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Removal of methyl tertiary butyl ether (MTBE) from contaminated water using UV-assisted nano composite materials

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ABSTRACT

This study was designed to examine the efficacy of UV-assisted nano material treatments to remove methyl tertiary butyl ether (MTBE) from contaminated water. The focus was to investigate the applicability of combining the degradation potential of nano TiO_2 photocatalysis and adsorption power of carbon nano tubes (CNTs). Effect of different combinations of two ultraviolet radiations (UVA and UVC) and three types of nano materials: TiO_2, CNTs, and TiO_2/CNTs on MTBE remediation was studied. Removal efficiency of different combinations varied significantly with highest removal (95%) achieved by UVC-TiO_2, followed by UVC-CNTs (75%) and UVA-TiO_2/CNT_S (60%). However, additive effect of UV/TiO_2/CNTs on MTBE removal from water was not observed. Major degradation byproducts formed were acetone, tertiary butyl formate, and tertiary butyl alcohol.

Keywords: MTBE; UV light; Nano materials; Photodegradation; Carbon nano tubes; Titanium dioxide

1. Introduction

Kingdom of Saudi Arabia is located in an arid region, characterized by limited rainfall and high-evaporation rates [1]. Due to the absence of conventional surface water resources, non-renewable groundwater is the major source of fresh water. Excessive withdrawal of water for agriculture and other domestic purposes has put these resources under severe pressure [2,3]. In addition, both organic and inorganic chemical pollutants have found their ways into the groundwater making it unfit for human consumption in many cases [4]. Therefore, decontamination of ground water resources has been top priority of scientific community and municipal authorities of the country.

Benzene, toluene, ethyl benzene, and xylenes as well as methyl tertiary butyl ether (MTBE) are the most common organic pollutants found in groundwater. MTBE is a fuel additive that enhances octane rating and helps to reduce harmful emissions [5–7]. Its presence in the environment, especially water, is however an issue of concern due to its potential human health implications. Some studies showed that exposure to high-MTBE levels may cause headache, cough, nausea, dizziness, and skin irritation [8,9]. Belpoggi et al. concluded that exposure to MTBE causes increased proliferation of tumor cells, lymphomas, and leukemia in laboratory rats [10]. United States Environmental Protection Agency has classified MTBE as a potential human carcinogen and has set a threshold of 20–40 $\mu g\,L^{-1}$ in drinking water to avoid undesirable odor and taste [11]. The California Department of Health Services has gone farther to set a secondary maximum contamination level of 5 μg L^{-1} for MTBE in community water systems [12].

Remediation of MTBE contaminated water by conventional methods is challenging due to its high-water solubility, low adsorption onto solids, and resistance to biodegradation, making it rather persistent in the environment [13,14]. Advanced oxidation processes (AOPs) have been tipped promising for treatment of such waters [15]. These processes use hydroxyl radicals ($OH^{\cdot}$) to oxidize organic pollutants and subsequently complete mineralization into carbon dioxide and water. AOPs are capable of removing both low and high levels of organic pollutants from water [16]. UV-Titanium dioxide (UV/TiO_2) is the best among photocatalytic AOPs [17,18]. Recently, other nano materials have also been successfully employed in treatment of contaminated water [19,20]. Combining the photocatalytic properties of TiO_2 and adsorption powers of carbon nano tubes (CNTs) is an area where research has been limited [21,22].

Current study was aimed to examine a novel approach to remove MTBE and its byproducts from water using combined effects of UV-assisted degradation by nano photocatalysts (nano TiO_2) and adsorption by nano sorbents (CNTs).

2. Materials and methods

2.1. Materials

Multi-walled carbon nano tubes with 95 wt.% purity were obtained from Cheaptubes Inc., USA and used as starting material. 99.5% MTBE solution was purchased from Sigma–Aldrich, USA. Titanium(IV) oxide 99% anatase powder was obtained from Acros Organics, USA as well as titanium(IV) isopropoxide which was used as a titanium precursor.

2.2. Synthesis of CNT–TiO_2 material

CNT–TiO_2 composite material was prepared using wet impregnation method [23]. Approximately 5–10% TiO_2 was deposited on the surface of CNTs. Titanium dioxide precursor (titanium isopropoxide) was dissolved in deionized water. CNTs were dissolved in 200 mL of ethanol to enable adequate mixing during sonication. Titanium isopropoxide and CNTs were mixed in ethanol solution and stirred to obtain a homogenous solution. The solution was sonicated using a prop sonicator (model) for 1 h. The mixture was filtered and rinsed with deionized water. Calcination at 350 °C was carried out for 3 h. CNT–TiO_2 composite was then dried and characterized.

2.3. Characterization of CNT–TiO_2 material

2.3.1. Field emission scanning electron microscopy (FE-SEM)

Scanning electron microscopy (SEM) was used to characterize the surface morphology of CNTs, TiO_2, and CNT–TiO_2 composites. Samples were sputtered with a thin layer of gold for 20 s to minimize charging effect during examination in a 30 kV FE-SEM (Model FEI Nova Nano SEM 230). Low-voltage backscattered electron (BSE) imaging was performed using an accelerating voltage of 5 kV at a short working distance of 2 mm. Low voltage, high-contrast BSE detector was mounted below the objective pole-piece and directly above the sample to obtain high-resolution images at low kV. FE-SEM examination was performed at magnifications ranging from 500 to 40,000×. Micro-chemical analysis of samples was carried out in order to detect the presence of TiO_2. Energy dispersive X-ray spectroscopy (EDS) detector (Model: Oxford INCA Penta FETx3 with 30 mm^2 detectable area coupled with INCA EDS software) was used to examine the samples. The Si(Li) EDS detector was equipped with an atmospheric thin window capable of detecting elements down to Beryllium (Be). The accelerating voltage of the SEM was maintained at 20 kV during micro-chemical analysis.

2.3.2. Preparation of MTBE solution

All aqueous MTBE solutions were prepared by mixing pure MTBE with Milli-Q deionized water and stirred overnight to achieve complete uniformity. The pH of deionized water was adjusted to 7.0 in order to avoid its effect on MTBE solubility. A 100 ppm of aqueous stock standards of MTBE was prepared from which dilutions were made to calibrate the GC/MS instrument and spike the water samples to a concentration of 500 ppb.

2.4. Treatment of MTBE-spiked water using UV-assisted nano materials

Separate experiments were performed with UVA and UVC lamps irradiating at wavelengths of 365 and 254 nm, respectively. Flux readings, measured with a UV/VIS power meter, were converted to power readings (mW/cm^2) by multiplying with a calibration factor of 0.0042 given by the manufacturer.

Accurately weighed 20 mg of nano composite materials (CNTs, TiO_2, and CNT–5% TiO_2) were added to quartz tubes containing 10 mL spiked water samples (500 ppb MTBE) inside the photoreactor. The quartz tubes were placed into the rotating portable carousel to provide even exposure to the UV radiation. From each treatment run, 1 mL water sample was collected at 0, 30, 60, 90, and 120 min for chemical analyses.

All experiments were performed inside Luzchem LZC-4X photoreactor that housed several UV light sources.

2.5. Chemical analyses

The collected water samples were allowed to settle for several hours at 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 byproducts (tertiary butyl alcohol (TBA), tertiary butyl formate (TBF), and acetone). 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, 0.32 mm ID, and film thickness of 1.8 µm was used for the analysis of MTBE and its byproducts. The initial GC temperature used was 50°C (1 min) increased to 220°C at a rate of 20°C min^{-1}. ISQ MS method utilized was based on EI ion source temperature of 200°C and acquisition time of 4.3–7.3 min with a detector gain of 5×10^4. Selected Ion monitoring was used for the detection and quantification of the target compounds. All chemical analyses were performed in duplicate.

3. Results and discussion

3.1. Characterization of the nano composite materials

3.1.1. SEM/EDS

The surface morphology of CNTs, TiO_2, and CNTs/TiO_2 specimens was examined using SEM/EDS as shown in Figs. 1–3, respectively. Fig. 1 shows that the CNTs exhibited winding, entangled, and relatively disordered structure. These variations in CNTs lengths can occur due to fluctuation of carbon concentration during synthesis [24]. The diameter of CNTs varied between 10 and 20 nm while their lengths varied from 1,000 to 10,000 nm. The EDS analysis of CNTs (Fig. 1) revealed that commercial CNTs contained traces of fine silver (Ag) particles on their surface as impurities.

Fig. 2 shows SEM image of the commercial TiO_2 particles as agglomerated in spherical shapes and their diameter ranges from approximately 100 to 200 nm. The EDS analysis of TiO_2 showed that the commercial TiO_2 is relatively pure and the traces of gold (Au) particles detected were possibly from sample preparation.

Fig. 3 shows SEM images and EDS spectrum of TiO_2 impregnated on CNTs surface. The size of TiO_2 nano particles impregnated on the CNTs surface vary from small to large particles with sizes ranging from 100 to 500 nm for the large particles and from 5 to 10 nm for the small particles. Micro-chemical analysis of 5% TiO_2–CNT specimen encompassing an area containing substantial presence of these fine particles revealed that the specimen was mainly composed of carbon along with considerable amounts of Ti and O as shown in the EDS spectrum of Fig. 3. This suggests that the fine particles present at the surface of CNTs are TiO_2.

3.2. Removal of MTBE

3.2.1. Removal of MTBE in dark conditions (no UV irradiation)

Fig. 4 demonstrates that the removal of MTBE was not significant when treated by TiO_2, CNT, and CNT–5% TiO_2 as compared to the blank sample where no material was used. The loss in MTBE (20–30%) could be due to its volatility or adsorption to the surface of the container.

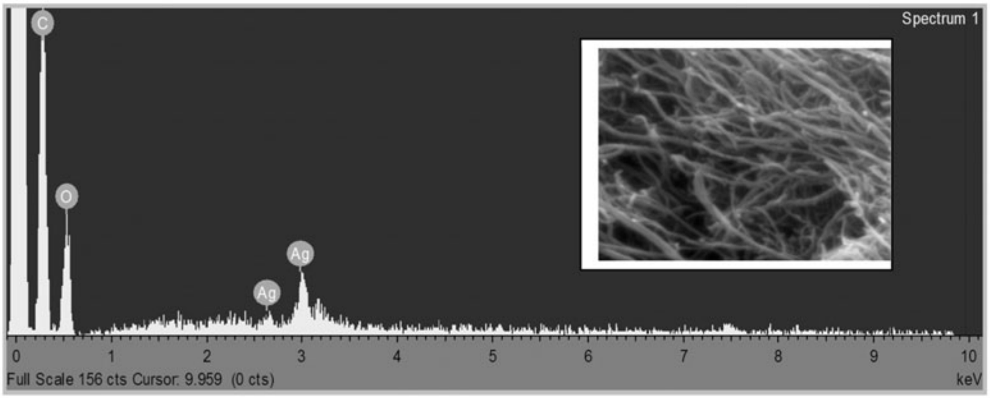

Fig. 1. SEM image and EDS spectrum of the CNTs material.

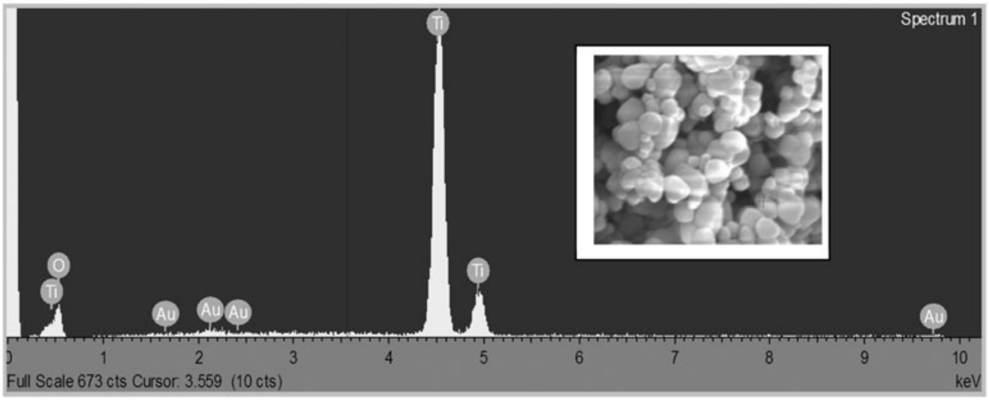

Fig. 2. SEM image and EDS spectrum of the TiO_2 material.

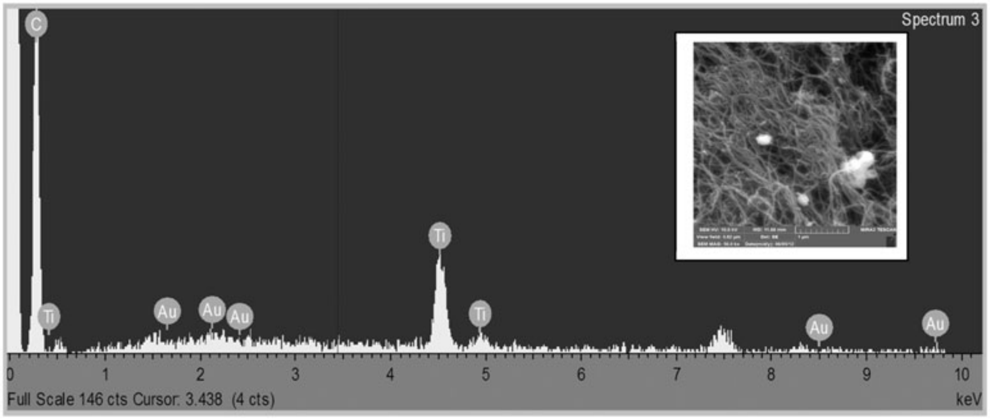

Fig. 3. SEM image and EDS spectrum of the TiO_2/CNTs.

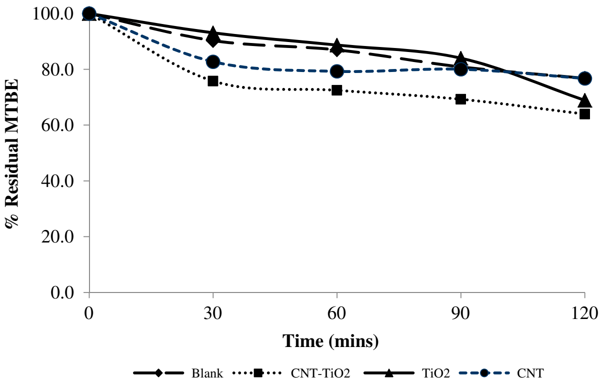

Fig. 4. Removal of MTBE from water with 20 mg of (1) CNT–5% TiO_2, (2) TiO_2, and (3) CNT after 30 min intervals up to 120 min.

Fig. 4 also proves that 20 mg of CNTs alone was not enough to remove MTBE by adsorption mechanism. Hence, absorption of MTBE to solid particles is rather poor, making it difficult to remove MTBE by normal adsorption. The absence of MTBE byproducts, such as acetone, TBF, and TBA species in the treated water samples further verified that no significant degradation of MTBE occurred under these conditions.

3.2.2. Removal of MTBE by UVA/UVC irradiation with TiO_2, CNT, and CNT–5% TiO_2

Fig. 5 shows 95% removal of MTBE within 30 min of reaction due to photocatalytic properties of UVA-irradiated TiO_2. It is in agreement with many previous studies that have reported TiO_2 as an excellent remediation agent [25]. About 50% of MTBE was removed by CNTs combined with UVA irradiation (UVA/CNTs) after reaction time of 120 min. It is thus a significant improvement in removal efficiency as compared to the 20% removal of MTBE with no UVA radiation in previous treatment (Fig. 4). This improved efficiency could be attributed to increase in the adsorption capability of CNTs by UVA irradiation.

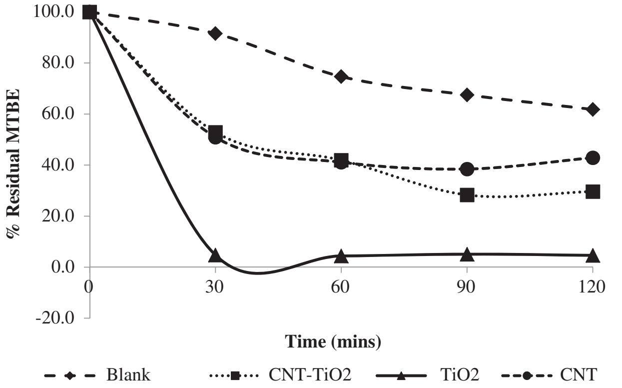

Fig. 5. Removal of MTBE from water with UVA light and 20 mg of (1) CNT–5% TiO_2, (2) TiO_2, and (3) CNT after 30 min intervals up to 120 min.

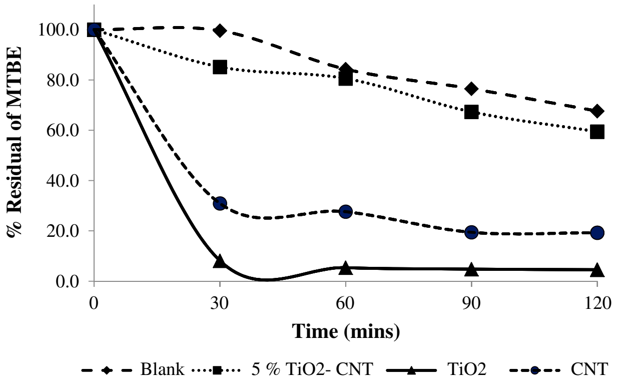

Fig. 7. Removal of MTBE after treatment by UVC light and 20.0 mg of (1) CNT–TiO_2, (2) TiO_2, and (3) CNT for a reaction time of 120 min.

Removal of MTBE in treatment with UVA light and 5% TiO_2 material placed on CNTs surface (TiO_2/CNTs) also improved as compared to the removal without UV (Fig. 4). More than 60% of MTBE was removed after 120 min by UVA/CNT–TiO_2 composite materials. However, highest removal of MTBE was achieved by the treatment UVA-TiO_2. The degradation of MTBE by UVA/TiO_2 was confirmed by the formation of acetone as one of the MTBE byproducts as indicated in Fig. 6.

Acetone was detected in the treatment of MTBE with UVA/TiO_2 only, while in treatments with other nano materials these byproducts were not detected. The reason may be that the byproducts formed were other than TBA, TBF, or acetone in samples treated with UVA-CNTs. Alternatively, CNTs did not work as a photocatalyst but rather its adsorption capacity was marginally enhanced by UVA irradiation.

Similarly, in experiment with UVC (Fig. 7) most efficient removal of MTBE was achieved by TiO_2 followed by CNTs and UV/CNT–TiO_2. More than 95% removal of MTBE was achieved in 30 min when water was treated with UVC/TiO_2 which agrees with many previous reports [25,26]. Similar results were also obtained when we used UVA (365 nm) as shown in Fig. 5, showing that photocatalytic properties of TiO_2 are independent of the type of UV irradiation. Degradation of MTBE by UVC/TiO_2 is further established by the detection of MTBE byproduct TBA (Fig. 8).

The hypothesis behind using impregnated nano material was the assumption that UV-TiO_2 will generate the radicals needed to degrade the MTBE, while resultant byproducts will be absorbed by the CNTs. It did not, however, produce the expected results. One likely reason could be the concentration of TiO_2 (5–10%) was inadequate to produce sufficient radicals. Alternatively, CNTs were probably absorbing the radicals once generated by TiO_2 particles by UV irradiation.

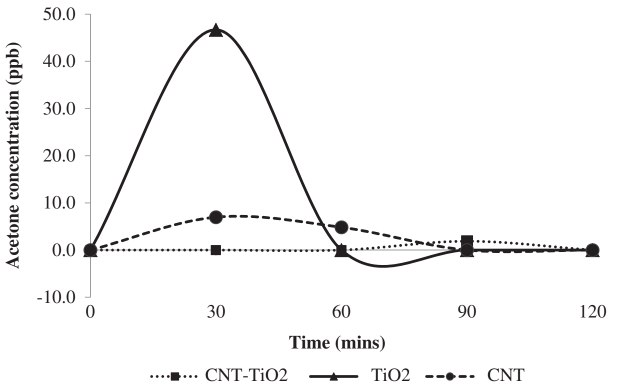

Fig. 6. Formation of acetone as a result of MTBE degradation using UVA light and 20 mg of (1) CNT–5% TiO_2, (2) TiO_2, and (3) CNT after 30 min intervals up to 120 min.

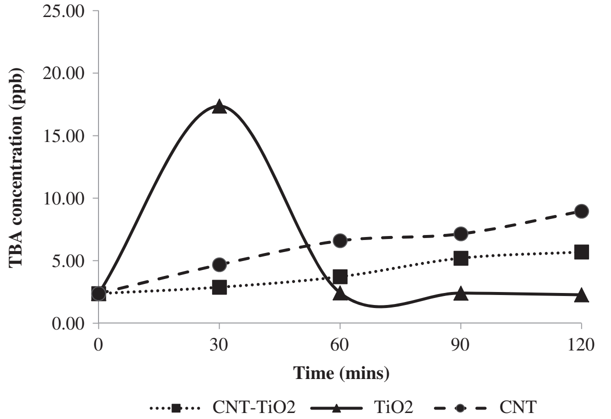

Fig. 8. Formation of TBA after treatment by the UVC light and 20.0 mg of (1) CNT–5% TiO_2, (2) TiO_2, and (3) CNT for a reaction time of 120 min.

4. Conclusion

Ultraviolet radiations (types A and C) can significantly increase MTBE removal efficiency of nano materials. Type C of the ultraviolet radiations showed significantly higher ability to enhance photocatalytic potential of TiO_2 and adsorption capability of CNTs. However, additive effect of UV/TiO_2/CNTs on MTBE removal from water was not observed. Further research in this area will be interesting and may lead to discovery of novel methods of conservation and remediation of water resources.

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