DEGRADATION OF METHYL TERTIARY BUTYL ETHER USING UV/TITANIUM DIOXIDE AND CARBON NANOTUBES

BY

MUSAH AHMED RUFAI MUHYEDEEN

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This thesis is written by Musah Ahmed Rufai Muhyedeen under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in **ENVIRONMENTAL SCIENCES.**

Thesis Committee

B.S. Tawabini 29 Sep 2012
Dr Bassam Shafiq Tawabini (Chairman)

3/10/2012
Dr Moataz Ali Atieh (Member)

8/10/2012
Dr Zain Hassan Yamani (Member)

Dr Abdulaziz Al-Shaibani
(Department Chairman)

Dr Salam A. Zummo
(Dean of Graduate Studies)

Date: 10/10/12

DEDICATION

To my family and friends...

ACKNOWLEDGEMENT

All praise and thanks is due to Allah; for it is by His Grace and Mercy that all things are possible.

Sincere and profound thanks go to my distinguished committee members; Dr Bassam Tawabini (Chairman), Dr Moataz Atieh and Dr Zain Yamani. Their guidance and motivation contributed to the successful completion of this work and I consider it an honour to have worked under their supervision. Also, the efforts of Dr Alaadin Bukhari, Dr Bassim Abussaud, Dr Anwar Ul Hamid, Dr Abbas Hakeem and Dr Mohammed Qamar are highly appreciated.

I am grateful to King Fahd University of Petroleum & Minerals for the opportunity to pursue my studies. I am especially thankful to everyone in the Earth Sciences Department, for the support and encouragement I received throughout the period of my study. I also appreciate the support I received from the Center of Excellence in Nanotechnology. The contributions of Messrs Abdul Rashid Mohammad, Ahmed Mahfouz, Mousa Amayreh, Jerwin Separa and Dan Cortes during sample preparation and characterization in this work are invaluable. To all my colleagues and friends; I appreciate all your advice, support and companionship.

Finally, I am deeply indebted to my family for being there for me.

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THESIS ABSTRACT

NAME: **MUSAH AHMED RUFAI MUHYEDEEN**

TITLE: **DEGRADATION OF METHYL TERTIARY BUTYL ETHER USING UV/TITANIUM DIOXIDE AND MULTI-WALLED CARBON NANOTUBES**

MAJOR FIELD: **ENVIRONMENTAL SCIENCES**

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The quality of water resources in a water-scarce country like the Kingdom of Saudi Arabia is an issue requiring a great deal of attention. Pollution from the production and use of chemicals poses a threat to the Kingdom's water resources. Methyl tertiary butyl ether (MTBE) is one such compound encountered in groundwater. MTBE is a fuel additive that replaced tetraethyl lead as the main anti-knocking agent and is used to enhance octane rating in refined fuels. Treatment of MTBE contaminated water by conventional methods (air stripping, adsorption onto activated carbon and biodegradation) is challenging due to its unique properties of high water solubility, low adsorption onto solids and resistance to biodegradation. Advanced oxidation processes (AOPs), however, seem to be a promising treatment option for water contaminated by MTBE and other organics. Photocatalysis is one form of AOPs that utilizes ultraviolet (UV) or visible light radiation in combination with a semiconductor photocatalyst. In this study, titanium dioxide (TiO_2), multi-walled carbon nanotubes (MWCNT) and TiO_2 supported on MWCNT (TiO_2-MWCNT) composites were used in combination with ultraviolet (UV) light radiation to photocatalytically degrade MTBE in spiked water samples. The removal of MTBE as well as its expected degradation by-products: acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF) were studied under different experimental conditions; TiO_2, MWCNT and TiO_2-MWCNT dosage (1 mg, 10 mg and 20 mg) and UV light intensity (0.98 mW/cm^2, 1.12 mW/cm^2 and 2.17 mW/cm^2) were examined. MTBE removal was found to be mainly due to the photocatalytic effect of TiO_2 (with removal rates reaching up about 95% after treatment). MWCNTs with UV light also demonstrated limited removal capabilities (with removal rates up to 68.21%); though the mechanism by which this happens is not fully understood. The prepared TiO_2-MWCNT composites however showed the lowest removal rates.

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ملخص الرسالة

الإسم: **موسى أحمد رفاعي محي الدين**

العنوان: **تحليل مادة م. ت. ب. إي. بإستخدام الأشعة فوق البنفسجية وثاني أكسيد التيتانيوم وأنابيب الكربون النانوية المتعددة الجدران**

التخصص: **العلوم البيئية**

التاريخ: **يوليو 2012 م**

إن نوعية الموارد المائية في بلد يعاني من ندرة المياه مثل المملكة العربية السعودية هي مسألة تتطلب قدرا كبيراً من الاهتمام. يشكل التلوث الناجم عن إنتاج واستخدام المواد الكيميائية تهديداً لموارد المياه في المملكة. وتعتبر مادة " الميثيل ثلاثي ايثر بوتيل " (م. ت. ب. إي.- MTBE) واحدة من هذه المركبات الكيميائية تتواجد أحيانا في المياه الجوفية. إن مادة م. ت. ب. إي. من مضافات الوقود والذي يحل محل رباعي إيثيل الرصاص وتستخدم أيضاً لتحسين نسبة الأوكتان. إن معالجة المياه الملوثة بمادة م. ت. ب. إي. بالطرق التقليدية (تجريد الهواء ، الامتصاص على الكربون المنشط والتحلل البيولوجي) تتصف بالتحدي بسبب خصائصها من حيث الذوبان العالي للماء ، والامتصاص المنخفض على المواد الصلبة ومقاومتها للتحلل. لكن تبدو عمليات الأكسدة المتقدمة خياراً واعداً لعلاج المياه الملوثة بمادة م. ت. ب. إي. والمواد العضوية الأخرى. كما يعتبر التحفيز الضوئي مثالا لعمليات الأكسدة المتقدمة التي تستخدم الأشعة فوق البنفسجية أو أشعة الضوء المرئي بالتوافق مع حافز ضوئي شبه موصل. في هذه الدراسة المعملية ، ُاستخدم كل من ثاني أكسيد التيتانيوم وأنابيب الكربون النانوية المتعددة الجدران وثاني أكسيد التيتانيوم المُدعم بأنابيب الكربون المصغرة المتعددة الجدران بالتوافق مع الأشعة فوق البنفسجية لتُحلل مادة م. ت. ب. إي. من خلال التحفيز الضوئي في عينات المياه. تمت دراسة عملية إزالة مادة م. ت. ب. إي. ، إضافة للمنتجات المصاحبة للتحلل الرئيسية: ثلاثي بوتيل الكحول والأسيتون تحت ظروف تجريبية مختلفة ، كما تم فحص جرعات من ثاني أكسيد التيتانيوم وأنابيب الكربون المصغرة المتعددة الجدران وثاني أكسيد التيتانيوم المُدعم بأنابيب الكربون المصغرة المتعددة الجدران ، بالإضافة إلي فحص شدة الأشعة فوق البنفسجية . وتم التوصل إلى أن السبب الرئيسي لإزالة مادة م. ت. ب. إي. كان نتيجة لتأثير التحفيز الضوئي لمادة ثاني أكسيد التيتانيوم (بمعدلات إزالة تصل إلي نحو 95 % بعد المعالجة). أوضحت القدرة الاستيعابية للإزالة والمُبينة من خلال أنابيب الكربون المصغرة المتعددة الجدران والأشعة فوق البنفسجية (بمعدلات إزالة تصل إلي نحو 68.21 %) على الرغم من عدم الفهم التام للطريقة التي تتم بها هذه العملية. بينما أظهرت مركبات ثاني أكسيد التيتانيوم المُدعم بأنابيب الكربون المصغرة المتعددة الجدران أدنى معدلات للإزالة.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران - المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Issues related to the availability and 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 but a few factors affecting the supply and quality of available water resources (Likodimos et al., 2010).

The Middle East and North African region is the most water-scarce in the world, having less than 1000 cubic meters of renewable freshwater per person per year (Roudi-Fahimi et al, 2002). The Kingdom of Saudi Arabia is located within this region of the world where the prevailing conditions are generally semi-arid to arid; characterised by high temperatures and evaporation rates. There are no permanent streams so groundwater and desalinated water are relied on heavily for water supply. The National Ground Water Association (NGWA) which is based in the United States of America estimates that about 32% of people living in the Asia-Pacific region depend on groundwater for drinking purposes. According to the United Nations Economic and Social Commission for

Western Asia, two-thirds of the water in Saudi Arabia comes from groundwater. It was estimated that total water withdrawal in the year 2006 was about 23.7 km^3 (an increase of 40% compared to 1992), and that groundwater constituted about 90% of this water withdrawn (AQUASTAT, 2008). This is shown in Figure 1 below.

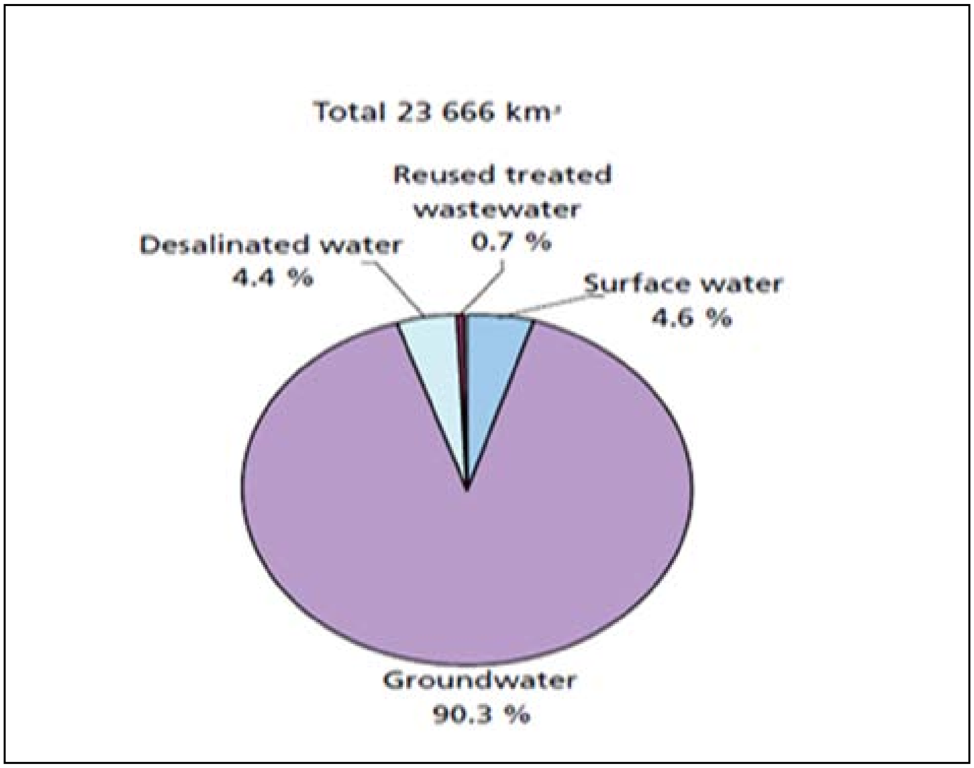


Figure 1: Water withdrawal by source in Saudi Arabia for 2006. (AQUASTAT, 2008)

Yet, excessive withdrawal is not the only threat to groundwater supply in Saudi Arabia. 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 (Manahan, 2005).

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 (Zang and Farnood, 2005). Its presence in the environment, particularly water, is however an issue of concern due to its human health implications. Remediation of water contaminated with MTBE by conventional treatment methods is challenging due to its high water solubility, low adsorption onto solids and resistance to biodegradation, thus making it quite persistent in the environment (Day et al., 2001; Eslami et al., 2009).

Saudi Arabia is highly endowed with oil and gas resources and as such ranks among the leading oil producing countries in the world (Organization of Petroleum Exporting Countries Annual Statistical Bulletin, 2009). Efforts to diversify the country's oil-based economy have led to rapid development of a petrochemical industry. The Kingdom is now among the world's leading manufacturers of petrochemicals including ethylene, methanol and MTBE (http://www.sabic.com). Due to continued production and use, MTBE has been released into the environment and thus poses a significant threat most especially to the Kingdom's non-renewable fossilized groundwater. The quest now is to seek sustainable, efficient and cost-effective approaches that can degrade recalcitrant organic compounds, such as MTBE, that are present in water.

Advanced oxidation processes (AOPs) have been identified as promising for treatment of water contaminated with pollutants such as MTBE (Squillace et al., 1997). These processes make use of hydroxyl radicals (OH•) and can oxidize all organic pollutants present in water (Ray et al., 2006). The hydroxyl radicals are generated either by one or a combination of the following sources: ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's reagent, ultraviolet (UV) radiation, electron beam, ultrasonic waves and photocatalysis with a semiconductor. AOPs are capable of removing both low and high levels of organic pollutants present in water. Studies using: ozone (Vel et al., 1994), hydrogen peroxide (Yeh and Novak, 1995), Fenton's reagent (Xu et al., 2004), UV/peroxide (Wagler and Malley, 1994) and gamma radiolysis (Hsieh et al., 2004) have yielded favourable outcomes. Among these forms of AOPs, photocatalysis is regarded as effective; with titanium dioxide (TiO_2) as the preferred photocatalyst (Chong et al., 2010).

Applications of nanomaterials in water treatment have also been promising. However, combining TiO_2 and CNTs could be considered a novel composite material where there are few publications on their photocatalytic properties (Woan et al., 2009). Considering the benefits in terms of safeguarding water resources and also reducing treatment costs, more research needs to be undertaken in this area.

1.2 SIGNIFICANCE OF THE STUDY

In a country like Saudi Arabia faced with shortage of freshwater resources, it is imperative that water is kept free from pollution in order to partly ease the effects of water scarcity. With the extensive industrialization drive being pursued in the country, the quality of limited groundwater resources is threatened by pollution from MTBE as a result of high production levels and widespread use of MTBE. Treatment options currently available for MTBE removal are inefficient and costly (Sutherland et al., 2004). Considering the health impacts associated with MTBE exposure identified in the Drinking Water Advisory of the United States Environmental Protection Agency (EPA, 1997), there is a need to develop techniques which are environmentally friendly and cost effective and also efficient in removing MTBE from water.

1.3 OBJECTIVES

The main aim of this study is to develop a bench-scale water treatment technique that efficiently removes MTBE and its main degradation by-products: acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF) from water using the combined mechanisms of TiO_2-photocatalysis and adsorption by multi-walled carbon nanotubes (MWCNTs). The specific objectives are:

1. To demonstrate the removal of MTBE as well as its degradation by-products from MTBE-spiked water using:
    - Titanium dioxide (TiO_2)
    - Multi-walled carbon nanotubes (MWCNTs)
    - TiO_2 deposited on MWCNTs (TiO_2-MWCNT)
2. To examine MTBE removal efficiency under varying conditions of TiO_2 and MWCNT dosage and UV light intensity
3. To identify the most efficient treatment condition in removing MTBE and its degradation by-products (acetone, TBA and TBF) from contaminated water.

CHAPTER 2

LITERATURE REVIEW

2.1 METHYL TERTIARY BUTYL ETHER (MTBE)

MTBE ($C_5H_{12}O$), shown in Figure 2, is an organic compound produced from methanol and isobutylene.

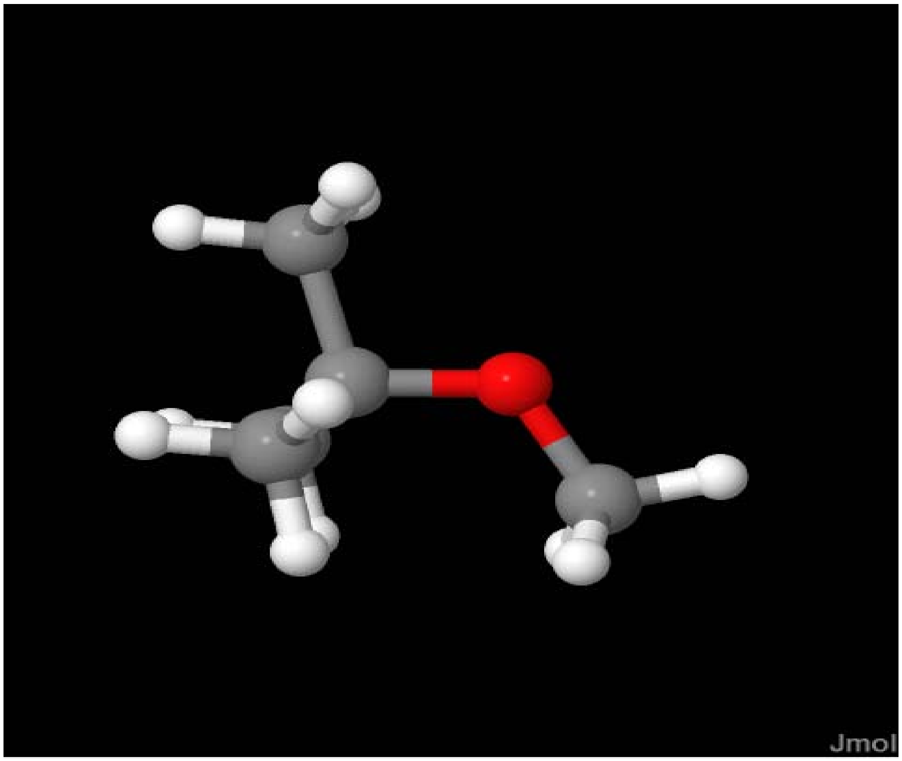


Figure 2: 3D chemical structure of MTBE (Source: http://www.chemspider.com)

It was introduced as a fuel additive in the late 1970’s to improve octane rating and replace tetraethyl lead as the main anti-knocking agent. It is a volatile, flammable and colourless liquid that is soluble in water. The California Office of Environmental Health Hazard Assessment (OEHHA) in a report in 1999 identified MTBE as being the preferred oxygenate in fuels because of its low production costs and the fact that it is readily miscible with other fuel components. Its addition has enhanced the burning of fuels and improved air quality by reducing harmful emissions such as nitrogen oxides (NO_x), carbon monoxide (CO) and ozone (O_3) (Zang and Farnood, 2005; Kuburovic et al., 2007). Kolb and Puttmann (2006) estimated that about 20 million tons of MTBE is used worldwide annually.

The use of MTBE is however not devoid of environmental implications; as it appears to have impacted negatively on groundwater supply (Rong, 2001). Its presence in aquatic environments is mainly through leaks from underground fuel storage tanks, transferring pipelines, fuel spills and defective construction at gas stations (Johnson et al., 2000). Emissions from gasoline use have also been suggested as a leading source of MTBE in the environment (MEF, 2001).

The main concern however is with its human health effects, symptoms of which include headache, cough, nausea dizziness and skin irritation (Barcelo and McGregor, 2007). Belpoggi et al., (1995) showed that exposure to MTBE caused an increase in cell tumours, lymphomas and leukaemia in rats. The United States Environmental Protection

Agency (EPA) has classified MTBE as a potential human carcinogen and recommended a concentration limit of 20 to 40 μg/L in drinking water in order to avoid undesirable odour and taste problems (USEPA, 1997). The California Department of Health Services has gone further to set a secondary maximum contaminant level of 5 μg/L for MTBE in community water systems (CDPH, 2009).

MTBE's high solubility in water, chemical and biological stability and poor adsorption onto solids makes it very persistent in the environment (Shaffer and Uchrin, 1997; Day et al., 2001; Eslami et al., 2007). These properties also make it difficult to treat water contaminated with MTBE using conventional treatment methods such as air stripping, activated carbon adsorption and biodegradation (Anderson, 2000).

Sutherland et al., (2004) concluded that air stripping was inefficient in removing MTBE from water at low temperatures. MTBE is capable of being adsorbed onto granular activated carbon as demonstrated by Shih et al., (2003). However, competition for adsorption sites with other compounds as well as higher treatment costs makes this option less desirable for MTBE removal. Bioremediation of MTBE is difficult and slow due to the presence of an ether bond and a tertiary carbon in its structure, which inhibits environmental degradation under normal conditions and natural biodegradation (Suflita and Mormille, 1993; Yeh et al., 1995; Steffan et al., 1997; Fayolle et al., 2001). Nonetheless, research has shown that some microbes are capable of metabolizing MTBE, even on the field-scale (Salanitro et al., 2000). However, there still the need for cost-effective and efficient methods for treating MTBE present in water.

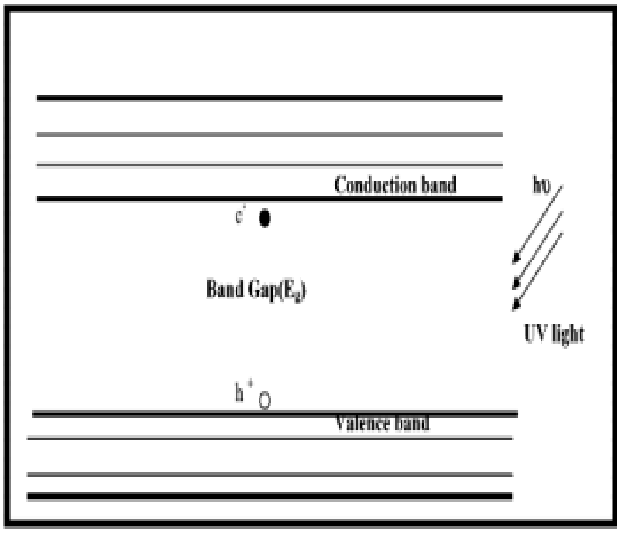
2.2 ADVANCED OXIDATION PROCESSES (AOPs)

AOPs have proven to be a feasible treatment option for water contaminated with refractory, toxic and non-biodegradable materials (Ray et al., 2006). Squillace et al., (1997) also highlighted these processes as a promising choice for removal of MTBE from water. The main merit of AOP's is the ability to completely mineralize organic compounds. AOP's can also be used as preliminary treatment to enhance the biotreatment of water containing recalcitrant organic pollutants (Kuburovic et al., 2007).

AOPs utilize highly reactive hydroxyl (OH•) radicals to degrade pollutants in water. The hydroxyl radicals are generated either by one or a combination of the following sources: ozone (O_3), hydrogen peroxide (H_2O_2), Fenton's agent, ultraviolet (UV) radiation, electron beam, ultrasonic waves and photocatalysis with a semiconductor (Ray et al., 2006). Previous studies on the effectives of O_3/UV (Garoma et al., 2008), O_3/H_2O_2 (Acero et al., 2001; Mitani et al., 2002), UV/H_2O_2 (Chang and Young, 2000; Stefan et al., 2000), Fenton's reaction (Ray and Selvakumar, 2000), electrocatalytic oxidation (Wu, 2007) and photocatalytic degradation with titanium dioxide (TiO_2) (Zang and Farnood, 2005; Xu et al., 2006), all yielded limited results. Optimally these techniques should completely degrade MTBE into carbon dioxide and water; however the by-products from incomplete oxidation of MTBE are of great concern due to their toxicity. Acetone, tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF) are the main intermediates detected during MTBE degradation (Selli et al., 2005; Eslami et al., 2007). Some toxicological studies suggest that TBF and TBA may present greater health hazards than MTBE (Froines, 1998).

2.3 TiO_2 PHOTOCATALYSIS

Photocatalytic degradation is one of the most widely preferred AOPs that utilize UV radiation in combination with a semiconductor photocatalyst (Kuburovic et al., 2007). The degradation process is based on the action of electron/hole (e^-/h^+) pairs which are formed in the conduction and valence bands of the semiconductor, respectively, when a semiconductor is irradiated with UV light with energy greater than its band gap as depicted in Figure 3 (Kabra et al., 2004).



$$h\nu + \text{semiconductor} \rightarrow h^+ + e^-$$

Figure 3: Band-gap diagram showing the formation of holes (h^+) and electrons (e^-) upon irradiation of UV on a semiconductor surface.

These charges move to the surface of the photocatalyst where they decompose water molecules into hydroxyl radicals and oxidize adsorbed organic molecules (Klauson et al., 2008; Eslami et al., 2008). Oxygen adsorbed onto the surface of the semiconductor is the main electron acceptor and also reacts to generate superoxide radicals, $O_2^{\bullet -}$, which also play a part in the degradation process. This reaction resulting in superoxide radicals is also very significant in reducing electron-hole recombination and thus enhancing the effectiveness of the oxidative process (Zalazar et al., 2005).

Semiconductor photocatalysis is expected to complement conventional treatment techniques. Ttitanium dioxide (TiO_2) is generally the preferred semiconductor (Eslami et al., 2007; Likodimos et al., 2010). TiO_2 is the most common compound of titanium and has many uses. It is close to being an ideal photocatalyst due to its relatively low cost, non-toxicity and photo-stability (Hoffman et al., 1995; Fujishima et al., 2000; Eslami et al., 2009).

Photocatalysis with TiO_2 under optimum conditions is capable of oxidizing organic pollutants without leaving harmful end products (Likodimos et al., 2010). The anatase and rutile forms of TiO_2 require radiation of wavelength between 300-400 nm in order to be activated. This can be provided by commercially available UV lamps. About 5% of solar radiation reaching the earth possesses this range of wavelength, thus making it possible to utilize sunlight to activate TiO_2 (Matthews, 1984; Likodimos et al., 2010). The energy required to activate the anatase form of TiO_2 is 3.25 eV. The activation leads to the formation of hydroxyl radicals (OH•) and superoxide ions ($O_2^{\bullet -}$) that are capable of degrading organic pollutants (Carp et al., 2004). Ray et al., (2006) and Eslami et al., (2009) summarized the main steps involved in this process in the equations below:

$TiO_2 + h\nu \rightarrow \text{(holes) } h^+_{vb} + e^-_{cb}$ .... (1)

$h^+ + H_2O\text{ (ads)} \rightarrow OH^{\bullet} + H^+$ .... (2)

$h^+ + OH^-\text{ (ads)} \rightarrow OH^{\bullet}$ .... (3)

$e^- + O_2 \rightarrow O_2^{\bullet -}$ .... (4)

where: $h\nu$ - incident radiation, h^+_{vb} – holes formed in the valence band of the semiconductor, e^-_{cb} – electrons formed in the conduction band of the semiconductor.

The photocatalytic properties of TiO_2 was improved by the doping with metals such as gold (Orlov et al., 2007) and copper (Arana et al., 2008). Also, doping with carbon, sulphur and nitrogen have all shown improved photocatalytic activity (Reddy et al., 2005). However, a challenge faced still during photocatalysis is the difficulty in separating the catalyst from the aqueous phase after treatment. This has led to the emergence of new techniques which focus on photocatalyst deposition on a solid support (Arana et al., 2008).

2.4 NANOMATERIALS

Nanomaterials have a structural feature of less than 100 nm in at least one dimension. They have improved properties which tend to change their optical, electrical and chemical functionalities (Gogotsi, 2006). For example, the very high surface area in nanomaterials increases the number of atoms on the surface thus making more electrons available for catalytic reaction on the surface. Nanomaterials therefore tend to be more reactive than bulk materials in catalytic processes.

Advances in nanotechnology have contributed to the discovery of various nanomaterials that have proven effective in the treatment of water (Upadhyayula et al., 2009). TiO_2-carbon nanotubes combination seems to be an attractive alternative in the removal of contaminants due to the remarkable optical, mechanical, electrical and thermal properties that TiO_2 and carbon nanotubes possess (Eder and Windle, 2008). Xia et al., (2007) demonstrated improved photocatalytic reactions for TiO_2 deposited on multi-walled carbon nanotubes (MWCNTs) in the reduction of carbon dioxide with water. Enhanced photocatalytic degradation of phenol by TiO_2-carbon nanotubes has also been reported by Yao et al., (2008).

A review of available literature revealed a dearth of information on the subject of MTBE degradation using TiO_2 and CNT combination. In this study, TiO_2, MWCNTs and impregnated TiO_2-MWCNTs composites were investigated in order to find their possible practical use in the photocatalytic degradation of MTBE in water.

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

- Tert-butyl methyl ether (MTBE) solution: 99.5% MTBE solution purchased from Sigma-Aldrich was used to prepare all the aqueous MTBE solutions.
- Tert-butyl alcohol (TBA): ≥ 99.5% Tert-Butanol anhydrous was purchased from Sigma-Aldrich
- Tert-butyl formate (TBF): 1000 µg/mL tert-butyl formate in methanol standard was obtained from SPEX CertiPrep.
- Acetone: analytical grade solution, assay (GC) – 99.5% was obtained from Scharlau.
- Nitric acid (HNO_3): assay – 69.0-71.0% was purchased from Loba Chemie PVT Ltd.
- Sodium hydroxide (NaOH) pellets were obtained from Merck
- Titanium (IV) isopropoxide - This was used as a titanium dioxide precursor for the synthesis of TiO_2-MWCNT composites; was obtained from Acros Organics.

- Titanium (IV) oxide 99% anatase powder - Titanium (IV) oxide 99% anatase powder was obtained from Acros Organics.
- Multi-walled carbon nanotubes (MWCNTs): 95 wt% purity MWCNT were obtained from Cheaptubes Inc. It was used as starting material (diameter: 8-15 nm, length: 10-50 µm).

3.2 SYNTHESIS OF NANOMATERIALS: TIO_2-MWCNT COMPOSITE

TiO_2-MWCNT composite was prepared using a modified sol-gel synthesis method (Eder and Windle, 2008). To prepare 5g of 5% TiO_2-MWCNT, 0.25g of titanium isopropoxide, was added to 4.75g MWCNT and dissolved in 200 ml of ethanol. The resulting mixture was then stirred to obtain a homogenous solution. The solution was sonicated using a probe sonicator for an hour. The mixture was then rinsed with deionized water. Calcination at 350°C was carried out for three hours. The resulting material was then cooled and stored.

The synthesized material was characterized using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). A Tescan Lyra 3 FE-SEM model was used to observe the surface morphology of the synthesized materials. The samples were sputtered with a thin layer of gold to minimize charging effect. Secondary electron (SE), as well as low voltage back scattered electron imaging were carried out. The high contrast BSE detector was mounted below the objective pole-piece and directly above the sample in order to obtain high resolution images at low kV. SEM micrographs were obtained at magnifications up to 100,000x.

An attached energy dispersive x-ray (EDX) detector (Oxford INCA Penta FETx3) was used to examine the elemental composition of the materials. This detector was equipped with an atmospheric thin window capable of detecting elements down to Be.

A Rigaku Ultima IV MPD X-ray diffractometer fitted with a monochromator was used to determine the phase constitution of the materials. The diffraction spectra were generated using a Cu Kα radiation ($\lambda = 1.54184$°A) source operating at 40 kV and 40 mA. Samples were scanned at a rate of 1 degree per minute for diffraction angles (2θ) between 10 to 100 degrees. Peaks shown in the generated spectra were indexed using Rigaku PDXL software.

3.3 PREPARATION OF AQUEOUS MTBE SOLUTION

All aqueous MTBE solutions were prepared using water from a Milli-Q Direct water purification system from Millipore Corporation. The solutions (with concentration of about 1 ppm) were prepared by mixing pure MTBE with deionized water and stirred overnight to achieve a uniform solution (May et al., 2003). The solution was buffered to a pH of 7 using 0.01 N NaOH and 0.01 N HNO_3.

3.4 TREATMENT OF MTBE-SPIKED WATER

The experiments were carried out in a Luzchem LZC-4X photoreactor (Figure 4) that houses UV-A lamps. Recommended safety practices such as use of protective eye glasses and gloves were followed. UV-A lamps with wavelength of 350 nm were used in this study. The lamps were turned on approximately five (5) minutes before the start of each experiment and were kept on during sampling. A battery-powered portable sample carousel (Figure 5) with a clock-wise rotating motion was used to hold the samples. The flux readings of the lamps were measured with a Smart Sensor Digital Lux meter (AR 823).

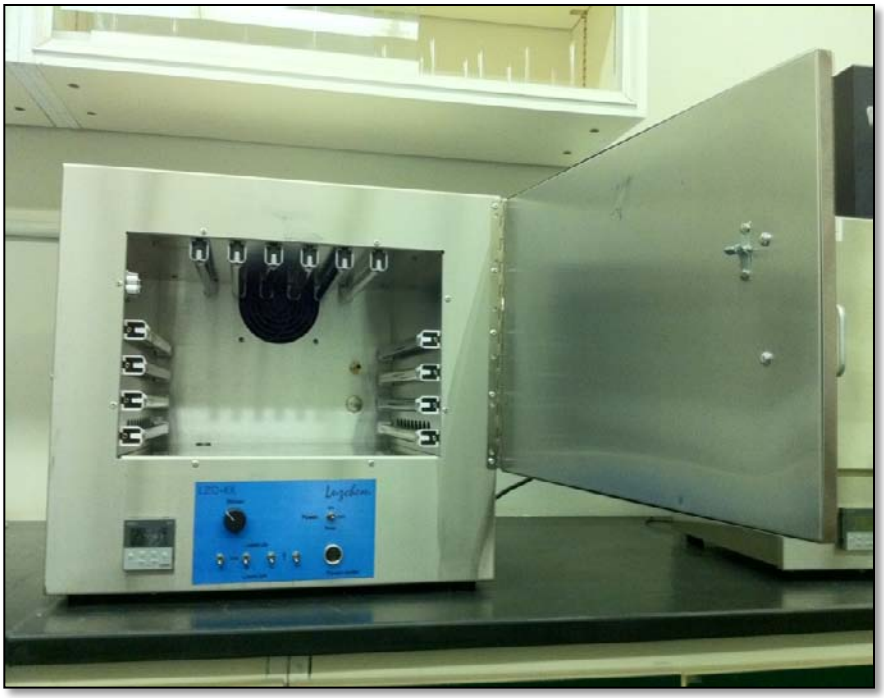


Figure 4: Luzchem LZC-4X UV Photoreactor.

All the experiments were performed in 10 mL quartz tubes. Specific doses (1 mg, 10 mg and 20 mg) of TiO_2, MWCNT and 5% TiO_2-MWCNT were separately measured into the quartz tubes and then aqueous MTBE solution was added. The quartz tubes were then placed in the portable carousel. The carousel was then turned on to begin rotating and then placed in the photoreactor with the lamps turned on. Each treatment run lasted for two hours. The quartz tubes containing TiO_2 had a milky colour; with the powder settled at the bottom of the tube shortly after addition of the MTBE solution. The tubes containing 5% TiO_2-MWCNT and MWCNT also had most of the materials settled at the bottom of the tube and few particles in suspension. The quartz tubes were agitated in order to release the settled particles into suspension. At half an hour intervals, 1 mL of the samples was collected from the tubes and filtered with a 0.22 µm membrane Millipore filter paper into vials. The collected samples were refrigerated at 4°C pending analysis.

Figure 5: Portable sample carousel holding the quartz tubes.

3.5 ANALYSIS OF MTBE AND ITS BY-PRODUCTS

The refrigerated samples were allowed to stand for several hours at room temperature before analysis to ensure that equilibrium between the vapour phase and the liquid phase had been reached. One (1) mL of the collected samples was transferred to the headspace vial and placed onto the GC-MS instrument for analyses.

A Thermo Scientific Trace GC ultra gas chromatograph coupled with an ISQ single quadrupole mass spectrometer and combined with a TriPlus headspace and autosampler (Figure 6) was used in the determination of MTBE, acetone, TBA and TBF.

Figure 6: Thermo Scientific Trace GC ultra with ISQ mass spectrometer and TriPlus headspace and autosampler.

A series of calibration standards of MTBE and its expected by-products (acetone, TBA and TBF), shown in Appendix A, were prepared from standard solutions by serial dilutions. These were used to develop external calibration curves for all analytes of interest.

The gas chromatograph was fitted with a fused silica capillary gas chromatography column; Rtx-502.2 from Restek Corporation (length: 60 m; internal diameter: 0.32 mm; 1.80µm thickness). The Rtx-502.2 stationary phase is diphenylidimethyl polysiloxane. The temperature was programmed at 50°C and held for 1 min; then it was ramped at a rate of 20°C/min to 220°C and held for 1 min. The injection temperature was 200°C and samples were injected in a split ratio of 10. The vials were incubated at 80°C for 15 min in the headspace autosampler in order to volatilize the samples and allow for the gas phase to be drawn and injected. Syringe temperature was set at 90°C.

The mass transfer line temperature of the mass spectrometer was 220°C whiles the ion source temperature was 200°C. Electron ionization (EI) mode was used for analysis. The set mass range for MTBE was 72.50-73.50 amu; 42.50-43.50 amu for acetone and 58.50-59.50 amu for TBA and TBF. Selected ion monitoring was used to acquire ion current at only the mass to charge ratio values of interest, thus increasing the instrument's sensitivity. Helium was used as the carrier gas at a constant flow rate of 1.7 mL/min. The analysis of all samples was repeated twice.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF NANOMATERIALS

Field-emission scanning electron microscopy (FE-SEM), energy dispersive x-ray (EDX) and x-ray diffraction (XRD) were the techniques used to examine the anatase TiO_2 powder, MWCNT and the 5% TiO_2-MWCNT composite.

4.1.1 Characterization of TiO_2

The FE-SEM micrograph of anatase TiO_2 powder (Figure 7) showed that TiO_2 particles were agglomerated in spherical shapes showing the orbicular structure of anatase TiO_2 powder. Their average grain diameter was approximately 200 nm.

The EDX spectrum of TiO_2 powder (Figure 8) showed that titanium (Ti) (46.29 wt %) and oxygen (O) (53.71 wt %) were the major constituents.

The XRD patterns obtained for anatase TiO_2 powder (Figure 9) showed sharp set of peaks at 25.46, 37.94, 48.18, 55.207 and 70.44 degrees. All peaks were indexed as anatase phase of titania (TiO_2).

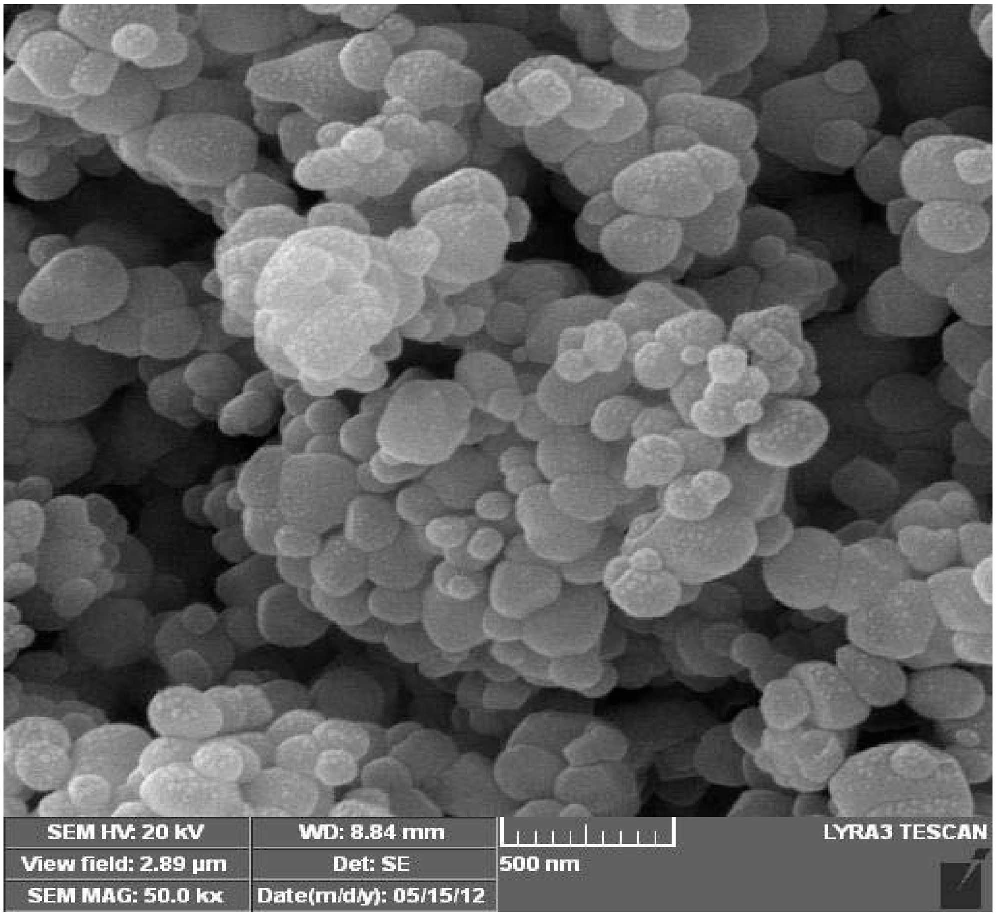


Figure 7: SEM-micrograph of anatase TiO_2 powder (Magnification: 50,000x)

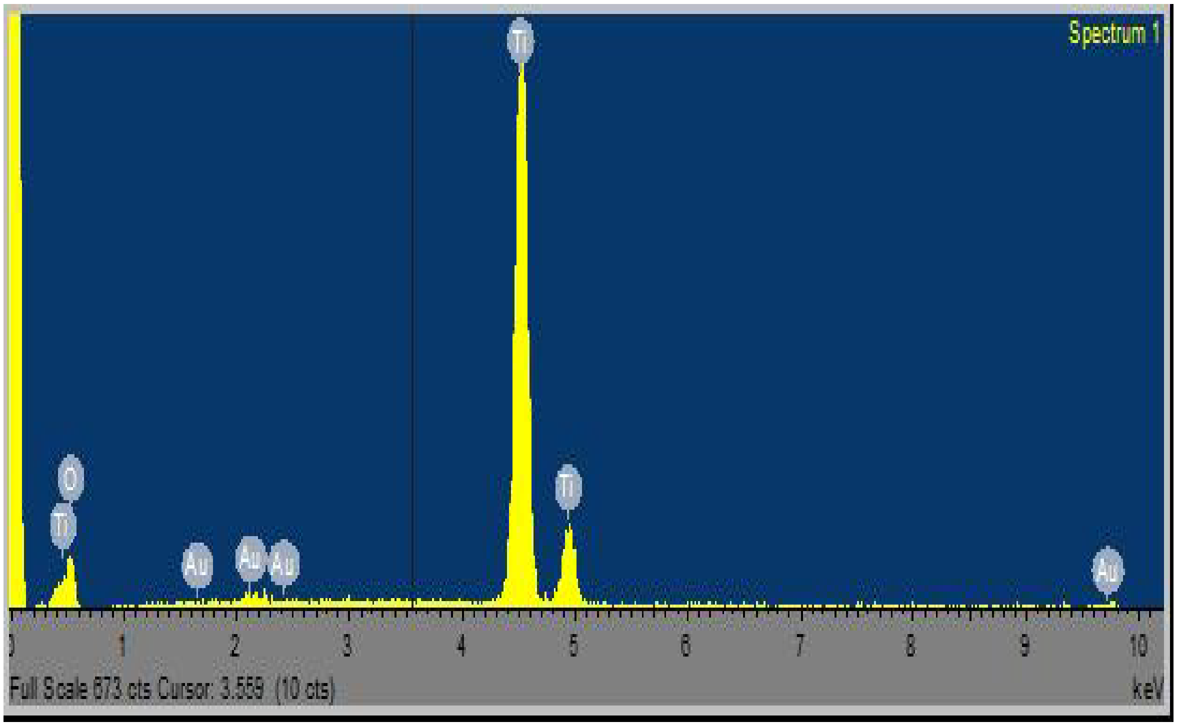


Figure 8: EDX spectrum of anatase TiO_2 powder

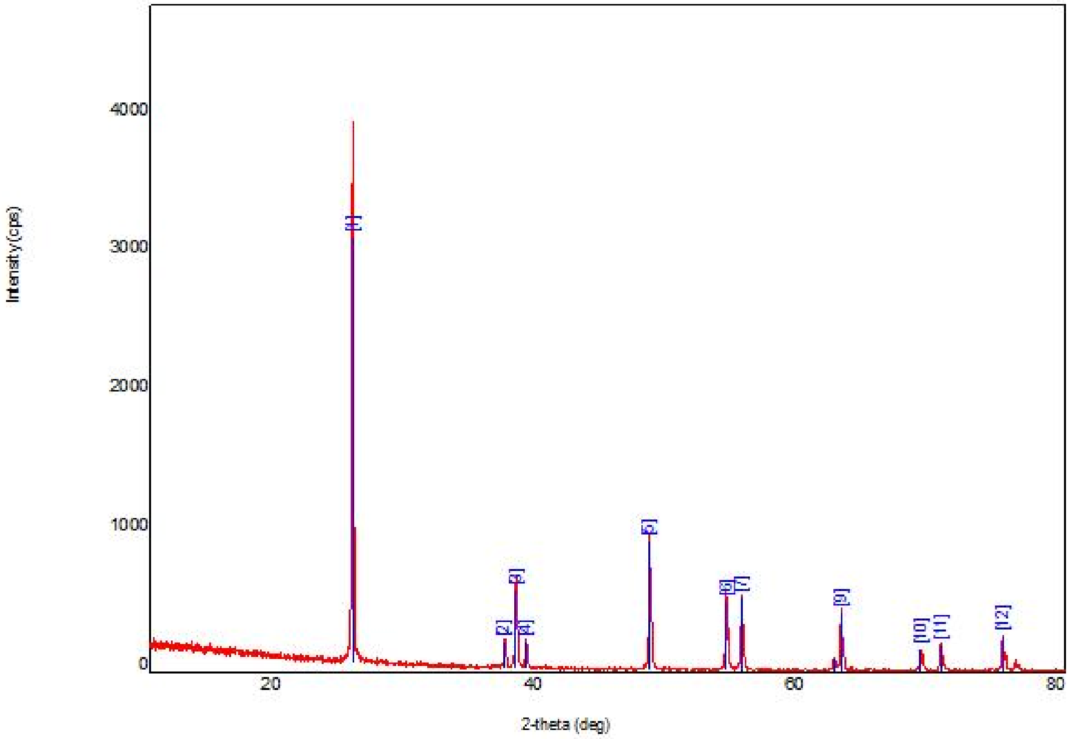


Figure 9: XRD spectrum for anatase TiO_2 powder

4.1.2 Characterization of MWCNT

MWCNT samples were seen to be winding, entangled and relatively disordered in constitution. Individual MWCNT with their cylindrical structure were more readily distinguishable at higher magnifications as shown in Figure 10. It is difficult to assess the exact dimensions of MWCNTs due to its interweaving structure but they appear to be approximately 50 nm in diameter.

The EDX spectrum of MWCNT (Figure 11) showed that carbon (C) (57.64 wt %) and oxygen (O) (53.71 wt %) were the major constituents.

The XRD spectrum for MWCNT (Figure 12) showed peaks at 25.62, 43.78 and 77.15 degrees corresponding to those of hexagonal graphite at 26.23 (002), 44.36 (101) and 77.18 (110) respectively. The peaks at 37.53 and 64.01 degrees could be attributed to the aluminium holder used to retain the sample during analysis.

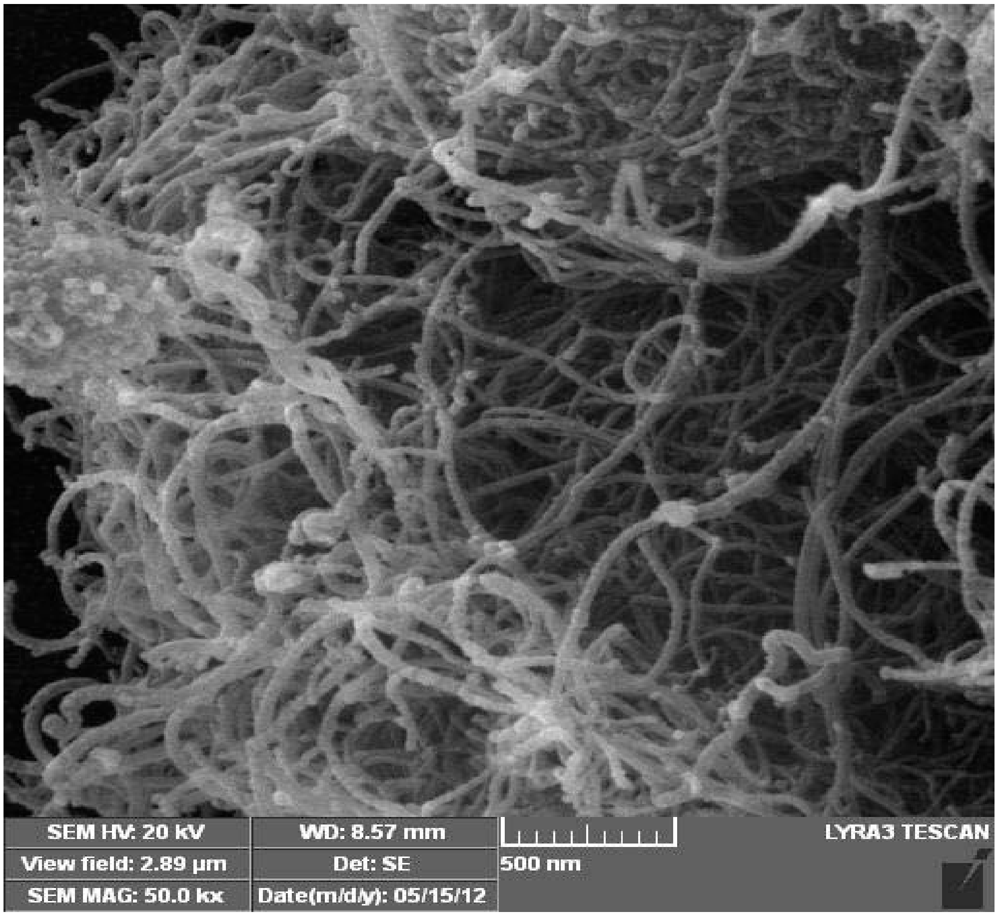


Figure 10: SEM-micrograph of MWCNT (Magnification: 50,000x)

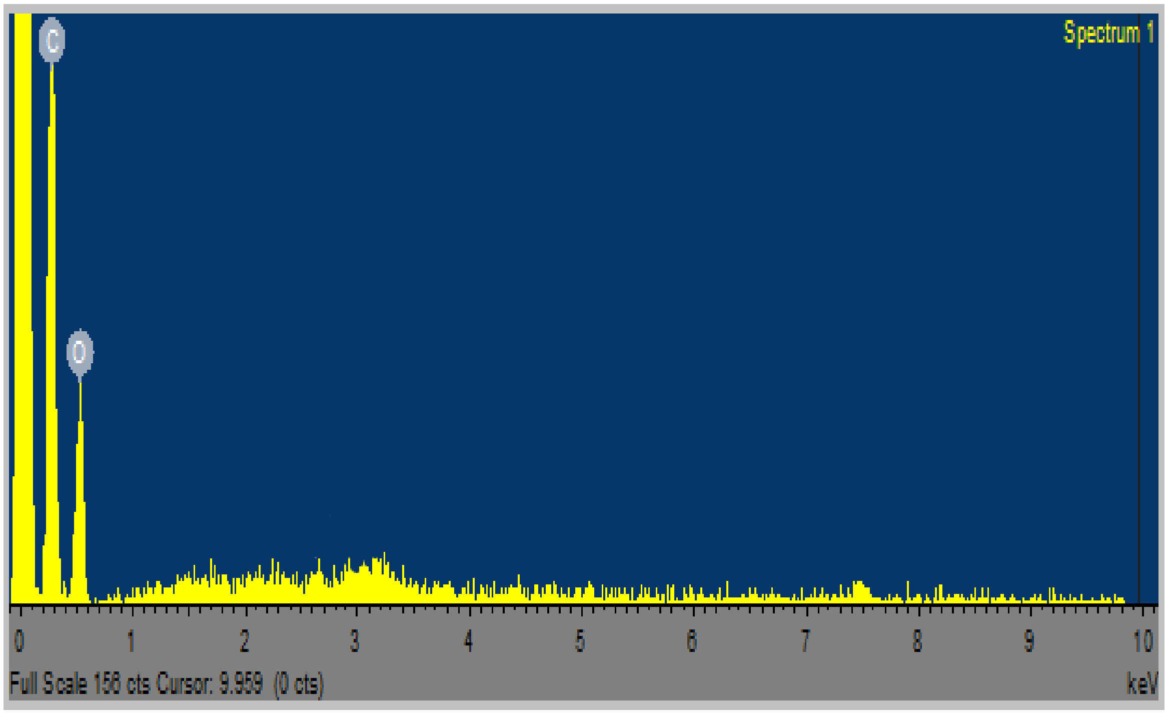


Figure 11: EDX spectrum of MWCNT

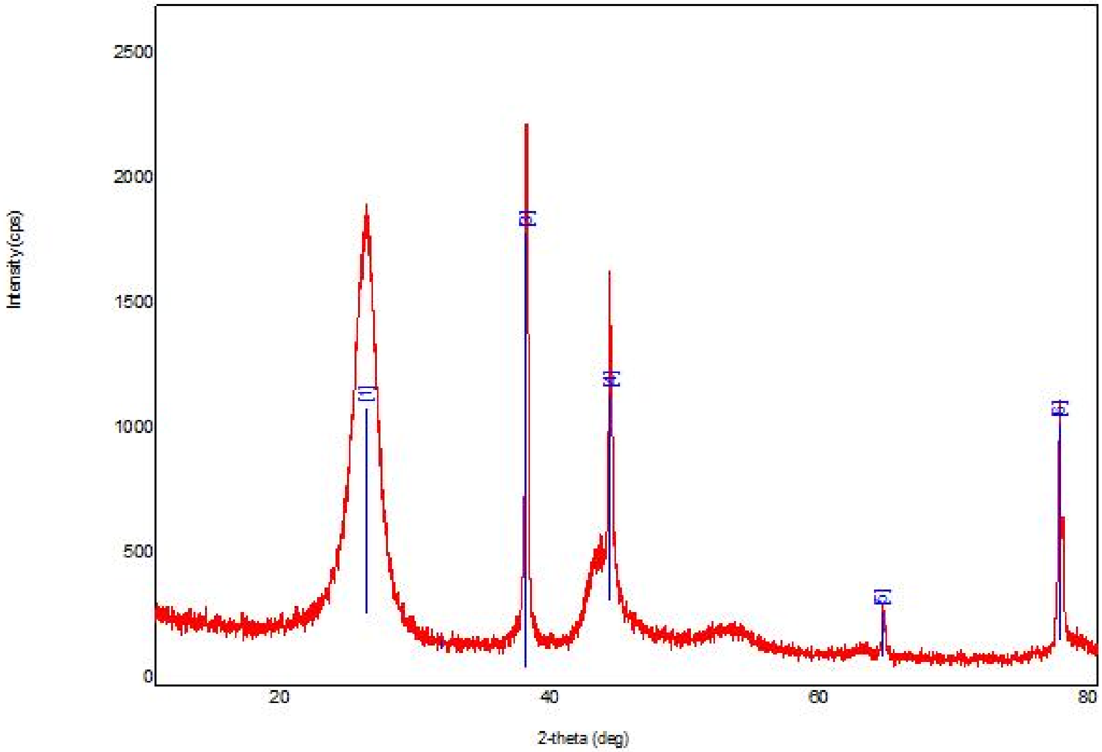


Figure 12: XRD spectrum for MWCNT

4.1.3 Characterization of 5% TiO_2

The micrograph of the 5% TiO_2-MWCNT composite showed that the surface structure of MWCNTs was primarily smooth, with low concentration of TiO_2 particles (highlighted in Figure 13) attached to its length. The TiO_2 particles had an average diameter of approximately 0.1 µm.

Microchemical analysis of the 5% TiO_2-MWCNT composite 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 EDX spectrum in Figure 14. This suggests that the fine particles found at the surface of the MWCNT were TiO_2. Generally, TiO_2 particles were dispersed homogeneously on the surface of MWCNTs with minimal agglomeration observed only at localized regions. Other unwanted peaks could be attributed to impurities.

The peaks in XRD spectrum of the 5% TiO_2-MWCNT composite (Figure 15) revealed that the graphite structure of the MWCNT (at these peaks: 25.98, 43.42 and 78.90 degrees) was still present after the deposition of TiO_2. TiO_2 peaks were also identified at 37.55 and 54.53 degrees. The peaks were broadened and lower in intensity compared to samples with anatase TiO_2 powder only and MWCNT only.

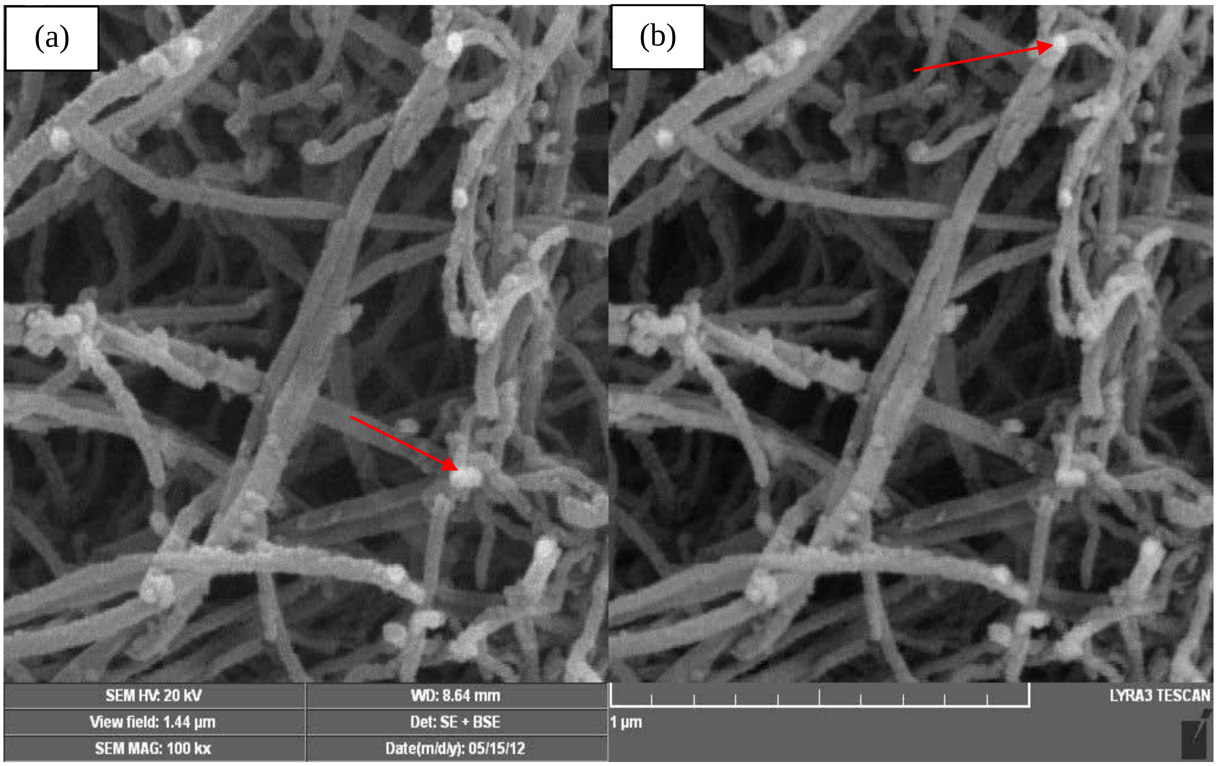


Figure 13: SEM-micrograph of 5% TiO_2-MWCNT – (a) Secondary electron image (b) Back scattered image (Magnification: 100,000x)

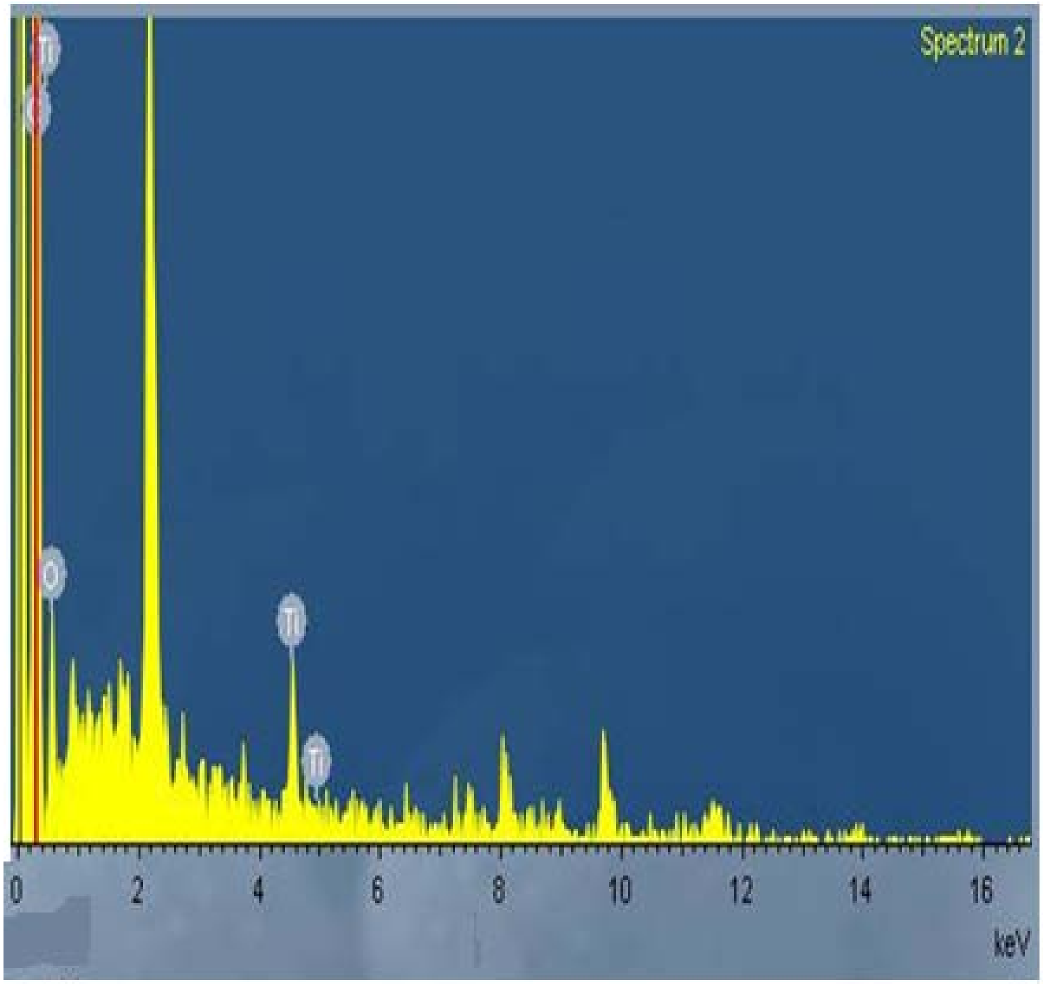


Figure 14: EDX spectrum of 5% TiO_2-MWCNT composite

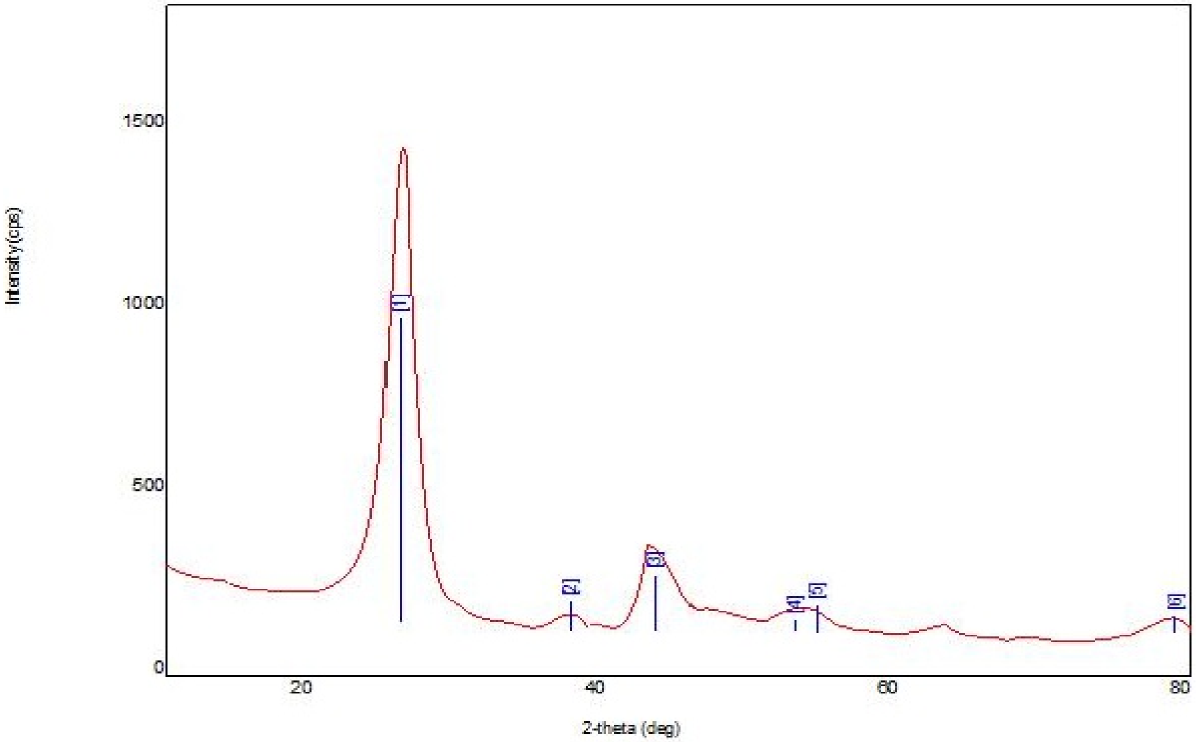


Figure 15: XRD spectrum for 5% TiO_2-MWCNT

4.2 DEGRADATION OF MTBE

The removal of MTBE as well as its expected degradation by-products (acetone, TBA and TBF) was studied under different experimental conditions; variation of TiO_2, MWCNT and TiO_2-MWCNT dosage and also UV light intensity.

4.2.1 Effect of pH on initial MTBE concentration

Experiments were carried out to ascertain the effect of pH on MTBE concentration. One (1) ppm MTBE solutions were prepared in buffer solutions of pH ranging from 4 to 9 and then analysed with the GC-MS to determine any change in the initial concentration. It was as observed, as seen in Figure 16 that it was only at approximately pH 7 that the concentration was optimum. Thus, all succeeding experiments were carried out at pH 7.

4.2.2 Blank Runs (Dark Experiments)

These experiments were conducted by running only aqueous MTBE solution, as well MTBE solutions with 5% TiO_2-MWCNT, TiO_2 and MWCNT in the photoreactor with the UV lamps turned off. This was to allow any system losses as well as other removal mechanisms such as adsorption to be quantified. Results of experiments showing residual MTBE after treatment with only 10 mg and 20 mg 5 % TiO_2-MWCNT, TiO_2 and MWCNT are depicted in Figure 17 and Figure 18 respectively.

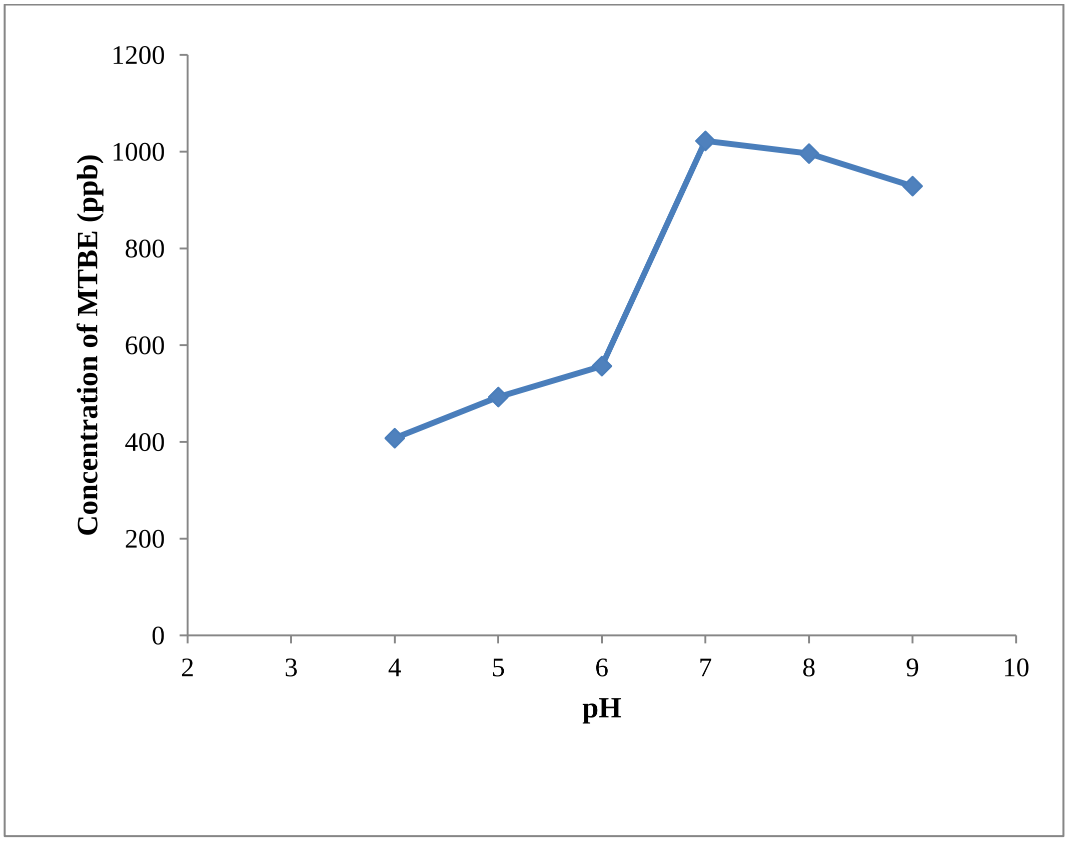


Figure 16: Effect of pH on initial MTBE concentration

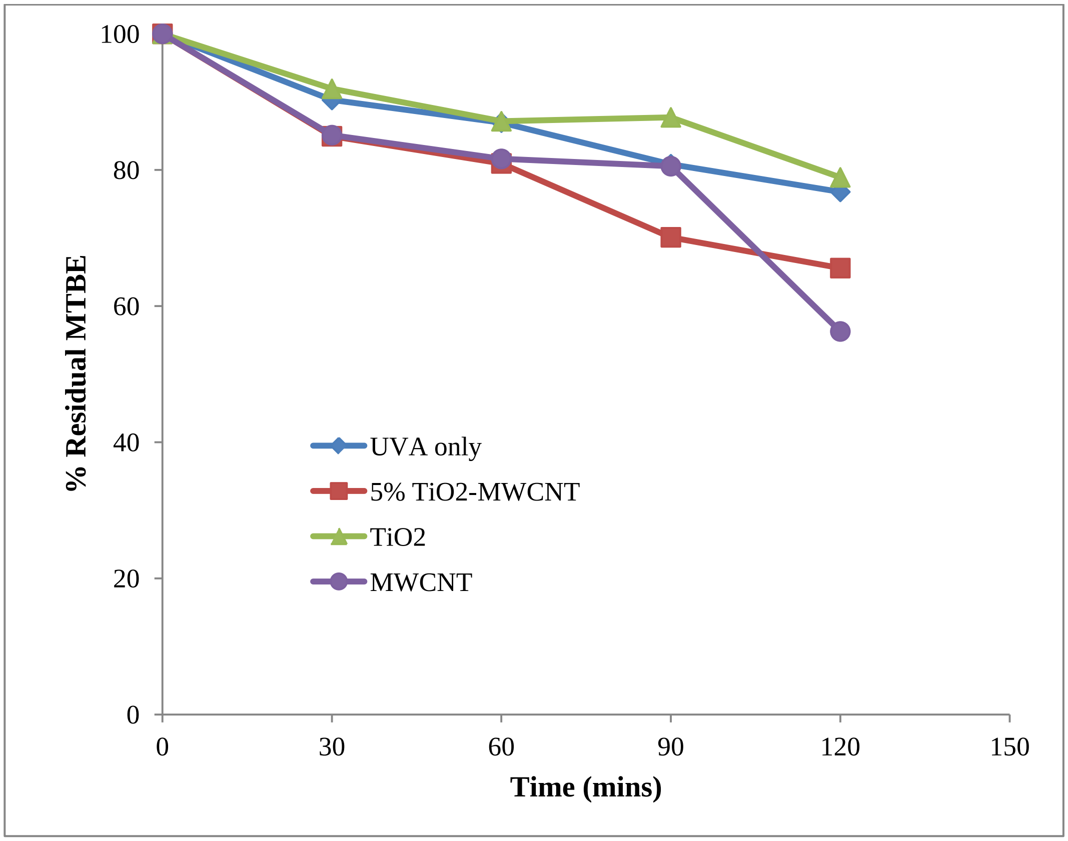


Figure 17: Dark experiment - % Residual of MTBE after treatment with 10 mg 5 % TiO_2-MWCNT, TiO_2 and MWCNT.

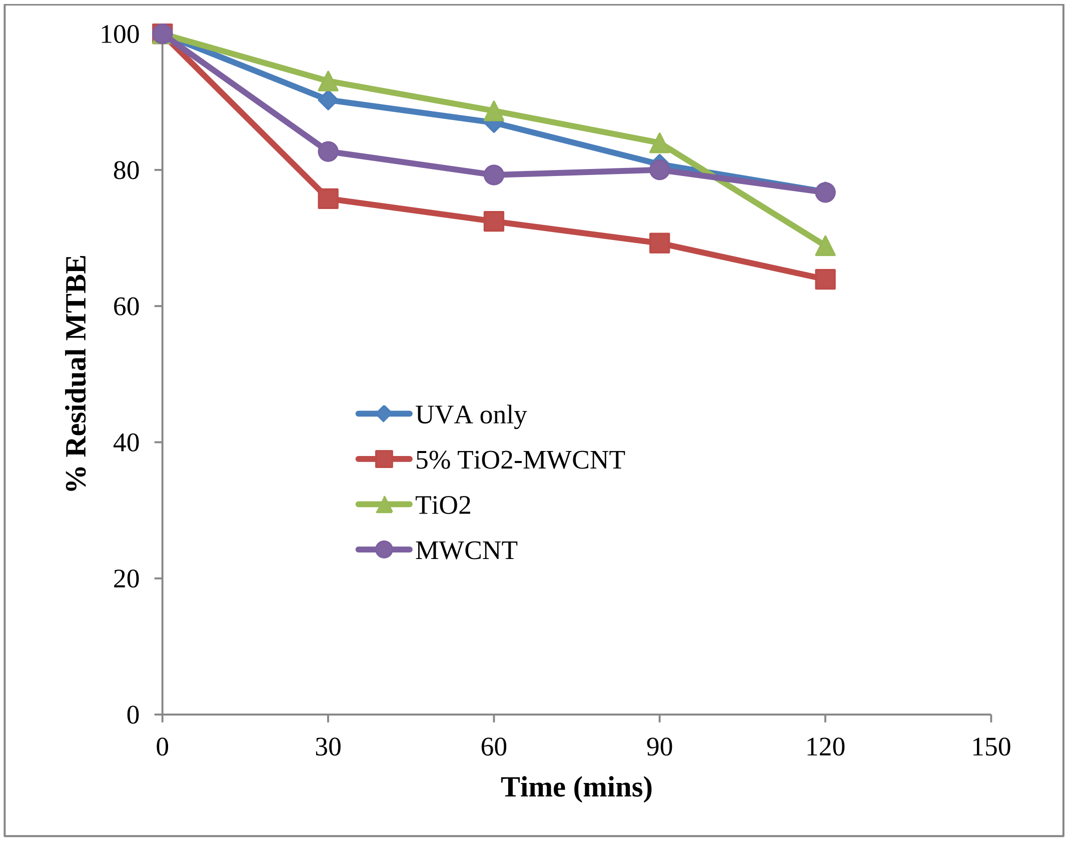


Figure 18: Dark experiment - % Residual of MTBE after treatment with 20 mg 5 % TiO_2-MWCNT, TiO_2 and MWCNT.

MTBE residual at the end of the two hour treatment run with 10 mg 5% TiO_2-MWCNT was 65%, 78% for TiO_2 and 56% for MWCNT. MWCNT showed a higher removal rate compared to 5% TiO_2-MWCNT and TiO_2. At the end of the treatment run with a dosage of 20 mg, 5% TiO_2-MWCNT yielded 63% while TiO_2 and MWCNT yielded a residual of 68% and 76% respectively. The performance of TiO_2-MWCNT and TiO_2 improved with increased dosage; however, this was not observed for MWCNT. The poor performance of TiO_2 can be explained by the fact that as a photocatalyst, it functions best when exposed to radiation sufficient enough to 'activate' it. MWCNTs are known adsorbents; hence the positive removal effect when used alone. Also the effect the 5% TiO_2-MWCNT in dark conditions could be due to the high percentage of MWCNT in it. Generally, there was significant removal of MTBE by all three materials and thus losses could be attributed to adsorption mechanisms or MTBE volatility. Also, increase in dosage was not effective enough to remove MTBE; indicating that sorption onto solid particles is not an efficient way of removing MBE in water (Anderson, 2000).

4.2.2 Degradation of MTBE with three 350 nm UV lamps

This experiment was to investigate the effect of using UV lamps of intensity 0.98 mW/cm^2. Three UV lamps positioned at the top of the photoreactor were used. In the treatment with a dosage of 1 mg (Figure 19), MTBE residual for 5% TiO_2-MWCNT was 89% after thirty minutes of treatment. This improved to 75% and 69% after one hour and ninety minutes of treatment respectively. A residual of 60% was recorded at the end of the treatment run. TiO_2 showed about 60% MTBE removal (a residual of 40%) after thirty minutes of treatment; this performance improved to 21% (79% removal) after an hour and 15% (85% removal) after an hour and a half of treatment. 10% was recorded at the end of the two hours of treatment. The MTBE residual for MWCNT was 53% after thirty minutes of treatment. There was an improvement after an hour; with a residual of 41%. After ninety minutes, a residual of 37% was recorded, however, performance decreased to 41% at the end of the run. TiO_2 demonstrated a higher removal rate compared to the other materials; MWCNT displayed a better performance than 5% TiO_2-MWCNT.

With an increased dosage of 10 mg (Figure 20), MWCNT showed about 58% removal (a residual of 42%) after half an hour of treatment; TiO_2 showed about 85% removal (a residual of 15%) whiles 5% TiO2-MWCNT showed 27% removal (a residual of 73%). There was improvement in terms of MTBE removal by each material: with residual rates of 54%, 8% and 38% respectively at the end of the treatment run.

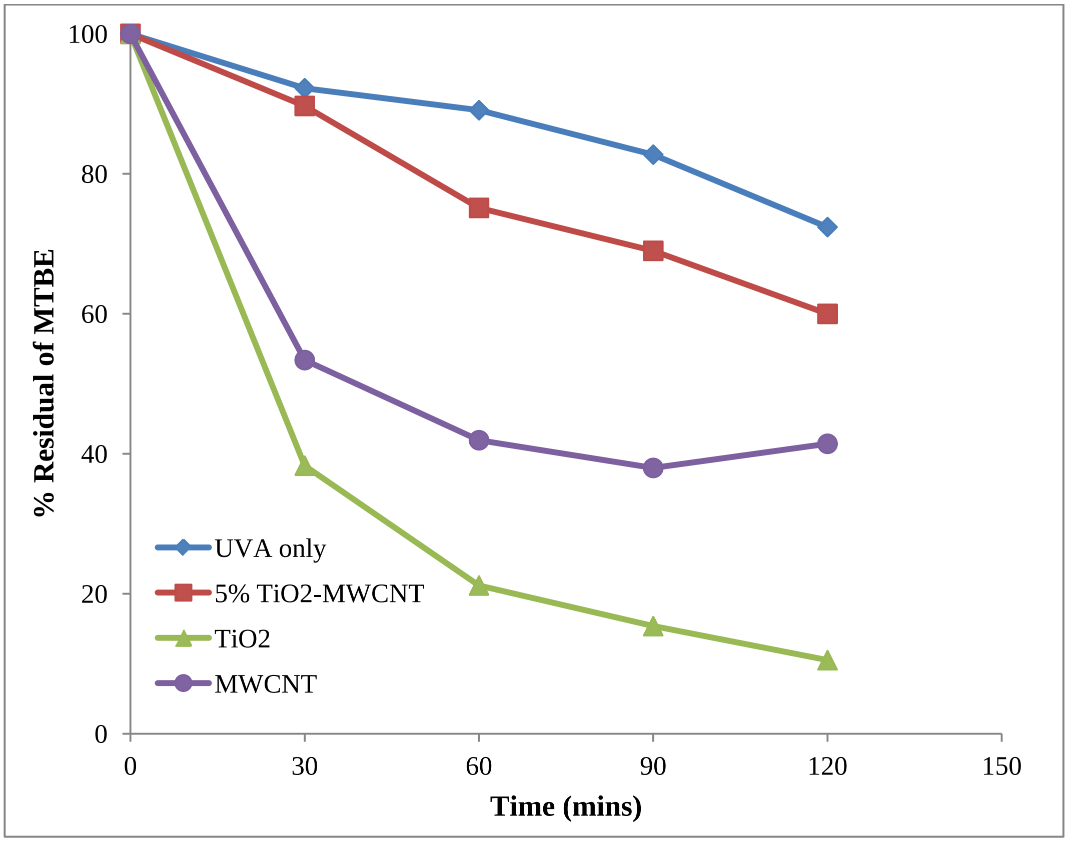


Figure 19: % Residual of MTBE after treatment by 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

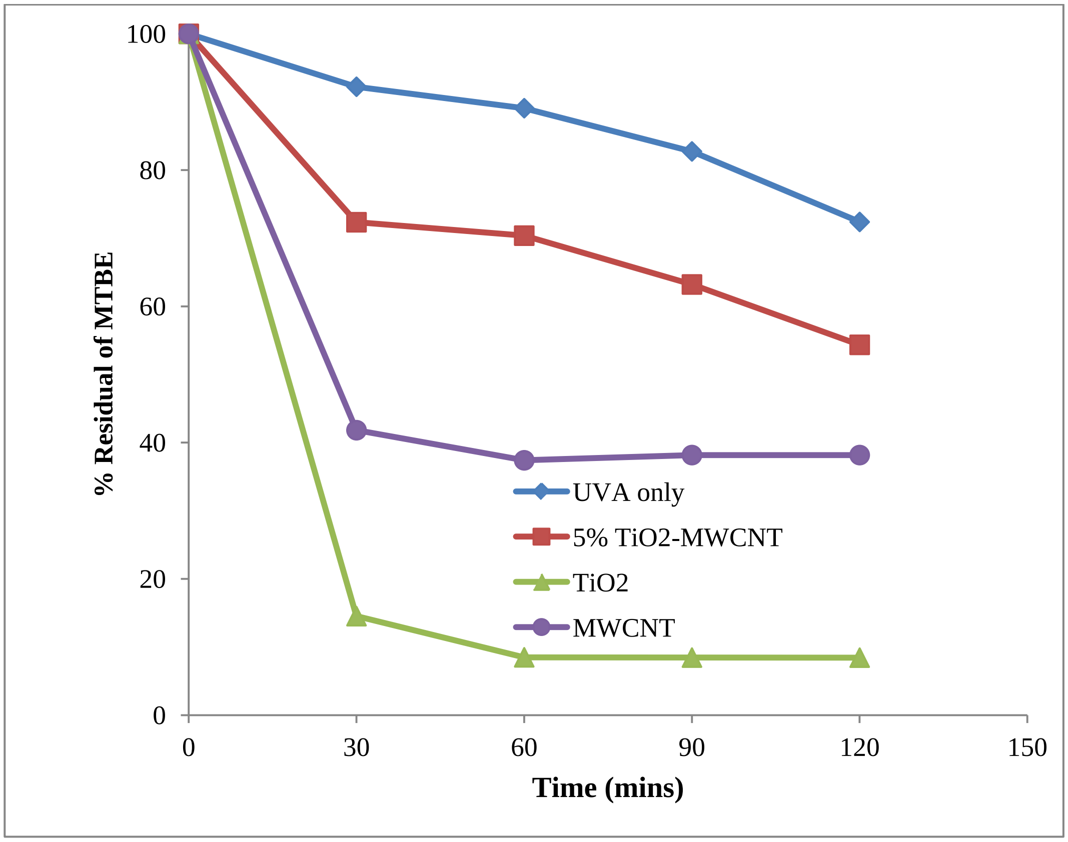


Figure 20: % Residual of MTBE after treatment by 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

At a dosage of 20 mg (Figure 21), removal by TiO_2 remained unchanged with a residual of 8%. The effect of 5% TiO_2-MWCNT and MWCNT marginally reduced at the end of the run; with residual rates of 64% and 42% respectively. The superior performance of TiO_2 as compared to the other materials was expected since it is a known photocatalyst (Likodimos et al., 2010). MWCNT showed a better performance compared to 5% TiO_2-MWCNT; this could be attributed to either improvement of the adsorption properties of the MWCNT or that MWCNTs have photocatalytic capabilities. The mechanism by which the latter point is based on still requires further studies. The poor performance of the 5% TiO_2-MWCNT with UV light could be attributed to the low dosage of TiO_2 (i.e. 5%) in the composite. It could also be due to the fact that MWCNTs are adsorbing the hydroxyl radicals (OH•) generated by the interactions of TiO_2 with UV light and thus preventing them from partaking in the removal of MTBE or its by-products. Generally, an increase in dosage reflected in an increase in MTBE removal; due to increased surface area for degradation and adsorption. This observation is also reported by Carp et al., (2004).

The main by-products detected during MTBE degradation are acetone, TBA and TBF (Selli et al., 2005; Eslami et al., 2007). The detection of by-products is thus an indication of the photocatalytic degradation of MTBE.

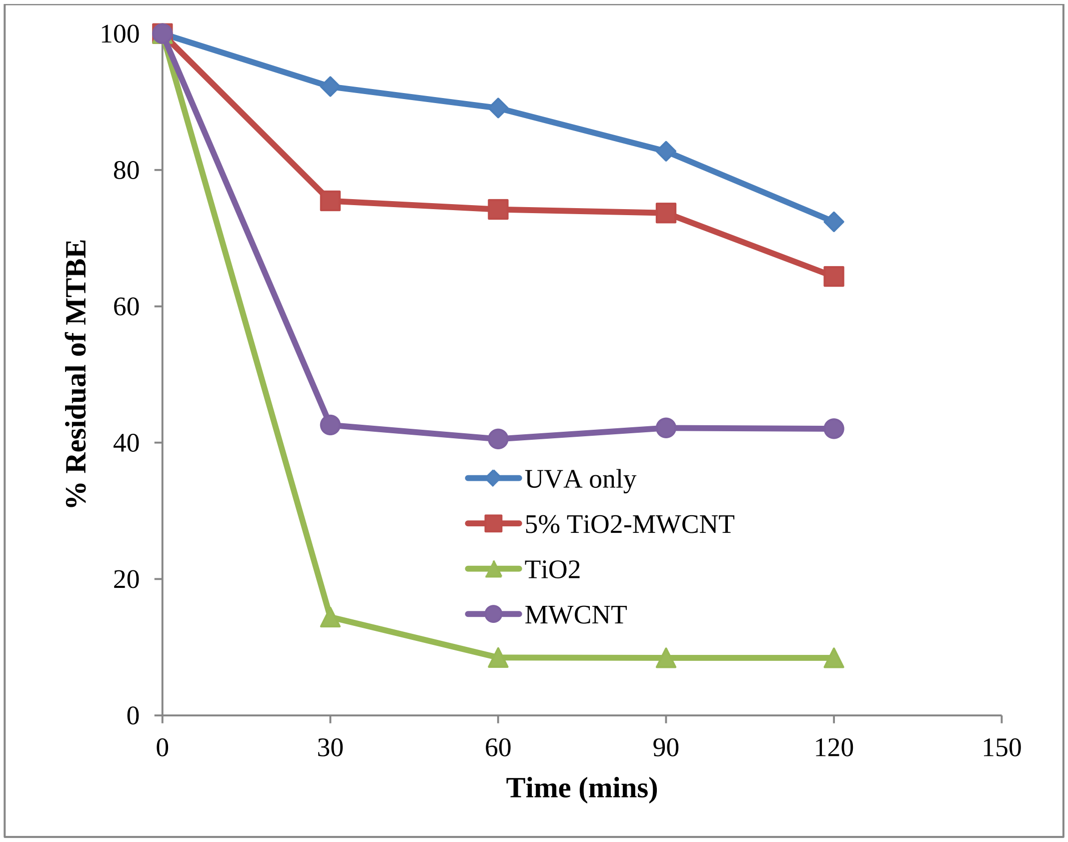


Figure 21: % Residual of MTBE after treatment by 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

Results obtained for analysis of acetone are shown in Figure 22, Figure 23 and Figure 24. At a dosage of 1 mg, acetone concentration after treatment with TiO_2 was 23 ppb. However, for the remainder of the conditions, acetone concentrations were below detectable levels at the end of each treatment run. The reason could be that all the acetone was degraded as in the case of TiO_2 and adsorption as in the case of 5% TiO_2-MWCNT and MWCNT.

TBA results (shown in Figure 25, Figure 26 and Figure 27) revealed that at the end of each treatment run for 5% TiO_2-MWCNT, TiO_2 and MWCNT, a concentration less than 10 ppb was recorded. This may be because adsorption was the main reaction taking place instead of photocatalysis; thus by-products formed were below noticeable levels.

Results of TBF analysis are depicted in Figure 28, Figure 29 and Figure 30. Treatment with 1 mg of TiO_2 yielded a maximum concentration of 112 ppb after ninety minutes of treatment; this however fell to 78 ppb at the end of the two hour run. At a dosage of 10 mg, 79 ppb was recorded after thirty minutes of treatment with TiO_2, this decreased sharply to a value less than 10 ppb at the end of the run. After treatment with a dosage of 20 mg, a concentration of 60 ppb was recorded for TiO_2; this decreased to a value less than 10 ppb at the end of the run. Treatment runs with 5% TiO_2-MWCNT and MWCNT all recorded values less than 5 ppb. The higher concentrations reported here supports the point that an increase in dosage could result in better removal of MTBE and thus the generation of more by-products.

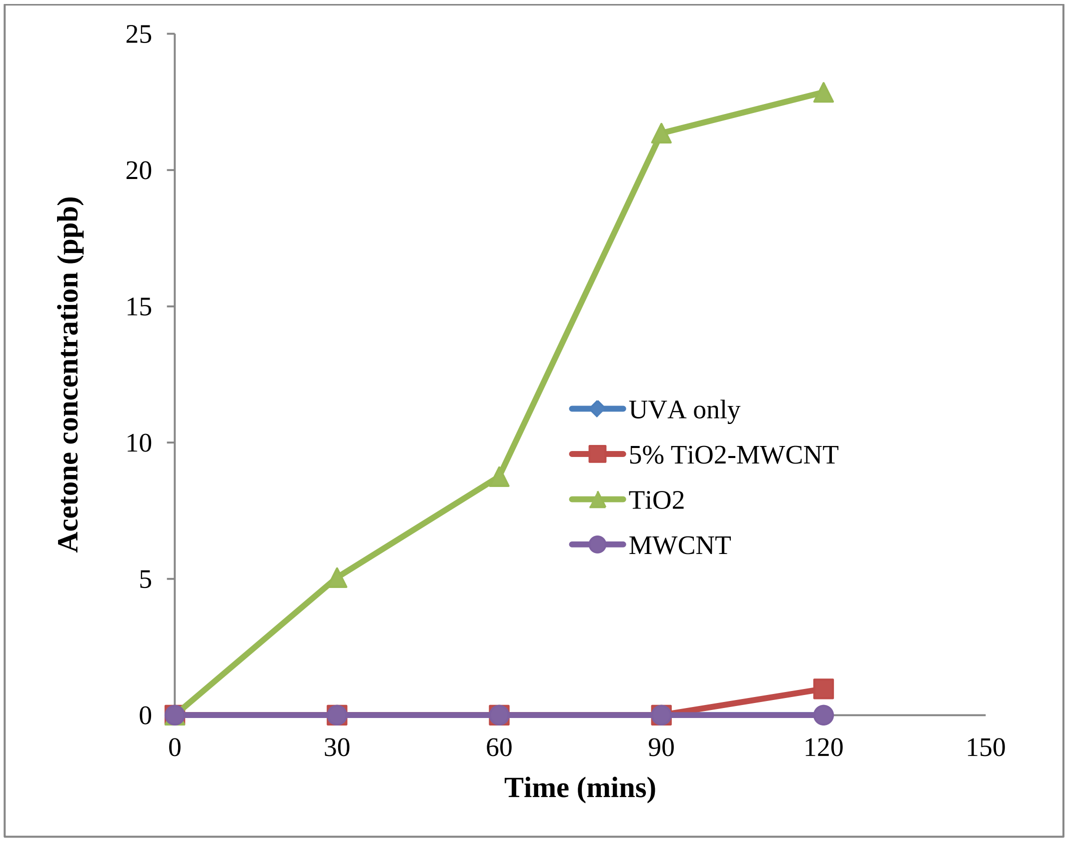


Figure 22: Acetone concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

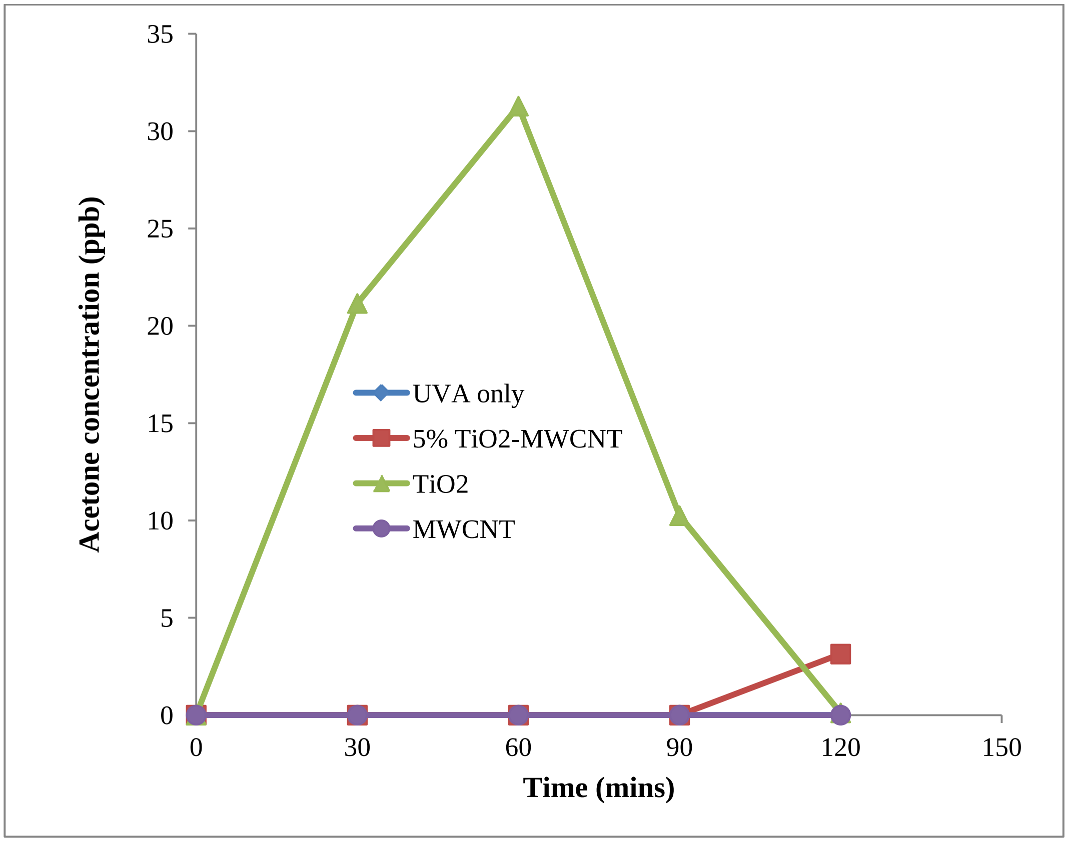


Figure 23: Acetone concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

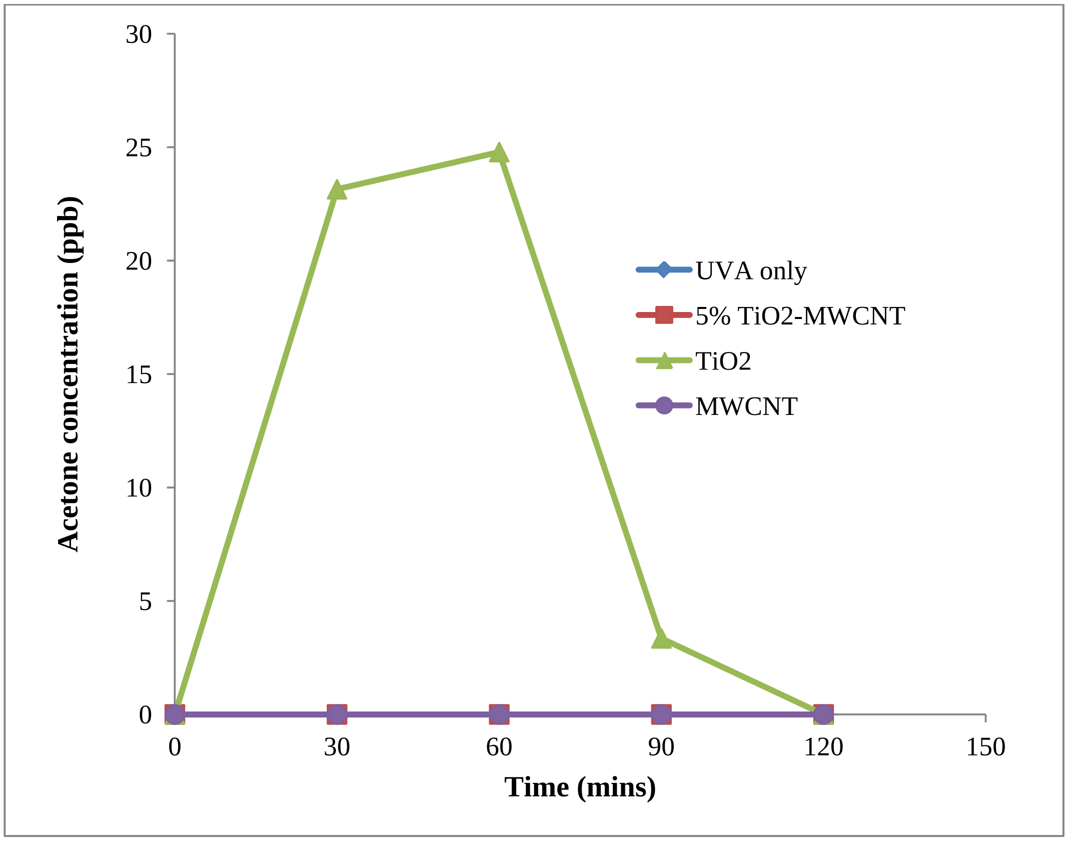


Figure 24: Acetone concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

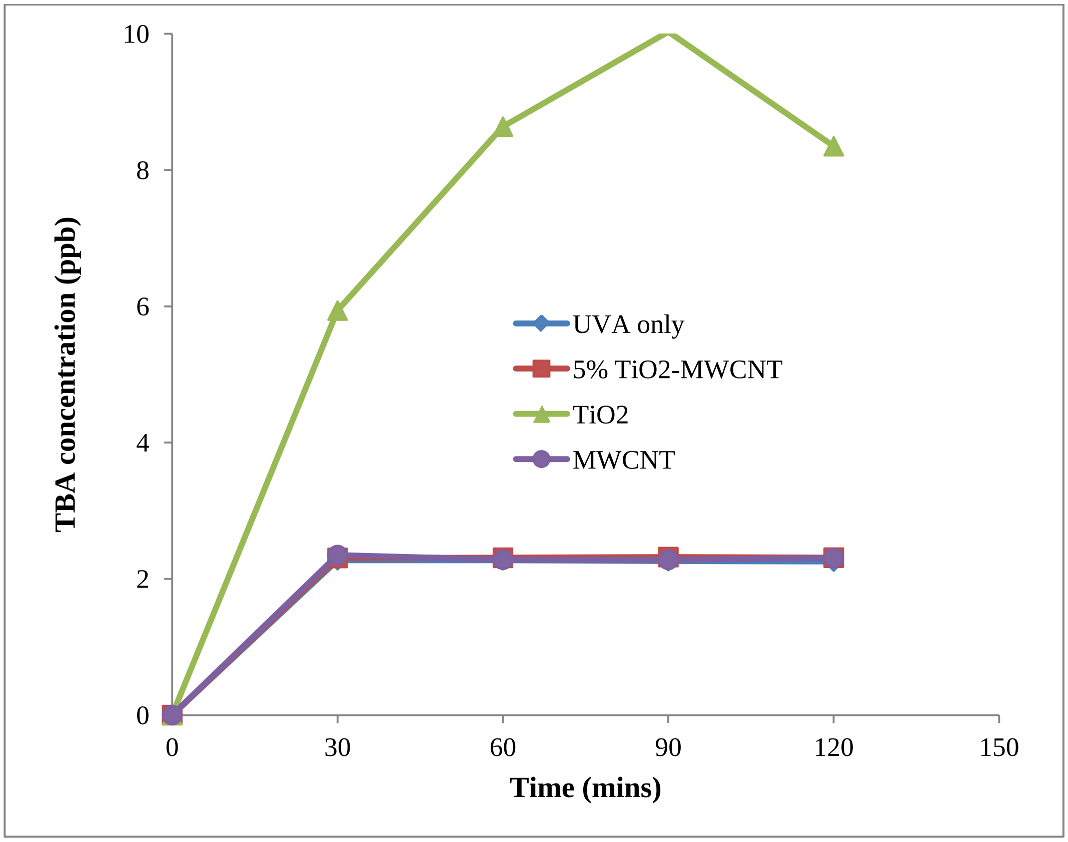


Figure 25: TBA concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

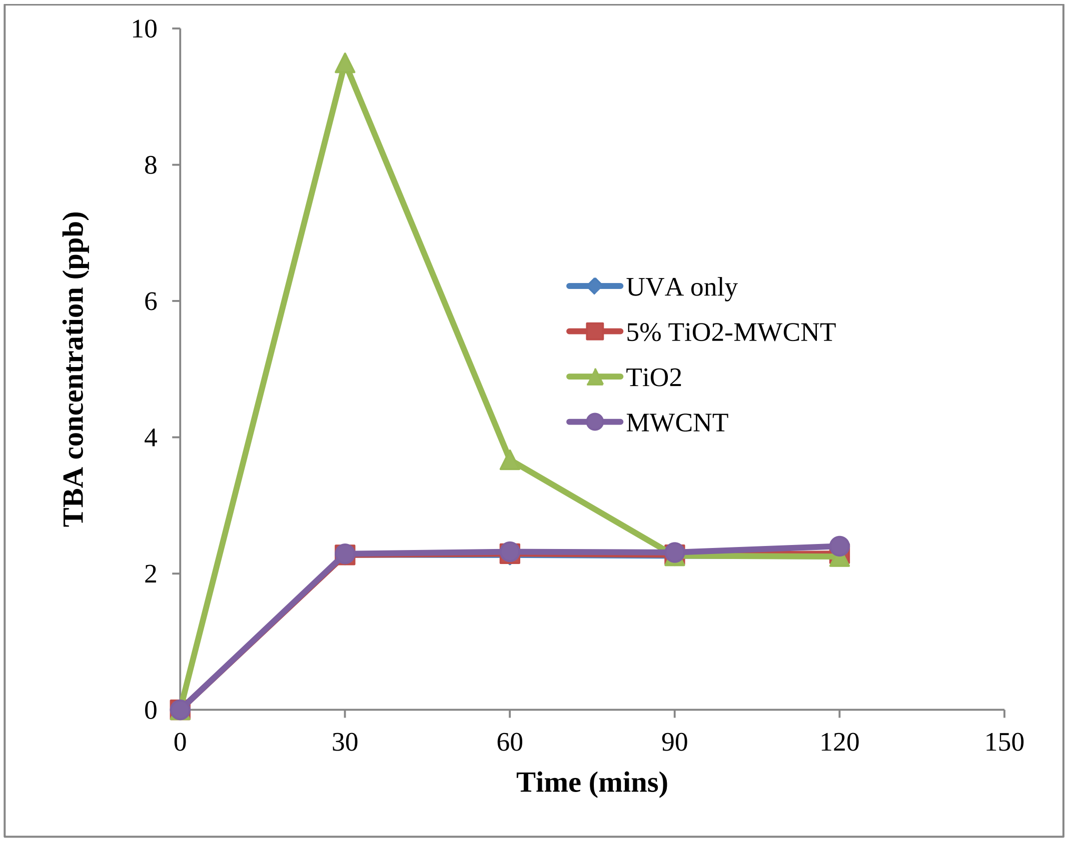


Figure 26: TBA concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

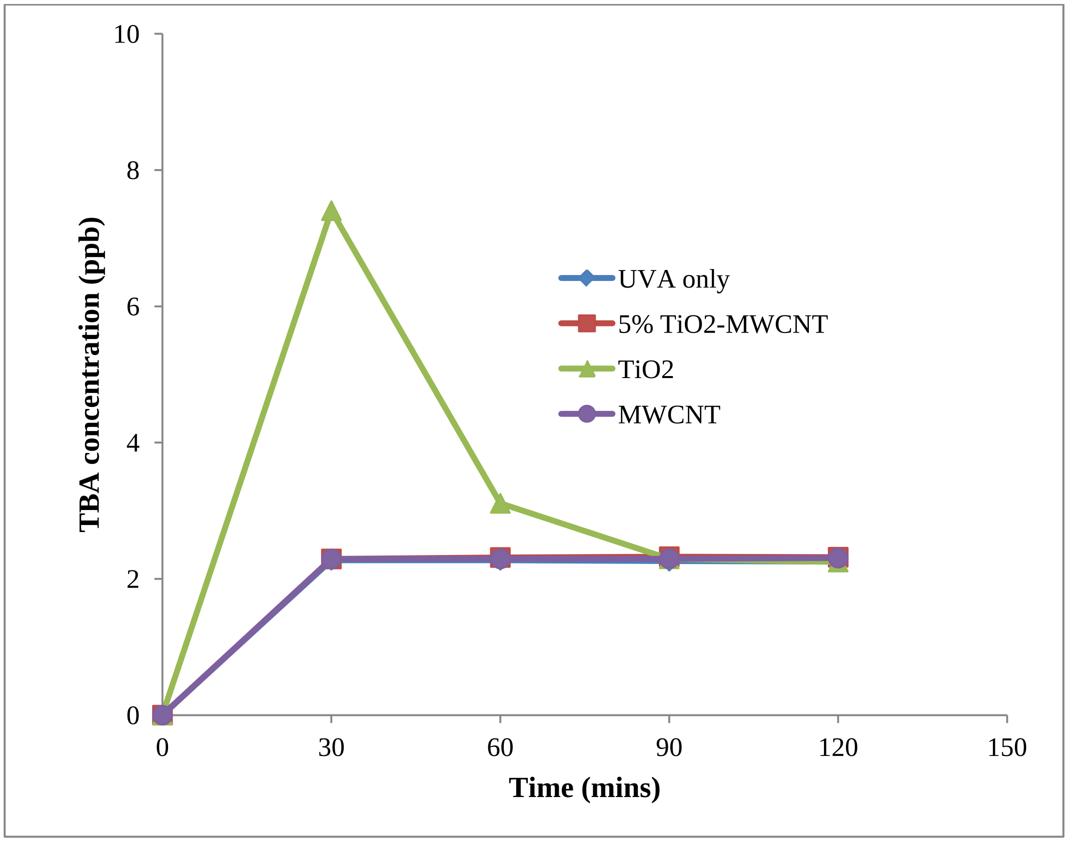


Figure 27: TBA concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

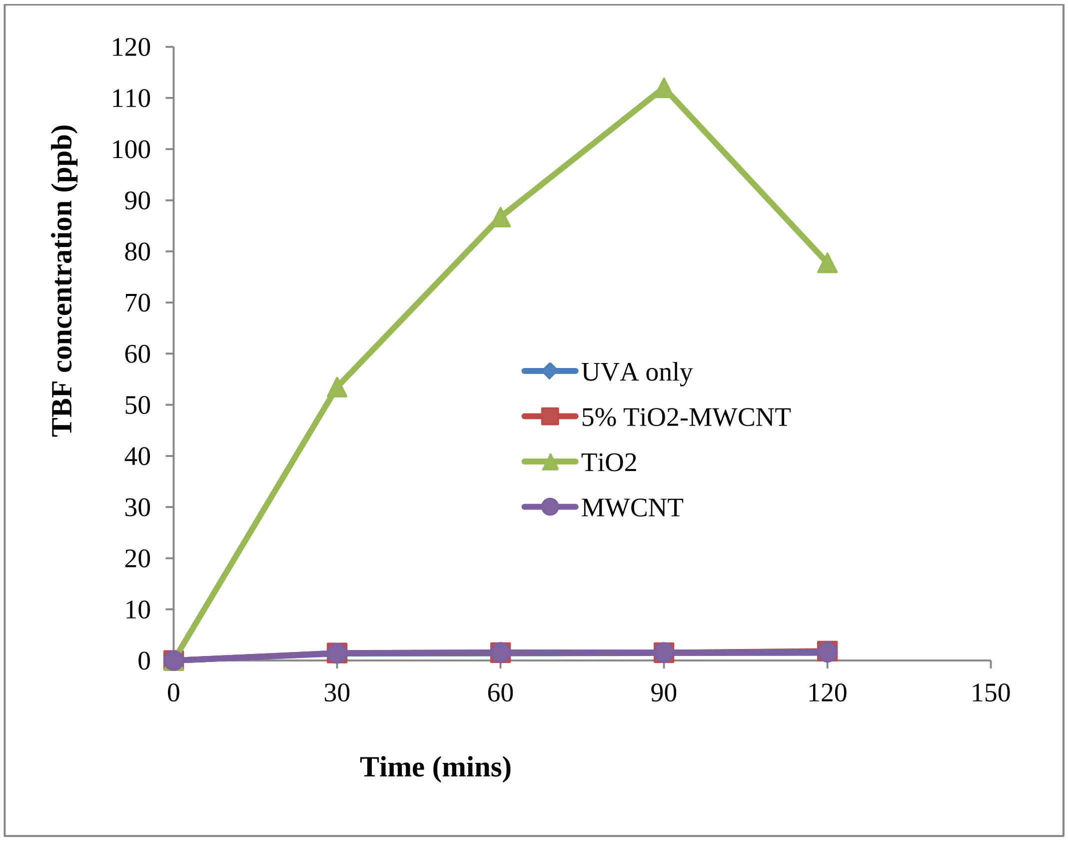


Figure 28: TBF concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

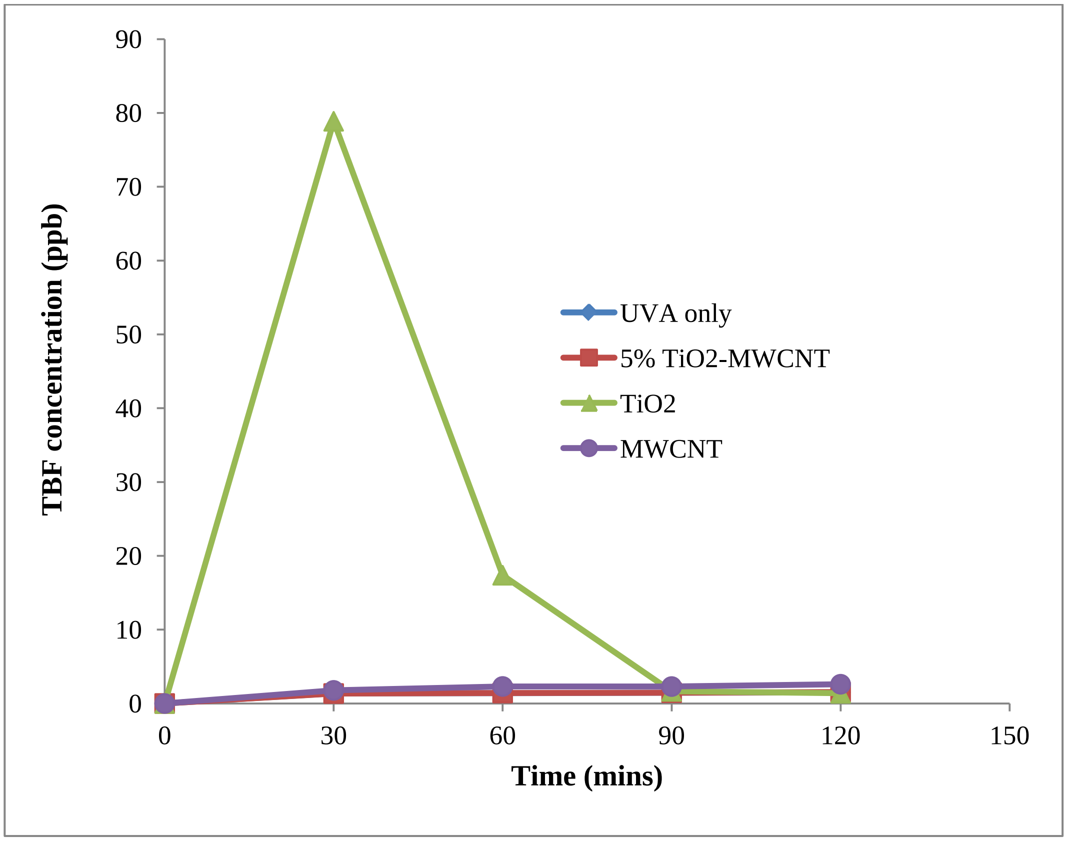


Figure 29: TBF concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

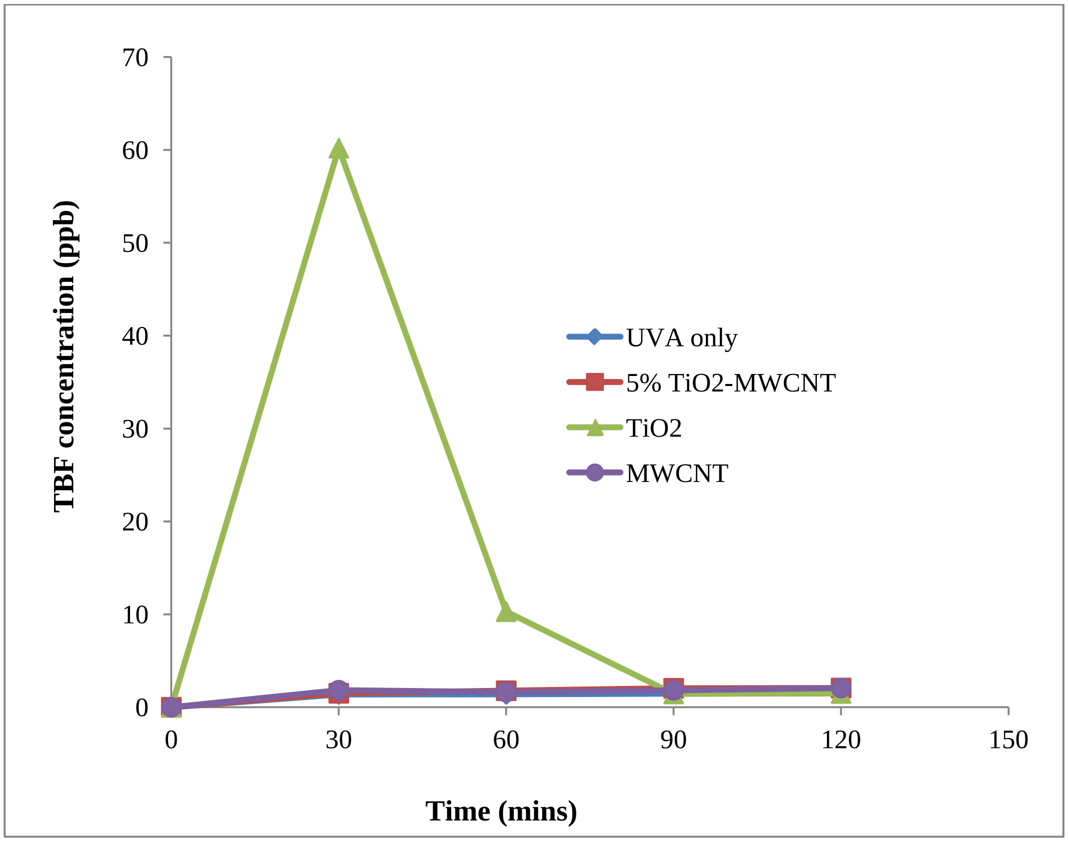


Figure 30: TBF concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 0.98 mW/cm^2 UV-A light.

4.2.3 Degradation of MTBE with four 350 nm UV lamps

This experiment was to find out the effect of using UV lamps of intensity 1.12 mW/cm^2. Four UV lamps; two positioned on each side of the photoreactor were used. MTBE after half an hour of treatment with a dosage of 1 mg yielded a residual of 55% for 5% TiO_2-MWCNT, TiO_2 was 4% and MWCNT yielded 41% (Figure 31). Removal of MTBE continued at a rate less than 10% for each material, until the end of the treatment run where 50% was recorded for 5% TiO_2-MWCNT, TiO_2 was 5% and 32% for MWCNT. TiO_2 showed higher removal rates compared to 5% TiO_2-MWCNT and MWCNT; whiles MWCNT also outperformed the 5% TiO_2-MWCNT. Removal rates were higher compared to when three UV lamps of intensity 0.98 mW/cm^2 were used. With an increased dosage of 10 mg (Figure 32); after thirty minutes of treatment, 5% TiO_2-MWCNT showed MTBE removal rate of 49% (a residual of 51%), TiO_2 showed 96% removal (a residual of 4%) while MWCNT showed 52% removal. MTBE residual by 5% TiO_2-MWCNT was 51% after an hour of treatment and then improved to 47% after an hour and a half. TiO_2 residual was 4% after one hour of treatment and remained unchanged after ninety minutes. The MTBE residual for MWCNT after an hour of treatment was 44%, marking an improvement. There was however a marginal decrease after an hour and a half of treatment; with a residual of 45%. At the end of the run residual rates were 47%, 5% and 35% for 5% TiO_2-MWCNT, TiO_2 and MWCNT respectively. The removal rates here were also higher compared to when three UV lamps of intensity 0.98 mW/cm^2 were used. TiO_2 removal rates were higher compared to the other materials. MTBE removal by MWCNT was better compared to the 5% TiO_2-MWCNT.

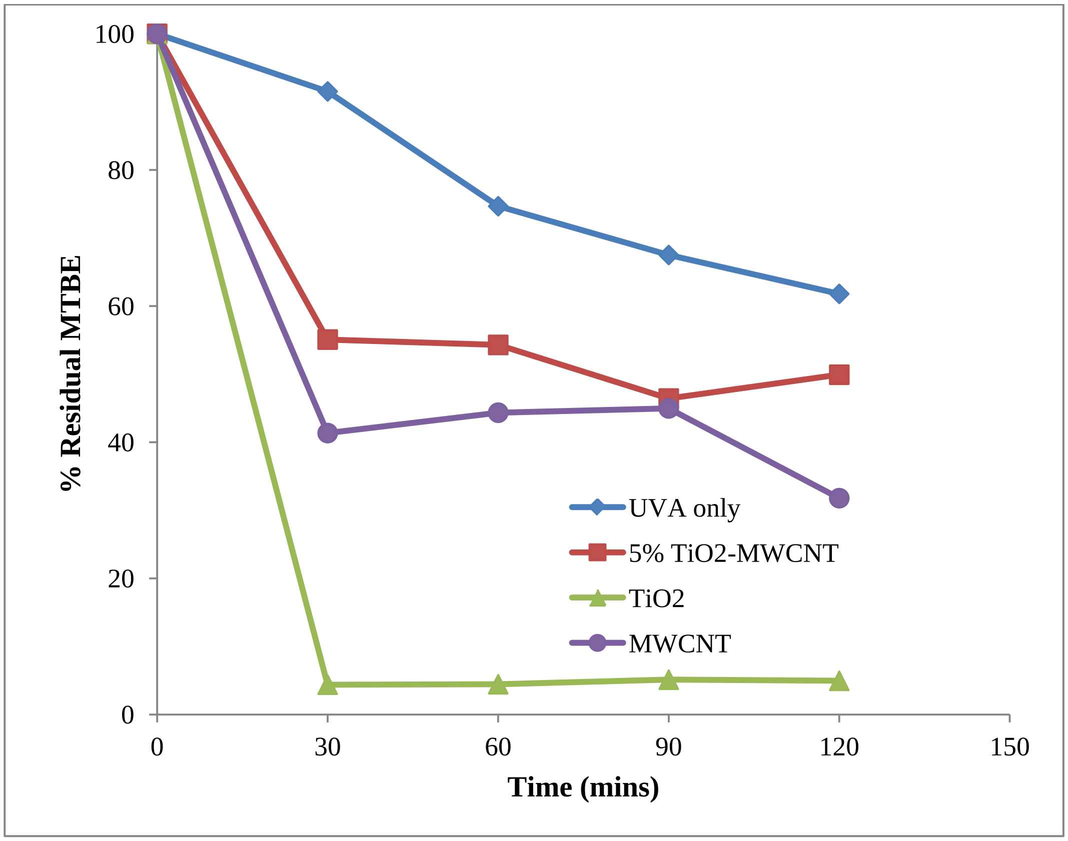


Figure 31: % Residual of MTBE after treatment by 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

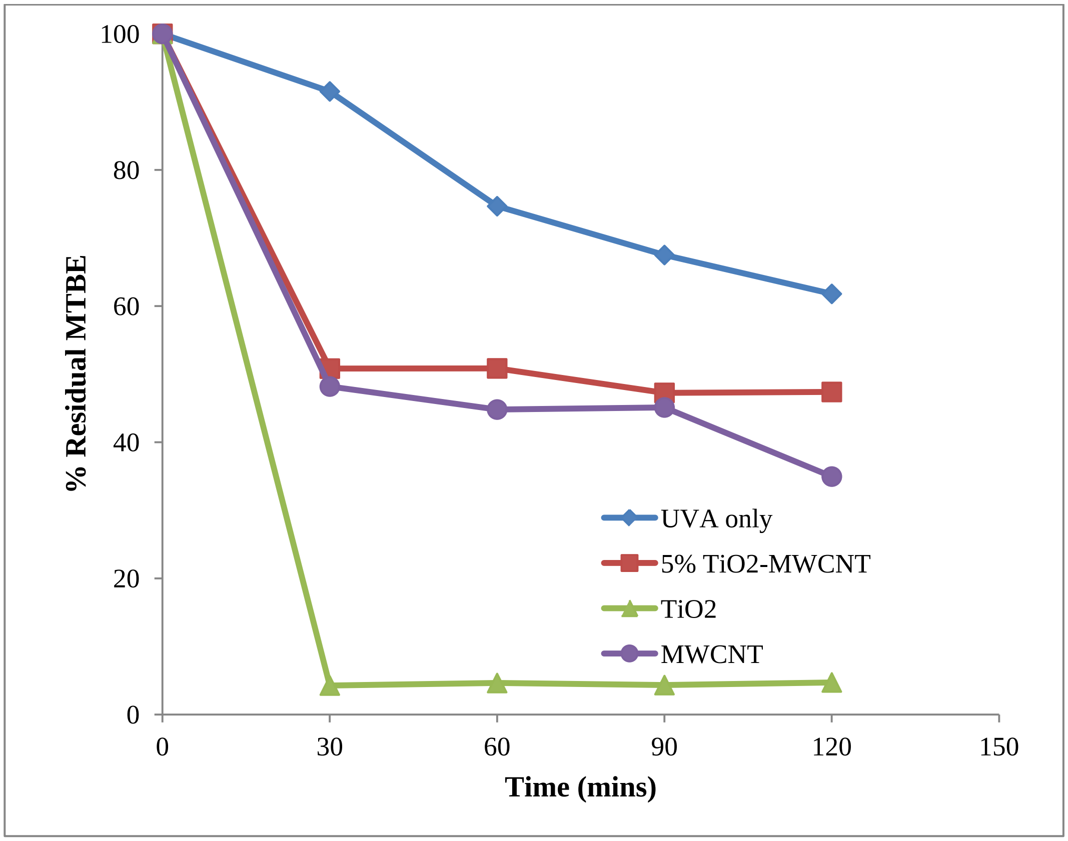


Figure 32: % Residual of MTBE after treatment by 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

At a dosage of 20 mg (Figure 33), the effect of 5% TiO_2-MWCNT after half an hour of treatment was a residual of 53%. This improved to 42% after an hour of treatment. After ninety minutes of treatment, a high removal rate of 72% (a residual of 28%) and then finally a residual of 30% at the end of the treatment run. Treatment with TiO_2 yielded MTBE residual of 5% after thirty minutes. There was an improvement after one hour of treatment with a residual of 4%. However, at ninety minutes, a decrease in performance was observed with a residual of 5%. At the end of the run, a residual of 4% was recorded. MWCNT yielded a residual of 51% after half an hour of treatment. This improved to 41% and 38% after an hour and an hour and a half of treatment respectively. At the end of the run a residual of 43% was observed. MTBE removal rates here were also higher compared to when three UV lamps of intensity 0.98 mW/cm^2 were used. This could be due to the increase in intensity of the UV-A light. TiO_2 removal rates were higher compared to MWCNT and 5% TiO_2-MWCNT as reported previously. MTBE removal by 5% TiO_2-MWCNT was however better compared to the MWCNT. This could also be attributed to the increased intensity of the UV-A light which resulted in more hydroxyl radicals (OH•) being generated to carry out the degradation.

Results of analysis of acetone are depicted in Figure 34, Figure 35 and Figure 36. Treatment with 1 mg of 5% TiO_2-MWCNT yielded a concentration of 20 ppb at the end of the run. A concentration of 148 ppb was measured after thirty minutes of treatment with 1 mg of TiO_2, this however was drastically reduced to 13 ppb at the end of the run. Also, 13 ppb was recorded for MWCNT.

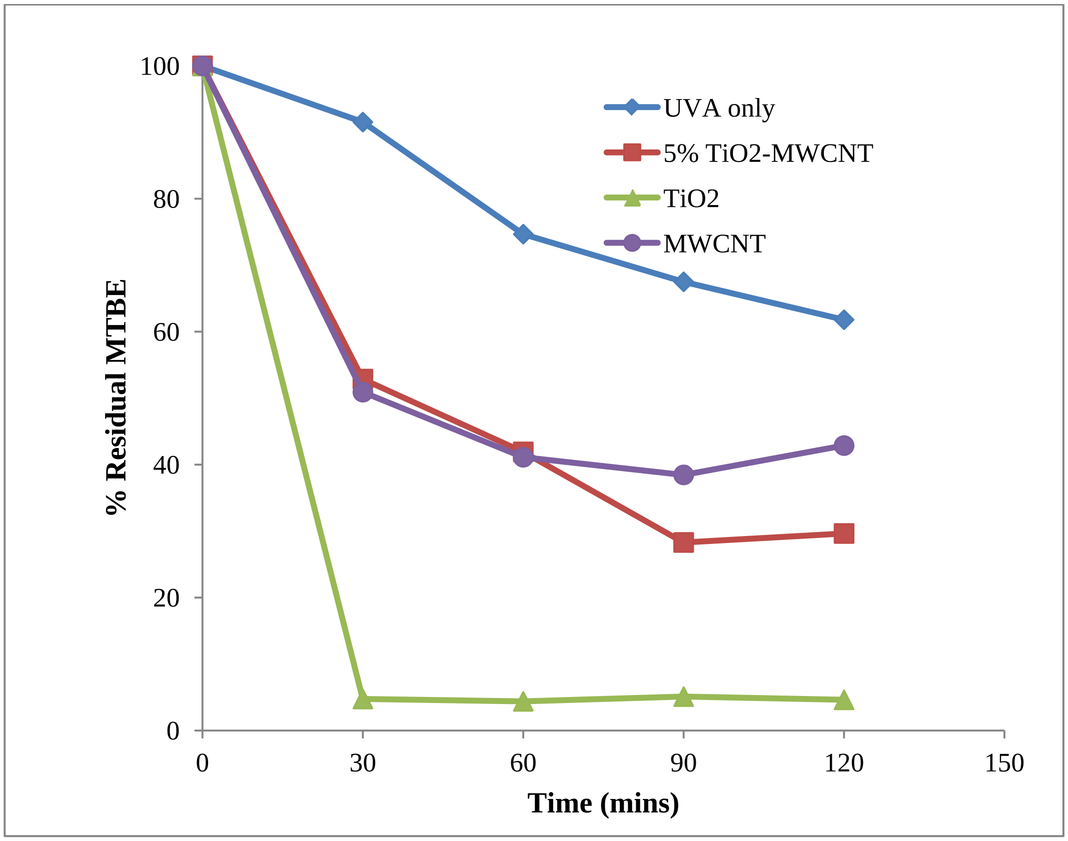


Figure 33: % Residual of MTBE after treatment by 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

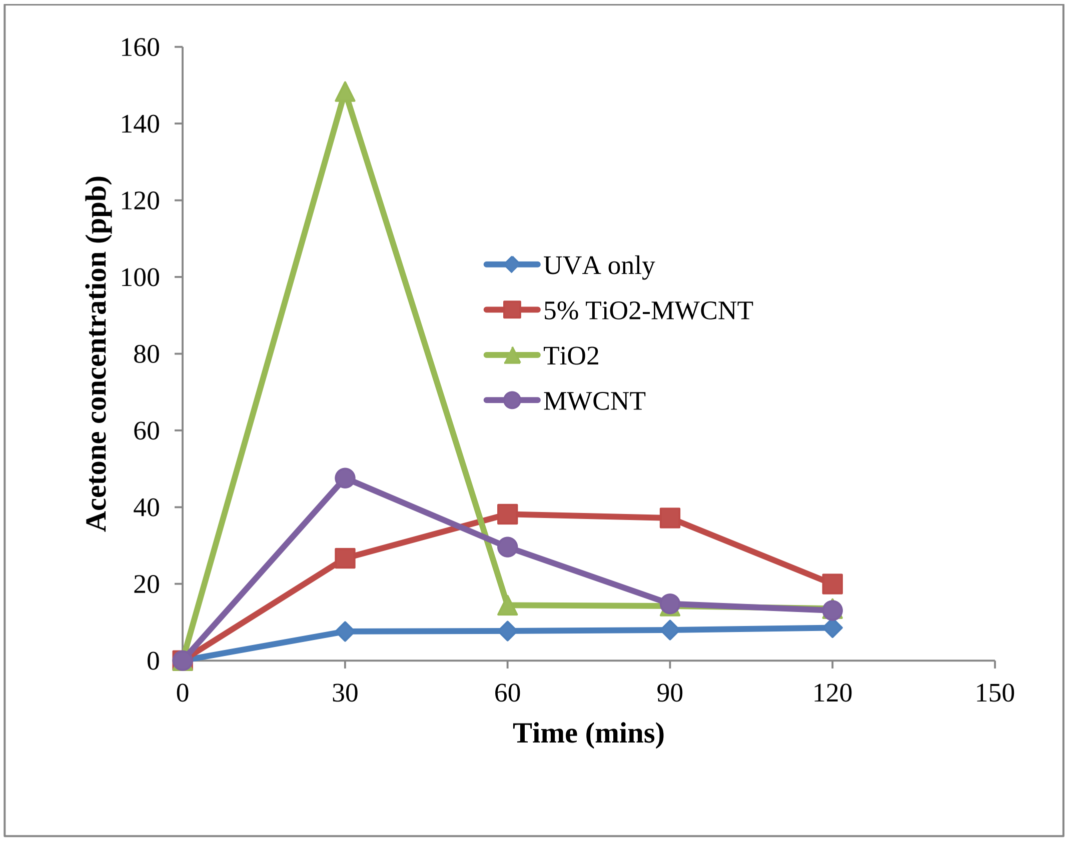


Figure 34: Acetone concentration after treatment with 1 mg 5 % TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

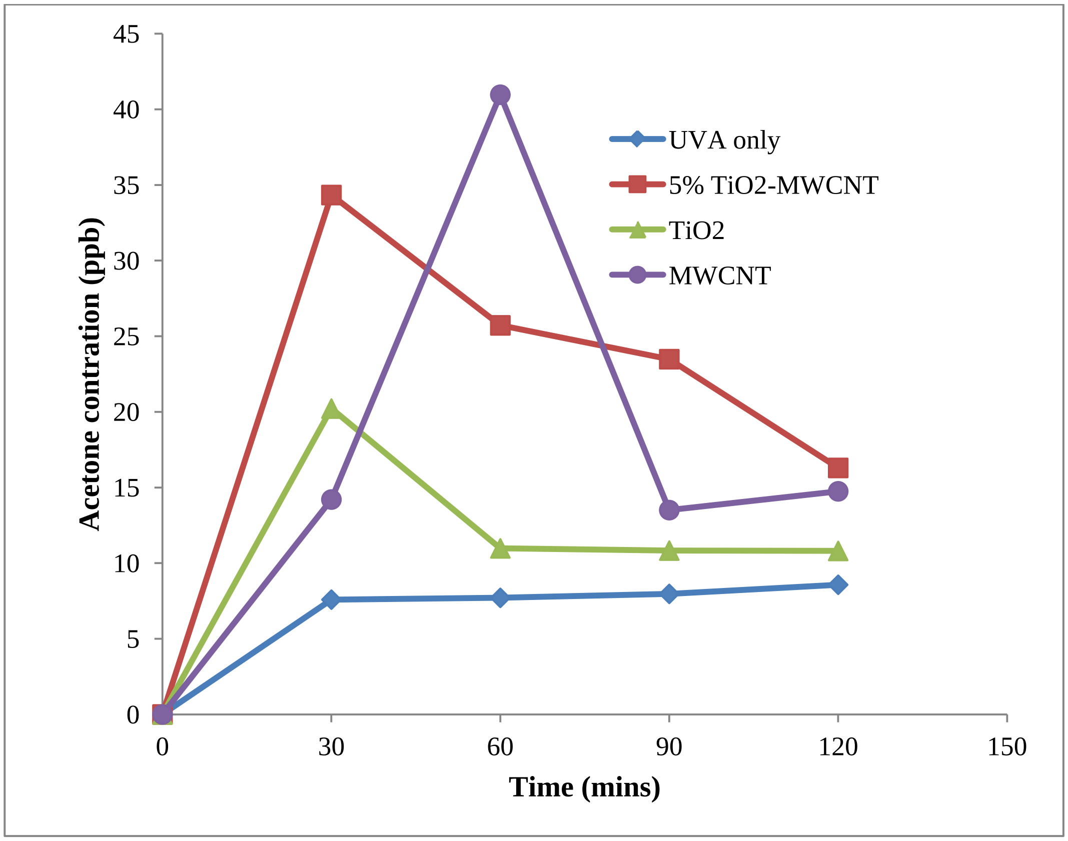


Figure 35: Acetone concentration after treatment with 10 mg 5 % TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

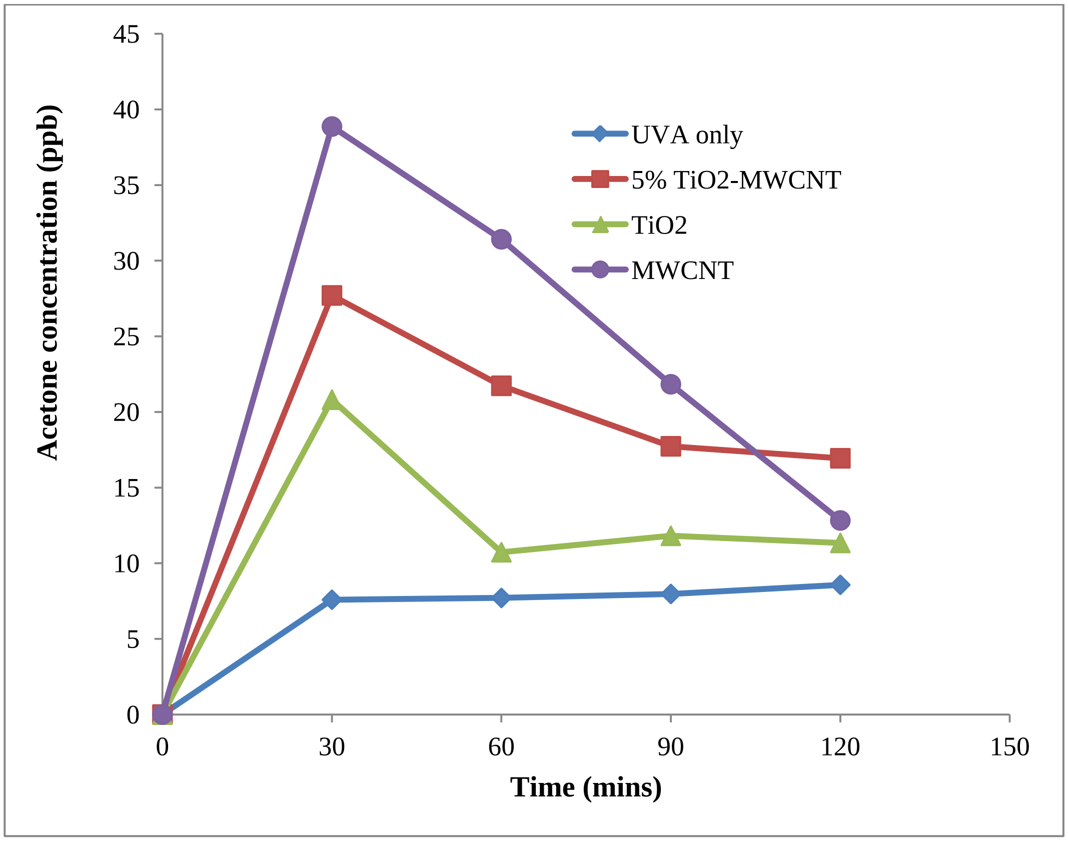


Figure 36: Acetone concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

At a dosage of 10 mg, acetone concentration was 16 ppb for 5% TiO_2-MWCNT and 15 ppb for MWCNT. A concentration of 11 ppb was measured at the end of the run after treatment with TiO_2. After treatment with a dosage of 20 mg, 17 ppb was measured for 5% TiO_2-MWCNT and 11 ppb for TiO_2. 13 ppb was detected for MWCNT. The levels of acetone recorded were higher as compared to when three UV lamps of intensity 0.98 mW/cm^2 were used; also an indication that there was increased photocatalytic activity.

Results for TBA analysis (shown in Figure 37, Figure 38 and Figure 39) showed a concentration less than 5 ppb for 5% TiO_2-MWCNT, TiO_2 and MWCNT, was recorded. This may be because adsorption was the main reaction taking place instead of photocatalysis; thus by-products formed were below noticeable levels.

TBF results are shown in Figure 40, Figure 41 and Figure 42. Also, concentrations less than 5 ppb were recorded. The reason could be that there was increased degradation of TBA due to generation of more hydroxyl (OH•) radicals, thus concentrations recorded at the end of the run were below detectable levels.

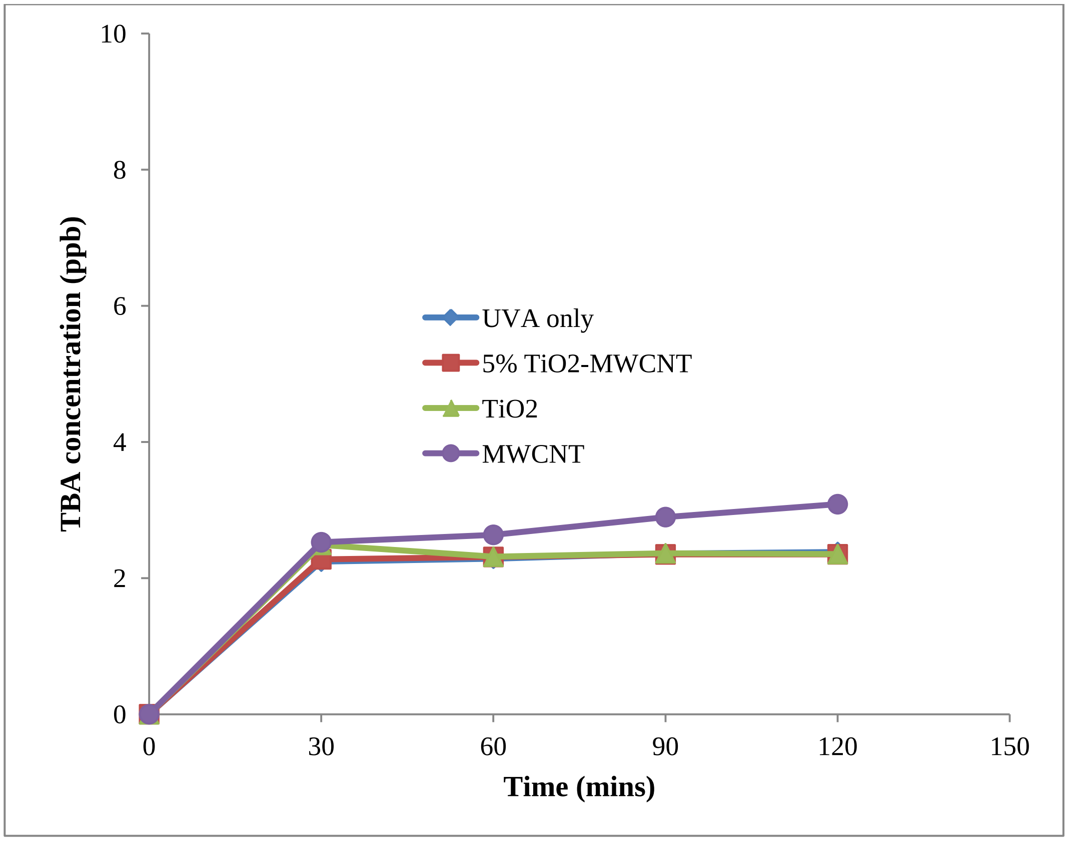


Figure 37: TBA concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

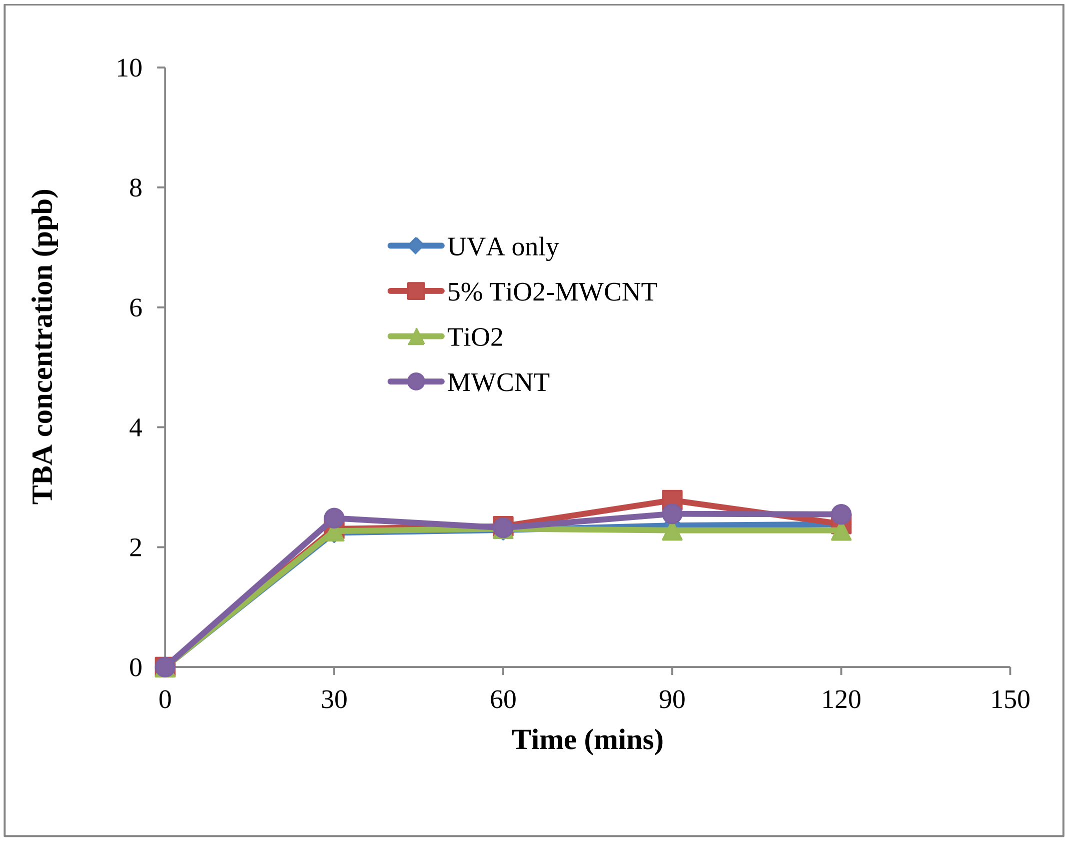


Figure 38: TBA concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

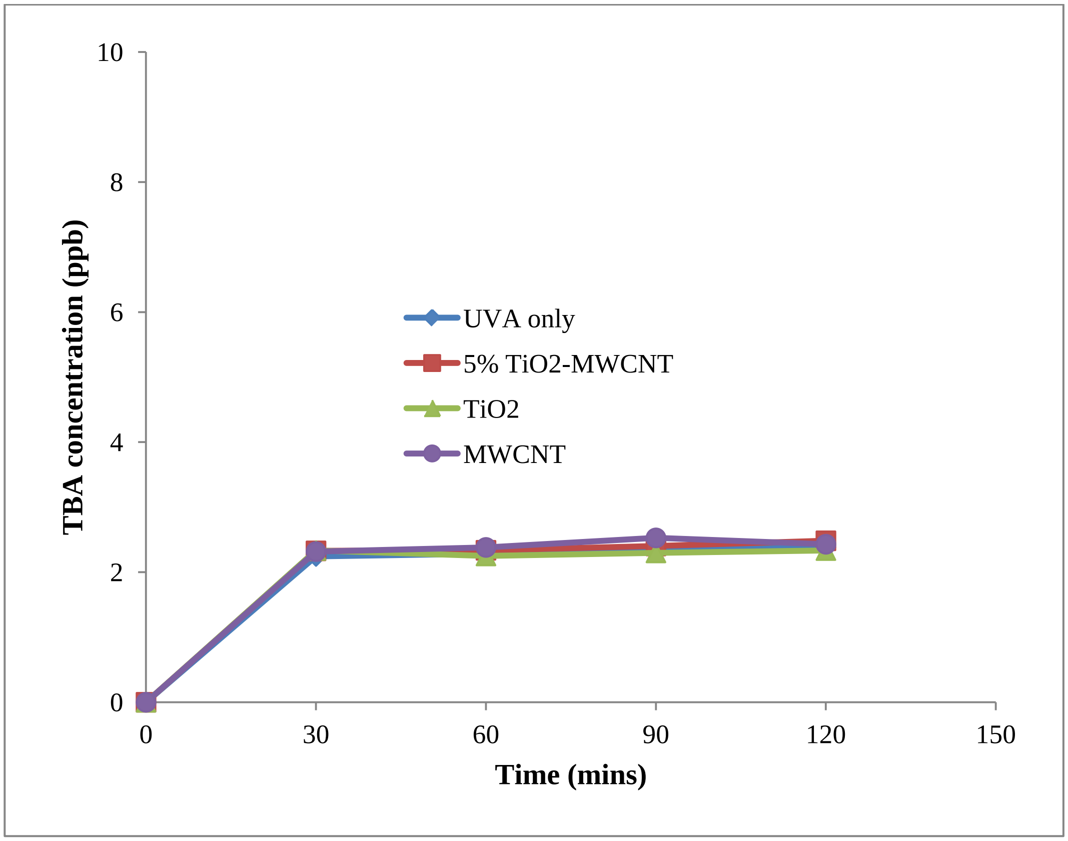


Figure 39: TBA concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

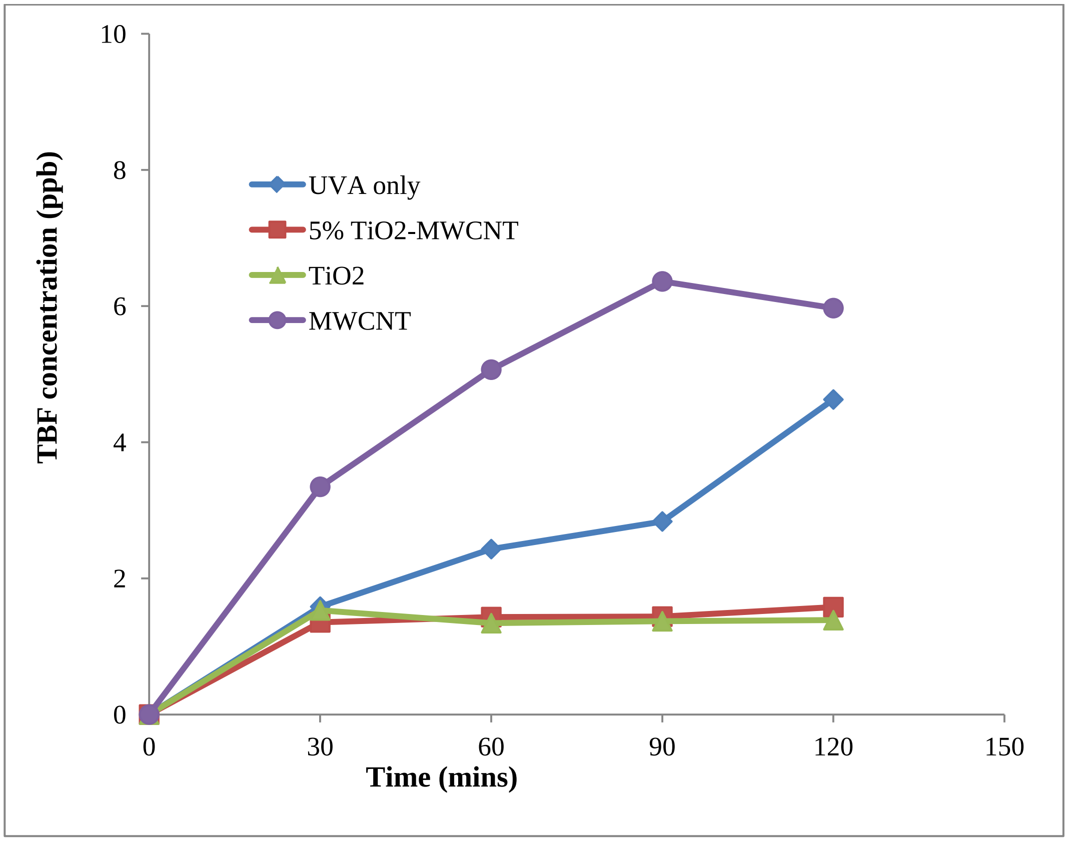


Figure 40: TBF concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

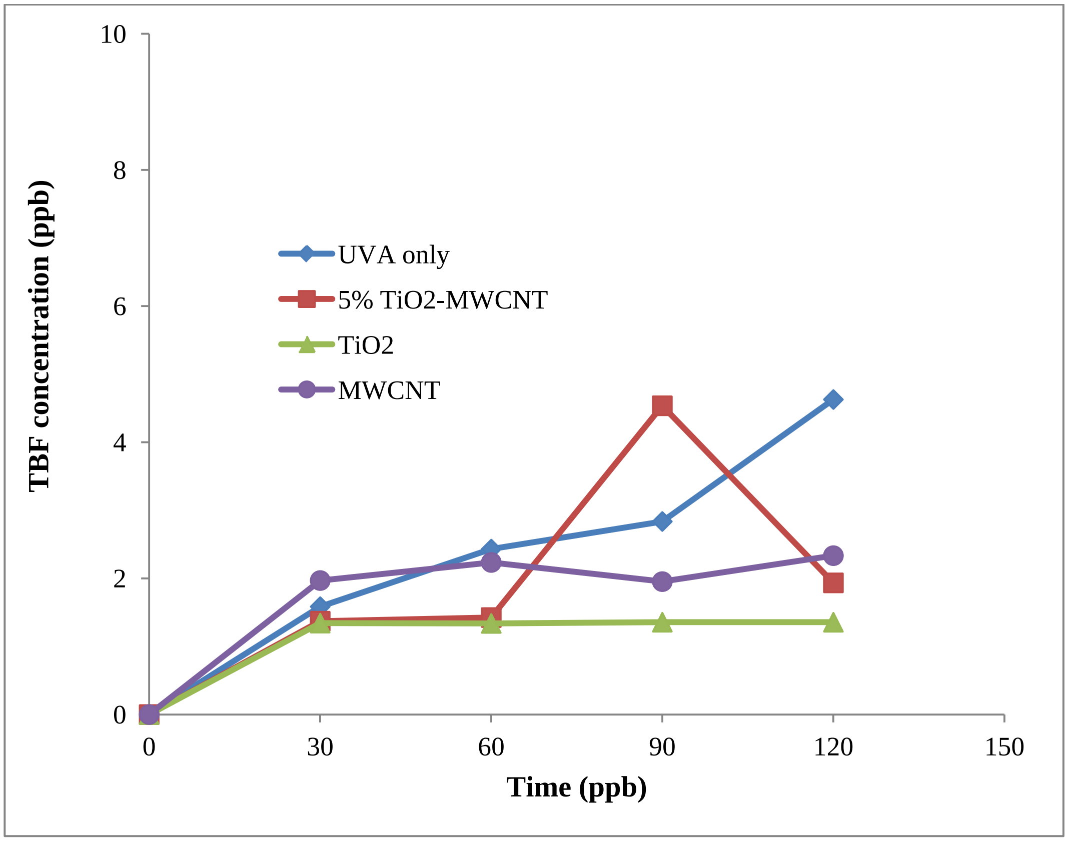


Figure 41: TBF concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

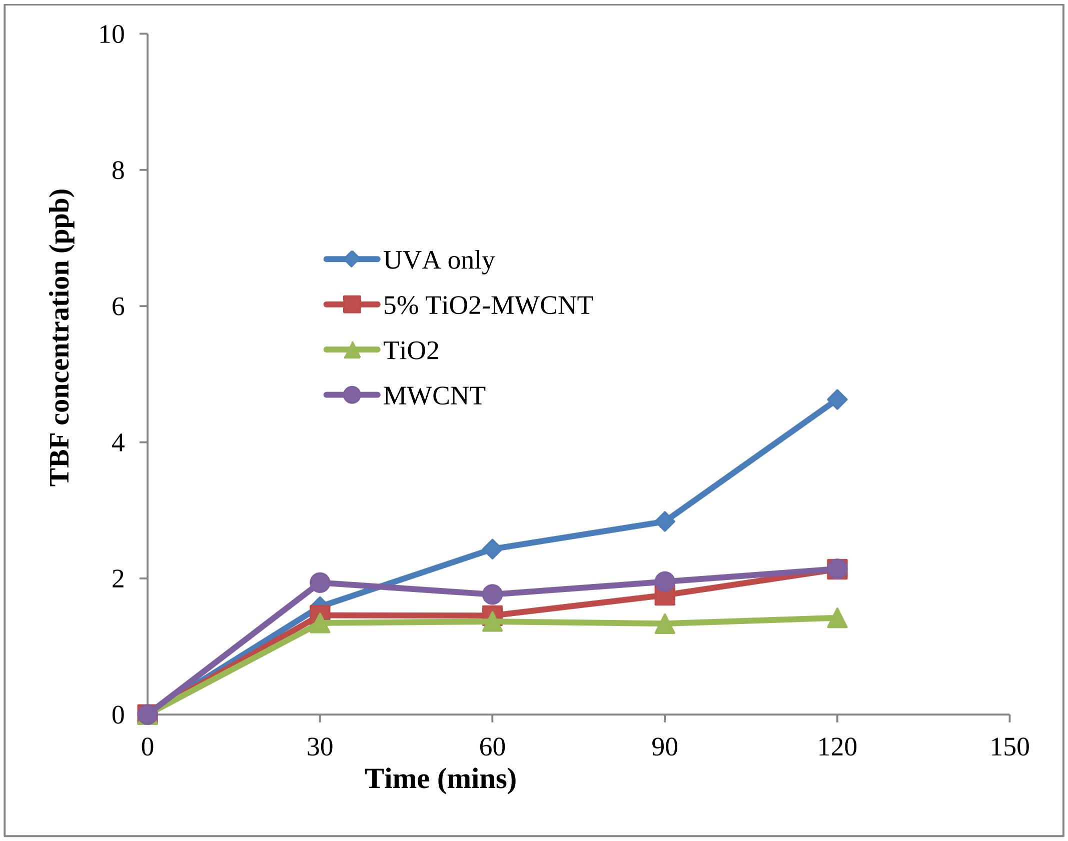


Figure 42: TBF concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 1.12 mW/cm^2 UV-A light.

4.2.4 Degradation of MTBE with seven 350 nm UV lamps

The goal of this experiment was to establish the effect of using UV lamps of intensity 2.17 mW/cm^2. Three lamps positioned at the top and four lamps (two on each side of the photoreactor) were used. After treatment with a dosage of 1 mg (Figure 43), MTBE residual for 5% TiO_2-MWCNT after half an hour of treatment was 87%; 50% for TiO_2 and 81% for MWCNT. There was an improvement in the performance of each material after an hour of treatment; with residual rates of 84%, 28% and 76% for 5% TiO_2-MWCNT, TiO_2 and MWCNT respectively. MTBE residual for 5% TiO_2-MWCNT was 78% after ninety minutes of treatment. Treatment with TiO_2 yielded a residual of 15% while treatment with MWCNT yielded a residual of 75%. At the end of the treatment run, residual rate for 5% TiO_2-MWCNT was 72%, TiO_2 was 8% and MWCNT yielded 71%; all showing a reduction in performance when compared to when UV-A lamps of intensity 0.98 mW/cm^2 (three lamps) and UV-A lamps of intensity 1.12 mW/cm^2 (four lamps) were used. The lower removal rates observed may be due to the fact that the intensity of UV-A light is not the optimum to result in degradation. However, more investigations are required to fully understand this observation. TiO_2 removal rates were higher compared to 5% TiO_2-MWCNT and MWCNT. MTBE removal by MWCNT was also better compared to the 5% TiO_2-MWCNT.

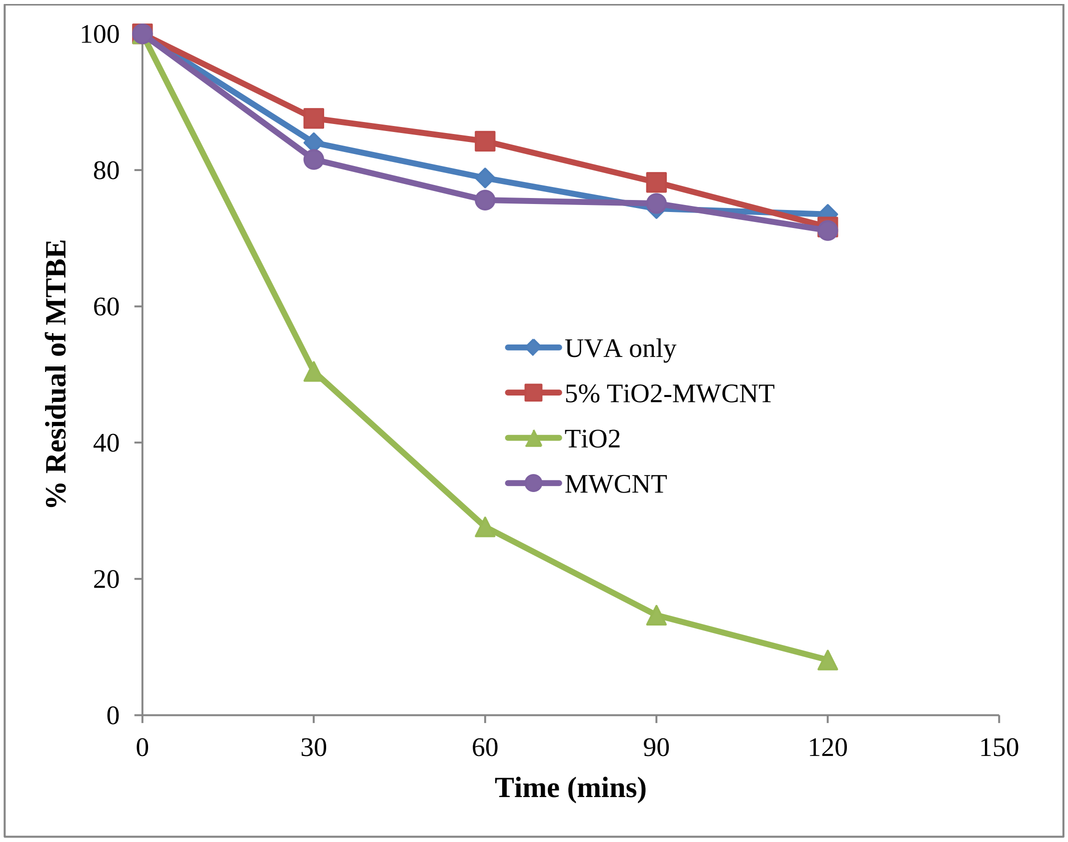


Figure 43: % Residual of MTBE after treatment by 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

With an increased dosage of 10 mg (Figure 44), 5% TiO_2-MWCNT effect after thirty minutes of treatment was a residual of 89%.This improved to 79% after an hour of treatment and then 78% after ninety minutes of treatment. At the end of the treatment run MTBE residual for 5% TiO_2-MWCNT was 72% (removal of 28%). TiO_2 yielded MTBE residual of 22% (removal of 78%) after half an hour of treatment. There was an improvement after one hour of treatment with a residual of 8% (92% removal). There was further improvement after an hour and a half or treatment; a residual of 7%. A residual of 6% (removal of 94%) was recorded at the end of the treatment run. Treatment with MWCNT yielded a residual of 77% after thirty minutes of treatment. MTBE residual was 73% after an hour of treatment, and 71% after ninety minutes. A residual of 67% (33% removal) was recorded at the end of the treatment. MTBE removal rates were also lower as compared to when UV-A lamps of intensity 0.98 mW/cm^2 (3 lamps) and UV-A lamps of intensity 1.12 mW/cm^2 (4 lamps) were used; the reason probably due to the fact that the intensity of UV-A light is not the optimum to result in degradation. TiO_2 removal rates were higher compared to 5% TiO_2-MWCNT and MWCNT. MWCNT showed a better performance compared to 5% TiO_2-MWCNT. Increase in dosage from 1 mg to 10 mg resulted in an increased removal; thus further supporting the point that higher material loading could result in increased degradation.

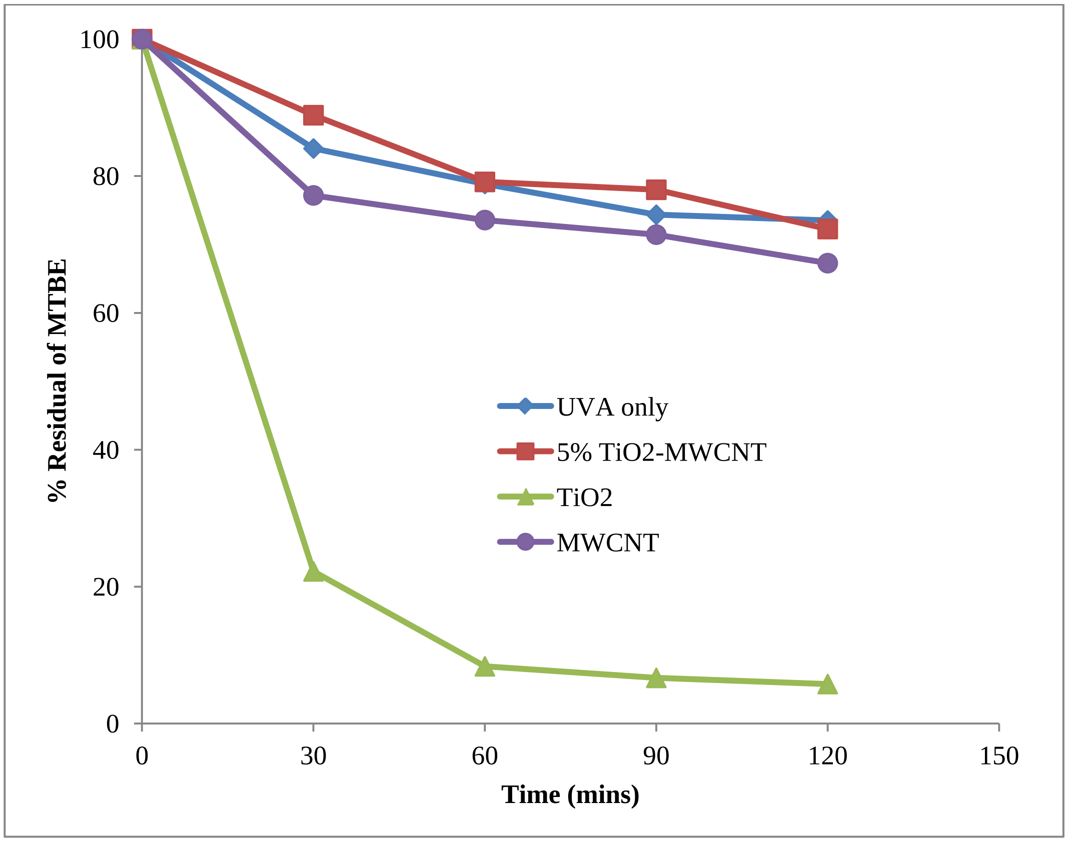


Figure 44: % Residual of MTBE after treatment by 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

At a dosage of 20 mg (Figure 45), MTBE residual after half an hour of treatment was 80% for 5% TiO_2-MWCNT, 18% for TiO_2 and 75% for MWCNT. 5% TiO_2-MWCNT yielded 76% after an hour of treatment and 73% after ninety minutes, while TiO_2 also showed residual of 10% and 6% after one hour and after an hour and a half of treatment respectively. Treatment with MWCNT showed MTBE residual of 72% after an hour of treatment and 67% after ninety minutes. At the end of the run, residual rates were 68%, 4% and 66% for 5% TiO_2-MWCNT, TiO_2 and MWCNT respectively. MTBE removal rates were also lower as compared to when UV-A lamps of intensity 0.98 mW/cm^2 (3 lamps) and UV-A lamps of intensity 1.12 mW/cm^2 (four lamps) were used. This could be because the intensity of UV-A light is not the optimum to result in degradation; further studies are needed to understand this observation. TiO_2 removal rates were higher compared to 5% TiO_2-MWCNT and MWCNT as previously reported. MTBE removal by MWCNT was also better compared to 5% TiO_2-MWCNT.

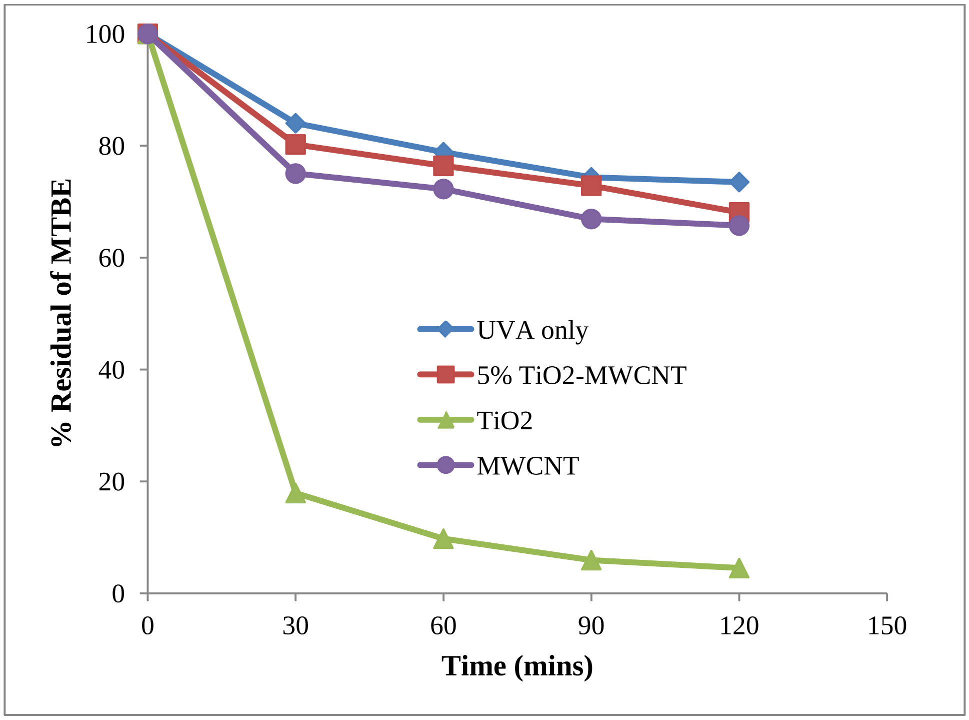


Figure 45: % Residual of MTBE after treatment by 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

Figure 46, Figure 47 and Figure 48 show results of acetone. A concentration of 25 ppb was recorded after thirty minutes of treatment with 1 mg TiO_2. At a dosage of 10 mg, 30 ppb was recorded after an hour of treatment. After treatment with 20 mg, concentrations of 19 ppb and 18 ppb were measured after half an hour and an hour of treatment respectively. For the remainder of the conditions, acetone was not detected at the end of each treatment run. Acetone was not detected when treatment was carried out with 5% TiO_2-MWCNT and MWCNT. The decreased MTBE degradation under this condition could be the reason for this.

For TBA analysis, depicted in Figure 49, Figure 50 and Figure 51, concentrations less than 5 ppb was recorded for 5% TiO_2-MWCNT, TiO_2 and MWCNT. This may be because adsorption was the main reaction taking place instead of photocatalysis; thus by-products formed were below noticeable levels.

TBF results are shown in Figure 52, Figure 53 and Figure 54. A concentration of 223 ppb was recorded after half an hour treatment with 1 mg TiO_2. However, concentrations less than 5 ppb were recorded for 5% TiO_2-MWCNT, TiO_2 and MWCNT for the remainder of the conditions. Increase in dosage initially resulted in higher concentrations but the generally lower photoactivity resulted in very low concentrations by the end of the treatment runs.

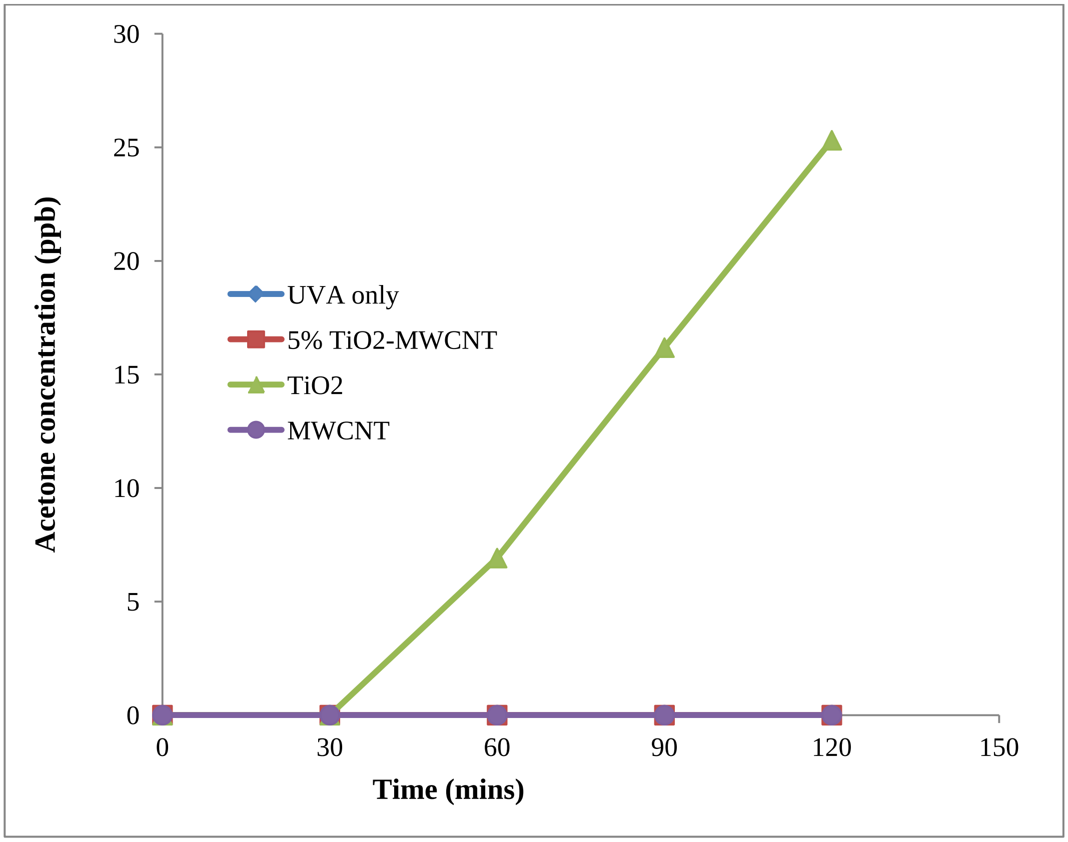


Figure 46: Acetone concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

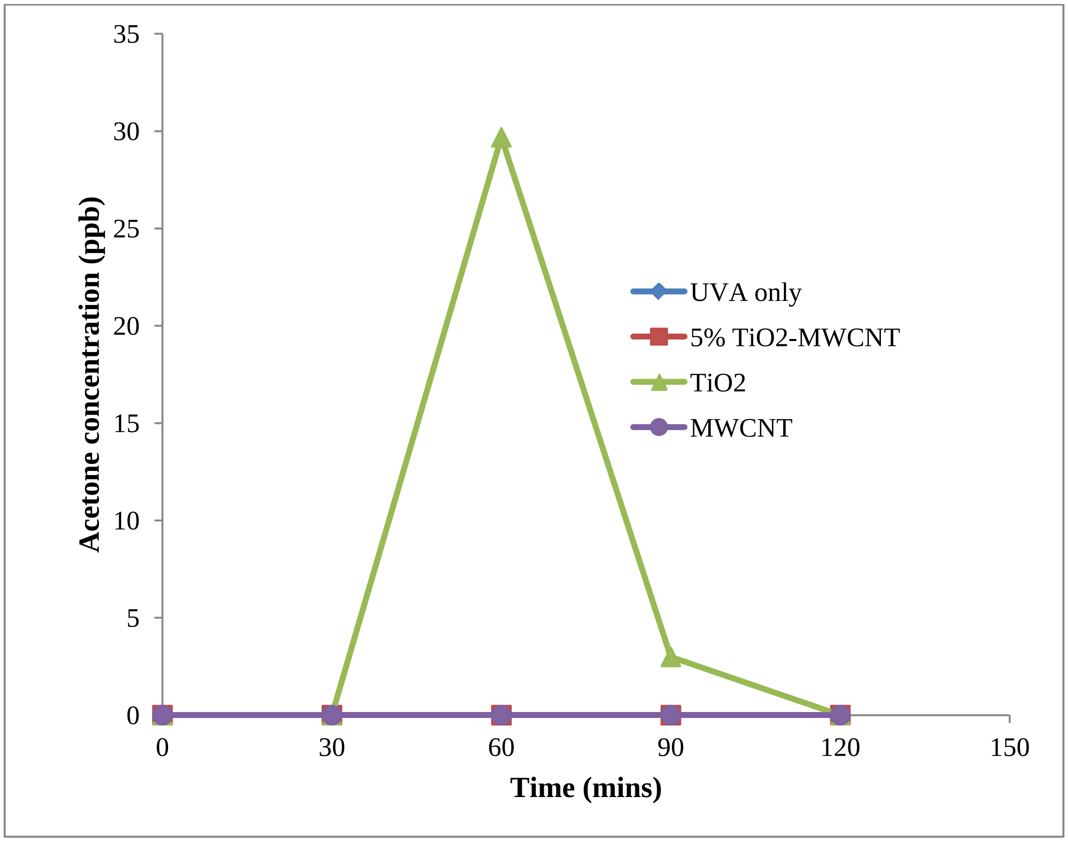


Figure 47: Acetone concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

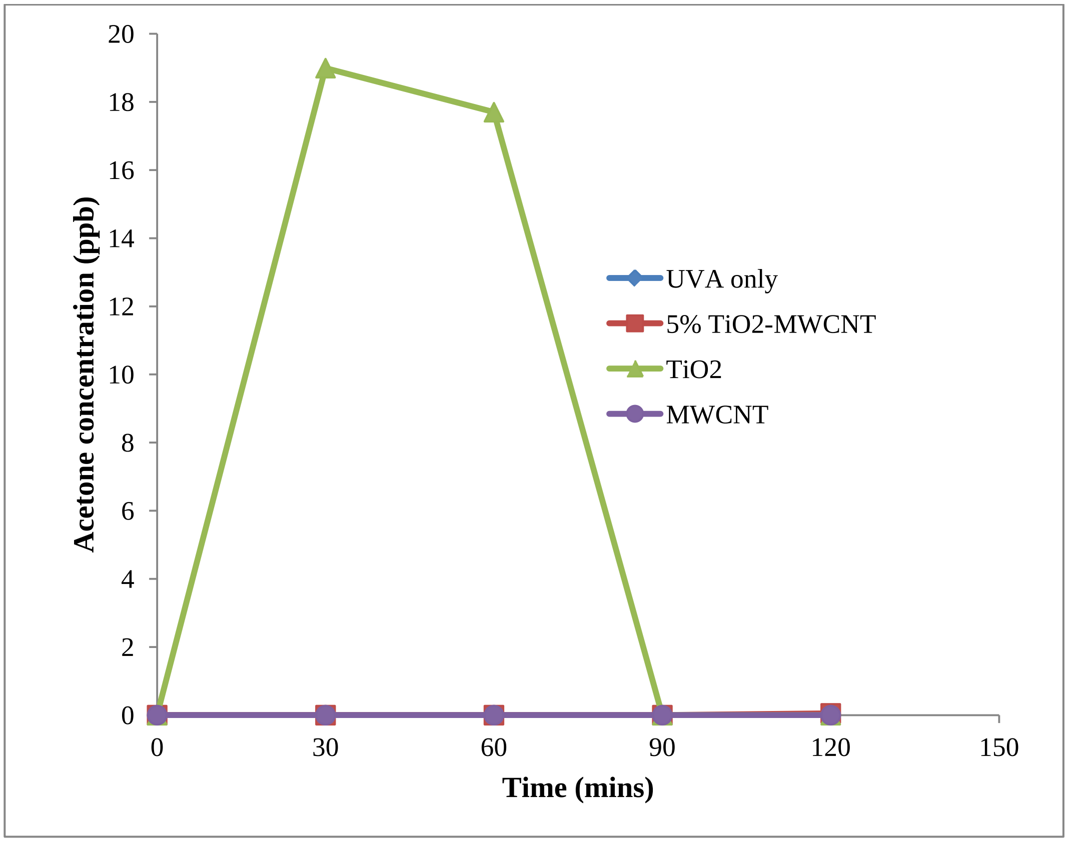


Figure 48: Acetone concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

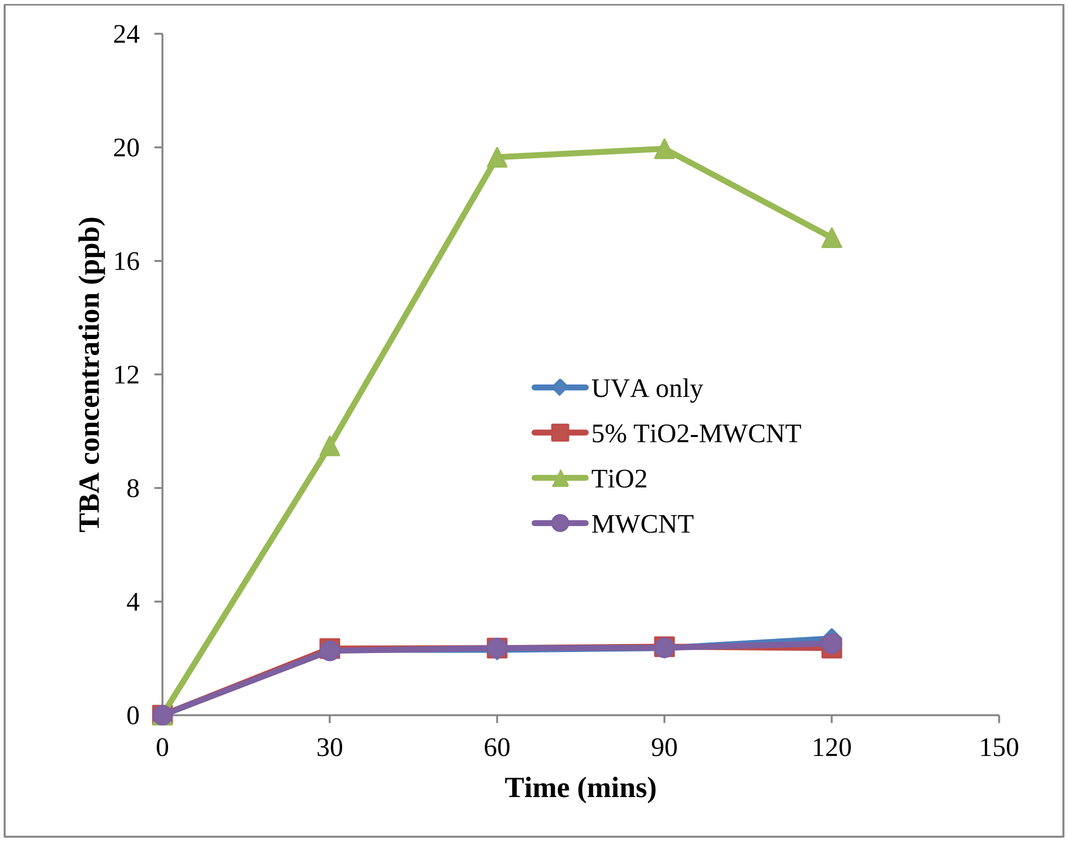


Figure 49: TBA concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

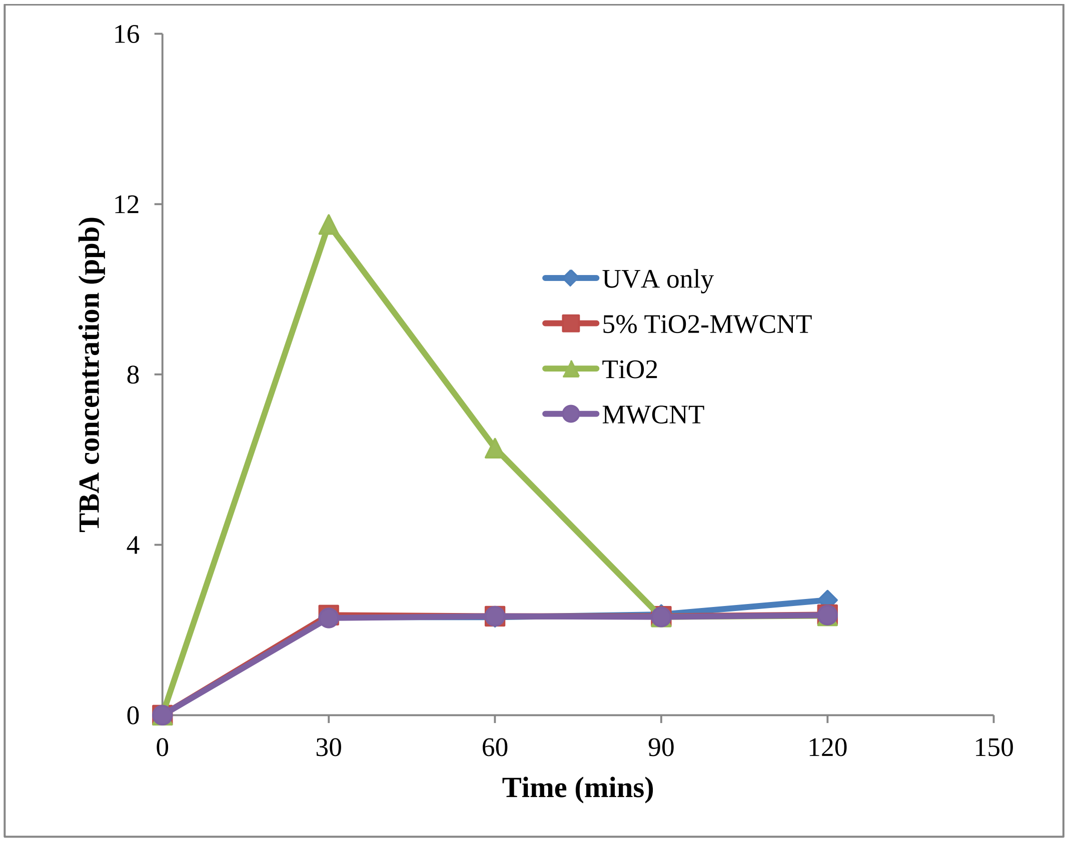


Figure 50: TBA concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

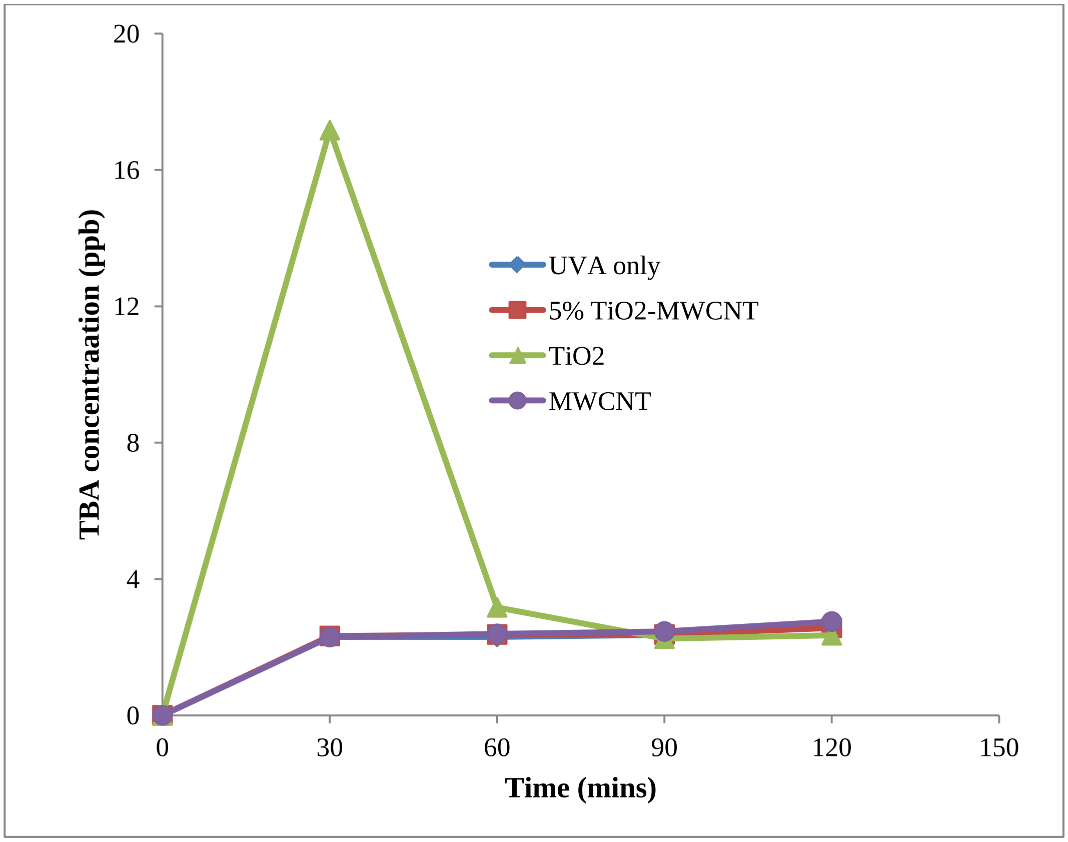


Figure 51: TBA concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

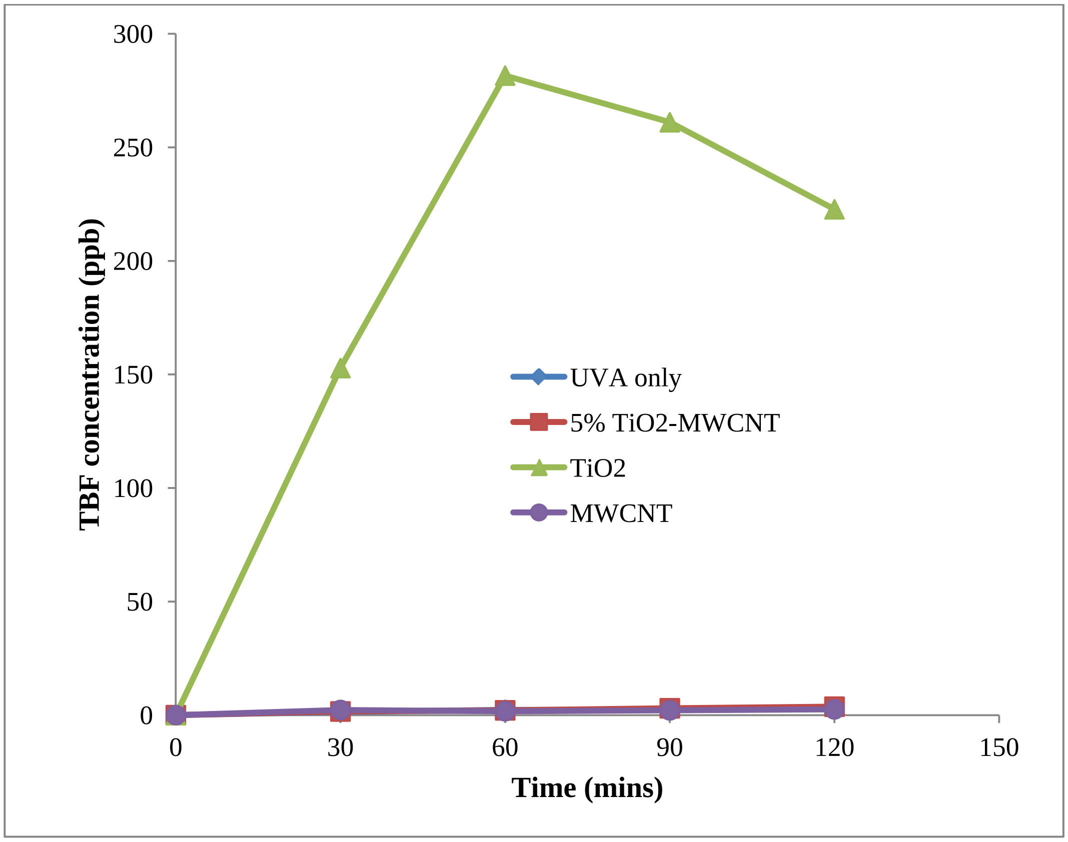


Figure 52: TBF concentration after treatment with 1 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

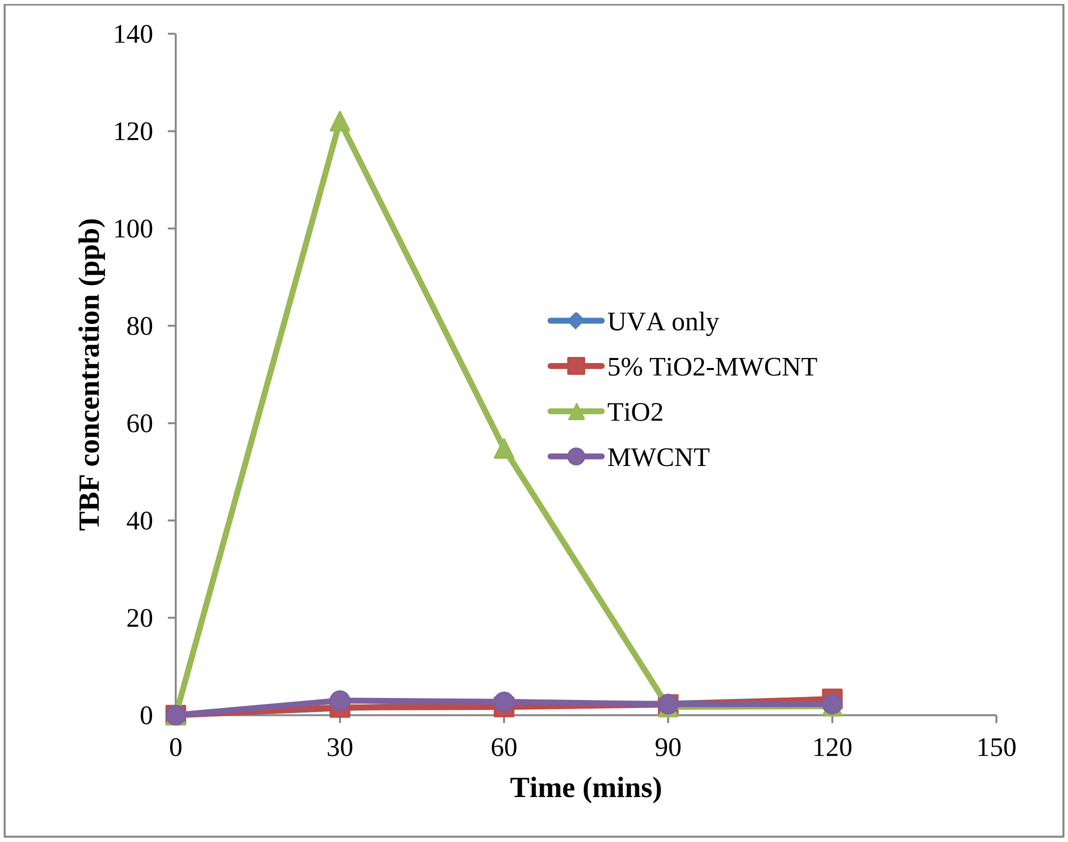


Figure 53: TBF concentration after treatment with 10 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

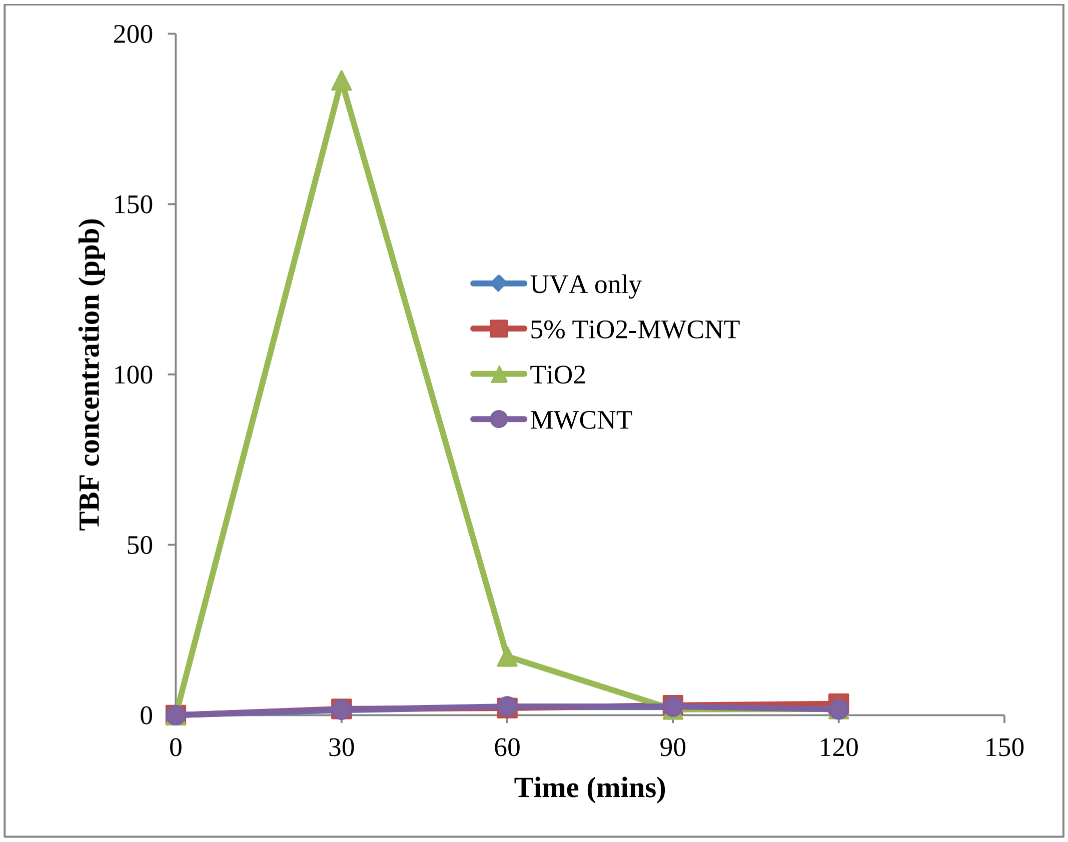


Figure 54: TBF concentration after treatment with 20 mg 5% TiO_2-MWCNT, TiO_2 and MWCNT irradiated with 2.17 mW/cm^2 UV-A light.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The aim of this study was to develop a water treatment technique that efficiently removes MTBE and its degradation by-products from water. The goal was to combine the mechanisms of TiO_2-photocatalysis and adsorption by multi-walled carbon nanotubes (MWCNTs). 5% TiO_2-MWCNT composites were synthesized and characterized by FE-SEM, EDX and XRD analysis. The photoactivity of 5% TiO_2-MWCNT composites as well as anatse TiO_2 powder and MWCNTs was tested using aqueous MTBE solutions under irradiation of UV-A lamps of wavelength of 350 nm at various intensities (0.98 mW/cm^2, 1.12 mW/cm^2 and 2.17 mW/cm^2).

MTBE degradation was estimated by the measurement of residual concentration in water. Degradation by-products; acetone, TBA and TBF, were also monitored. It was observed that degradation with UV-A lamps at intensity of 1.12 mW/cm^2 resulted in a better removal of MTBE and a consequent increase in by-product formation.

From the results it could be deduced that the decomposition of MTBE in aqueous solution with TiO_2 was much better compared to MWCNT and 5% TiO_2-MWCNT. TiO_2

is a known photocatalyst and its effectiveness has been widely reported (Keshmiri et al., 2004; Eslami et al., 2007; Chong et al., 2010). In the case of MWCNTs, the photo-induced-electron absorption effect reported by Oh et al., (2010), could explain the photocatalytic activity observed in the experiments. Though the mechanism by which this occurs is not fully understood. Generally, MWCNT showed a better performance at removing MTBE compared to 5% TiO_2-MWCNT, except under irradiation by UV-A lamps at intensity of 1.12 mW/cm^2 with a dosage of 20 mg. The prepared 5% TiO_2-MWCNT composites generally exhibited the lowest removal rates, which could be due to the low TiO_2 loading in the composite; as a low TiO_2 loading would reduce the amount of hydroxyl radicals generated and thus lower degradation.

5.2 RECOMMENDATIONS

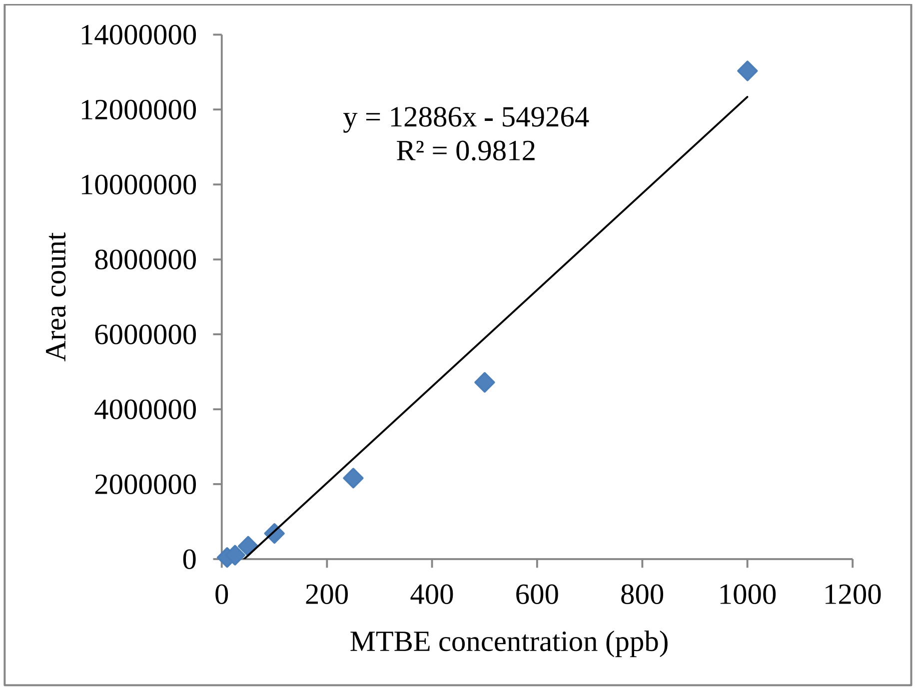
To build upon the findings made in this study and add to the knowledge base in this subject area, the following recommendations are proposed:

1. TiO_2-MWCNT composites with higher TiO_2 loadings should be synthesized and their photodegradation capabilities investigated.
2. A detailed analysis of the by-products generated is required in order to ensure that potentially harmful contaminants are not generated.
3. Adopting the procedure used in this study to test the effectiveness of removal of other contaminants such as benzene.
4. Finding techniques of overcoming the problem of settling of the materials.

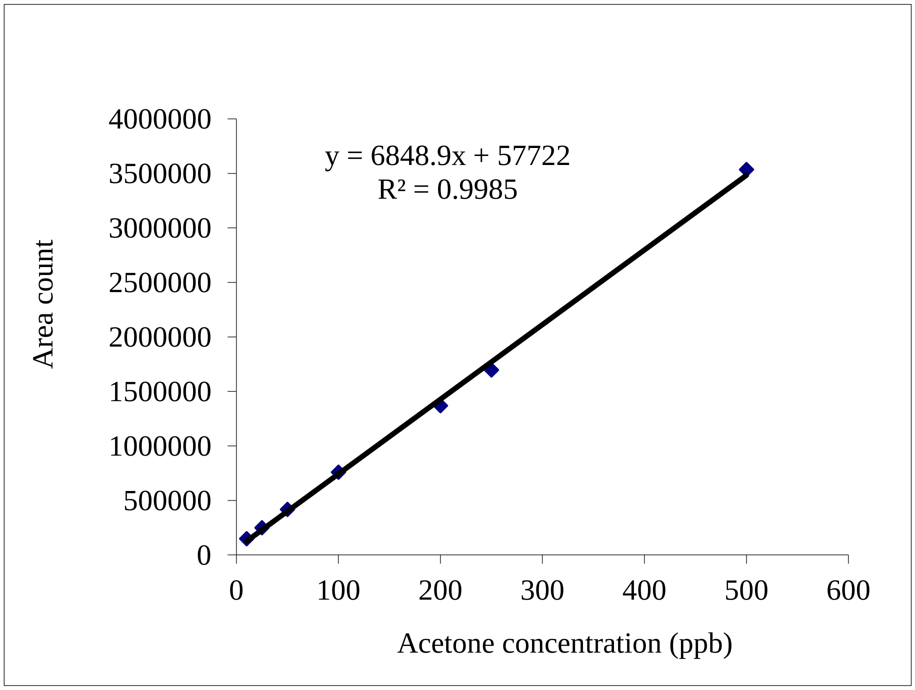
APPENDIX

APPENDIX A: CALIBRATION CURVES

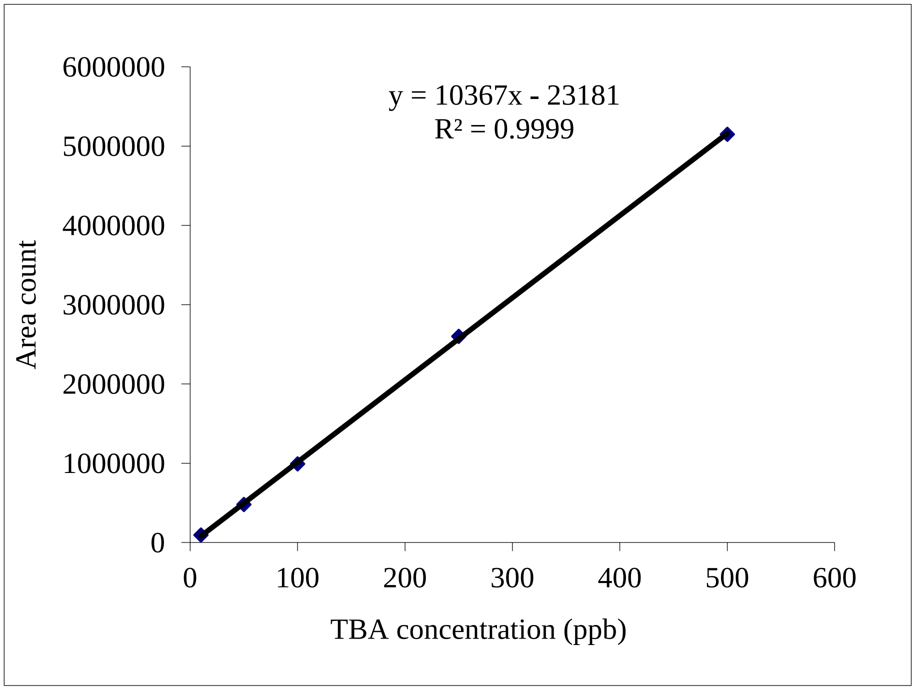
MTBE CURVE



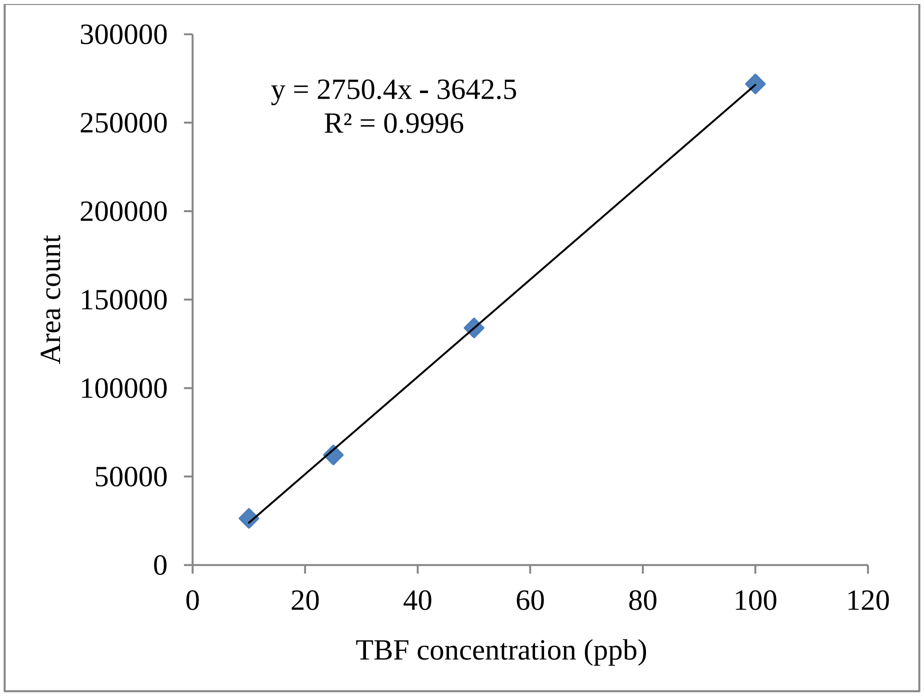
ACETONE CURVE



TBA CURVE



TBF CURVE



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VITAE

Name: Musah Ahmed Rufai Muhyedeen

Nationality: Ghanaian

Email: mformusah@yahoo.com

Mailing Address: P.O Box AN 8246 Accra-North, Accra – Ghana

Education:

2004-2008 KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY (KUMASI, GHANA)

- Bachelor of Science Degree – Environmental Science

2009 -2012 KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS, (DHAHRAN, SAUDI ARABIA)

- Master of Science Degree – Environmental Sciences