Photocatalytic Degradation of Methyl Tert-Butyl Ether (MTBE) from Aqueous Solution: A Review

Ali Assadi a, Tohid Soltani a,*, Mohammad Reza Mehrasbi a

a Department of Environmental Health Engineering, School of Public Health, Zanjan University of Medical Sciences, Zanjan, Iran.

*Corresponding author: Tohid Soltani
Department of Environmental Health Engineering, School of Public Health, Zanjan University of Medical Sciences, Zanjan, Iran.
Tell: +98-9147162518.
E-mail address: soltanitohid071@gmail.com

ARTICLE INFO

Article Type: Review article

Article history:
Received October 9, 2017
Revised November 22, 2017
Accepted December 2, 2017

DOI: 10.29252/jhehp.3.1.5

Keywords:
Photo Catalysis
Nanoparticles
MTBE Removal
AOPs
Water Pollution

ABSTRACT

Nowadays, underground water is the main source of drinking water that contamination to organic pollutants such as MTBE is an important issue. One of the suitable methods for these types of pollutants is the advanced oxidation methods. Advanced oxidation processes (AOPs) are involved in the production of highly reactive hydroxyl radicals that oxidize organic matter such as MTBE and even lead to its full mineralization. The use of light in the presence of catalysts is one of the methods of advanced oxidation processes. Photocatalytic methods widely used for a wide range of toxic and none degradable pollutants. Recent advances in the fabrication and characterization of Nano scale materials have extensively developed research into methods for the preparation of highly effective Nano-sized catalysts for the removal of chemical contaminants. This review article discusses the work on the photo catalysis of MTBE in water using different types of photo catalysts.

1. Introduction

For several years, lead was added to raise the octane number and burn fuel to gasoline. But after confirming its health aspects in the environment and in humans, in recent years, the substance MTBE (C₅H₁₂O) has been used to replace it [1]. Over the past decade, MTBE has been accepted as an additive to gasoline. The addition of MTBE to unleaded gasoline reduces atmospheric CO emission levels by 10 to 15% [2, 3]. The use of MTBE in the new formulation of gasoline to improve the combustion process and reduce the amount of carbon monoxide emissions from cars exhaust was proposed by the Clean Air Act (1990) [4]. This combination was first used in Iran in 2000 and from the beginning of 2002, it was added to petrol from around the country [5]. MTBE inside fuel systems increases the incidence of surface and groundwater pollution. Water pollution can be mainly due to high leakage of MTBE on the ground or underground from fuel storage tanks, pipelines, and refueling points. In addition, flotation activities can also cause pollution in ports, lakes, and open water reservoirs. As regards to other gasoline compounds (such as benzene, toluene, and ethylene benzene-waist lean (BTEX)), MTBE has a relatively high solubility in water (43 to 54 g/L) and has a slight tendency to enter the soil as a result of leakage from fuel tanks or chronic effects.

Nervous system reactions and symptoms such as dizziness, lack of concentration, difficulty in breathing, nausea, vomiting and forgetfulness as well as skin irritation have been reported as a result of exposure to this compound [7]. The US Environmental Protection Agency has classified MTBE as a potential carcinogenic agent due to its rapid solubility in water and unpleasant smell and odor, and its maximum permitted level in drinking waters has been proposed to be 20 to 40 ppb [8, 9]. One of the important characteristics of this oxygen material is the high polarity and low Henry’s constant (0.022) [10]. These materials can easily penetrate the soil without absorption and cause groundwater pollution. Also, MTBE can easily evaporate into the air and then return to water environments through precipitation. Owing to these properties and the presence of ether band and long (over one carbon) material in structure, it is known as a highly resistant material for natural degradation [11]. Remediation of groundwater contaminated with MTBE is a major problem in physicochemical and biological properties. MTBE is a microbial absorbent material in typical waters both in aerobic and anaerobic conditions. In addition, bioremediation is not widely accepted. For purification of drinking water, evaporative evaporation techniques, such as dehydration by steam and steam extraction, have limited success in high water solubility (50 g/L) and low Henry’s constant [12, 13]. MTBE is a common pollutant with a significant environmental impact and in recent years it has been highlighted.

Therefore, the photocatalytic method for the degradation of MTBE is less developed than other pollutants. The existence of low emission in relation to this subject is the evidence of its confirmation [9].

Recent advances in the fabrication and characterization of nano scale materials have extensively explored into methods for producing highly effective nano-sized catalysts for the removal of chemical contaminants [14]. Nanoparticles have been widely used in optical, resonant, electrical, and chemical fields. Various chemical methods have been used to produce nanoparticles with small size distribution, including microemulsion and hydrothermal methods [15]. In recent decades, many technologies have been used to decompose MTBE in aquatic environments. Some of these technologies include granular activated carbon (GAC), absorption, aeration, advanced oxidation processes (AOPs), and biological decomposition. In the last decade, AOPs are effective methods for the degradation of organic pollutants [2]. One of these advanced oxidation processes are the photocatalytic processes that decompose and mineralize organic pollutants [16-18].

Different types of advanced oxidation processes including Fenton, H₂O₂/UV, H₂O₂/O₃, O₃, O₃/UV, synolysis, and heterogeneous photocatalyst, process various mechanisms to produce highly reactive hydroxyl radicals that mineralize pollutants [17, 19-21].

ZnO and TiO₂ are two ideal photocatalyst in photocatalytic systems and they provide high-oxidizing photogenes with their broadband fission energy. As the oxide on the energy of fissile bonding is approximately the same (3.2 eV) than TiO₂, its photocatalytic capacity, similar to TiO₂, is predicted to be the biggest advantage of zinc oxide as compared to titanium oxide, which absorbs more than a fraction larger than the UV spectrum, and the corresponding threshold of zinc oxide is 425 nm [22]. This research is a systematic review. The study was conducted by gathering information from the Web of Science, Google scholar, and Science Direct sites with the keywords "AOPs, Groundwater, MTBE, Organic Contaminants, and Nano-photo catalyst.” Articles reviewed were from the period of 1995 to 2017. The criteria for the entry of the documentation are the appropriateness of the title and the abstract (related to the subject matter). A total of 35 documents were used for the write-up.

2. Mechanism of Photocatalytic Degradation of MTBE

MTBE contains methoxy groups (–CH₃) that can absorb hydrogen atoms by producing radicals resulting from photocatalytic stimulation of light. For absorption of hydrogen atoms owing to the lower separability of energy, the C-H bond, in the methoxy group is easier than the methyl group. Accordingly, the degradation reaction begins with the absorption of the hydrogen atom from the methoxy group.

\[(\text{CH}_3\text{)}\text{COCH}_3 + \text{OH}^+ \rightarrow (\text{CH}_3\text{)}\text{COCH}_2^+ + \text{H}_2\text{O}\]

\[(\text{CH}_3\text{)}\text{COCH}_2 + \text{O}_2 \rightarrow (\text{CH}_3\text{)}\text{COCH}_2\text{OO}^−\]

\[(\text{CH}_3\text{)}\text{COCH}_2^− \rightarrow (\text{CH}_3\text{)}\text{C}^+ + \text{HCHO}\]

\[(\text{CH}_3\text{)}\text{C}^+ + (\text{CH}_3\text{)}\text{CO} \rightarrow (\text{CH}_3\text{)}\text{CH} + (\text{CH}_3\text{)}\text{COCH}_2^−\]

\[(\text{CH}_3\text{)}\text{C}^+ \rightarrow (\text{CH}_3\text{)}\text{C} = \text{CH}_2 + \text{H}^+\]
The intermediate products following the reactions include: tert-butyl formate (TBF), tert-butyl alcohol (TBA), formic acid, acetone, and acetic acid [19].

3. Study of the Effective Parameters in Photocatalytic Processes on MTBE Degradation

3.1. Effect of $H_2O_2$

The results a study on $H_2O_2$ showed that the addition of $H_2O_2$ in the photocatalyst system increases the rate of degradation, in order for the efficiency of TiO$_2$ catalyst to increase in the presence of $H_2O_2$ [23]. The results of Beretelly et al. (2004) showed that the simultaneous presence of $H_2O_2$ and TiO$_2$ (UV/TiO$_2$/H$_2O_2$) at 254 nm wavelengths resulted in total MTBE degradation in less than 2 h. Therefore, the combination of these processes has a synergistic effect on MTBE degradation [24]. Zang et al., (2006) examined the effect of hydrogen peroxide on UV/TiO$_2$ on the rate of MTBE degradation and found that the constant reaction rate ($k_0$) in the UV/TiO$_2$/H$_2O_2$ process increased by increasing catalyst load and its optimum (0.03 min$^{-1}$) was obtained in 0.5 g TiO$_2$/L. At higher levels of hydrogen peroxide (> 0.15 g/L), peroxide itself produces hydroxyl radicals under the UV irradiation, such that MTBE degradation is improved and reaches a plateau depending on the amounts of TiO$_2$ in the solution [25]. The role of the initial concentration of $H_2O_2$ in the range of 5, 10, 15, and 20 mM was investigated. The optimum concentration results for this parameter was reported to be 15 mM [13].

At optimal pH and catalyst concentration, different ratios of $[H_2O_2]/[MTBE]$ were studied in the range of 5 to 14 and the results showed that degradation efficiency increased from ratio 4 to 10 and then decreased later. Thus, the ratio of 10 was obtained as the optimal ratio [2]. Chih-Hsiu et al. (2009) studied photocatalytic degradation of MTBE using Fe$_3$O$_4$/TiO$_2$ magnetic nanoparticles under visible light. The results showed that hydroxyl radicals in aqueous solutions increase with increasing pH and usually result in a high removal of organic pollutants. Therefore, the control of pH was very important for the general treatment efficiency during the operation [26]. In a study conducted 2013, the role of molar ratio [H$_2$O$_2$]/[MTBE]$_0$ in different concentrations was studied and it was reported that by increasing this ratio to 4 the removal efficiency increases, then with an excessive increase in efficiency there is decrease in the degradation, as such its optimum is reported at 4 [16].

In 2014, the effect of $H_2O_2$ on photocatalytic activity of the process UV/Fe$_3$O$_4$/ZnO was investigated. The maximum decomposition rate in molar ratio $[H_2O_2]/[MTBE]$ was reported to be 5. Furthermore, higher concentrations of $H_2O_2$ can have a negative effect on the process efficiency. This effect can be due to the formation of a less active Hu species in higher concentrations of $H_2O_2$ [27].

3.2. Effect of Modifier Agent

Orlov et al. (2007), investigated the photocatalytic degradation of MTBE by modifying TiO$_2$ with gold nanoparticles. They reported that TiO$_2$ modification with golden nanoparticles increases its photocatalytic activity. In the best condition for loading the particles of gold at a size of 3 nm, the constant MTBE degradation rate was three times higher than that of the typical TiO$_2$ [28]. Seddigi et al. (2014), examined the effect of palladium-modified zinc oxide nanoparticles (ZnO) in the MTBE photocatalytic degradation process. According to the results, when the percentage of palladium used for zinc oxide modification increases, the reaction rate constant ($k_0$) increases. MTBE degradation in water was studied by 0.5, 1 and 1.5% modified palladium. According to the results of 1% palladium modified ZnO, the best result was obtained in the system and almost complete degradation of MTBE with 1% Pd/ZnO after 5 h [29].

Vicente et al., (2008) examined the efficiency of MTBE degradation under visible light with Au/TiO$_2$ and Au/TiO$_2$-Al$_2$O$_3$. In this study, MTBE degradation for Au/TiO$_2$ catalyst was 57%, for Au/P25 it was 80%, and for Au/TiO$_2$-Al$_2$O$_3$ it was 100% for 150 min [30].

In the study of Kuburovic et al., Photocatalytic activity of TiO$_2$ (P-25) and coated with iron and La were investigated. The rate of degradation of MTBE with p25 in 45 minutes was 49.6%, while the p25 coated with iron and La degradation rate was 44.2 and 48.6% at 30 minutes [31]. In a study of photocatalytic systems such as UV, Ag/TiO$_2$, UV/TiO$_2$, UV/Ag/TiO$_2$, TiO$_2$ under [MTBE] = 1mM, pH =3, 2 g/L TiO$_2$, 2 g/L Ag/TiO$_2$ and $\lambda$ = 254 nm they were compared. They results shown that modified TiO$_2$ catalyst had better performance than single processes [13]. According to the results of various studies, suitable coating of...
catalysts increases their efficiency and the amount of degradation of pollutants is achieved in a short time.

3.3. Effect of PHs

The photocatalytic degradation of MTBE using the UV-vis/ZnO/H₂O₂ process was studied in 2008. The showed that by increasing the pH from 4 to 7, the degradation rate increases, then from 7 to 9 the degradation efficiency decreases. Therefore, the optimal pH was reported to be 7 and as such the highest removal percentage was 89.5% [2]. Chih-Hsiu et al. (2009) studied photocatalytic degradation of MTBE using Fe₃O₄/TiO₂ magnetic nanoparticles under visible light. They showed that hydroxyl radicals in aqueous solutions increased with increasing pH and usually result in a high removal of organic pollutants. Therefore, the control of pH was very important for the overall treatment efficiency during the operation [26].

In the study of Safari et al., the pH range studied at an initial concentration of MTBE, 75ppm, catalyst concentration, 2g/L, [H₂O₂]₀/[MTBE]₀, 0.05, UV intensity of 24W (254 nm wavelength) and irradiation time 1h, was evaluated in range 3 to 9. The results showed that the degradation efficiency increased from pH 3 to 7, with the increase of pH from 7 to 9, the degradation rate decreased, so pH 7 was reported as optimal [16]. To find the optimal pH and obtain the maximum process efficiency, this parameter was evaluated in the range of 6, 7, 8 and 9. Based on the results, the optimal parameter was near to 7 and 8 [32].

One of the important parameters in the photocatalytic processes for degradation of organic pollutants is pH. This parameter was evaluated in the range of 4, 7, and 10. Based on the results, the MTBE degradation rate from pH 4 to 7 increased and then decreased by increasing it to 10, thus, pH 7 was obtained as the optimal pH [33]. The role of pH as one of the important parameters in UV/TiO₂ and UV/H₂O₂ systems was investigated in 2008. In the UV/H₂O₂ system, acidic pH responded better and pH 3 was considered as the optimal pH. In the UV/TiO₂ system, when different pH values are evaluated, the optimum value reported was near to 7 [13]. The role of pH in oxidation processes is very difficult, owing to its multiple roles in electrostatic reactions between semiconductor surfaces, solvent molecules substrate, and charged radicals produced during the reaction. In general, the pH effect depends on the type of pollutant and zero point charge (ZPC) of semiconductor (catalyst) in the oxidation process [13, 16].

3.4. Effect of Initial Concentration of MTBE

The effect of initial concentration of MTBE on UV/TiO₂ and UV/H₂O₂ systems was investigated in the study of Zhang et al. (2008). Under identical conditions, in both systems, the efficiency of removal is reduced by increasing the initial concentration of MTBE. In the UV/H₂O₂ system, MTBE removal was achieved after 60 min at an initial concentration of 0.5 mM to 87%, but when the initial concentration of the pollutant increases from 1 to 1.5 mm, the percentage of removal is reduced from 69 to 59. Similar results were also reported in the UV/TiO₂ system when the TiO₂ concentration of the catalyst was fixed [13]. In the study of Eslami et al. (2008), the effect of the initial concentration of MTBE in the range of 10 to 500 mg/L was investigated and they showed that the complete degradation of MTBE increased from 15 to 150 min, when the initial concentration of MTBE increases from 10 to 500 mg/L, as such the amount of degradation is reduced by increasing the initial concentration of the pollutant; in other words, the time required for degradation increases [2]. The initial concentration of 50, 100, 200, and 400 ppm was studied in 2015.

According to the results, they showed that complete degradation of MTBE at initial concentration of 50 ppm was obtained, but by increasing the initial concentration, degradation rate decreased [32]. The initial concentration of the pollutant (MTBE) was studied as an important parameter in photocatalytic processes in the study of Mansouri et al., (2017). They observed that by increasing the initial concentration of the pollutant, the process degradation and efficiency decreased [33]. In low concentrations of MTBE, a large number of water molecules is absorbed onto the catalyst, which results in the production of hydroxyl radicals, which also accelerates the oxidation process. In more concentrations, a few molecules of water are placed on active sites. As a result, competition between the concentrations of MTBE and water molecules increases on absorption and leads to reduction in the amount of decomposition [2, 33].

3.5. Effect Catalyst Load

In 2007, photocatalytic process was investigated for MTBE degradation. The result showed that by increasing the catalyst load, the rate of degradation increased, such that by increasing the catalyst to 5 g/L in 150 min, MTBE degradation was almost complete [34]. The role of catalyst concentration on the process was studied in different concentrations. Low
concentration of catalyst in the range of 0.5 to 1 g/L, leads to low MTBE degradation, and also excess concentrations of catalyst (4 to 5 g/L), reduced the degradation rate. At catalyst concentrations of 2 to 3 g/L, the values were less than 2 mg/L, and the concentration of 2 mg/L was obtained as the optimum amount [13]. Catalyst load was evaluated under room temperature (24 to 26°C), optimal pH of 10, flow rate of 100 mL min⁻¹, 419 nm visible light, and light intensity of 724 lx. By increasing the catalyst load up to 5 g/L, the degradation of MTBE increased (91.6%).

Then, with excess catalytic load, the degradation rate decreased, so the optimal amount of catalyst was reported to be 5 g/L [26]. In the study of Safari et al. (2013), catalyst load was evaluated in the range of 1 to 4 g/L [16]. They showed that, by increasing catalyst loading, the amount of degradation increases from 1 to 2 mg/L, then the amount of degradation decreases by increasing catalyst loading from 2 to 4 mg/L. Catalyst loading in the range of 100 to 400 mg/L was studied in order to obtain the optimal catalyst level. By increasing catalyst loading from 100 to 200 mg/L, degradation increased and then degradation rate was reduced by excessive catalyst loading; so, optimal catalyst concentration of 200 mg/L was obtained [32]. The effect of catalytic loading in the range of 1, 2, and 3 g/L was investigated and according to the results, the rate of degradation from the loading rate of 1 to 2 increases and then decreases by increasing it to 3 g/L. Therefore, loading more than the optimal range could have a negative effect. The optimal amount of catalyst in this study was reported to be 2 g/L [33]. With a further increase in the catalyst load, some photocatalyst particles may not receive sufficient energy for the MTBE oxidation, as well as the excess catalyst load can be a barrier to UV radiation. It may also result from Nano aggregation, increasing obscurity, reducing the active points on its surface to adsorb organic compounds and UV, thereby reducing the quantity of e-h+ and OH radicals and affecting the degradation [34, 35].

<table>
<thead>
<tr>
<th>Pure catalyst</th>
<th>Catalyst/</th>
<th>Catalyst/</th>
<th>pH_{opt}</th>
<th>Efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>H₂O₂</td>
<td>TiO₂/Au</td>
<td>pH_{opt}</td>
<td>Degradation rate was higher than of the pure catalyst</td>
<td>[13,28, 29,31]</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>ZnO/Pd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO₂/Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO₂/Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>ZnO/H₂O₂</td>
<td></td>
<td>Increased degradation in the presence of H₂O₂</td>
<td>[2, 24, 26]</td>
</tr>
</tbody>
</table>

4. Conclusions

This review study is the result of the photocatalytic processes used for the degradation of MTBE in aqueous solutions. The use of photocatalytic processes is an effective and efficient way for a variety of toxic and non-degradable pollutants. Improving the efficiency of these processes is possible by optimizing parameters such as pH, catalyst load, initial concentration of the pollutant, duration time, and H₂O₂ concentration. Modifying the level of catalysts using metals (such as gold, iron, silver, copper, carbon, etc.) has also been reported to be more efficient than the pure catalyst. Therefore, modifying catalyst with suitable coatings and finding the optimal level of the effective parameters in the photocatalytic processes of the two key elements.

References


Photocatalytic Degradation of MTBE
Assadi A, et al.


