

# Effect of Ultraviolet Light on the Efficiency of Nano Photo-Catalyst (UV/ CNTs/TiO<sub>2</sub>) Composite in Removing MTBE from Contaminated Water

B. S. Tawabini, M. Atieh, and M. Mohyeddin

**Abstract**—In this study, the removal efficiency of methyl tertiary butyl ether (MTBE) by: (1) UV-Titanium dioxide (UV/TiO<sub>2</sub>), (2) UV-Carbon Nanotubes (UV/CNT) and (3) 5% TiO<sub>2</sub> impregnated on CNTs surface (UV/CNTs/5%TiO<sub>2</sub>) was investigated. Two types of UV irradiation were utilized in this study namely: UVA irradiating at wavelength of 365nm and UVC irradiating at a wavelength of 254 nm. Dosage of 20 mg of nano materials was used in these experiments. The fate of MTBE's main degradation by-products were also investigated in this study. Results of the study showed that MTBE removal in the dark was very low for the three types of nano materials under the study conditions used. However, appreciable removal of MTBE was observed when using UV/TiO<sub>2</sub> for both types of UV lights, with UVC showing slightly better than UVA. On the other hand, the removal of MTBE by UV/CNTs and UV/CNTs/TiO<sub>2</sub> were much lower than that of UV/TiO<sub>2</sub>.

**Index Terms**—CNTs, MTBE, photo-catalysis, UV, TiO<sub>2</sub>, TiO<sub>2</sub>/CNTs.

## I. INTRODUCTION

The quality of freshwater resources is receiving a great deal of attention worldwide. Increasing demand for clean water due to rising population and pollution from industrial, agricultural and domestic activities are among the factors affecting the quality of available water resources [1]. Chemical pollutants in the form of organics, inorganics and heavy metals are usually present in water bodies at generally low levels; however it is their high toxicity and potential to cause harm to humans that is of greater concern. Benzene, toluene, ethyl benzene and xylene (BTEX) as well as methyl tertiary butyl ether (MTBE) are organic compounds frequently encountered in groundwater. MTBE is a fuel additive that enhances octane rating and helps lower harmful emissions [2], [3], [4]. Its presence in the environment, particularly water, is however an issue of concern due to its potential human health implications.

MTBE has been found to raise the toxic effects of other pollutants in the environment, particularly pesticides [5]. The main concern however is with its potential adverse human health effects, symptoms of which include headache, cough,

nausea dizziness and skin irritation [6]. Reference [7] showed that exposure to MTBE caused an increase in cell tumors, lymphomas and leukemia in rats. The United States Environmental Protection Agency (USEPA) has classified MTBE as a potential human carcinogen and recommended a concentration limit of 20 to 40µg/L in drinking water in order to avoid undesirable odor and taste problems [8]. The California Department of Health Services has gone further to set a secondary maximum contaminant level of 5µg/L for MTBE in community water systems [9].

Remediation of water contaminated with MTBE by conventional treatment methods is challenging; due to the compound's high water solubility, low adsorption onto solids and resistance to biodegradation, thus making it quite persistent in the environment [10], [11]. Advanced oxidation processes (AOPs) have been identified as promising for treatment of water contaminated with pollutants such as MTBE. These processes make use of hydroxyl radicals (OH•) to oxidize all organic pollutants present in water; leading to complete mineralization into carbon dioxide and water [12]. AOPs are capable of removing both low and high levels of organic pollutants present in water. Among the effective AOPs in removing contaminants from water is photocatalysis; with titanium dioxide (TiO<sub>2</sub>) as the preferred photocatalyst [13]. Recent applications of nano-materials in water treatment have also been promising. Combining the photocatalytic properties of TiO<sub>2</sub> and adsorption powers of carbon nanotubes (CNTs) is an area where research has been limited. Considering the benefits in terms of safeguarding water resources and also reducing treatment costs, more research needs to be undertaken in this area.

The main aim of this study is to develop a bench-scale water treatment technique that can effectively remove MTBE and its degradation by-products from water using the combined mechanisms of TiO<sub>2</sub>-photocatalysis and adsorption by multi-walled carbon nanotubes (MWCNTs).

## II. MATERIALS AND METHODS

Multi-walled carbon nanotubes (MWCNT) with 95 wt% purity obtained from Cheaptubes Inc. was used as starting material. 99.5% tert-butyl methyl ether (MTBE) solution was purchased from Sigma-Aldrich.

Titanium (IV) oxide 99% anatase powder was obtained from Acros Organics as well as titanium (IV) isopropoxide which was used as a titanium precursor.

The CNT-TiO<sub>2</sub> composite material was prepared using wet impregnation method. An approximate concentration of 5% of TiO<sub>2</sub> was deposited on the surface of the CNTs. The

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titanium dioxide precursor (titanium isopropoxide) was dissolved in deionized water. The CNTs were dissolved in 200 ml of ethanol to enable adequate mixing during sonication. The titanium isopropoxide and CNTs in ethanol solutions were mixed and then stirred to obtain a homogenous solution. The solution was sonicated using a prop sonicator for an hour. The mixture was filtered and rinsed with deionized water. Calcination at 350°C was carried out for three hours. The CNT- TiO<sub>2</sub> composite was then dried and characterized.

All aqueous MTBE solutions were prepared using Milli-Q deionized water. The solutions were prepared by mixing pure MTBE with deionized water and stirred overnight to achieve a complete and uniform solution. The pH of the de-ionized water used for preparing the MTBE-spiked water samples were adjusted to about 7.0 to avoid its effect on MTBE solubility. A 100 ppm of aqueous stock standards of MTBE was prepared from which dilutions were prepared to calibrate the GC/MS instrument and spike the water samples to levels of 500 ppb.

All experiments were carried out in the Luzchem LZC-4X photoreactor that houses several UV light sources. UV-A lamps with wavelength of 350 nm were used that were arranged in 3 top and 4 side positions inside the photoreactor. The flux readings, measured with a UVA/VIS power meter, were converted to power readings (mW/cm<sup>2</sup>) by multiplying with a calibration factor of 0.0042. The UV-A lamps MTBE-spiked water samples were placed into quartz tubes of 10 mL capacity on a portable carousel for liquid samples ("merry-go-round"). The experiments with UV light were performed with different doses (0.5, 5, and 20 mg) of TiO<sub>2</sub>, CNTs and CNT- TiO<sub>2</sub> materials added to the aqueous MTBE solution. One (1) ml samples were collected at 30 minutes intervals for 120 minutes during the treatment runs.

The collected samples were allowed to stand for several hours at a room temperature before analysis to ensure that equilibrium between the vapor phase and the liquid phase had been reached. Each sample was analyzed for MTBE as well as its degradation by-products (TBA and acetone). All analyses were duplicated. A Thermo Scientific Trace GC Ultra Gas Chromatograph coupled with an ISQ single quadrupole mass spectrometer was used. Headspace technique was utilized for sample introduction. Helium was used as the carrier gas. A 60 m long, 0.32mm ID and film thickness of 1.8 um was used for the analysis of MTBE and its by-products. The initial GC temperature used was 50°C (1 min) increased to 220°C at a rate of 20°C/min. An ISQ MS method utilized was based on EI Ion source temperature of 200°C and acquisition time from 4.3 min to 7.3 min with a detector gain of 5 x 10<sup>4</sup>. Selected Ion monitoring (SIM) was used for the detection and quantification of the target compounds (i.e. acetone and Tertiary Butyl Alcohol (TBA)).

### III. RESULTS AND DISCUSSION

#### A. Removal of MTBE in Dark Conditions

Fig. 1 show the removal of MTBE in dark conditions (i.e. without UV irradiation) when water spiked with 500 ppb MTBE is treated with 20 mg of (1) CNT-5%TiO<sub>2</sub>, (2) TiO<sub>2</sub> and (3) CNTs respectively. The results depicted in Fig. 1,

indicate that there is no significant removal of MTBE when treated by the TiO<sub>2</sub>, CNT and CNT-5%TiO<sub>2</sub> as compared to the blank sample where no material was used. The marginal loss in MTBE could be due to its volatility or adsorption mechanisms. Fig. 1 also shows that 20 mg of CNTs alone was not enough to remove MTBE by adsorption mechanisms. This shows that absorptivity of MTBE to solid particles is not good which represent one of the challenges to the removal of MTBE by normal adsorption unit. Fig. 1, shows that less than 10% of MTBE was removed via adsorption by CNTs, TiO<sub>2</sub> and CNT/TiO<sub>2</sub> nano composite materials when compare to the blank sample. The poor adsorption of MTBE by these nano materials is mainly due to the fact that MTBE has relatively high solubility in water (48,000 ppm at 25°C) and low octanol : water distribution coefficient (log K<sub>ow</sub> = 1.2) [14].

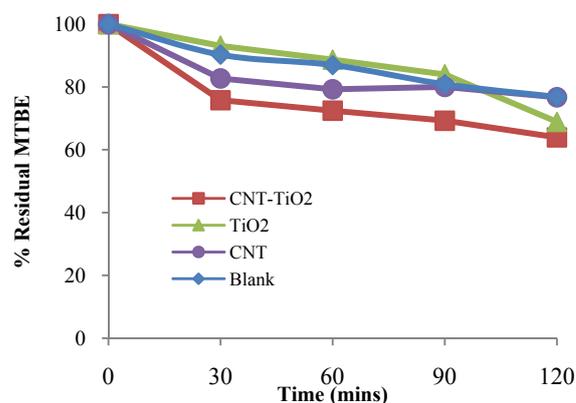


Fig. 1. Removal of MTBE with 20 mg of CNT-5%TiO<sub>2</sub>, TiO<sub>2</sub> and CNT

The proof that no significant degradation of MTBE occurred under dark conditions was the absence of any degradation by-products.

#### B. Removal of MTBE by UVA Irradiation TiO<sub>2</sub>, CNT and CNT-TiO<sub>2</sub>

A series of experiments were carried out to assess the effect of utilizing the UVA light in irradiating the catalysts (i.e. CNTs, TiO<sub>2</sub> and CNT/TiO<sub>2</sub>) to generate the hydroxyl radicals necessary to breakdown the MTBE compound. Results of these experiments are depicted in Fig. 2.

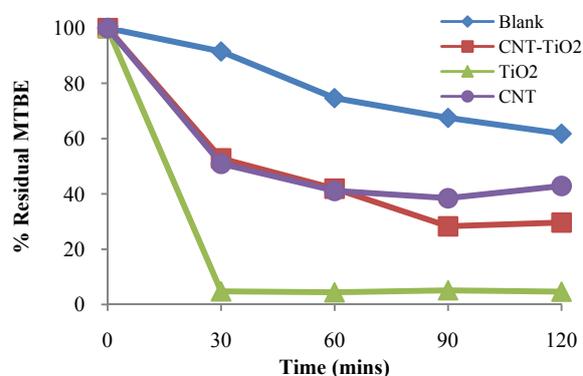


Fig. 2. Removal of MTBE by UVA light and 20 mg of CNT-TiO<sub>2</sub>, TiO<sub>2</sub> and CNT

Results in Fig. 2 show that about 35% of MTBE was removed due to photolysis by UVA only. However, more than 99% of MTBE removal was obtained by UV/TiO<sub>2</sub> owing to the excellent photocatalytic properties of TiO<sub>2</sub>. This comes

in agreement with many previous studies that have reached to the same conclusion (Refs). When studying the removal of MTBE by CNTs combined with UV irradiation (UV/CNTs), it was noticed that only about 20% of MTBE was removed in 120 minutes. This shows a slight improvement in the removal efficiency of MTBE compared to the 20% removal with no UV radiation as shown in Fig. 1. The increase in removal of MTBE by UV-assisted CNTs could be attributed to the enhancement of the adsorption capability of the CNTs.

Similarly, Fig. 2 show that the 5%TiO<sub>2</sub> material impregnated on CNTs surface showed similar behavior to the removal by CNTs. Results showed that more than 60% of MTBE was removed after 120 min by UV/CNT-TiO<sub>2</sub> composite materials. The reason behind trying to use the impregnated material was the assumption that the UV-TiO<sub>2</sub> will generate the radicals needed to degrade the MTBE while formed by-products will be adsorbed by the CNTs. The results indicate that either the 5% TiO<sub>2</sub> material was not enough to improve the removal efficiency of MTBE by the impregnated materials or the CNTs materials was absorbing the radicals once generated by irradiating TiO<sub>2</sub> particles with UVA sources.

In addition, the degradation of MTBE by UV-TiO<sub>2</sub> was confirmed by the formation of some by-products as shown in Fig. 3 which shows that some Tertiary Butyl Ether (TBA) were detected during the treatment of MTBE with UV/TiO<sub>2</sub> only, while treatment with other nano materials did not form these by-products to noticeable levels. The reason behind this is may be that other by-products are formed during the degradation of CNTs with the aid of UV. The other reason could be that CNTs did not work as a photocatalyst but rather its adsorption capacity was enhanced by the irradiation with UV. Further investigation is needed in this case to study the mechanism of MTBE removal by UV-assisted CNTs.

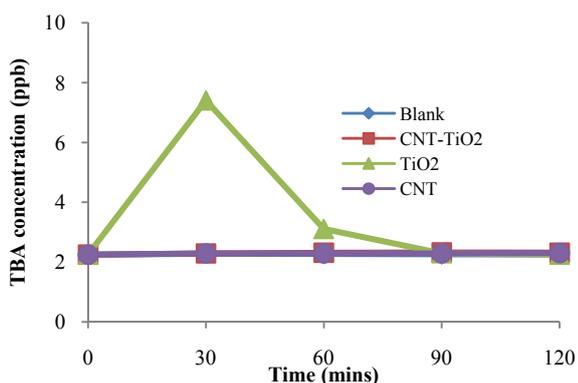


Fig. 3. Formation of TBA by UVA light and 20.0 mg of CNT-5%TiO<sub>2</sub>, TiO<sub>2</sub> and CNT

In order to study the effect of the UV type irradiation, several experiments were carried out in the lab using the UVC lamps irradiating at wavelength of 254 nm to irradiate the nano composite materials (i.e. CNTs, TiO<sub>2</sub> and CNT/TiO<sub>2</sub>). The water samples spiked with 500 ppb MTBE were first dosed with 20 mg of each composite materials and were irradiated with UVC for 120 minutes. Water samples were collected every 30 min up to 120 min and analyzed for MTBE and TBA. The results of MTBE residual concentrations with treatment time are depicted in Fig. 4.

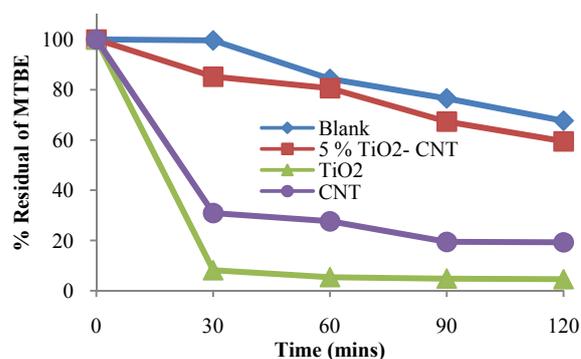


Fig. 4. Removal of MTBE after treatment by UVC light and 20 mg of CNT-TiO<sub>2</sub>, TiO<sub>2</sub> and CNT

#### A. Removal of MTBE by UVC Irradiation TiO<sub>2</sub>, CNT and CNT-TiO<sub>2</sub>

The results in Fig. 4 show excellent removal of MTBE by UV/TiO<sub>2</sub> followed by UV/CNTs. However, removal by UV/CNT-TiO<sub>2</sub> was not showing good removal of MTBE. More than 95% removal of MTBE was achieved in 30 min when water was treated with UV/TiO<sub>2</sub> which agreed with other studies. Similar results were also obtained when we use UVA (365nm) as shown in Fig. 2 above. This confirms the excellent photocatalytic properties of TiO<sub>2</sub> irrespective of the UV type used. Degradation of MTBE by UVC/TiO<sub>2</sub> is shown by the formation of the by-product of MTBE (i.e. TBA) as shown in Fig. 5. On the other hand, the removal of MTBE by UVC/CNTs was noticeably improved as shown in Fig. 4. In fact about 70% removal of MTBE was achieved within 30 min. Comparing results in Fig. 2 and 4 clearly indicate better removal of MTBE by UVC/CNTs than UVA/CNTs. Some degradation of MTBE is shown by the formation of TBA as shown in Fig. 5. However, removal of MTBE by UVC/CNTs/TiO<sub>2</sub> was lower than removal when using UVA irradiation source shown in Fig. 2. This may be due to more absorption of hydroxyl radicals taken place in this case.

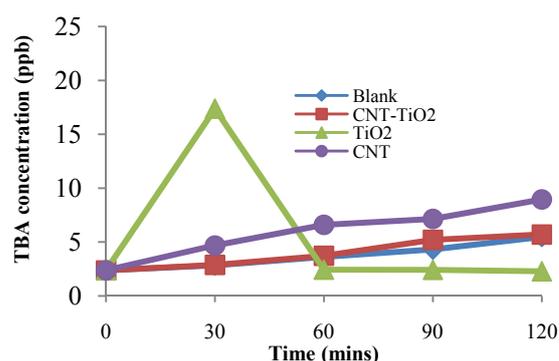


Fig. 5. Formation of TBA after treatment by the UVC light and 20.0 mg of CNT-5%TiO<sub>2</sub>, TiO<sub>2</sub> and CNT

#### IV. CONCLUSION

The present study demonstrated the ability of different nano-materials in combination with UV radiation to remove MTBE from contaminated water. These materials were: CNTs, TiO<sub>2</sub>, and 5% TiO<sub>2</sub>/CNTs. The TiO<sub>2</sub> nanoparticles were impregnated on the surface of carbon nanotubes. The results of the study showed that under the conditions used,

UV/TiO<sub>2</sub> process had higher removal efficiency of MTBE compared to UV/CNTs and UV/TiO<sub>2</sub>/CNTs. However, results also indicated that CNTs show some efficiency in removing MTBE when irradiated by UV light. Results also show better removal of MTBE using UVC/CNTs than UVA/CNTs.

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