



## Photocatalytic Removal of Methyl Tert-Butyl Ether by C-N-TiO<sub>2</sub> Nanoparticles from Aqueous Solution

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### ABSTRACT

**Background:** The elimination of methyl tert-butyl ether (MTBE) from water resources remains a main environmental concern. In the present study, photo-assisted process for removal of MTBE was examined in the solutions containing C-N-TiO<sub>2</sub> nanoparticles under UV irradiation in the batch mode.

**Methods:** The effects of operational factors such as pH, initial catalyst concentration, and initial MTBE concentration on MTBE removal was investigated.

**Results:** The optimum degradation condition for MTBE was obtained at pH 7, catalyst load of 100 mg/L, air flow rate = 0.1 L/min and C<sub>0</sub> = 5 mg/L with 73 percent degradation of MTBE at 60 min. In addition, Analytical profiles on MTBE removal were based on the first-order kinetics model. However, the removal rate decreased by increasing initial concentration of MTBE.

**Conclusion:** The findings showed that UV/C-N-TiO<sub>2</sub> system is an efficient method for MTBE degradation from aqueous solution.

## 1. Introduction

MTBE is an organic oxygen substance that is primarily used as an octane additive in gasoline. The most important sources which release MTBE into the environment are leaking underground storage tanks, pipes, and pipelines that lead to the contamination of water [1-3]. MTBE is not absorbed in the soil. It penetrates into the ground and re-enters the environment through water cycle. MTBE is considered to be resistant to the environmental decomposition because of the existence of ether bond and long sub branches (more than one carbon) in its structure [4, 5]. It is considered as a

carcinogen by inhalation routes which causes other detrimental health problems including dizziness, nausea, eye irritation, skin irritation, and headache [6-8]. Concentrations of MTBE is limited in the range of 20 to 40 ppb in drinking water. [9, 10]. Existing technologies for MTBE decomposition, including granular activated carbon, adsorption, anaerobic/aerobic bioremediation, air-stripping, and advanced oxidation processes (AOPs) have been employed in recent decades [11, 8]. Recently, AOPs has come to be widely used to eliminate the refractory and xenobiotics from the solutions [8, 12]. These processes produce highly reactive hydroxyl radicals, which can cause a wide range of



pollutants, including all types of colors and MTBE, without any specific properties. Different photocatalysts have been used (e.g., TiO<sub>2</sub>, ZnO, CDs, and ZnS) to remove different pollutants from water. TiO<sub>2</sub> is used enormously for the decomposition of organics in the air and water due to its properties such as insolubility in reaction, medium size, non-toxicity, great photocatalytic activity, and low cost of production [13, 14]. One of the significant issues in utilizing pure TiO<sub>2</sub> is the reintegration among electrons and holes. Several studies about metallic and nonmetallic coatings have been conducted to enhance the performance of TiO<sub>2</sub> photocatalytic. [15-21]. Wang *et al.* (2009) investigated N-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) anatase catalyst which illustrated high performance in the reduction of o-nitrophenol (ONP) [22]. Kakroudi *et al.* (2014) have studied the role of nitrogen and carbon co-doped TiO<sub>2</sub> (C-N-TiO<sub>2</sub>) in reproducing the carbonyl compounds from oximes [15]. Despite considerable achievements in the elimination of MTBE, efficient and low-priced approaches are needed. Notably, there is an ongoing demand to introduce effective methods. The present study aimed to evaluate the efficiency of the UV/C-N-TiO<sub>2</sub> system. The impacts of pH, initial MTBE concentration, and the dose of catalyst on MTBE degradation rate were also determined.

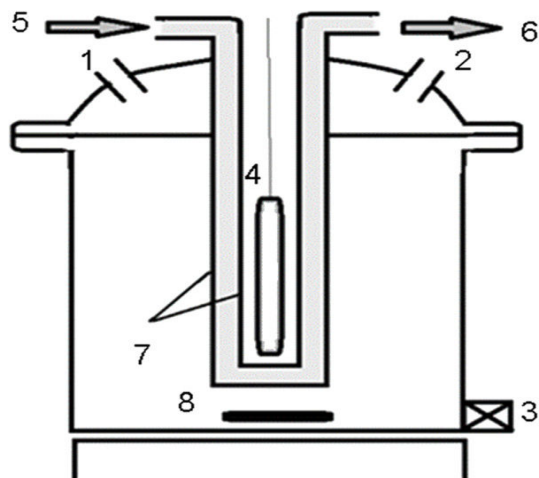
## 2. Materials and Methods

### 2.1. Experimental Method

Mesoporous C-N Codoped Nano TiO<sub>2</sub> with a crystal size of 15 nm, 109 m<sup>2</sup>/g surface area, and anatase phase, were prepared according to the study by Kakroudi *et al.* (2014) [15]. First, 10 mL of pure ethanol, 0.5 mL acetic acid, and 1 mL TPT (solution of Ti (OPri)<sub>4</sub>) were added and mixed for 1 hour at ambient temperature (solution A). Then, a solution of 5 mL deionized water and 5 mL ethanol in a sonication bath (solution B), 1.2 g (20 mM) urea was added. Afterwards, solution B was increased to solution A drop by drop. Sonication was performed using a direct plunge of the admixture container in the bath at ambient temperature for 150 min. The obtained mixture was retained at ambient temperature for one night. Thereafter, the gel was dehumidified at the 100 °C for 8 h. Finally, a fine catalyst powder was obtained by crushing and calcinating in a furnace at the 400 °C for 2 h. The pale yellow rectified Titania defined as mesoporous C-N co-doped Nano TiO<sub>2</sub> was generated.

### 2.2. Experimental Set up

All the steps were taken to eliminate MTBE with UV/C-N-TiO<sub>2</sub> in a batch mode with a volume of one liter (Figure 1). To



**Figure 1:** Schematic of the reactor: 1 and 2: feed of chemical; 3: sample withdrawn port; 4: UV lamp; 5-6: inlet and outlet of water; 7: water circulating system; 8: mixer.

adjust the reaction temperature, the reactor was equipped with a circulating water system around the lamp that continuously cooled the system. A 150 W UVC lamp was used to provide UV. In order to homogenize the reaction system, a magnetic stirrer was used. In addition, the air was added to the system to provide the oxygen for the catalyst.

Therefore, air flow rate (AFR) was used to investigate its role in the reaction. Then, the effects of factors such as pH, catalyst dose and, the initial MTBE concentration were examined.

### 2.3. Analytical Method

MTBE samples were taken from different heights of the reactor. All samples were collected, covered with an airtight cap and, kept in the refrigerator at 4 °C temperature before analysis. MTBE concentration was measured using Gas Chromatography (GC) device made by the Agilent Company. It was equipped with the Flame Ionization Detector (FID) according to the U.S EPA502.2 test method to analyze MTBE in the liquid phase through GC with the purge and trap system [17]. The absorption column of HP-5 with a length of 30 m and inner diameter of 0.32 mm was used. A temperature program of the column as the following: initial temperature of the column was 35 °C and after 4 min, at the rate of 10 °C per minute was up to the 150 °C. By reaching to this temperature, the method was finished. The FID temperature, hydrogen flow and, air flow was selected 300 °C, 25 mL/min and 250 mL/min, respectively. The three-step purge and trap, purge, desorb and, bake have been performed. Purging time was 11 minutes the flow was 40 mL/min, temperature was 25 °C and, dry purge flow was 200 mL/min. The time of desorb and bake were 2min, flow was 300 mL/min and, temperature was 250 °C. Temperature of the bake was 270 °C and flow was 400 mL/min. To determine the accuracy and precision of MTBE measurement, known concentration

samples were analyzed triplicate in identical condition. The relative standard deviation (RSD) in this method did not exceed more than 2%.

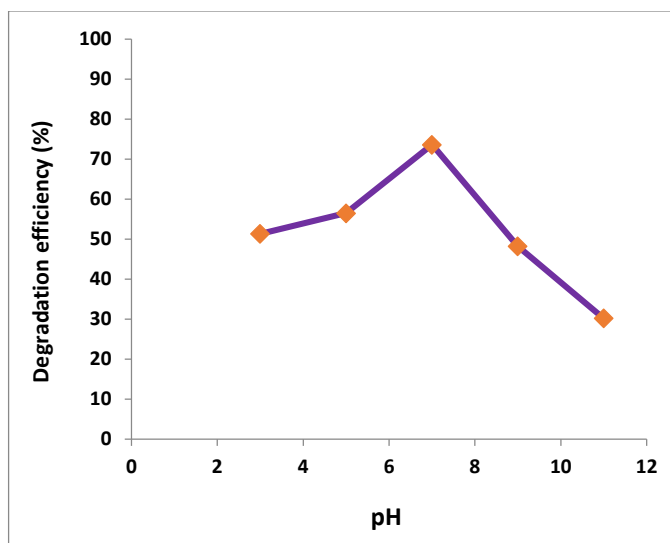
### 3. Results and Discussion

#### 3.1. Effect of pH

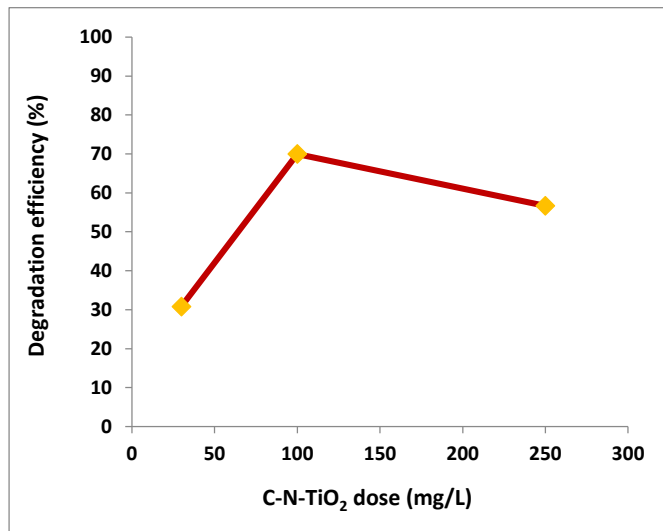
Determining pH in photocatalytic process performance is very important. The effect of pH on the MTBE removal was investigated in the range of 3 to 11. Figure 2 shows the MTBE degradation in several different ranges. The efficiency of the process improves as the pH dose e increases from 3 to 7, followed by a decrease by the increment of pH from 7 to 11. The pH of the reaction has serious effects on the photocatalytic oxidation, zero point charge (ZPC) of nanoparticle, and pollution. The process can be described according to the place of the point of zero charge (isoelectric point) of the C-N-TiO<sub>2</sub> [4, 2, 20, and 19]. Also, the findings of other works have indicated that pH impacts the generation of OH radicals, the oxidation efficiency, and the oxidation of organic pollutants both directly and indirectly [23, 24]. According to the results, the optimum pH=7 is selected for the removal of MTBE.

#### 3.2. Effect of Catalyst Dose

The quantity of catalyst is a main factor in photocatalytic system [25]. The effect of catalysts load on the MTBE degradation in the range of 30 to 250 mg/L was investigated. Figure 3 shows the percentage of removal of MTBE in different catalyst ranges. The degradation percentage increases by adding catalyst amount from 30 to 100 mg/L, then decreases from 100 to 250 mg/L. This process indicates that some nanoparticles may not receive adequate energy to generate hydroxyl radical to begin MTBE degradation.



**Figure 2:** Effects of pH variation on photocatalytic removal of MTBE ( $C_0 = 5$  mg/L, C-N-TiO<sub>2</sub> dose = 100 mg/L, AFRs = 0.1 L/min, t = 1 h)



**Figure 3:** Effect of C-N-TiO<sub>2</sub> dose on photocatalytic degradation of MTBE ( $C_0 = 5$  mg/L, pH = 7, AFRs = 0.1 L/min, t = 1 h)

Furthermore, when the quantity of catalyst is high, it increases the turbidity of the water phase and decreases the Penetration of the light into the solution completely. Therefore, the removal of MTBE is reduced. [4, 18, 16, 26]. The findings show that the best catalyst dose for degradation of MTBE under mentioned condition is 100 mg/L.

#### 3.3. Effect of the Initial MTBE Concentration

According to Figure 4, the rate of oxidation is decreased by increasing the initial MTBE concentration. Due to increasing initial MTBE concentration, their intermediates, and the limited number of produced OH, the interaction probability and oxidation will reduce. Consequently, the efficiency of the removal of MTBE will decrease [2, 20, and 27].

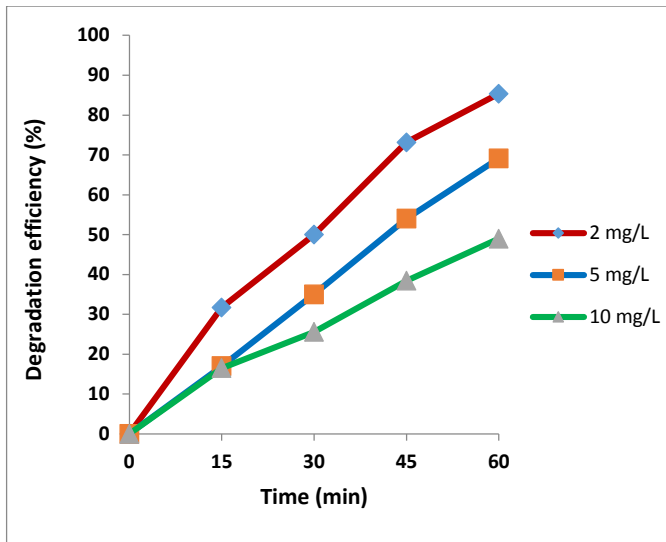
#### 3.4. Kinetics of MTBE Degradation

Based on the optimal conditions of MTBE removal by UV/C-N-TiO<sub>2</sub> system, the kinetics of photocatalytic degradation were evaluated for different initial concentration of MTBE which is shown in Figure 5. Normally, first-order kinetic is suitable for photocatalytic oxidation according to the following equation [28, 29].

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (1)$$

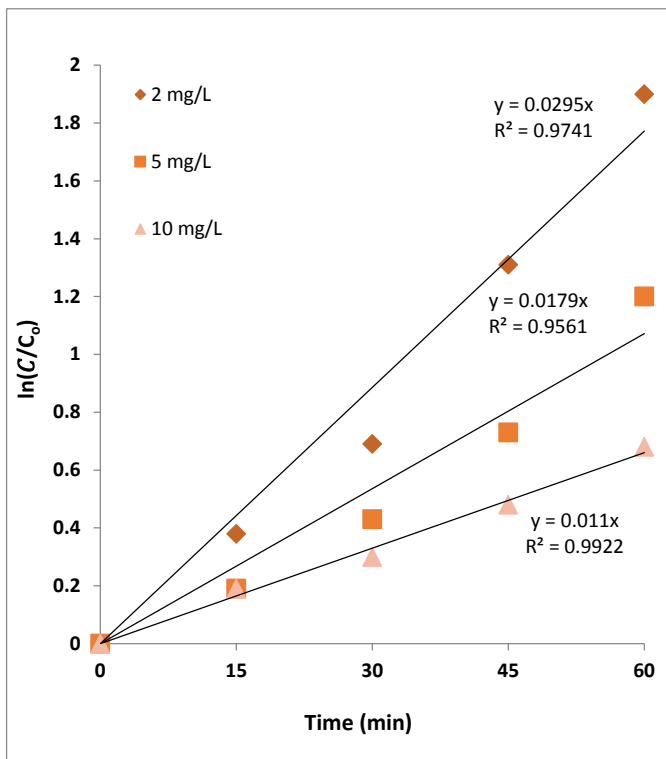
Where, k is the constant of the reaction rate (the constant of first order reaction), C is the remained concentration of the MTBE (mg/L), C<sub>0</sub> is the initial MTBE concentration (mg/L), and (t) shows the time of the reaction (min) respectively.

The slope of the ln (C/C<sub>0</sub>) against time under optimized conditions shows the constant reaction rate (k) for MTBE degradation [30]. Table 1 demonstrates the amounts of the and R<sup>2</sup> values of the linear regression.



**Figure 4:** Variation of different initial MTBE concentrations on degradation rate (PH = 7, C-N-TiO<sub>2</sub> dose = 100 mg/L, AFRs = 0.1 L/min, t = 1h)

While the initial MTBE concentration increases, constant rate of degradation decreases. The initial constant rates decreased from 0.0295 to 0.011 (1/min) as the MTBE concentration increased from 2 to 10 mg/L. The profiles on MTBE degradation rate were based on the first-order kinetics model.



**Figure 5:** The effect of initial MTBE concentration on constant reaction rate (k) using UV/C-N-TiO<sub>2</sub> system (PH = 7, C-N-TiO<sub>2</sub> dose = 100 mg/L, AFRs = 0.1 L/min, t = 1h)

**Table 1:** Effect of initial MTBE concentration on degradation rate constant (k)

C <sub>0</sub> (mg/L)	k (1/min)	R <sup>2</sup>
2	0.0295	0.9741
5	0.0179	0.9561
10	0.011	0.9922

#### 4. Conclusion

In this work, C-N-TiO<sub>2</sub> nanoparticles were used as a nanoparticle for photocatalytic oxidation of MTBE under UV irradiation. The effects of different operational factors such as pH, catalyst loading, and initial concentration of MTBE on removal rate were investigated in a batch mode. The obtained results indicated that pH=7, catalyst amounts of 0.1 g/L, air flow rate (AFRs) = 0.1 L/min, and 60-minute UV irradiation could be an optimum condition to achieve to 80% MTBE removal. The profiles on MTBE oxidation rates were followed by the first-order kinetics model. The findings presented that UV/C-N-TiO<sub>2</sub> process is a reliable system for MTBE oxidation from aqueous solution.

#### Authors' Contributions

T.S., drafted the manuscript and analyzed the samples. A.A., supervised the study and wrote the manuscript. F.K., performed data Analysis. M.R.M., designed the study, directed the analysis of the study, and wrote the manuscript.

#### Conflicts of Interest

The Authors declare that there is no conflict of interest.

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