

## APPLICATION OF PHOTOCATALYTIC PROCESS FOR REMOVAL OF METHYL TERT-BUTYL ETHER FROM HIGHLY CONTAMINATED WATER

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### ABSTRACT

The oxygenate methyl tert-butyl ether is added to gasoline to increase the octane level and to reduce carbon monoxide and hydrocarbon emissions by vehicles. The high mobility, water solubility, and resistance to natural attenuation associated with methyl tert-butyl ether may result in contamination of ground and surface waters. In this research the degradation of aqueous methyl tert-butyl ether at relatively high concentrations was investigated by UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> photocatalytic process. The effect of important operational parameters such as pH, amount of H<sub>2</sub>O<sub>2</sub>, catalyst loading, and irradiation time were also studied. Concentrations of methyl tert-butyl ether and intermediates such as tert-butyl formate and tert-butyl alcohol were measured over a 180 min period using a gas chromatograph equipped with flame ionization detector and combined with headspace sampler. Results showed that the time required for complete degradation increased from 30 to 180min, when the initial concentration was increased from 10 to 500mg/L. The first order rate constant for degradation of methyl tert-butyl ether from the hydroxyl radical was estimated to be 0.177 to 0.022 1/min as the concentration increased from 10 to 500mg/L. Study on the overall mineralization monitored by total organic carbon (TOC) analysis showed that in the initial concentration of 100mg/L methyl tert-butyl ether, complete mineralization was obtained after 110min under UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> photocatalytic process.

**Key words:** Photocatalysis, methyl tert-butyl ether, Titanium dioxide, Hydrogen peroxide

### INTRODUCTION

The addition of methyl tert-butyl ether (MTBE) to gasoline as an additive to replace tetraethyl lead has brought about a significant improvement in air quality (Zang and Farnood, 2005a). MTBE raises the oxygen content of gasoline thus helps reduce harmful agent of CO, NO<sub>x</sub> and hydrocarbon emissions from vehicle exhausts (Jacobs *et al.*, 2001; Zang and Farnood, 2005b; Guillard *et al.*, 2003). About 20 million tons (t) are used worldwide mainly for this purpose (Kolb and Puttmann, 2006). Unfortunately, this improvement also leads to a negative environmental impact. Since MTBE has high water solubility, the occurrence of fuel spills or leaks from underground storage tanks or transferring pipeline has led to the contamination

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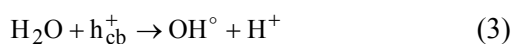
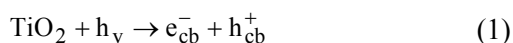
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of water sources. The United States Environmental Protection Agency (EPA) has classified MTBE as a suspect human carcinogen, and suggested the health limit of 20–40µg/L in drinking water (USEPA, 1997).

MTBE is poorly adsorbed, chemically and biologically stable, and very soluble in water, making it very persistent in the environment. Conventional treatment including air stripping, Granular Activated Carbon (GAC) adsorption and biodegradation processes using for MTBE-contaminated groundwater have been inefficient and unsatisfactory (Zang and Farnood, 2005b; Anderson, 2000). Advanced oxidation processes (AOPs), on the other hand, provide promising treatment alternative for MTBE removal (Squillace *et al.*, 1997). These processes rely on the

generation of highly reactive hydroxyl radicals ( $\text{OH}^\circ$ ) that react indiscriminately with most organic compounds such as MTBE, and even result in complete mineralization with a very high reaction rate (Zang and Farnood, 2005b; Rong Xu *et al.*, 2004). One of the most important methods in AOPs is the photocatalytic degradation, which was extensively studied worldwide over the past three decades. The process couples low-energy ultraviolet lamp radiation and a semiconductor photocatalyst (Kuburovic *et al.*, 2007). Upon illumination of the semiconductor with light of energy greater than the semiconductor band gap, electron-hole pairs ( $e^-/h^+$ ) are formed in the conduction and the valence bands of the semiconductor, respectively (Kabra *et al.*, 2004). These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential (Rong Xu *et al.*, 2006).

The first environmental application of  $\text{TiO}_2$  as one of such photocatalysts in aqueous solution was reported 30 years ago (Zang and Farnood, 2005a). The energy needed to activate anatase form of  $\text{TiO}_2$  is 3.2 eV, which corresponds to UV radiation wavelength of  $\lambda \leq 380\text{nm}$  (Zang and Farnood, 2005a). This catalyst has been widely employed due to its photo-stability, non-toxicity, low cost, and water insolubility. Earlier studies have indicated that a wide range of organic substrates can be completely photomineralized in the presence of this semiconductor. In the aqueous slurry, several possible reactions occur on  $\text{TiO}_2$  surface under UV illumination ( $\lambda < 388\text{nm}$ ), as shown below:



The organic pollutants are attacked and oxidized by the radicals formed through the above mechanisms. In addition to hydroxyl radicals, superoxide radical anions and in some cases the positive holes are also suggested as possible oxidizing species that could attack organic contaminants present at or near the surface of  $\text{TiO}_2$  (Zang and Farnood, 2005a).

Several studies have been conducted involving the degradation of MTBE in aqueous solution using

AOPs. These studies have considered photolytic, photocatalytic and microbiological degradation by Kuburovic *et al.*, (2007); UV/ $\text{TiO}_2$  process by Rong *et al.*, (2006); photochemical, biological, and combined processes by Asadi and Mehrvar (2006); effect of hydrogen peroxide concentration and ultraviolet light intensity by Zang and Farnood (2005b), oxidation kinetics and effect of pH on the degradation with Fenton reagent by Burbano *et al.*, (2005); ozonation an UV-Ozonation by Graham *et al.*, (2004); Fenton's reagent by Ray *et al.*, (2002);  $\text{O}_3/\text{H}_2\text{O}_2$  by Safarzadeh-Amiri (2001); UV/ $\text{H}_2\text{O}_2$  by Cater *et al.*, (2000); UV/ $\text{TiO}_2$  by Barreto *et al.*, (1995).

Based on MTBE degradation mechanism, it is clear that the addition of hydrogen peroxide in this process has two competing effects: (1) increasing the concentration of hydroxyl radicals in the reaction media and (2) decreasing the average light intensity within the solution due to the absorption of UV light by  $\text{H}_2\text{O}_2$ . It has been shown earlier that the heterogeneous photocatalytic oxidation processes can be used for removing the pollutants using UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$  and solar/ $\text{TiO}_2/\text{H}_2\text{O}_2$  systems (Bertelli and Selli, 2004; Bozzi *et al.*, 2004; Sreedhar Reddy and Kotaiah, 2005).

In this work, specific emphasis is given to obtain kinetic results of MTBE degradation in water under UV-vis/ $\text{TiO}_2/\text{H}_2\text{O}_2$  system. The effects of factors such as pH, amount of  $\text{H}_2\text{O}_2$ , catalyst loading, and irradiation time were investigated to obtain the optimum conditions. Moreover, the concentration profiles of the reaction intermediates and Total Organic Carbon (TOC) content (for overall mineralization) have been monitored under optimized degradation conditions. Almost all of the studies to date have dealt with the destruction of MTBE in spiked tap water or distilled water. However, the last objective of the present study was to investigate the kinetic and efficiency of degradation of MTBE in an actual gasoline contaminated water, obtained from drainage water of a gas station in Zanzan city which is located at north-west of Iran.

## MATERIALS AND METHODS

### Materials

All chemicals were analytical or reagent grade, or the highest purity available from several suppliers. Analytical grade MTBE and hydrogen

peroxide (30% w/w) were purchased from Merck. tert-butyl formate (TBF) (Aldrich) and tert-butyl alcohol (TBA) (Fluka) were also analytical grade reagents. Titanium dioxide (98% anatase, 2% rutile with an average particle size of 35 nm) was obtained from Merck.

#### Experimental set-up

A 25 mL Pyrex tubular batch reactor with a magnetic stirrer placed under the reactor was designed and used. Fig. 1 shows the schematic

diagram of the experimental set-up. Irradiation was achieved by applying a 400W high-pressure mercury lamp used as the UV-vis light source. In order to keep the reaction mixture at room temperature, a cooling water jacket was placed around the Pyrex reactor. In the present set-up, the bulk solution was about 25cm away from the lamp. During irradiation, the solution was magnetically stirred.

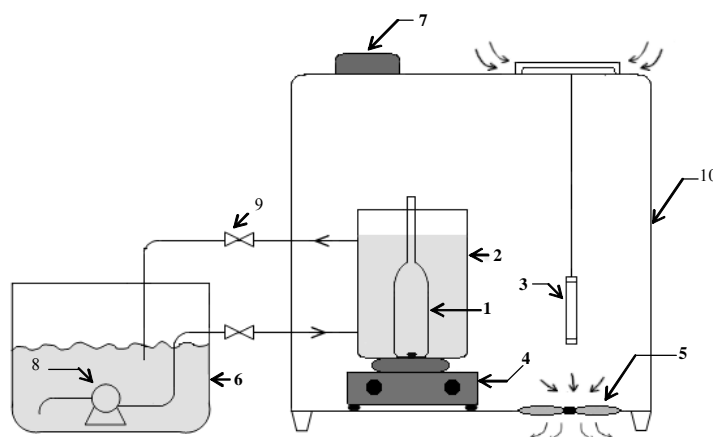


Fig. 1: Experimental set-up for photocatalytic process:

1- Photocatalytic degradation cell (Photo batch reactor), 2-2 L Pyrex beaker, 3- 400 W high-pressure Hg lamp, 4- Magnet stirrer, 5- Fan, 6- Cooling water tank, 7- Power supply, 8- Recirculating pump, 9- Control valve, 10- Pilot box

#### Analytical methods

The analysis of MTBE and its intermediates, TBF and TBA was carried out using a gas chromatograph (GC, 3800 Varian) equipped with a flame ionization detector (FID) and combined with headspace sampler (model Com BI pal). Fused silica capillary gas chromatography column (cp-sil 8CB, 30m×0.32mm i.d., 0.25µm film thickness) was purchased from Varian Inc. The vials were incubated at 70°C with shaking at 500 rpm for 1min. The temperature was programmed at 35°C for 2min; then it was ramped at a rate of 4°C/min to 75°C and held for 2min. The injection temperature was 150°C and samples were injected in a split ratio of 25. The detector temperature was 250°C and Helium was used as the carrier gas at a flow rate of 30mL/min and the flow rate of air was 300mL/min. The minimum detection limit of this method was 5µg/L and can be used for headspace and direct injection method. The

incident UV light intensity at the vicinity of the bulk solution was measured using a digital UV-A radiometer (Hagner, model EC1 UV-A). The intensity of irradiation at  $\lambda > 300$  nm measured with a digital UV-A radiometer was 6.28W/cm<sup>2</sup>. pH monitoring for the initial solution and samples was performed using a pH meter (Mettler Toledo MP 225). The extent of mineralization was determined through TOC analysis using a Shimadzu, model TOC-CSH analyzer. Prior to analysis, TiO<sub>2</sub> was separated from suspensions using a Hettich EBA 20 centrifuge.

A Philips X'pert X-ray diffractometer with Cu K $\alpha$  radiation was used to determine the crystallinity and phase purity of the TiO<sub>2</sub> catalyst. The X-ray diffraction (XRD) patterns were recorded in the 2 $\theta$  range of 30–70°, with a scan speed of 2°/min (Fig. 2). The XRD pattern of TiO<sub>2</sub> shows the presence of two peaks (2 $\theta$ =25.35,

27.48), which were regarded as an attributive indicators of anatase and rutile form of  $\text{TiO}_2$ . The first peak ( $2\theta=25.35$ ), which is an indicator of anatase form, shows much higher intensity than peak of rutile form due to high content of anatase. Moreover, the average particle size  $D$  of  $\text{TiO}_2$  can be estimated from the width of the diffraction curves in the XRD pattern using the Scherrer formula:  $D = K\lambda/(\beta\cos\theta)$ , where  $\lambda$  is the wavelength of the X-ray used,  $\beta$  the width of the curve at the half-maximum intensity, and  $K$  is a constant. The calculated value of the particle size was 35nm.

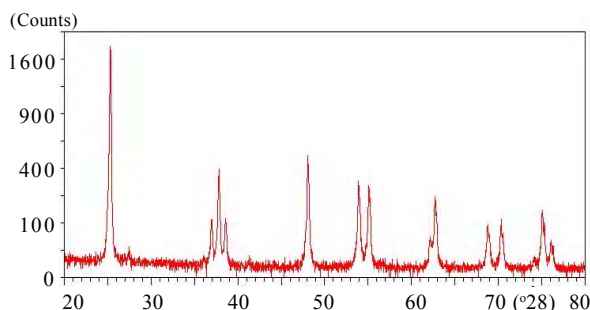


Fig. 2: XRD pattern of  $\text{TiO}_2$  nanoparticles

#### Control experiments

A series of control experiments were conducted to quantify the possible loss of MTBE through volatilization or oxidation by UV-vis,  $\text{H}_2\text{O}_2$ , and  $\text{TiO}_2$  alone. Separate application of each of UV,  $\text{H}_2\text{O}_2$ , and  $\text{TiO}_2$  in a solution with initial concentration of 100mg/L, did not show any considerable decrease of MTBE after 1 hour. These experiments showed only 2-9% decrease in MTBE during 1 hour. Previous investigations have found MTBE to be similarly non-reactive with respect to oxidation by hydrogen peroxide or photolysis by UV light (Zang and Farnood, 2005b; Asadi and Mehrvar, 2006; Burbano *et al.*, 2005; Chang and Young, 2000). No measurable oxidation of MTBE by hydrogen peroxide was observed over a 50-day period in batch microcosms (Yeh and Novak, 1995). A 10-30% removal of MTBE from aqueous solution was reported upon exposure to a low-pressure mercury lamp; however, it is

unclear if the results of their experiment took into account volatile or system losses (Wagler and Malley, 1994).

## RESULTS

### Optimizing of the reaction conditions

#### Effect of pH

Under the initial condition of MTBE Concentration = 100mg/L,  $\text{TiO}_2$  concentration = 2.4 g/L,  $\text{H}_2\text{O}_2/\text{TiO}_2$  molar ratio=10, and irradiation time=1h, the effect of pH on the photocatalytic degradation efficiency of MTBE was examined in the range 4–9. The results showed that the pH for the best MTBE degradation was at 6. The photocatalytic degradation efficiency of MTBE was 86% at pH=6, selected as the best reaction pH value for the oxidation of MTBE for the rest of study.

#### Effect of $\text{TiO}_2$ concentration

The effect of varying concentrations of  $\text{TiO}_2$  on the degradation rate of MTBE was obtained.  $\text{TiO}_2$  loading rang from 0.8 to 3.2g/L were prepared and the optimum catalyst loading was determined for the degradation of MTBE. It was found that degradation rate increased with the increase in catalyst concentration upto 1.6g/L; further increase in catalyst concentration led to decrease in degradation rate.

#### Effect of $\text{H}_2\text{O}_2$ concentration

The effect of  $\text{H}_2\text{O}_2$  addition on the photodegradation efficiency of MTBE was investigated by varying the amount of  $\text{H}_2\text{O}_2$  from  $\text{H}_2\text{O}_2/\text{MTBE}$  molar ratio of 5 to 15. The elimination percentage of MTBE reached to 96% when  $\text{H}_2\text{O}_2/\text{MTBE}=12$ .

#### Degradation rates

The photocatalytic degradation of MTBE was investigated at different concentrations in the range 10-500mg/L. The degradation of MTBE as a function of time was shown in Fig. 3. The time required for complete degradation increased from 30 min to 180 min, when the MTBE concentration was increased from 10-500mg/L.

The plot of  $\ln(c/c_0)$  versus irradiation time was linear suggesting that the photocatalytic degradation reaction follows the first order kinetic model (Fig. 4). Values of the first order degradation constants ( $k$ ) and  $r^2$  values of the linear regression are reported in Table 1.

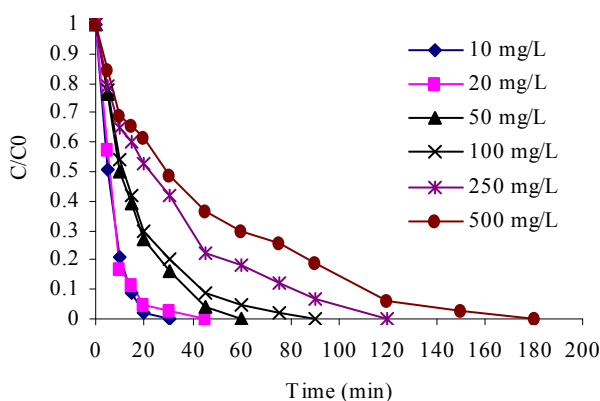


Fig. 3: Effect of initial concentration on the photocatalytic degradation of MTBE. Initial MTBE concentration=100 mg/L; pH=6; TiO<sub>2</sub> concentration=1.6 g/L; H<sub>2</sub>O<sub>2</sub>/MTBE molar ratio=12

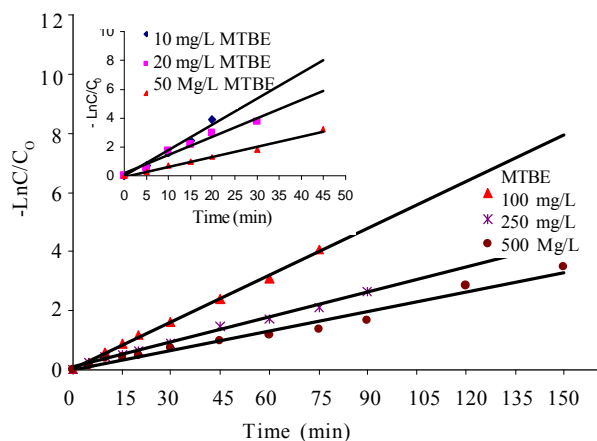


Fig. 4: Plot of  $-\ln C/C_0$  vs. time for photocatalytic degradation of MTBE

Table 1: First order kinetic values for MTBE degradation at different initial MTBE concentrations

MTBE concentration (mg/L)	Synthetic sample						Field sample
	10	20	50	100	250	500	95.9
Rate constant (1/min)	0.177	0.135	0.067	0.053	0.029	0.022	0.027
Correlation coefficient	0.96	0.96	0.98	0.97	0.98	0.97	0.76

*Degradation intermediates and mineralization monitoring*

Fig. 5 shows the concentration profile of the reaction intermediates detected during photocatalysis process. TBF was the main degradation intermediate at the beginning of the run; its concentration continuously increased in the first 45min and then declined. By contrast, after an initial increase at the very beginning of the degradation process, TBA concentration remained almost constant.

Overall mineralization, monitored by TOC analysis; also it is proceeded at a lower rate with respect to MTBE degradation. For instance, mineralization proceeded only up to 85% after 90min, while MTBE complete degradation occurred in a same time. Complete mineralization was obtained after 110min under UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> photocatalytic process (Fig. 5).

*Application of the optimized UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process for degradation of MTBE in actual gasoline contaminated water*

To investigate the kinetic and efficiency of

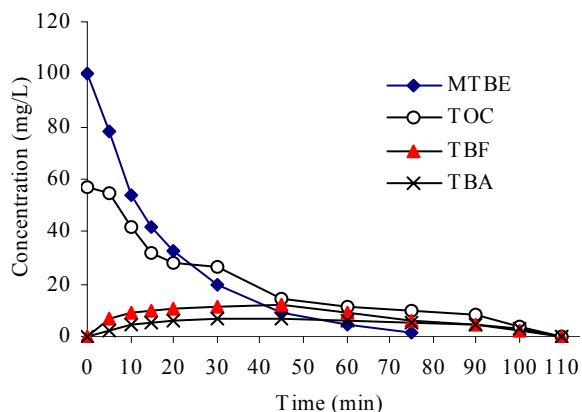


Fig. 5: MTBE degradation and concentration profiles of TBF and TBA over time by UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process. Initial MTBE concentration=100 mg/L; pH = 6; TiO<sub>2</sub> concentration=1.6 g/L; H<sub>2</sub>O<sub>2</sub>/MTBE molar ratio=12

degradation of MTBE in an actual gasoline contaminated water, samples were obtained from the drainage water of a gas station in Zanjan city. The initial characteristics of water such as pH, Alkalinity, total iron, COD, and TOC were 6.5, 126.5 (mg/L as CaCO<sub>3</sub>), 0.1, 703, and 153mg/L

respectively. As shown in Fig. 6, concentrations of MTBE, TBF, TBA and TOC of field samples during the time under the optimized UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> reaction process are illustrated.

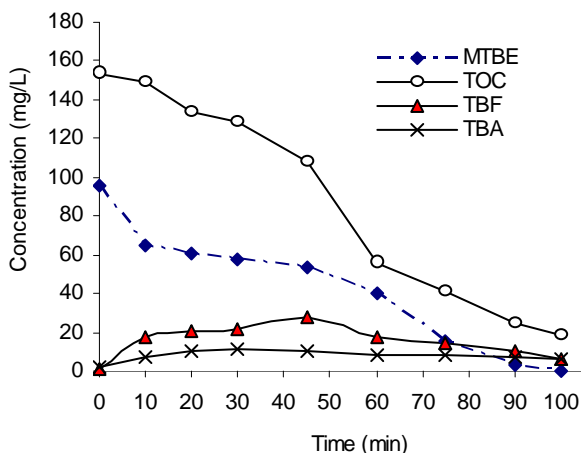
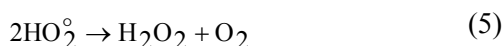
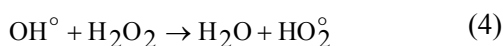


Fig. 6: MTBE degradation and concentration profiles of TBF and TBA in actual contaminated water using optimized UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process. Initial MTBE concentration=100 mg/L; pH=6; TiO<sub>2</sub> concentration=1.6 g/L; H<sub>2</sub>O<sub>2</sub>/MTBE molar ratio=12

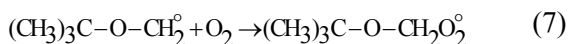
## DISCUSSION

According to the results in the degradation of MTBE by UV-vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, the pH of solution dropped gradually over the time of reaction, suggesting that H<sup>+</sup> ions are released during the reaction process. The similar trend was also reported by Rong *et al.*, in the oxidation of MTBE by fenton's reagent (Rong Xu *et al.*, 2004). It was found that degradation rate increased with increasing catalyst concentration. A similar trend was observed by Zang and Farnood (2005a). However, above this optimum range, the interaction between catalyst particles became significant, reducing the site density for surface holes and electrons. Moreover, the increase in solution turbidity blocks the light passage and decreases the formation of electron/hole pairs. Results were shown, the removal percentage of MTBE increased with the increase of concentration of H<sub>2</sub>O<sub>2</sub>. When H<sub>2</sub>O<sub>2</sub>/MTBE>12, the removal percentage of MTBE showed a decrease. However, at higher peroxide concentrations, the excessive hydrogen peroxide can act as the OH<sup>•</sup> scavenger (Chu, 2001; Ghaly *et al.*, 2001; Stefan and Hoy, 1996):



A similar observation has been reported for other organic pollutants (Chen and Liu, 2007; Chen and Cao, 2002; So *et al.*, 2002; Chu and Wong, 2004). Therefore, the proper addition of hydrogen peroxide may accelerate the photodegradation rate of MTBE. However, in order to keep the efficiency of the added hydrogen peroxide, it was necessary to choose the proper dosage of hydrogen peroxide, according to the kinds and the concentrations of the pollutants. Thus, we chose H<sub>2</sub>O<sub>2</sub>/MTBE molar ratio of 12 for the rest of study. Fig. 3 shows that the rates of degradation of MTBE at the initial period of reaction were rapid but the rate slowed down later on. As shown in Fig.4 the photodegradation reactions followed the first order kinetic model, as is commonly found in the literature (Asadi and Mehrvar, 2006; Bertelli and Selli, 2004; Chang and Young, 2000; Selli *et al.*, 2005). Rate constants were estimated from the slope of the -LnC/C<sub>0</sub> versus time plot in the optimized conditions. Based on the results shown in table1, the initial rates decreased from 0.177 to 0.022 1/min as the MTBE concentration increased from 10 to 500mg/L. In the initial period of reaction, rate was higher because of the presence of high concentration of produced oxidant species (OH<sup>•</sup>, O<sub>2</sub><sup>-•</sup>, HO<sub>2</sub><sup>•</sup>) and MTBE. Afterwards, a number of intermediates are formed competing with MTBE to react with available oxidants and vice versa. *Tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), and acetone were the main reaction intermediates evidenced during MTBE degradation. Other compounds also formed, such as formic and acetic acid, responsible for the pH decrease observed during the runs, which could hardly be detected by the adopted analytical procedure. TBF was identified as the primary degradation by-product and *tert*-butyl alcohol and acetone were identified as secondary by-products during photocatalytic degradation of MTBE with TiO<sub>2</sub> (Barreto *et al.*, 1995). TBF, TBA and acetone were already identified as major intermediates in MTBE degradation by different AOPs (Bertelli and Selli, 2004; Chang and Young, 2000; Selli *et al.*, 2005). Their presence supports the two

reaction mechanisms proposed for the process, both involving  $\text{OH}^\circ$  radicals. The prevailing one, initiated by  $\text{OH}^\circ$  radical attack at the methoxy group of MTBE, leads to TBF formation through the following reaction sequence:



TBA can form either from TBF, through both hydrolysis and further hydroxyl attack, or as an intermediate of the minor reaction path involving  $\text{OH}^\circ$  radical attack at the *tert*-butyl group of MTBE. Both TBF and TBA were shown to react with  $\text{OH}^\circ$  radicals under the conditions of MTBE degradation, both finally yielding acetone as most stable intermediate (Barreto *et al.*, 1995; Bertelli and Selli, 2004; Chang and Young, 2000). Results showed that TBF concentrations continuously increased in the first 45 min and then declined while after an initial increase at the very beginning of the degradation process, TBA concentration remained almost constant. Similar results have been reported by Bertelli and Selli (2004), Seli *et al.*, (2005) and Hsieh *et al.*, (2004). Fig. 6 shows that the complete removal of MTBE in the actual gasoline contaminated water occurred after 100 min while in the spiked distilled water (synthetic solution) it happens 70 min after the reaction has started. It can be due to the presence of other hydrocarbons occurring in gasoline which have entered the actual contaminated water sample. Furthermore, according to table 1 and comparison of reaction rate constants in the synthetic and actual samples we come to the conclusion that the degradation rate of MTBE in the actual samples is lower. Results show that at the first 60 min of reaction, degradation of MTBE in the actual sample proceeds gradually but takes place at high rate after then, up to the complete removal of MTBE within 100 min. On the other hand the degradation rate of MTBE in the synthetic solutions is occurred constantly over time. In addition, the profile of formation of intermediates during the degradation of MTBE such as TBF and

TBA shows that the maximum concentration of intermediates is higher in UV-vis/ $\text{TiO}_2/\text{H}_2\text{O}_2$  process. In order to degrade MTBE by UV-vis/ $\text{TiO}_2/\text{H}_2\text{O}_2$  process in the actual samples which are contaminated with gasoline, longer reaction time was required compared to synthetic solutions. Also, after the complete elimination of MTBE, the extent of mineralization in actual samples was lesser than synthetic solution. Therefore, in order to make sure about the complete removal of hazardous intermediates of photocatalytic degradation process, it is continued until the complete mineralization of those compounds has been occurred.

Finally, the data presented in this paper clearly indicated that UV-vis/ $\text{TiO}_2/\text{H}_2\text{O}_2$  as advanced oxidation process provides an efficient treatment alternative for the remediation of MTBE contaminated waters. Since the reaction pathways in photocatalytic process are complex and likely to yield hazardous intermediates, especially in actual samples, it is recommended to continue the degradation process after the complete elimination of MTBE until complete mineralization.

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## REFERENCES

- Anderson, M. A., (2000). Removal of MTBE and other organic contaminants from water by sorption to high silica zeolite. *Environ. Sci. Technol.*, **34**: 725-727.
- Asadi, A., Mehvar, M., (2006). Degradation of aqueous methyl tert-butyl ether by photochemical, biological, and combined processes. *Int. J. Photoenergy.*, 1-7.
- Barreto, R. D., Anders, K., Gray, K. A., (1995). Photocatalytic degradation of methyl tert-butyl ether in  $\text{TiO}_2$  slurries: a proposed reaction scheme. *Water Res.*, **29** (5): 1243-1248.
- Bertelli, M., Selli, E., (2004). Kinetic analysis on the combined use of photocatalysis,  $\text{H}_2\text{O}_2$  photolysis, and sonolysis in the degradation of methyl tert-butyl ether. *Appl. Catal. B: Environ.*, **52**: 205-212.
- Bozzi, A., Dhanaanjan, M., Guasaquillo, I., Parra, S., Pulgarin, C., Weins, C., Kiwi, J., (2004). Evolution of

- toxicity during melamine photocatalysis with TiO<sub>2</sub> suspensions. *J. Photochem. Photobiol. A: Chem.*, **162**: 179-185.
- Burbano, A. A., Dionysiou, D. D., Suidan, M. T., Richardson, T. L., (2005). Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent. *Water Res.*, **39**: 107-118.
- Cater, S. R., Stefan, M. I., Bolton, J. R., Safarzadeh-Amiri, A., (2000). UV/H<sub>2</sub>O<sub>2</sub> treatment of methyl *tert*-butyl ether in contaminated waters. *Environ. Sci. Technol.*, **34**: 659-662.
- Chang, P. B. L., Young, M. T., (2000). Kinetics of methyl *tert*-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment. *Water Res.*, **8**: 2233-2240.
- Chen, S. F., Cao, G. Y., (2002). The effects of H<sub>2</sub>O<sub>2</sub>, metal ions on the photocatalytic reduction of Cr (VI) and photocatalytic oxidation of dichlorvos. *Photogr. Sci. Photochem.*, **20**: 435-440.
- Chen, S. h., Liu, Y., (2007). Study on the photocatalytic degradation of glyphosate by TiO<sub>2</sub> photocatalyst. *Chemospher.*, **67**: 1010-1017.
- Chu, W., (2001). Modeling the quantum yields of herbicide 2, 4-D decay in UV/H<sub>2</sub>O<sub>2</sub> process. *Chemosphere.*, **44**: 935-941.
- Chu, W., Wong, C. C., (2004). The photocatalytic degradation of dicamba in TiO<sub>2</sub> suspensions with the help of hydrogen peroxide by different near UV irradiations. *Water Res.*, **38**: 1037-1043.
- Ghaly, M. Y., Hartel, G., Mayer, R., Haseneder, R., (2001). Photochemical oxidation of *p*-chlorophenol by UV/ H<sub>2</sub>O<sub>2</sub> and photo-Fenton process: a comparative study. *Waste Manage.*, **21**: 41-47.
- Graham, J. L., Striebich, R., Patterson, C. L., Radha Krishnan, E., Haught, R. C., (2004). MTBE oxidation by products from the treatment of surface waters by ozonation an UV-Ozonation. *Chemosphere.*, **54**: 1011-1016.
- Guillard, C. h., Charton, N., Pichat, P., (2003). Degradation mechanism of methyl *tert*-butyl ether (MTBE) in atmospheric droplets. *Chemosphere.*, **53**: 469-477.
- Hsieh, L. L., Lin, Y. L., Wu, C. H., (2004). Degradation of MTBE in dilute aqueous solution by gamma radiolysis. *Water Res.*, **38**: 3627-3633.
- Jacobs, J., Guertin, J., Herron, C., (2001). MTBE: Effects on Soil and Groundwater Resource. Lewis Publishers, Boca Raton, 7-21.
- Kabra, K., Chaudhary, R., Sawhney, R. L., (2004). Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: A review. *Ind. Chem. Res.*, **43**: 7683-7696.
- Kolb, A., Puttmann, W., (2006). Comparison of MTBE concentrations in groundwater of urban and nonurban areas in Germany. *Water Res.*, **40**: 3551-3558.
- Kuburovic, N., Todorovic, M., Raicevic, V., Orlovic, A., Jovanovic, L., Nikolic, J., Kuburovic, V., Drmanic, S., Solevic, T., (2007). Removal of methyl *tert*-butyl ether from wastewaters using photolytic, photocatalytic and microbiological degradation processes. *Desalination*, **213**, 123-128.
- Ray, A. B., Selvakumar, A., Tafuri, A. N., (2002). Treatment of MTBE contaminated waters with Fenton's reagent. *Remediation J.*, **12**: 81-93.
- Rong Xu, X., Bin Li, H., Dong Gu, J., (2006). Simultaneous decontamination of hexavalent chromium and methyl *tert*-butyl ether by UV/TiO<sub>2</sub> process. *Chemosphere*, **63**: 254-260.
- Rong Xu, X., Ye Zhao, Z., Yan Li, X., Dong Gu, J., (2004). Chemical oxidative degradation of methyl *tert*-butyl ether in aqueous solution by Fenton's reagent. *Chemospher.*, **55**: 73-79.
- Safarzadeh-Amiri, A., (2001). O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment of methyl *tert*butyl ether (MTBE) in contaminated waters. *Water Res.*, **35**: 3706-3714.
- Selli, E., Bianchi, C. L., Pirola, C., Bertelli, M., (2005). Degradation of methyl *tert*-butyl ether in water: effects of the combined use of sonolysis and photocatalysis. *Ultrason. Sonochem.*, **12**: 395-400.
- So, C.M., Cheng, M.Y., Yu, J.C., Wong, P. K., (2002). Degradation of azo dye procion Red MX-5B by photocatalytic oxidation. *Chemosphere*, **46**, 905-912.
- Squillace, P. J., Pankow, J. F., Korte, N. E., Zogorski, J. S., (1997). Review of the environmental behavior and fate of methyl *tert*-butyl ether. *Environ. Toxicol. Chem.*, **16**: 1836-1844.
- Sreedhar Reddy, S., Kotaiah, B., (2005). Decolorization of simulated spent reactive dye bath using solar/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>. *Int. J. Environ. Sci. Technol.*, **2**: 245-262.
- Stefan, M. I., Hoy, A. R., Bolton, J. R., (1996). Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. *Environ. Sci. Technol.*, **30**: 2382-2390.
- USEPA, (1997). Office of Water. EPA-822-F-97-009.
- Wagler J. L., Malley J. P. Jr., (1994). The removal of methyl *tert*-butyl ether from a model ground water using UV/ peroxide oxidation. *J. NWWA*. September, 236-260.
- Yeh C. K., Novak J. T., (1995). The effect of hydrogen peroxide on the degradation of methyl and ethyl *tert*-butyl ether in soils. *Water Environ. Res.*, **67**: 828-834.
- Zang, Y., Farnood, R., (2005). Photocatalytic decomposition of methyl *tert*-butyl ether in aqueous slurry of titanium dioxide. *Appl. Catal. B: Environmental*, **57**: 275-282
- Zang, Y., Farnood, R., (2005). Effects of hydrogen peroxide concentration and ultraviolet light intensity on methyl *tert*-butyl ether degradation kinetics. *Chem. Eng. Sci.*, **60**: 1641-1648.