

Photocatalytic Degradation of Methyl *tert*-Butyl Ether (MTBE): A review

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Abstract. Advanced oxidation processes using UV and catalysts like TiO₂ and ZnO have been recently applied for the photocatalytic degradation of MTBE in water. Attempts have been made to replace the UV radiation by the solar spectrum. This review intends to shed more light on the work that has been done so far in this area of research. The information provided will help in crystallizing the ideas required to shift the trend from UV photocatalysis to sunlight photocatalysis. The careful optimization of the reaction parameters and the type of the dopant employed are greatly responsible for any enhancement in the degradation process. The advantage of shifting from UV photocatalysts to visible light photocatalysts can be observed when catalysts like TiO₂ and ZnO are doped with suitable metals. Therefore, it is expected that in the near future, the visible light photocatalysis will be the main technique applied for the remediation of water contaminated with MTBE.

Keywords: photocatalysis; degradation; MTBE; doping; TiO₂; ZnO

1. Introduction

The alarming rise in the environmental pollutants encourages the demand to control and reduce the pollution load (Tabrez *et al.* 2011, Wasi *et al.* 2013). Oxygenates as gasoline additives have been used since 1979. The use of oxygenates rose tremendously after the passage of 1990 Clean Air Act, which recommends that they could be added to gasoline either seasonally (15% by volume) or yearly around (11% by volume) (Kim *et al.* 2012, Wu *et al.* 2012). In the year 1997, fifty five nations have agreed for Kyoto Protocol to reduce the emission of greenhouse gases such as carbon dioxide, nitrous oxides, methane, perfluorocarbons, hexafluorides, hydrofluorides and

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sulfur hexafluoride (Arana *et al.* 2008). Consequently, the use of fuel oxygenates got further impetus to improve the quality of fuel and its octane value (Guillard *et al.* 2003). To improve octane and reduce vehicular emissions two types of fuel oxygenate can be blended with gasoline (aliphatic alcohols or ethers). While gasoline containing alcohol requires careful handling to avoid or minimize water content, ethers tend to be trouble free as gasoline blend components, for this reason methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME) were preferably blended in gasoline (Kanai *et al.* 1994). With the excessive use of MTBE in gasoline, it became prominent in environment (An *et al.* 2002). MTBE was considered as an environmental pollutant due to the following reasons: 1) its large annual production for use as a fuel oxygenate, 2) reports of various studies have indicated the presence of MTBE in atmosphere, 3) its solubility in water is high (48 g l^{-1}) and it is the most frequently detected organic pollutant which is not adsorbed by the soil particles (Park *et al.* 2003). In addition, it can be detected sensitively by human senses due to its unique odor in a concentration range of $13.5\text{-}45.5 \mu\text{g l}^{-1}$ (Cooper *et al.* 2009).

MTBE has relatively low Henry's law constant (vapor/aqueous phase concentration) compared with other organic compounds like benzene, toluene, ethylbenzene and xylene (Wu *et al.* 2012). The Henry's law constant of MTBE ranges from 0.012 to 0.029 in the temperature range 10°C to 25°C (Fischer *et al.* 2003). Volatile organic substances with their Henry's law constant less than 0.05 tend to be more soluble in water than to escape in the atmosphere (Lim and Lynch 2011a). When MTBE enters into the groundwater, its migration rate is similar to the rate of migration of water. Regarding its interaction with the organic fraction of soil, MTBE, shows a weak partition with the soil. The chemical stability of MTBE and its resistance to biodegradation are responsible for its persistence in the environment. Once released from an underground source, MTBE has high tendency to spread extensively and rapidly in groundwater (Chan and Lynch 2003). The presence of MTBE in water poses potential health problems. It has been shown that MTBE can accumulate in blood stream and can be detected in breath. Symptoms of MTBE exposure include headaches, vomiting, dizziness, fever, cough, muscular ache, sleepiness, disorientation and skin & eye irritation (Arana *et al.* 2008, Baus *et al.* 2005, Amir *et al.* 2012). According to United States Environment Protection Agency (USEPA), MTBE is a potential human carcinogenic and adversely affects the odor and taste quality of water. The EPA has issued an advisory for drinking water limiting the concentration of MTBE to the range 20-40 ppb based on taste and odor (Lim and Lynch 2011a).

The overall characteristics and problems raised by the presences of MTBE in water pose a greater challenge towards its treatment. Many techniques have been applied to remove MTBE from water. Traditional techniques were not successful when applied for the treatment of water containing pollutants like MTBE (Selli *et al.* 2005). For instance, the use of activated carbon to adsorb MTBE from water was found to be of high cost because other organics will preferentially occupy the adsorption sites and thereby increase carbon usage rates (Mascolo *et al.* 2008). In addition, these processes do not represent an environmentally sustainable solution because they merely transfer the organic pollutants from one phase to another. Biological oxidation as a cost-effective remediation technology for cleaning up hydrocarbon contaminated sites has become of an increasing interest in recent years. The synthetic additive MTBE is particularly recalcitrant to biodegradation, because it contains an ether bond and a tertiary carbon, leading to a low biodegradation rate. Nevertheless, a variety of microbial species have been shown to be capable of metabolizing MTBE, mostly in aerobic conditions (Deeb *et al.* 2000, Fayolle *et al.* 2001) and field-scale bioremediation studies have already given promising results. However, long

degradation times that last for several months are required to show a significant decrease in the concentration of MTBE (Salanitro *et al.* 2000). On the contrary, advanced oxidation processes (AOPs) using UV radiation and certain types of photocatalysts have shown successful results in the photodegradation of MTBE in water. Advanced oxidation processes (AOPs) are the type of chemical reactions that lead to the production of hydroxyl radicals in sufficient quantities. These radicals act to degrade most of the complex organic molecules. AOPs include Fenton's Process, $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{O}_3$, O_3 , O_3/UV , sonolysis, heterogeneous photocatalysis etc (Gogate and Pandit 2004). All of these processes act to produce the hydroxyl radicals by different mechanisms. Hydroxyl radicals have high oxidation potential; therefore, they are highly unstable and reactive. The reactions between the organic species/pollutants and the hydroxyl radicals are very fast and nonspecific (Esplugas *et al.* 2002). The semiconductor photocatalysts have been found to work in presence of the UV radiation and visible light as well.

2. Photocatalytic degradation of MTBE

Photocatalytic degradation of contaminants in waste water treatment/purification has attracted the attention of many researchers. This is attributed to the fact that the photocatalytic process within ambient conditions can come to completion and the contaminant could be totally removed (Gogate and Pandit 2004). In addition, the photocatalytic process is an appropriate technique and could be applied in case of a sensitive environment. Photocatalytic reactions can proceed only in presence of suitable light, dissolved oxygen and a photocatalyst. However, there are few reports which have discussed the use of oxidizing agents like O_3 and H_2O_2 to optimize the photocatalytic process (Mascolo *et al.* 2008). Such process is usually initiated by radiating the semiconductor with light, which promotes the valence band electrons to the conduction band. The electron deficiencies, or holes, left behind in the valence band can either be filled by adsorbed organic molecules or hydroxide anions, to form hydroxyl radicals. Moreover, adsorbed dioxygen acts as a sink for the electrons of the photo-promoted conduction band, as a result superoxide anions and hydrogen peroxide radicals will be formed (Fig. 1). All of these species can play important roles in the photocatalysis of the organic compounds (Zang and Farnood 2005a, Li *et al.* 2005). The photocatalysts TiO_2 , ZnO and their derivatives are commonly used as photocatalysts for the degradation/removal of MTBE from water using UV radiation. There are few reports that have discussed the photocatalytic degradation of MTBE in water where the more friendly visible light has been applied instead of UV. The photocatalytic degradation of MTBE can be classified into two groups namely TiO_2 based group and the ZnO based group. The literature shows that the TiO_2 based group has more applications compared to the ZnO based group. Chan and Lynch (2003) studied the degradation of MTBE in water using TiO_2 in a supported cylindrical photoreactor. They have used UV light in the range of 320-400 nm. Park *et al.* (2003) have reported the photocatalytic degradation of MTBE in vapor phase onto TiO_2 coated plates in presence of UV radiation at 360 nm. They have also studied the degradation mechanism of MTBE by using gas chromatography equipped with flame ionization detector (FID) and FTIR technique. This study has highlighted the feasibility of the degradation process in presence of sun light.

Bertelli and Selli (2004) have studied the kinetic parameters of MTBE degradation under various experimental conditions. For instance, they have applied TiO_2 in presence of radiations of different wavelengths. They have also undertaken the photolysis of MTBE in presence of hydrogen peroxide and the sonolysis at a frequency of 20 KHz ultrasonic wave. They have also performed photocatalysis in presence of TiO_2 and UV irradiation at 254 nm and 315 nm. They

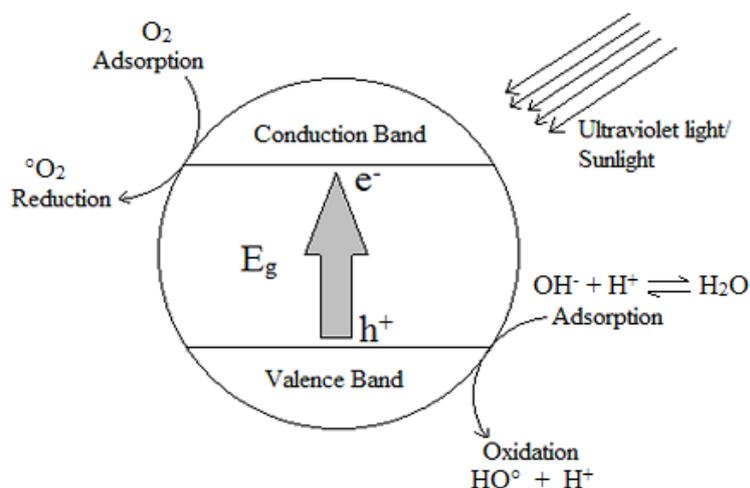


Fig. 1 Schematic diagram of photoexcitation of semiconductor by UV/solar irradiation

have identified the intermediates of the degradation process by means of a gas chromatography with an FID and the total organic carbon (TOC) analyzer. As a result, they have reported the degradation mechanism. In another study, Selli *et al.* (2005) have compared the effectiveness of MTBE degradation, using photocatalysis, photolysis and sonolysis degradation techniques. Zang and Farnood (2005b) have carried out the photocatalytic degradation of MTBE using TiO₂ slurry in water where a xenon lamp has been applied as a UV irradiation source. They have combined the gas chromatograph with an FID detector using head space micro-extraction system. Arana *et al.* (2008) have studied the comparative photocatalytic degradation of MTBE using TiO₂ and Cu doped TiO₂ as photocatalysts. They have used fluorescent tubes with emission spectrum in the range of 300 to 400 nm as UV light source. Jo and Yang (2010) have utilized S- and N- doped TiO₂ as photocatalysts for the degradation of very low concentration MTBE using visible light. They have applied a gas chromatograph equipped with FID for the analysis of the degradation products and UV-VIS-NIR spectrophotometer for the characterization of the doped TiO₂. Kuburovic *et al.* (2007) have reported the degradation of MTBE in wastewater using various techniques like photocatalytic, photolytic and biological degradation. They have applied TiO₂ during the photocatalytic degradation of MTBE and used a gas chromatograph with an FID detector for the analysis. Orlov *et al.* (2007) have undertaken the degradation of MTBE in presence of gold modified TiO₂. They have applied advanced analytical techniques like high resolution electron microscopy, X-ray photoelectron spectroscopy for the characterization of the catalyst and a gas chromatograph with an FID detector for the MTBE analysis using head space technique. Arana *et al.* (2008) have reported the photocatalytic degradation of MTBE over gold deposited TiO₂ and TiO₂-Al₂O₃ in presence of visible light using krypton lamp. They have used nitrogen adsorption, XRD, UV-VIS and STEM-EDAX spectroscopic techniques for the characterization of the photocatalysts. Total organic carbon analyzer and gas chromatography-mass spectrometry (GC/MS) analysis have been utilized to study the by-products of the degradation process.

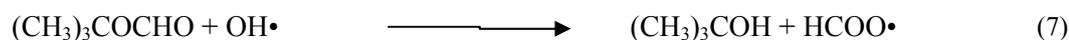
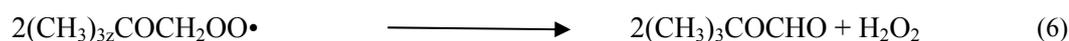
The utilization of ZnO based group as a photocatalyst in the degradation of MTBE has been recently reported. For example, Eslami *et al.* (2008) have discussed the photocatalytic degradation of MTBE in presence of UV-vis/ZnO/H₂O₂ and used a gas chromatograph with an FID detector. The ZnO based group could be easily activated by small amount of energy compared to TiO₂ based group (Shinde *et al.* 2011). Very recently, Seddigi *et al.* (2013, 2014) have highlighted the effect of the particle size of ZnO on the photocatalytic degradation of MTBE. They have also studied the photocatalytic degradation of MTBE in presence of Pd doped CeO₂-ZnO nanoparticles. Samples of the employed catalyst have been characterized using high resolution electron microscopy, XRD, EDX, X-ray photoelectron spectroscopy & N₂ sorptometry. Bagal and Gogate (2013) recently investigated sonolysis, photocatalysis, and sonophotocatalysis for the degradation of alachlor using TiO₂ (mixture of anatase and rutile), TiO₂ (anatase) and ZnO.

This review article discusses the work on the photocatalysis of MTBE in water using different types of photocatalysts. In addition, the work related to the use of visible light in the photodegradation of MTBE instead of UV was also emphasized.

2.1 Mechanism of photocatalytic degradation of MTBE

The photocatalytic degradation of MTBE is considered to be a complex process of consecutive reactions, which proceed through several intermediate steps. The reaction between MTBE and the hydroxyl radicals was reported to be the dominant pathway in the degradation process which is initiated by the UV radiation (Mezyk *et al.* 2004). The hydroxyl radical reaction gives a transient carbon-centered radical, which subsequently reacts with the dissolved oxygen to form peroxy radicals. The formation of both carbon-centered and peroxy radical have been considered as second order reactions (Achten *et al.* 2002).

Methyl tert-butyl ether contains –CH₃ groups from which a hydrogen atom can be abstracted by the hydroxyl radical, which is generated as a result of the photo-excitation of the photocatalyst. The abstraction of a hydrogen atom from the methoxy group is easier than that from a methyl group. This is because the bond dissociation energy of the C-H bond in the methoxy group is less than that of the methyl group. Accordingly, the degradation reaction starts with the abstraction of H atom from the methoxy group as shown below (Guillard *et al.* 2003, Bertelli and Selli 2004, Arana *et al.* 2008).



The main intermediate that will be formed is the *tert*-butyl formate (TBF) which produces

tert-butyl alcohol (TBA), formic acid, acetone and acetic acid, all of which were detected during the analysis. The formation of acids during the course of the reactions is responsible for the decrease in the pH during the photodegradation process. The formation of intermediates in the photodegradation reactions depends on several factors like the type of the catalyst and its amount, the presence of oxygen and the technique used etc. (Selli *et al.* 2005, Arana *et al.* 2008).

2.2 Reaction parameters

2.2.1 Initial concentration of MTBE

The initial concentration of MTBE is considered an important parameter in the photocatalytic process. The concentrations of MTBE vary in the environmental waters as well as in the processed effluents. This will in turn affect the time required for the total conversion of MTBE (Boulamanti and Philippopoulos 2008). In case of effluents of high concentrations of MTBE, the degradation is negligible and dilution is considered to be an essential solution to such a situation. In a solution with a high concentration of MTBE, the removal efficiency was found to decrease (Herrmann 1999, Hu *et al.* 2008, Eslami *et al.* 2009) have reported a similar pattern in the removal of MTBE using UV/TiO₂ system with a constant amount of TiO₂. To completely remove the MTBE, its initial concentration should be about 0.1 mM (Xu *et al.* 2004, Zang and Farnood 2005b). The reduced reaction rate at high MTBE concentrations might be attributed to the availability of adsorption sites on the surface of the catalyst. These adsorption sites depend on the geometry of the reactor and on the competition between MTBE molecules and/or the MTBE intermediates which are formed during the oxidation process. MTBE and its intermediate products both can compete in the consumption of the hydroxyl radicals ($\bullet\text{OH}$) which result from the photoexcitation of the catalyst (Hu *et al.* 2008, Boulamanti and Philippopoulos 2008). This type of competition will lead to a decrease in the concentration of $\bullet\text{OH}$ radicals which are essential for the degradation process.

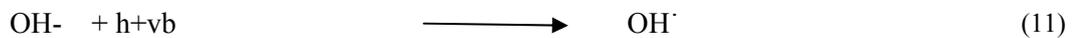
2.2.2 Effect of pH of the reaction medium

The pH of the reaction medium plays a very important role in photocatalytic degradation reactions. However, the effect of pH on the rate of the photocatalytic reactions is considered to be a bit complex phenomenon. This is due to the electrostatic properties of both the catalyst and the pollutant molecules. The pH of the solution will affect the surface charge of the catalyst, the interfacial electron transfer and the photoredox processes (Zhu *et al.* 2005). In case of a weakly acidic pollutant, a slight decrease in the pH of the solution plays a favorable role in the photocatalytic process. However, some researchers were not convinced with the previously mentioned effect of lowering the pH of the solution (Vohra and Davies 2000, Subramanian *et al.* 2000). Most of the semiconducting oxides are amphoteric in nature, as a result, the pH will affect the surface-charge properties of the photocatalysts (Chakrabarti and Dutta 2004) which will in turn controls the rate of the reaction taking place on the surfaces of the semiconductor particles. Eslami *et al.* (2008) have reported a linear increase in the efficiency of the photodegradation of MTBE when the pH of the solution was changed from 4-6. However, by increasing the pH from 6 to 9, the efficiency of the photodegradation of MTBE has shown a gradual decrease. Based on these observations, they have suggested that a pH value of 7 was considered to be optimum for the oxidation of MTBE. On the contrary, Hu *et al.* (2008) have reported that the highest removal efficiency of MTBE using UV/TiO₂ system was obtained at pH ~3. Lu and Chiang (2009) have found that a pH ~9 was considered optimum for the photocatalytic degradation of ETBE. Safari *et*

al. (2013) have suggested that a pH of 7 is optimum for the photocatalytic degradation of 75 ppm MTBE using Fe doped TiO₂ as a photocatalyst. It is obvious that the change in the pH of the solution has a significant effect on the MTBE removal. At higher values of pH, more hydroxide ions will be available to induce the generation of the hydroxyl radicals. Such radicals will result from the photooxidation of the OH⁻ ions by the holes formed on the catalyst surface as a result of photoexcitation (Wong and Chu 2003). However, an explicit interpretation of the effect of the initial pH on the photocatalytic degradation is very difficult because of several factors like electrostatic interactions between the surface of the catalyst, the solvent molecules and the charged radicals formed during the course of the reaction.

2.2.3 Effect of the presence of O₂

In addition to the effect of the pH, oxygen also plays an important role in the degradation of MTBE (Eslami *et al.* 2009). The rate of MTBE degradation increases to a certain extent in presence of oxygen. For instance, an increase in the flow rate of oxygen will increase the supply of oxygen by means of enhanced turbulence, gas-liquid interfacial area, gas holdup and mass transfer coefficient. However, further increase in the oxygen flux leads to a decrease in the degradation efficiency of MTBE (Lim and Lynch 2011a, Mehrjouei *et al.* 2012). Boulamanti and Philippopoulos (2008) have reported Langmuir-Hinshelwood-Hougen-Watson characteristic kinetic behavior for the gas-solid heterogeneous reactions. They have shown that under a particular set of fixed conditions an increase in the concentration of O₂ increases the rate of the oxidation process up to a certain limit. However, beyond that limit any increase in the concentration of O₂ will have no effect on the oxidation process. Gerischer and Heller (1991) have suggested that the reaction of photo-generated electron and oxygen adsorbed on the surface of a solid semiconductor is slow and could become the controlling step in the photocatalytic oxidation reaction. It is also known that a limitation in the photocatalytic degradation efficiency is attributed to the recombination of the photogenerated hole-electron pairs. Oxygen adsorbed on the surface of titanium dioxide prevents the recombination process as electrons scavenger. The mechanism pathways involved are given below (Eslami *et al.* 2009).



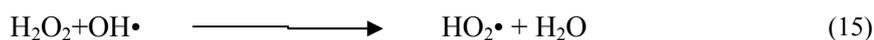
2.2.4 Effect of the presence of H₂O₂

Hydrogen peroxide (H₂O₂) plays two important roles in the photocatalytic degradation of MTBE. It increases the concentration of hydroxyl radicals in the reaction mixture and absorbs some of the UV light; hence, it decreases the light intensity within the solution (Andreozzi *et al.* 2000). Accordingly the concentration of H₂O₂ should be optimized during the degradation of MTBE. The consumption of H₂O₂ usually leads to a decrease in the concentration of MTBE. This

indicates the role of H_2O_2 in forming the hydroxyl radicals when it is radiated with UV light. These hydroxyl radicals will oxidize the organic molecules available in the reactor (Zang and Farnood 2005a). Due to the absorption of UV light by H_2O_2 , the O-O bond is ruptured, leading to the production of activated $\bullet\text{OH}$ and atomic oxygen. An increase in the concentration of H_2O_2 will increase the amount of energy absorbed, as a result more $\bullet\text{OH}$ radicals will be produced. This will in turn lead to a rise in the oxidative destruction of MTBE. The following reactions show the role of H_2O_2 .



However, if the MTBE solution contains excessive amounts of H_2O_2 , then the hydrogen peroxide itself becomes a significant competitor for $\bullet\text{OH}$ (Cater *et al.* 2000). Accordingly, less reactive $\text{HO}_2\bullet$ species will be formed (Pérez *et al.* 2002, Safari *et al.* 2013) as can be seen from the following equation



2.2.5 Effect of the catalyst concentration

The amount of the catalyst affects both the rate of the reaction as well as its mechanism. As a result the amount of the catalyst has to be optimized (Lu and Chiang 2009). It has been reported that the photocatalytic efficiency increases linearly with an increase in the catalyst loading to a certain limit. However, beyond that limit, the photocatalytic efficiency decreases. This has been attributed to the surface of the catalyst and the light absorbed which are considered to be the limiting factors in case of low amount of catalyst. However, when a large amount of the catalyst is used, the reaction mixture becomes turbid and it will reduce the penetration of UV light into the solution (Andreozzi *et al.* 2000, Dijkstra *et al.* 2001). Moreover, it is difficult to maintain the homogeneity of slurry solution as the catalyst start settling at the bottom of the reactor. The variation in the degree of settling may also influence the consistency of the total amount of light absorbed, the scattering of the incident light by the catalyst particles and the sampling process (Lu and Chiang 2009, Rabindranathan *et al.* 2003), consequently, the photocatalytic efficiency will decrease. Therefore, it is obvious that a higher dose of a catalyst will enhance the aggregation of the particles, which will in turn reduce the intensity of the UV irradiation. Several researchers have reported an optimum amount of the catalyst loading under different experimental conditions (Xu *et al.* 2004, Hu *et al.* 2008). In presence of insufficient amount of the catalyst, the produced $\bullet\text{OH}$ radicals will not be effective in completing the oxidation process. However, excessive amounts of the catalyst slurries adversely affect the photoreaction due to the scattering of light which reduces the UV permeation in the reactor system (Chan *et al.* 2009). Barreto *et al.* (1995) have also reported the reduction of light transmission at a high TiO_2 loading and a limited catalyst surface when less TiO_2 is used.

2.2.6 Effect of the presence of organics and inorganics

The photo-degradation of MTBE is greatly affected by the presence of dissolved ions because of the competitive behavior of these ions to the catalyst. The dissolved ions may be adsorbed on

the surface of the catalyst thus they will deactivate the active sites and they may also behave as a scavenger for the hydroxyl radicals (Lim and Lynch 2011b, Liao *et al.* 2001). Inhibition in photocatalytic oxidation of MTBE was also observed in case of comparative study between actual groundwater sample and synthetic samples in distilled water by Sahle-Demessie *et al.* (2002). The inhibition in groundwater samples was attributed to the presence of dissolved ions. Similar inhibitions in case of an actual gasoline contaminated water sample and distilled water samples have been reported by Eslami *et al.* (2008). These studies have suggested that the observed inhibition in the photocatalytic degradation of MTBE is due to the presence of traces of hydrocarbons in the contaminated water. The advantage of having iron up to a certain limit during the photocatalytic oxidation of organic contaminants has also been reported (Hua *et al.* 1995). Within the suggested concentration limit, iron (III) (Fe^{3+}) reduces the electron hole recombination, thereby increasing the rate of the hydroxyl radical ($\bullet\text{OH}$) generation. Fe^{2+} and Fe^{3+} have been reported to have similar effect on the photocatalytic oxidation of organic contaminants. This has been attributed to the equilibrium state that will be established between Fe^{2+} and Fe^{3+} in an acidic aqueous solution in the presence of dissolved oxygen (Xin *et al.* 2007, Vamathevan *et al.* 2001). Lim and Lynch (2011b) have reported that the removal efficiency of MTBE has decreased in presence of dissolved ions like chloride ion.

Klauson *et al.* (2005) have reported that a better degradation efficiency of MTBE can be obtained in presence of a certain concentration of Fe^{3+} (Vamathevan *et al.* 2001). On increasing the concentration Fe^{3+} , as light decrease in MTBE removal efficiency has been noted. This is because Fe^{3+} ions, could be adsorbed onto the TiO_2 surface and scavenge the photo-generated electrons to form Fe^{2+} ions (Eq. (16)), which will compete for photo-generated holes (Equation 17) resulting in “short-circuit” phenomenon and reducing $\bullet\text{OH}$ radical formation, however, Butler and Davis during their study (1993) did not detect Fe^{2+} ions in their reactor. The Fe^{3+} ion can also deposit on the catalyst and precipitate out of the bulk solution as $\text{Fe}(\text{OH})_3$ which will probably act to decrease the rate of the photocatalytic oxidation by reflecting UV illumination through increased solution opacity.



2.3 Photocatalysts in photodegradation of MTBE

Fujishima and Honda (1972) have introduced TiO_2 as a catalyst for the electrochemical splitting of water. Many researchers have directed their research interests to semiconducting oxides which have been applied in both photochemistry and photophysics. One of the most important aspects of photocatalysis is to consider the relation between the redox potential required for the evolution of H_2 , O_2 , (OH^\bullet), (H_2O_2) and super oxides (O_2^\bullet) and the band gap of the semiconductor (Eslami *et al.* 2008). This redox potential should be within the band gap of the selected semiconductor photocatalyst. Since the photocatalytic reactions take place in water saturated with air, the employed catalyst must also be stable in such conditions.

TiO_2 and ZnO are relatively inexpensive, non-toxic, chemically stable and insoluble in water. These two oxides have similar band gaps of 3.2 eV and considered to be the most preferred semiconductor photocatalysts for the degradation of toxic and hardly degradable chemicals (Shinde *et al.* 2011). ZnO is preferred sometimes over TiO_2 due to its higher quantum efficiency

and photoactivity in sunlight (Fujishima *et al.* 2000) however; it undergoes photo-corrosion in acidic medium. Both oxides, when irradiated with UV light, show high efficient photocatalytic activities and can generate highly oxidizing and reducing electrons and holes (Wu *et al.* 2011). If, for instance, TiO₂ is irradiated with UV, then electrons from the valence band will be excited to the conduction band leading to the creation of highly oxidative holes on the valence band and the formation of $\cdot\text{OH}$ radicals. Organic species are degraded on the surface of the photocatalyst as well as by the radicals that are generated in the solution (Miyachi *et al.* 2002). ZnO and TiO₂ both have wide band gaps and the energy associated with the visible light will not be sufficient to efficiently excite the electrons. To overcome this problem, various techniques have been studied in order to enhance the photocatalytic activities of these two oxides (Song *et al.* 2007). These techniques include surface modification (Ho and Yu 2006), semiconductor coupling (Anpo and Takeuchi 2006), band gap modification by creating oxygen vacancies and oxygen sub-stoichiometry by non-metal including co-doping of non-metal and metal doping (Rehman *et al.* 2009, Hariharan 2006). The parameters that could affect the oxidation of the contaminant include: the concentration of the catalyst, the wavelength of the light employed and its intensity. In addition, the presence of H₂O₂, the pH of the solution and its matrix will also affect the photocatalytic process. In aqueous slurry, several possible reactions could transpire on the TiO₂ surface being illuminated by UV as shown below:

The generally accepted mechanism for a heterogeneous photocatalysis process using ZnO as a catalyst is very similar to that of TiO₂. It includes the redox reactions of adsorbed water, hydroxyl anions and oxygen molecules or other substances. Upon irradiation, valence band electrons (e^-) are promoted to the conduction band, leaving a hole (h^+) behind. These electron-hole pair can either recombine or interact separately with other molecules (Kuburovic *et al.* 2007).

2.3.1 Doping of the photocatalyst

Doping of photocatalysts/semiconducting metal oxides usually creates impurity levels in the band gap of the semiconductor. When these newly created levels are close to the band edges they might overlap with the band states causing narrowing of the band gap. However, they may also act as recombination centers for the photogenerated electron/hole pairs if present deep in the band gap. Photoactivity of any catalyst may be determined by the competition between the rate of promotion of the charge carrier to the surface and to the recombination rate. If the rate of recombination is too high then these charge carriers will not be involved in a redox reaction at the surface of the catalyst. Thus, optimum level of doping is always required for a desired activity (Rehman *et al.* 2009). The two catalysts TiO₂ and ZnO both have their own inherent drawbacks. For instance, TiO₂ is mainly used as a catalyst when is being irradiated with UV light. In case of being used in solar spectrum, only 4-5% of the spectrum could be utilized. However, in case of ZnO, which gets corroded in UV, a larger portion of the solar spectrum can be used. To solve this problem, doping of a semiconducting metal oxide or mixed metals oxides (Zhu *et al.* 2011, Wang *et al.* 2011) with a suitable element can reduce the band gap of the catalyst. This will result in an imbalance in the charge carriers which are either electrons or holes that have enough energy to create new energy levels. These levels can be either donor or acceptor levels inside the band gaps depending on the type of the dopant. When subjected to electromagnetic radiation, the electrons of the donor or acceptor level can be excited and displaced to the conduction band from an energetic level inside the band gap with less energy required for electron excitation. Thus, paving the way to use light of greater wavelength, like the solar spectrum, to be used in the photocatalytic reactions (Rehman *et al.* 2009).

2.3.2 Non-metallic doping

Both TiO₂ and ZnO have been stimulated by non-metallic doping to investigate their photocatalytic properties in visible light. Doping of semiconductors by non metal atoms generates a new band between the valence band and the conduction band, however, this new band will be closer to the valence band of the metal oxide (Rehman *et al.* 2009, Jo and Yang 2010). Modifying TiO₂ by doping it with an anion has resulted in introducing localized states in the band gap, consequently, the absorption of the visible light has increased (Chen and Burda 2008). The intrinsic defects including those associated with oxygen vacancies have been found to enhance the photochemical activity of TiO₂ in visible region (Serpone 2006). Gopal *et al.* (2008) have proposed that doping the interstitial positions of TiO₂ with boron atoms favors the formation of oxygen with two excess electrons, which makes Ti⁴⁺ ions to be reduced to Ti³⁺. Doping TiO₂ with boron (B-TiO₂) will lead to a red shift in its optical absorption because of the formation of oxygen vacancies. Low levels of boron doping have been found to result in a significant absorption of visible light and a better photo-activity degradation of MTBE compared to the normal TiO₂ (In *et al.* 2007). The photochemical oxidation of MTBE using the artificial visible light has been found to be more efficient in an acidic medium than in an alkaline or neutral media. This trend has been observed in case of all S (Sulfur)-containing catalysts (Jo and Yang 2010). The photocatalytic oxidation efficiency of MTBE, in case of S-doped catalysts, has been reported to be two fold higher than that of the Degussa P25 (Zhong *et al.* 2012). In regards B-TiO₂, the dependence of the efficiency of the photocatalytic oxidation of MTBE on the pH was similar to that of S-TiO₂ (Klauson *et al.* 2005). Wu *et al.* (2011) have noted a little red shift in the band gap energy of B-TiO₂ (2.98 eV). The overall performance of S-TiO₂ was found to be slightly better than that of B-TiO₂.

2.3.3 Metallic doping

Several studies have been conducted to improve the photocatalytic efficiency of TiO₂ by doping it with certain elements (Colón *et al.* 2006, Bellardita *et al.* 2007, Prei *et al.* 2005). Similarly ZnO has also been doped with metals like Co, Cu, Mn and Ni (Fitzgerald *et al.* 2005, Naeem *et al.* 2008, Shinde *et al.* 2006, Kanade *et al.* 2007). Doping of the semiconducting photocatalyst induces a defect state and decreases the band gap of the catalyst. However, in case of Mn, a higher doping level causes an increase in the band gap of ZnO due to Burstein-Moss effect (Wang *et al.* 2006, Srinivasana *et al.*, 2008). On increasing the Co content in ZnO, the absorption of visible light and the surface oxygen vacancies both have been found to increase (Xiao *et al.* 2007). ZnO doped with Co has better crystallinity and narrower band gap (Ekambaram *et al.* 2007), thus it offers better visible light activity than ZnO doped with either Mn or Ni. TiO₂ doped with Fe generates impurity states within its band gap and induces visible light absorption, however, at higher doping levels, Fe ions serve as recombination centers leading to lower visible light activity (Hung *et al.* 2007). One of the goals of the metal doping of the semiconductor catalyst was to reduce the electron-hole recombination by reacting the metal with the photo-generated electrons, consequently the metal will be reduced. However, the resulting reduced species were found to be oxidized by the holes, thus, inhibiting the formation of radicals (Ou and Lo 2007). Most of the studies have been centered on the noble metals like Pt, Pd, Au etc (Callén *et al.* 2007, Orlov *et al.* 2007, Arana *et al.* 2008, Sun *et al.* 2008, Zhong *et al.* 2012). Due to an appropriate Fermi level position, metallic Pt particles have been photodeposited on TiO₂ surface to control the recombination process by scavenging photogenerated electrons. Pt doping also cause introduction of intra-gap impurity states which favor the absorption in visible region by valence electrons. These states improve the

photoactivity in both UV and visible light for TiO₂ doped with Pt. The catalyst's surface area and the alteration of surface hydroxyl group distribution may be among the negative effects of doping process. Arana *et al.* (2008) have studied the degradation of MTBE in presence of TiO₂ doped with Cu and reported that these catalysts have better efficiency compared with the normal TiO₂. They have suggested that doping of TiO₂ with Cu remarkably improves the photocatalytic activity and minimizes the deactivation process. The reaction of Cu²⁺ ions deposited on the catalyst surface with the photo-generated electrons seems to be the key process to photoactivity improvement. Recently, Orlov *et al.* (2007) have reported that modification of TiO₂ with gold nanoparticle can increase the photocatalytic activity in case of the degradation of both 4-chlorophenol and MTBE.

It has been reported that the gold nanoparticles in contact with TiO₂ will act as sinks for the photo-generated electrons, thus reducing the e⁻/h⁺ recombination rate and enhancing the photocatalytic rate. This mechanism explains the activity observed in case of the photo-degradation of MTBE at TiO₂ doped with high gold loadings compared to the activity of the pure TiO₂ (Salhe-Demessie *et al.* 2002). Orlov *et al.* (2007) have indicated that the rate decrease observed at higher gold loadings is attributed to the elimination of the hole-trapping of OH groups at the TiO₂ surface. In case of very high metal loadings shadowing of the TiO₂ become prominent by the large number of gold particles which reduce the TiO₂ surface area available for the both the MTBE adsorption and the photo-excitation process, as a result, the photo-catalytic activity will be suppressed.

The most interesting results have been obtained by using very small gold nanoparticles (< 3 nm) (Arana *et al.* 2008). These nanoparticles are expected to demonstrate semiconducting properties rather than metallic properties. Therefore, this may invoke a mechanism based on semiconductor-semiconductor contact in which photoelectrons are injected from gold nanoparticles into the TiO₂ conduction bands. As a result, separated electrons and holes will be created which will then undergo charge transfer reactions with the adsorbates. However, very little is known about the charge-transfer dynamics of the electrons and the holes within the molecules adsorbed at the surface of the semiconductor. It is obvious that this research area is promising and needs more efforts.

Arana *et al.* (2008) have reported a complete degradation of MTBE by the visible-light photocatalytic using the composite TiO₂/Al₂O₃ doped with gold as a photocatalyst. However, Gómez *et al.* (2012) have used TiO₂/Al₂O₃ doped with Pt as a catalyst for the degradation of *p*-cresol. Few dyes have also been degraded using the concept of doped catalysts in fenton based processes (Panda *et al.* 2011, Liu *et al.* 2012).

3. Future perspective in the field of MTBE photocatalysis

The objective of any photocatalytic degradation process is to completely mineralize the toxic contaminants or transform them into non-toxic or biodegradable molecules with minimum capital investment. The catalyst should be non-toxic and able to utilize the sunlight as an energy source for the photo-excitation and generation of photo-excited electron-hole pairs. This could be achieved by carrying out further work in the catalyst doping research to find the most effective catalysts that can utilize the radiation of the sunlight. We also suggest the utilization of the combined treatment technologies. Photocatalytic degradation of toxic molecules undergoes a series of chemical reactions and their byproducts could lead to modulate the local environment of the photodegradation of a contaminant under investigation. Therefore, a good insight of in-situ changes during the photodegradation reactions is also required to have proper optimization. The

application of photocatalytic degradation of gaseous contaminants like MTBE is in an early stage of development and more dedicated research is required to elucidate its mechanism of action and application on industrial scale. Most of the studies have been carried out in batch and continuous reactors have revealed that these techniques could be effective only if the previous knowledge of aqueous phase experiment is applied. In view of the above mentioned facts, the development of a novel photocatalyst is required for the MTBE photocatalytic degradation.

4. Conclusions

This review summarizes the studies that have been made so far in the area of the photocatalytic degradation of MTBE in water using semiconducting metal oxides. Recently, the TiO₂ and ZnO have been found to be effective photocatalysts in MTBE remediation using artificial UV radiation. Recent developments have been made to apply TiO₂ and ZnO using the visible light instead of UV as an energy source in the photocatalytic process. It is obvious that a simple single semiconductor catalyst might not be effective to support the future needs to degrade and remove toxic molecules. However, a carefully doped catalyst that works in the visible light is considered as a promising area of research that might offer good opportunities in the remediation of wastewaters containing toxic chemicals. The applications of mixed oxide doped photocatalysts are in their initial stages of research studies and are being solely designed to use solar spectrum for their photocatalytic action. This strategy will offer a wide application range in the field of visible light photocatalysis for the degradation of complex molecules. It is also expected that optimization of the effective parameters will offer a better control of the photocatalytic reactions which will result in obtaining better efficiencies in the photocatalytic degradation of the contaminants.

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