

# Evaluation of UV/O<sub>3</sub> process for removal of methyl tertiary-butyl ether in aqueous solutions

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## INTRODUCTION

The methyl tertiary-butyl ether (MTBE) with ((CH<sub>3</sub>)<sub>3</sub>COCH<sub>3</sub>) formula is a colorless and transparent liquid which has a terbutin - like smell.<sup>[1,2]</sup>

Having unique properties, MTBE is used as a substitute of

## ABSTRACT

**Aims:** In the present investigation, the methyl tertiary-butyl ether (MTBE) removal efficiency from the synthetic solutions by the means of advanced oxidation process of UV/O<sub>3</sub> was studied.

**Materials and Methods:** To study the efficiency of process, the following variables were studied: ozone concentration, pH, MTBE initial concentration, and radiation duration. As The radiation source, a Mercury vapor UV lamp with moderate pressure (400W) was used which was immersed vertically in the solution containing MTBE, in a glass reactor (Volume: 2 L).

**Results:** The results showed that the efficiency of UV radiation and ozone alone in 50 mg/L concentration and pH: 7 on MTBE removal was 4 and 53%, respectively. The UV/O<sub>3</sub> compound process removal efficiency in 60 minutes was 63%. The pH played a significant role in the process, as with the increase in pH, the removal rate increased as well. The removal rates for the initial concentrations of 10, 20, 50, and 100 mg/L of MTBE were 98, 81.5, 72.8, and 63.8%, respectively.

**Conclusion:** The results of the present survey indicated that the efficiency of the UV/O<sub>3</sub> combination process was more than ultraviolet (UV) and Ozone alone. In the UV/O<sub>3</sub> combination process, the MTBE removal efficiency increased as the O<sub>3</sub> concentration and pH increased, while the efficiency decreased as the MTBE concentration decreased.

**Key words:** MTBE, OH radical, removal rate, UV/O<sub>3</sub> process, water pollution

Tetra-ethyl Lead in petrol. The compound nicely increases the octane rating of petrol (up to 110).<sup>[3]</sup> On the other hand, it has oxygen in its molecular structure, and conveys the oxygen content of petrol to 2.7 (which is normally 5% of the total weight). Hence, petrol combustion matures and emission of the air polluting materials (like carbon monoxide, ozone, and especially lead) dramatically decreases.<sup>[4-6]</sup>

The compound is being used from late 1970's in the US and European countries<sup>[3,6-8]</sup>, and in Iran the use of this compound has been initiated since 2000.<sup>[3]</sup> Physical contact with this compound causes severe and chronic consequences. Reactions of the nervous system and symptoms like dizziness, lack of concentration, nausea, and amnesia have been reported. Also with the metabolism of MTBE in the body, compounds

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like tertiary butyl alcohol (TBA) and formaldehyde are produced in the body and according to the announcement by the international agency for research on cancer (IARC), formaldehyde is known as a Tumor Maker substance in humans.<sup>[9, 10]</sup>

The US environmental protection agency (EPA) has announced 20 – 40 µg/L as the allowance of MTBE in drinking water,<sup>[4, 5, 7]</sup> and has announced that this compound as may cause tumors in humans.<sup>[3, 6, 7]</sup> Two major sources of underground water contamination with compound are leakage from underground tanks and transmittance by means of air.<sup>[11]</sup> MTBE is not absorbed in the soil, therefore, it can be penetrated in the soil and contaminate underground water resources.<sup>[9]</sup>

The conventional methods of purification of soils contaminated by MTBE, are insufficient and inefficient. Air stripping is difficult and as the Henry's constant of the compound is low, high ratio of air to water is needed.<sup>[6, 7, 12]</sup> Also the low tendency of MTBE for active carbon absorption makes the method inconvenient and uneconomic.<sup>[6, 12]</sup> The general characteristic of MTBE is inactivity and stability in diverse biological degradation situations. Even as most researchers believe that MTBE degradation is difficult, some others even categorize it to be in a group of compounds that are resistive to biological degradation.<sup>[3, 6, 7, 10, 11]</sup>

A group of new oxidation processes, under the common name of advanced oxidation technologies (AOTs) are commonly used in the ratification of quality of the waters containing organic compounds resistive to degradation.<sup>[12, 13]</sup> AOTs have the general characteristic of creating hydroxyl radicals (OH•) such radicals are extremely unstable and have high redox (oxidation) potential.<sup>[6, 13]</sup> In advanced the producing of hydroxyl radicals using the following method has been studied: photo catalysis with TiO<sub>2</sub> solution radiation, using UV and H<sub>2</sub>O<sub>2</sub>, Oxidation with ozone or ozone/hydrogen peroxide, potassium permanganate, per sulfate and 4- Fenton's reaction.<sup>[6, 8, 10]</sup> Although ozone is a relatively selective and potent oxidizer, the hydroxyl radical is a much stronger oxidizer and is non-selective. Hence, its reaction rate is often nine times faster (compared to ozone) for the same organic compound. The advanced oxidation processes that are based on ozone, create radicals of hydroxyl in a self-degradation cycle, which is accelerated by the hydroxyl ion (high value of pH), H<sub>2</sub>O<sub>2</sub> or UV.<sup>[13]</sup> MTBE is a common pollutant with a significant environmental effect and in the present years has been discussed as a major consequence of technological development.<sup>[14]</sup>

In a study by Sadeghi *et al.* a degradability increase of MTBE with ozonation in high pH was investigated. The empirical results showed that during ozonation, MTBE was removed completely in 100 minutes, and,<sup>[15]</sup> the efficiency of the compound removal was surveyed in a study conducted by Safarzadeh by using the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> method, in 2001. MTBE degradation was discussed with a pseudo-first-order reaction, in two stations. The oxidation

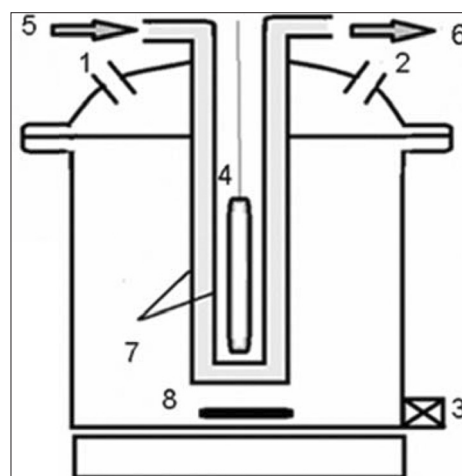
rate of MTBE (in the lowest level of the first phase) was limited by the ozone mass transfer, and increased with an increase in the ozone flow. The data collected during the study showed that MTBE removal in underground water reservoirs using O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was quite efficient and cost less than the UV/H<sub>2</sub>O<sub>2</sub> process.<sup>[12]</sup> In 2004, degradation by-products of the compound (using ozonation alone and ozonation accompanied with UV radiation) were compared by Graham *et al.* The results indicated that the efficiency of degradation doubled with UV radiation, when compared to merely ozonation.<sup>[16]</sup> The main goal of this study was to investigate the degradation of MTBE in an aqueous solution using the UV/O<sub>3</sub> process.

## MATERIALS AND METHODS

In the present study the removal ability of MTBE, by means of the advanced oxidation process is investigated. The MTBE used in the study is provided by MERK (Germany), and has a purity of 97%. Other chemical materials used are also laboratory-grade materials. A low pressure UV lamp (400 W) was used as the radiation source. The reactor used in the study with a volume of 2 L (13cm (d) and 15cm (L)) [Figure 1]. As it can be observed, the reactor has an internal shield and the UV lamp is placed within it with a double-layered quartz wrap. The cooling process takes place when the water passes through the double-layered wrap. The experiments have been conducted in 10, 20, 50 and 100 mg/L concentrations of MTBE in 50, 100, 150 mg/L of ozone in a pH range of 5-9 under normal room-temperature.

An electronic mixer has been used in the reactor to achieve a thorough mixture. In order to adjust the pH, sulfuric acid and soda ash (1 N) has been used.

For determining the amount of MTBE, the gas chromatography (GC) method and the purge and trap



**Figure 1:** Schematic diagram of photolytic oxidation system experimental set-up, 1. Ozone entry, 2. Ozone exit, 3. Sampling tap, 4. UV lamp, 5. Cooling water's entry, 6. Water exit, 7. Magnet, 8. Two-layer Quartz coat

(P and T) concentrator system were used. The gas chromatography device was by Agilent (US) and equipped with a flame ionization detector (FID). The column used was HP-5 with a length of 3 m and of internal diameter of 0.320 mm. The Thermal column program was as follows:

The initial temperature of the column was 35°C and increases by the rate of 10°C/min, then reaching 150°C. The temperatures of the detector and injector were 300°C and 200°C, respectively. The carrier gas was hydrogen.

Calibration was done with solutions containing 0, 0.5, 1, 5, 10, 25, and 50 mg/L. The calibration curve achieved is presented in [Figure 2].

The MTBE was being injected in the desired concentrations with a Pyrex © syringe (Volume: 5 mL).

In order to determine the concentration of the ozone output in the ozone generator, 2 Trap heads or K1 (A and B Traps) were used and the gas was passed through them for one minute. Each TRAP was a Gas Wash Bottle containing a distinguished amount of iodide (Min: 200 mL), then the remaining concentration of ozone was measured by means of the indigo method.<sup>[17]</sup> Gathering the adequate data, the analyses were done using the Microsoft Excel software.

## RESULTS

### The effect of ultraviolet radiation and ozone alone

In order to survey the effect of UV radiation and merely ozone, in MTBE removal, 50 mg/L solution of the compound was prepared and exposed to UV radiation and ozone. At the beginning and final phases of the test, and also in distinctive time periods, sample were taken. The result showed that efficiency of MTBE removal in 60 min with pH: 7 for 50 mg/L concentration for UV and merely ozone were 4 and 53%, respectively [Figure 3].

### The effect of different concentrations of ozone

To investigate the effect of different concentrations of

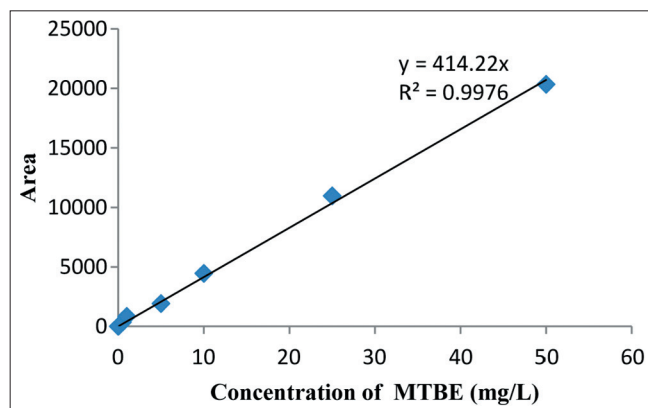


Figure 2: The MTBE calibration curve with GC-FID

ozone on UV/O<sub>3</sub>, a solution of 50 mg/L concentration (pH: 7) was prepared. Thereafter, 50, 100, 150, and 200 mg/L concentration of ozone were to the above solution and exposed to UV radiation for 60 minute time. Several samples were taken from the solution in different time intervals and the results were read by a gas chromatograph device (GC). The results with the UV/O<sub>3</sub> process indicated that MTBE oxidation was directly bearing with the ozone concentration. The removal percentages for 50, 100, 150, and 200 mg/L concentrations were 27.5, 42.5, 62, and 67.5%, respectively. The results indicated that with an increase in the concentration ozone concentration from 50 mg/L to 200 mg/L, the efficiency of process in MTBE removal increased from 27.5 to 67.5%. However, as it is presented in Figure 4, the difference in removal efficiency in the 150 and 200 mg/L concentration is insignificant. Therefore, the 150 mg/L concentration was chosen from among the mentioned concentrations as an optimum concentration for the further steps

### The effect of pH change

For investigating the effect of pH changes on the UV/O<sub>3</sub> process, a 50 mg/L MTBE solution with 150 mg/L efficient ozone concentration, in the acidic to base pH range, was experimented. The results showed that with the increase of pH (ranging 5 to 9) the MTBE removal efficiency increased. Therefore, according to [Figure 5] the optimum pH to MTBE removal with the UV/O<sub>3</sub> process is the alkali condition, and in the pH: 9 it is equal to 72.8%.

### The effect of the initial concentration of methyl tertiary – butyl ether

To investigate the effect of the initial concentrations of MTBE) in the UV/O<sub>3</sub> process, several solution of MTBE, with different concentration of 10, 20, 50, and 100 mg/L, in efficient condition of process were used.

The results are shown in Figure 6. The removal percent for the above-mentioned MTBE concentration are 98, 81.5, 72.8, and 63.8%, respectively. Therefore, the result show that the efficiency process for low concentrations is

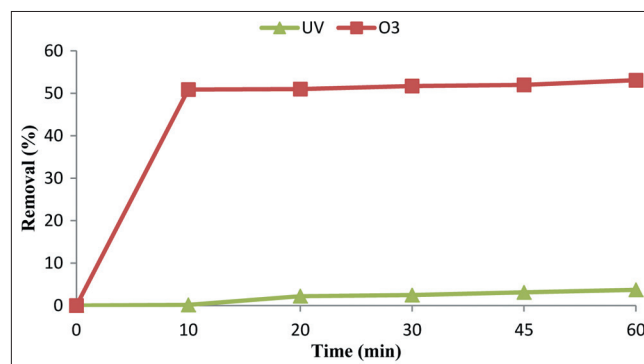
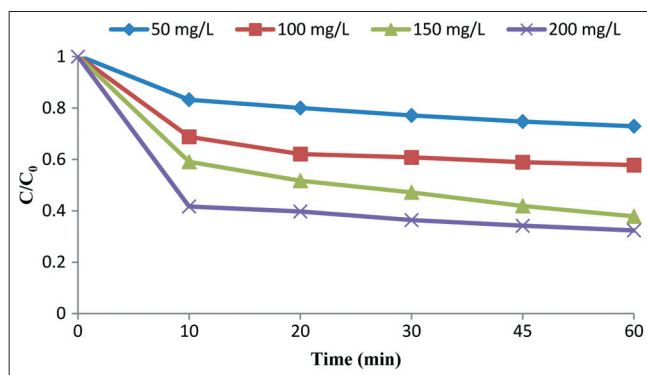
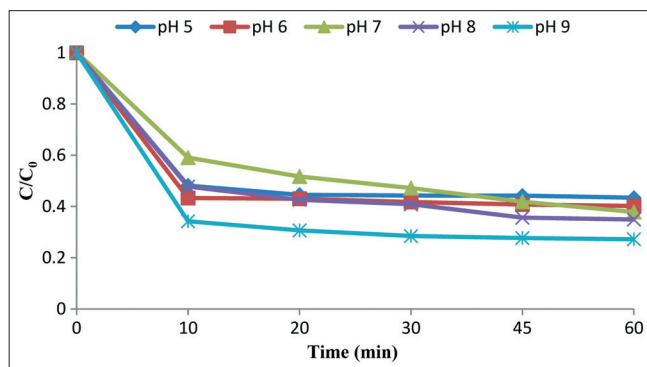


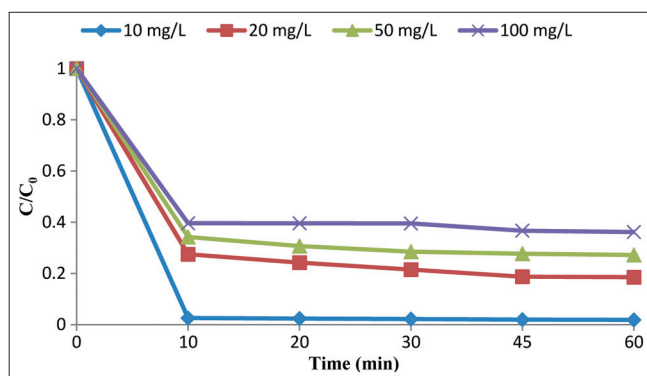
Figure 3: Efficiency of UV and ozone process alone in eliminating MTBE (C<sub>0</sub>: 50 mg/L, O<sub>3</sub>: 150 mg/L, pH: 7)



**Figure 4:** The effect of changes in ozone concentration on MTBE elimination in the UV/O<sub>3</sub> process. (C<sub>0</sub>: 50 mg/L, pH: 7)



**Figure 5:** The effect of pH changes on MTBE elimination in the UV/O<sub>3</sub> process. (C<sub>0</sub>: 50 mg/L, O<sub>3</sub>: 150 mg/L)



**Figure 6:** The effect of changes in the initial concentration of MTBE on its elimination in the UV/O<sub>3</sub> process (O<sub>3</sub>: 150 mg/L, pH: 7)

high and decreases significantly when the MTBE initial concentration increases.

## DISCUSSION

The results of the experiment proved that mere MTBE exposure to UV radiation has a very low effect on its removal [Figure 3]. These findings agree with the previous findings of other researchers, which are in accordance with the findings by

other researchers.<sup>[4, 6, 7, 18]</sup> Alnaizy *et al.*, investigated the effect of UV radiation on the UV/H<sub>2</sub>O<sub>2</sub> process with two lamps, high pressure and low pressure UV lamps, on MTBE removal. The results have testified a trivial role of UV radiation alone in removing the compound.<sup>[18]</sup> Ozone itself is a potent oxidizer (especially in alkali pH) and has a significant effect on MTBE removal. The potent characteristic of ozone as an oxidizer in alkaline pH has been investigated by Sadeghi *et al.*<sup>[13, 15]</sup> The findings of the study show that using a combination process of UV/O<sub>3</sub> in MTBE removal is highly and effective and useful in purifying sewage and waste water. In a study conducted by Graham *et al.*, a simultaneous utilization of UV/O<sub>3</sub> with O<sub>3</sub> alone has been surveyed, which indicates that the removal efficiency of the UV/O<sub>3</sub> combination process is almost twice that of O<sub>3</sub> alone, in degrading organic compound.<sup>[16]</sup>

The present study the efficient concentration of ozone was considered to be 150 mg/L among four other concentrations. Although the MTBE removal rate increased with the increase in ozone concentration from 50 to 200 mg/L, the difference in removal rate in 150 mg/L and 200 mg/L was insignificant. This indicated that increasing the ozone concentration would merely increase the removal efficiency to a distinctive rate [Figure 4]. Salari *et al.*, by utilizing H<sub>2</sub>O<sub>2</sub> as an oxidizer, concluded: that with increasing the H<sub>2</sub>O<sub>2</sub> concentration from 60 mg/L, the MTBE removal rate decreased.<sup>[6]</sup> This following was simultaneously announced in other studies as well: increasing the ozone amount boosted the reaction time (RT), but on the other hand, decreased the time needed for achieving the desired quality of waste water. The reason was probably an increase in the oxidizer percent available in stable circumstances.<sup>[12]</sup>

The results of the present study indicate that pH plays a prominent role in the UV/O<sub>3</sub> process. The findings of the experiments show that with pH increase from 5 to 9, the MTBE removal rate (with ozone efficient degree of the 150 mg/L) increases [Figure 5]. It also indicates that in alkaline pH, probably the OH• concentration increases and the oxidation process facilitates.<sup>[13]</sup> Sadeghi *et al.* in a study indicated that pH: 11.5 has the highest efficiency in MTBE removal.<sup>[13, 15]</sup>

The results showed that the efficiency of the UV/O<sub>3</sub> process is high for low MTBE concentrations and significantly decreases with an increase in the initial concentration of MTBE [Figure 6]. The initial concentration of MTBE is an important factor as varied quantities of this compound exist in environmental waters.<sup>[7]</sup> In study conducted by Eslami in 2007 (the application of photo catalyst in MTBE removal from highly contaminated waters); degradation of this compound by means of the UV/Vis/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> photocatalytic process has been analyzed. The effects of important parameters like pH, amount of H<sub>2</sub>O<sub>2</sub>, concentration of the catalyst, and aeration, have been investigated. The results indicate, that the time duration needed for degradation increases from 30 to 180 minutes as the concentration increases from 10 mg/L

to 500 mg/L.<sup>[4]</sup> This provides further support to the earlier study, which has been shown that in the high initial MTBE concentration, the removal rate reduces and it is due to the competition between various MTBE molecules and / or the MTBE intermediates formed during the oxidative process.<sup>[7]</sup> These findings agree with many other studies conducted on the effect of the MTBE initial concentration.<sup>[7, 12, 15]</sup>

As noticed, the MTBE removal rate in this combination process is based on the ozone efficient concentration, initial concentration of MTBE, pH, and radiation duration. The efficient condition for MTBE removal (with the influence of UV/O<sub>3</sub>) is as follows: 150 mg/L concentration of ozone, alkaline pH, and low concentration of MTBE. Sadeghi *et al.*, in their 2005 study, conclude that least time and ozone needed for the degradation of 90% of each MTBE mole, are 70 minutes and 5.3 moles, respectively (happened in pH: 11.5). They have found that the shortest time (70 minutes) and the smallest amount of ozone (5.3 M) required to remove 90% MTBE per mole occurred at pH: 11.5.<sup>[15]</sup>

The findings of the present study indicate that the utilizing UV/O<sub>3</sub> combination process is significantly beneficial in MTBE removal, utilizing UV radiation and ozone separately is less efficient for MTBE removal compared to the UV/O<sub>3</sub> combination process. In varied concentration of ozone and pH range used in this study, with any increase, the MTBE removal rate increase. It is also indicated, among concentration investigated that with decreasing the initial concentration of MTBE, the removal efficiency increase up to 98% in stable conditions for UV/O<sub>3</sub>.

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