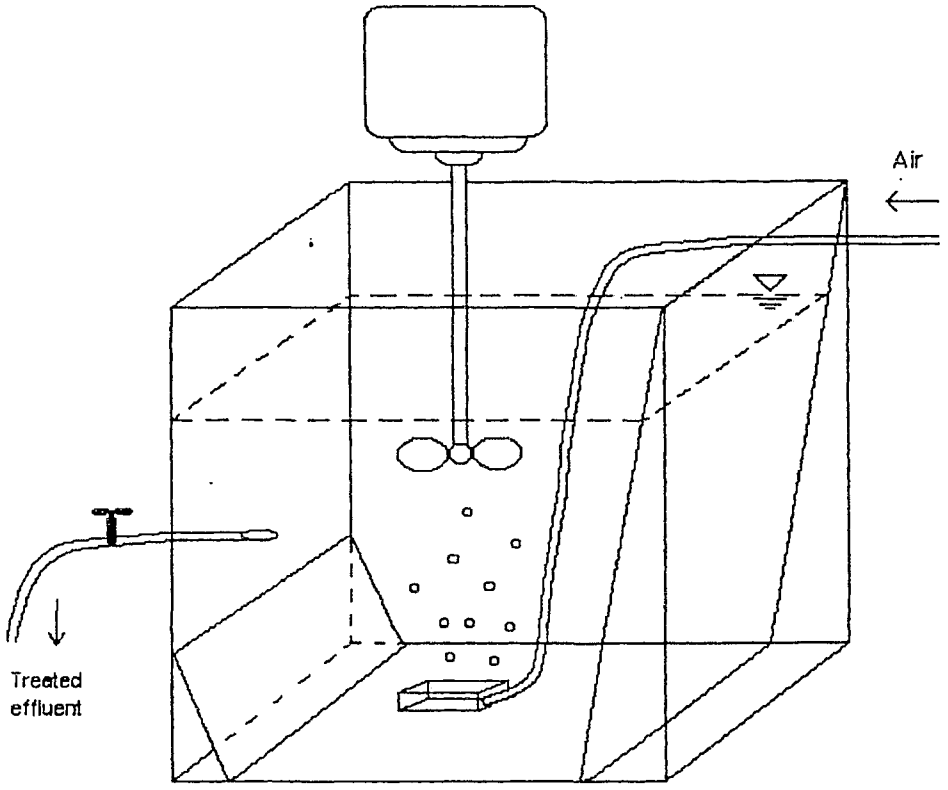

Figure 3.2. Experimental Set-up for the biological treatment of MTBE.

of SBR in these series of experiments is explained in details in Section 3.2.2.3.2. A stone air-diffuser aerated the culture through a tube through which air was flowing gently to avoid MTBE stripping. To ensure no disappearance of MTBE was occurred due to the aeration, the loss of MTBE was determined with different flow rates of air and the appropriate one was set for the reactor. A mechanical paddle stirrer with rotating speed of 350-400 rpm, which was measured by Tachometer (DT-105 A, Electronic Equipment Co., Inc.), distributed the sludge and materials in the reactor evenly.

3.2.2.3.1. Microorganisms Acclimation Experiments

Acclimatization is the physiological and behavioural adjustments of microorganisms to changes in its environment (EPA, 1999). The acclimation process was applied to maximize the efficiency of biodegradation of bioresistant compounds. In this process over a period of time, increasing concentration of the compound of interest was introduced as feed to microorganisms and makes them to gradually utilize the compound as a carbon source (Scott and Ollis, 1995). As MTBE is not known as a readily used carbon source by microorganisms, a previous process of acclimatization was necessary to be carried out.

To achieve the endpoint concentration of 30 mg/L MTBE for acclimation procedure, the bioreactor was primarily filled with 7 L synthetic wastewater containing 10 mg/L MTBE and 5 mg/L sodium acetate as carbon sources, which had BOD_5 of 4 mg/L. To ensure adequate nutrients for microorganisms, the ratio of BOD: N: P equal to 100: 5: 1 was provided in the solution by addition of 3 ml phosphate buffer with supplementary

nutrients including 1.5 ml of each magnesium sulphate, calcium chloride, and ferric chloride. The same amounts of these nutrients were added whenever the wastewater was refreshed until the end of the acclimatization period. For microbial growth in the solution, it was inoculated with activated sludge. Microbial growth was tracked by the measurement of MLVSS (Section 3.5.8). The bioreactor operated at room temperature, which was $25 \pm 1^{\circ}C$. To ensure the adequate aeration in the bioreactor, DO was daily monitored which was in the range of 7.15 to 8 mg/L and confirmed the presence of aerobic condition in the SBR. To acclimatize the microorganisms to MTBE, a feeding strategy was applied by which the introduction of increasing concentrations of this substrate to the reactor was defined during acclimation period. In this way, 10 mg/L of MTBE and 5 mg/L of sodium acetate were introduced to SBR in the first day and as acclimation proceeded, the concentration of MTBE was increased 1 mg/L and of sodium acetate was decreased 0.25 mg/L per successive additions (Figure 3.3). Steady state was assumed to be achieved when the MTBE concentration in the bioreactor became constant and close to zero. At the time, new mixture of MTBE and sodium acetate was added and samples were taken for measurement of BOD_5. This process was continued until the concentration of MTBE and sodium acetate in the feed reached to 30 and 0 mg/L, respectively. This process took more than 50 days. The acclimatization was finally attained when removals of MTBE with initial concentration of 30 mg/L in different conducted experiments were similar.

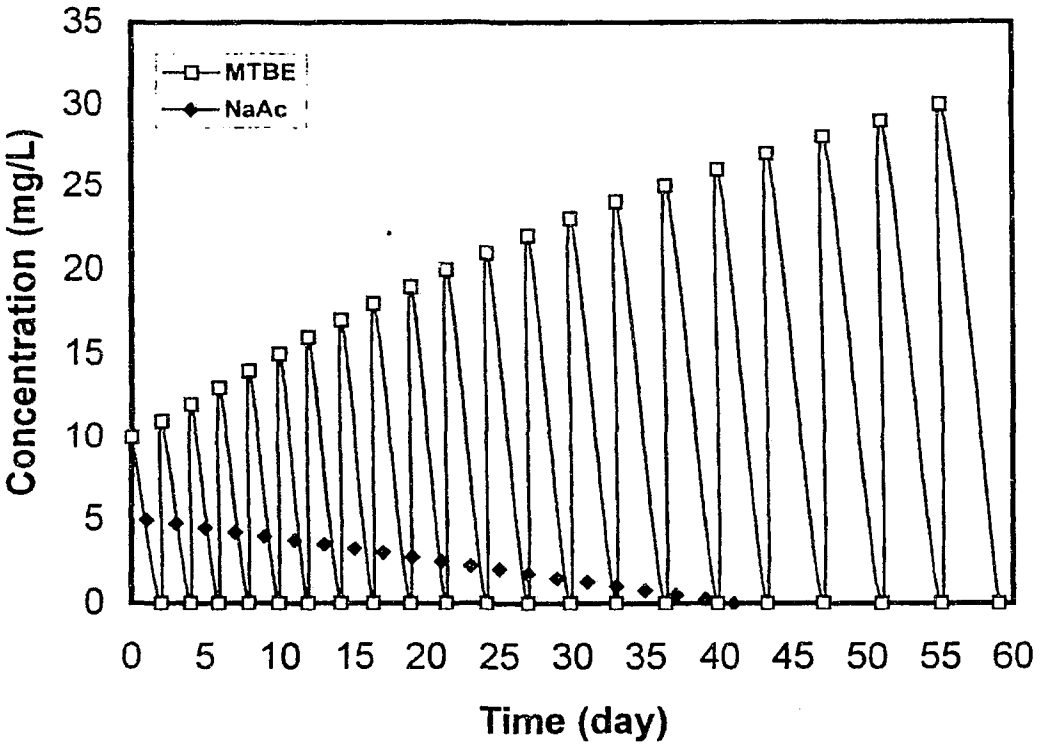

Figure 3.3. Schematic diagram of MTBE and sodium acetate (NaAc) changes during the acclimatization period of microorganisms taken from activated sludge unit of municipal wastewater treatment plant of Toronto.

3.2.2.3.2. Biodegradation Experiments

After the acclimation phase, the feasibility of the remained biomass for biodegradation of MTBE was investigated. For this purpose, the 7-L batch reactor was applied as a sequential batch reactor (SBR). Following a 10-h settlement, the remaining solution in the bioreactor was removed. To compensate the discharge of nutrients with discharge of supernatant, phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride were added to fresh MTBE solution to supply the suggested ratio of BOD: N: P. A fill-and-draw cycle was considered at room temperature. A complete cycle began with a 6-h aerated fill period, in which fresh MTBE solution with concentration of 30 mg/L and nutrients were introduced to the bioreactor, and followed by a 65-h react period including aeration and mixing. The amount of MTBE was determined in specific time intervals of 10-15 hours. This period lasted until the desired concentration of MTBE was achieved. To avoid biomass losses, 7 hours was dedicated to the settle period without any aeration or mixing. A clear supernatant was obtained after this period, which was the treated effluent. The process continued by 3.5-h draw period with no aeration and mixing, in which the treated effluent was removed from the reactor. The cycle ended by idle phase of 3.5 hours without any mixing and aeration. MTBE, MLVSS, DO, BOD, COD and pH were the parameters obtained to evaluate the performance of the process. The trend of degradation of MTBE during this process is shown in Figure 4.31.

3.3. Combination of Photocatalytic and Biological Processes for the Degradation of MTBE in Water

The removal of MTBE was performed by the combined processes of photochemical and biological treatment. The decomposition of MTBE was carried out by photocatalytic reaction as a pre-treatment followed by biodegradation. For this purpose, the effluent obtained from photoreactor was introduced into the biological reactor.

Initial concentration of 50 mg/L MTBE and 1.5 g/L TiO_2 were introduced to the photoreactor. Experiments were conducted in the same way that has been described before (Section 3.1.2) for a 1.5-h period of time. In a similar way to that for the single biological process (Section 3.2.2.3.2), the supernatant of centrifuged pre-treated solution was fed into the SBR, which was the final MTBE concentration in photoreactor and its initial concentration in biological experiments (Figure 3.4).

3.4. Materials and Analytical Techniques

3.4.1. Reagents and Materials

HPLC grade MTBE, *tert*-butyl alcohol (TBA, $C_4H_{10}O$), and *tert*-butyl formate (TBF, $C_5H_{10}O_2$), as intermediates, were obtained from Aldrich Co. (Canada). Dionized water produced by ~~produced by~~ MILLI-RX-75 deionizer was used for all experiments. BOD seed inoculum's capsules (Polyseed microorganisms) were obtained from InterLab Co. (VWR, Canada). For COD tests, 16 mm Accu - TEST twist-cap vials with digestion

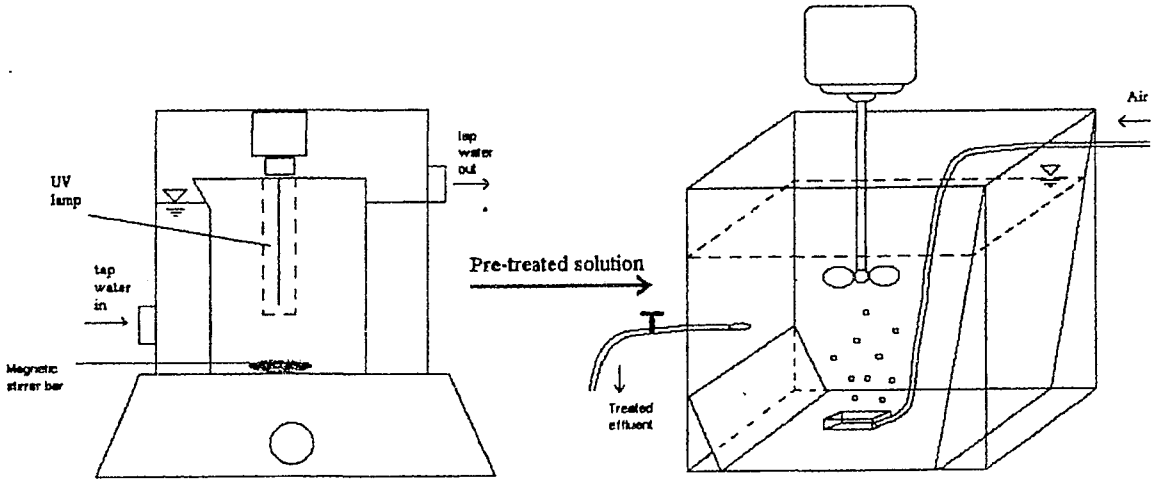

Figure 3.4. Schematic diagram of experimental set-up for the combined photochemical and biological processes.

reagent were purchased from BioScience Inc. TiO_2 Degussa P25 was obtained from Kontrollnummer (Germany). DMP and Catalase were purchased from ACROS and Sigma, respectively. H_2O_2 50% wt solution in water, all chemicals for BOD experiments and for H_2O_2 measurement were obtained in reagent grade from Aldrich, Canada.

3.5. Analytical Techniques

3.5.1. Determination of MTBE Concentration

MTBA concentrations were analyzed by GC with conditions as follows: MTBE was transferred from 10 ml aqueous samples to the vapour phase by bubbling an inert gas, He, for 11 min through the aqueous samples contained in purging chamber of a Tekmar 2016 purge and trap autosampler at ambient temperature. After completion of purging, the trap was heated and the compound was desorbed and transferred into a DB-WAX column ($30m \times 0.25mm \times 0.5\mu m$) in a Perkin Elmer Autosystem XL, which was equipped with flame ionization detector. Both the injector and detector temperatures were set at 300°C. The temperature of the oven was set at 45°C and remained constant for 15 min. Helium was used as the carrier gas with the flow rate of 1-2 ml/min. The retention time for MTBE was at 2.73 min (Figure 3.5).

3.5.2. pH

Buffer solutions with pH 4 and 7 were used each day to calibrate the pH meter before the beginning of experiments because they bracketed the expected sample range. pH was monitored with a Thermo Orion model 230A plus.

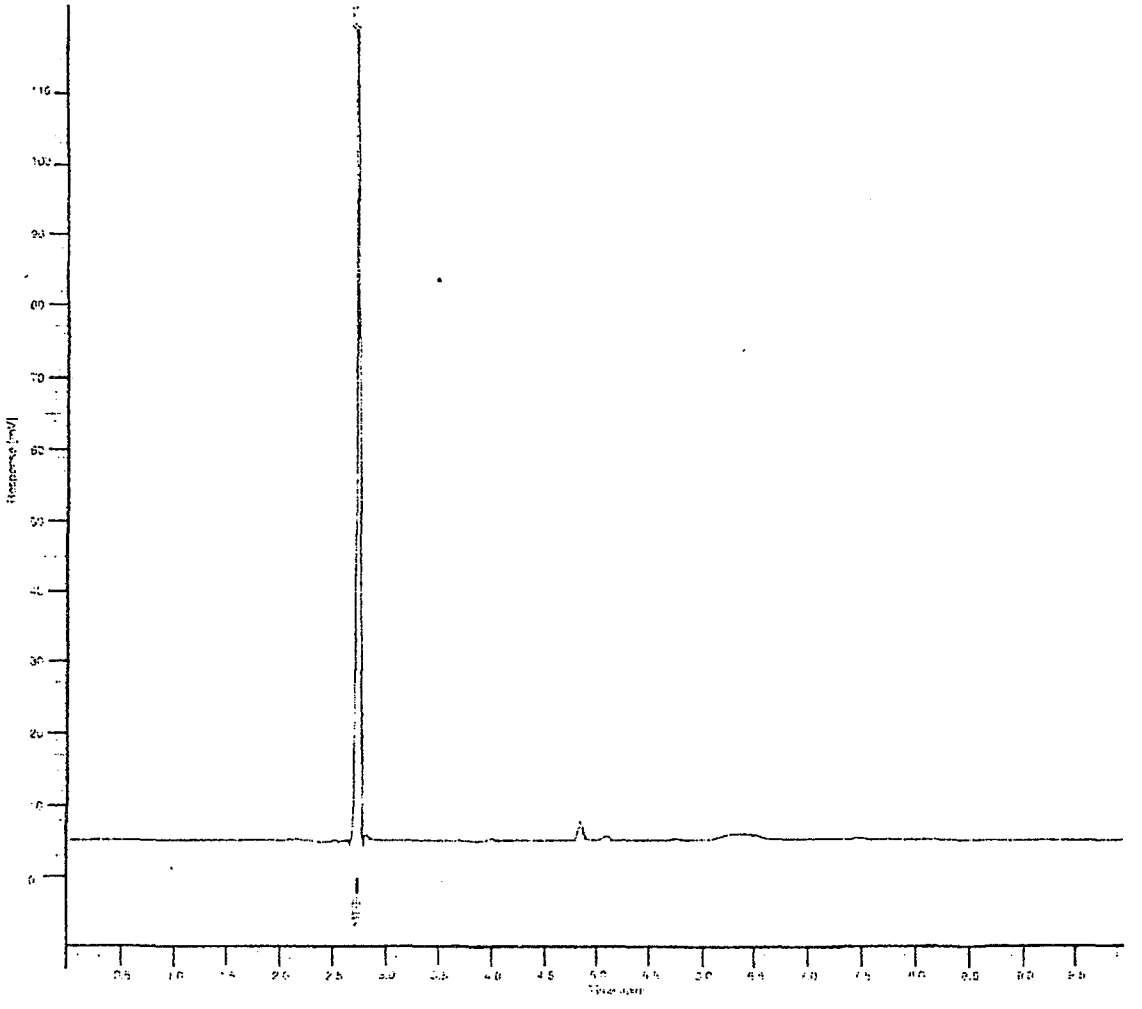

Figure 3.5. GC chromatogram for identification of MTBE in the solutions.

3.5.3. H_2O_2

H_2O_2 in the range of 2-500 μM was determined by 2,9-dimethyl-1,10-phenantroline (DMP) method (Kosaka et al., 1998). Different standard solutions of H_2O_2 were prepared by addition of its desired amount to distilled water. By dissolving of 1 g DMP in 100 ml ethanol, DMP reagent was made and stored in a brown bottle at 4°C. By dissolving copper (II) sulphate pentahydrate in water, a 0.01 M copper (II) sulphate solution was prepared. 13.5 g K_2HPO_4 and 12 g NaH_2PO_4 were added to water to make 0.1 M phosphate buffer and then its pH was adjusted to 7.0 by H_2SO_4 1 N and NaOH 1 N. In a 10-ml volumetric flask, 1 ml each of DMP, copper (II) sulphate, phosphate buffer and 3 ml of desired standard solution of hydrogen peroxide was added. Flask was filled up with distilled water and solution was mixed. Blank solution contained 1 ml DMP reagent, 1 ml copper (II) sulphate, and 1 ml phosphate buffer and was filled up with distilled water. By comparing the absorbance of blank and standards at 454 nm in a Biochrom spectrophotometer model Ultrospec 1100pro a calibration curve was obtained, which was used further for determination of H_2O_2 in samples (Figure 3.6).

3.5.4. H_2O_2 Removal

To stop the reaction by hydrogen peroxide and to remove its detrimental effect on microbial culture, H_2O_2 had to be decomposed by catalase. In this experiment, the used catalase with molecular weight of 250,000 was bovine liver type and was purchased from SIGMA Company. H_2O_2 with 200 mg/L concentration was removed by addition of 2.5 unit of catalase per ml of solution. Each mg of catalase was equivalent to 2380 units. The solution was kept for 2 hours without mixing and the concentration of H_2O_2 was

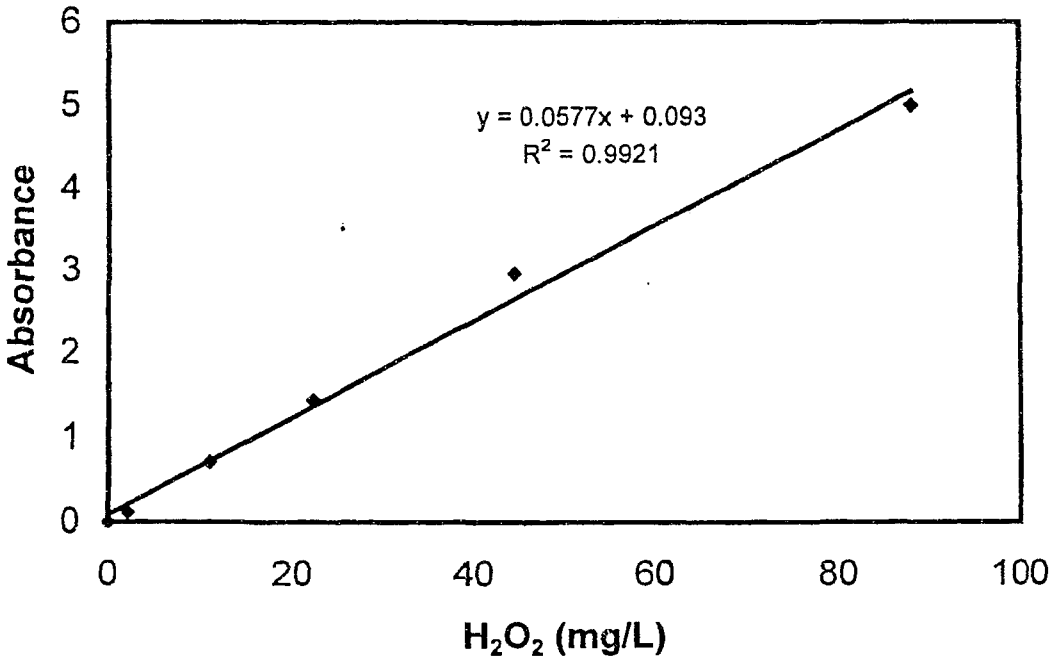

Figure 3.6. Calibration curve for determination of H_2O_2. Absorbance is equal to logarithm of the ratio of incident light to transmitted light and is a measure of the amount of light absorbed by a solution.

measured to ensure its complete removal (Ito et al., 1998).

3.5.5. Chemical Oxygen Demand (COD)

To measure the oxygen equivalent to the organic matter content of a sample, COD tests were used. In this method, organics were oxidized by $K_2Cr_2O_7$ in acidic condition, which was provided by sulphuric acid in follow reaction:

$$C_nH_aO_bN_c + dCr_2O_7^{-2} + (8d+c)H^+ \rightarrow nCO_2 + (a+8d-3c)/2H_2O + cNH_4^+ + 2dCr^{3+} \quad (3.1)$$

Where d = 2n/3 + a/6 – b/3 – c/2. Usually 0.25 N solution of potassium dichromate is used for COD determination, although for samples with COD below 50 mg/L a lower concentration of potassium dichromate is preferred. In this experiment, 2.5 ml of sample solution was added into COD vials contained sulphuric acid, potassium dichromate, silver sulphate (catalyst), mercuric sulphate and sulphamic acid. After screwing the cap, vials were placed in the heater block of an Accu-TEST COD reactor (BioScience, Inc.) at 150°C for 2 h. Then, unopened vial was put into the light path of a Biochrom spectrophotometer model Ultrospec 1100pro, which was set at 600 nm. The absorbance was measured and compared to the calibration curve and corresponding amount of COD was reported in mg/L (Figure 3.7). Standard solution had been prepared by dissolving of 425 mg of potassium hydrogen phthalate (KHP) in 1000 ml distilled water, which had a theoretical COD of 500 mg/L O_2. Different concentrations for standard solutions were prepared by dilution of this solution (Standard methods for the examination of water and wastewater, 1998).

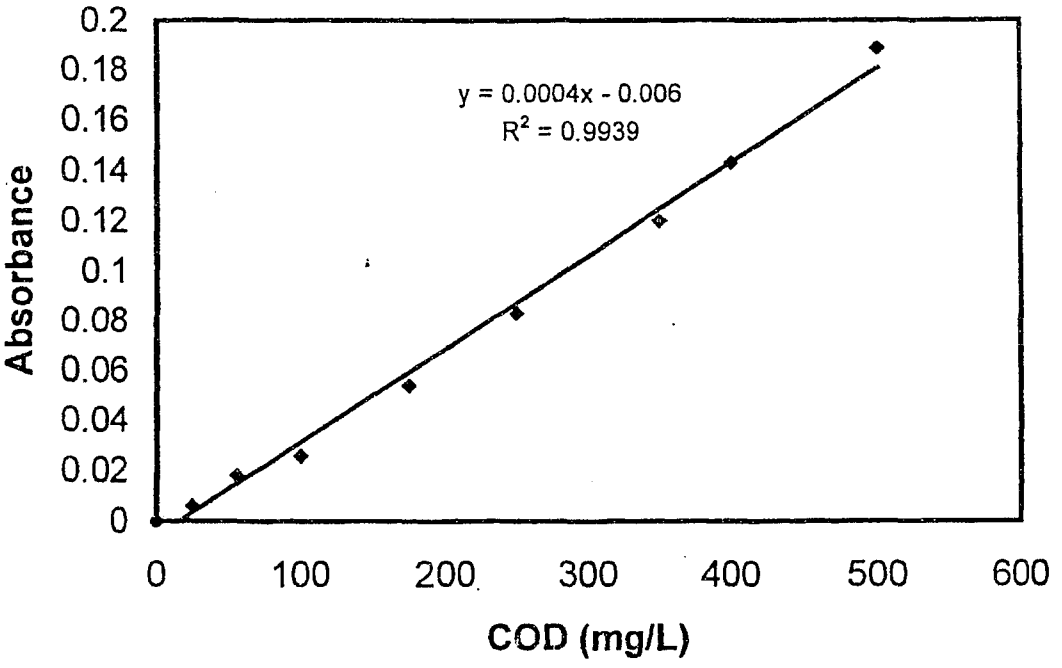

Figure 3.7. Calibration curve for determination of COD. Absorbance is equal to logarithm of the ratio of incident light to transmitted light and is a measure of the amount of light absorbed by a solution.

3.5.6. Dissolved Oxygen (DO)

Dissolved oxygen was measured by a YSI dissolved oxygen meter model 58 equipped with a YSI 5739 field probe. Each day before the beginning of experiments, DO meter was adjusted to obtain a meter reading corresponding to the calibration value for the local altitude.

3.5.7. Biological Oxygen Demand (BOD)

BOD tests were performed according to the Standard Methods for the Examination of Water and Wastewater (Standard Methods for the Examination of Water and Wastewater, 1998). For this purpose, phosphate buffer solutions were prepared by dissolving 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4.7H_2O$, and 1.7 g NH_4Cl in about 500 ml distilled water and diluted to 1 L. Magnesium sulphate solution was made by dissolving 22.5 g $MgSO_4.7H_2O$ in distilled water and diluted to 1 L. Calcium chloride solution was prepared by dissolving 27.5 g $CaCl_2$ in distilled water and diluted to 1 L. Ferric chloride solution was prepared by dissolving 0.25 g $FeCl_3.6H_2O$ in distilled water and diluted to 1 L. For preparation of dilution water, 1 ml of each phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solution was added per litre of desired volume of distilled water and saturated with DO by aerating before BOD experiments.

3.5.7.1. Seeding

To provide a population of microorganisms to oxidize the organic matters, one capsule of polyseed, containing 100 mg of special microbial cultures capable of

degradation of industrial and municipal wastes, was added to 500 ml of distilled water and was aerated for 30 minutes before BOD experiments.

3.5.7.2. Filling the BOD Bottles

Since BOD_5 tests were conducted for various concentrations of MTBE, different volumes of MTBE solutions were used in each test. Necessary volume of samples was added to 300-ml BOD bottles individually. 5 ml of aerated seed material was added to each bottle and the bottle was filled with aerated dilution water. Initial DO measurement was performed by DO meter. As a rough check of experimental conditions, a dilution water blank including only seed material and dilution water in BOD bottle was used with each batch of samples. Bottles of samples were incubated in a New Brunswick scientific C25KC incubator at 20°C without any shaking. After 5 days, the final DO of samples and blank were measured and BOD_5 was calculated. A sample of calculation of BOD_5 is provided in Appendix A.

3.5.8. Mixed Liquor Volatile Suspended Solid (MLVSS)

A well-mixed sample of sludge was filtered through a weighed 934-AH Whatman glass microfiber filter (Made in England by W & R Balston Limeted) by using buchner funnels connecting to vacuum system. Removed from filtration apparatus, filter was transferred to an aluminium-weighing dish and placed in an oven at 103-105°C for 1 hour. Dried filter was weighed. By considering the weight of filter paper and the volume of sample, the total suspended solid (TSS) was determined in mg/L (Standard Methods for the Examination of Water and Wastewater, 1998):

$$TSS(mg/L) = \frac{Weight\ \ of\ \ dried\ \ filter(mg)}{Volume\ \ of\ \ sample(L)} \qquad (3.2)$$

Mixed Liquor Volatile Suspended Solid (MLVSS) was calculated as 80% of TSS in each sample (Metcalf and Eddy, 1991).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Photochemical Treatment of MTBE

4.1.1. Dark Reaction

A series of control experiments were conducted to quantify the loss of MTBE through volatilization or oxidation by dissolved oxygen. In these dark experiments, solutions of MTBE were stirred in the reactor without UV lamp, H_2O_2, or TiO_2 for 5 hours to verify if other processes such as volatilization or adsorption contribute to MTBE disappearance. A cooling system around the reactor maintained the temperature at 15-20°C. The results of these experiments are depicted in Figure 4.1. These experiments indicated only 5% decrease of MTBE during 5 hours, which is negligible.

Since UV lamp produces heat in the photoreactor, the necessity of cooling system was indicated by conducting a dark reaction experiment along with a heating system (instead of cooling system) with the same heating trend that UV lamp produced during the reaction. The temperature examined in the range of 20-41°C accelerated the rate of disappearance. 95% loss of MTBE in 5 hours was observed, which can be the result of volatilization (Figure 4.2). It is found that the Henry's law constant is temperature dependent and generally increases with increasing temperature. This fact caused less solubility of MTBE in water with increasing the temperature and, therefore, resulted in its high disappearance in the solution. This control test showed that constant temperature

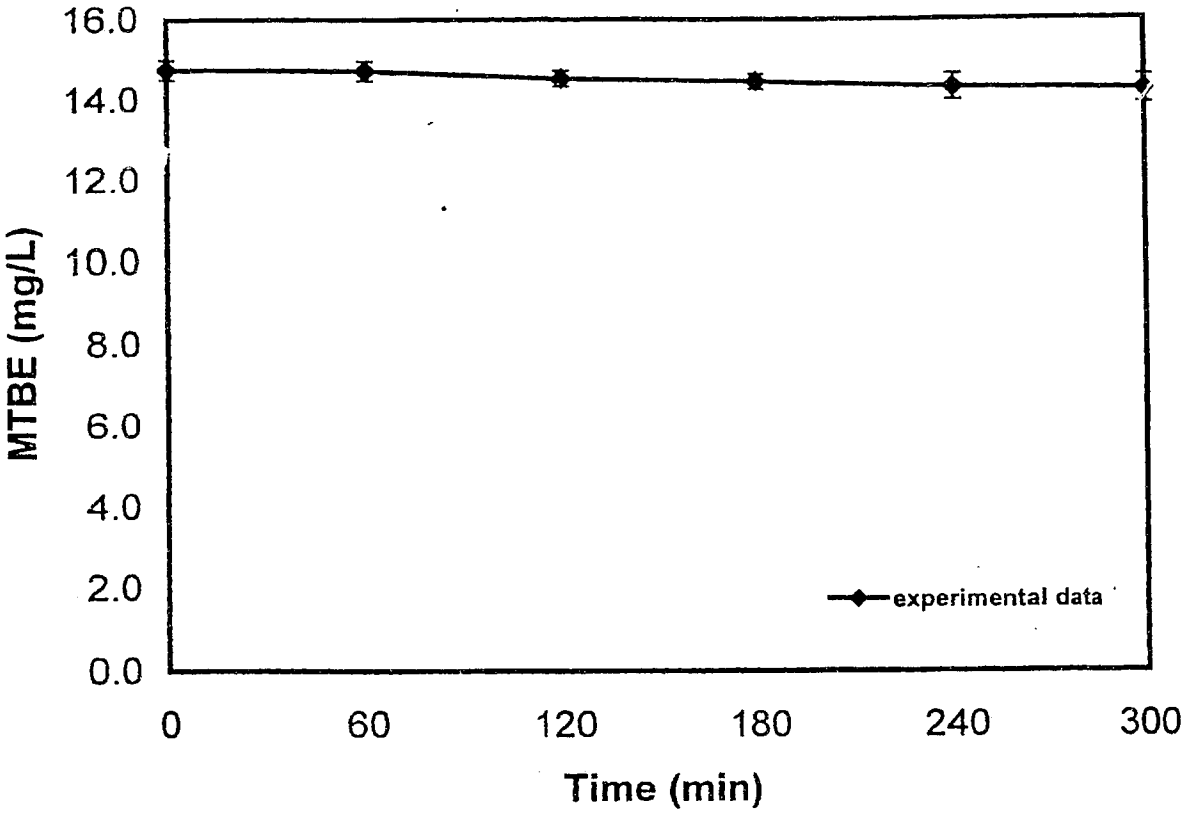

Figure 4.1. Removal of MTBE in dark reaction. $C_{o,\,MTBE}$=15 mg/L, no UV lamp, TiO_2, and H_2O_2 were used. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

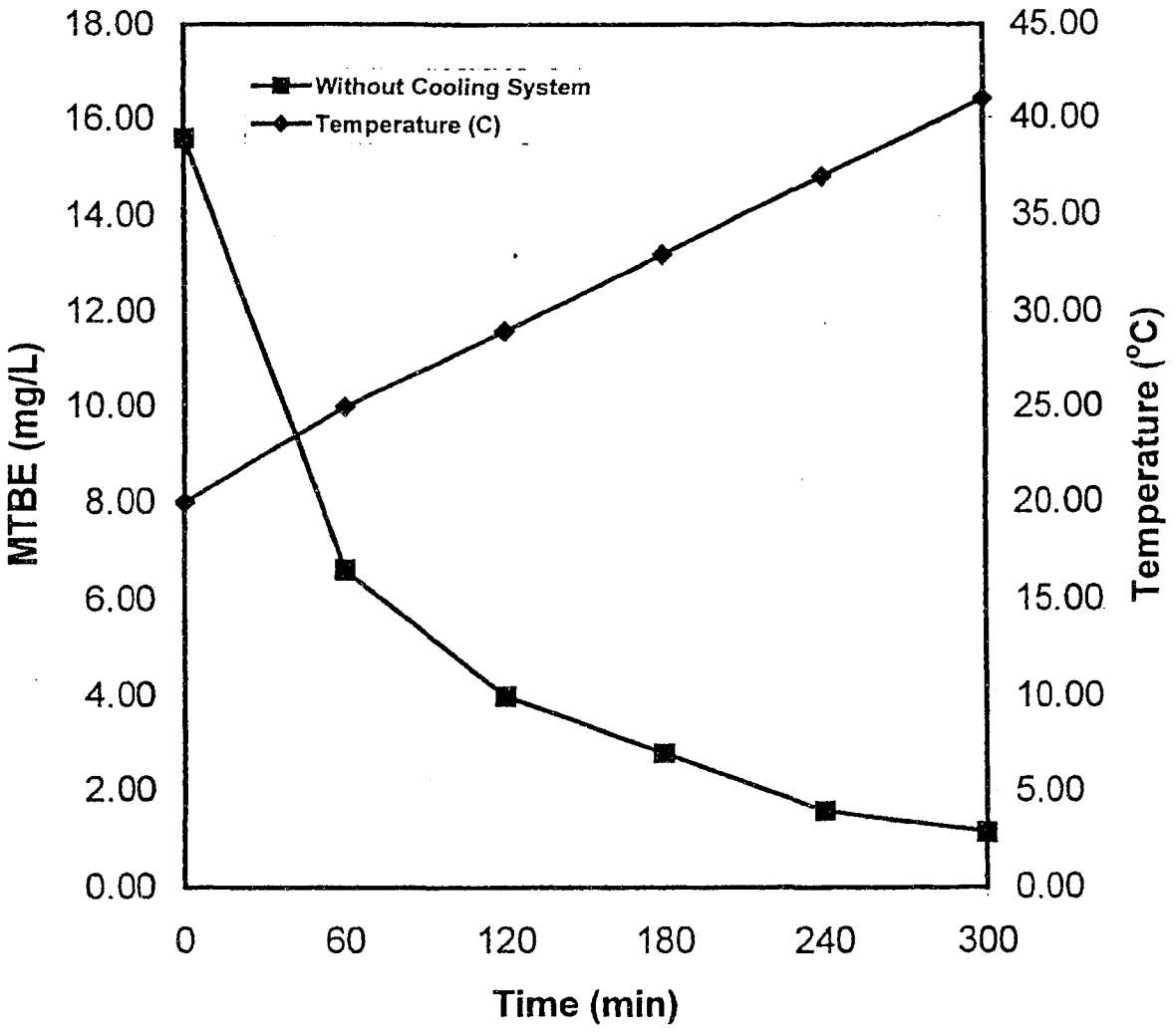

Figure 4.2. Removal of MTBE in dark reaction without cooling system. $C_{o,\,MTBE}$ =15 mg/L, no UV lamp, TiO_2, and H_2O_2 were used. A heating system was used to keep the heating trend the same as what UV lamp produced.

was necessary for these series of experiments.

4.1.2. Photoreaction

In order to determine whether photolysis contributes to MTBE degradation, its solutions were put in contact with UV light. As Stefan et al. (2000) reported MTBE does not absorb UV light greater than 200 nm, so direct photolysis of MTBE does not occur. Figure 4.3 shows the disappearance of MTBE due to photolysis by 254 nm UV light. Almost 10% decrease in the residual of MTBE was observed with UV light illumination during 5 hours. It may arise from oxidation by oxygen and volatilization. These results point out that photolysis of MTBE is not an appropriate way for its removal.

4.1.3. The Effect of Hydrogen Peroxide on MTBE Degradation

The effect of H_2O_2 on the MTBE solution in the absence and presence of the UV light (Figure 4.4) was examined. As illustrated in Figure 4.4, dark experiments conducted on a mixture of MTBE/H_2O_2 did not show any significant reaction between the two compounds and less than 10% of MTBE was disappeared after 4 hours.

4.1.3.1. Combination of UV Light and H_2O_2

In the next step, the photodegradation of MTBE, with the aim to investigate the effect of a supplementary oxidant was conducted. The use of a strong oxidant such as H_2O_2 improved the single UV radiation efficiency and considerably increased the destruction of MTBE. Considering the facts of negligible decrease of MTBE by UV and H_2O_2 alone and H_2O_2 photoactivity at 185-400 nm, it can be concluded that

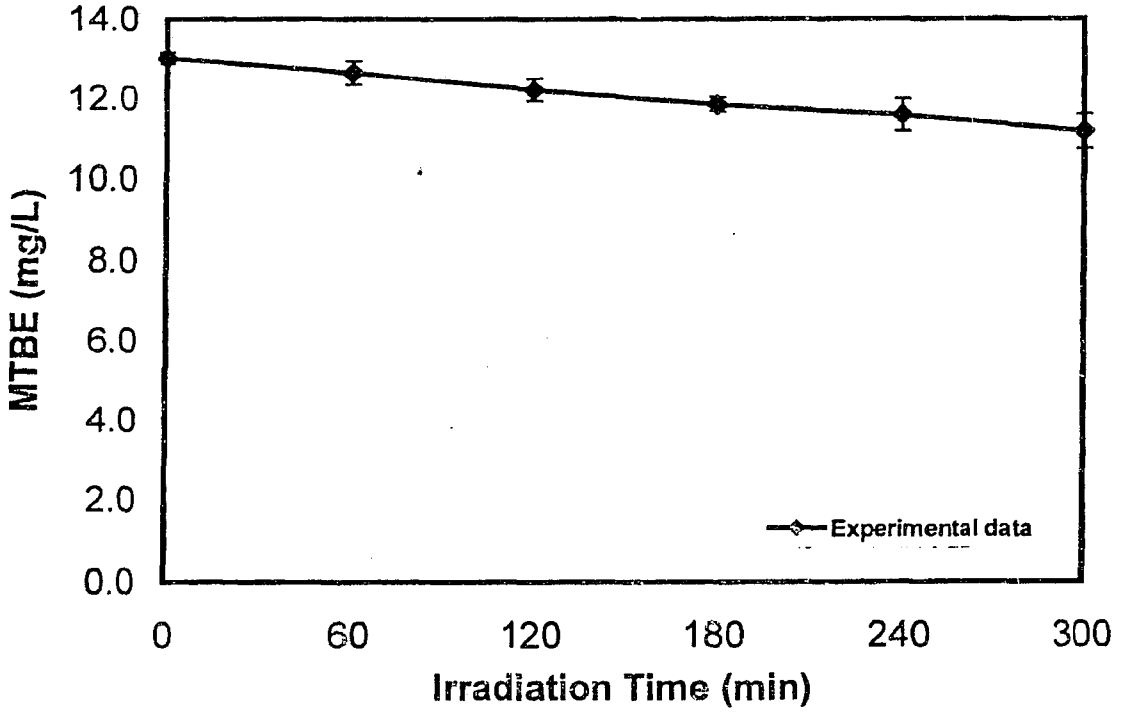

Figure 4.3. Removal of MTBE by UV-254. $C_{o,\,MTBE}$ = 13 mg/L, no TiO_2 and H_2O_2 was used. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

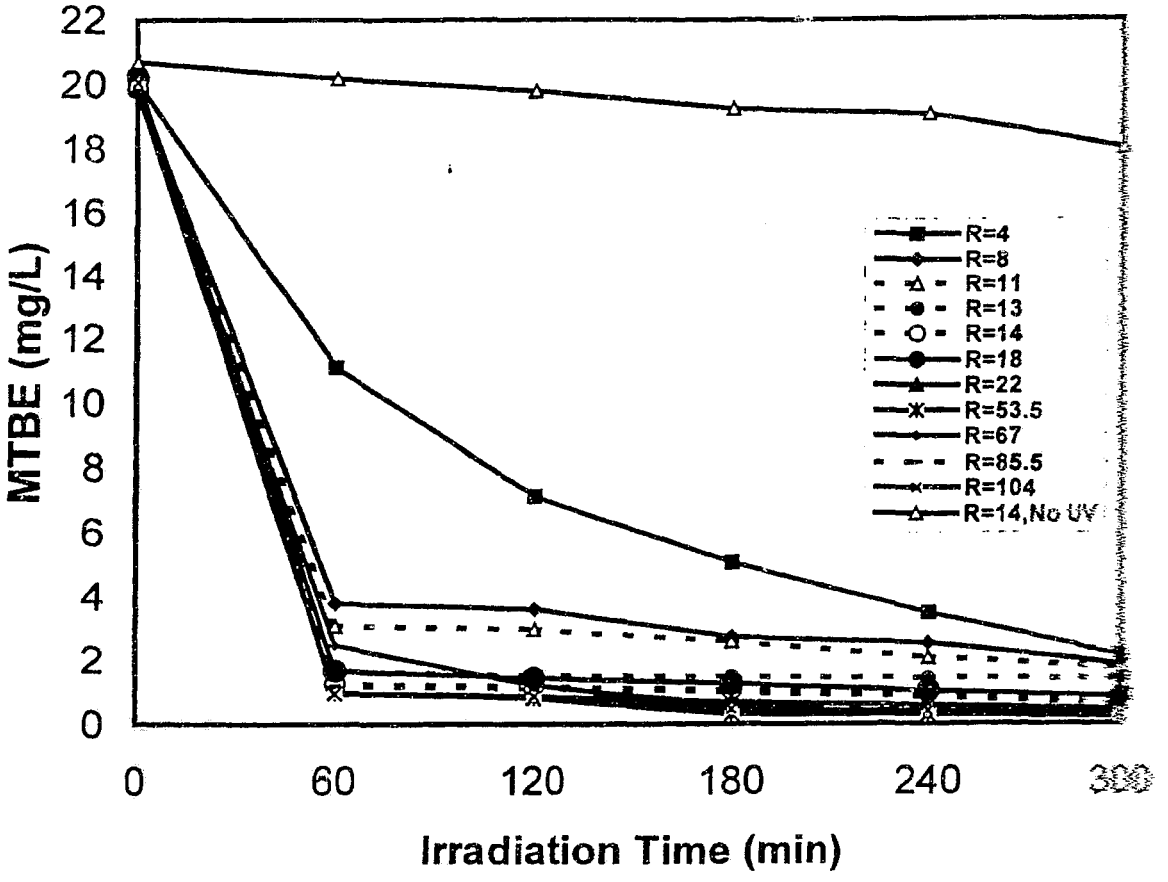

Figure 4.4. Removal of MTBE by H_2O_2 and UV-254/H_2O_2 with various molar ratio of H_2O_2 / MTBE. $C_{o,\,MTBE}$ = 20 mg/L, $C_{o,\,H2O2}$ = 0.9 - 24 mM, R = Molar ratio of $[H_2O_2]$ / [MTBE] = 4-104. A cooling system was used to keep the temperature constant at 15-20°C.

degradation process must occur by direct photolysis of H_2O_2. Because of the increased amount of hydroxyl radicals, combination of UV and H_2O_2 results in more rapid degradation of MTBE according to the following reaction:

$$H_2O_2 \xrightarrow{h\nu<400nm} 2^{\bullet}OH \qquad (4.1)$$

At low concentrations of H_2O_2, it can absorb light, but not sufficient $^{\bullet}OH$ is produced. Increasing concentration of H_2O_2 increases the absorbance, which in turn increased the production of $^{\bullet}OH$. Hydroxyl radicals enhanced significantly the reduction of MTBE in the range 90-98%. The initial concentration of MTBE was 20 mg/L and the concentration of H_2O_2 was in the range of 0.9-24 mM, therefore, the molar ratio of H_2O_2 to MTBE was in the range of 4-104. In all cases, more than 90% conversion was observed during the first hour of irradiation followed by a very slow rate of degradation (Figure 4.4). This phenomenon can be justified by the production of hydroperoxyl radicals ($HO_2^{\bullet}$), which are much less reactive than hydroxyl radicals.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (4.2)$$

Another speculation, which can contribute to the decrease of the rate of the reaction is the influence of by-products through their competition for either scavenging the hydroxyl radicals or absorbing the UV light. *tert*-butyl alcohol (TBA) and *tert*-butyl formate (TBF) are two major by-products of MTBE decayed by UV/H_2O_2 (Stefan et al., 2000). Hardison et al. (2002) reported the rate constant of $(4.1\pm0.2)\times10^8$ $M^{-1}s^{-1}$ for

reaction of TBF with hydroxyl radicals, and the attack of these radicals on TBA occurs at rate constant of 6×10^{8} $M^{-1}s^{-1}$ (Stefan et al., 2000), which are similar to that of MTBE reaction with hydroxyl radicals (2×10^{9} $M^{-1}s^{-1}$).

4.1.3.2. The Effect of H_2O_2 Concentration on MTBE Degradation

Since $^{\bullet}OH$ reacts with H_2O_2, the selection of appropriate concentration of H_2O_2 is important to minimize the loss of process efficiency. Optimum concentration of H_2O_2 was obtained by the comparison between the percentages of degraded MTBE with different amounts of H_2O_2. It was observed that the molar ratio of H_2O_2 to MTBE had more effect on MTBE degradation than only concentration of H_2O_2. Figure 4.5 shows that the optimum molar ratio of H_2O_2 to MTBE was 14. Balanced equation of the reaction between MTBE and H_2O_2 shows that theoretically for complete mineralization the molar ratio of 15 is required, which confirms the accuracy of obtained result:

$$C_5H_{12}O(aq)+15H_2O_2(aq)\rightarrow 5CO_2(g)+21H_2O(l) \qquad (4.3)$$

The initial rate of reaction reached a plateau with increasing the molar ratio of H_2O_2 to MTBE, likely because the extra H_2O_2 competed with MTBE for the hydroxyl radicals and scavenges them by the following reaction:

$$H_2O_2+{}^{\bullet}OH\rightarrow HO_2{}^{\bullet}+H_2O \qquad (4.4)$$

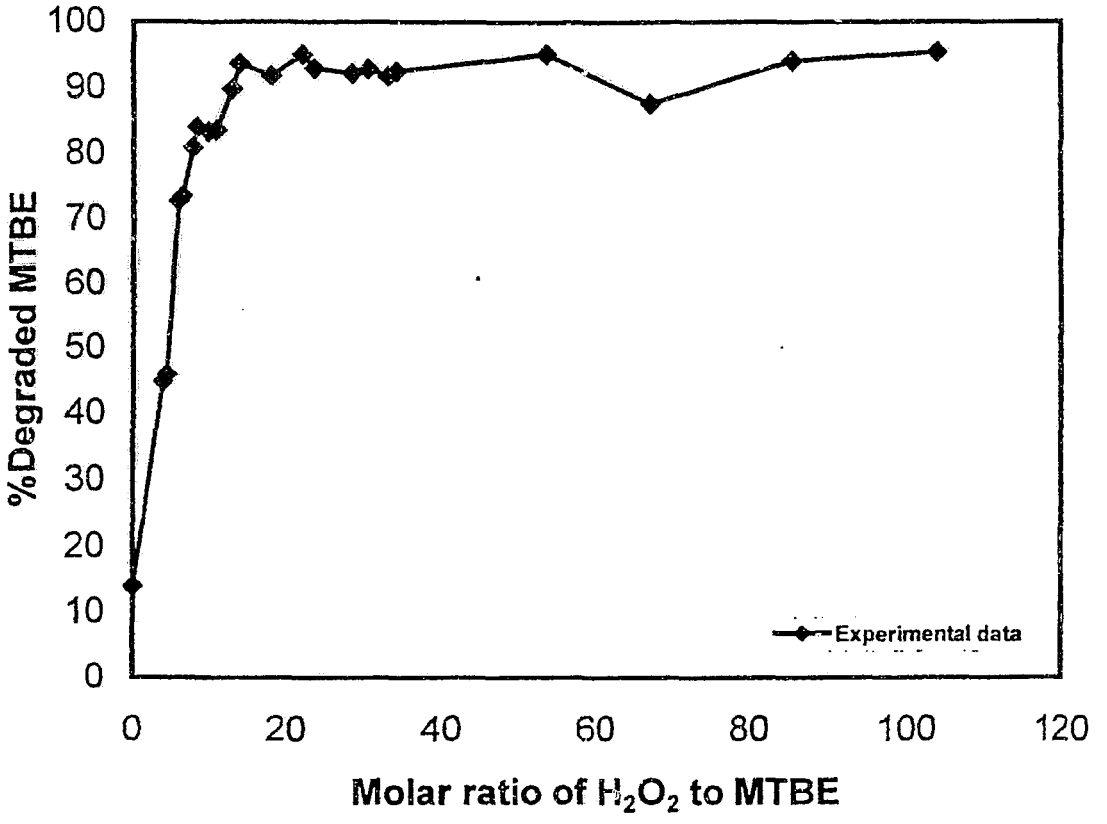

Figure 4.5. Effect of molar ratio of H_2O_2/MTBE on the photodegradation of MTBE using UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 20 mg/L, $C_{o,\,H2O2}$ = 0.9 - 24 mM corresponded to the molar ratio of [H_2O_2] / [MTBE] = 4-104. A cooling system was used to keep the temperature constant at 15-20°C.

In addition, the increase of H_2O_2 entailed the increase of intermediates, which may have higher absorption coefficient than that of H_2O_2 and act as an inner filters. The presence of such intermediates resulted in their competition with H_2O_2 for absorbing the UV light and, therefore, less light would be provided for H_2O_2 to absorb.

After determination of optimum molar ratio of H_2O_2/MTBE, a series of experiments were conducted by this optimum molar ratio to observe the removal of MTBE in details in one-hour period of time. For this purpose, the initial concentration of 30 mg/L MTBE with 155 mg/L H_2O_2 was considered to provide the molar ratio of H_2O_2/MTBE = 14. The samples were taken every 10 minutes for analysis. The obtained results showed more than 90% removal of MTBE in the first 20 minutes of reaction (Figure 4.6). One mechanism for hydrogen-abstraction is suggesting a radical attack to methoxy group of MTBE (Stefan et al., 2000):

$$H_2O_2 \leftrightarrow 2^{\bullet}OH \qquad (4.5)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + ^{\bullet}O_2H \qquad (4.6)$$

$$(CH_3)_3C-OCH_3 + ^{\bullet}OH \rightarrow (CH_3)_3C-OCH_2^{\bullet} + H_2O \rightarrow Products \qquad (4.7)$$

There are different pathways for reaction (4.7) that result in many different products, which are suggested in Stefan et al.'s study (2000). To find the kinetic rate constants for the initial photochemical degradation of MTBE in the presence of H_2O_2, more studies about the mechanisms of the reaction was necessary. In the lack of such information, the overall degradation rate constant was estimated by application of a mathematical model:

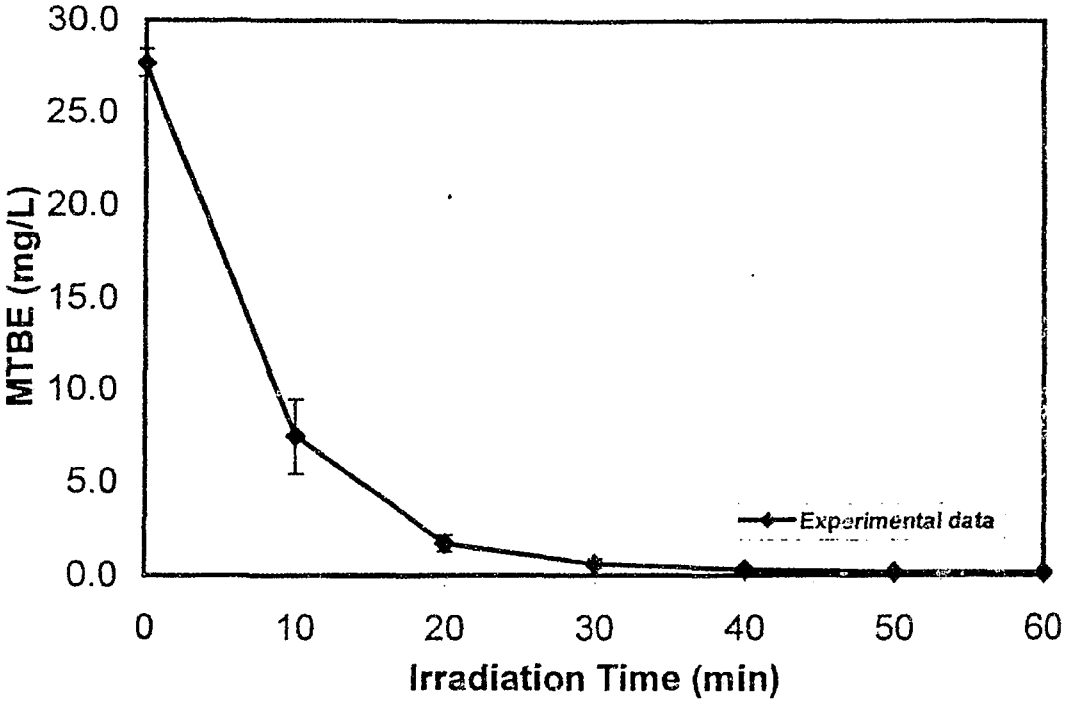

Figure 4.6. Removal of MTBE by UV-254/H_2O_2 in first 60 minutes of reaction. $C_{o,\,MTBE}$ = 30 mg/L, $C_{o,\,H2O2}$ = 155 mg/L, Molar ratio of H_2O_2 / MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

$$\ln C = \ln C_0 - kt \qquad (4.8)$$

Linear regression on natural logarithm of C/C_0 versus time showed consistency of experimental data with the model within 30 minutes of reaction but after this time, the data did not follow the first-order model completely. This discrepancy can be explained by the hypothesis of the competition between H_2O_2 and intermediates for both $^{\bullet}OH$ and UV light. As mentioned before, the rate constant for reaction of TBF and TBA with hydroxyl radicals are close to that of MTBE. On the other hand, intermediates such as acetone and oxalic acid, with absorption coefficients much higher than that of H_2O_2, can absorb UV light considerably and decrease the rate of reaction. In fact, the light absorbed by organics can be considered as wasted light. The apparent rate constant for degradation of MTBE by UV/H_2O_2 was attained during the first 30 minutes (Appendix C) (Figure 4.7), which was equal to 1.37×10^{-1} min^{-1}. Stefan et al. (2000) performed their experiments at molar ratio of H_2O_2/ MTBE equal to 18.26/ 0.92 and suggested a first-order reaction for decay of MTBE in 20 minutes by UV/H_2O_2 with rate constant of 3.47×10^{-1} min^{-1}. Disappearance of hydrogen peroxide within 5 hours followed a zero-order reaction with rate constant of 2.13×10^{-1} mg L^{-1} min^{-1} (Figure 4.8). In the same study, it was suggested a zero-order rate constant of 3.09×10^{-1} mg L^{-1} min^{-1} for consumption of H_2O_2 in a period of 80 minutes. It can be observed that during the first hour of reaction the amount of H_2O_2 was almost constant. The general form of the reaction between MTBE and H_2O_2 Can be defined by following equation:

$$A + B \rightarrow products \qquad (4.9)$$

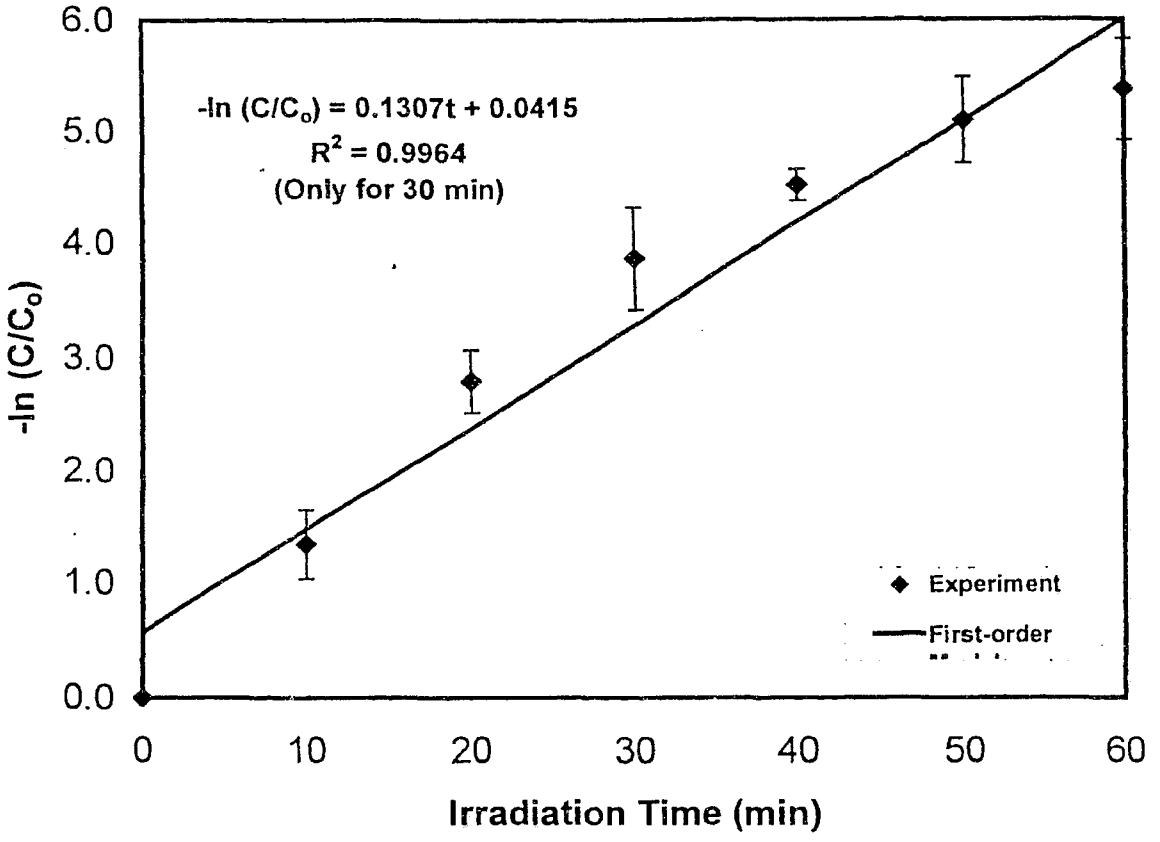

Figure 4.7. Degradation of MTBE by UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 30 mg/L, $C_{o,\,H2O2}$ = 155 mg/L, Molar ratio of H_2O_2 / MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

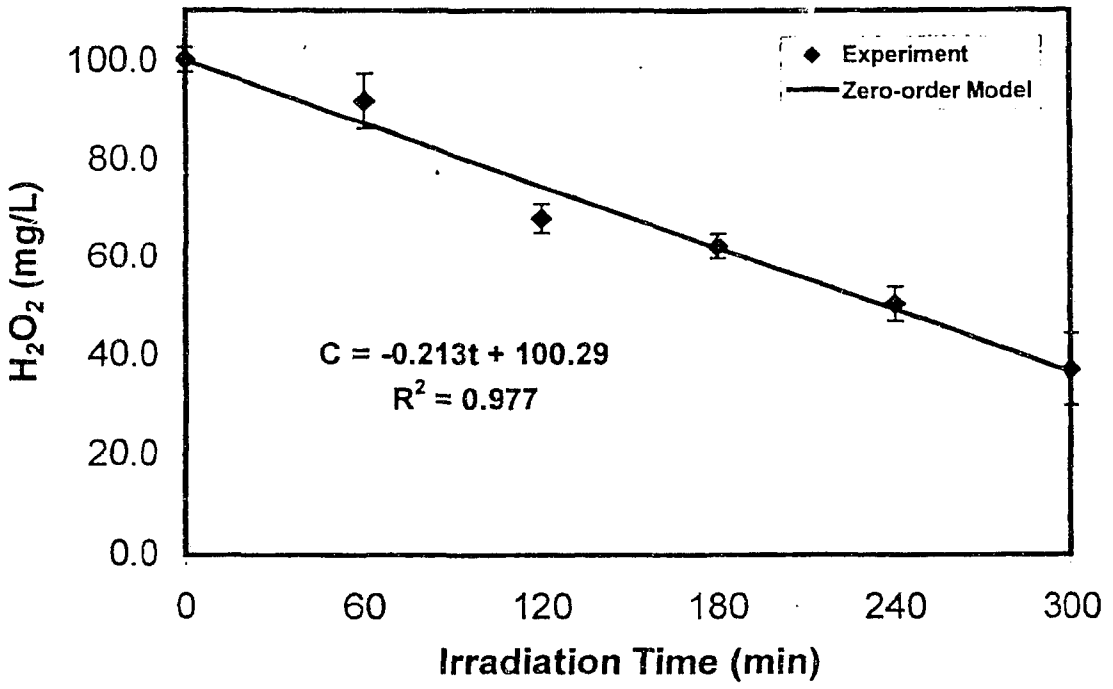

Figure 4.8. Disappearance of H_2O_2 in degradation of MTBE by UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 30 mg/L, $C_{o,\,H2O2}$ = 155 mg/L, Molar ratio of H_2O_2/MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

and the rate of reaction can be calculated as follows:

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = kC_A C_B \qquad (4.10)$$

$$\ln\frac{C_B C_{A_0}}{C_{B_0} C_A} = (C_{B_0} - C_{A_0})kt \qquad (4.11)$$

Since the amount of H_2O_2 was higher than that of MTBE, the degradation rate can turn to a first-order reaction with respect to MTBE. This explanation is consistent with the suggested models for both MTBE and H_2O_2.

Changes in MTBE along with the changes in COD are illustrated in Figure 4.9 A decrease of COD was observed during the time of reaction, which was the result of photooxidation of both MTBE and intermediates by UV/H_2O_2 process. Figure 4.11 also showed the decrease of pH, which can be the result of the formation of acidic compounds in the presence of UV/H_2O_2. Stefan et al. (2000) also confirmed the presence of short chain carboxylic acid such as pyruvic, oxalic and formic acid. The amount of BOD had a steady decrease. At the beginning of experiments, was 2 mg/L, changed to 1.5 mg/L within 60 minutes, which corresponded to BOD/COD ratio of 0.03 and 0.36, respectively (Figure 4.10). Assuming the suggested mechanism by Stefan et al. (2000), it can be interpreted that removal of MTBE was accompanied by the formation of its non-biodegradable intermediates And degradation of primary intermediates resulted in the formation of more biodegradable compounds such as formic, pyruvic, and oxalic acid,

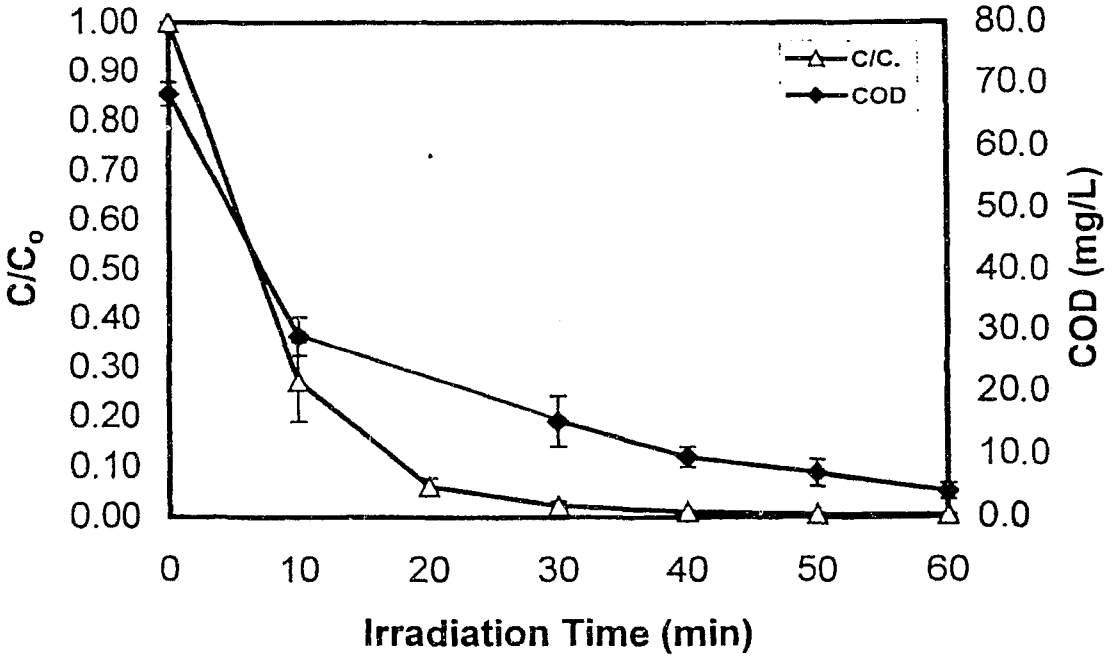

Figure 4.9. Changes of COD along with MTBE during the degradation of MTBE by UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 30 mg/L, $C_{o,\,H2O2}$ = 155 mg/L, Molar ratio of H_2O_2 / MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

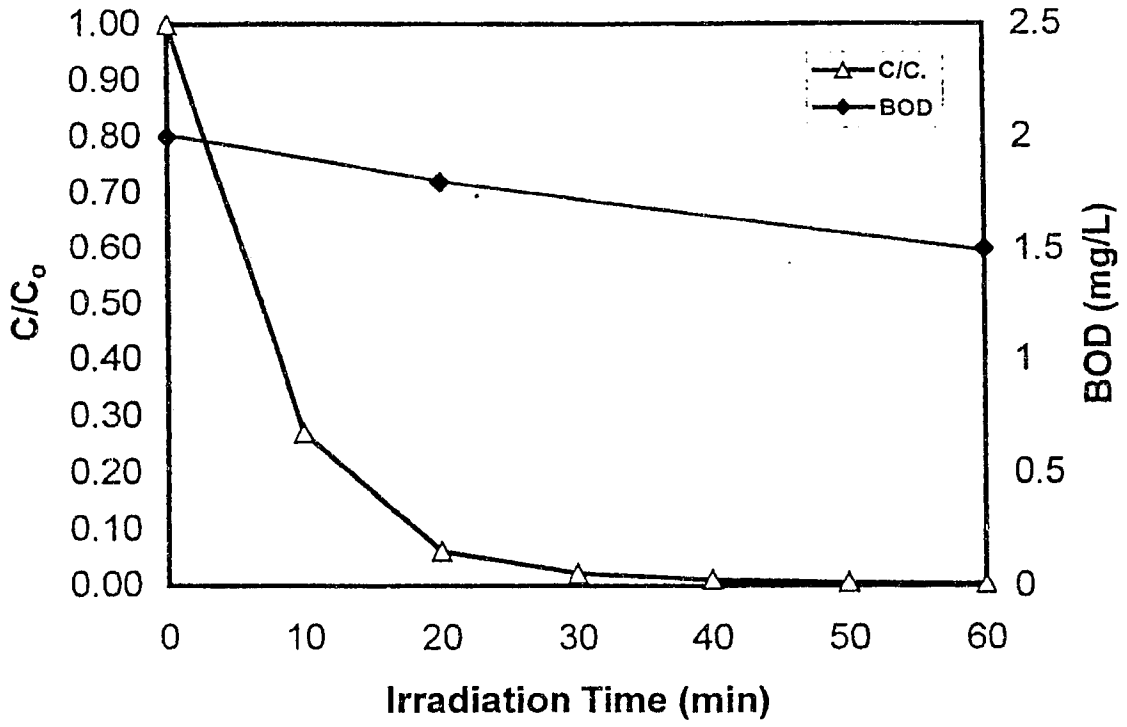

Figure 4.10. Changes of BOD during the degradation of MTBE by UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 30 mg/L, $C_{o,\,H2O2}$ = 155 mg/L, Molar ratio of H_2O_2 / MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C.

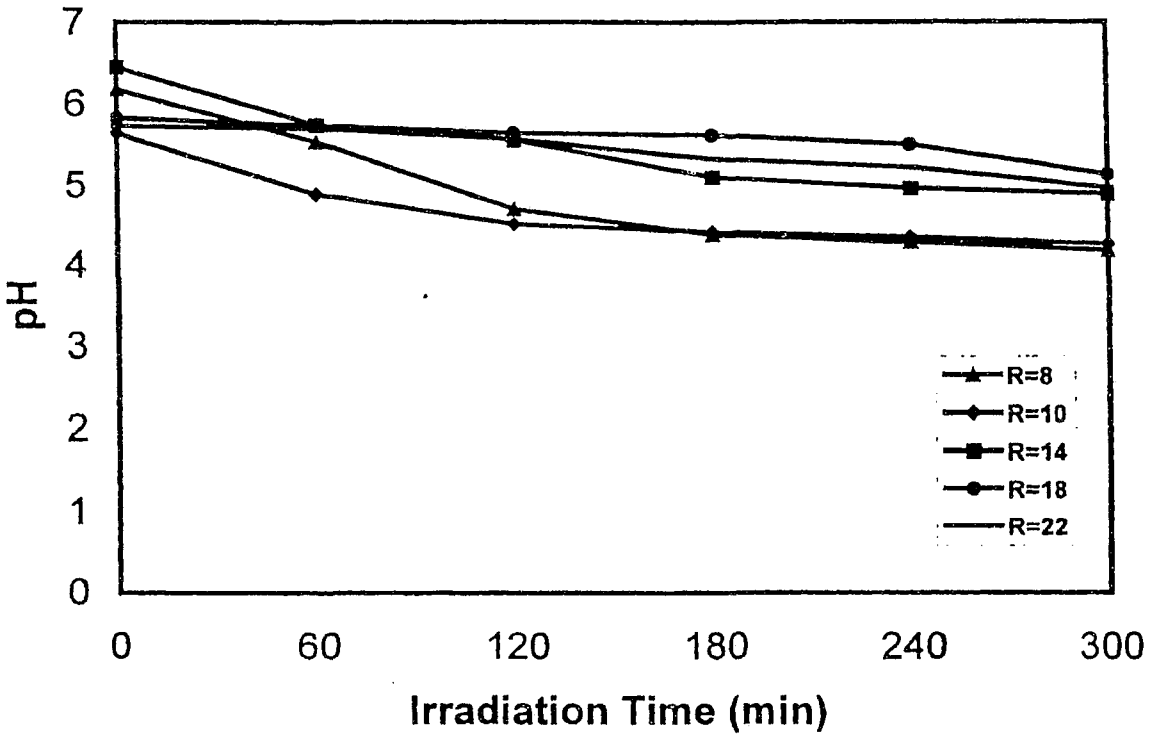

Figure 4.11. pH changes during the degradation of MTBE by UV-254/H_2O_2 process. $C_{o,\,MTBE}$ = 30 mg/L, R=Molar ratio of H_2O_2/MTBE = 8-22. A cooling system was used to keep the temperature constant at 15-20°C.

which could improve the biodegradability of solution in term of BOD/COD (Marco et al., 1997). Since the degradation of MTBE was the main goal of this experiment, which was achieved in 20 minutes, this improvement could not affect its removal from water although the obtained result can be applied for complete mineralization.

4.1.3.3. Comparison of Different UV-Lights in the Degradation of MTBE by H_2O_2

To compare the efficiencies of different UV lights in the degradation of MTBE by H_2O_2, two series of experiments were conducted in which UV lamps with 254 nm and 365 nm wavelength were inserted in the reactor, separately. As illustrated in Figure 4.12, the degradation of MTBE by UV_{254}/H_2O_2 was faster than that of the UV_{365}/ H_2O_2. This Figure showed that after 5 hours reaction the UV_{254}/H_2O_2 system could degrade almost 97% of initial MTBE while UV_{365}/ H_2O_2 system degraded 54% of MTBE at the same period of time. The necessary energy to break the O-O bond of H_2O_2 and to produce $^{\bullet}OH$ is high and equal to 48.5 kcal.mole^{-1} (Clarke and Knowles, 1982). UV-254 has the radiation energy of 112.7 kcal.mole^{-1}, while this factor for UV-365 is equal to 78.5 kcal.mole^{-1} (Appendix D). Both of these UV lights have the capability of breaking the bond in H_2O_2, as is illustrated in Figure 4.12, but higher level of energy in UV-C lamps with 200-280 nm makes it efficient for higher degradation rate of MTBE.

4.1.4. Photocatalytic Degradation of MTBE

4.1.4.1. Dark Reaction

To quantify the contribution of catalyst adsorption, catalytic reaction was conducted by using TiO_2 Degussa P25 in the absence of UV light. Almost 10% decrease of MTBE

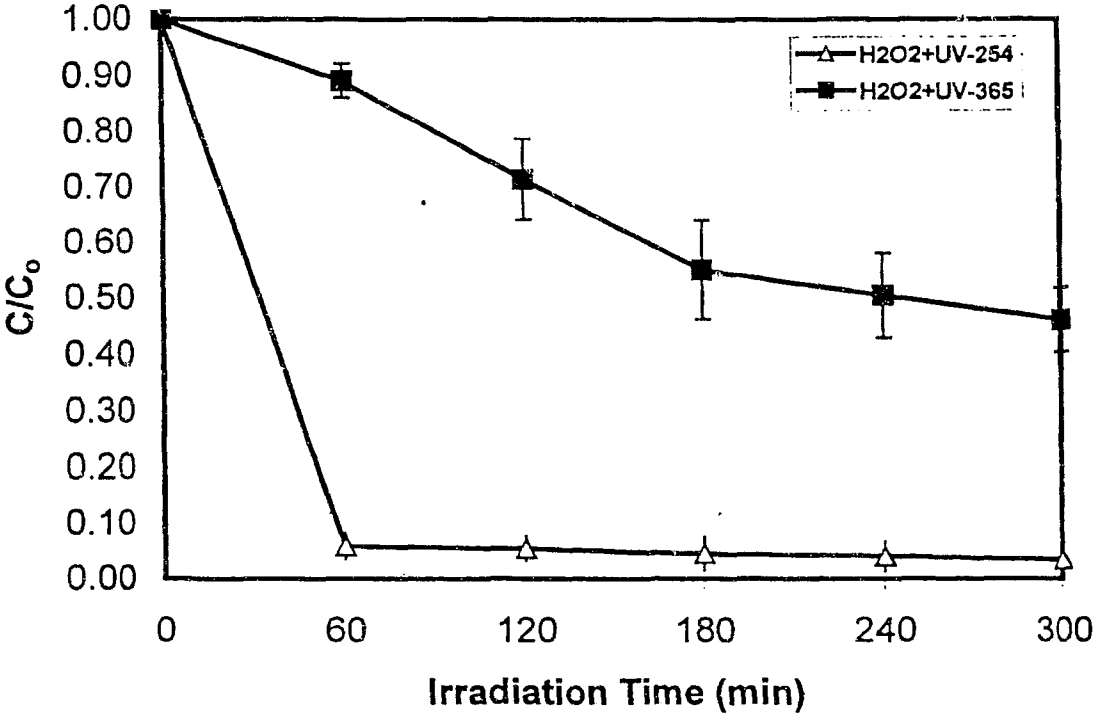

Figure 4.12. Removal of MTBE by H_2O_2/UV-254 and H_2O_2/UV-365. $C_{o,\,MTBE}$ = 10 mg/L, Molar ratio of H_2O_2/MTBE = 14. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

concentration could be the result of its oxidation by oxygen and volatilization and adsorption. The possibility of a dark reaction between MTBE and TiO_2 is shown in Figure 4.13.

The experiments in the presence of UV lamp with wavelength of 254 nm alone (The results are discussed in Section 4.1.3 and illustrated in Figure 4.3) suggested that MTBE had negligible photoactivity and the molecules did not absorb light effectively at 254 nm. On the other hand, the small decrease of MTBE during its dark reaction with TiO_2 showed the lack of tendency for TiO_2 to react with MTBE and degrade it (Figure 4.13), so the effect of the presence of both UV and TiO_2 for degradation of MTBE was investigated in next step.

4.1.4.2. Combination of UV Light and TiO_2

UV radiation in the presence of TiO_2 highly contributed to the removal of MTBE (Figure 4.14). The effect of TiO_2 concentration was studied in the range of 0.1 to 5 g/L. Figure 4.15 shows the optimum amount of TiO_2, which was found to be 1.5 g/L. This value was different from what was suggested by Barreto et al. (1995). In their study, it was found that the optimum concentration of TiO_2 for a 1 mM solution of MTBE was 0.125 g/L. In high concentrations of TiO_2, suspended catalyst particles scattered the light and resulted in lower rates because of lower light transmission in the presence of increased solid catalyst. Below this optimum level the surface area of the catalyst was a limiting factor (Barreto et al., 1995).

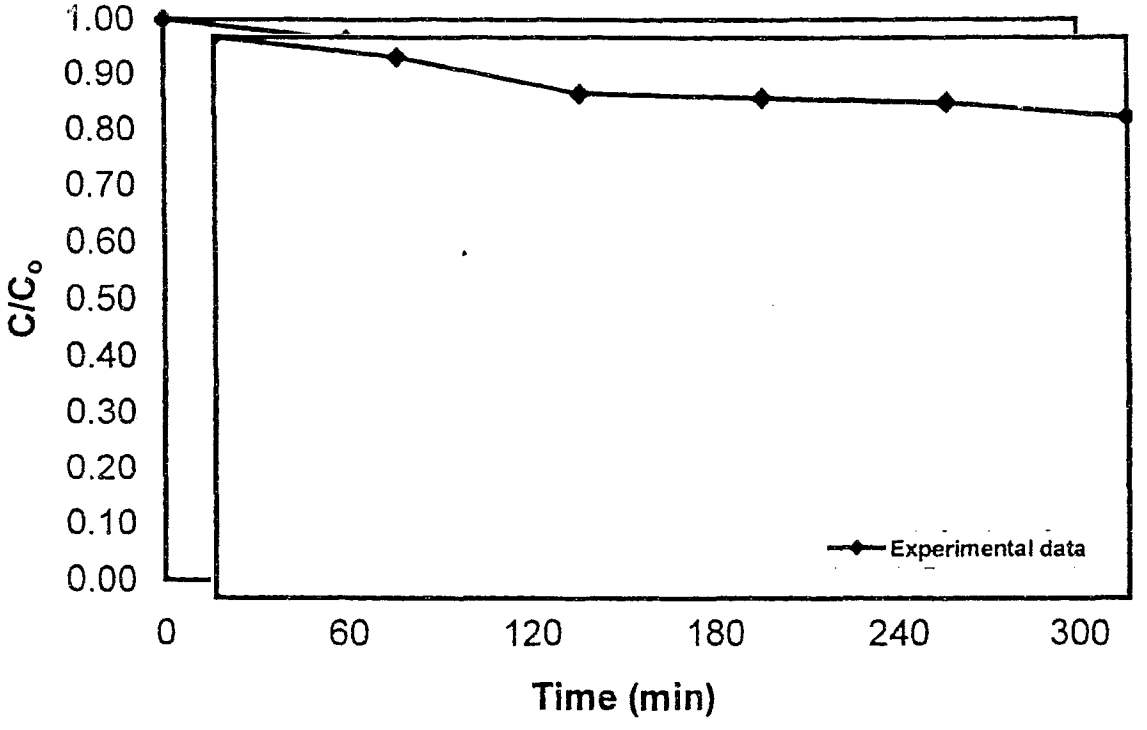

Figure 4.13. Dark reaction for MTBE by TiO_2 Degussa P25 alone. Neither H_2O_2 nor UV light was used, $C_{o,\ MTBE}$ = 8 mg/L. A cooling system was used to keep the temperature constant at 15-20°C.

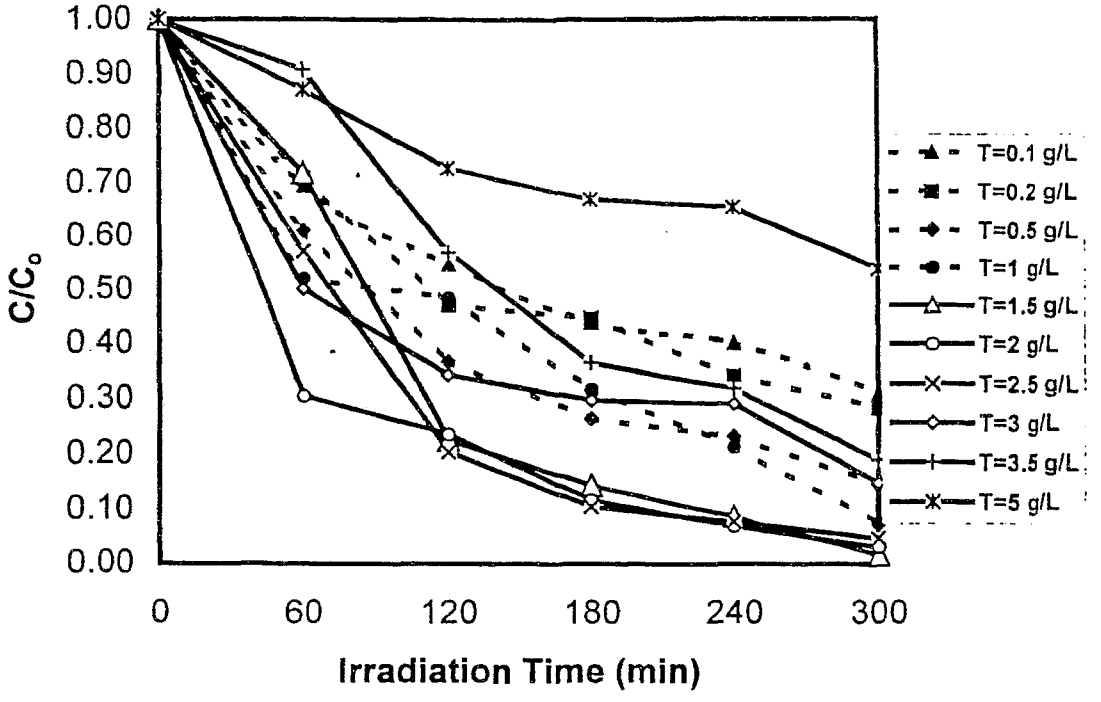

Figure 4.14. Removal of MTBE by UV-254/TiO_2. $C_{o,\,MTBE}$ = 8 mg/L, T = [TiO_2 Degussa P25] = 0.1-5 g/L. A cooling system was used to keep the temperature constant at 15-20°C.

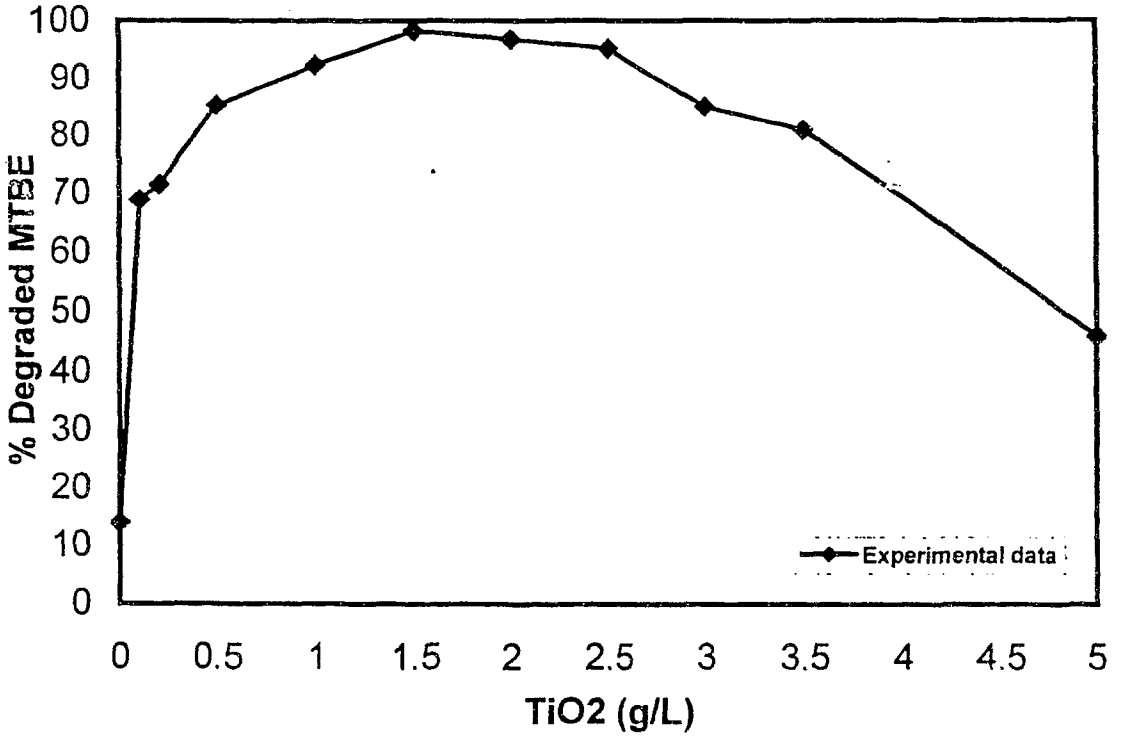

Figure 4.15. Effect of TiO_2 concentration on the photodegradation of MTBE. $Co_{,MTBE}$ = 8 mg/L, [TiO_2 Degussa P25] = 0.1-5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

During photocatalytic reaction, COD was decreased, but it was slower than that of MTBE (Figure 4.16). While 84% of MTBE was degraded within 5 hours, 67% of COD was removed at the same time. This implied that MTBE was not completely mineralized and new organic matters were produced. This conclusion is consistent with the results of Barreto et al.'s (1995) study, which demonstrated the presence of TBF, TBA, and acetone in the solution after 300 min. BOD was almost constant, 2 ± 0.1 mg/L, and did not show any improvement in biodegradability of the solution.

The pH of the solution was decreased slowly from 6.2 to 5 during the degradation of MTBE by UV-254 in different concentrations of TiO_2 (Figure 4.17). Barreto et al. (1995) reported the formation of acidic products such as acetic or formic acids during the reaction, which were consistent with this observation.

4.1.4.3. Photocatalytic Degradation Rate of MTBE

Oxidization of MTBE in a chain mechanism is suggests an initial radical attack to the methoxy group of MTBE as follows (Barreto et al., 1995):

$$(CH_3)_3COCH_3 + O_2 \xrightarrow{TiO_2, h\nu} (CH_3)_3CO(CH_2)OOH \qquad (4.12)$$

$$(CH_3)_3CO(CH_2)OOH \xrightarrow{H^+ / H_2O} (CH_3)_3CO(CO)H + H_2O \qquad (4.13)$$

The production of TBA and formic acid are the next steps. To find the kinetic rate constants, mechanism of the photocatalysis should be studied. In the absence of such information about the mechanism of the photocatalysis of MTBE, performed experiments

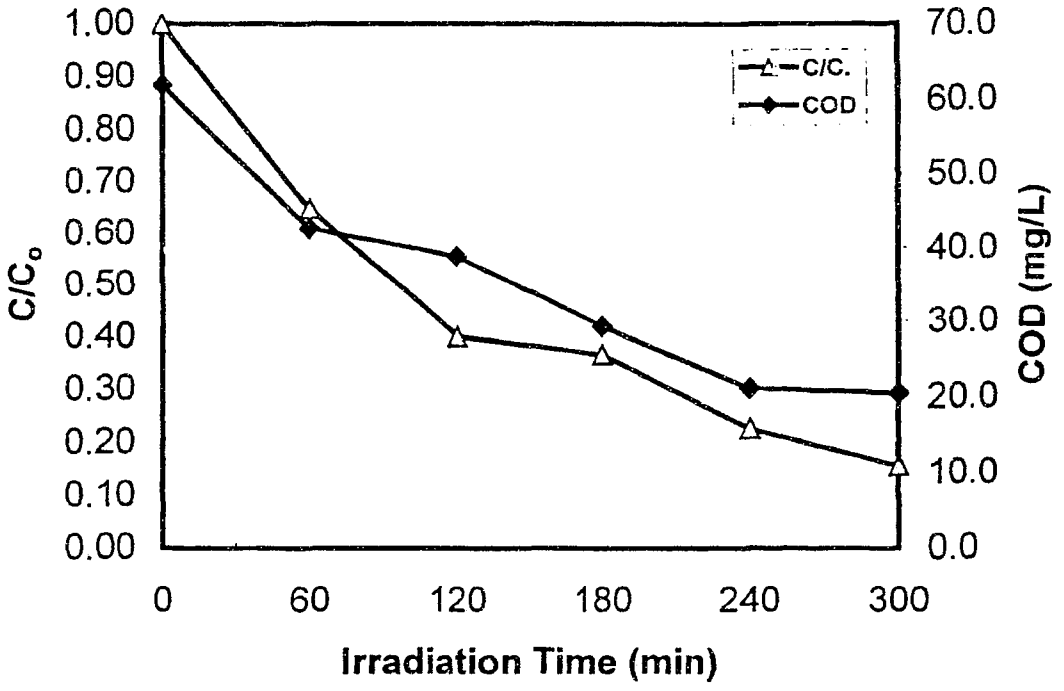

Figure 4.16. Changes of COD during the photodegradation of MTBE by TiO_2. $C_{o,\,MTBE}$ = 26 mg/L, [TiO_2 Degussa P25] = 1.5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

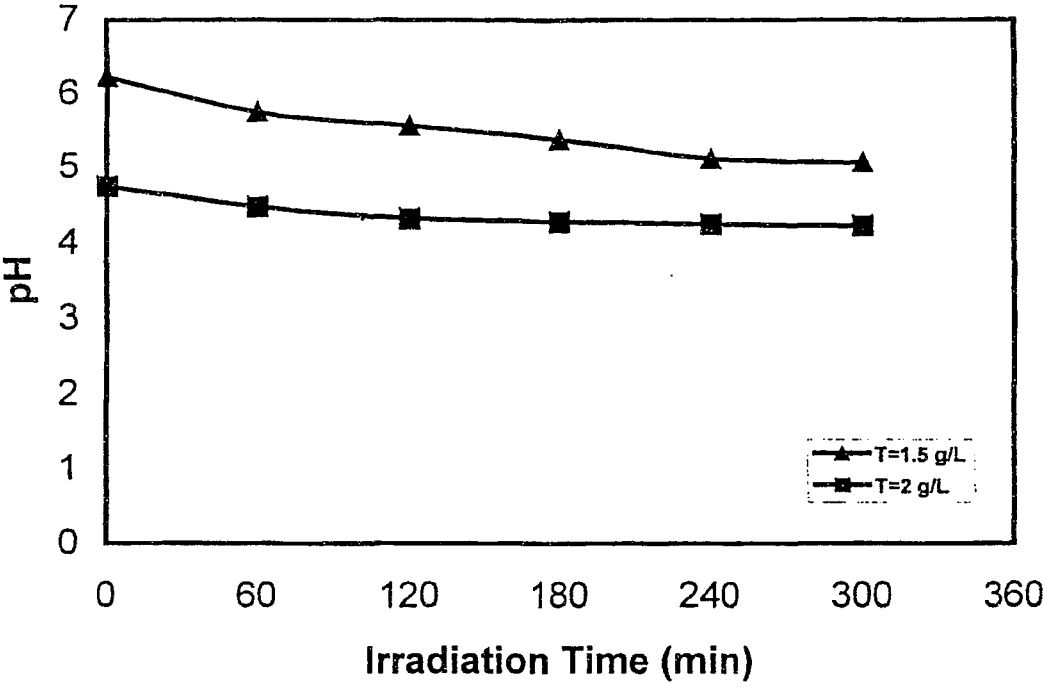

Figure 4.17. pH changes during the photodegradation of MTBE by TiO_2. $C_{o,\,MTBE}$ = 26 mg/L, T= [TiO_2 Degussa P25] = 1.5-2 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

in present study were considered for the study of the overall photocatalytic reaction rate. As shown in Figure 4.18, the linear regressions of $-\ln (C/C_o)$ versus time plots were determined in which regression coefficients were greater than 0.9 in all cases. This implied that the removal of MTBE by UV/TiO_2 followed a first-order model with apparent rate constant of 1.32×10^{-2} min^{-1}. Barreto et al. (1995) calculated an initial rate constant of 7.2×10^{-2} min^{-1} for the first 20 minutes of reaction and beyond this time, the rate constant was measured to be 7.8×10^{-3} min^{-1}. As it will be discussed later, initial concentration of MTBE had an inverse effect on the rate constant. Barreto et al. (1995) made a 1 mM solution for their experiments. This difference in initial concentration can justify the difference between obtained values in the two studies. In addition, the value of 1.32×10^{-2} min^{-1} in this study corresponded to a complete 5-h reaction time.

Generally, the kinetic of heterogeneous photocatalytic reactions follow the Langmuir-Hinshelwood mechanism (Herrmann, 1999):

$$-\frac{dC}{dt}=\frac{kKC}{1+KC} \qquad (4.14)$$

Where k is the reaction rate constant and K is the equilibrium constant of adsorption. In low concentrations of C, $KC \leq 1$ and the reaction becomes the first-order. This explanation is consistent with the obtained experimental data and suggested model.

4.1.4.4. The Effect of Initial Concentration of MTBE on Apparent Rate Constant

Initial concentrations of 2.7, 3.8, 6.8, and 7.6 mg/L of MTBE were considered to

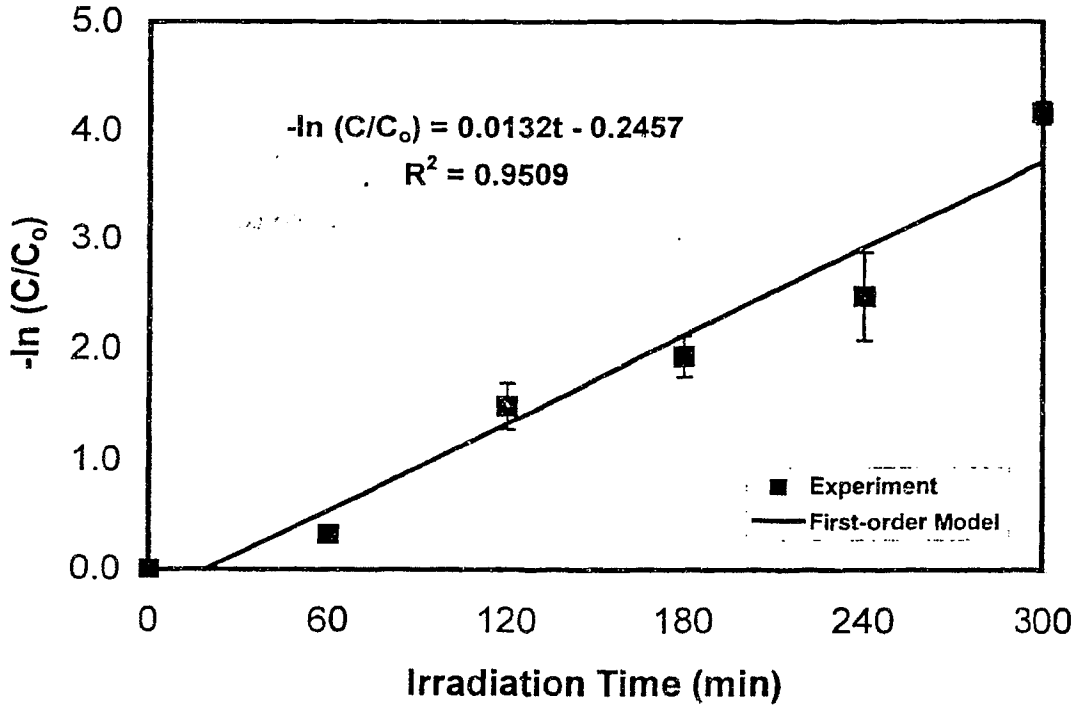

Figure 4.18. Photodegradation of MTBE by first-order reaction in UV-254/TiO_2 process. $C_{o,MTBE}$ = 8 mg/L, [TiO_2 Degussa P25] =1.5 g/L. A cooling system was used to keep the temperature constant at 15-20°C. Calculation of error bars is explained in Section 3.1.2.

examine the effect of initial concentrations on the degradation rate of MTBE. Since MTBE degradation follows a first-order reaction, plots of $-\ln (C/C_o)$ versus time resulted straight lines with different slops depending on the initial concentration of MTBE. As shown in Figures 4.19-4.22, the apparent rate constants decreased with increasing MTBE concentration. As these Figures illustrate, in the presence of 1.5 g/L TiO_2, the apparent rate constants for solutions with initial concentration of 3.8 and 6.8 mg/L MTBE were 0.023 and 0.0174 min^{-1}, respectively. Also, in the presence of 0.5 mg/L TiO_2, the apparent rate constant for solutions with initial concentration of 2.7 and 7.6 mg/L MTBE were 0.0155 and 0.0081 min^{-1}, respectively. These can be explained by assuming that the by-products were competing with MTBE for the site of the surface of TiO_2. The main intermediate products of the photocatalytic reaction of MTBE were identified to be TBF, TBA, and acetone (Barreto et al., 1995).

4.1.4.5. Comparison of Different UV-Lights in Degradation of MTBE by TiO_2 Photocatalysis

The comparison between degradation rate in application of UV_{254} and UV_{365} revealed that the light with 254 nm wavelength had more effectiveness on degradation of MTBE than 365 nm. Figure 4.23 shows more than 90% decrease for the degradation of MTBE by UV_{254}/TiO_2 system while the removal of MTBE by UV_{365}/TiO_2 was less than 70%. TiO_2 has band-gap energy of 3.02 eV, which means the electrons in valance band can be promoted to conduction band by UV with $\lambda \leq 400$ nm. Although considerable removal of MTBE was observed with both UV-254 and UV-365, the higher level of energy in former could contribute to the degradation and improved its rate, therefore,

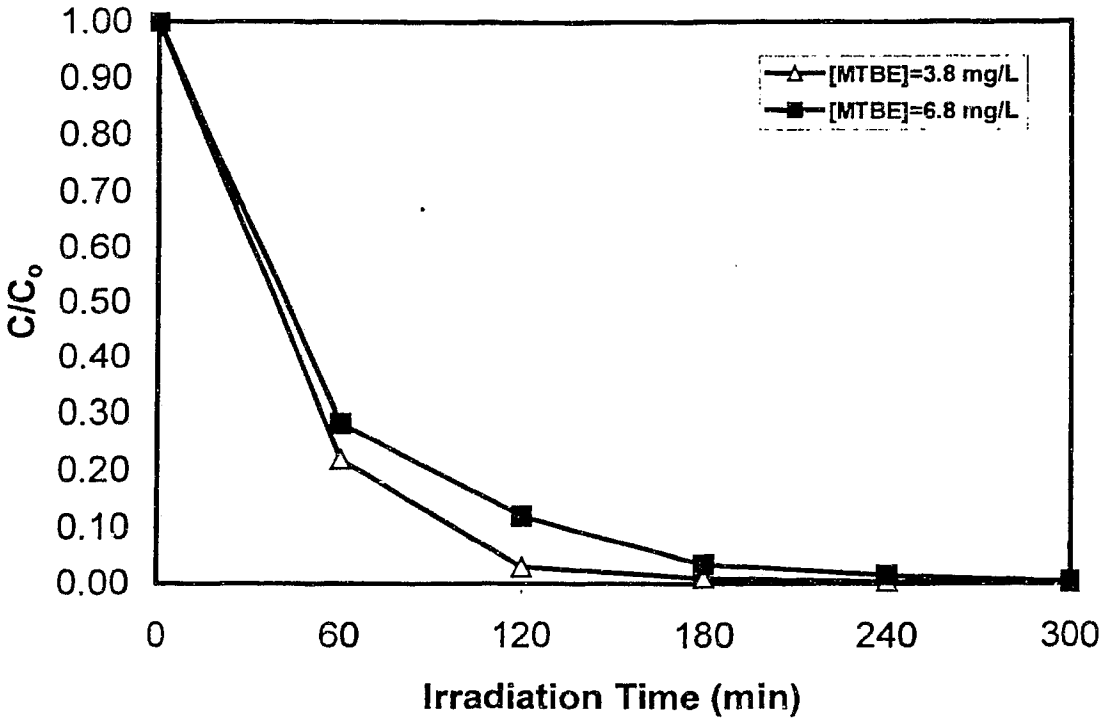

Figure 4.19. Effect of initial concentration of MTBE on its photodegradation. $C_{o,\,MTBE}$ = 3.8, 6.8 mg/L, [TiO_2 Degussa P25] = 1.5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

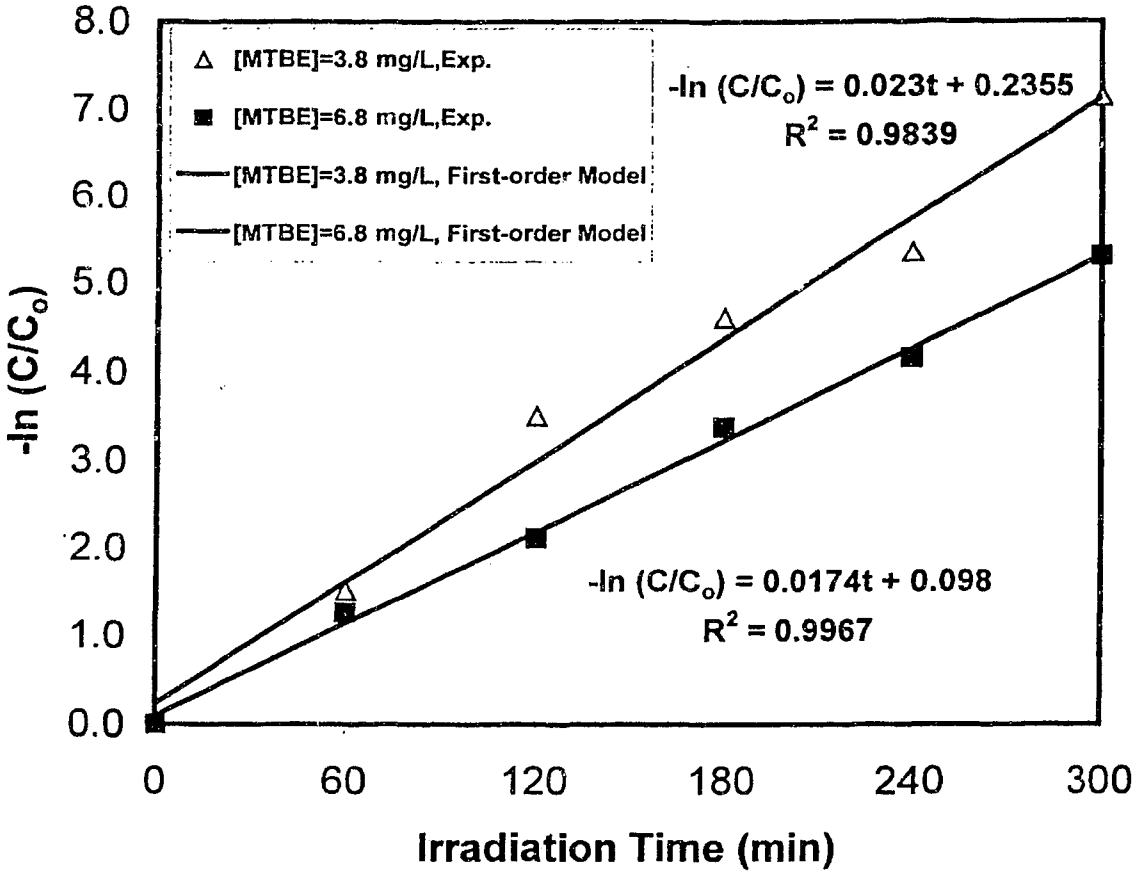

Figure 4.20. Effect of initial concentration of MTBE on the rate constant of its photodegradation. $C_{o,\,MTBE}$ = 3.8, 6.8 mg/L, [TiO_2 Degussa P25] = 1.5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

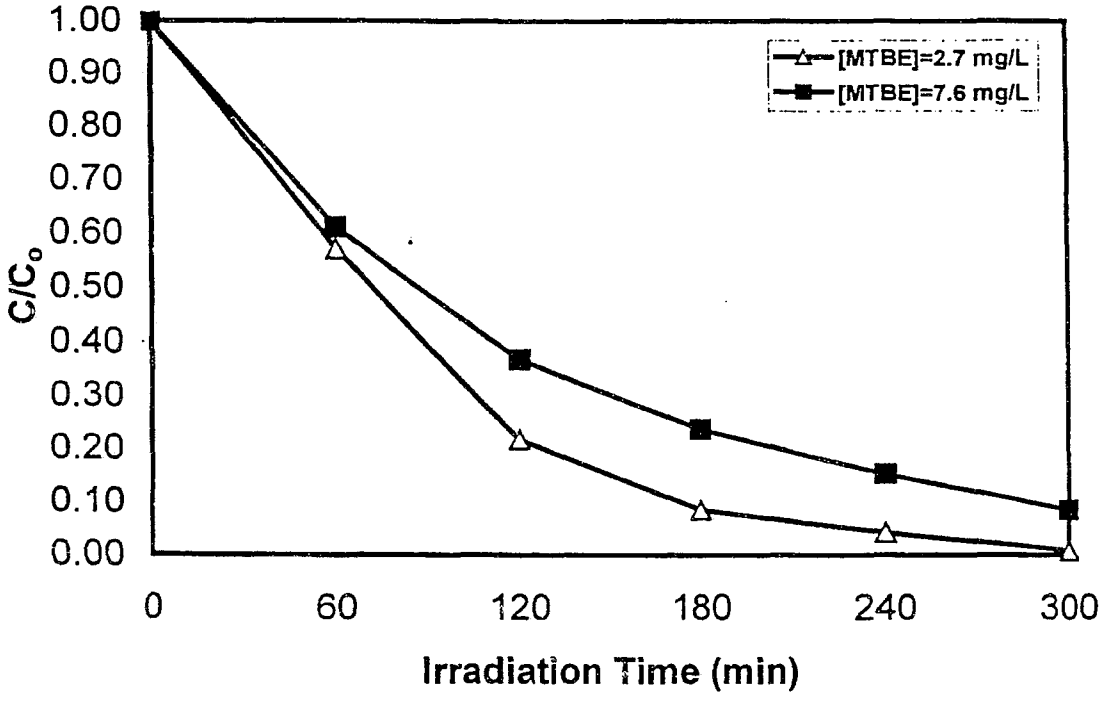

Figure 4.21. Effect of initial concentration of MTBE on its photodegradation. $C_{o,\,MTBE}$ = 2.7, 7.6 mg/L, [TiO_2 Degussa P25] = 0.5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

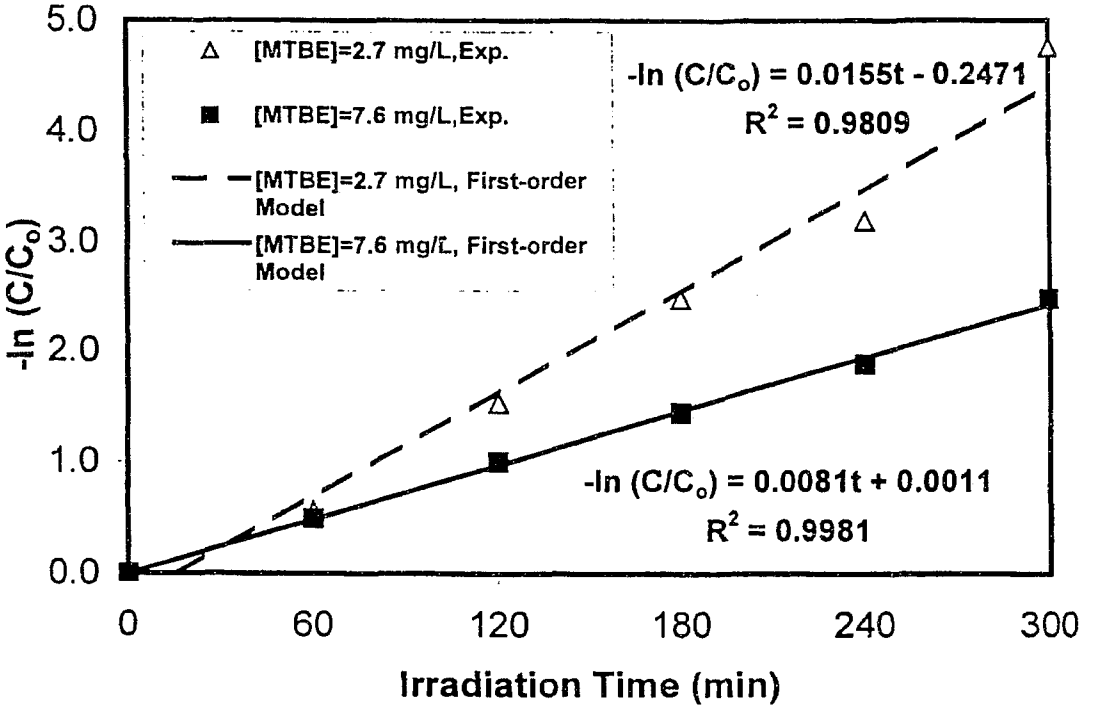

Figure 4.22. Effect of initial concentration of MTBE on the rate constant of its photodegradation. $C_{o,\,MTBE}$ = 2.7, 7.6 mg/L, [TiO_2 Degussa P25] = 0.5 g/L, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

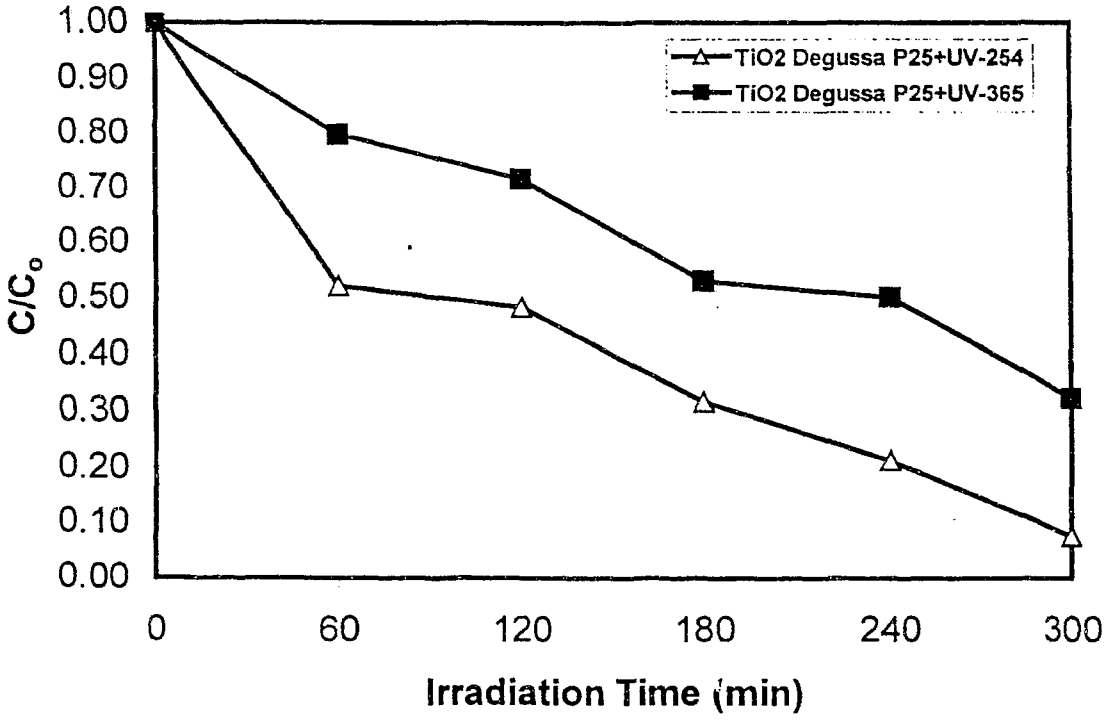

Figure 4.23. Removal of MTBE by TiO_2/UV-254 and TiO_2/UV-365. $C_{o,\,MTBE}$ = 8 mg/L, [TiO_2 Degussa P25] = 1.5 g/L. A cooling system was used to keep the temperature constant at 15-20°C.

after 5 hours 20% more decrease was observed by UV-254.

4.1.5. Combination of UV-Light 254 nm, TiO_2 and H_2O_2

The system of TiO_2/ H_2O_2/UV-254 even with the optimum amount of TiO_2 and H_2O_2 did not involve a clear advantage over using UV/H_2O_2 or UV/TiO_2 (Figure 4.24). The results showed that 1.5 g/L TiO_2 in the presence of UV_{254} could degrade 72% MTBE after 1 hour. In the other hand, solution with molar ratio of H_2O_2 / MTBE = 14 could degrade 96% MTBE at the same time, but addition of 1.5 g/l TiO_2 to this solution decreased the rate of degradation and only 27% MTBE was degraded within 1 hour. Also, degradation rate of solution with molar ratio of H_2O_2 / MTBE = 18 decreased from 93% to 26% by addition of 1.5 g/L TiO_2 during 1 hour. As Figure 4.25 illustrates, the highest degradation rate in 1 hour of reaction corresponded to UV/H_2O_2 and the lowest belonged to UV/TiO_2/H_2O_2.

Addition of H_2O_2 to the system of UV/TiO_2 could result the following reactions:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (4.15)$$

$$H_2O_2 + h^+ \rightarrow HO_2^{\bullet} + H^+ \qquad (4.16)$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \qquad (4.17)$$

Competition of H_2O_2 with MTBE for hole region in TiO_2 can justify the decrease of degradation after addition of H_2O_2 to TiO_2. In addition, $HO_2^{\bullet}$, which can oxidize

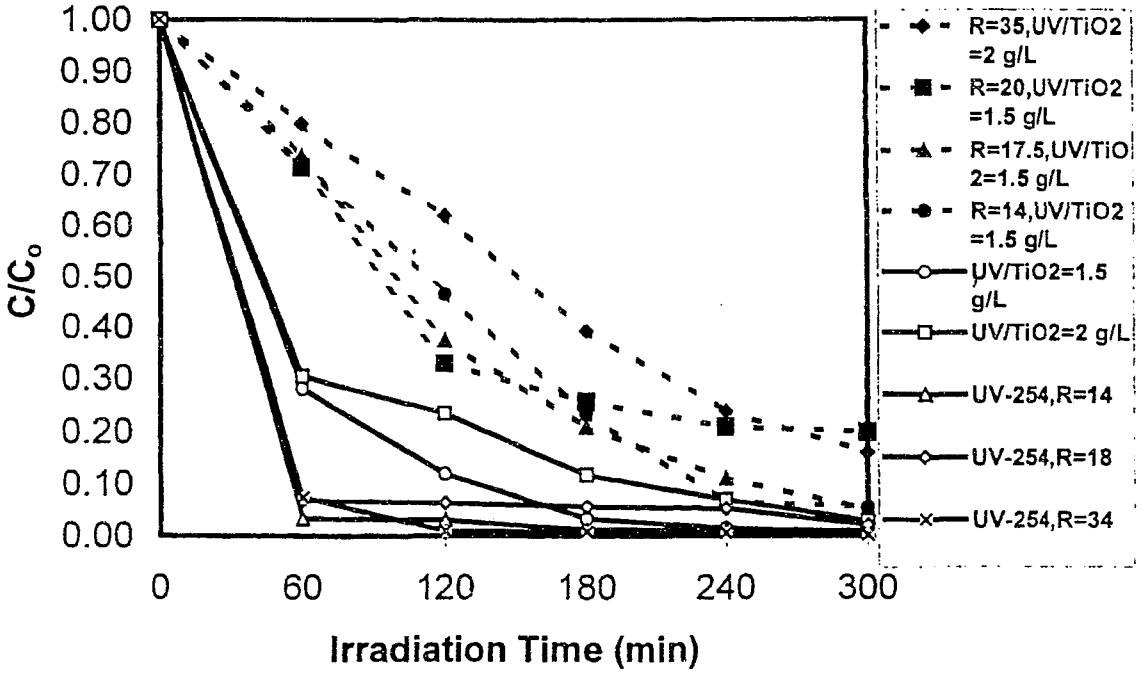

Figure 4.24. Effect of addition of H_2O_2 on photocatalytic degradation of MTBE. $C_{o,\,MTBE}$ = 2-30 mg/L, [TiO_2 Degussa P25] =1.5-2 g/L, $C_{o,\,H2O2}$ = 35 – 265 mg/L, R = Molar ratio of H_2O_2 / MTBE =14-35, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

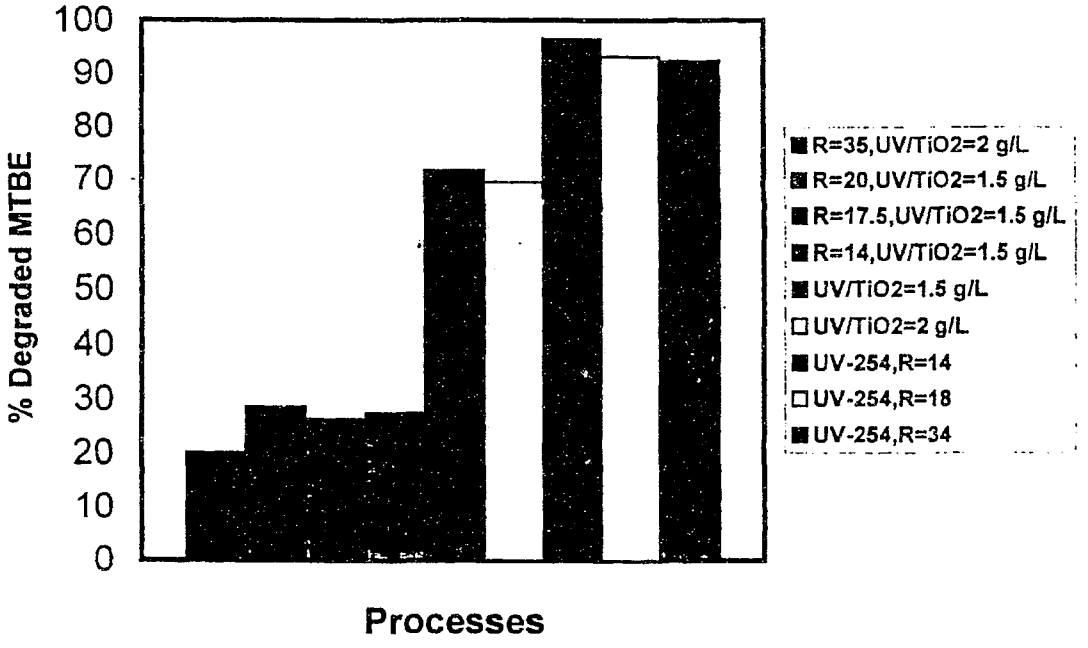

Figure 4.25. Initial degradation of MTBE by various AOPs. $C_{o,\ MTBE}$ = 2-30 mg/L, [TiO_2 Degussa P25] =1.5-2 g/L, $C_{o,\ H2O2}$ = 35 – 265 mg/L, R = Molar ratio of H_2O_2 / MTBE =14-35, the light source was a UV-254 lamp. A cooling system was used to keep the temperature constant at 15-20°C.

organics, can also be reduced by e^-, therefore, the rate of oxidation would be decreased. H_2O_2 may also absorb photons and compete with photocatalyst for light absorption (Bolduc and Anderson, 1997). Another possibility is the competition between H_2O_2 and MTBE for $^{\bullet}OH$, which could result in decrease of degradation rate after addition of H_2O_2 to UV/TiO_2.

4.2. Biological Treatment of MTBE

4.2.1. Inhibitory Effects of MTBE and its Intermediates

Application of AOPs may entail the production of more toxic intermediates than the parent compounds. Therefore, to evaluate the effects of AOP products on their biodegradation, inhibitory tests are necessary. To verify the inhibitory effects of MTBE, TBA, and TBF on microbial activity, a source of carbon, easily used by polyseed microorganisms, was added to BOD bottles and the oxygen consumption by microorganisms was compared in the absence and presence of different concentrations of pollutants (Bolduc and Anderson, 1997). For this purpose, sodium acetate was chosen as a readily utilized carbon source. BOD bottles without/with 10, 30, 50, 100, 150, 200, and 5 mg/L of MTBE were prepared containing seed materials, dilution water, and 5 mg/L sodium acetate. The same procedure was followed for TBA and TBF with 10, 50, and 100 mg/L solutions. In the presence of constant amount of sodium acetate and with increasing of pollutants, the results of BOD_5 interpreted in three ways: decrease of the oxygen demand corresponded to an inhibitory or toxic effect of pollutant on the microorganisms, slightly lower consumption of oxygen than that of the pure sodium acetate suggested that pollutant neither had toxic effect nor were easily consumed by

microorganisms, and finally, increase of oxygen consumption corresponded to oxidation of pollutant by microorganisms. The details of the method and calculations are explained in Section 3.2.7 and Appendix A.

Table 4.1 and Figure 4.26 present the result of these experiments. As this Table and Figure show, increasing the amounts of MTBE, TBA, and TBF in the solution of 5 mg/L sodium acetate did not have a great impact on the microorganisms for their oxygen consumption.

Table 4.1. Biodegradability assessment of MTBE, TBA, and TBF.

(NaAc = sodium acetate).

Compound	**Concentration of pollutant (mg/L) in presence of 5 mg/L NaAc**	**BOD_5 (mg/L)**
MTBE	200	2.62
	150	2.59
	100	3.12
	50	3.21
	30	3.89
	10	3.45
	5	3.49
	0	3.04
TBA	100	3.71
	50	3.69
	10	3.15
	0	3.04
TBF	100	3.33
	50	3.27
	10	3
	0	3.04

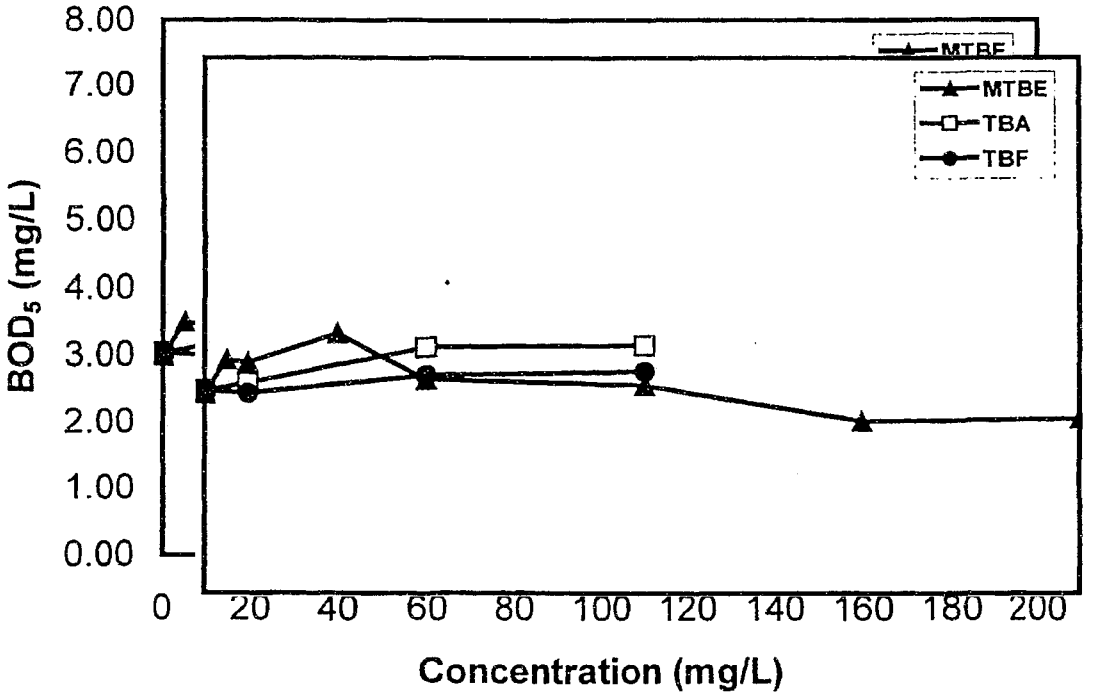

Figure 4.26. Assessment of biodegradability for different concentrations of MTBE, TBA, and, TBF by measuring BOD_5 in the presence of sodium acetate (NaAc). BOD bottles were incubated for 5 days at 20°C, C_{NaAc} = 5 mg/L.

The highest BOD_5 was corresponded to the solution containing 5 mg/L sodium acetate and 30 mg/L MTBE. Interpretation of the obtained results leads to this conclusion that these compounds do not have toxic effects on living organisms and their consumption by microorganisms can be observed under certain conditions.

4.2.2. Ultimate BOD Determination

Table 4.2 and Figure 4.27 and illustrate that the BOD_U, determined by the daily-difference method (Section 3.2.2.1), for solutions containing 5, 10, 30, and 50 mg/L of MTBE were 3.55, 3.76, 4 and, 4.89 mg/L, which resulted in the first-order rate constants of 0.099, 0.096, 0.118, and 0.101 day^{-1} at 20°C, respectively. Although the value of BOD_5 and therefore the value of BOD_U were higher for solution of 50 mg/L MTBE, the highest rate of oxygen consumption corresponded to the solution with 30 mg/L MTBE, which meant more tendencies of microorganisms for usage of this concentration. Calculations for determination of rate constants are presented in Appendix E.

Table 4.2. Ultimate BOD for MTBE obtained by daily-difference method.

MTBE (mg/L)	**BOD_5 (mg/L)**	**BOD_U (mg/L)**	**k (day^{-1})**
5	1.39	3.55	0.099
10	1.43	3.76	0.096
30	1.78	4	0.118
50	1.94	4.89	0.101

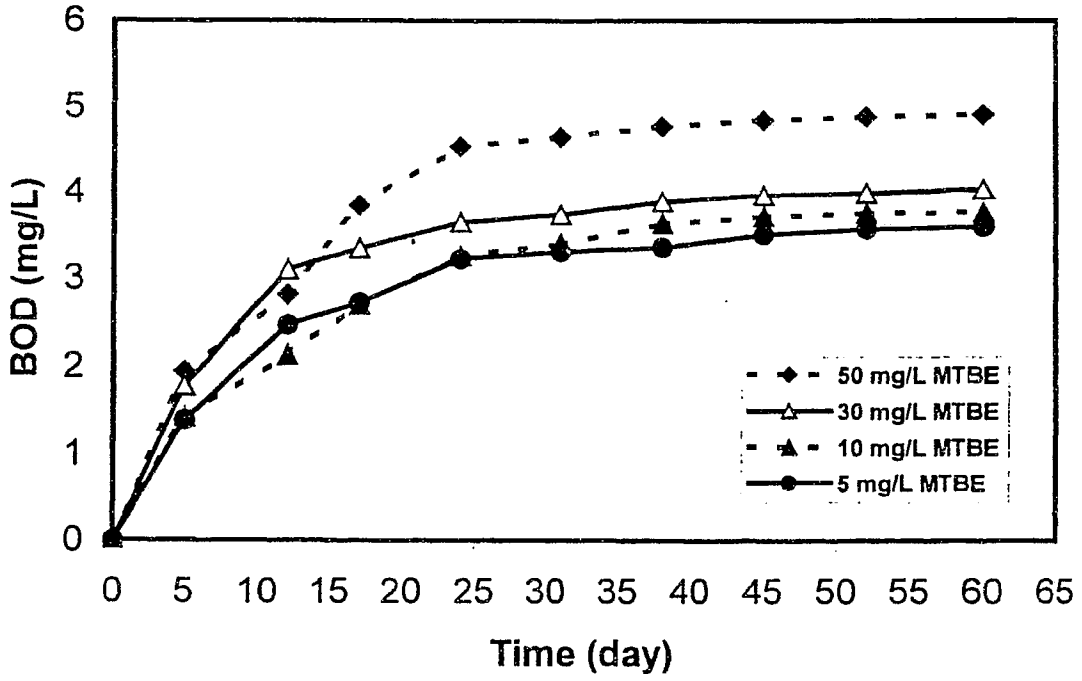

Figure 4.27. Determination of BOD_U for various solutions of MTBE by daily-difference method. $C_{o,\,MTBE}$ = 5-50 mg/L. BOD bottles were incubated for 5 days at 20°C.

4.2.3. Biodegradation of MTBE by Mixed Culture

The possibility of degradation of MTBE by mixed culture was studied and its biodegradation was tracked by measurement of MTBE. Details of procedure are explained in Section 3.2.2.2. Liquid culture was collected and filtered, and cell-free aqueous sample was injected into GC to determine MTBE concentration in liquid phase.

During a 30-day time-course, almost 70% of initial amount of MTBE was decreased. To study the rate of biodegradation, a Monod model was modified and applied. Following equation defines the rate of bacterial growth (Metcalf and Eddy, 1991):

$$r_g = \mu X \qquad (4.18)$$

Where:

r_g = Rate of bacterial growth, mass/ volume . time

μ = Specific growth rate, time^{-1}

X = Concentration of microorganism, mass/ volume

The specific growth rate has a relationship with the substrate concentration, which is experimentally proposed by Monod:

$$\mu = \mu_m \frac{S}{K_S + S} \qquad (4.19)$$

Where:

μ_m = Maximum specific growth rate, time^{-1}

S = Substrate concentration, mass/ volume

K_S = Monod saturation constant, mass/ volume

In a microbial system the rate of bacterial growth is proportional to the rate of substrate consumption by following relationship:

$$r_g = Yr_s \qquad (4.20)$$

Where:

Y = Maximum yield coefficient, the ratio of mass of formed cells to the mass of consumed substrate, mg/ mg

$r_s = \frac{dS}{dt}$ = Substrate consumption rate, mass/ volume . time

Therefore:

$$\frac{dS}{dt} = -\frac{\mu_m XS}{Y(K_S + S)} \qquad (4.21)$$

At low concentration of substrate $K_S >> S$, which leads to the simplification of dominator. Previous studies show that maximum yield coefficient for MTBE is very low (Deeb et al, 2000) and as result X can remain constant. All these parameters can be

substituted by a new constant as k which leads to the following first-order equation for substrate consumption by microorganisms:

$$\frac{dS}{dt} = -kS \qquad (4.22)$$

Figure 4.28 depicts that biodegradation followed a first-order reaction rate with low rate constant of 4.36×10^{-2} day^{-1}. It means that more than 150 days are required to achieve the MTBE concentration in the range set by EPA at Drinking Water Advisory (EPA, 2003).

During the biodegradation period in shake flasks, a decrease of pH from 7 to 4.5 was observed, which suggested the formation of some acidic compounds. Figure 4.29 shows the COD changes in the biodegradation period. COD declined at a slower rate than did MTBE. While 70% of MTBE was degraded within 30 days, 40% of COD was removed at the same time. This result implied the accumulation of intermediates that were not readily biodegradable. Although the amount of MTBE was decreased, the biodegradation could not proceed with the new products and resulted in their accumulation. Many researchers studied the mechanism of bioremediation of MTBE and identified TBA and TBF as the primary products (Steffan et al., 1997; Salanitro et al., 1994; Hernandez-perez et al., 2001; and Fayolle et al., 2003), which are not readily biodegradable and rarely take part in biological reactions.

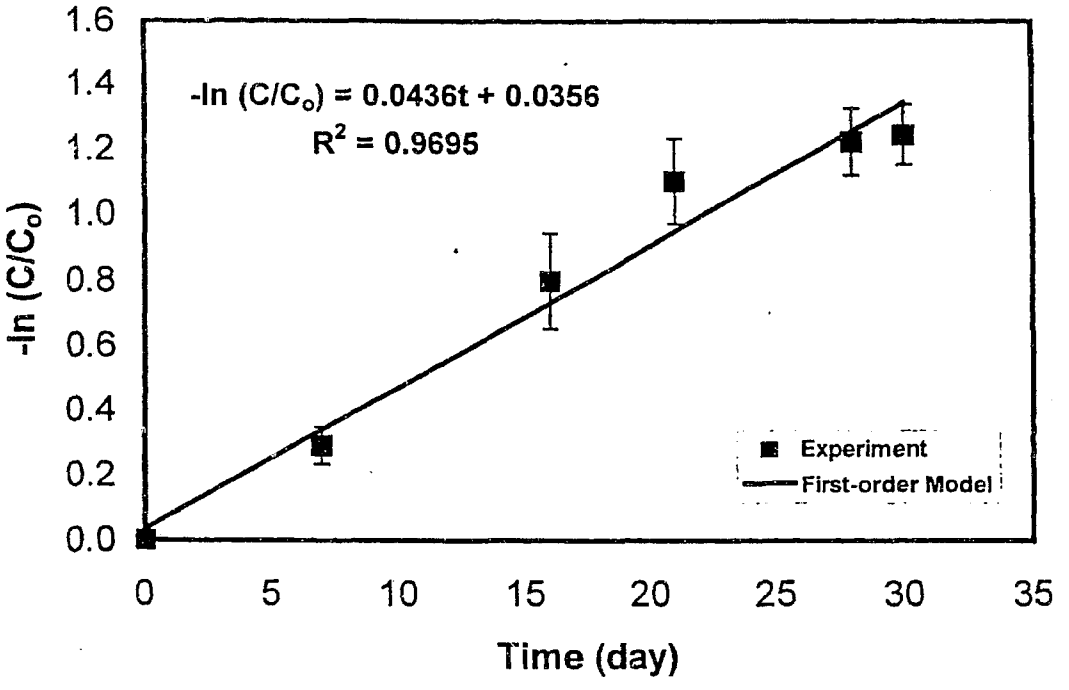

Figure 4.28. Biological treatment of MTBE in shake flask by non-acclimated activated sludge taken from activated sludge unit of municipal wastewater treatment plant of North Toronto. $C_{o,\,MTBE}$ = 30 mg/L, T = 20°C. Calculation of error bars is explained in Section 3.1.2.

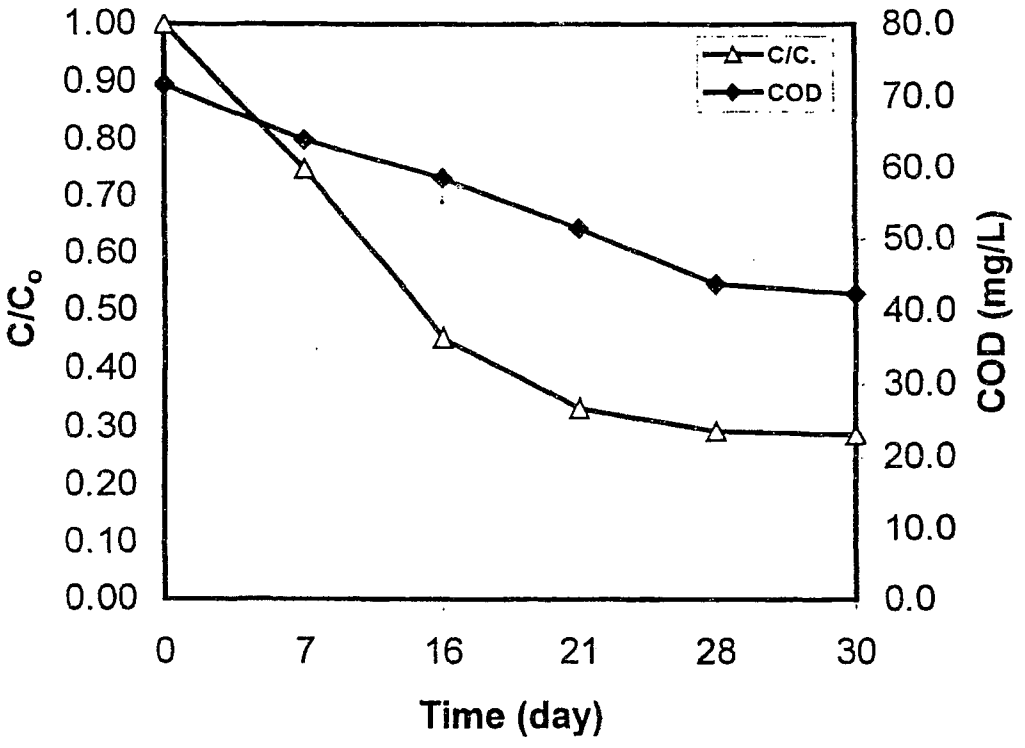

Figure 4.29. COD changes in biological treatment of MTBE in shake flask by non-acclimated activated sludge taken from activated sludge unit of municipal wastewater treatment plant of North Toronto. $C_{0,\,MTBE}$ = 30 mg/L, T = 20°C.

4.2.4. Biodegradation of MTBE by Acclimated Activated Sludge

As explained in Section 3.2.2.3.1, an acclimatization process was followed by gradually increasing the concentration of MTBE from 10 mg/L to 30 mg/L. Addition of MTBE during acclimation period resulted in almost constant amount of BOD_5 of 4 ± 0.15 mg/L, which meant that in spite of the decreasing amount of sodium acetate, the biodegradable part of nutrients was not changed, in other words, microorganisms could adjust themselves with new changes in their environment and could switch their carbon consumptions from sodium acetate to MTBE. Although microorganisms showed a slow growth rate, which could not be tracked by the present analytical balance in the laboratory, the increase of 100 mg/L cell dry weight at the end of acclimation period still confirmed their adjustment with new conditions. The initial and final values of pH were 7.5 and 6.3, respectively, which gives the conclusion of increasing amount of acidic products.

As it was mentioned in Section 3.2.2.3.1, the endpoint of acclimation process was the presence of 30 mg/L MTBE in the bioreactor. After accomplishment of acclimation phase, the main biological treatment started (Section 3.2.2.3.2). The initial BOD_5 for 30 mg/L solution of MTBE was 4.95, which was higher than that of the non-acclimated culture. This implied that with the same initial concentrations of MTBE in both bioreactors, microorganisms in SBR are exposed to more available nutrients and had more tendencies for MTBE consumption. Figure 4.30 illustrates the trend of biodegradation of MTBE in SBR. Acclimation led to the increase of biological activity and eventually greater degradation. A zero-order model can have the best fit with

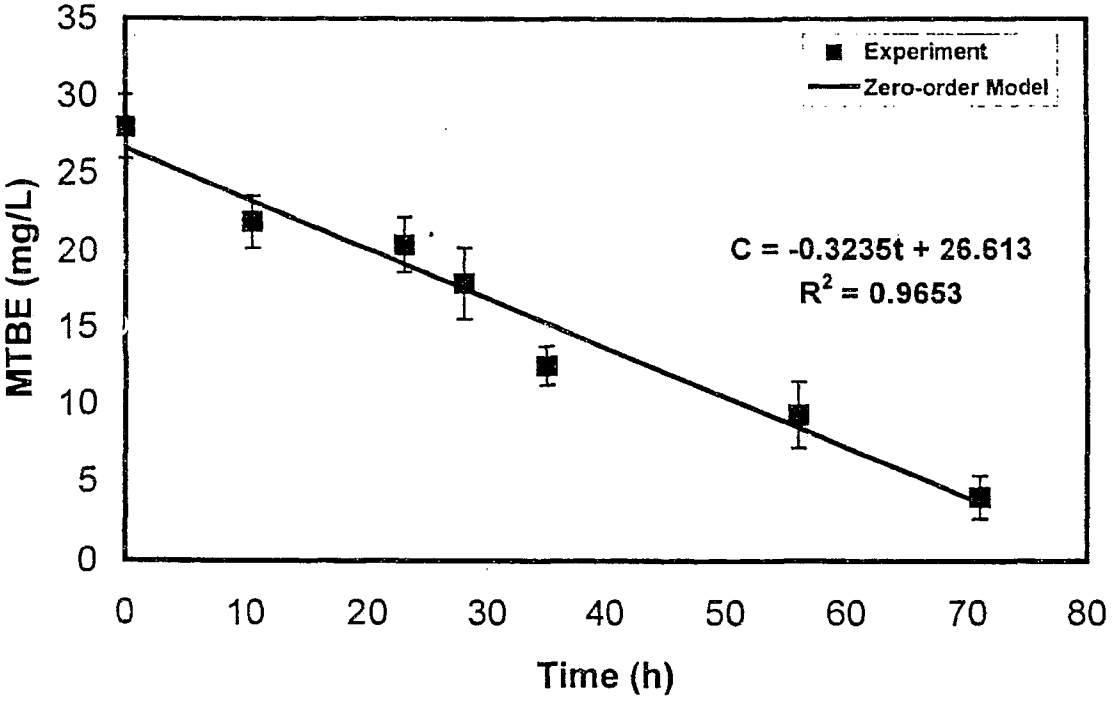

Figure 4.30. Biological treatment of MTBE in SBR by microorganisms taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. $C_{o,\,MTBE}$ = 30 mg/L, T = 25 ± 1°C. Calculation of error bars is explained in Section 3.1.2.

obtained results. Compared with degradation rate constant in non-acclimated case, it had considerable improvement and became equal to 3.235×10^{-1} mg L^{-1} h^{-1}. This comparison showed that while a solution of 30 mg/L of MTBE can be treated by non-acclimated organisms in 150 days to reach to the level set by EPA for MTBE in drinking water, the same removal of MTBE can be occurred in 90 h with acclimated microorganisms. Fortin et al. (2001) suggested a zero-order constant rate of 2.8 $mgL^{-1}h^{-1}$ for the degradation of up to 100 mg/L MTBE by a microbial consortium cultivated in liquid system designated as F-consortium.

In this study, the amount of cell growth was so small for each run that could not be measured with the present analytic balance in the laboratory, but after three consecutive runs, 7 mg/L microbial growth was observed. All these facts implied that the acclimation phase was successfully implemented. pH decrease from 6.5 to 6 during the degradation of MTBE by acclimated microorganisms indicated the production of acidic compounds. The result of BOD and COD tests for acclimated microorganisms during removal of MTBE are illustrated in Figures 4.31 and 4.32. 85% degradation of MTBE during 71 h was accompanied with 45% and 75% removal of COD and BOD, respectively. One hypothesis that could be suggested from the analysis of these results was that acclimated microorganisms, which could degrade MTBE effectively, were not capable of degrading by-products and therefore these compounds accumulated in the system and slowed down the rate of COD removal. The rate of decrease of MTBE was the same as of BOD, which implied that the only biodegradable source for living microorganisms in this system was MTBE. At the same time, removal of COD was not significant and 55% COD remained

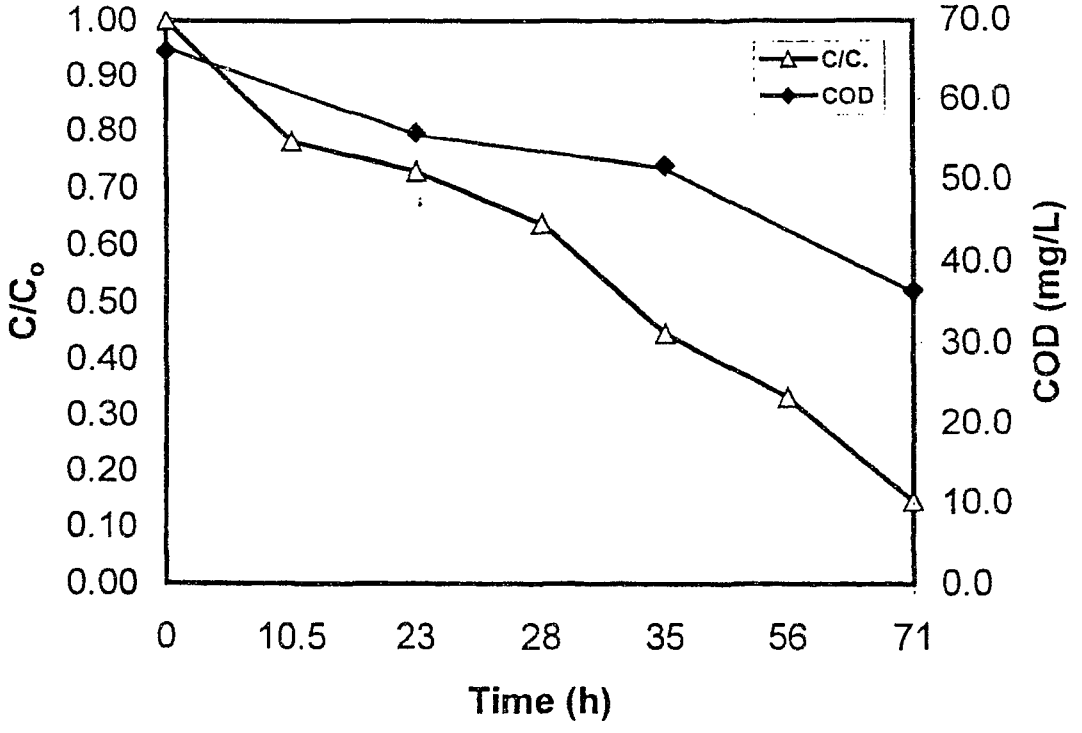

Figure 4.31. COD changes in biological treatment of MTBE in SBR by microorganisms taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. $C_{o,\,MTBE} = 30$ mg/L, $T = 25 \pm 1^{\circ}C$.

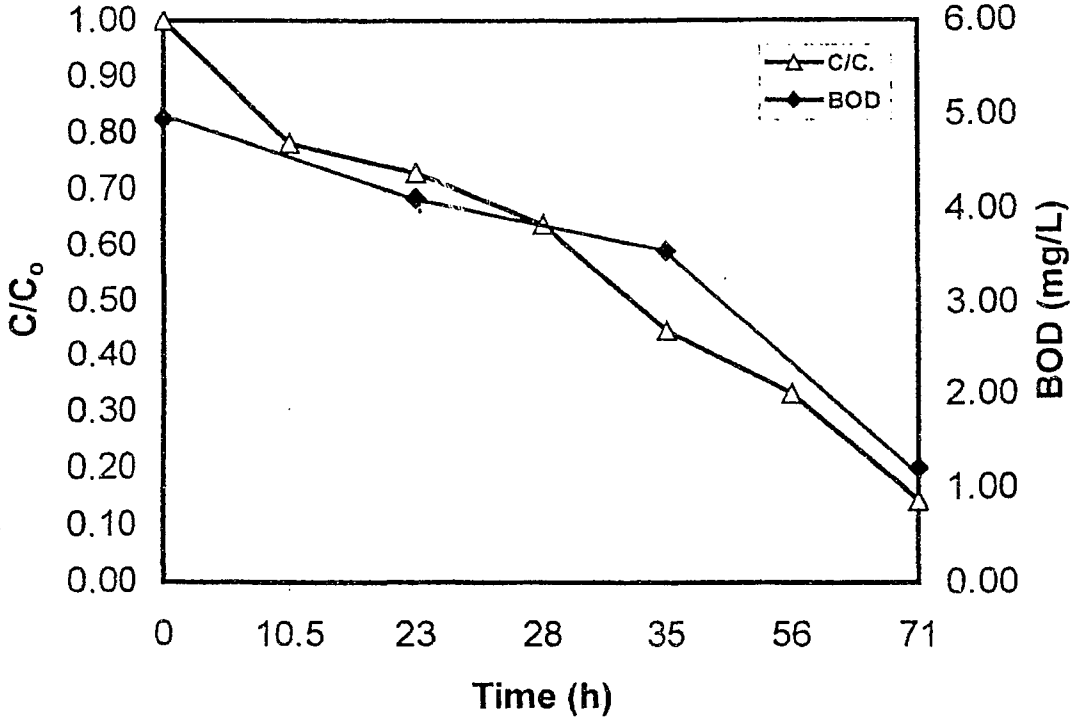

Figure 4.32. BOD changes in biological treatment of MTBE in SBR by microorganisms taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. $C_{o,\,MTBE}$ = 30 mg/L, T = 25 ± 1°C.

after removal of MTBE. Like non-acclimated situation, here again biotreatment led to formation of the non-biodegradable products, which was the reason for by-products accumulation. The BOD/COD ratio, which is a good indication of biodegradability, decreased from 0.07 to 0.03. The change of this ratio can be explained by this fact that BOD decreased because MTBE was consumed but at the same time the rate of COD reduction became slower because non-biodegradable by-products were formed. Assembling all these results confirms that the intermediates were not biodegradable and could not be consumed by these acclimated microorganisms.

4.2.5. Combination of Photochemical and Biological Processes for the Treatment of MTBE

In combination process, first a solution with 50 mg/L MTBE and 1.5 g/L TiO_2 was introduced to photochemical reactor and after 1.5 h the effluent containing 30 mg/L of MTBE centrifuged and the supernatant transferred to SBR to be treated by acclimated microorganisms (Section 3.3). A similar study was conducted in SBR and the zero-order rate constant was equal to 2.825×10^{-1} mg L^{-1} h^{-1} (Figure 4.33). The removal of COD was similar to what occurred in non-treated solution (Figure 4.34), which was slower than degradation rate of MTBE. 68% degradation of MTBE occurred with decrease of COD, but still 65% COD was not treated and remained in the solution. This implied that the acclimation and the adjustment of microorganisms to MTBE did not necessarily entail their adjustment to by-products, therefore, the biodegradability of photoreaction products must be taken into account. As a result, they were accumulated since the time they entered to bioreactor. In addition, formation of new intermediates in biological reactor, as

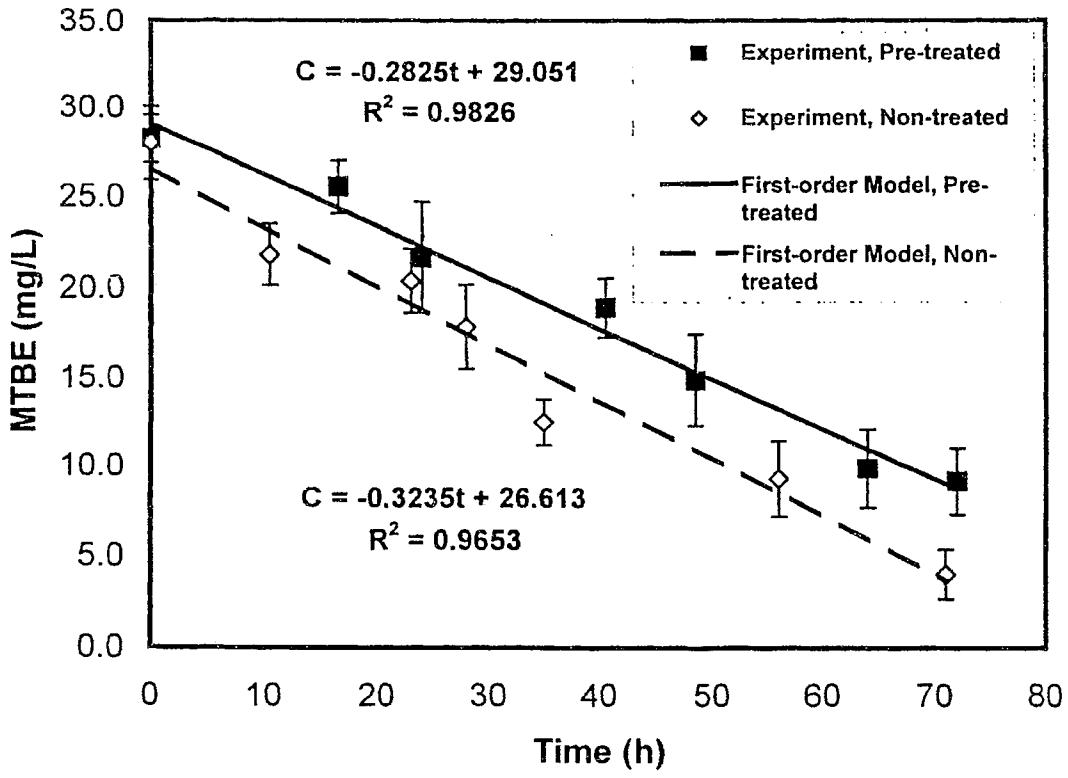

Figure 4.33. Comparison between biological treatment of non-treated and pre-treated of MTBE solution in photoreactor by microorganisms in SBR. Microorganisms were taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. In photoreactor $C_{o,\,MTBE}$ = 50 mg/L and was degraded there by UV/TiO_2 for 1.5 hours and then was transferred to bioreactor, in bioreactor for both non-treated and pre-treated $C_{o,\,MTBE}$ = 30 mg/L, T = 25 ± 1°C. Calculation of error bars is explained in Section 3.1.2.

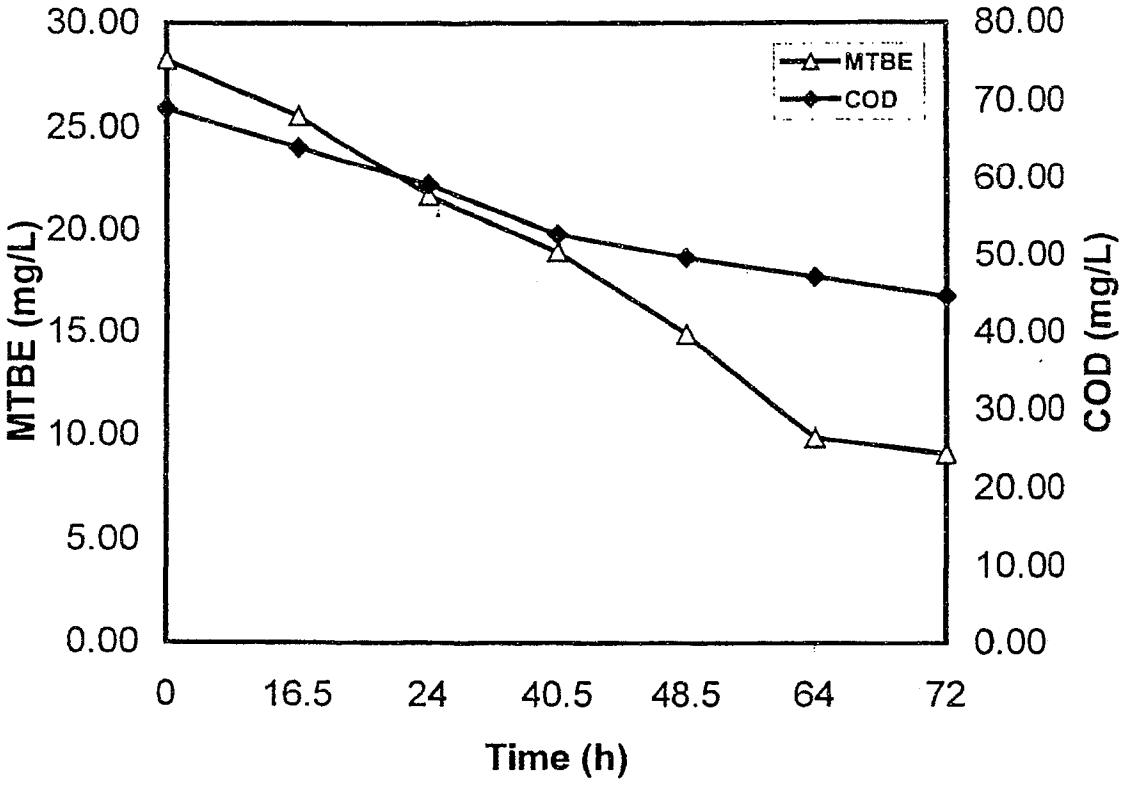

Figure 4.34. COD changes in biological treatment of pre-treated solution of MTBE in photoreactor by microorganisms in SBR. Microorganisms were taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. In photoreactor $C_{o,\,MTBE}$ = 50 mg/L and was degraded there by UV/TiO_2 for 1.5 hours and then was transferred to bioreactor while C_{MTBE} = 30 mg/L, T = 25 ± 1°C.

was assumed in single bioreactor in previous section, reflected in COD values. Change of BOD with the decrease of MTBE is illustrated in Figure 4.35. The trend of BOD decrease was the same as for MTBE, which was observed and discussed in non-treated case before.

When the biodegradation rate of non-treated solution was compared to that of the pre-treated one (Figure 4.33), the value of 0.041 min^{-1} slower rate constant in non-treated case gave this conclusion that pre-treatment by UV/TiO_2 did not enhance the performance of the biodegradation of MTBE. The lower rate of MTBE consumption can be interpreted that the presence of intermediates coming from chemical treatment interfered the biotreatment of MTBE and made its degradation slower. Since in combination process microorganisms confront with intermediates as well as MTBE, in acclimation phase the presence of intermediates must be considered.

4.2.6. Cost Optimization for Combined Photochemical and Biological Processes for the Treatment of MTBE

In the last part of this study, by the knowledge of degradation rate in each photochemical and biological phase, the combined processes were optimized for relative cost in order to find an economic and efficient method of treatment. This part of current study did aim to provide a cost optimization and not a cost estimation, because a comprehensive estimation of costs needed more studies and was out of the defined goals of this study. The purpose of the optimization was a simply comparison between different possible treatments of MTBE, therefore, the relative cost, and not the real cost, was

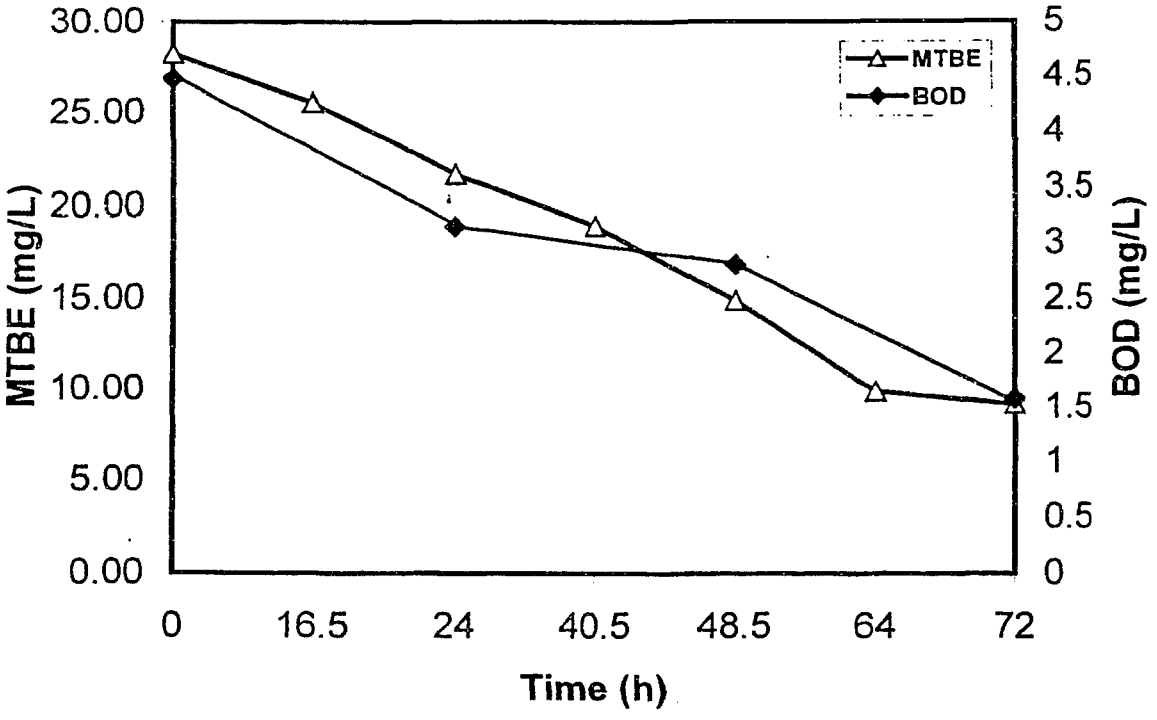

Figure 4.35. BOD changes in biological treatment of pre-treated solution of MTBE in photoreactor by microorganisms in SBR. Microorganisms were taken from activated sludge unit of municipal wastewater treatment plant of North Toronto and acclimated to MTBE. In photoreactor $C_{o,\,MTBE}$ = 50 mg/L and was degraded there by UV/TiO_2 for 1.5 hours and then was transferred to bioreactor while C_{MTBE} = 30 mg/L, T = 25 ± 1°C.

estimated for each process and this term was compared. The values of relative costs for various methods of treatment were used as a tool to compare them from the economic point of view. Since this term is only used for comparison, it is not expressed in any units. The high values correspond to expensive methods and low values indicate less expensive method of treatment. For example, a photochemical process with relative cost of 1000 is 5 times more expensive than a biological process with relative cost of 200.

An important step in the combination process is the determination of a goal in order to define the efficiency of the process. The efficiency values are good tools to optimize the conditions in a combined system (Scott and Ollis, 1995). In a combined process, efficiency of each chemical and biological process determines the global efficiency (Scott and Ollis, 1996). Measurement of efficiency should be conducted within the definition of constraints. Without constraints, process with higher efficiency would have an indefinite reaction time until the global goal is achieved (Scott and Ollis, 1995).

The most crucial part of the optimization process is the appropriate formulation of the problem. Optimization in the operation of the process includes the formulation of a suitable objective function and a mathematical description of the processes, which form a set of constraints. The objective of optimization in this study was the cost minimization in a coupled photochemical-biological system by achieving the required amount of MTBE through the definition of the residence time in each photochemical or biological reactor.

Since there are inherent differences between chemical and biological treatments, the following considerations and simplifications were considered:

- The estimation included the cost of reactors within the reaction time, therefore, the cost of additional operations such as neutralization, centrifuge, filtration, reutilization of TiO_2, acclimatization, and transfer of solution between reactors were not included. Also, chemical costs and capital investment were ignored. This assumption made the cost optimization be primarily based on the reaction time.

- The effect of initial concentration of MTBE on both chemical and biological reaction rates was ignored and for constants reaction rate in photoreaction, the value of 1.32×10^{-2} min^{-1} and in bioreaction for non-treated and pre-treated solutions values of 3.235×10^{-1} and 2.825×10^{-1} mg L^{-1} h^{-1} were considered, respectively.

- For degradation of TBF, as the primary and major product of MTBE degradation by UV/TiO_2, a psuedo first-order reaction with the rate constant of 1.1×10^{-2} min^{-1} was considered (Barreto et al., 1995).

- For estimating the process cost, logarithmic relationship, known as the six-tenths-factor rule (Peters and Timmerhaus, 1991), was used as a volumetric cost scale. In this rule, when the cost of a unit at given volume is known, the cost of similar unit with X times volume of the first one is about $(X)^{0.6}$ times the cost of initial unit. This is the reason that is called volumetric cost scale. Using this factor is an oversimplification of cost model because the cost capacity factor differs from 0.2 to greater than 1 (Peters and Timmerhaus, 1991), but in the lack of other information, 0.6 factor can be an appropriate estimation.

These assumptions led to the optimization scenario as follows:

MTBE with the initial concentration of C_0 was partially degraded to its intermediate TBF under a first-order reaction:

$$MTBE \xrightarrow{k_1} TBF \xrightarrow{k_2} product$$

$$\frac{dC}{dt_C} = -k_1 C \qquad (4.23)$$

$$Initial\ condition\ of\ treatment: C(0) = C_0 = 30\ \text{mg/L} \qquad Boundary\ condition: C(t_C) = C_C$$

$$-\ln\frac{C_C}{C_0} = k_1 t_C \Rightarrow t_C = \frac{\ln C_0 - \ln C_C}{k_1} \qquad (4.24)$$

$$\Rightarrow C_C = C_0 e^{-k_1 t_C} \qquad (4.25)$$

Where:

C_0 = Initial concentration of MTBE in photoreactor, 30 mg/L

C_C = Residue of MTBE in photoreactor at time t_C, mg/L

k_1 = MTBE degradation rate constant in photoreactor, 1.32×10^{-2} min^{-1}

k_2 = TBF degradation rate constant in photoreactor, 1.1×10^{-2} min^{-1}

t_c = Residence time in photoreactor, min

$$\frac{dC_T}{dt_C} = k_1 C_C - k_2 C_T \qquad (4.26)$$

$$\frac{dC_T}{dt_C} = k_1 C_0 e^{-k_1 t_C} - k_2 C_T \qquad (4.27)$$

Where:

C_T = Concentration of TBF in photoreactor at time t_C, mg/L

With considering following conditions, the integration of Equation (4.27) resulted in:

$$Initial\ \ condition: C_T(0) = 0 \qquad Boundary\ \ condition: C_T(t_C) = C_T$$

$$C_T = C_0 k_1 \left(\frac{e^{-k_1 t_C} - e^{-k_2 t_C}}{k_2 - k_1}\right) \qquad (4.28)$$

For equilibrium, Equation (4.24) was substituted into Equation (4.28):

$$C_T = \frac{k_1 C_0}{k_2 - k_1}\left(\frac{C_C}{C_0} - \left(\frac{C_C}{C_0}\right)^{\frac{k_2}{k_1}}\right) \qquad (4.29)$$

As it was discussed before, the intermediates produced in the chemical treatment could not be consumed by microorganisms and, therefore, were accumulated in the bioreactor. As a result, the value of C_T in the bioreactor would be constant. The effluent of this reactor, which had the concentration of C_C, entered to the bioreactor:

$$\frac{dC}{dt_B} = k_3 \qquad (4.30)$$

$$Initial\ \ condition: C(0) = C_C \qquad Boundary\ \ condition: C(t_B) = C_B$$

$$C_C - C_B = k_3 t_B \Rightarrow t_B = \frac{C_C - C_B}{k_3} \qquad (4.31)$$

Where:

C_C = Initial concentration of MTBE in bioreactor, mg/L

C_B = Residue of MTBE in bioreactor at time t_B, mg/L

k_3 = MTBE degradation rate constant in bioreactor with pre-treatment, 4.7×10^{-3} mg L^{-1} min^{-1}

t_B = Residence time in bioreactor, min

Since individual reactor volume is proportional to individual residence time (Esplugas and Ollis, 1997), the six-tenths-factor rule was applied and a model for estimation of the relative cost in the combined processes was developed (Esplugas and Ollis, 1997):

$$f = Cost \quad function: t_B^{0.6} + at_C^{0.6} \qquad (4.32)$$

Where a is the volumetric cost ratio between AOP and biological reactor, which must be equal or greater than 1. With increasing the parameter a above unity, the chemical reactor cost exceeds that of the bioreactor (Esplugas and Ollis, 1997). Esplugas and Ollis (1997) studied $1 \le a \le 10$ for ozone and peroxide combined with activated sludge treatment, but in the absence of the information about the relative cost in UV/TiO_2 and biological processes, for this study a assumed to be 5, although the effect of a will be discussed later. The new cost function, as an objective function, was defined as:

$$f = Objective \quad function: t_B^{0.6} + 5t_C^{0.6} \qquad (4.33)$$

The optimum amount of the residence time in each reactor depended on the required overall efficiency. Based on the first assumption of this optimization, the optimum

residence time can result in the optimum amount of the operation cost. The efficiency of the individual and overall processes was defined as the ratio of the amount of the converted MTBE to its initial amount (Scott and Ollis, 1996).

$$\eta_C = (C_0 - C_C)/C_0 \qquad (4.34)$$

$$\eta_B = (C_C - C_B)/C_0 \qquad (4.35)$$

$$\eta_T = (C_0 - C_B)/C_0 = \eta_C + \eta_B \qquad (4.36)$$

Where:

η_C = Efficiency in photoreactor

η_B = Efficiency in bioreactor

η_T = Overall efficiency

The favourite efficiency for integrated system makes the objective function to have a response within the constraints, and optimal operating times in each reactor were identified under given constraints. Since the cost of each process was assumed to be proportional to the cost of reactor within the residence time, the optimization was primarily based on the reaction time, and, therefore the cost optimization could be accomplished through the measurement of the optimal residence time in each reactor. The final goal of treatment was to achieve the MTBE concentration set by EPA at Drinking Water Advisory (EPA, 2003), which means that the residue of this compound after biological treatment (C_B) should be less than 0.04 mg/L. This value defined the overall efficiency and imposed a constraint to the objective function. In addition, there

was no production of MTBE in the system, so C_B must be equal or less than C_C. For the same reason C_C must be equal or less than C_0. Also the only source of TBF was the degradation of MTBE in photoreactor, therefore C_T must be less than or equal to C_0. The standard formulation form of this optimization problem would be:

Minimize: $$f = t_B^{0.6} + 5t_C^{0.6} \qquad (4.33)$$

Subject to:

$$C_B \le 0.04 \qquad (4.32) \quad , \qquad C_B \le C_C \qquad (4.38)$$

$$C_T = \frac{k_1 C_0}{k_2 - k_1}\left(\frac{C}{C_0} - \left(\frac{C}{C_0}\right)^{\frac{k_2}{k_1}}\right) \qquad (4.39)$$

$$0 \le C_C \le C_0 \qquad (4.40)$$

$$0 \le C_T \le C_0 \qquad (4.41)$$

$$t_C \ge 0 \qquad (4.42) \quad , \qquad t_B \ge 0 \qquad (4.43)$$

The optimization problem was solved by Generalized Reduced Gradient (GRG2) non-linear optimization method (Appendix F). C_C, C_T and C_B were adjusted until the constraints in the problem were satisfied and the objective function was minimized. The results showed that the minimum relative cost would be 158 if solution remained in photoreactor for 176 minutes, which resulted in 2.93 and 8.54 mg/L concentrations of

MTBE and TBF, respectively. The solution then would be transferred to the bioreactor and remained there for 617 minutes to reduce the MTBE concentration to 0.04 mg/L.

The changes of minimum objective function with different values of ratio of volumetric cost, a, were investigated. The results are summarized in Table 4.3.

Table 4.3. Effect of various values of ratio of volumetric cost on combined treatment.

	$a = 1.5$	$a = 3$	$a = 5$	$a = 10$
t_C (min)	376	262	176	0
t_B (min)	36	192	617	6374
$t_C + t_B$ (min)	412	454	793	6374
Relative cost	61	108	158	192
C_C (mg/L)	0.21	0.94	2.93	30
C_B (mg/L)	0.04	0.04	0.04	0.04
C_T (mg/L)	1.66	4.53	8.54	0
Organic removal %	94.34	84.77	71.41	99.87
t_C / t_B	10.51	1.367	0.285	0

As it was mentioned before, the increase of the parameter a above unity results in the chemical reactor cost exceeds that of the bioreactor (Esplugas and Ollis, 1997), Therefore in the cost optimization, the increase of a decreased the tendency of chemical reaction until the biological treatment completely dominated the process at $a = 10$. Although the chemical portion decreased by increase of a, at the same time the overall cost was increased, which meant that a had important roll in the cost estimation. If

residue of MTBE and produced TBF were the only compounds remained in the bioreactor after completion of combined process, organic removal would be defined as:

$$organic\ \ removal = \frac{C_0 - (C_B + C_T)}{C_0} \times 100 \qquad (4.44)$$

Table 4.3 shows that the decrease of a and consequently the increase of chemical residence time increased the organic removal. Considering $a = 5$, the same optimization procedure was followed with the value of rate constant in non-acclimated microorganisms process. In that case, the effect of the presence of chemical by-products on the rate of biological reaction was ignored. Because of the low rate of biological reaction, optimization resulted in an almost 500-minute single photoreaction with relative cost of 208; therefore, the combination process was meaningless.

Another scenario was optimized by reversed sequence of biological and photochemical reactions in the combined system:

$$\frac{dC}{dt_B} = k_4 \qquad (4.45)$$

$$Initial\ \ condition: C(0) = C_0 = 30\ \ \text{mg/L} \qquad Boundary\ \ condition: C(t_B) = C_B$$

$$C_0 - C_B = k_4 t_B \Rightarrow t_B = \frac{C_0 - C_B}{k_4} \qquad (4.46)$$

Where:

C_0 = Initial concentration of MTBE in bioreactor, 30 mg/L

C_B = Residue of MTBE in bioreactor at time t_B, mg/L

k_4 = MTBE zero-order reaction rate constant in bioreactor without pre-treatment, 5.4×10^{-3} mg L^{-1} min^{-1}

t_B = Residence time in bioreactor, min

The effluent of this reactor, which had the concentration of C_B, was sent to photoreactor in which MTBE was partially degraded to its intermediate TBF under a first-order reaction:

$$MTBE \xrightarrow{k_1} TBF \xrightarrow{k_2} product$$

$$\frac{dC}{dt_C} = -k_1 C \qquad (4.47)$$

$$Initial\ \ condition: C(0) = C_B \qquad Boundary\ \ condition: C(t_C) = C_C$$

$$-\ln\frac{C_C}{C_B} = k_1 t_C \Rightarrow t_C = \frac{\ln C_B - \ln C_C}{k_1} \qquad (4.48)$$

$$\Rightarrow C_C = C_B\, e^{-k_1 t_C} \qquad (4.49)$$

$$\frac{dC_T}{dt_C} = k_1 C_C - k_2 C_T \qquad (4.50)$$

$$\frac{dC_T}{dt_C} = k_1 C_B e^{-k_1 t_C} - k_2 C_T \qquad (4.51)$$

$$Initial\ \ condition: C_T(0) = 0 \qquad Boundary\ \ condition: C_T(t_C) = C_T$$

$$C_T = C_B k_1 \left(\frac{e^{-k_1 t_C} - e^{-k_2 t_C}}{k_2 - k_1}\right) \qquad (4.52)$$

Where:

C_B = Initial concentration of MTBE in photoreactor, mg/L

C_C = Residue of MTBE in photoreactor at time t_C, mg/L

C_T = Concentration of TBF in photoreactor at time t_C, mg/L

k_1 = MTBE degradation rate constant in photoreactor, 1.32×10^{-2} min^{-1}

k_2 = TBF degradation rate constant in photoreactor, 1.1×10^{-2} min^{-1}

t_c = Residence time in photoreactor, min

For equilibrium, Equation (4.48) was substituted into Equation (4.52):

$$C_T = \frac{k_1 C_B}{k_2 - k_1}\left(\frac{C_C}{C_B} - \left(\frac{C_C}{C_B}\right)^{\frac{k_2}{k_1}}\right) \qquad (4.53)$$

With the same objective function and similar constraints of previous case, the standard formulation form of this optimization problem would be:

Minimize: $f = t_B^{0.6} + 5t_C^{0.6}$ (4.33)

Subject to:

$C_C \le 0.04$ (4.54) , $C_C \le C_B$ (4.55)

$$C_T = \frac{k_1 C_B}{k_2 - k_1}\left(\frac{C}{C_B} - \left(\frac{C}{C_B}\right)^{\frac{k_2}{k_1}}\right) \qquad (4.56)$$

$0 \le C_B \le C_0$ (4.57)

$$0 \le C_T \le C_B \qquad (4.58)$$

$$t_B \ge 0 \qquad (4.59) \quad , \qquad t_C \ge 0 \qquad (4.60)$$

Optimization in this sequence did not result in a combined system but led to a single photochemical or a single biological process with relative cost of 208 and 176, respectively. The single step photoreaction required almost 500 minutes time while bioreaction alone by acclimated microorganisms would be completed within 5548 minutes.

Table 4.4. Performance and relative cost of various combined treatment of MTBE.

	chemical+biological treatment (acclimated)	biological+chemical treatment (acclimated)		Single chemical treatment	Single biological treatment (acclimated)	Single biological treatment (non-acclimated)
		Chem.	Bio.			
t_C (min)	176	502	0	502	0	0
t_B (min)	617	0	5548	0	5548	220000
$t_C + t_B$ (min)	793	502	5548	502	5548	220000
Relative cost	159	208	176	208	176	1605
C_C (mg/L)	2.93	0.04	-------	0.04	-------	-----
C_B (mg/L)	0.04	------	0.04	-------	0.04	0.04
C_T (mg/L)	8.54	0.499	0	0.499	0	0
Organic removal %	71.41	98.2	99.87	98.2	99.87	99.87

Table 4.4 shows a comparison between different combinations of photochemical and biological treatment. The optimization showed that the most cost-efficient process was a chemical/biological treatment with relative cost of 159. A single biological treatment by

acclimated microorganisms can be the next option, which lasts for 5548 minutes and has the relative cost of 176. Single chemical reaction takes 502 minutes, and its relative cost would be 208. The longest and the most expensive process would be the treatment of MTBE by non-acclimated microorganisms which can be completed in 220000 minutes and has 1605 relative cost. Optimization of biological/chemical process resulted in either single chemical or single biological treatment; therefore, the cost-efficiency of these processes had the following order (Figure 4.36):

Chemical/biological, single biological (acclimated), single chemical, and single biological (non-acclimated).

The difference between the cost of non-acclimated treatment and of the one in which acclimated microorganisms are used should be compared with the costs of the acclimatization to justify the selection of any of these processes. As mentioned before, the relative cost, not the real cost, was defined for this optimization to compare the cost of different process of treatment. For example this tool shows that the cost of treatment of MTBE by non-acclimated microorganisms is about 9 times more than that of treatment by acclimated microorganisms ($1605 \div 176 = 9.1$), or single photochemical treatment costs about 1.3 times more than combined treatment ($208 \div 159 = 1.3$).

Predictably, the shortest and the longest treatment were single chemical and single biological (non-acclimated) processes, respectively (Figure 4.37). Obtained results from optimization showed that the chemical/biological process had the lowest level of organic

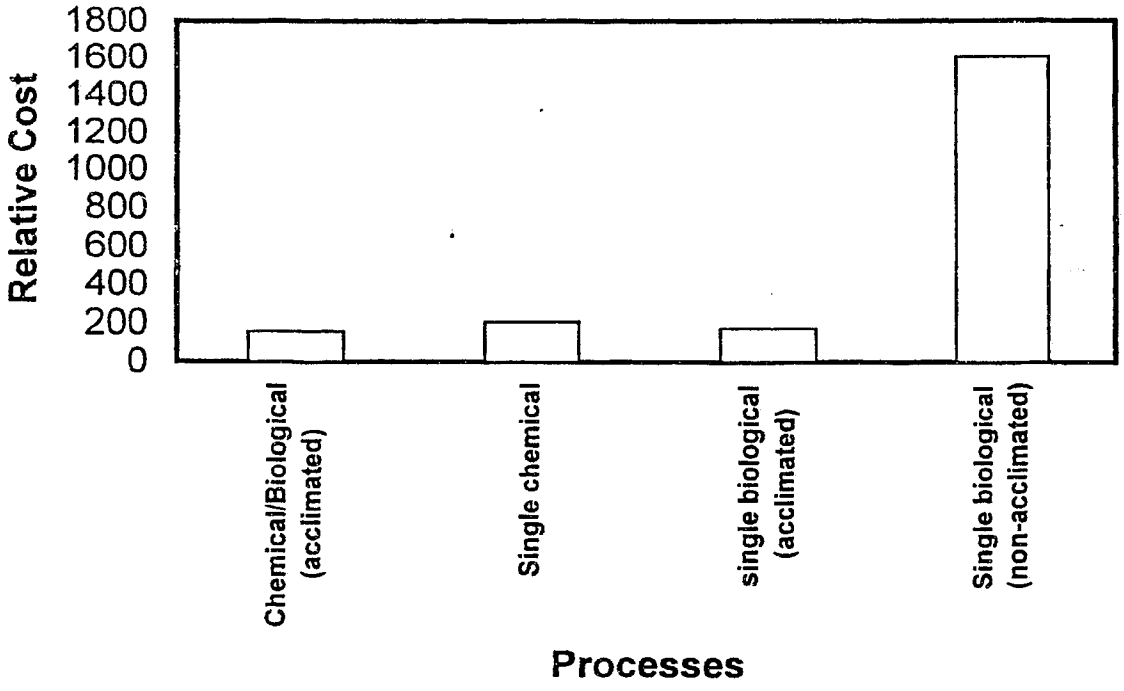

Figure 4.36. Comparison of relative cost in various methods of treatment of MTBE.

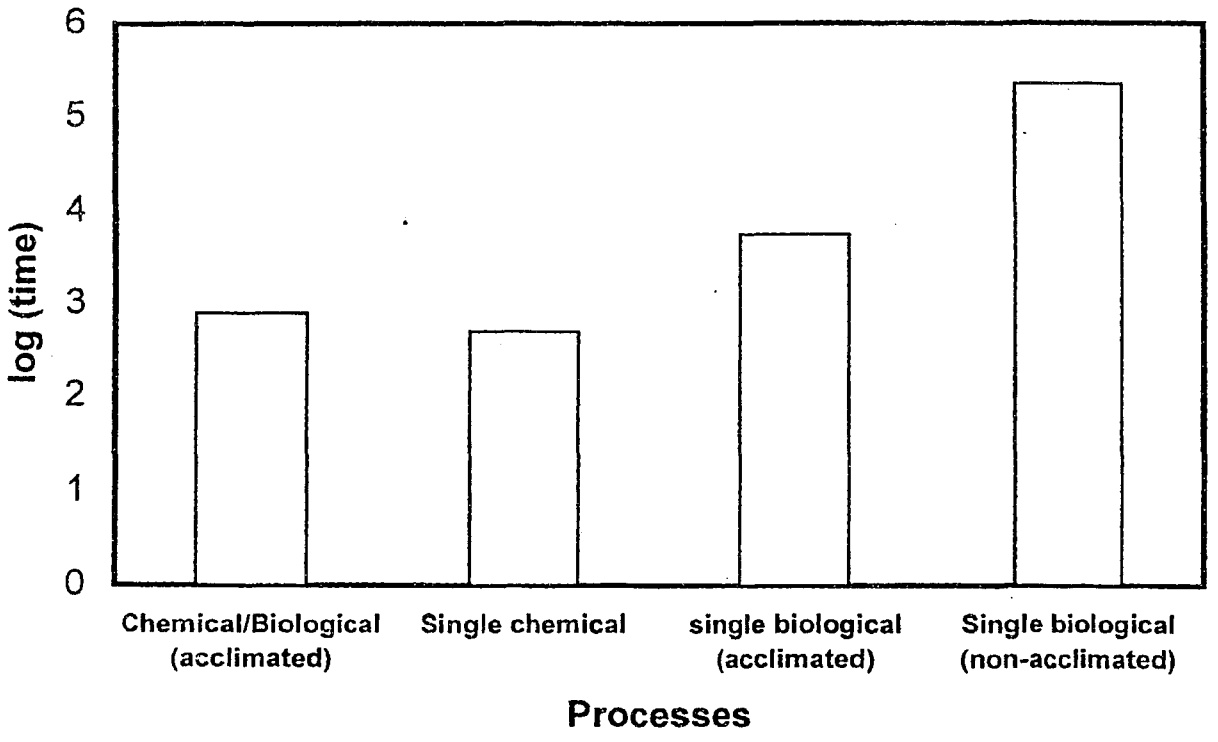

Figure 4.37. Comparison of treatment time in various methods of MTBE removal. Because of big difference between residence times in different processes, the logarithm of time is shown in Y-axis

removal while the single biological treatments, either by acclimated or non-acclimated microorganisms, were the most efficient processes for this purpose. It should be noticed absence of information, it was assumed that in the biological phase no organic matter was produced and in chemical phase, TBF was the only by-product. More studies about the mechanisms of chemical and biological treatments may change this assumption and consequently change the conclusion about the performance of processes in organic removal.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The following conclusions were drawn from this thesis:

- An important result emerging from this study was that UV/H_2O_2 and UV/TiO_2 could be used to remove MTBE from water. Degradation of MTBE with H_2O_2 in the presence of UV was a first-order reaction with respect to MTBE and the apparent rate constant was found to be 1.307×10^{-1} min^{-1} during the first 30 minutes of reaction. The disappearance of H_2O_2 followed a zero-order reaction with rate constant of 2.13×10^{-1} mg $L^{-1}min^{-1}$. For treatment of MTBE the highest effective amount of TiO_2 in UV/TiO_2 process was 1.5 g/L and the reaction was modeled by a first-order equation with apparent rate constant of 1.32×10^{-2} min^{-1}.

- Combination of UV/H_2O_2 and UV/TiO_2 did not have any advantages over each of them alone. Competition between MTBE and H_2O_2 for the surface of TiO_2 could be the reason of this decrease in rate of reaction.

- Since MTBE is a poor substrate as sole carbon source, it should be biodegraded under controlled aerobic conditions. Acclimation of

microorganisms to MTBE could improve its rate of biodegradation and promote the apparent rate constant from 4.36×10^{-2} day^{-1} to 3.235×10^{-1} $mg\,L^{-1}\,h^{-1}$.

- Pre-treatment of MTBE by photocatalytic process did not improve its bioderadability. The obtained results support this hypothesis that intermediates in primary phase have important role in the efficiency and proceeding of the combined process because their property can enhance or deter the next step.

- When the costs in photoreactor are much more than that in bioreactor (such as $a=5$), a combination of photochemical/biological treatment can be suggested as an economic option. Although chemical pre-treatment cannot enhance the biodegradability, the high difference in costs can justify this combination.

- Optimization of different combinations of chemical and biological processes showed that only with acclimated microorganisms, the biological treatment (either single or in conjunction with chemical treatment) could be an economic option; otherwise, a single chemical treatment would be the most cost-effective process.

5.2. Recommendations

- Studies should be performed to identify and quantify the intermediates and to define the mechanisms in both chemical and biological processes. The complete mineralization should be tracked by measurement of total organic carbon (TOC) to ensure the removal of initial and produced organic compounds.

- The intermediates, which are formed in photoreactor, are introduced into the bioreactor in a combined system, therefore the presence of these intermediates should be considered in the process of acclimatization.

- To have more precise optimization, detailed studies are required to estimate the cost in each process and consequently propose a comprehensive model. By considering all existing costs in both processes, this model can prevent some simplifications that were unavoidable in this study in the absence of adequate information.

- Since natural waters contain many other chemical species, studies should be conducted to investigate the interaction between various substrates and the effect of their presence on the efficiency of the treatment.

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APPENDICES

A: Determination of BOD_5

In BOD test after 5 days incubation at 20°C, the final DO of samples and blank were measured and BOD_5 was calculated as follows:

$$BOD_5, mg/L = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \qquad (a.1)$$

Where:

D_1 = DO of diluted sample immediately after preparation, mg/L

D_2 = DO of diluted sample after 5 day incubation at 20°C, mg/L

P = Decimal volumetric fraction of sample used

B_1 = DO of seed control before incubation, mg/L

B_2 = DO of seed control after incubation, mg/L

f = Ratio of seed in diluted sample to seed in seed control

To measure the BOD_5 for a solution of 10 mg/L of MTBE, BOD bottle was filled with 295 ml of aerated MTBE solution, 5 ml of aerated seed material, and nutrients. All details for BOD test are in Section 3.5.7. The initial and final DO were 7.60 and 6.17 mg/L, respectively. At the same time, the initial and final DO in blank bottle were 7.82 and 7.80 mg/L, respectively, therefore:

$$BOD_5 = \frac{(7.60 - 6.17) - (7.82 - 7.80)}{295/300} = 1.43 \quad mg/L$$

B: Determination of Removal Efficiency

In this study, the percentage of degradation was considered as the performance of the system, which can be expressed as removal efficiency (RE) (Fortin and Deshusses, 1999):

$$RE = \frac{C_0 - C_t}{C_0} \times 100 \qquad (b.1)$$

Where:

C_0 = Initial concentration of MTBE in the reactor, mass/ volume

C_t = Residual concentration of MTBE in the reactor at time t, mass/ volume

If the concentration of MTBE decreases from initial amount of 8.06 mg/L to 0.12 mg/L within 5 hours, the removal efficiency during this time will be:

$$RE = \frac{8.06 - 0.12}{8.06} \times 100 = 98.5\%$$

C: Determination of Reaction Rate Constant

In a batch reactor, the substrate is added and during the retention time it is well mixed. A mass balance for the substrate in a complete-mixed reactor can be written as follow (Reynolds and Richards, 1996):

$$Accumulation\ of\ substrate = -(the\ rate\ of\ reaction\ of\ substrate)$$

In a batch reactor with first-order reaction, the terms of accumulation and reaction are $\frac{dC}{dt}$ and kC, respectively:

$$\frac{dC}{dt} = -kC \qquad (c.1)$$

$$\int_{C_0}^{C_t} \frac{dC}{C} = -k\int_0^t dt \qquad (c.2)$$

$$\frac{C_t}{C_0} = e^{-kt} \qquad (c.3) \qquad or \qquad -\ln\frac{C_t}{C_0} = kt \qquad (c.4)$$

Where:

C_0 = Initial concentration of MTBE in the reactor, mass/ volume

C_t = Residual concentration of MTBE in the reactor after the reaction time of t, mass/ volume

t = Reaction time, time

k = First-order rate constant, $time^{-1}$

By linear regression on natural logarithm of C_t/C_0 versus time, the first-order rate constant can be calculated from the slope of the graph (Figure C.1).

Table C.1. Experimental data for determination of rate constant.

C (mg/L)	t (min)	C/C_o	$-\ln (C/C_o)$
27.66	0	1.00	0.00
7.43	10	0.27	1.34
1.72	20	0.06	2.80
0.61	30	0.02	3.87

The same procedure for a zero-order reaction can be followed:

$$\frac{dC}{dt} = -k \qquad (c.5)$$

$$\int_{C_0}^{C_t} dC = -k\int_0^t dt \qquad (c.6)$$

$$\frac{C_t}{C_0} = kt \qquad (c.7)$$

By linear regression on C_t/C_0 versus time, the zero-order rate constant can be calculated from the slope of the graph (Figure C.2).

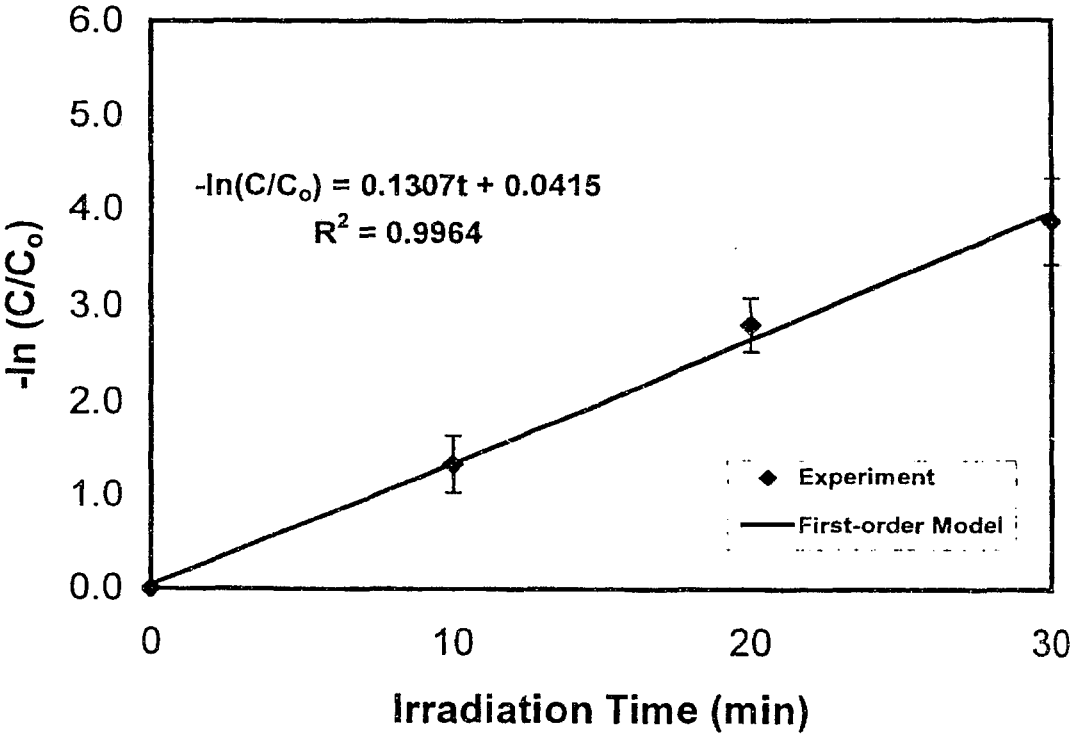

Figure C.1. Determination of rate constant in a first-order reaction. Calculation of error bars is explained in Section 3.1.2.

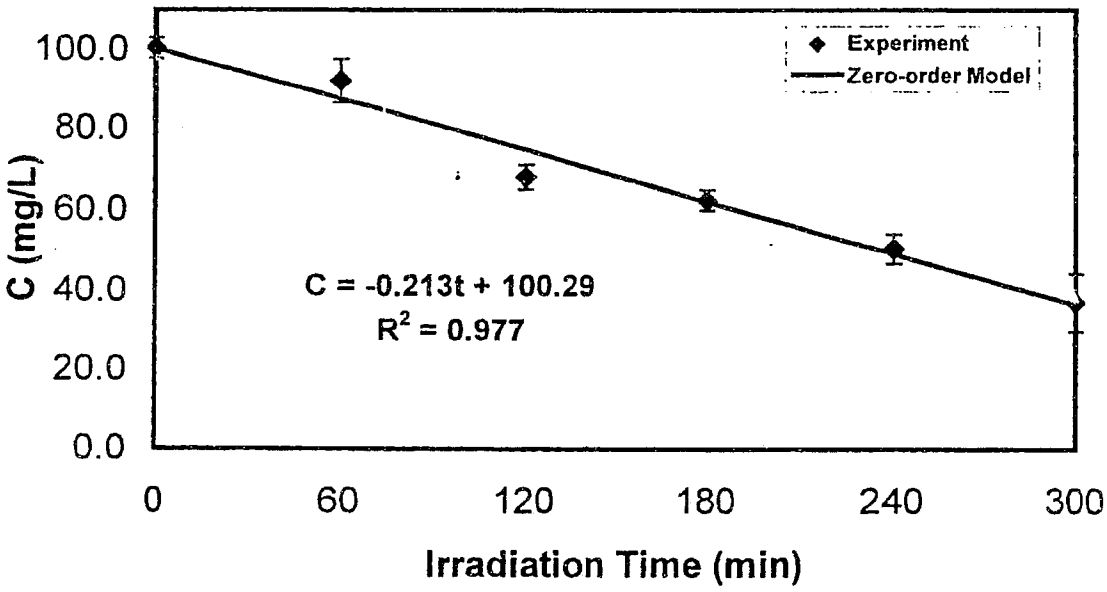

Figure C.2. Determination of rate constant in a zero-order reaction. Calculation of error bars is explained in Section 3.1.2.

Table C.2. Experimental data for determination of rate constant.

C (mg/L)	t (min)
100.33	0
92.00	60
68.00	120
62.33	180
50.33	240
37.00	300

D: Determination of Radiation Energy of a Photon

For a given wavelength, the radiation energy is determined by equation (Ranby and Rabek, 1975):

$$E = h\nu = h\frac{c}{\lambda} \qquad (d.1)$$

Where:

h = Planck's constant, 6.62×10^{-27} erg sec

λ = Wavelength, $\overset{o}{A}$, nm or cm

c = Velocity of light, 3×10^{10} cm

$$E = \frac{1.986 \times 10^{-8}}{\lambda}(erg) = \frac{4.634 \times 10^{-16}}{\lambda}(cal) = \frac{2.86 \times 10^{5}}{\lambda}(kcal/mol) \qquad (d.2)$$

E: Determination of Ultimate BOD

A first-order reaction is considered for the kinetics of the BOD reaction (Metcalf and Eddy, 1991):

$$\frac{dL_t}{dt} = -kL_t \qquad (e.1)$$

Where:

L_t = Amount of BOD remaining in the water at time t, mg/L

k = Reaction rate constant, day^{-1}

This equation can result in:

$$\frac{L_t}{L} = e^{-kt} \qquad (e.2)$$

Where:

$L = BOD_{ultimate}$ = BOD remaining at time t_0, mg/L

The amount of BOD that has been exerted at any time t equals:

$$L - L_t = L(1 - e^{-kt})$$
$$= BOD_{ultimate}(1 - e^{-kt}) \qquad (e.3)$$

Therefore, the 5-day BOD equals:

$$BOD_5 = BOD_{ultimate}(1 - e^{-5k}) \qquad (e.4)$$

Using the obtained values of BOD_5 and BOD_U in this formula, results in reaction rate constants of 0.099, 0.096, 0.118 and 0.101 day^{-1} for 5, 10, 30 and 50 mg/L solution of MTBE, respectively.

F: Optimization Results

GRG2 uses an implementation of the generalized reduced gradient (GRG) algorithm, which solves nonlinear optimization problems. It seeks a feasible solution first (if one is not provided) and then retains feasibility as the objective is improved. It uses the quasi-Newton algorithm as its default choice for determining a search direction. There are two essential steps that must be taken in order to present an optimization problem to GRG2. First, a function must be written to compute values of the constraint functions and the objective function for given values of the variables. Next, the data that describe the optimization problem must be created, organized, and passed to GRG2. The data consist of the variables, lower and upper bounds on the variables and the functions (constraint functions plus the objective function). A tool in Microsoft Excel, called solver, was used to solve the optimization problem in this study by GRG2.

Tables f.1, f.2, f.3.1, and f.3.2 show the obtained results of solution of optimization problem for cost estimation by GRG2:

Table f.1. Obtained results for optimization of cost estimation in a Photochemical + biological (acclimated microorganisms) treatment.

Microsoft Excel 9.0 Answer Report					
Worksheet: [opt.xls]Sheet1					
Report Created: 6/14/04 9:56:11 PM					
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Cell	**Name**	**Original Value**	**Final Value**		
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Adjustable Cells					
Cell	**Name**	**Original Value**	**Final Value**		
$G$2	Cc	5	2.936473647		
$H$2	Ct	2	8.536327233		
$I$2	Cb	1	0.04		
Constraints					
Cell	**Name**	**Cell Value**	**Formula**	**Status**	**Slack**
$K$2	Con 1	8.53632727	$K$2=$H$2	Binding	0
$I$2	Cb	0.04	$I$2<=$G$2	Not Binding	2.896473647
$E$2	Tb	616.9488868	$E$2>=0	Not Binding	616.9488868
$D$2	Tc	176.042088	$D$2>=0	Not Binding	176.042088
$G$2	Cc	2.936473647	$G$2<=$F$2	Not Binding	27.06352635
$H$2	Ct	8.536327233	$H$2>=0	Not Binding	8.536327233
$G$2	Cc	2.936473647	$G$2>=0	Not Binding	2.936473647
$H$2	Ct	8.536327233	$H$2<=$F$2	Not Binding	21.46367277
$I$2	Cb	0.04	$I$2<=0.04	Binding	0
$I$2	Cb	0.04	$I$2>=0	Not Binding	0.04

Table f.2. Obtained results for optimization of cost estimation in a Photochemical + biological (non-acclimated microorganisms) treatment

Microsoft Excel 9.0 Answer Report					
Worksheet: [opt.xls]Sheet1					
Report Created: 6/16/04 12:40:46 PM					
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Adjustable Cells					
Cell	**Name**	**Original Value**	**Final Value**		
$G$2	Cc	0.04	0.04		
$H$2	Ct	10	0.499557008		
$I$2	Cb	0.04	0.04		
Constraints					
Cell	**Name**	**Cell Value**	**Formula**	**Status**	**Slack**
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$I$2	Cb	0.04	$I$2<=$G$2	Binding	0
$D$20	Tc	501.4705454	$D$20>=0	Not Binding	501.4705454
$E$20	Tb	0	$E$20>=0	Binding	0
$G$2	Cc	0.04	$G$2<=$F$2	Not Binding	29.96
$H$2	Ct	0.499557008	$H$2>=0	Not Binding	0.499557008
$G$2	Cc	0.04	$G$2>=0	Not Binding	0.04
$I$2	Cb	0.04	$I$2>=0	Not Binding	0.04
$H$2	Ct	0.499557008	$H$2<=$F$2	Not Binding	29.50044299
$I$2	Cb	0.04	$I$2<=0.04	Binding	0

Table f.3.1. Obtained results for optimization of co[illegible]esi[illegible]ation in a biological (acclimated microorganisms) + Photochen[illegible]catment

Microsoft Excel 9.0 Answer Report					
Worksheet: [opt.xls]Sheet2					
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Target Cell (Min)					
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Adjustable Cells					
Cell	**Name**	**Original Value**	**Final Value**		
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$I$2	Ct	2	0.499557008		
Constraints					
Cell	**Name**	**Cell Value**	**Formula**	**Status**	**Slack**
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$I$2	Ct	0.499557008	$I$2<=$G$2	Not Binding	29.50044299
$D$2	Tb	0	$D$2>=0	Binding	0
$E$2	Tc	501.4705454	$E$2>=0	Not Binding	501.4705454
$G$2	Cb	30	$G$2<=$F$2	Binding	0
$I$2	Ct	0.499557008	$I$2>=0	Not Binding	0.499557008
$G$2	Cb	30	$G$2>=0	Not Binding	30
$H$2	Cc	0.04	$H$2<=0.04	Binding	0
$H$2	Cc	0.04	$H$2>=0	Not Binding	0.04

Table f.3.2. Obtained results for optimization of cost estimation in a biological (acclimated microorganisms) + Photochemical treatment

Microsoft Excel 9.0 Answer Report					
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Report Created: 6/14/04 11:48:13 PM					
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Adjustable Cells					
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Constraints					
Cell	**Name**	**Cell Value**	**Formula**	**Status**	**Slack**
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$I$2	Ct	0	$I$2>=0	Binding	0
$G$2	Cb	0.04	$G$2>=0	Not Binding	0.04
$H$2	Cc	0.04	$H$2<=0.04	Binding	0
$H$2	Cc	0.04	$H$2>=0	Not Binding	0.04