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Original Article

Removal of Methyl Tert-Butyl Ether (MTBE) from Contaminated Water by Photocatalytic Process

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Abstract

Background: Methyl *tert*-butyl ether (MTBE) has been commercially used as an octane enhancer to replace tetraethyl lead in gasoline since 1979. The high mobility, water solubility, and resistance to natural attenuation associated with MTBE may result in contamination of ground and surface waters. In this investigation the degradation of aqueous MTBE at relatively high concentrations was studied by UV-vis/TiO_2/O_2 photocatalytic process. The effect of important operational parameters such as pH, oxygen flow, catalyst loading, and irradiation time were also studied.
Methods: Concentration of MTBE and intermediates such as tert-butyl formate (TBF) and tert-butyl alcohol (TBA) were measured using a gas chromatograph equipped with flam ionization detector and combined with headspace sampler.
Results: The time required for complete degradation increased from 15 to 150 min, when the initial concentration was increased from 10 to 500 mg/L. The first order rate constant for degradation of MTBE from the hydroxyl radical was estimated to be 0.266 to 0.033 min^{-1} as the concentration increased from 10 to 500 mg/L. Study on the overall mineralization monitored by total organic carbon (TOC) analysis showed that in the initial concentration of 100 mg/L MTBE, complete mineralization was obtained after 110 min under UV-vis/TiO_2/O_2 photocatalytic process.
Conclusion: The data presented in this paper clearly indicate that UV/TiO_2/O_2 advanced oxidation process provides an efficient treatment alternative for the remediation of MTBE contaminated water.

Keywords: *Photocatalytic degradation, MTBE, Water, Titanium dioxide, Oxygen*

Introduction

MTBE (methyl *tert*-butyl ether) has been commercially used as an octane enhancer to replace tetraethyl lead in gasoline since 1979 (1). Unfortunately, the high mobility, water solubility, and resistance to natural attenuation associated with MTBE may result in contamination of ground and surface water resources (2). Besides leaking underground fuel tanks and leaking pipelines, other sources of MTBE in groundwater resources include tank overfilling and faulty construction at gas stations, spillage from vehicle accidents, and home owner releases (3, 4). The US Environmental Protection Agency (USEPA) has classified MTBE as a possible human carcinogen and set a drinking water advisory at 20-40 µg/L to prevent taste and odor problems and to protect against potential health effects (3). The toxicity of MTBE to animals and humans is well documented. It has been established that MTBE is carcinogenic to animals (5). MTBE is poorly adsorbed, chemically and biologically stable, and very soluble in water, making it very persistent in the environment. Conventional treatments of MTBE contaminated groundwater have been inefficient and unsatisfactory. In search of a viable method for the degradation of the fuel oxygenate MTBE in contaminated groundwater, several application of advanced oxidation processes (AOP_s) have reportedly achieved promising results (6-8). Under suitable operating conditions final products in AOPs are CO_2, H_2O and low molecular weight aliphatic acids (9). These processes rely on the generation of highly reactive hy-

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***Corresponding author:** Tel.: +98 21 8889414, Fax: +98 21 88950188, E-mail: simnasseri@hotmail.com droxyl radicals ($OH^\bullet$) that react indiscriminately with most organic compounds at very high rate constant (10). This process is based on the formation of high-energy-state electron/hole pairs (e^-/h^+) while the photocatalyst (a semiconductor) is exposed to the UV irradiation with the photon energy greater than the band gap energy of the semiconductor ($h_v > E_g$). The first environmental application of TiO_2 as one of such photocatalysts in aqueous solution was reported 30 yr ago (11). This catalyst (especially in the anatase form) has been widely employed due to its photostability, non-toxicity, low cost, and water insolubility. In the aqueous slurry, several possible reactions occur on TiO_2 surface under UV illumination (λ<388nm), as shown below:

[1] $TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-)$

[2] $H_2O_{(ads)} + h^+ \rightarrow OH^\bullet + H^+$

[3] $OH + h^+ \rightarrow OH^\bullet$

[4] $O_2 + e^- \rightarrow O_2^\bullet$

[5] $O_{2(ads)} + e^- + H^+ \rightarrow HO_2^\bullet$

The organic pollutants are attacked and oxidized by the radicals formed through the above mechanisms. Although the quantum yield for the Eq. 2 is only about 0.04-0.05, the ability of TiO_2 to adsorb and concentrate pollutants on the surface of catalyst particles balances this low yield (1).

Literature reports on the influence of adsorbed oxygen in the photocatalytic degradation of MTBE are not many. Zalazar et al. (12) has ivestigated the effect of oxygen on the reaction kinetics of the photocatalytic oxidation of dichloroacetic acid at pH below the titanium dioxide isoelectric point. A kinetic scheme based on the direct hole attack to the dichloracetate ion in conjunction with the classical role of oxygen acting as an electron acceptor is proposed. Comparative studies of phenol and salicylic acid photocatalytic degradation and influence of adsorbed oxygen have been reported (13). Photocatalytic degradation of model textile dye wastewater using ZnO irradiated with UV-radiation in the presence of air/O_2 (14). Kim et al. carried out the photocatalytic degradation of volatile organic compounds at the gas-solid interface of TiO_2 photocatalyst as a function of water vapor, molecular oxygen and reaction temperature (15).

In this work, specific emphasis is given to obtain kinetic results of MTBE degradation in water under UV-vis/TiO_2/O_2 system. Influence of factors such as pH, oxygen, catalyst loading, and irradiation time investigated to obtain the optimum conditions. Moreover, the concentration profiles of the reaction intermediates have been monitored under achieved optimum degradation conditions. Overall mineralization monitored by Total Organic Carbon (TOC) analysis.

Material and Methods

Materials

All chemicals were analytical or reagent grade, or the highest purity available from several suppliers. Analytical grade MTBE was purchased from Merck. TBF (Aldrich) and 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. UV-vis irradiation was provided by applying a 400W high-pressure mercury lamp. In order to keep the reaction mixture at room temperature, a cooling water jacket was placed around the Pyrex reactor. Oxygen was introduced to the solution from a gas cylinder (puriity 99.9%) at regulating flow rate through a needle valve and gas flow meter ranging from 5 to 50 mL/min. In the present set-up, the bulk solution was about 25 cm away from the lamp. During irradiation, the solution was magnetically stirred. pH of the solution was adjusted initially by adding 0.1 N NaOH or 0.1 N HCl.

Analytical methods

The analysis was carried out according to the modified method of Chrompack 1313. MTBE and its intermediates, TBF and TBA was quantified by 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, 30 m×0.32 mm i.d., 0.25 µm film thickness) was purchased from Varian Inc. The vials were incubated at 70^o C with shaking at 500 rpm for 1 min. The temperature was programmed at 35^o C for 2 min, and then it was ramped at a rate of 4^o C/min to 75^o C and held for 2 min. The injection temperature was 150^o C and samples were injected in a split ratio of 25. The detector temperature was 250^o C and Helium was used as the carrier gas at a flow rate of 30 mL/min and the flow rate of air was 300 mL/min. The minimum detection limit of this method was 5 µg/L and can be used for headspace and direct injection method. The incident UV light intensity at the vicinity of bulk solution was measured using a digital UV-A radiometer (Hagner, model EC1 UV-A). The intensity of irradiation at λ>300 nm measured with digital UV-A radiometer was 6.28 W/cm^2. 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_2 was separated from suspensions using a Hettich EBA 20 centrifuge.

Results

Control experiments

A series of control experiments were conducted to quantify the possible loss of MTBE through volatilization or oxidation by dissolved oxygen. In these experiments, solution containing 100 mg/L of MTBE were stirred in the reactor with oxygen flow rate of 20 mL/min and without UV lamp and TiO_2 for 1 h. Results indicated only 6% decrease of MTBE during that time. Also, Separate application of each of UV-vis, and TiO_2 (by adding 2.4 g/L TiO_2 into the solution with initial concentration of 100 mg/L) did not show any considerable decrease of MTBE after 1 h. These experiments showed only 2-9% decrease in MTBE during 1 h. Previous investigations have found MTBE to be similarly non-reactive with respect to photolysis by UV light (1, 11, 16, 17) and low interaction with TiO_2 particles in the dark (11, 16).

Effect of pH

The effect of pH value on the degradation efficiency was studied in the pH range 4-9 at TiO_2 concentration= 1.6 g/L, oxygen flow rate=20 mL/min and irradiation time= 1 h. The results showed a slow increase in the degradation of MTBE with increase of the pH value from 4 up to 6 and gradually decreases upon increasing the pH value from 6 to 9 (Fig. 2). Therefore the best reaction pH value for the oxidation of MTBE was chosen to be 6.

Effect of catalyst concentration

To investigate the effect of catalyst loading on the final degradation efficiency, a series of experiments were carried out by varying the catalyst from 0.8 to 4.8 g/L in the solution with 100 mg/L MTBE concentration. The relationship between the photodegradation of MTBE and concentration of phocatalyst is shown in Fig. 3. It is demonstrated that when the illumination time is fixed, as the concentration of the catalyst increases from 0.8 to 2.4 g/L the photodegradation efficiency of MTBE increase rapidly from 46.1% to 96% and a further increase of catalyst concentration beyond 2.4 up to 3.2 g/L leads to slightly increase in the photodegradation efficiency of MTBE. Then, further increase leads to decrease in degradation rate. Therefore, the optimum concentration of TiO_2 was chosen 2.4 g/L.

Effect of oxygen flow rate

Experiments with a controlled flux of oxygen in aqueous solution were obtained. As the results are presented in Fig. 4, it can be seen that MTBE degradation increases in the presence of oxygen with flux from 5 up to 25 mL/min. An increase in the oxygen flow rate increased the supply of oxygen by way of enhanced turbulence, gas holdup, gas–liquid interfacial area, and the mass transfer coefficient. Then, as shown in Fig. 4, further increase of oxygen flux beyond 25 mL/min leads to decrease in degradation efficiency of MTBE.

Degradation rates

The photocatalytic degradation of MTBE was investigated at different concentrations in the range 10-500 mg/L. Fig. 5 shows the degradation of MTBE as a function of time. The time required for complete degradation increased from 15 min to 150 min, when the MTBE concentration was increased from 10-500 mg/L. Values of the first order degradation constants (k) and r^2 value of the linear regression are reported in Table 1.

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

MTBE concentration (mg/L)	**10**	**20**	**50**	**100**	**250**	**500**	**83.2 (actual sample)**
Rate constant (min^{-1})	0.266	0.226	0.139	0.067	0.043	0.033	0.027
Correlation coefficient	0.93	0.90	0.91	0.98	0.92	0.98	0.86

Degradation intermediates and mineralization monitoring

Fig. 6 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 30 min 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 preceded only upto 82% after 75 min, while MTBE complete degradation occurred in a same time. Complete mineralization was obtained after 110 min under UV/TiO_2/O_2 photocatalytic process (Fig. 6).

Application of the optimized UV/TiO_2/O_2 process for degradation of MTBE in actual gasoline contaminated water

To investigate the kinetic and efficiency of 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, 132.6 (mg/L as $CaCO_3$), 0.09, 659, and 144.6 mg/L, respectively. Concentrations of MTBE, TBF, TBA and TOC, of field samples during the time under the optimized UV/TiO_2/O_2 reaction process are shown in Fig. 7.

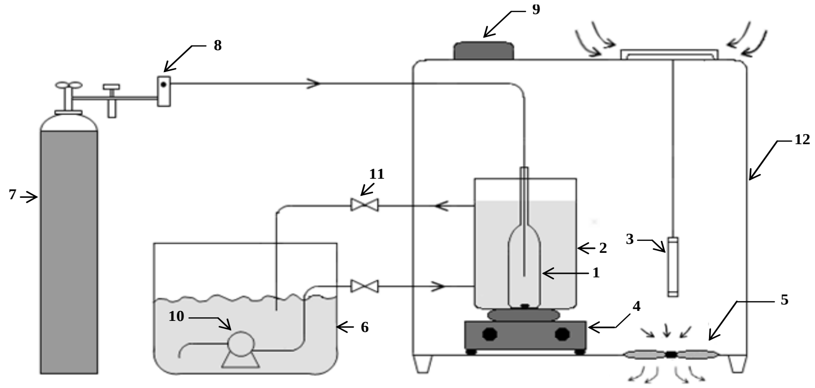

Fig. 1: Experimental set-up for photocatalytic process: 1-Photocatalytic degradation cell (Photo batch reactor),2- 2 L pyrex beaker, 3- 400 W high-pressure Hg lamp, 4- Magnet stirrer, 5-Fan, 6-Cooling water tank, 7-Oxygen cylinder, 8-Gas flow meter, 9-Power supply, 10-Recirculating pump, 11-Control valve, 12-Pilot box

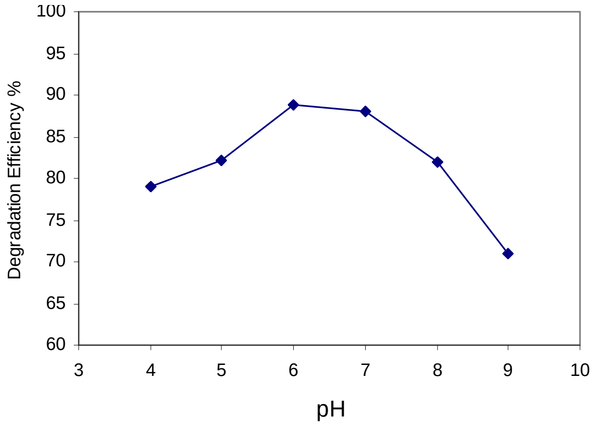

Fig. 2: Effect of pH on the photocatalytic degradation efficiency of MTBE. Initial MTBE concentration= 100 mg/L; TiO_2 concentration= 1.6 g/L; oxygen flow rate= 20 mL/min; irradiation time= 1h

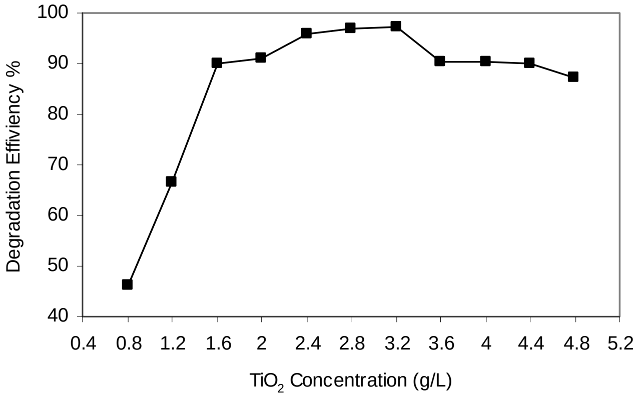

Fig. 3: Effect of TiO_2 concentration on photocatalytic degradation efficiency of MTBE. Initial MTBE concentration = 100 mg/L; pH = 6; oxygen flow rate = 20 mL/min; irradiation time = 1h

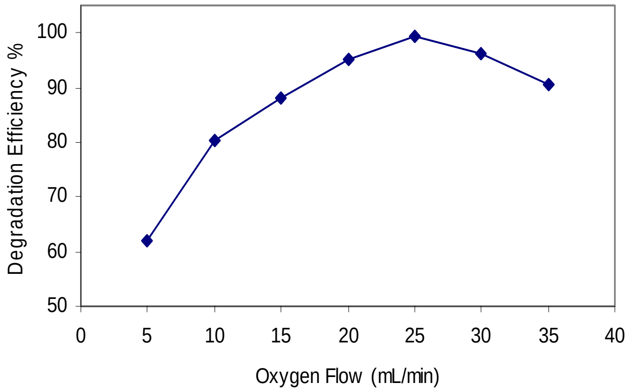

Fig. 4: Effect of oxygen flow rate on photocatalytic degradation efficiency of MTBE. Initial MTBE concentration= 100 mg/L; pH= 6, TiO_2 concentration= 2.4 g/L; irradiation time= 1h

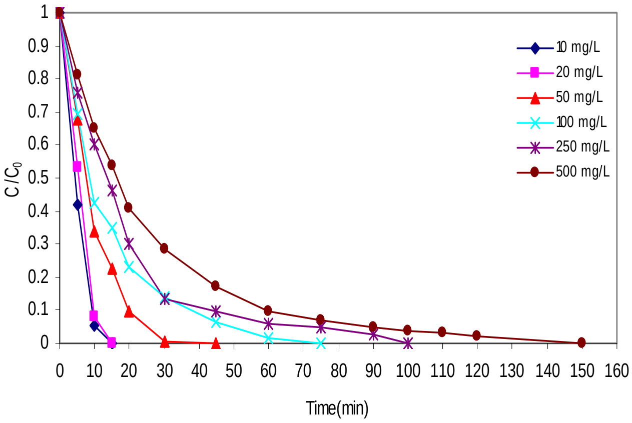

Fig. 5: Effect of initial concentration on the photocatalytic degradation of MTBE. pH = 6; TiO_2 concentration = 2.4 g/L; oxygen flow rate = 25 mL/min

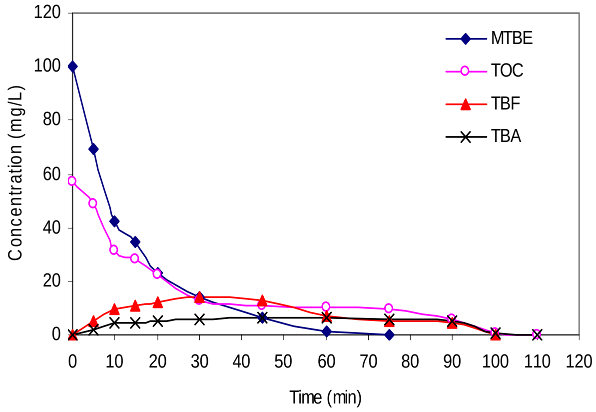

Fig. 6: MTBE degradation and concentration profiles of TBF and TBA by $UV/TiO_2/O_2$ process. Initial MTBE concentration = 100 mg/L; pH= 6; TiO_2 concentration= 2.4 g/L; oxygen flow rate=25 mL/min

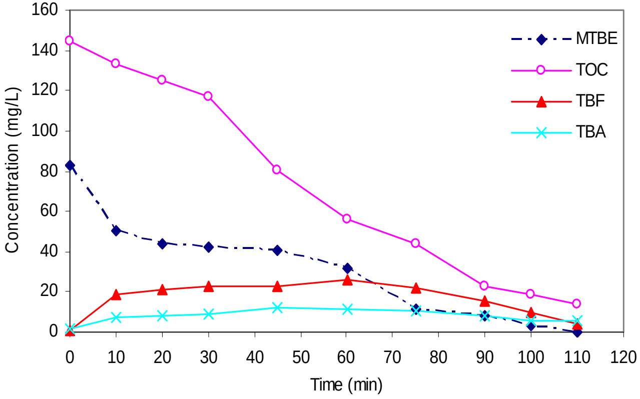

Fig. 7: MTBE degradation and concentration profiles of TBF and TBA in actual contaminated water using optimized $UV/TiO_2/O_2$ process. Initial MTBE concentration= 83.2 mg/L; pH= 6; TiO_2 concentration= 2.4 g/L; oxygen flow rate= 25 mL/ min

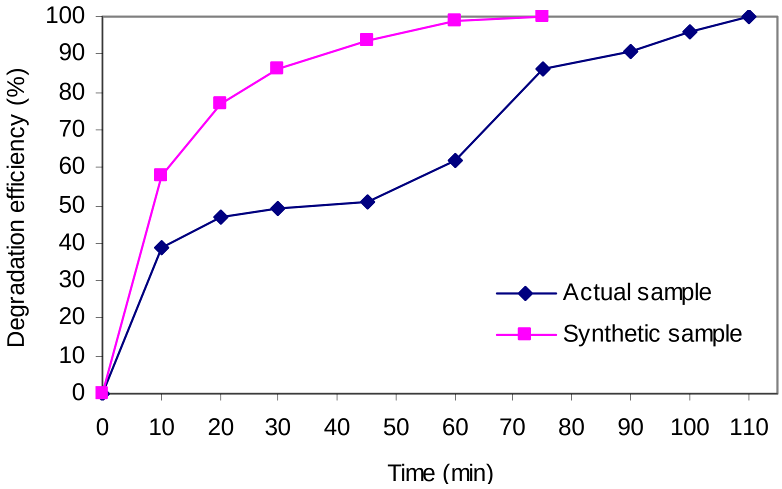

Fig. 8: Comparison of MTBE degradation in actual contaminated water and synthetic samples using optimized UV/TiO_2/O_2 process. Initial MTBE concentration of synthetic samples = 100 mg/L; Initial MTBE concentration of actual contaminated water = 83.2 mg/L; pH = 6; TiO_2 concentration=2.4 g/L; oxygen flow rate = 25 mL/min

Discussion

According to the results in the degradation of MTBE by UV-vis/TiO_2/O_2, the pH of solution dropped gradually over the time of reaction, suggesting that H^+ 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 (10). It was found that degradation rate increased with increasing catalyst concentration. A similar trend was also observed (1). Many other researches have been verified that there was an optimum amount of catalyst loading under different experimental conditions. Due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering (18).

It is well known that limitation in photocatalytic degradation efficiency is attributed to the recombination of photogenerated hole-electron pairs. Oxygen adsorbed on the surface of titanium dioxide prevents the recombination process as electrons scavenger. The mechanistic pathway, generally admitted, was as below:

[6] $e^- + O_2 \rightarrow O_2^{\bullet -}$

[7] $O_2^{\bullet -} + O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2$

[8] $O_2^{\bullet -} + h_{vb}^+ \rightarrow O_2$

[9] $OH^- + h_{vb}^+ \rightarrow OH^\bullet$

[10] $OH^\bullet + OH^\bullet \rightarrow H_2O_2$

According to Gerischer and Heller (19) the reaction of the adsorbed oxygen with the photogenerated electron on the surface of the solid semiconductor is rather slow and could become the controlling step in photocatalytic oxidations. Despite the rate, it is clear that this reaction is important to reduce the significance of electron-hole recombination and thus improving the effectiveness of the oxidative path with the hole participation. Consequently, if electrons are not removed, the oxidative degradation of the organic compound could be stopped. Besides the electron acceptor function, oxygen may participate directly in its molecular form in the oxidation path (12, 20, 21).

As shown in Fig. 5, the rates of degradation of MTBE at the initial period of reaction were rapid but the rate slowed down later on. This is similar to another report (6). The plot-LnC/C_0 versus irradiation time in initials concentration of MTBE was linear suggesting that the photodegradation reaction follows the first order kinetic model as is commonly found in the literature (17, 22, 23). Rate constants were estimated from the slope of the-LnC/C_0 versus time plot in the optimized conditions. Based on the results shown in table1, the initial rates decreased from 0.266 to 0.033 min^{-1} as the MTBE concentration increased from 10 to 500 mg/L. In the initial period of reaction, rate was higher because of the presence of high concentration of produced oxidant species ($OH^•$, $O_2^{-•}$, $HO_2^•$) 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_2 (6). TBF, TBA and acetone were already identified as major intermediates in MTBE degradation by different AOPs (22-24). Their presence supports the two reaction mechanisms proposed for the process, both involving $OH^•$ radicals. The prevailing one, initiated by $OH^•$ radical attack at the methoxy group of MTBE, leads to TBF formation through the following reaction sequence:

$$[11]\quad (CH_3)_3C-O-CH_3+OH^\bullet \rightarrow (CH_3)_3C-O-CH_2^\bullet+H_2O$$

$$[12]\quad (CH_3)_3C-O-CH_2^\bullet+O_2 \rightarrow (CH_3)_3C-O-CH_2O_2^\bullet$$

$$[13]\quad 2(CH_3)_3C-O-CH_2O_2^\bullet \rightarrow 2(CH_3)_3C-O-CHO+H_2O$$

TBA can form either from TBF, through both hydrolysis and further hydroxyl attack, or as an intermediate of the minor reaction path involving $OH^•$ radical attack at the *tert*-butyl group of MTBE. Both TBF and TBA were shown to react with $OH^•$ radicals under the conditions of MTBE degradation, both finally yielding acetone as most stable intermediate (6, 22, 24). Similar results have been reported earlier (22-24).

It can be seen that the complete removal of MTBE in the actual gasoline contaminated water occurred after 110 min while in the spiked distilled water (synthetic solution) it happens 75 min after the reaction has started. It can due to the presence of other hydrocarbons occurring in gasoline which have entered the actual contaminated water sample. Further more, according to table 1 and comparison or 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. Fig. 8 shows 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 110 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/TiO_2/O_2 process. In order to degrade MTBE by UV/TiO_2/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 indicate that UV/TiO_2/O_2 advanced oxidation process provides an efficient treatment alternative for the remediation of MTBE-contaminated water. 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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