Remediation and by-products of MTBE in groundwater by a photochemical process

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Abstract

MTBE has been used as an octane number enhancer in gasoline, and blended with gasoline to about 15% by volume. High concentrations of MTBE have been discovered in the groundwater at a number of petrol stations in Iran. MTBE exhibits very high mobility in groundwater. Due to its solubility, groundwater contaminated with MTBE poses many problems for remediation. The properties of MTBE, including water solubility, vapour pressure, soil adsorption coefficient, retardation factor and Henry's law constant affect the selection and design of remediation technologies. Although MTBE is difficult to treat economically with conventional techniques, it readily degraded photocatalytically. The degradation of MTBE at high concentration (10,000 μg/l) was investigated in batch nanocrystalline TiO_2 slurries. The optimum loading of TiO_2 was found experimentally. In this experiment MTBE degradation proceeded with a pseudo first order reaction. The primary by-products have been identified. Mass balance calculation has shown that MTBE is completely mineralised. A reaction pathway is proposed.

Keywords: photocatalysis, advanced oxidation process, nanocrystalline titanium dioxide, hydroxyl radical, tert-butyl format, tert-butyl alcohol, MTBE.

1 Introduction

MTBE has been widely used as an octane enhancer in gasoline in Iran since 2000. The gasoline has been stored in aboveground and underground storage tanks at refineries and service stations, and has been transferred via pipeline, barge, rail and truck. As a result of leaks and splits, MTBE has been detected in groundwater supplies more than 2 μg/l [1]. The physical properties of MTBE

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including its solubility in water and volatility from the free product phase cause a big mobility in the environment. Due to MTBE's physical properties, it has been difficult to treat contaminated groundwater with conventional methods. MTBE is approximately 10 times less volatile than benzene making air stripping less efficient. Also MTBE does not adsorb well to granular activated carbon (GAC) compared to benzene, GAC is about five times less effective at removing MTBE [2,3]. Two bio recalcitrant functional groups in MTBE structure, ether link and branched, make it resistant to biodegradation. Since bioremediation strategies are often used to degrade petroleum hydrocarbons, it would be advantageous to either enhance the biodegradability of MTBE or to find a destruction process, which could be combining well with bioremediation.

Advanced oxidation processes (AOPs), which involve the generation of the hydroxyl radical ($^{\cdot}OH$) to degrade a chemical, have recently emerged as an important class of technologies for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water and soil. An advantage of AOPs over activated carbon and air stripping is that, if effective, the contaminant is degraded into other compounds, removing the contaminant from the environment, not just from the aqueous phase.

In this research, photocatalytic degradation of MTBE in nanocrystalline TiO_2 slurry was investigated by (i) quantifying the kinetics of MTBE degradation, (ii) identifying the by-products formed, (iii) proposing a reaction scheme.

2 Materials and methods

MTBE (Merck), t-butyl format (TBF, Aldrich) were reagent grade. Nanocrystalline Titanium dioxide (TiO_2) was obtained from Degussa corp. (p25).

Photochemical experiments were carried out in a 700ml batch slurry photoreactor with a UV lamp immersed in the centre of photoreactor. Slurry was circulated with a pump through the reactor in a constant rate. A reaction run involved the addition of TiO_2 700 ml of deionised water and 10 µl of MTBE (10750 µg/l) to the reactor. TiO_2 particles were allowed to be settling down overnight in 4 ºC [4].

Reaction kinetics was followed using gas chromatography (GC). Compounds were extracted from the aqueous solution with a Lekmar ISC 200 purge and trap apparatus, with conditions as specified in EPA methods 8015, 5030. The trapped compounds were auto-injected into a Varian model 3400 gas chromatograph with flame ionisation detector (FID). CP.CIL5, 60 m, 0.75 i.d. capillary columns were used with the following temperature program; initial temperature 150 ºC, rate of increasing temperature 5 ºC/min, final temperature 200 ºC. Unknown reaction by-products were identified by Head-Space gas chromatography-mass spectrometry (HS/GC-MS). Chromatographic analysis was performed using a Varian model 1200 GC equipped with a Quadrupole mass spectrometer. Samples were introduced into the GC with HS system. Separation of the analytes was performed using a 60 m × 0.25 µm I.D. VF5 column with a film thickness of 0.25 µm. The column oven temperature was initially at 50 ºC Temperature increased at a rate of 5 ºC /min to 100ºC and then at a rate of 20ºC to final temperature 275°C. Mass spectra were scanned in the range of 32-450 m/e. identification of the individual compounds was made by comparing the resulting spectral pattern with those of the information service spectra library.

Soluble organic acids were analysed using a metrohm modular Ion chromatograph with a metrosep A SUPP 5-250 column and conductivity detector. The eluent for the process was a 1mmole/l solution of $NaHCO_3$ and 3.2 mmole/l solution of $Na_2 CO_3$ with a flow rate of 0.7 ml/min. Peak identification was performed by peak matching using 1 mg/l solution of acetic acid and formic acid.

3 Result and discussion

A series of experiment was carried out to find an optimum catalyst loading. By varying the amount of TiO_2 in the reaction from 0.01 g to 0.3 g. it was found that the optimum loading of catalyst was 0.05 g per 700 ml of solution (0.07 g/l). Above this amount increased turbidity of the solution reduced the light transmission through the solution. Below this amount, catalyst surface was limiting and photocatalytic efficiency decreased. Photocatalytic degradation of MTBE at this optimum loading is shown in Fig. 1. It was observed that more than 80% of MTBE was removed in the first 20 min of the reaction. Nearly complete removal of MTBE (>99.99%) was achieved after 120 min. A first order model according to Fig. 2 with the rate constant of 6.4×10^{-2} min^{-1} estimated the degradation rate constant. After 2 h MTBE was no longer detectable in the reaction solution.

By-products of photocatalytic degradation of MTBE were identified by HS/GC/MS. As shown in fig. 3, seven components exist in the chromatogram. By comparing the spectrum of each component (fig 4-8) with the standard spectrum of instrument service spectra library, five by products were identified.

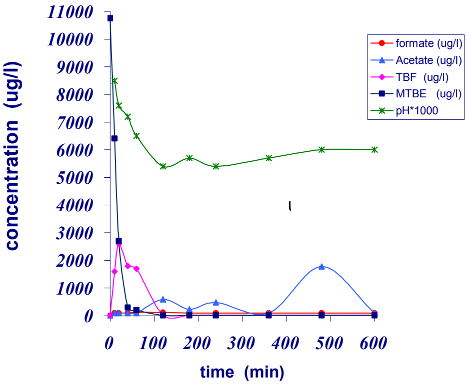

Figure 1: The variation with time of the concentration of MTBE and its by-products and the pH solution.

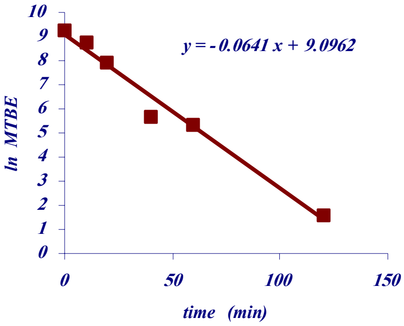

Figure 2: The photocatalytic reaction rate of MTBE.

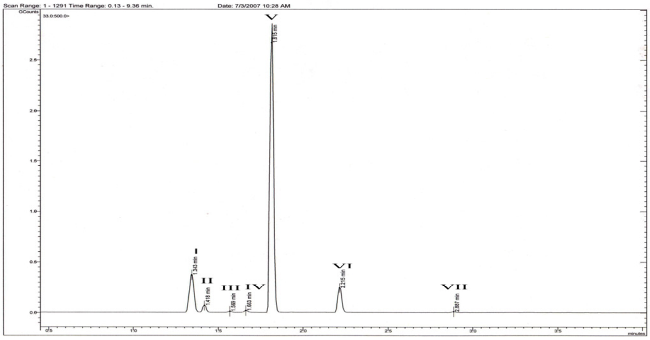

Figure 3: Chromatogram of reaction mixture; I) CO2, II) 2-methyl-1-propene, III) acetone, IV) TBA, V) MTBE, VI) TBF, VII) 2-methyl propanoic acid.

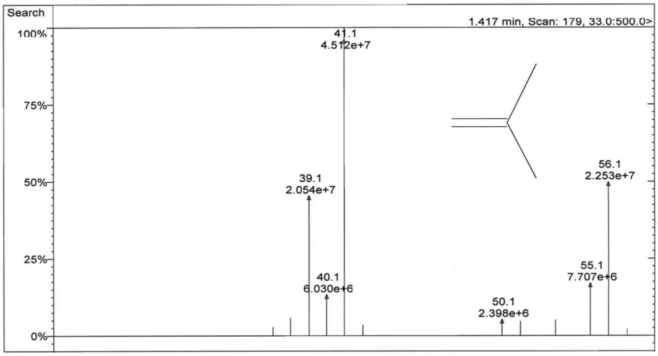

Figure 4: Mass spectrum of 2-methyl-1-propene.

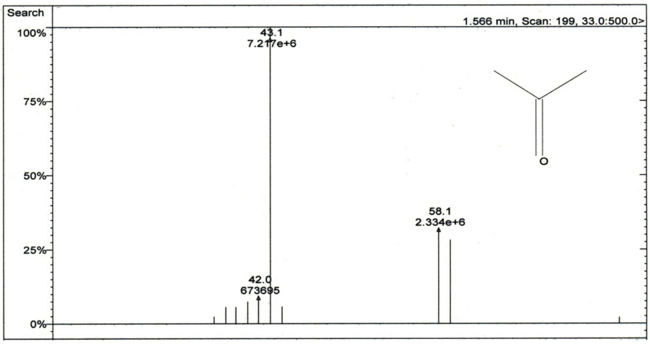

Figure 5: Mass spectrum of acetone.

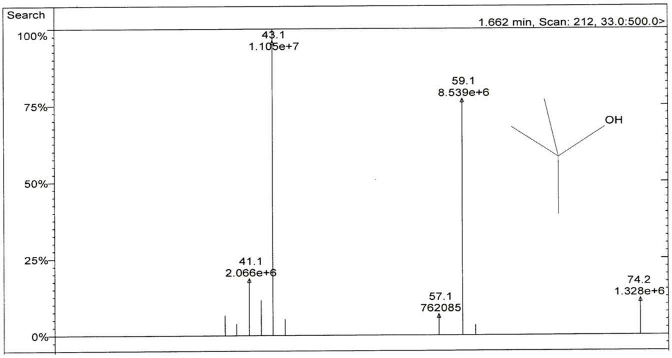

Figure 6: Mass spectrum of TBA.

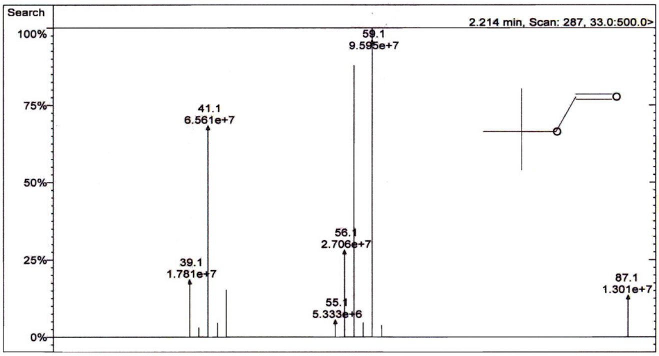

Figure 7: Mass spectrum of TBF.

Two peaks in 1.318, 1.815 min related to dissolved carbon dioxide and MTBE respectively. The major by-products were t-butyl format (TBF), t-butyl alcohol (TBA), and acetone. Two other by-products were 2-methyl-1-propene and isopropanoic acid. TBF is the first by-product of degradation with higher toxicity than MTBE. It appeared rapidly and reached to a maximum at 20 min. However TBF is also mineralised and after 3 h the concentration of TBF decreased to a trace level.

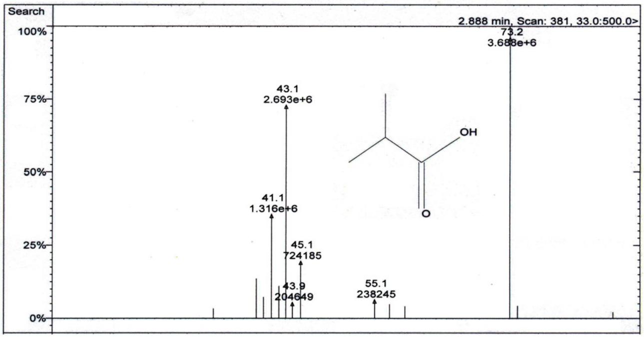

Figure 8: Mass spectrum of 2-methyl propanoic acid.

The decreasing of pH during the reaction suggested the presence of acidic compounds. Ion chromatography showed the presence of two organic acid acetic acid and formic acid were identified by retention time matching with external standards. The formation acidic product was consistent with pH changes. The initial pH of solution was 8.5 and gradually decreased. After 1 h of reaction the pH dropped to 6.5 due to formation of formic acid. Over the reminder of the degradation the pH slowly dropped to 5.4 because of appearance of acetic acid. However the pH reached to 6 after 8 h and no pH changes was detected in control reaction. At 10 h of reaction no organic products were detected. A mass balance on organic carbon was determined for the reaction solution at 10 h and approximately 99.9% of MTBE was mineralised to CO_2 and water. According to above information, a reaction scheme was proposed (Fig 9).

It is well accepted that the initial process for photocatalysis of organic compounds by semiconductors is the generation of electron-hole pairs in the TiO_2 particles [5,6].

$$Tio_2 \xrightarrow{hr} \bar{e} + h^+$$

TiO_2 is a semiconductor with a band gap of 3.2 eV; when excited by light of energy equal to or exceeding that value, electrons are promoted from the valance band to the conduction band, leaving positive holes in the valance bands. These electrons and holes are capable of reducing and oxidizing compounds at the TiO_2 surface. The hole is quickly converted to the hydroxyl radical ($^{\cdot}OH$) upon oxidation of surface adsorbed water. This radical is the major reactant responsible for the oxidation of organics. The first step in the destruction of MTBE is abstraction of an α-hydrogen by hydroxyl radical to form an organic radical. This radical reacts with dissolved oxygen in the reaction solution to convert a proxy radical as an unstable intermediate. The most important oxidation of ethers is conversion to esters. Therefore the unstable intermediate

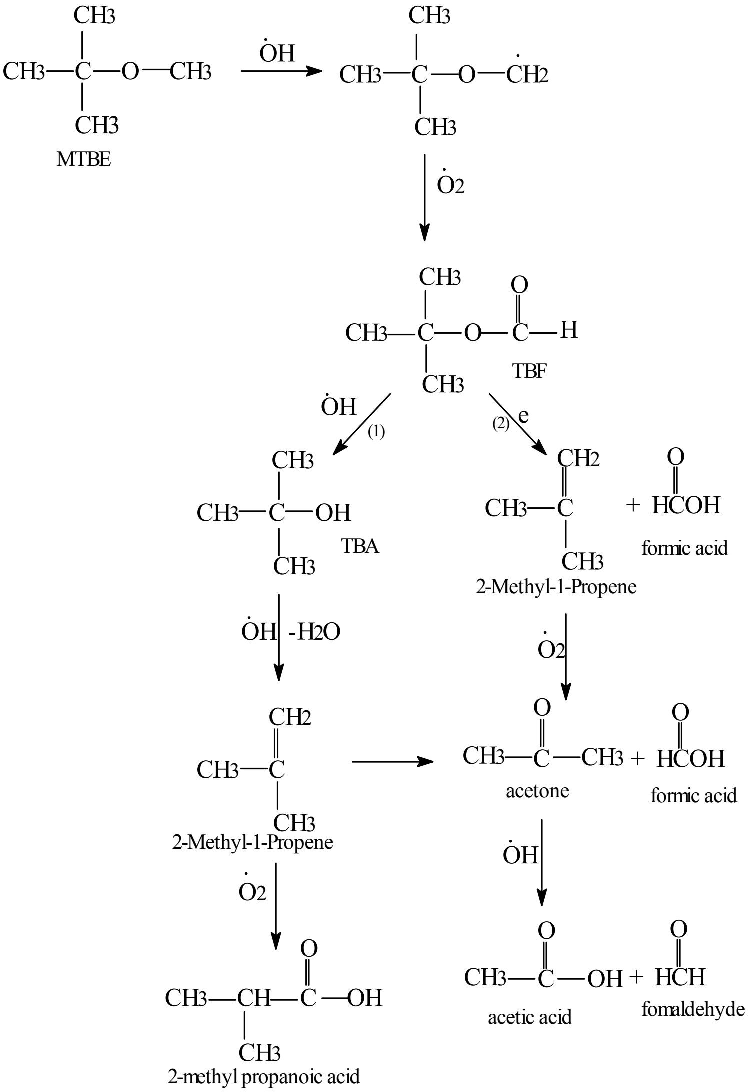

Figure 9: Proposed reaction pathway for photocatalytic destruction of MTBE.

rapidly was converted to TBF by heterolysis of the O-O band. Although hydroxyl radicals are strong oxidants in this reaction, other active species such as electron and super oxide anions can react with organic compounds. Due to this fact, TBF degraded in two ways. Esters are subject to both acid and base catalysed hydrolysis to produce carboxylic acid and alcohol. Therefore in the first way, TBF would produce TBA and formic acid. Formic acid is photocatalytically oxidized by oxygen to CO_2 and water on the surface of TiO_2.

In the second way, TBF reduced with electron to form 2-methyl-1-propene and formic acid. Under acidic condition and in the presence of hydroxyl radicals, TBA was dehydrated to alkenes, which easily oxidized and produced acetone and formic acid. Then acetic acid, like other by-product, was photocatalytically degraded to acetic acid and formaldehyde. When the time of reaction proceeded, all organics was degraded to CO_2 and water.

The degradation of TBF was a first order reaction with a rate faster than MTBE. The stoichiometry of reaction confirmed this fact, because the concentration of TBF at 10 min in the reaction solution was not equal to the concentration of destruction MTBE. Also TBF disappeared after 3 h.

Investigation of the concentration of acetic acid is useful to predict the rate of degradation of TBA. As shown in Fig.1, there are a maximum at the curve for acetic acid at 6 h that relate to degradation of TBA to acetone and then to acetic acid. It means the rate of degradation of TBA is slower than MTBE and TBF and this step was the limiting step in the photocatalytic process.

4 Conclusion

It has been found that MTBE is readily and rapidly degraded photocatalytically by nanocrystalline TiO_2 under batch slurry conditions with first order rate constant of 6.4×10^{-2} min^{-1}. The primary intermediates of this reaction have been identified to be t-butyl format, t-butyl alcohol and acetone, which are easily degraded photocatalytically. TBF is degraded faster and TBA slower than MTBE. A reaction scheme has been proposed by considering the action of active species generated when TiO_2 excited by UV radiation. MTBE completely degraded to biodegradable products. Upon which to consider using photocatalysis reaction as a method to convert a non-biodegradable compound such as MTBE and it's the first by-product, TBF, to products such as TBA and acetone which can be treated biologically [7].

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