

Removal of High Concentration of Methyl *tert*-Butyl ether in Synthetic Wastewater by Employing High Frequency Ultrasound Waves

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In this study, the proposed ultrasound technique at high frequency of 2.4 MHz for removal of methyl *tert*-butyl ether has been investigated. The ultrasonic removal mechanism of methyl *tert*-butyl ether in aqueous solution is complex because of the competition between hydroxyl radical attack, pyrolysis and hydrolysis reactions. An investigation of removal of methyl *tert*-butyl ether using sonolysis has performed here with a kinetics models study. Chemical destruction by sonolysis is rationalized using hydroxyl radical chemistry, in which methyl *tert*-butyl ether transfers into the cavitating bubbles and decomposed. The kinetics study indicates that the removal of methyl *tert*-butyl ether at different initial concentration namely (2000, 1000 and 500 ppm) is the best fitted with first order kinetic model with a reaction rate constant of 0.034 min⁻¹. The removal of methyl *tert*-butyl ether investigated at different reactant volumes inside the ultrasound reactor found that the lower volume of reactant is preferable on higher volume. The results of removal of methyl *tert*-butyl ether show that more than 85 % has obtained, at only 50 min of exposing to ultrasound irradiation even with high initial concentrations.

Keywords: Ultrasound, Degradation, Methyl *tert*-butyl ether, Wastewater treatment.

INTRODUCTION

Methyl *t*-butyl ether (MTBE) has been used as a fuel oxygenate worldwide due to its good properties as octane enhancers and helping in preventing engine knocking. Methyl *tert*-butyl ether was firstly used in the USA since 1979 to replace tetra-ethyl lead which was known to its serious effect on human health resulted from air borne pollution. Since that date and over decades of years MTBE has been used as an octane enhancer and fuel oxygenation additive in gasoline to provide a cleaner burning fuel. Despite the several technological benets of using MTBE [1-5], but recently there is warning sign of having a serious environmental problem with regard to water quality [6-10]. Methyl *t*-butyl ether has become one of the most common contaminants in shallow ground waters and drinking water, mainly as a consequence of petroleum leakage from underground tanks [11]. Methyl *t*-butyl ether according to USEPA classification is considered a risk chemical compound on human health with a high potential of carcinogen [11]. The environmental fate of MTBE depends closely on its excellent solubility in water and its very low soil sorption coefficient [9,12,13]. This means that MTBE is only retained by soil layers in a weak concentration and is rapidly transported

to ground waters. Another reason for MTBE's persistence to be more mobile in groundwater systems than other gasoline components If groundwater is moving gradually downward, the chemicals dissolved in it will also gradually move downward, because MTBE may migrate over greater distances, the magnitude of dive may be greater [6,11].

Several studies have reviewed the different technologies used to the treatment or removal of MTBE from underground water. These technologies may include both *ex situ* technologies (pump and treat) and *in situ* technologies (airsparging, bioremediation, chemical oxidation, phytoremediation and monitored natural attenuation) [14-17]. Methyl *tert*-butyl ether can be biologically degraded under both aerobic and anaerobic conditions and both *in situ* and *ex situ*, however, removal of MTBE can be incomplete, resulting in the formation of *tert*-butyl alcohol. Generally, aerobic conditions have been shown to be far more effective in the complete biological treatment and removal of these compounds but still expensive [18-21].

The use of ultrasound technology to remove or decomposition of MTBE is still under investigation [22]. Matouq *et al.* [1-5] have employed the use of high frequency of ultrasound wave for the removing of different pollutants from wastewater, the use of such process to decompose of MTBE under high

frequency is a new technique. Kim *et al.* [23] have studied the removal of MTBE and other oxygenated fuel, by employing the ultrasound at low frequency in the presence of saturated oxygen with removal mechanisms proposed for each gasoline oxygenate. They reported that the common degradation pathways involve abstraction of α -hydrogen atoms by hydroxyl radicals generated during ultrasound cavitation at low temperature. The ultrasound at either low or high frequency will be a new area for researchers to investigate since the process of MTBE removal by conventional remediation technologies, is costly and ineffective. Therefore, much attention will be focused on other methods such as advanced oxidation processes (AOPs) [24,25] and ultrasound techniques for its degradation.

There are less studies dealing with the degradation of MTBE at high frequency of ultrasound more than 1 MHz [23] that directly applied to a solution of MTBE and water. In this study, the process of using such ultrasound techniques will be introduced here to investigate the ability of ultrasound wave to remove MTBE at high concentration. The use of ultrasound with high frequency alone in the removal of MTBE from is a new topic, here both the removal and the kinetics of MTBE removal will be investigated using a simulated wastewater.

EXPERIMENTAL

Methyl *tert*-butyl ether obtained with 99 % purity from Saudi Basic Industries Corporation, (SABIC) (www.sabic.com) Table-1 enlisted these properties. The experimental results analysis performed using gas chromatography PYE-UNICOM 4900-FID, with a stainless steel column 2 m long and 2 mm diameter, filled with chromosorb C03 as packing material. The detection temperature was set at 300 °C and the injection set 250 °C while the oven was set at 200 °C. Calibration of a gas chromatography device was done carefully with a solution with a known amount of MTBE. The results are then plotted generating a calibration curve as a reference for future results. After that, different concentration samples of MTBE were prepared.

TABLE-1
MTBE PROPERTIES BY SABIC

| Parameter | Unit | Quantity |
|----------------------------|------|----------|
| Purity | wt % | 98 min |
| C4-hydrocarbons | wt % | 0.5 max |
| C5-hydrocarbons | wt % | 1 max |
| Methanol | wt % | 0.7 max |
| <i>tert</i> -Butyl alcohol | wt % | 0.6 max |
| Di-isobutene | wt % | 0.6 max |
| Water | ppm | 500 max |

Sources: <http://www.sabic.com/corporate/en/productsandservices/chemicals/mtbe>

In 1 L, volumetric flask a measured amount of pure MTBE is added to in order to obtain the target concentration needed. The required concentrations in this study was adjusted at 2000, 1000 and 500 ppm by volume (v/v %). These concentrations are corresponding to 1480.8, 740.4 and 370.2 ppm by mass respectively. The usual concentration of MTBE in water is actually less than of those specified above concentrations, in order to investigate the ability of ultrasound to remove MTBE

at high concentration with very short period. Ray *et al.* [26] investigated the reduction of MTBE in groundwater with an initial concentration of 1300 ($\mu\text{g/L}$) ppm to decompose into final concentration of 20 ppm or less, this value is specified by USEPA [27].

A 50 mL sample with certain concentration of MTBE placed in a cylindrical tube reactor attached with ultrasound cell at the bottom. The solution irradiated with ultrasound for a fixed period around 50 min. Each 10 min a sample with a syringe (0.5 mL), was taken from the solution and directly injected to the gas chromatography for analysis. To prevent any MTBE escape from the solution to the atmosphere a watch glass fitted at the top of the cylindrical reactor as shown in Fig. 1.

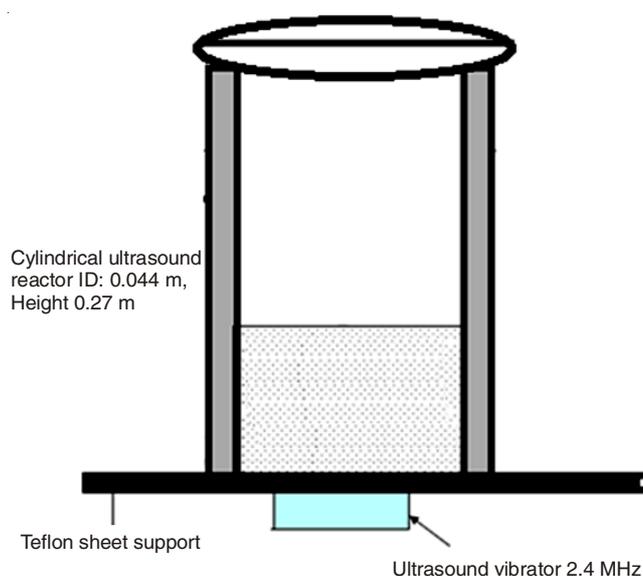


Fig. 1. Experimental setup for cylindrical ultrasound reactor

The experimental apparatus demonstrated in Fig. 1, which consists of a cylindrical vessel with 44 mm inside diameter and 270 mm height. Watch glass cover attached to the cylindrical ultrasound reactor. Electrical source with variable voltage supply ranges from 0 to 40 volts was attached to the apparatus. The electrical supply can also be adjusted to control the electrical current source from 0 to 600 mA. All experiments conducted at 24 volts and 500 mA, according to the specified condition by ultrasound device wave generator manufacture. Ultrasonic vibrator comprised of 20 mm diameter transducer, which contains piezoceramics (sandwich) with titanium end masses leading the face from which the ultrasonic emitted. It has a frequency of 2.4 MHz and electric input power 9.5 Watt and it supplied by Honda electronics Co. Ltd., of Japan, type HM-2412.

RESULTS AND DISCUSSION

Fig. 2 shows the concentration profile for MTBE removal at 2.4 MHz ultrasound waves and 50 mL volume of MTBE as solution. It shows that the profiles are decreasing with the increasing of time for three different concentrations, 2000, 1500, 500 ppm. This means that the MTBE in the solution is removing with time due to the effect of irradiation by ultrasound.

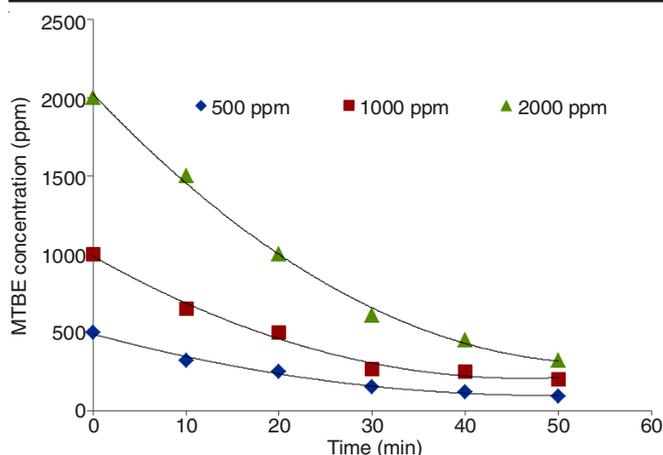


Fig. 2. Concentration profiles for MTBE removal at 2.4 MHz ultrasound waves and 50mL volume of MTBE

The final solution tested by gas chromatography didn't show any sign of other compounds which means MTBE should have either been broken down into gaseous molecules or degraded into water or both. Literature suggests that it is possible for MTBE to be oxidized into CO_2 and water [28]. The results of MTBE removal shown in Fig. 2, indicates that when the MTBE concentration at higher the removal is almost the same for MTBE at lower concentration. For example when the initial concentration of MTBE is 2000 ppm and after 50 min the concentration reaches 318 ppm with more than 84 % removal. However, when the initial concentration of MTBE of 500 ppm the final concentration reaches 90 ppm and after 50 min with a removal percentage of 81 %. This percentage of removal in such short time is acceptable to reach the standard regulation for MTBE in groundwater according to USEPA, bearing in mind that in actual case the initial concentration of MTBE does not reach the investigated concentration in this study.

The effect of changing the liquid volumes inside the ultrasound reactor on removal of MTBE is shown in Fig. 3 at three different volumes 50, 40 and 30 mL. It is clear from the figure that the relation between the removal rate and the liquid volume inside the ultrasound reactor is an inverse function. When the liquid volume (solution level) was 50 mL (for the different MTBE concentrations 2000, 1000 and 500 ppm) the removal of MTBE reaches more than 80 % for all MTBE concentration at 50 mL volume, compared to more than 95 % for all MTBE concentrations, at 30 mL liquid volume and after 50 min. Therefore, the removal process of MTBE under ultrasound effect is more preferable toward a low volume inside the ultrasound reactor.

Chemical kinetic removal models: The suitable chemical removal model will be investigated here in which the process will be tested for different kinetics order. The obtained results fitted with different kinetics models namely first and second order. The following simulation will show the best results fitting for the obtained experimental results.

First order kinetics model: In this model the experimental data were fitted according to simple first order rate:

$$C(t) = C_0 e^{-k_1 t} \quad (1)$$

To obtain a liner fitting eqn. 1 rearranged to:

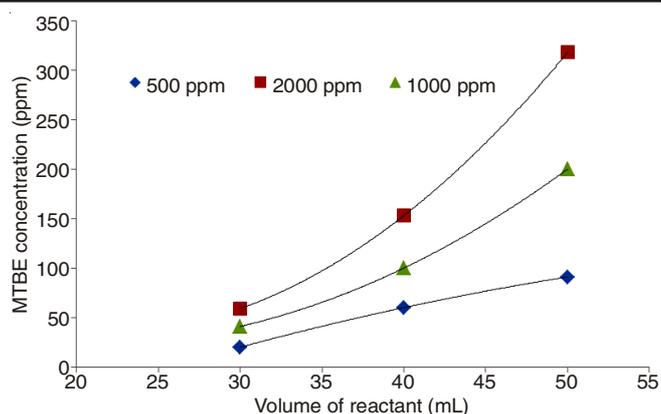


Fig. 3. Effect of changing MTBE volume inside reactor after 50 min of irradiation at different initial concentration

$$\ln C(t) = \ln C_0 - k_1 t \quad (2)$$

where k (min^{-1}) is the first order rate constant can be estimated from the slope by plotting $\ln C(t)$ versus time (t) as shown in Fig. 4. The figure shows a consistency between the plotted experimental data and the proposed model kinetics, where the correlation factor (R^2) is higher than 98 %.

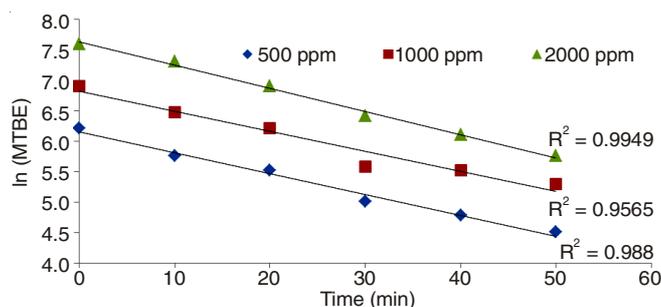


Fig. 4. First order model results fitting at 50 mL liquid volume and constant frequency wavelength of 2.4 MHz at different concentrations of MTBE

Second order kinetics model: The proposal of having a second order kinetic model will be examined here. The change in the removal concentration can be fitted by using the second order kinetic equation model described by eqn. 3:

$$-r = \frac{dC}{dt} = -kC^2 \quad (3)$$

For linear fitting the equation can be rearranged as:

$$\frac{1}{C} = kt + \frac{1}{C_0} \quad (4)$$

where k is the second order removal rate constant and it can be estimated from the slope after plotting $1/C$ vs. t . as demonstrated in Fig. 5.

The experimental result shows that the fitted $1/C$ versus t , for different initial concentrations of MTBE. Although the fitting looks in a good consistency, still the R^2 , for the first order is higher for all experimental data at different initial concentrations. This means in this experimental work and at these conditions the best kinetics model for the removal of MTBE at 2.41 MHz ultrasound is best fitted with a first order kinetics. The average reaction rate constant is estimated to be 0.035 min^{-1} according to results obtained from Fig. 4, at first

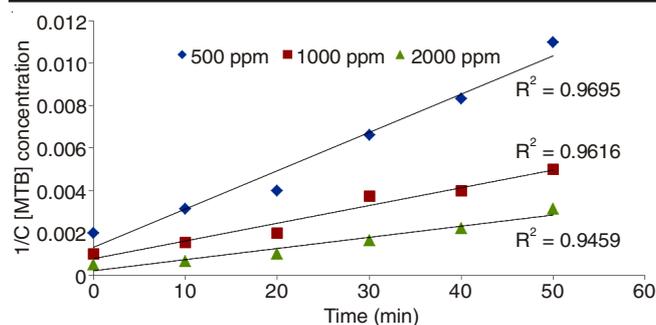


Fig. 5. Second order model data fitting at 50 mL liquid volume and constant frequency wave length of 2.4 MHz at different concentrations of MTBE

order. Table-2 summaries the reaction rate constant at different initial concentrations of MTBE.

| Initial concentration of MTBE (ppm) | k (min ⁻¹) |
|-------------------------------------|------------------------|
| 2000 | 0.038 |
| 1000 | 0.033 |
| 500 | 0.034 |

Conclusion

The removal of methyl *tert*-butyl ether by employing the high frequency of ultrasound has successfully obtained. The experimental conditions selected in this study is fixed at three different MTBE initial concentrations (2000, 1000 and 500 ppm), with three different volume solutions at ultrasound reactor volume (50, 40 and 30 mL) has given a good results for removal of MTBE within in a short period, during the irradiation process. The results show that the removal process of MTBE at 2.4 MHz and after only 50 min has exceeded 85 % of its initial concentration. The results also demonstrate that the removal of MTBE could be obtained at lower initial liquid volume 30 mL, regarding to the initial concentration of MTBE, since the percentage of removal is almost the same for three different initial concentrations. The kinetics model study shows that removal of MTBE is following the first order kinetics model with reaction rate constant k equal to 0.035 (min⁻¹).

REFERENCES

- M.A.-D. Matouq and Z.A. Al-Anber, *J. Ultrasonics Sonochem.*, **14**, 393 (2007).
- M. Matouq, Z.A. Al-Anber, T. Tagawa, S. Aljbour and M. Al-Shannag, *Ultrason. Sonochem.*, **15**, 869 (2008).
- M. Matouq, N. Susumu, Z. Al-Anber, O. Markarian, O. Al-Ayed and T. Tagawa, *Res. J. Pharm. Biol. Chem. Sci.*, **5**, 940 (2014).
- M. Matouq, T. Tagawa and N. Susumu, *J. Global Network Environ. Sci. Technol.*, **16**, 805 (2014).
- M. Matouq, Z. Al-Anber, N. Susumu, T. Tagawa and H. Karapanagioti, *Sep. Purif. Technol.*, **135**, 42 (2014).
- P.B.L. Chang and T.M. Young *Water Res.*, **34**, 2233 (2000).
- M.D. Einarson and D.M. Mackay, *Environ. Sci. Technol.*, **35**, 66A (2001).
- EFOA, The European Fuel Oxygenates Association (2001); <http://www.efoa.org>.
- J.W. Antony, in eds.: B.C. Alleman, A. Leeson, Methodology to Evaluate Natural Attenuation of MTBE, In: Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds, Columbus Batelle Press, pp. 121-133 (1999).
- J. Jacobs, J. Guertin and C. Herron, MTBE: Effects on Soil a Ground-water Resource, Lewis Publishers, Boca Raton (2001).
- P.J. Squillace, J.F. Pankow, N.E. Korte and J.S. Zogorski, *Environ. Toxicol. Chem.*, **16**, 1836 (1997).
- B.C. Alleman and A. Leeson, Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds, Columbus Batelle Press, pp. 121-133 (1999).
- A. Azadpour-Keeley, Envirogen Propane Biostimulation Technology for *in situ* Treatment of MTBE-Contaminated Ground Water, EPA/600/R-02/092 (2002); <http://www.epa.gov/ORD/NRMRL/Pubs/600R02092/600R02092.pdf>.
- C.L. Bruce, C.D. Gilbert, R.L. Johnson and P.C. Johnson, Methyl *tert*-Butyl Ether Removal by *in situ* Air Sparging in Physical Model Studies, in Proceedings, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, Calif., Columbus, Batelle Press, Ohio, USA, May 18–21, pp. 293-298 (1998).
- A.P. Mortensen, K.H. Jensen, T.O. Sonnenborg and E. Arvin, *Ground Water Monit. Remed.*, **20**, 87 (2000).
- K.W. Rutherford and P.C. Johnson, *Ground Water Monit. Remed.*, **16**, 132 (1996).
- P.C. Johnson, *Environ. Sci. Technol.*, **32**, 276 (1998).
- T.C. Schmidt, M. Schirmer, H. Weiß and S.B. Haderlein, *J. Contam. Hydrol.*, **70**, 173 (2004).
- R.J. Steffan, K. McClay, S. Vainberg, C.W. Condee and D. Zhang, *Appl. Environ. Microbiol.*, **63**, 4216 (1997).
- M.I. Stefan, J.R. Mack and J.R. Bolton, *Environ. Sci. Technol.*, **34**, 650 (2000).
- X.R. Xu, Z.Y. Zhao, X.Y. Li and J.D. Gu, *Chemosphere*, **55**, 73 (2004).
- D.K. Kim, K.E. O'Shea and W.J. Cooper, *Sci. Total Environ.*, **430**, 246 (2012).
- D.K. Kim, K.E. O'Shea and W.J. Cooper, *Ultrason. Sonochem.*, **19**, 959 (2012).
- A.A. Burbano, D.D. Dionysiou, M.T. Suidan and T.L. Richardson, *Water Res.*, **39**, 107 (2005).
- W.M. Glaze, J.W. Kang and D.H. Chapin, *Ozone Sci. Eng.*, **9**, 335 (1987).
- A.B. Ray, A. Selvakumar and N.T. Anthony, Treatment of Methyl Tertiary-butyl Ether (MTBE) Contaminated Waters with Fenton's Reagent, Urban watershed Management Branch, United State Environmental Protection Agency (2003).
- USEPA, Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-butyl Ether (MTBE), EPA 822-F-97-008, Office of Research and Development, Washington D.C. (1997).
- C. Guillard, N. Charton and P. Pichat, *Chemosphere*, **53**, 469 (2003).