PHOTOCHEMICAL DEGRADATION OF BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENES (BTEX) USING UV/H_2O_2

Durkhani Kakar

(B.Eng., Ryerson University, ON, Canada, 2003)

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ABSTRACT

Photochemical Degradation of Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) Using UV/H_2O_2

Durkhani Kakar

MASc., Environmental Applied Science and Management Program

Ryerson University

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The oxidation of benzene, toluene, ethylbenzene, and xylenes (BTEX) by advanced oxidation processes in water was investigated. The degradation of BTEX by UV-185 and UV-254 nm in conjunction with H_2O_2 was studied. It was observed that the recommended H_2O_2 concentration to degrade 100 mgTOC/L of BTEX was 250 mg/L and 300 mg/L for UV-185 and UV-254 nm, respectively. In addition, it was observed that using the lamps in series did not have any advantages in the TOC removal of BTEX. Under acidic condition, pH 3, UV-$185/H_2O_2$ removed 10% more than UV-$254/H_2O_2$. At the recommended H_2O_2 concentration, 90% of BTEX mineralization was occurred with UV-185 nm/ H_2O_2 under acidic condition of pH 3. It was observed that 21-32% BOD/TOC ratio of BTEX was decreased with an increase in residence time (within 140 min) in the photoreactor.

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NOMENCLATURE

B_1	DO of seed control before incubation, mg/L
B_2	DO of seed control after incubation, mg/L
COD_i	COD concentration of influent or inlet wastewater sample, mg/L
COD_f	COD concentration of effluent or outlet wastewater sample, mg/L
d	diameter of feed reservoir, cm
D_1	DO of a diluted sample immediately after preparation, mg/L
D_2	DO of a diluted sample after 5 days incubation at 20°C, mg/L
f	ratio of the volume of seed solution in glucose glutamic acid test to the volume of seed solution in seed control
HRT	Hydraulic retention time in ABR (days)
k	the rate constant $M^{-1} s^{-1}$
k_{RH}	the second-order rate constant, L/mg.h
k_{Sn}	the second-order rate constant, L/mg.h
p	power rating for system, W
P	decimal volumetric fraction of sample used (dimensionless)
TOC_i	TOC concentration of influent or inlet wastewater sample, mg/L
TOC_f	TOC concentration of effluent or outlet wastewater sample, mg/L

Greek Letters

ε	molar absorptivity, $(M.m)^{-1}$
ξ	a constant that depends on an AOP process, mg/h.W
φ	quantum yield constant, (mol of H_2O_2 or target compound)/photon

Abbreviations

ABR	Anaerobic Baffled Reactor
AOP	Advanced Oxidation Process
ATSDR	Agency for Toxic Substances and Disease Registry
BOD	Biological Oxidation Demand
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CAS	Chemical Abstract Service
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EPA	Environmental Protection Agency
EIA	Energy Information Administration
GC	Gas chromatography

HR	Higher range
HRT	Hydraulic retention time
LR	Lower range
MCL	Maximum Contaminant Level
N/A	Not applicable
NDIR	Non-dispersive infrared
RCB	Romy Chakraborty (Indexing of bacteria, bacteria is named after the person that discovered/isolated. The strain RCB was isolated by Romy Chakraborty, Ph D. at the University of Berkeley California in 2005)
RH	Target compound
TCOD	Total Chemical Oxygen Demand
TOC	Total Organic Carbon
UV	Ultraviolet
VOC	Volatile Organic Compound
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

Preserving and protecting the environment have become of prime importance. Due to the exponential increase in human population, industrial developments, and human activities, there are higher levels of environmental pollutants. Water, one of the most valuable resources, is polluted by these organic contaminants. In the United States, the treatment of wastewater did not receive much attention before the 1900, because the release of wastewater into large bodies of water did not present such a nuisance and health problems as it does today. In the early 1900s, the health problems caused by wastewater brought about an increased demand for more effective means of wastewater management (Metcalf and Eddy, 1991).

Wastewater treatment technologies including physical, chemical, and biological methods are classified into three main categories: primary, secondary, and tertiary treatments. They are widely used to remove contaminants from wastewater to achieve different levels of contaminant removal. These treatment processes include screen, oil, and grease removal units, dissolved air floatation, adsorption, stripping, coagulation, flow equalization, filtration, disinfection, biological treatment including any combination of aerobic lagoon, anaerobic lagoon, facultative lagoon, activated sludge process, and/or other biological treatment processes (US EPA, 2002).

In 2008, the world's total daily production of crude oil was over 73 million barrels (EIA, 2009). Over 9 million barrels of 73 million barrels were processed into gasoline (EIA, 2009). Benzene, toluene, ethylbenzene, and xylenes (BTEX) are components of gasoline-

derived contaminants. BTEX are also widely used as industrial solvents for organic synthesis and equipment cleaning (Shim et al., 2005). The BTEX components of petroleum products are of particular concern because of their toxicity. These chemicals are prone to be released to the environment through continuous accidental spills from road surface, domestic waste, and major leakage from tankers, pipelines, industrial activities, and storage tanks. BTEX are relatively soluble and they migrate with the groundwater (Lovley, 1997).

The biodegradation of BTEX has been studied both aerobically (Zilverntant; Mason et al., 2000; Schreiber and Bahr, 2002; Shim et al., 2006) and anaerobically (deNardi et al., 2007; Lovley, 1997, Shim et al., 2006). The results of these studies show that the biodegradation is a common degradation process for BTEX in aquifers and soils. The aerobic processes are commonly utilized in the contaminated fields and research to degrade BTEX. Under proper conditions, microorganisms can be cultivated to remove BTEX. However, biodegradation processes take a long time to degrade BTEX. Borden et al. (1997) demonstrated that toluene can be biodegraded in a petroleum contaminated site under methanogenic condition only after a lag phase of 60 to 246 days. Aquifer materials from contaminated sites can degrade low concentration (1-4 mg/L) of BTEX aerobically (Cho et al., 2006; Bahr and Schreiber, 2002). It has been shown that in nitrate reducing experiments, benzene and ethylbenzene were not degraded by indigenous microorganisms during the course of 4 months of experiment (Alvarez and Vogel, 1995).

Most existing water treatment processes have limitations and are not cost-effective. Among other chemical processes, an attractive alternative to the degradation of toxic and recalcitrant chemicals in wastewater is advanced oxidation processes (AOP). AOPs are fairly new technologies, which have developed in the last 35 years (Zhou and Smith, 2001). AOPs have become predominately important due to their ability to rapidly remove pollutants from

wastewater. AOP has emerged as an effective method for purifying water and air (Mathew, 1987). AOP produce highly reactive intermediates, mainly hydroxyl radicals (·OH), which oxidize chemicals unselectively. These processes can be combined with UV irradiation. The energy from the UV wavelength is able to break a chemical bond and hence produce a free radical. These radicals henceforth attack the organic pollutants and mineralize them. Though relatively expensive, complete mineralization of organic compounds is possible through the photolytic reaction. Lee et al. (2001) reported that using AOP to treat 400 m^3/day textile wastewater would cost 55% more compared to the use of the intensified biological treatment. Therefore, it is important to optimize the parameters of the AOP to render it cost-effective.

BTEX were chosen for this study because these compounds are notorious as pollutants in groundwater, soil, and air. Available data support that BTEX are hazardous to human health and benzene is a possible carcinogen.

CHAPTER 2

LITERATURE REVIEW

This chapter contains three parts. Section 2.1 describes the properties of BTEX. Section 2.2 presents a review of experimental and field work performed on BTEX, and Section 2.3 is a review of AOP processes.

2.1. BTEX

2.1.1. Presence of BTEX in Environment

BTEX (benzene, toluene, ethylbenzene, and xylenes) are hazardous pollutants that are found in the air, water, and soil. BTEX are volatile mono-aromatic hydrocarbons, which are commonly found together in crude petroleum and petroleum products. Benzene can be found in synthetic rubber, plastic, nylon, insecticides, paints, dyes, resins-glues, furniture wax, detergents, cosmetics, and cigarette smoke. Toluene is used as a solvent for paints, coatings, gums, oils and resins. Ethylbenzene can be found in paints, inks, plastic, and pesticides. Printing, rubber, and the leather industries use xylenes as solvent. In addition, BTEX are used as diluents in nuclear hot laboratory cells (Skarabakova et al., 1994). Typically, BTEX make up about 18% of gasoline. The breakdown of BTEX in gasoline is as follows: 11% benzene, 26% toluene, 11% ethylbenzene, and 52% xylenes by weight (Health Assessment Section, 2008). When gasoline contacts water, BTEX accounts for 90% of the soluble fraction of the gasoline components in water (Bolduc et al., 2002).

2.1.2. Health Effects

To limit human risks and to attain the aesthetic quality of drinking water, the World Health Organization (WHO) defined guideline values for these components as follows: benzene, 10 µl/L; toluene, 700 µl/L; ethylbenzene, 300 µl/L ; and xylenes, 500 µl/L (WHO, 1993). Exposure to any of the individual chemicals can cause neurological impairment via parent chemical-induced changes in neuronal membranes. In addition, benzene can cause hematological effects, which may ultimately lead to aplastic anemia and acute myelogenous leukemia. There is evidence that ethylbenzene is carcinogenic in other tissues (ATSDR, 2004). The potential health effects of exposure to BTEX at levels higher than the Maximum Contaminant Level (MCL) are presented in Table 2.1.

2.1.3. Properties of BTEX

At room temperature, BTEX are colourless and flammable volatile organic compounds (VOCs). Most people can begin to smell benzene in air at 1.5-4.7 parts of benzene per million parts of air and smell benzene in water at 2 mg/L. Most people can begin to taste benzene in water at 0.5-4.5 mg/L. One part per million is approximately equal to one drop in 40 gallons (ATSDR, 1997). For toluene, Alexander et al. (1982) reported that the odour threshold is 0.024 mg/L and two taste threshold measurements of 0.12 and 0.16 mg/L (average value 0.14 mg/L). They reported two odour thresholds of 0.0016 and 0.0032 mg/L (average value 0.0024 mg/L) for ethylbenzene and two taste threshold measurements of 0.064 and 0.08 mg/L (average value 0.072 mg/L). For xylenes, Middleton et al. (1958) stated that taste and odour could be detected at concentrations ranging from 0.3 to 1.0 mg/L.

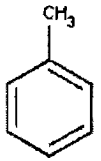
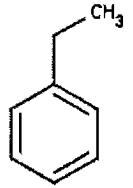
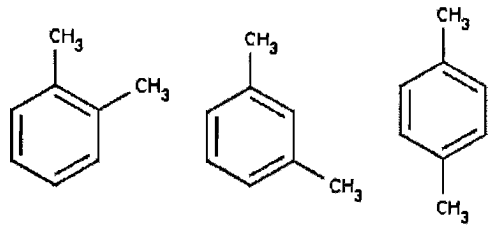
The molecular weights of BTEX range between 78-107 g/mol. The BTEX have a low solubility in water except for benzene (1755mg/L). The physical properties of BTEX are

Table 2.1: The Health Effects of BTEX (Adapted from MDE, 2007)

Parameter	Benzene	Toluene	Ethylbenzene	Meta, ortho, and para-Xylene
Maximum Contaminant Level (MCL)	0.001 mg/L	1 mg/L	0.7 mg/L	10 mg/L

Short Term Exposure	• nervous system disorder
	• immune system depression
	• anemia
		• minor nervous system disorders
		  ○ fatigue
		  ○ nausea
		  ○ weakness
		  ○ confusion
			• drowsiness
			• fatigue
			• headache
			• mild eye and respiratory irritation
				• disturbances of cognitive abilities, balance, and coordination.

Long Term Exposure (life time)	• chromosome aberration cancer	• pronounced nervous disorders
		  ○ spasms
		  ○ tremors
		  ○ impairment of speech hearing vision memory coordination
		  ○ liver
		  ○ kidney damage
			• liver
			• kidneys
			• central nervous system
			• eyes
				• damage to the central nervous system, liver and kidneys

Chemical Structure				

listed in Table 2.2. The vapor pressure and the Henry's law constants are listed. The vapor pressure of a liquid is the pressure of the gas in equilibrium with respect to the liquid at a given temperature. The vapour pressure dictates compound's tendency to evaporate. High vapour pressures mean that the compound is more likely to volatilize out of solution. The o-xylene has the lowest vapour pressure (8.72×10^{-3} atm). This means that the o-xylene will volatilize slower compared to the other BTEX. The property of a chemical that expresses its partition between water and air is the Henry's law constant, which predicts the behaviour of an organic compound in the environment. It also predicts the movement of organic matter from water to air and vice versa. High values means that the chemical compound will move toward the gas phase, while low values predicts that it will stay in the aqueous phase (Petrucci and Harwood, 1997). The Henry's law constant of toluene is relatively greater than the other BTEX; this indicates that toluene will escape a water solution faster than benzene, ethylbenzene, and xylenes.

2.2. Previous Work on the Degradation of Aqueous BTEX

The natural attenuation of BTEX has been documented at many sites where the BTEX were biodegraded primarily by indigenous microorganisms. Laboratory work has been performed in a closed system to demonstrate the biodegradability of BTEX by various microorganisms. Several peer reviewed papers (deNardi et al., 2007; Shim et al., 2005; Chakraborty et al., 2005; Schreiber and Bahr, 2002; Flyvbjerg et al., 1993; Prenafeta-Boldu, 2002) have been published to demonstrate the biodegradation of BTEX under aerobic and anaerobic conditions.

deNardi et al. (2007) demonstrated that 75-90% of BTEX can be removed when

Table 2.2: Physicochemical Properties of BTEX (Adopted from Chemical Properties Handbook, 1999)

Parameter	Molecular Formula	Molecular Weight [g/mol]	Solubility in water at 25°C [mg/L]	Density at 25°C [mg/L]	Boiling point [°C]	Henry's law constant [atm m^3/mol]	Vapor Pressure at 25°C [atm]
Benzene	C_6H_6	78.114	1755	0.873	81.09	5.55×10^{-3}	1.25×10^{-1}
Toluene	C_7H_8	92.141	542.4	0.865	111.63	6.35×10^{-3}	3.74×10^{-2}
Ethylbenzene	C_8H_{10}	106.167	165.1	0.865	137.2	8.14×10^{-3}	1.27×10^{-2}
m-Xylene	C_8H_{10}	106.167	174	0.861	140.12	6.78×10^{-3}	1.11×10^{-2}
o-Xylene	C_8H_{10}	106.167	220.8	0.876	145.43	4.19×10^{-3}	8.72×10^{-3}
p-Xylene	C_8H_{10}	106.167	201.7	0.858	139.36	6.15×10^{-3}	1.17×10^{-2}

treated in conjunction with the addition of protein, carbohydrates, and ethanol in a bench scale horizontal-flow anaerobic immobilized biomass reactor. Shim et al. (2005) have studied the degradation of BTEX as the sole carbon source under aerobic and hypoxic condition by the coculture of *P. putida* and *P. flurorescens* in a defined mineral salts medium. H_2O_2 dissolved in water with catalase were used as the additional O_2 source and no aeration was provided to avoid stripping of the BTEX. Concentrations of BTEX up to 150 mg/L were used. The results of the aerobic studies of BTEX show that the biodegradation is a common process in aquifers and soils. Aerobic processes are more commonly utilized for the degradation of BTEX. However, in soil and groundwater, oxygen is often depleted. Due to the low water solubility of oxygen in groundwater, the flux of oxygen will not be enough to support aerobic degradation.

Depending on the experiments under proper conditions, microorganisms are able to degrade the components of the BTEX. Chakraborty et al. (2005) demonstrated that *dechloromonas aromatica* (strain RCB) is capable of anaerobic degradation of benzene under nitrate reduction. In addition to nitrate, *dechloromonas aromatica* could alternatively degrade benzene both aerobically and anaerobically with perchlorate or chlorateas as suitable electron acceptors. Furthermore, with nitrate as the electron acceptor, strain RCB could also utilize toluene, ethylbenzene, and all three isomers of xylene (ortho, meta, and para) as electron donors.

Under anaerobic conditions, the biodegradation pattern for these compounds israther complex. Under strict anaerobic and sulfate reducing conditions, benzene and ethylbenzene were not degraded by aquifer-derived miroorganisms (Edwards et al., 1992; Wilson et al., 1986). Under strict anaerobic conditions, where sulfate was the terminal electron acceptor, Edward et al. (1992) demonstrated that toluene and the three isomers of xylene were

completely mineralized to CO_2 and biomass by aquifer-derived microorganisms. The biodegradation under denitrifying conditions are less favorable. Benzene cannot be degraded with nitrogen as the terminal electron acceptor (Schreiber and Bahr, 2002). The degradation of *o*-xylene often depends on the existence of primary substrates, either toluene or phenol (Flyvbjerg et al., 1993). Due to this cometabolic behavior, lag periods are prolonged for degradation of xylenes and ethylbenzene (Hutchins et al., 1991). Table 2.3 summarizes the removal efficiency of the BTEX degradation under different conditions. The studies on the degradation of BTEX demonstrate that BTEX can be consumed by microorganisms under aerobic and anaerobic conditions. These two processes can take several days to several months. On the other hand, degradation of BTEX under AOP takes only a few minutes to a few hours.

Table 2.3: Studies on the Degradation of BTEX

Treatment Technology	System	Acclimation time / Source of sludge	Initial BTEX concentration [mg/L]	Removal Efficiency (%; otherwise specified)	Reaction time	References
Biodegradation in 500 mL closed reactor	Closed system	3-20 days / consortium from landfill	100 (25 mg/L each of BTEX)	~100	below detection limit 0 mg/l after 15 h; T: 7 h; B in 12 h; X in 16 h	Goudar and Strevett, 1998
Biodegradation in 160 mL serum bottles with Minnert septa	Closed system	6 months / enrichment culture grown on phenol	14-43	81	5 days	Bielefeldt and Stensel, 1999

Treatment Technology	System	Acclimation time / Source of sludge	Initial BTEX concentration [mg/L]	Removal Efficiency (%; otherwise specified)	Reaction time	References
Continuously mixed reactor with powdered activated carbon	Closed system	sludge from refinery	50	67	N/A	Mason et al., 2000
Biodegradation in three geochemically distinct areas enriched with bromide and nitrate.	Under-ground water	Contaminated site	0.1-5.3	100	in a distance of 9.70 m from sources 50 days	Schreiber and Bahr, 2002
Biodegradation in bench-scale horizontal-flow anaerobic immobilized biomass reactor;	Closed System	65 days	48	75-99	N/A	deNardi et al., 2007
Biodegradation by four different aquifer materials nitrate reducing condition	Closed System	330 days	Benzene 19.6 ±0.3 Toluene 19.2±0.8 Ethylbenzene 3.7±0.1 *o*-Xylene 3.8±0.1 *m*-Xylene 9.3±0.3 *p*-Xylene 3.7±0.1	~ 0 ~ 100 ~ 0 ~ 53 ~ 0 ~ 0	N/A[1] 27 days N/A[1] 27 days N/A[1] N/A[1]	Alvarez and Vogel, 1995
Field and laboratory experiment were conducted to examine the anaerobic degradation of BTEX in two petroleum contaminated site under ambient condition	Closed system and under-ground water	Contaminated site	2	no evidence of BEX degraded and toluene removal 98.5-99.75	60-246 days	Borden et al., 1997

Treatment Technology	System	Acclimation time / Source of sludge	Initial BTEX concentration [mg/L]	Removal Efficiency (%; otherwise specified)	Reaction time	References
Biodegradation of BTEX at a spill site	Spill site	Contaminated site	60	93.1% iron reducing zone; 5.6% nitrate zone and 1.3% oxidized zone	N/A	Kao and Wang, 1999
Biodegradation in Chemostat experiment under ethanol enriched	Closed system	N/A	1	0.25-0.64 pg/cell/h	N/A	Lovanh et al., 2002
Biodegradation in serum bottles by *Pseudomonas putida* and *Pseudomonas fluorescensunder*	Closed System	N/A	150	77	500 h	Shim et al., 2005
Biodegradation by soil in an anaerobic chamber containing pure dinitrogen gas	Closed system	Contaminated soil + 5 months incubation in nitrogen chamber	10-150	47-100	50 days	Dou et al., 2008
Biodegradation in a glove box containing nitrogen	Closed system	Petroleum contaminated coastal plain	1-3	98	388 days	Hunt et al., 1998
Batch photoreactor contained a bundle of TiO_2-coated quartz fiber was used to photo catalytically oxidize gaseous benzene in air stream,	Closed system	N/A	20	80	4 h	Wang and Ku, 2003

Treatment Technology	System	Acclimation time / Source of sludge	Initial BTEX concentration [mg/L]	Removal Efficiency (%; otherwise specified)	Reaction time	References
Homogeneous degradation of BTEX in aqueous solution, at pH 3, of hydrogen peroxide under UV irradiation in a photoreactor equipped with 300 nm light	Closed system	N/A	100 (25 mg/L each of BTEX)	90	10 min	Daifullah, and Mokhtar, 2004
BTEX contaminated water from wells were pumped into a solar photocatalytic degradation reactor containing TiO_2 slurry or H_2O_2 to remove BTEX.	Closed system	N/A	46.9-103	> 70	4 h	Cho et al., 2006

[1] Not applicable because degradation was not significant

Daifullah and Mohamed (2004) studied the degradation of BTEX by the UV irradiation of the magnetically stirred clear solutions containing 100 mg/L BTEX in a quartz cylindrical flask (12 cm^3) at 20°C. The UV lamp (high pressure mercury lamp) emitted 300 nm light. The oxidant used in their experiments was H_2O_2. More than 90% of BTEX were removed within the first 10 minutes irradiation.

Cho et al., (2006) studied solar photocatalytic degradation of BTEX. The solar reactor had 8 quartz tubes (1.524 cm diameter), which were connected to 8 modules with width and length of 75 cm and 100 cm respectively. The total volume of the 8 quartz was 0.73 L. The quartz tubes were packed with 1.0 wt% TiO_2 slurry. The 8 modules and 8 quartz tubes were connected in series, the contaminated water flow through these modules and

quartz then back to the 10L reservoir at a rate of 3 L/min. The UV wavelength from the sun was 365 nm. In their study, the solar light/TiO_2 slurry system degraded more than 70% of BTEX within 4 h.

2.2.1. BTEX Intermediates

Some of the potential aromatic and aliphatic metabolites of BTEX are benzoate ($C_6H_5CO_2$), catechol ($C_6H_4(OH)_2$), 3-methylcatechol ($C_7H_8O_2$), 4-methylcathechol ($C_7H_8O_2$), succinate ($C_4H_6O_4$) and adipate (Alvarez and Vogel, 1995). Phenolic intermediates are produced during high dosage of H_2O_2 with *p*-xylenes (Stephan et al., 2000). During toluene oxidation, benzaldehyde (C_7H_6O) and benzoic acid (C_6H_5COOH) have been detected (Hisahiro et al. 2002). Ouidri and Khalaf (2009) reported that during photo-oxidation of toluene, the major intermediates formed are benzaldehyde (C_7H_6O) and *p*-cresol (C_7H_8O). In addition, traces of benzyl alcohol ($C_6H_5CH_2OH$), benzoic acid (C_6H_5COOH), pyrogallol ($C_6H_6O_3$), and hydroquinone ($C_6H_4(OH)_2$) were also found. A t the early stage of photocatalytic degradation of gaseous benzene in the air streams experiment, phenol (C_6H_6O) was identified to be the major intermediate produced (Wang, and Ku, 2003).

2.3. Advanced Oxidation Processes

Advanced oxidation processes (AOPs) refer to a set of chemical treatment processes designed to remove organic and inorganic materials by oxidation in wastewater and drinking water. The AOPs are promising technologies for the removal of contaminated ground and surface water as well as wastewater containing non-biodegradable or inhibitory organics to microbial growth. These processes generate free radicals (•OH), which are highly reactive and therefore attack organic chemicals mineralizing them or converting them into less harmful or lower chain compounds (Gogate et al., 2004; Legrini et al., 1993; Zhou and Smith,

2002). In AOPs, the organic radicals are formed either by photolysis of the organic substance or by reaction with hydroxyl radicals (•OH) (Legrini et al., 1993).

The products of the organic molecules could be intermediates, or at the final stage, HCO_3^-, Cl^-, NO_3^-, CO_2, and H_2O. The oxidation of organics is defined by the extent of their degradability to the final oxidation products as follows (Braun and Oliveras, 1997):

- Primary degradation, which causes structural change in the parent compounds.
- Satisfactory degradation, a primary degradation that reduces the toxicity or converts non-biodegradable organics to biodegradable ones.
- Complete mineralization or ultimate degradation, changing the organics into CO_2 and water.
- Improper degradation, a change in the structure of the parent compounds in a way that increases the toxicity of the wastewater.

The major advantages of the AOPs are their ability to remove a wide range of chemicals (Stefan et al., 1996; Aye et al., 2004), and their ability to destroy the organic compounds without transferring them to another medium or generating secondary waste disposal problems. In wastewater treatment, UV/O_3 and UV/H_2O_2 have been successfully used to degrade organic compounds (Bolduc and Anderson, 1997). To improve the generation of radicals, UV-light can be coupled with different chemicals: UV- H_2O_2; UV-TiO_2; UV-O_3; and UV-Fenton reagent. The radicals generated by different AOPs are listed in Table 2.4 (Gulyas, 1997).

2.3.1. UV/ H_2O_2 Process

In this research, UV and UV with H_2O_2 were used to degrade BTEX. The UV/H_2O_2 combination is one of the most widely used AOP for various wastewater treatment methods. For instance, Beltran et al. (1993) studied the treatment of atrazine in water using a

Table 2.4: AOPs that Generate Free Radicals

PROCESSES	Advantages and Disadvantages	Free Radicals	References
O_3 O_3/UV O_3/H_2O_2 $O_3/UV/ H_2O_2$ H_2O_2/UV TiO_2/UV (Photocatalysis) $TiO_2/UV/ H_2O_2$ H_2O_2/Fe^{2+} (Fenton) $H_2O_2/Fe^{2+}/UV$(Photo-Fenton)	Advantages: • H_2O_2 renders ozone unselective by production of other radicals • UV strengthens the oxidation of organics by H_2O_2 • H_2O_2 is unselective to degrade contaminant; stable; slow self decomposition and therefore requires UV or a catalyst to produce hydroxyl radical • TiO_2 is stable, it lacks toxicity Disadvantages: • O_3 is selective; needs reactor to dissolve it in water before it reacts with chemicals ; unstable gas • foaming due to O_3 blocks UV transmittance • $H_2O_2/Fe^{2+}/UV$ produces sludge by the precipitation of iron hydroxide; high operational cost; solid layer forms on UV lamp	·OH	Kurniawan et al., 2006 and Gulyas, 1997
O_3 O_3/H_2O_2 H_2O_2/UV $O_3/UV/ H_2O_2$		HO_2·	
O_3 O_3/H_2O_2 $O_3/UV/ H_2O_2$		O_2·- HO_2· HO_3·	

UV/H_2O_2 process and reported that more than 99% of atrazine degradation occurred in less than 15 minutes. Aye et al. (2003) reported that the decolourization and mineralization of cotton dyeing effluent containing textile dye (reactive yellow 2) were significantly improved by using an optimum H_2O_2 concentration of 15 mM with UV, and it followed the first order kinetics. Toor and Mohseni (2007) studied the treatment of raw surface water containing disinfection byproducts using a UV/H_2O_2 process with a H_2O_2 concentration of 0-23 mg/L. It was observed that the UV/H_2O_2 process was effective in reducing disinfection byproducts at a UV dosage greater than 1,000 mJ/cm^2. Tabrizi and Mehrvar (2006) reported

an optimum H_2O_2 concentration of 720 mg/L for the degradation of a 100 mg/L solution of aqueous linear alkylbenzene sulfonate in a pilot-plant photoreactor with the UV - 254 nm.

Depending on the photochemical properties of the pollutants, UV alone may be used to remove pollutants from the water if they can absorb light at the specified wavelength. In order to improve this process, H_2O_2 can be added to enhance the generation of hydroxyl radical. The major reactions including literature values of relevant quantum yields or rate constants for organic compounds (RH) involved in a UV/ H_2O_2 process are summarized in Table 2.5 (Legrini et al., 1993; Crittenden et al., 1999; Johnson and Mehrvar, 2008).

The mechanism most commonly accepted for the photolysis of H_2O_2 is the cleavage of one H_2O_2 molecule into two hydroxyl radicals ($^{\bullet}OH$) per quantum of radiation absorbed, which is shown in Reaction (2.1) (Legrini et al., 1993; Crittenden et al., 1999; Tabrizi and Mehrvar, 2004). When an organic compound (RH) presented in water and wastewater, the reactions between generated hydroxyl radicals and organic pollutants may be differentiated by the mechanisms of Reactions (2.1) to (2.10). The final step in the reaction is the combination of radical-radical (Reaction (2.3) (Legrini et al., 1993). Due to its highly reactive nature, other water constituents such as carbonate and bicarbonate can react with hydroxyl radicals, where hydroxyl radicals react to H_2O_2, therefore causing a reduction in the overall efficiency of oxidation process with respect to the contaminant of interest.

Hydrogen peroxide is commercially available. It has a minimal capital investment, thermally stable, and very soluble in water. The energy required for the O-O bond to break in hydrogen peroxide is 48.5 kcal/mol. The energy supplied by the short wavelength UV light is sufficient to break O-O bond (Clarke and Knowles, 1982). These properties make H_2O_2 an advantageous oxidant for the industrial wastewater. Hydroxyl radicals are able to attack

pollutants unselectively by adding to the double bond (Reaction 2.11), extracting a hydrogen atom (Reaction 2.12), transferring an electron to a halogenated compound (Reaction 2.13) or by producing an organic radical (Reaction 2.14) as listed in Table 2.5.

Table 2.5: Major Reactions in the UV/H_2O_2 Process

Reaction	Rate constants	Reference	Reaction No.
$H_2O_2 + h\nu \xrightarrow{\varphi_1} 2^{\bullet}OH$	φ_1 = 0.5 mol photon^{-1}	Beltrán et al., 1999	(2.1)
$H_2O_2 + h\nu \xrightarrow{k_1} 2^{\bullet}OH$	k_1 = 1.4-4.5×10^7 M^{-1}s^{-1}	Buxton et al., 1988	(2.2)
$2^{\bullet}OH \xrightarrow{k_2} 2H_2O_2$	k_2 = 5.0-8.0×10^9 M^{-1}s^{-1}	Staehelin et al., 1984	(2.3)
$2HO_2^{\bullet} \xrightarrow{k_3} H_2O_2 + O_2$	k_3 = 0.8-2.2×10^6 M^{-1}s^{-1}	Bielski et al., 1985	(2.4)
$HO_2^{\bullet} + {}^{\bullet}OH \xrightarrow{k_4} H_2O_2 + O_2$	k_4 = 1.4×10^{10} M^{-1}s^{-1}	Koppenol et al., 1978	(2.5)
$RH + {}^{\bullet}OH \xrightarrow{k_5} CO_2 + H_2O$	k_5 varies	Legrini et al., 1993	(2.6)
$RH + h\nu \xrightarrow{\varphi_2} CO_2 + H_2O$	φ_2 varies	Legrini et al., 1993	(2.7)
$HCO_3^- + {}^{\bullet}OH \xrightarrow{k_6} CO_3^{\bullet-} + H_2O$	k_6 = 2×10^7 M^{-1}s^{-1}	Buxton et al., 1988	(2.8)
$CO_3^{2-} + {}^{\bullet}OH \xrightarrow{k_7} CO_3^{\bullet-} + OH^-$	k_7 = 3.7×10^8 M^{-1}s^{-1}	Buxton et al., 1988	(2.9)
$CO_3^{\bullet-} + H_2O_2 \xrightarrow{k_8} HCO_3^- + HO_2^{\bullet}$	k_8 = 8.2×10^5 M^{-1}s^{-1}	Crittenden et al., 1999	(2.10)
${}^{\bullet}OH + X_2C = CX_2(OH) \xrightarrow{k_9} X_2C(OH)_2CX_2$	k_9 varies	Legrini et al., 1993	(2.11)
${}^{\bullet}OH + RH \xrightarrow{k_{10}} H_2O + R^{\bullet}$	k_{10} varies	Legrini et al., 1993	(2.12)
${}^{\bullet}OH + RX \xrightarrow{k_{11}} OH^- + R^{\bullet}$	k_{11} varies	Legrini et al., 1993	(2.13)
${}^{\bullet}OH + RX \xrightarrow{k_{12}} OH^- + XR^+$	k_{12} varies	Legrini et al., 1993	(2.14)
${}^{\bullet}OH + HO_2^- \xrightarrow{k_{13}} HO_2^{\bullet} + OH^-$	k_{13} = 7.5×10^9 M^{-1}s^{-1}	Christensen et al., 1982	(2.15)
$H_2O_2 + {}^{\bullet}OH \xrightarrow{k_{14}} HO_2^{\bullet} + H_2O$	k_{14} =2.7×10^7 M^{-1}s^{-1}	Buxton et al., 1988	(2.16)

Where φ is the quantum yield constant, (mol of H_2O_2 or RH)/photon; and k is reaction rate constant, M^{-1}s^{-1}, R is an organic compound and X is a halogenated group

The removal of organic chemical through advanced oxidation processes can be complex. It involves a number of elementary chemical steps. Bolton et al., (2001) proposed a simple overall kinetics. The rate of a specific component and even the

reduction of the TOC that are either zero-order or first-order with respect to the organic contaminant can be expressed as follows:

$$H_2O_2 \longrightarrow 2^{\bullet}OH \qquad R_1 = \frac{\xi P}{V} \tag{2.17}$$

$$^{\bullet}OH + RH \rightarrow products \qquad R_2 = k_{RH}\left[^{\bullet}OH\right][RH] \tag{2.18}$$

$$^{\bullet}OH + S_1 \rightarrow products \qquad R_{3a} = k_{s_1}\left[^{\bullet}OH\right][S_1] \tag{2.19}$$

$$^{\bullet}OH + S_2 \rightarrow products \qquad R_{3b} = k_{s_2}\left[^{\bullet}OH\right][S_2] \tag{2.20}$$

.....

$$^{\bullet}OH + S_i \rightarrow products \qquad R_{3i} = k_{s_n}\left[^{\bullet}OH\right][S_n] \tag{2.21}$$

Where R = a rate (M h^{-1})

ξ = a constant [usual unit: $mg.h^{-1}W^{-1}$] that depends on the AOP

P = the electric power [W] input to the system

V = the treated volume, volume of reactor [L]

RH = a particular organic contaminant

S_1, S_2, ... S_i are a series of scavengers for the $^{\bullet}OH$

k_{RH} and k_{sn} are second-order rate constants [L/mg.h]

At steady state the overall rate law for the above mechanism is as follows:

$$-\frac{d[RH]}{dt} = \frac{\xi P k_{RH}[RH]/V}{k_{RH}[RH] + \sum_i k_{s_i}[S_i]} \tag{2.22}$$

Equation 2.22 can be used to determine the effect of each of the parameter on the TOC removal of the target contaminants during an AOP, provided that all parameters are available from literature or measured during experiments.

2.4. Biodegradability of Organic Chemicals

Many factors affect the organic biodegradability of chemicals. The most important factors to consider in biodegradability tests are: chemical structure a nd concentration; source and quantity of microorganisms; and the physicochemical conditions in which the test is performed.

The structure of the chemical compounds is important because it determines the solubility and volatility of the substance, which determine its bioavailability. It also dictates the accessibility of active sites in molecules, which are attacked by enzymes of degrading microorganisms (Boethling and Alexander, 1979). The concentration of chemicals establishes the toxicity of a substance to microorganisms (Madsen et al., 1991).

Various species of microorganisms live in different environmental conditions. Some are able to immediately degrade chemicals, completely or to an extent. Other microorganisms have to develop appropriate enzymatic mechanisms for degradation (Grady, 1985). Biodegradation could be a result of action of a single species of microorganisms, but more often it occurs due to the combined activity of several microbial species. In addition, a mixed culture usually has a higher biodegradation potential and is the actual carrier of biodegradation processes in the environment (Broholm et al., 1993).

Physicochemical conditions are important because they determine the behaviour of substances and microorganisms. The quantity and the quality of nutrients (phosphorus, nitrogen, etc.) affect the growth of microorganisms. The quantity of oxygen present, pH, temperature, and light affect the performance of microorganisms and the compounds in waste water (APHA, 1998).

2.5. Theoretical Chemical Oxygen Demand (TCOD)

The theoretical COD value of a specific compound is calculated from a stoichiometric ratio. If this theoretical value corresponds to the experimental value, it is concluded that the oxidation of the organic material is complete. The theoretical COD of a compound with a structural formula, $C_xH_yO_z$, can be determined from the two redox equations that describe the overall oxidation reaction (Petrucci and Harwood, 1997).

- **Oxidation reaction:**

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + (4x + y - 2z)H^+ + (4x + y - 2z)e^- \quad (2.23)$$

- **Reduction reaction:**

$$e^- + H^+ + \frac{1}{4}O_2 \rightarrow \frac{1}{2}H_2O \quad (2.24)$$

Combining Reactions 2.15 and 2.16 results to the following equation:

$$C_xH_yO_z + \frac{1}{4}(4x + y - 2z)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad (2.25)$$

From Reaction 2.25, it can be noted that the theoretical oxygen demand of one mole of a compound $C_xH_yO_z$ demands to ¼·(4x+y-2z) moles of O_2. The molar mass of $C_xH_yO_z$ can be expressed as (12x+y+16z) g/mol and the molar mass of oxygen is 32 grams. It is concluded that the COD of (12x+y+16z) grams of the compound $C_xH_yO_z$ is equal to ¼·(4x+y-2z)·32 = 8·(4x+y-2z) g O_2. Hence the theoretical COD per unit mass of $C_xH_yO_z$ is given by (Petrucci and Harwood, 1997):

$$COD_{theoritical}\left[\frac{gCOD}{gC_xH_yO_z}\right] = \frac{8(4x + y - 2z)}{(12x + y + 16z)} \quad (2.26)$$

When the procedure of the COD test is strictly followed, for almost all compounds, the experimental result will not differ more than a few percent from the theoretical value. This leads to the following two conclusions:

1. During the COD test, the organic materials are completely oxidized
2. The precision and reproducibility of the test are good

Equation (2.26) can be used to calculate the theoretical COD per unit mass for different structural formulas $C_xH_yO_z$. Equation (2.26) was used to calculate the theoretical oxygen demand of BTEX.

The total theoretical COD of a solution was calculated by multiplying the concentration of benzene, toluene, ethylbenzene and xylenes by its COD per compound value as shown in Table 2.6. The total organic carbon (TOC) of a solution was determined by multiplying its concentration by the carbon to molecular weight ratio.

Table 2.6: Theoretical Chemical Oxygen Demand (COD) and the Total Organic Carbon (TOC) per mg of Compound (BTEX)

Molecular formula	Name	Molecular weight (g/mol)	mg Carbon / mg Compound	mg COD/ mg Compound
C_6H_6	benzene	78.11	0.92	3.08
C_7H_8	toluene	92.14	0.91	3.13
C_8H_{10}	ethylbenzene	106.17	0.90	3.17
C_8H_{10}	xylene	106.17	0.90	3.17

Based on the literature review, biological process is a common process to degrade BTEX, however it is a slow process that could take up to months. It can only treat low concentration of organic contaminants. It is difficult to apply to the remediation of highly contaminated sites. BTEX are also hazardous and volatile therefore, it is necessary to treat them immediately to avoid any health and environmental effect. AOP can be used as an ex-

situ remediation method. To date limited studies have been performed on BTEX with AOP. Therefore the objectives of this study were as follows:

- To determine the degradability of BTEX by UV-185 and UV-254 nm
- To determine the recommended concentration of H_2O_2 to degrade 100 mgTOC/L of BTEX using UV-185 and UV-254 nm
- To assess the biodegradability enhancement of BTEX after photochemical pretreatment

CHAPTER 3

EXPERIMENTAL SETUP AND METHODOLOGY

3.1. Materials

Materials used in experiments are as follows:

3.1.1. BTEX

The following BTEX were used in experiments: benzene manufactured by EMD with GC assay of 99.0%; toluene manufactured by BDH with GC assay of 99.5%; ethylbenzene manufactured by Alfa Aesar with GC assay of 99%; and xylenes manufactured by J.T.Baker with GC assay of 99.9%.

3.1.2. Hydrogen Peroxide

Hydrogen peroxide is a pale blue liquid that appears colourless when in dilute aqueous solution. It has a molecular weight of 34.04 g/mol with a density of 1430 g/L. It is used as a disinfectant, an oxidizer, and a bleaching agent. It is a weak acid with strong oxidizing capability. In this study, hydrogen peroxide (30 wt% with density of 1110 g/L) was used as the oxidizing agent.

3.1.3. Catalase

The catalase enzyme is available in two forms, namely bovine liver and *Aspergillis niger*. Catalase bovine liver manufactured by Calbiochem with a molecular weight of 250,000 kDa was used in this study. Each mg of catalase consisted of 2380 units (1 unit is the amount of enzyme that catalyses the reaction of 1 nmol of substrate per minute) and it was stored at 5°C. The bovine liver catalase has the ability to decompose hydrogen peroxide into water and oxygen. Hydrogen peroxide concentration less than 200 mg/L can be removed effectively by adding 2.5 units/mL of catalase and leaving it undisturbed for 2 h (Ito et al., 1998).

Each molecule of catalase is a tetramer of four polypeptide chains composed of more than 500 amino acids. Four porphyrin heme groups are located within this tetramer. The heme group is responsible for the catalase enzymatic activity. To date, the exact mechanism of the catalase catalysis has not been precisely determined, but the reaction is believed to occur in two steps (Boon et al., 2008).

$$H_2O_2 + Fe(III) - E \rightarrow H_2O + O = Fe(IV) - E \tag{3.1}$$

$$H_2O_2 + O = Fe(IV) - E \rightarrow H_2O + Fe(III) - E + O_2 \tag{3.2}$$

Where Fe-E represents the iron center of the heme (the cofactor) attached to the rest of the enzyme (E). The heme consists of a proptoporyphyrin ring and a central iron (Fe) atom. A protoporphyrin ring is made up of four pyrrole rings linked by methane bridges. Four methyls, two vinyls, and two propionate side chain are attached.

The bovine liver catalase was used prior to the BOD testing. The concentration of H_2O_2 was measured using the H_2O_2 kit (Section 3.2.5). Once the concentration of H_2O_2 was determined, catalase was added to the sample and the sample was left undisturbed for 2 h.

Subsequently, the sample was used for BOD analysis.

3.1.4. Removal of Hydrogen Peroxide

Hydrogen peroxide is a known bactericide and therefore it should be removed from the solution prior to using it for the biological oxygen demand (BOD) testing. In the experiments of this study, the bovine liver catalase was used to remove H_2O_2 from the BTEX solution treated with UV/ H_2O_2. The structure of catalase and its mechanism for H_2O_2 removal is explained in section 3.1.3. Hydrogen peroxide Lovibond CHECKIT was used to determine the concentration of H_2O_2 in solution, refer to Section 3.2.4 for method of measurement of H_2O_2. According to Ito et al. (1998), when solution contains less than 200 mg/L of H_2O_2, the H_2O_2 can be removed by adding catalase and leaving it undisturbed for 2 h. This procedure was pursued in the following experiments.

3.1.5. Methanol

Methanol manufactured by EM Science with a GC assay of 99.99% was used in the preparation of gas chromatography calibration solutions.

3.1.6. Other Reagents and Materials

The deionized water produced by the MILLI-RX-75 deionizer was used for all experiments. Polyseeds, the BOD seed inoculum capsules, manufactured by Interlab Co were used in the BOD tests. The procedure for using the Polyseeds is discussed in Section 3.2.5.2. The H_2O_2 measurement kits were used to quantify H_2O_2 in the samples, as discussed in Section 3.2.5. The Accu-Test Twist caps vials with digestion reagent manufactured by Bioscience Inc. were used for the COD tests, as discussed in Section 3.2.7. All chemicals (KH_2PO_4, K_2HPO_4, $NaHpO_4.7H_2O$, NH_4Cl, $MgSO_4.7H_2O$, $FeCL_3.6H_2O$, $CaCl_2$) for the BOD experiments were purchased from Aldrich Canada as discussed in Section 3.2.6.

The parameters and conditions for the experiments are listed in Table 3.1

Table 3.1: Experimental Parameters and Conditions

Parameter /Condition	Range	Comments
BTEX, [mgTOC/L]	45-135	95% of experiment were performed with initial BTEX concentration of 100 mgTOC/L
Benzene, [mass %]	11	gasoline contains BTEX in the following mass ratio: 11:26:11:52 mass ratio
Toluene, [mass %]	26	
Ethylbenzene, [mass %]	11	
Xylenes, [mass %]	52	
H_2O_2, [mg/L]	0-400	different concentrations of H_2O_2 were used to determine the recommended concentration of H_2O_2 for the removal of 100 mgTOC/L of BTEX
Sulfuric Acid (H_2SO_4), [mg/L]	0-2.45 × 10^{-3}	sulfuric acid was used to render the solution acidic, pH 3
Sodium hydroxide (NaOH) [mg/L]	0-2.0 × 10^{-3}	sodium hydroxide was used to render the solution basic, pH 11
Flow rate [L/min]	$6.75\times10^{-2} - 3.75\times10^{-4}$	N/A
Residence Time (min)	20-3600	N/A
Temperature (°C)	20-25	room temperature
Initial pH	3, 5.3, and 11	95% of the experiments were performed without adjusting the pH (pH=5.3)

3.2. Analytical Methods

Wastewater is characterized in terms of its physical, chemical, and biological compositions. The analysis used to characterize wastewater varies from precise quantitative determination of chemicals to the more qualitative determination of biological species. In the next section, the analytical methods used during these experiments are described.

3.2.1. Determination of BTEX Concentrations

The BTEX concentration was analyzed using a Gas Chromatography (GC), PE AutoSystem GC with built-in Autosampler. BTEX were transferred from 10 mL aqueous samples to the vapor phase by bubbling helium (He) gas for 11 min through the aqueous samples contained in the purging chamber of Tekmar 2016 purge and trap auto sampler at ambient temperature. After purging, the trap was heated and the compound was desorbed and transferred into BD-WAX column (30 m × 250 μm) in a Perkin Elmer Autosystem XL, which was equipped with flame ionization detector. Both the injector and detector temperatures were set at 200°C. The temperature of the oven was set at 45°C remaining constant for 3 min, after it was ramped up at a rate of 10°C/min to a maximum temperature of 350°C. The total run time was set to 10 min. Helium was used as the carrier gas at a flow rate of 45 mL/min and the retention time for BTEX was 2-8 min.

Figure 3.1illustrates a sample of GC chromatogram for the determination of BTEX concentration.

3.2.1.1. Sample Preparation for GC Calibration

The stock solutions for BTEX were prepared by dispensing 9.8 mL of methanol into a 10 mL glass-stoppered volumetric flask. The flask was undisturbed for about 10 min or until all methanol wetted surfaces were dried. The flask was weighed to the nearest 0.1 mg at ambient temperatures; one or two drops of the pure liquid standards (benze ne, toluene, ehtylbenzene, and xylenes) were added to the flask using a 50 μL syringe.

The flask was then reweighed and capped and the solution was mixed by inverting the flask several times (Kessels, 1992). The concentration of the BTEX standard in mg/L was calculated from the net gain in weight. These stock standards were transferred into a Teflon

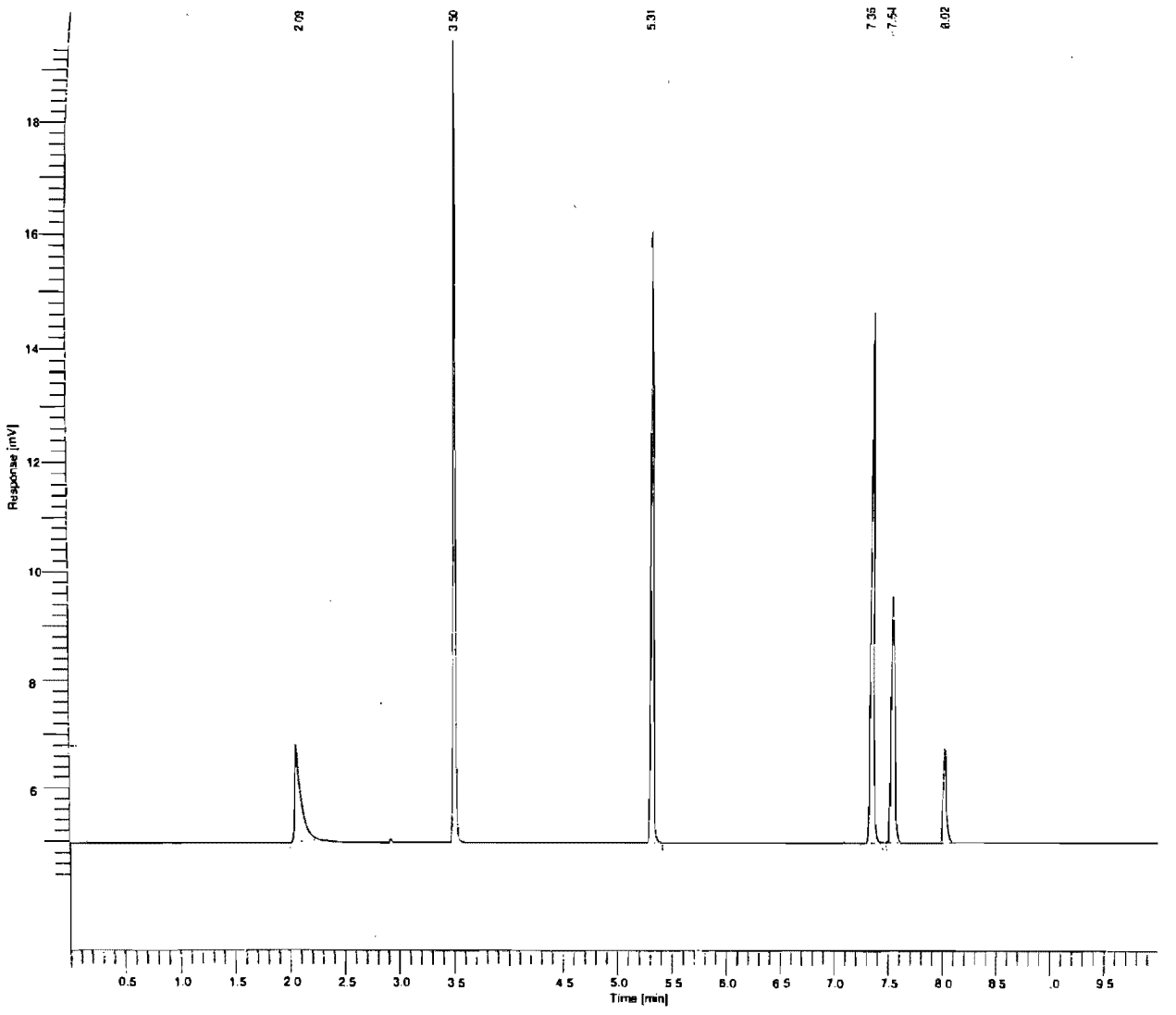


Figure 3.1: A sample of GC chromatogram for determination of BTEX concentration in the solutions. The peaks at retention time of 2.05, 3.50, 5.32, 7.37, 7.55 and 8.02 min represent benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene and *o*-xylene, respectively.

sealed screw cap bottle with minimal headspace and stored in the refrigerator. The stock standards were used to prepare the standards for calibration by dilution with methanol and water. The standards were analyzed in the GC. From the GC results obtained, the area under the peak was plotted against the known concentration of BTEX used. The concentrations of the samples were obtained from the calibration curve (Figure 3.2). Triplicate samples were prepared and analyzed to demonstrate the reproducibility of this technique. The results fell within 5-10% standard error.

3.2.2. pH and Temperature Measurement

The measurement and control of pH and temperature are highly important in the water treatment systems. The most significant environmental impact of pH involves synergistic effects. Synergy is the process whereby two or more substances combine and produce effects greater than their sum. For example when acidic waters (low pH) come into contact with certain chemicals and metals, this often makes them more poisonous than normal. To exemplify this concept, fish that usually can withstand pH values as low as 4.8 will die at pH 5.5 if the water they are swimming in contains as little as 0.9 mg/L of iron. Mixing acidic water with small amounts of aluminum, lead, or mercury, and one have a similar problem - one that far exceeds the usual dangers of these substances (DCNR, 2010).

The steps involved in wastewater treatment require specific pH levels. In order for coagulation (a treatment process) to occur, pH and alkalinity must fall within a limited range. Chlorination, a disinfecting process for drinking water, requires a pH range that is temperature dependent. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients (phosphorus, nitrogen, and carbon) and heavy metals (lead, copper, cadmium, etc.) (U.S. Geological Survey, 2010). Furthermore, in advance oxidation processes, measurements of pH can indicate that the reaction is moving

toward completion (for example, organic acid and carbon dioxide are produced and hence, the pH drops).

The temperature and pH of the samples were measured by a portable pH and pH/ISE Meter (230A plus, Thermo Orion). Before use, this measuring device was calibrated using either pH 4.01 and 7.00 or 7.00 and 10.01 buffer solutions, depending on the expected sample range, at room temperature. During pH measurement, the temperature was displayed automatically at the same time. The measurements were done immediately at room temperature after collecting wastewater sample.

3.2.3. Dissolved Oxygen (DO) Measurement

The YSI Dissolved Oxygen Meter model 58 equipped with an YSI 5739 BOD probe was used to measure the DO in the BOD bottles. The DO membrane and electrolyte were changed prior to the calibration and adjustment of the probe. The DO probe was adjusted before its use to obtain the DO readings that corresponded to the calibration values for the local altitude and temperature. The DO membrane was visually inspected (for wear, tear and/or presence of air bubbles) and replaced, if necessary.

3.2.4. Hydrogen Peroxide CHECKIT

The Lovibond Hydrogen Peroxide CHECKIT unit has three compartments, which functions as both a sample container and a comparator in a compact unit. The outer compartments are used for the analysis of low (0.2-2 mg/L) and high (10-100 mg/L) concentrations of H_2O_2. The middle compartment is used as a reference. It was filled with the water to be tested without addition of any reagent tablet in order to compensate for any inherent color or turbidity present in the sample. Three types of reagent tablets are part of this CHECKIT: LR (lower range), HR (high range), and acidifying tablet, which are used to detect the concentration of H_2O_2 in the sample.

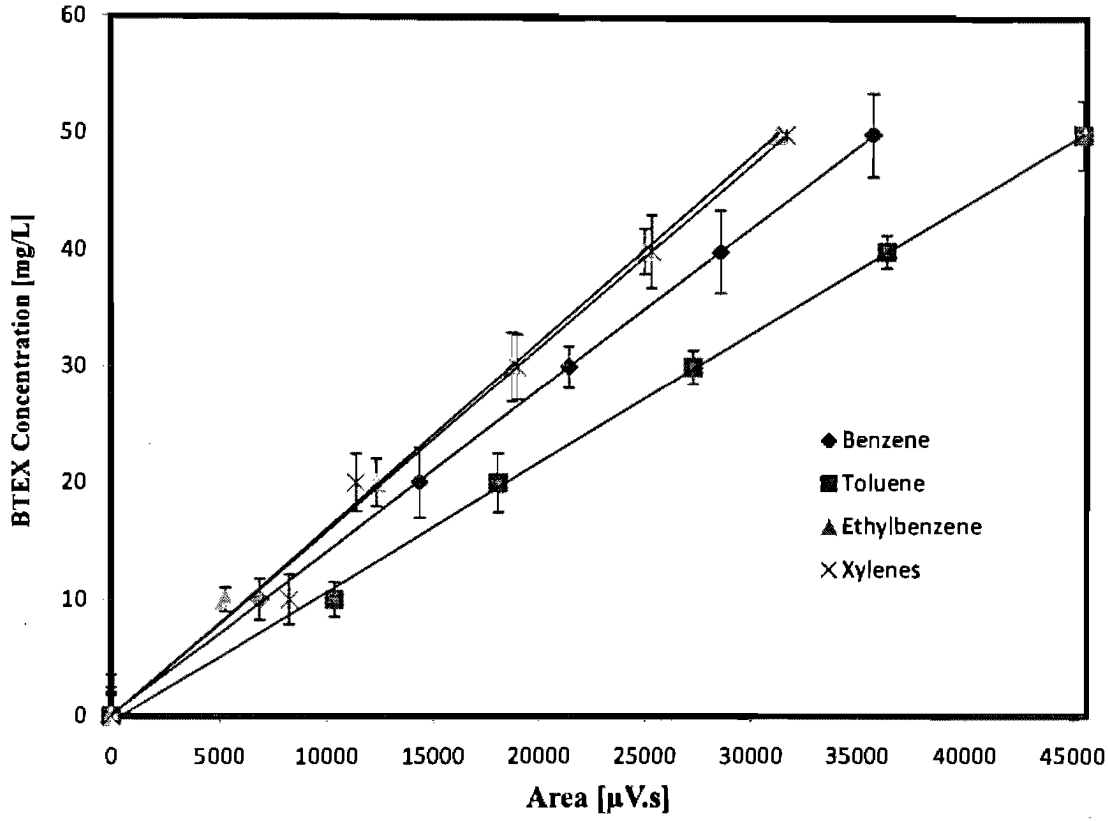


Figure 3.2: A sample of GC calibration curve for benzene, toluene, ethylbenzene, and xylenes. The calibration equations are as follows:

Benzene = 0.001x + 0.136 $R^2 = 0.999$
Toluene = 0.001x - 0.483 $R^2 = 0.999$
Ethylbenzene = 0.001x + 0.71 $R^2 = 0.999$
Xylenes = 0.001x $R^2 = 0.992$

To measure the concentration of H_2O_2, each compartment was filled to the 10 mL mark with the sample water. LR reagent tablet was added to the low range compartment and HR and the acidifying tablets were added to the high range compartment. The tablets were crushed with a clean stirring rod and the stopper was placed. The unit was inverted several times until the tablets were fully dissolved. Next, it was allowed to stand for 2 minutes. Then, CHECKIT was given a final shake and the colour produced was compared against the standards using daylight. The resulting sample colour was visually matched with the coloured plastic foils to indicate the concentration of the H_2O_2 under test. For example, if the colour of sampled water is unchanged when the tablets were added to the sample water in the kit, the solution did not contain H_2O_2 in the range of detection (<0.2 mg/L). If the colour changes to pink, then the solution contains H_2O_2. For example, if the colour of the sample is dark orange, based on the nomenclature of the kit, the concentration of H_2O_2 of the sample is 100 mg/L. In contrast, if the colour of sample changes to light pink, the concentration is 0.2 mg/L

3.2.5. Biological Oxygen Demand (BOD)

The biological oxygen demand (BOD) is a biochemical procedure for determining the uptake of dissolved oxygen by biological microorganisms in a sample of water. BOD tests were performed as per Standard Methods (APHA, 1998) for the examination of wastewater.

The following four buffers were required for BOD analysis: phosphate buffer, magnesium sulfate, ferric chloride, and calcium chloride. These buffers were prepared by dissolving the required chemicals in distilled water, diluted to 1L. The chemicals required for each stock solution are as follows:

- Phosphate buffer: 8.5 g KH_2PO_4; 21.75 g K_2HPO_4, 33.4 g $NaHpO_4.7H_2O$ and 1.7 g NH_4Cl
- Magnesium sulfate buffer: 22.5 g $MgSO_4.7H_2O$

- Ferric chloride: 0.25 g $FeCL_3.6H_2O$
- Calcium chloride: 27.5 g $CaCL_2$

Dilution water for BOD was produced by aliquoting 1 mL of each of the above stock buffer into 1 L of distilled water and saturated with DO by aeration. The diluted water must have a pH falling between 6.5 and 7.5. The pH for unknown samples must be verified. If the pH of the sampled water is not within the range, the sample must be neutralized by 1 N sulfuric acid (H_2SO_4) or 1 N sodium hydroxide (NaOH). The phosphate buffer has the ability to bring the pH of the diluted sample between 6.5 and 7.5. The sample should not be diluted by more than 0.5 % of total volume of the BOD bottle of 300 ml.

3.2.5.1. Standard Check Solution

Standard check solution was made of glucose-glumatic acid. Glucose ($C_6H_{12}O_6$) and glutamic acid ($C_5H_9NO_4$) were first dried for 1 h in an oven at 103°C and the solution was made by dissolving 150 g glucose and 150 g glutamic acid in distilled water, diluted to 1 L.

3.2.5.2. Seed Source

Polyseed, manufactured by InterLab, was the seed source for the BOD tests. Each capsule of Polyseed contains specialized microbial cultures ideal for use in a broad range of areas involving the degradation of industrial and municipal wastes. One capsule was added to 500 mL distilled water and was aerated for 30 minutes before BOD analysis.

Different volumes of BTEX solutions were used in each test. The necessary volume of samples was added to the 300 mL BOD bottles. Four mL of aerated seed solution were added to each of the BOD bottle and then each BOD bottle was filled by slowly adding sufficient dilution water such that the stopper could be inserted without leaving an air bubble but not so much that it would overflow. Initial DO concentration was measured using the

dissolved oxygen meter (YSI 58 Dissolved Oxygen Meter, YSI Inc.) equipped with a BOD bottle probe (YSI 5750 Non-Stirring BOD Bottle Probe, YSI Inc.)

As a reference test, two bottles were filled with dilution water and incubated with the rest of the bottles. In addition, four bottles with different seed volumes and dilution water were also incubated to determine the effect of Polyseed. Two bottles of glutamic acid and glucose with seed and dilution water were prepared for each batch of samples. This allowed for testing of the seed against a prepared standard.

The samples were incubated in a C25K Classic series refrigerated incubator shaker (New Brunswick Co., Inc). Final DO was measured after 5 days of incubation for all BOD bottles and the blanks. BOD then was calculated using the following equation:

$$BOD = \frac{(D_1 - D_2) - SCF}{P} \tag{3.3}$$

$$SCF = (B_1 - B_2) f \tag{3.4}$$

Where D_1= dissolved oxygen of diluted sample immediately after preparation [mg/L]
D_2 = dissolved oxygen of diluted sample after 5 days of incubation at 20°C [mg/L]
P = volumetric fraction of sample used
B_1= initial dissolved oxygen of seed control [mg/L]
B_2 = dissolved oxygen of seed control after 5 days of incubation [mg/L]
SCF = seed correction factor [mg/L]
f = ratio of seed in the sample to seed in the control, respectively (Metcalf and Eddy, 1991)
See Appendix A for a sample calculation of the BOD.

3.2.6. Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is defined as the amount of oxygen required to oxidize the organics in a solution by a strong oxidizing chemical under acidic condition. The unit of measure for COD normally is mg/L, which implies the oxygen uptake per litre of the

solution. The theoretical oxygen demand oxidizing an organic compound to carbon dioxide, water, and ammonia, can be calculated by the stoichiometry of oxidation (Petrucci and Harwood, 1997):

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{2}c\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3 \qquad (3.5)$$

Where n, a, b, and c are the number of carbon, hydrogen, oxygen and nitrogen atom, respectively per unit organic molecule. The chemical Equation (3.4) is balanced; the coefficient of O_2 determines the theoretical oxygen demand for the organic molecule.

The COD can be determined by different methods. Given that the samples in this experiment had no suspended solids present and the predicted COD value was above 50 mg/L, the closed refluxed method was chosen, because it is economical (APHA, 1998). In the closed refluxed method, a mixture of potassium dichromate and sulphuric acid is used to oxidize the organic compounds. The oxidation of organic compounds by potassium dichromate under acidic condition is as follows:

$$C_nH_aO_bN_c + dCr_2O_7^{-2} + (8d + c)H^+ \rightarrow nCO_2 + \left(\frac{a + 8d - 3c}{2}\right)H_2O + cNH_4^+ + 2dCr^{3+} \qquad (3.6)$$

Where n = the number of carbon per unit organic molecule

a = the number of hydrogen per unit organic molecule

b = the number of oxygen per unit organic molecule

c = the number of nitrogen per unit organic molecule

$$d = \frac{2n}{3} + \frac{a}{3} - \frac{c}{2}$$

The COD analysis was measured by the pre-packaged, mercury-free and premixed COD vials (Bioscience Inc.) based on Section 5220 of Standard Methods (APHA, 1998).

Bioscience Inc. manufactures three types of COD vials with low, medium, and high ranges COD. The chemical composition of these pre-packaged vials is listed in Table 3.2.

Table 3.2: Chemical Composition of the MICRO-COD Test Method Accu-Test Vials

Chemicals	Low Range: 5-150 mgCOD/L	Medium Range: 20-900 mgCOD/L	High Range: 100-4500 mgCOD/L
Sulphuric acid (H_2SO_4 [1 mg/m^3] CAS# 7664-939)	77%	75%	54%
Potassium dichromate ($K_2Cr_2O_7$, [0.0235 mg/L] as Cr^{+6}, CAS# 7778-50-9)	0.05%	0.20%	0.14%
Silver sulphate ($AgSO_4$, [0.01 mg/m^3]as Ag, CAS# 10294-26-5)	0.40%	0.40%	0.29%
Mercuric sulphate ($HgSO_4$, [0.05 mg/m^3]as Hg, CAS# 7783-35-9)	0.60%	0.60%	0.43%
Sulfuric acid (NH_2SO_3H, CAS# 5329-14-6)	0.002%	0.002%	0.0001%

In the preparation of a 10 gCOD/L of stock standard solution, potassium hydrogen phthalate (KHP) was pre-dried to a constant weight at 110°C, and 8.5034 g of it were dissolved in distilled water and diluted to 1 L. A series of working standard solutions, covering the expected range of sample concentrations (20-900 mgCOD/L) were prepared by accurately diluting the 10 gCOD/L of stock standard solution with distilled water. A standard calibration curve was prepared using potassium hydrogen phthalate (KHP). At least five standard KHP solutions with COD equivalent to 5 - 150 mgCOD/L were used, the same reagent volumes, tube and digestion procedures were used as for the samples.

According to the requirements of the test method for using the COD vials (Bioscience, Inc.), blanks of the ranges 20-900 and 100-4,500 gCOD/L were used to zero the spectrophotometer before sample testing. The highest standard (150 mg/LCOD) of the range 5-150 mgCOD/L was used to zero the spectrophotometer (λ = 440 and 600 nm were used for

low and high range, respectively). The standard curve of the range 5-150 mgCOD/L had a negative slope and the 150 mg/L standard would read a negative absorbance if using a blank for zeroing the spectrophotometer (the spectrophotometer cannot read negative absorbance). If the samples could not be tested within 5 h of collection, they were preserved with concentrated sulphuric acid, to a pH no greater than 2, and were refrigerated at 4°C until analysis.

The MICRO-COD Test Method accu-Test TM Low Range (5-150 mg/L COD) developed by Bioscience was used in this study, which is a colourimetric method of measuring COD. 2.5 mL of sample solution were added to the COD vial. The tubes were sealed and then thoroughly mixed by inverting them several times. The twist cap vials were heated in COD heater block (Bioscience Inc., preheated to 150±2°C) for 2 h. After 2 h, the vials were removed and allowed to cool down in a rack. The outsides of the vials were wiped to remove dust and then placed into the light path of the spectrophotometer (Ultrospec 1110 Pro, Biochrom Ltd.) to measure their CODs under a standard curve covering the expected range of sample concentrations.

The software, SWIFT II 1000, installed in a computer connected to the spectrophotometer was used for COD analysis. A wavelength of 600 nm for COD range 100-4,500 gCOD/L was first set and the absorbance was zeroed by a blank. A standard curve for this COD range was generated by selecting 'Run' and then 'Standards' to get the absorbance readings of a series of standards with known COD concentrations. Absorbance (optical density) is a measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light. Each replicate of each standard was measured and stored, and the mean values were calculated. A standard curve (Figure 3.3) was then created using the mean absorbance values. The standard curve showed linearity between absorbance values and known standards concentrations, and was displayed in a graph view,

with the results of samples superimposed upon it. The measured absorbance was compared to the calibration curve and corresponding COD was reported in mg/L. An unknown COD concentration was measured by selecting 'Open', selecting 'Standards', and then selecting 'Run Samples'. The samples were only run after the standard curve was created. Each replicate of a sample was measured and compared to the standard curve. Each sample's result was displayed as it was collected. The calibration curve was checked every time a sample was measured.

Eckenfelder (2000) states that there are some drawbacks to the COD method of determining the contents of organic carbon in a sample: aromatics compounds and volatile straight-chain aliphatic compounds cannot be oxidized using the COD method. Therefore, using the COD method for these compounds would give a lower COD value than the actual theoretical oxygen demand. The percentage removal of COD can be calculated as follows:

$$COD\% = \left(\frac{COD_i - COD_f}{COD_i} \right) \times 100\% \qquad (3.7)$$

Where COD_i = the influent or initial COD concentration (mg/L) of the sample

COD_f = the effluent or final COD concentration (mg/L) of the sample

3.2.7. Total Organic Carbon (TOC)

The TOC is another test to measure the organic content present in water. The test is performed by injecting a known quantity of a sample into a high-temperature furnace or chemically oxidizing environment. Through catalytic oxidation, the sample is completely

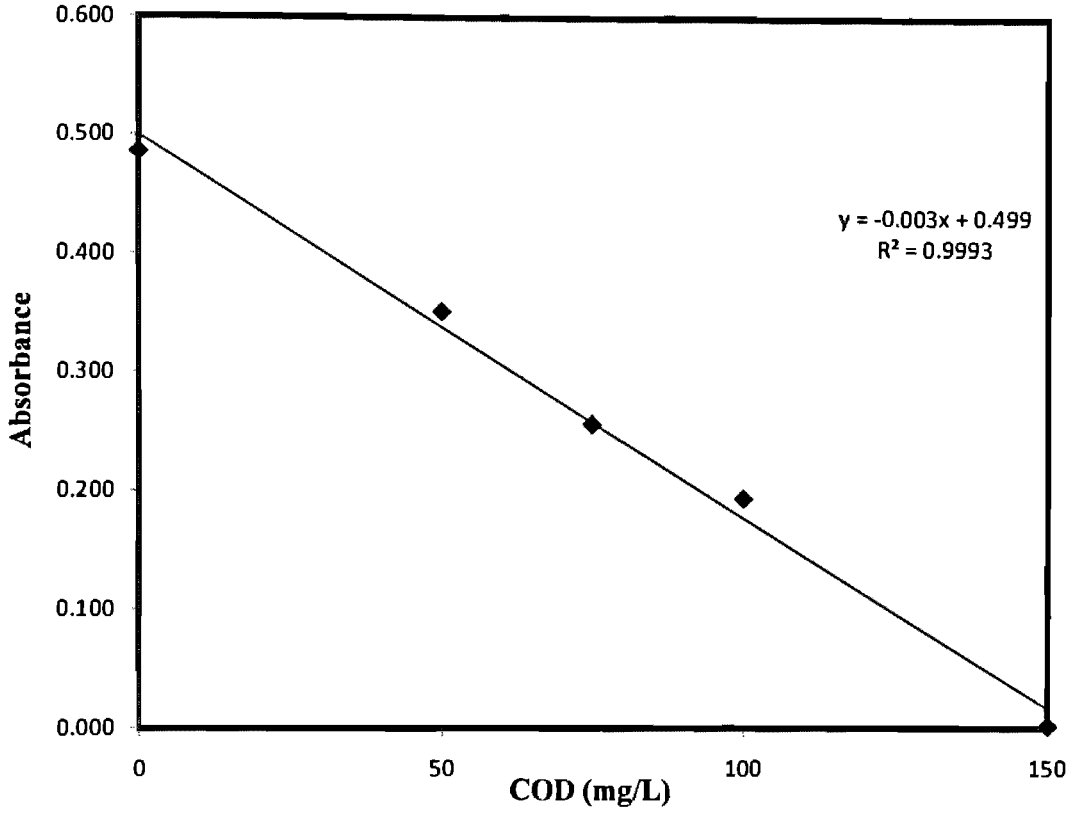


Figure 3.3: Calibration curve for determination of COD, based on the closed refluxed method. The slope is negative because the absorbance of the high COD (150 mCOD/L) was set to zero. Since Absorbance cannot be negative, the value of low COD (0 mgCOD/L) was measured to be approximately 0.500. Plotting these set of points (150, 0) and (0, 0.500) gives a negative slope.

oxidized to CO_2 and H_2O. The quantity of carbon dioxide produced is measured by means of an infrared analyzer.

In these experiments, the Apollo 9000 Total Organic Carbon (TOC) Analyzer was used, which utilizes combustion (680 to 1000°C) with a reusable platinum catalyst for the lowest detection limits while maximizing TOC recovery. Due to the presence of the catalyst, the organic matter is completely oxidized to CO_2 and H_2O. The non-dispersive infrared sensor (NDIR) quantifies the amount of CO_2 produced by the catalytic reaction in the TOC analyzer (Apollo 9000, 2003).

Before sample analysis, the TOC analyzer was calibrated using standards prepared using potassium hydrogen phthalate (KHP) as an organic carbon source for TOC calibration. The KHP was dried in an oven (Binder-World) at 105°C for 2 h before the preparation of stock standard solution and stored in a desiccator. In the preparation of a 1,000 mg/L of KHP stock standard solution, an accurate 2.125 mg of KHP was dissolved in distilled water and was diluted to 1 L. A series of accurate dilutions were performed, using the stock solution of 1000 mg/L to obtain working standard solutions, covering the expected range of sample concentrations i.e. 1-400 mg/L (Figure 3.4). Through running TOC standard calibration analysis, a TOC calibration curve for the range of 1-400 mg/L was obtained for analyzing TOC concentrations. A response factor correlates the raw counts of the instrument to a known amount of carbon in the standard.

Both stock and working standard solutions were capped and stored in a 2 to 8°C refrigerator. The percentage removal of TOC can be calculated as follows:

$$TOC\% = \left(\frac{TOC_i - TOC_f}{TOC_i} \right) \times 100\% \tag{3.8}$$

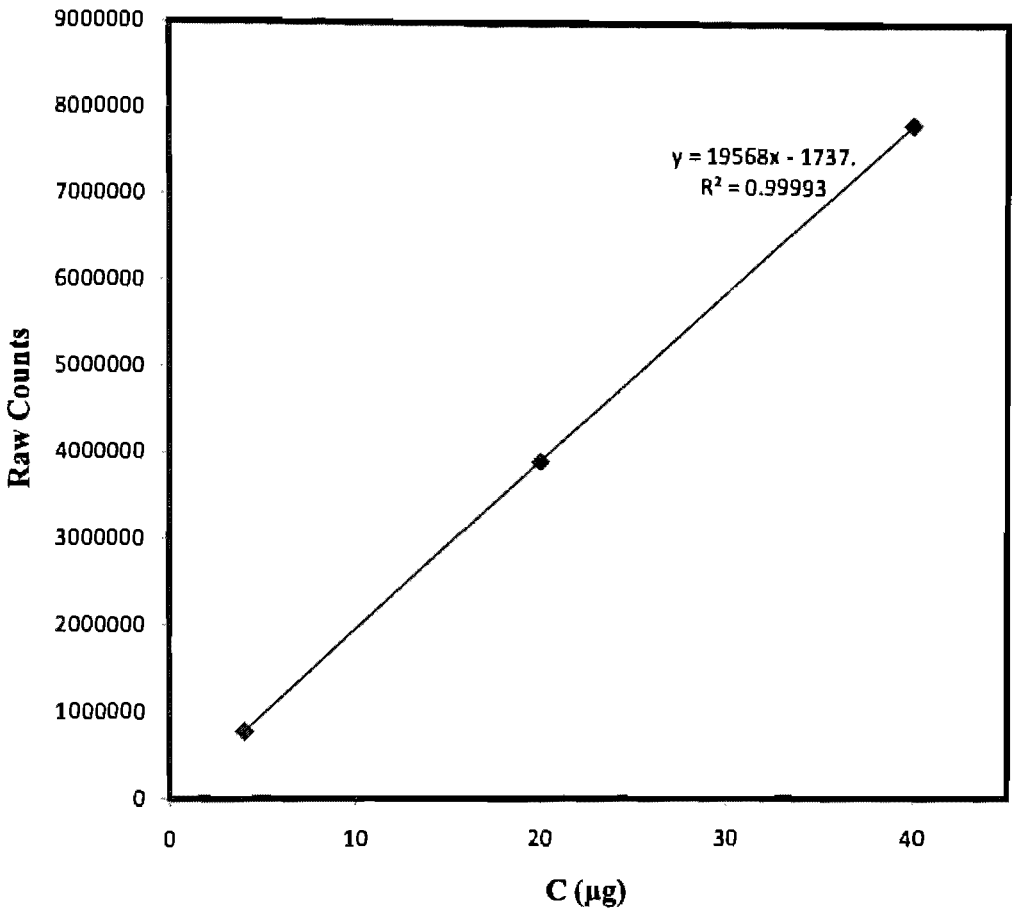


Figure 3.4: TOC calibration curve for 1-400 mgTOC/L

where TOC_i = the influent or initial TOC concentration (mg/L) of the sample

TOC_f = the effluent or final TOC concentration (mg/L)

3.3. Photochemical Treatment

Two experimental setups were used in this study: batch and continuous, as described in the following sections.

3.3.1. Batch Photochemical Setup

Figure 3.5 shows the photoreactor setup used in all batch photochemical experiments. The reactor in these experiments was a 300 mL glass Erlenmeyer. The working volume was 250 mL. A Philips UV lamp (PL-S 9W TUV) with wavelength of 254 nm was immersed in the reactor filled with the prepared synthetic BTEX wastewater. The reactor was wrapped by aluminum foil to prevent the transmission of UV light from the reactor. The vessel contained a magnetic stirring bar placed on a magnetically stirred plate to thoroughly mix the solution and to avoid any mass transfer limitation.

3.3.1.1. Batch Photochemical Experiments

A series of experiments were performed to determine whether a closed or open system should be used for the treatment of BTEX and to show the role of H_2O_2 in the degradation of BTEX using a UV-254 nm lamp in the batch reactor.

A typical degradation experiment was performed in a 250 mL test solution containing BTEX in deionized water in the presence or absence of H_2O_2. The concentration of BTEX used was 90-300 mgCOD/L. Samples were withdrawn periodically (every 20 min) by pipitting out 5-10 mL from the sample port and they were analysed for COD, BOD, and GC.

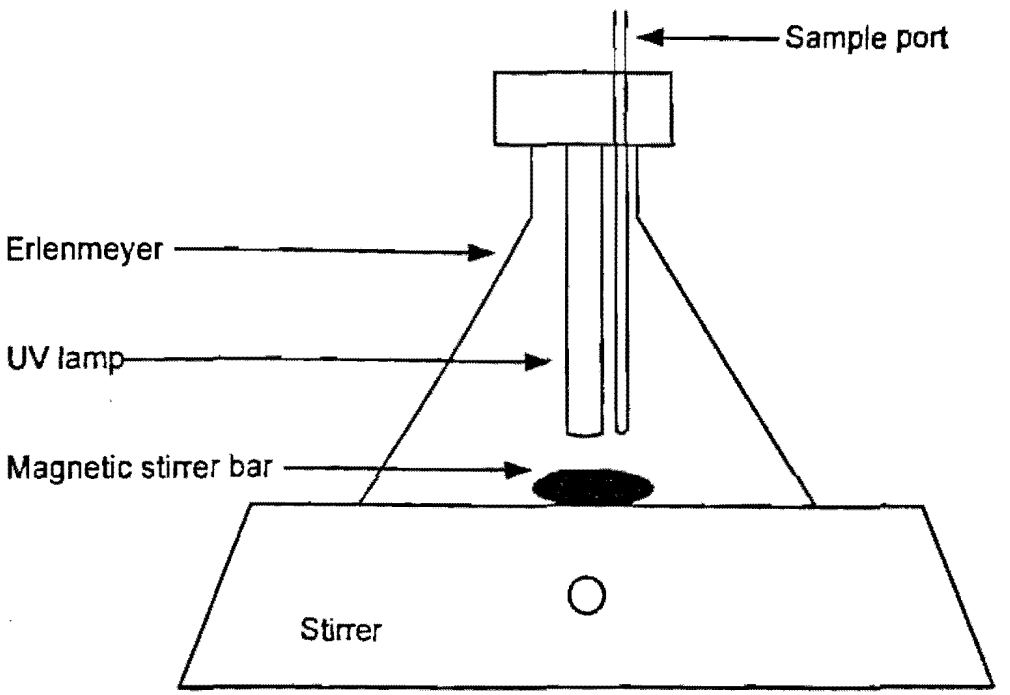


Figure 3.5: Experimental setup for the batch photochemical treatment of *BTEX*

3.3.2. Continuous Photoreactor Setup

Figure 3.6 shows the experimental setup for all the continuous photochemical experiments. The feed reservoir had a volume of 4 L. The flow of the synthetic water to the UV photoreactor was adjusted with a valve located at the outlet of the feed reservoir. The feed reservoir was filled to capacity (4L) and during each run only 1.5 L was used to avoid any pressure head change. The UV reactor purchased from Siemens Company (SL-1S) had a total working volume of 1.35 L with an 8 cm external diameter and a 34 cm total length. The power of the UV lamp was 17 W with a 1 cm diameter and a 30 cm length. The quartz sleeve of the UV lamp was 2.5 cm in diameter and 34 cm long. Two wavelengths of UV light (254 and 185 nm) were used.

3.3.2.1. Continuous Photochemical Degradation Experiments

A number of experiments was performed to show the degradation and/or disappearance of BTEX under different conditions. A 4-L glass spherical container (feed reservoir) with a sampling port was used to prepare the BTEX solution. The container was filled its capacity (4 L) with the deionized water placed on a magnetically stirred plate. 0.4632 mL of BTEX was injected into the glass feed reservoir. The solution was stirred with a Teflon-coated magnetic bar overnight to solubilize BTEX into the deionized water.

Prior to the start of photolytic experiment, a sample was taken for the TOC measurement. The required amount (0-350 mg/L) of 30% H_2O_2 was added to the BTEX water solution and stirred for 5 min to ensure that the solution was well mixed. Another sample was taken to measure the TOC. The feed reservoir outlet valve was adjusted to feed the BTEX solution into the 1.35 L UV reactor. The flow was adjusted such that the residence

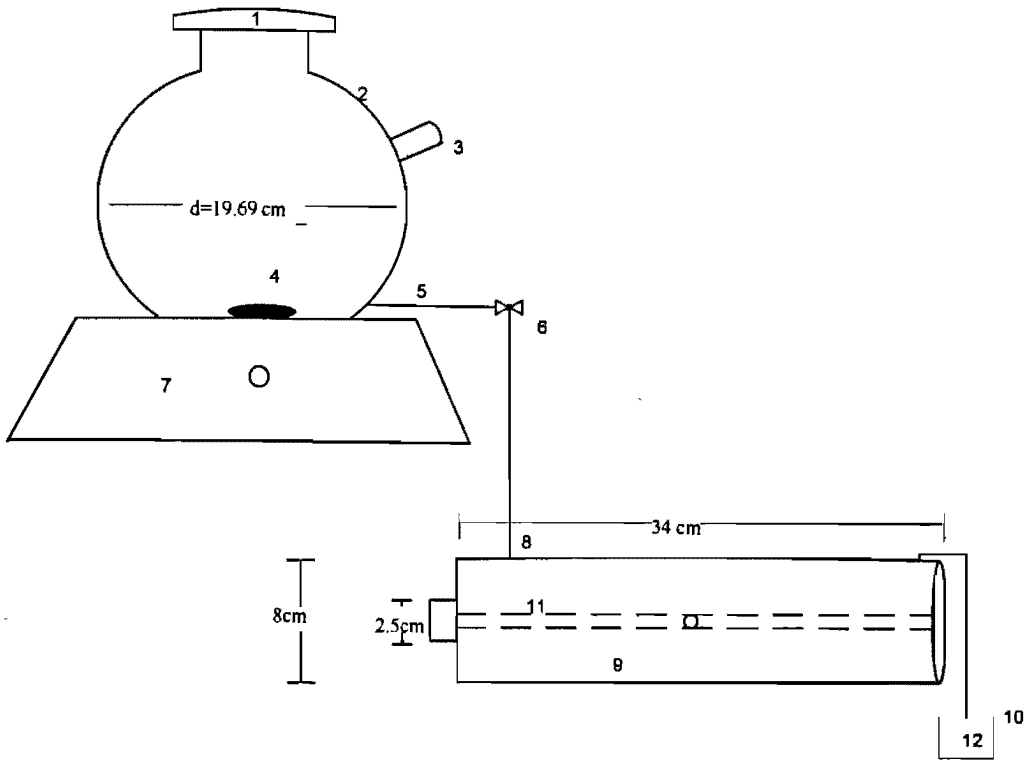


Figure 3.6: Experimental setup for the continuous photochemical treatment of BTEX, (1) the head plate; (2) the glass bottle: feed reservoir; (3) sample port; (4) magnetic stirrer bar; (5) outlet of the glass bottle; (6) valve; (7) stirrer plate; (8) inlet to UV reactor; (9) UV reactor; (10) UV reactor outlet; (11) = UV light; (12) = Sample vial

time of solution in the UV reactor was in the range of 20 min to 6 h. These residence times were chosen to determine the time for the mineralization of BTEX. Literature values show that in batch, the degradation of BTEX occurred in 10 min (Daifullah and Mohammed, 2004) and in a continuous flow, the solution was circulated for 4 h in the UV reactor (Cho et al., 2006). The reaction time or the residence time was not exactly the same as the literature, because the setup and equipment were not the same. Daifullah and Mohammed's (2004) reactor had a power rating of 500W; while the power supplied by the sun to reactor used by Cho et al., (2006) was 15 W. A timer was set from the time the first drop flowed to the UV reactor (marked as number 8 in the diagram) until the first drop was collected at location 10. The timer ensured that the residence time was indeed as set by the valve. Samples were collected from the UV outlet port and analyzed. The initial TOC of the BTEX used in each experiment was 100 ± 10 mg/L, unless otherwise specified. Triplicate runs were performed for each residence time and analyzed using the TOC analyzer and BOD.

Both COD and TOC give an indication of how much organic carbon is present in the sample. Since COD analysis takes approximately 3 h to attain results, COD was not used for all experiments. The process of analyzing the sample with TOC is less time consuming than COD; TOC analysis takes approximately 20 minutes. In addition, H_2O_2 has COD as well. Since H_2O_2 was used in these experiments, it interfered with the true COD value of the BTEX. Experiments were performed on each individual compound in a similar manner.

The temperature and pH were also monitored during each experiment. Each experiment was conducted in triplicates. The average results were reported and the value of standard error was calculated. A sample calculation of standard error is shown in Appendix B.

To assess the biodegradability of BTEX, a series of BOD tests were performed on the BTEX solution and the UV treated BTEX solution. For the BOD test of BTEX, oxygen

consumption was measured. To measure biodegradability of a chemical its ratios of BOD/COD or BOD/TOC must be measured. A high ratio of BOD/COD and BOD/TOC would translate into high growth and activity of the microbial community. Therefore, if the BOD/COD and BOD/TOC value is high, one can conclude that the BTEX and its intermediates are biodegradable.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results obtained from photochemical degradation of benzene, toluene, ethylbenzene, and xylenes (BTEX) using both batch and continuous photoreactors are presented. BTEX were degraded by UV-254 nm, UV-185 nm, and a combination of UV and H_2O_2 to determine which one has the ability to degrade BTEX at a faster rate.

4.1. Photochemical Degradation of BTEX

4.1.1 Dark Reaction

A series of control experiments were conducted to quantify the loss of BTEX through volatilization. In the dark experiments, solutions of BTEX were used in the batch reactor without light and with no H_2O_2 for an hour to verify whether volatilization and/ or deposition contributed to the loss of BTEX. The results of these experiments are illustrated in Figures 4.1, 4.2, and 4.3.

In the dark experiments, solutions of benzene, toluene, ethylbenzene and xylenes were placed into an open batch system. The COD of each solution was measured at the beginning of the experiment and three samples were taken within an hour. Figure 4.1 illustrates that when these solutions were left open to the air with no UV- light and no H_2O_2, the COD of each of the solution had decreased with time.

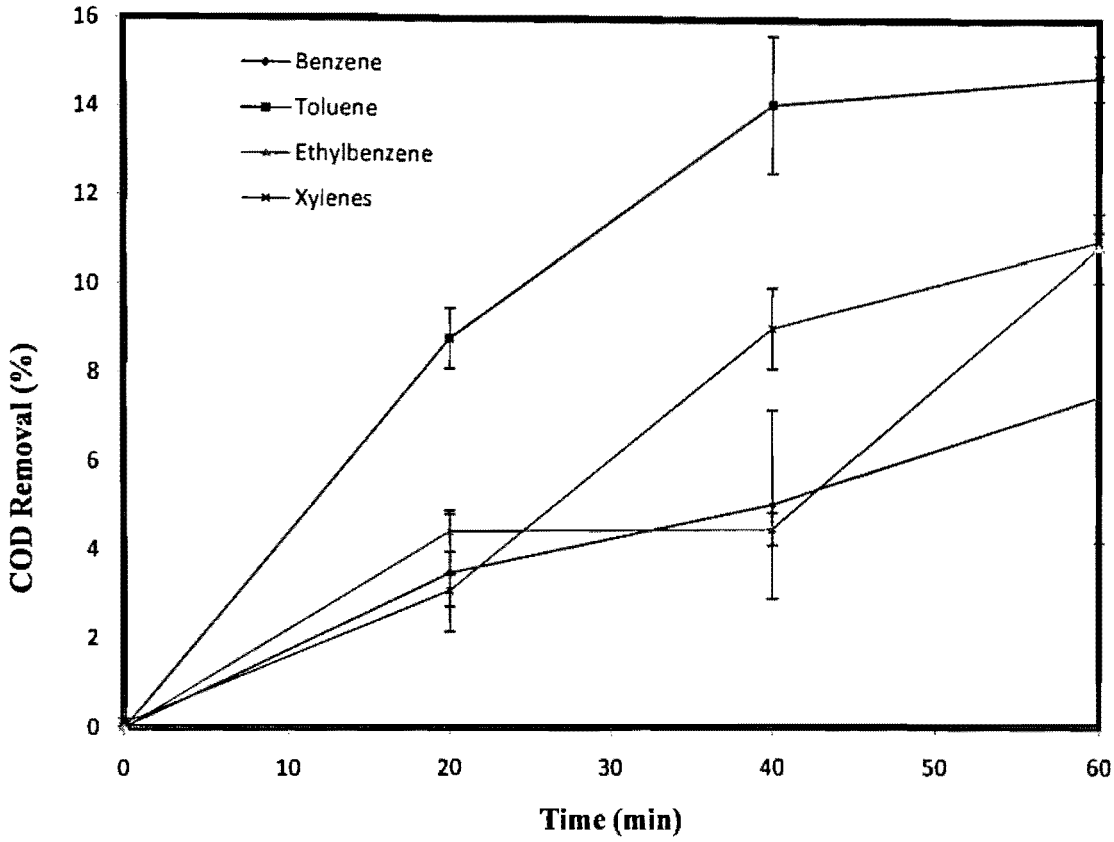


Figure 4.1: COD removal (%) of BTEX during the dark batch reaction in an open system without stirring. The initial COD concentration for benzene, toluene and ethylbenzene and xylenes were 144, 108, 94, and 172 mg/L, respectively. Each of the components was individually tested. No UV lamp or H_2O_2 was used.

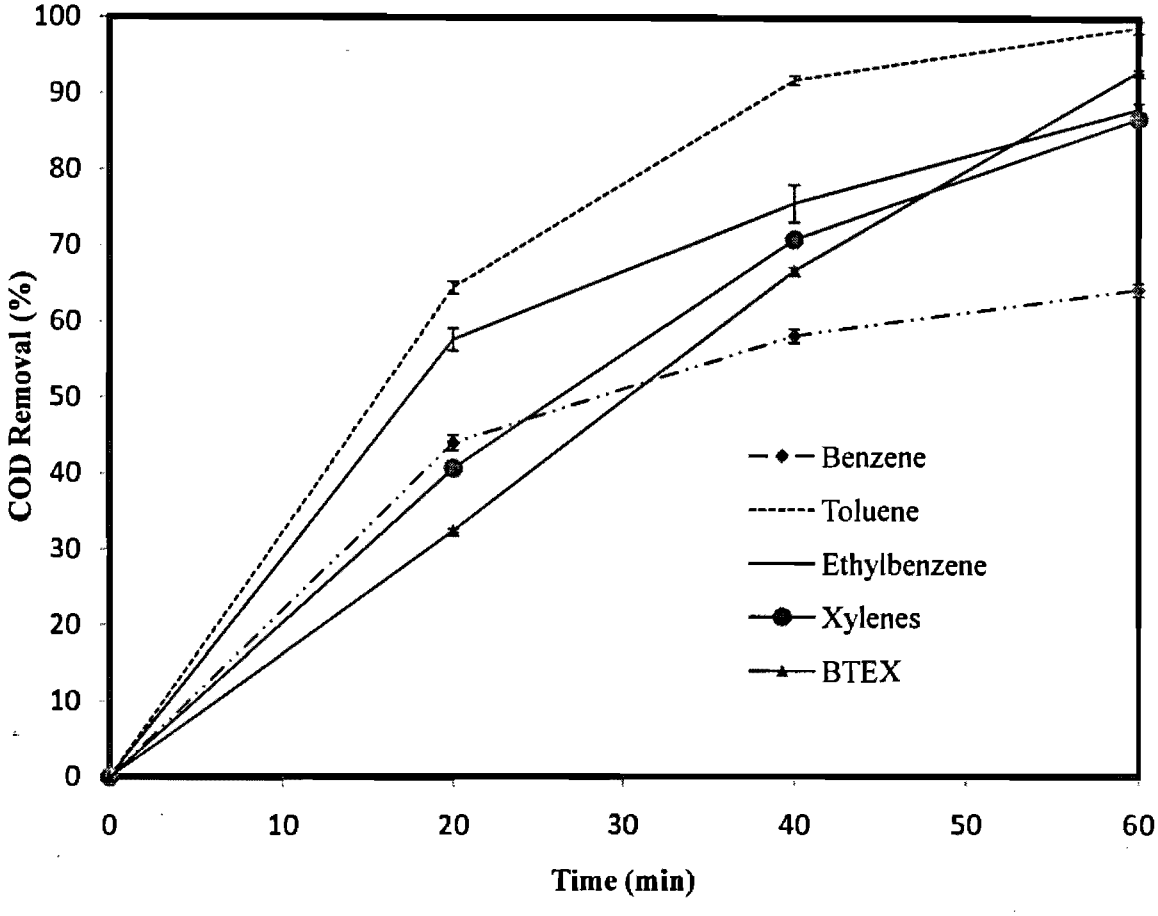


Figure 4.2: COD removal (%) of BTEX during the dark reaction in a stirred batch reactor. The initial concentration COD for benzene, toluene, ethylbenzene, xylenes, and BTEX were 139, 110, 91, 172, and 274 mg/L, respectively. Each of the data line represents a separate experiment. Neither UV lamp nor H_2O_2 were used.

At 20 min, 2.9%-4.1% COD of each of the solution had evaporated. After an hour in the open system, 10-15% COD of the BTEX had escaped from the solution.

Figure 4.2 illustrates that when the solution was stirred in an open batch system with no light and no H_2O_2, the rate of disappearance of COD of BTEX increased by 76-85%. After 20 min of stirring in the open system, the COD concentration dropped by 32.5-45% for each of the solutions. After an hour of stirring, 65-100% of COD of BTEX disappeared. Toluene was entirely volatilized out of the solution within an hour of stirring in an open system, while 65% of benzene volatilized. The results of these experiments demonstrated that a closed reactor system was required to avoid the loss of BTEX due to volatilization. The purpose of these experiments was to show the requirement of a closed system for the degradation of BTEX.

A solution of BTEX was stirred, for an hour, in the batch photoreactor (closed system) with the UV light off and with no H_2O_2. The results of the closed dark reaction are illustrated in Figure 4.3. It was observed that there was a 0.5% (2.5 mgCOD/L) change in the COD concentration of BTEX. Comparing a 0.5% loss of COD in a closed batch system to a 65-100% loss of COD in open batch system, it was concluded that a closed system would avoid the changes in concentration of BTEX due to evaporation. Therefore, a closed reactor system was used as depicted in Figure 3.5 for the photodegradation of BTEX.

A series of dark reactions were conducted with the BTEX solutions in the continuous flow photoreactor to determine the evaporation of BTEX in the continuous setup. The results of these experiments are illustrated in Figure 4.4. Each bar represents an experiment. It was observed that the change in the TOC concentration increased with an increase in the residence time.

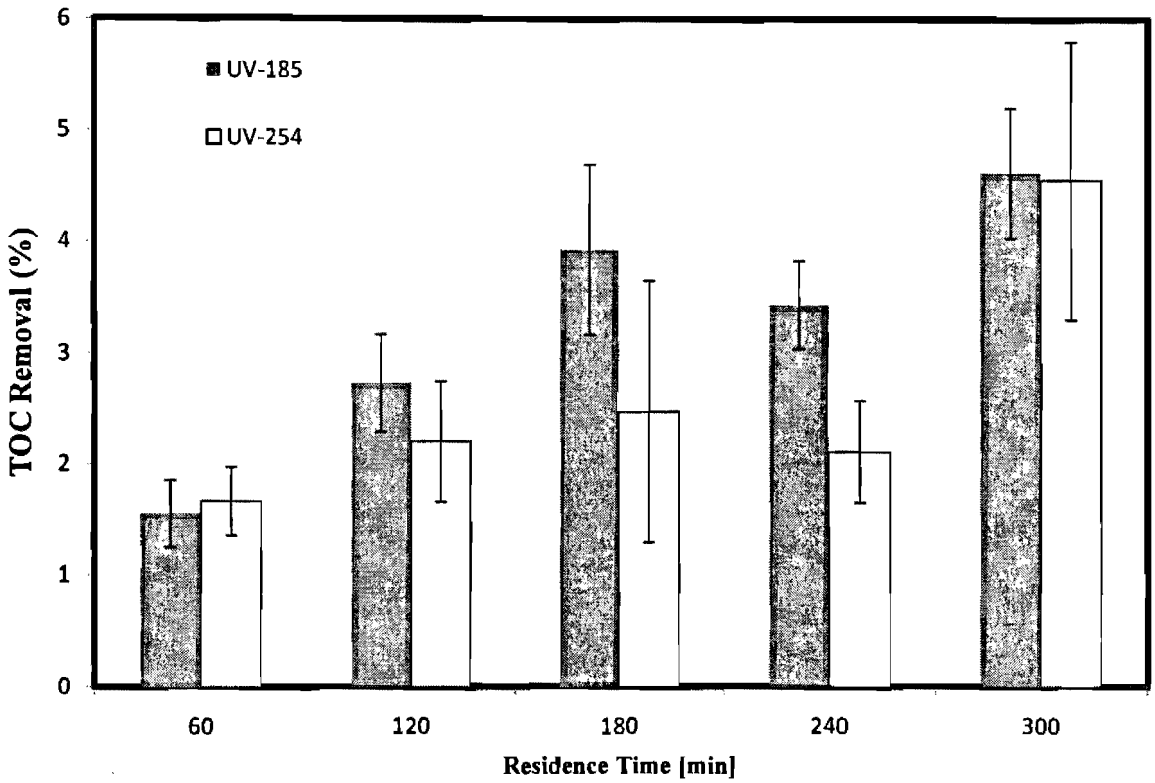


Figure 4.4: TOC Removal (%) of BTEX during the dark reaction in the continuous flow system. The inlet concentration TOC of BTEX was 100 mgTOC/L. The UV reactors were off and no H_2O_2 was used for any of the 12 experiments (triplicate experiments were run for each condition).

Experiments with longer residence time (i.e. 6 h) demonstrated changes in the TOC concentration in the range of 3.2-5%.; while experiments with residence time of 1 h showed changes in the TOC concentration in the range of 0.9-1.1%. Therefore, there was no significant degradation of BTEX in the absence of UV light.

4.1.2. Photoreaction of BTEX

In order to determine whether photolysis contributed to the degradation of BTEX, BTEX solutions were exposed to UV light in both batch and continuous reactor without any H_2O_2.

The average COD, TOC or concentration of BTEX values of triplicate experiments were calculated and graphed. In addition, the standard error for each data point was calculated. Refer to standard error calculation in Appendix B. The standard error for all data was less than 5%, with the exception of the BOD test results, for which the standard error was as high as 9.9% (see data points at 10 min in Figure 4.10, 40 min and 120 min in Figure 4.23).

In the closed stirred batch system, BTEX solutions were irradiated by UV-254 nm for a period of 3 h. As illustrated in Figure 4.5, the COD removal (%) increased with an increase in the treatment time. For example, the COD removal of the solution within the first hour of reaction was 14.8%. After 3 h of treatment time, it was 26.8%.

Different concentrations of BTEX [mgTOC/L] were irradiated by UV-254 with TOC/H_2O_2 = 1/3. It was observed that the percentage removal decreased as the TOC of BTEX increased (refer to Table 4.1).

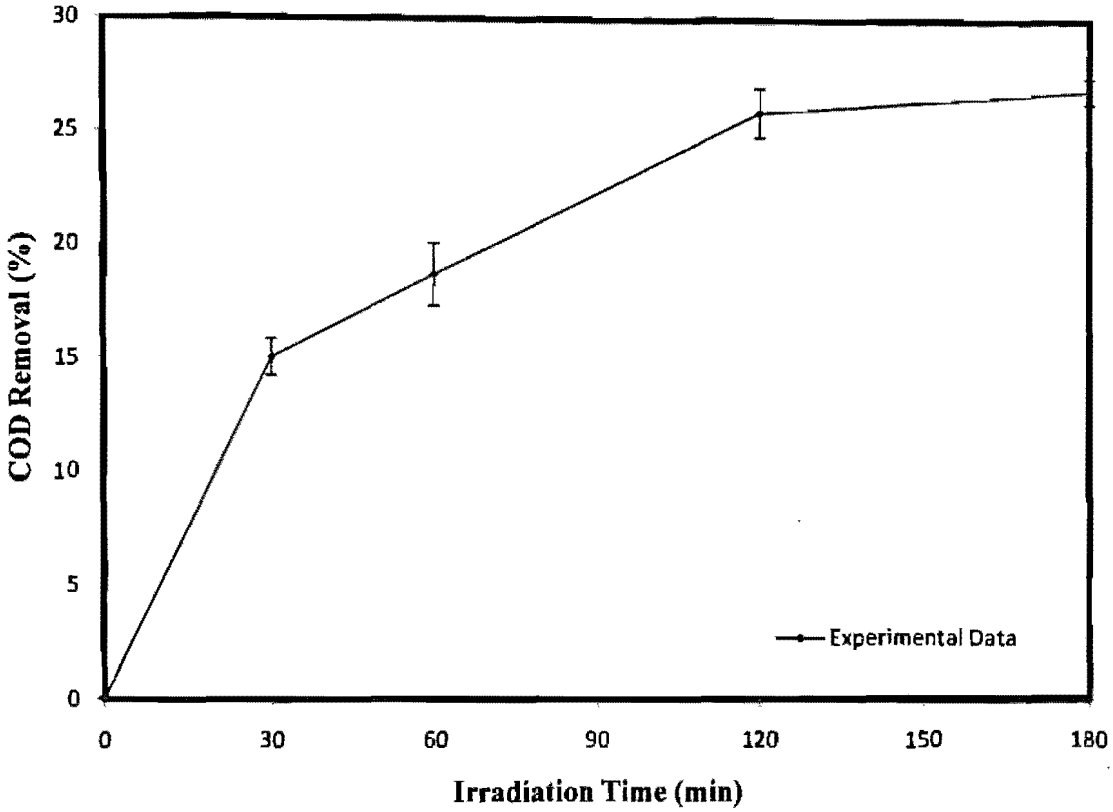


Figure 4.5: COD removal of BTEX during a stirred batch with UV-254 nm light reaction, the initial COD concentration of BTEX was 291 mg/L. No H_2O_2 was used.

Table 4.1: TOC Removal of Various BTEX Concentrations under the Irradiation of UV-254 in the Continuous Flow Reactor

BTEX [mgTOC/L]	Mass ratio of B:T:E:X	TOC Removal (%)
77	11:26:11:52	34.8
100	11:26:11:52	34.1
135	11:26:11:52	21.5

In the continuous photoreactor, the BTEX solutions were exposed to UV-185 and UV-254 nm with no H_2O_2 for a period of 4 h. As exemplified in Figure 4.6, the degradation of BTEX with UV-185 nm was higher than that of UV-254 nm, because water has a continuous UV adsorption spectrum between 175 and 190 nm and in this wavelength range, a direct decomposition of water is the source of hydroxyl radicals (Reaction 4.1) (Chen et al., 2002; Wang and Ray, 2000; Millipore, 2000) which can then attack the BTEX compounds thus degrading them. In addition, UV-185 carries more energy than the longer UV-254 wavelength. UV-185 not only breaks organic bonds, but also generates chemical species called free radicals (Byron, 2000).

When the residence time was 1 h, the removal of BTEX with UV-254 nm was 0.3%. UV-185 nm had a TOC removal of 6.94%. The removal for both wavelengths increased with an increase in the residence time. When the residence time was 4 h, the removal of TOC by UV-254 nm and UV-185 nm was 8.6% and 12%, respectively.

$$H_2O + h\nu_{185\,nm} = H^{\bullet} + OH^{\bullet} \qquad (4.1)$$

The difference in removal of TOC between UV-185 and UV-254 in the first hour was 6.91%, while the difference in removal at 4 h of residence was 3.4 %. This difference is due

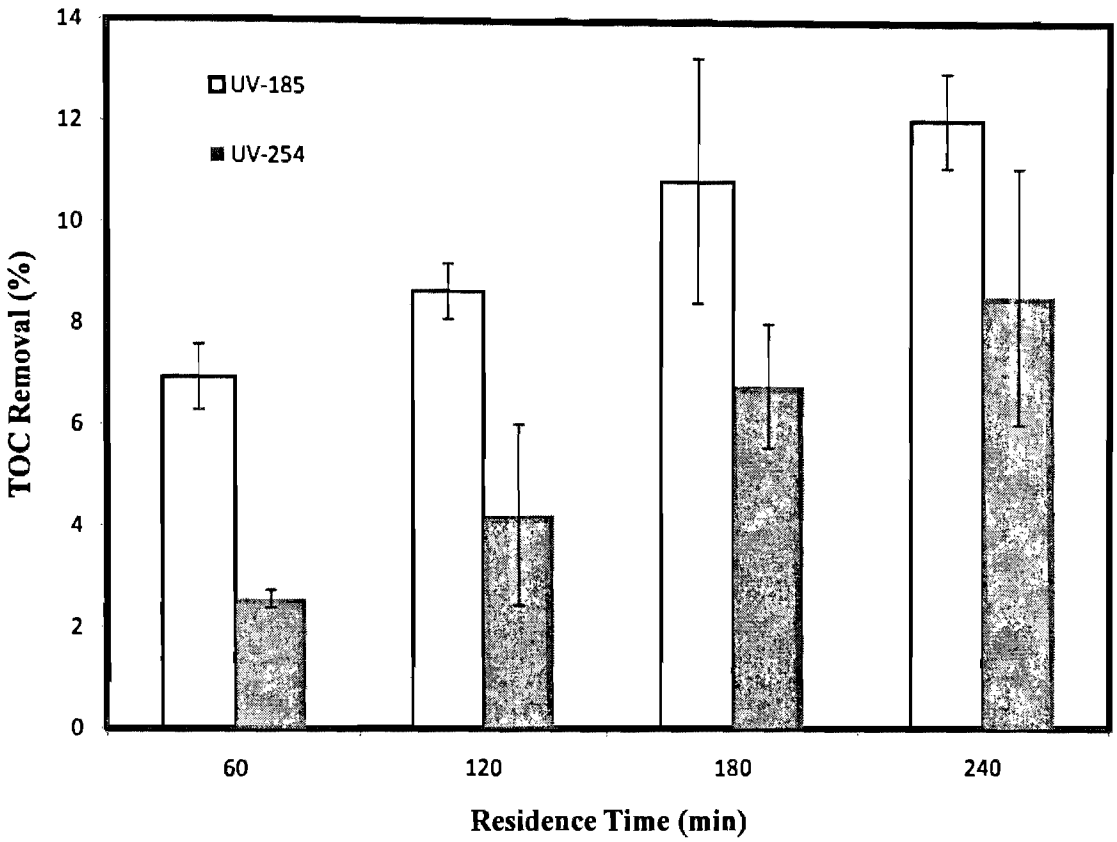


Figure 4.6: Degradation of BTEX in the continuous flow photoreactor under UV-185 nm and UV-254 nm without H_2O_2. The inlet concentration of BTEX was 100 mgTOC/L. Each of the data bar represents a separate experiment.

to the initial supply of hydroxyl radical, which as mentioned above, UV-185 is able to break water molecules into hydroxyl radical (Chen et al., 2002; Wang and Ray, 2000; Millipore, 2000). Therefore, it can be concluded that the difference in removal of BTEX by UV-185 and UV-254 nm decreased with time.

4.1.3. Effects of Hydrogen Peroxide on the Degradation of BTEX

The effect of H_2O_2 alone in the absence of UV light on the BTEX solution in the photoreactor was tested by taking samples from the reactor every 20 min for 3 h to measure the COD of the solution. In a closed system with BTEX concentration of 100 mgCOD/L, a 300 mg/L of H_2O_2 sample was added and the reactor was continuously stirred. The results of this experimental run are illustrated in Figure 4.7. The COD concentration decreased with an increase in time. This dark experiment was conducted on a mixture of BTEX/H_2O_2 showing a 15.3% COD concentration change within 3 h.

The results show that the mineralization of BTEX by H_2O_2 was a slow process. As exhibited in Section 4.1.2, the photolysis of BTEX without an oxidizing agent was also a slow process. Therefore, UV was combined with H_2O_2 to speed up the degradation process of BTEX, as described next.

4.1.4. Combination of UV and H_2O_2

The photodegradation of BTEX, with the aim to investigate the effect of oxidant (H_2O_2), was conducted. H_2O_2 in combination with UV-254 was used in the batch setup. The results demonstrated that the addition of oxidants enhanced the removal of BTEX. As shown in Figure 4.8, more than 90% of BTEX was degraded within 40 min irradiation under UV-254 nm. The COD value also decreased. After 105 min irradiation, BTEX was not detected in the solution, but the COD had not reached to zero. In a complete mineralization of BTEX, the

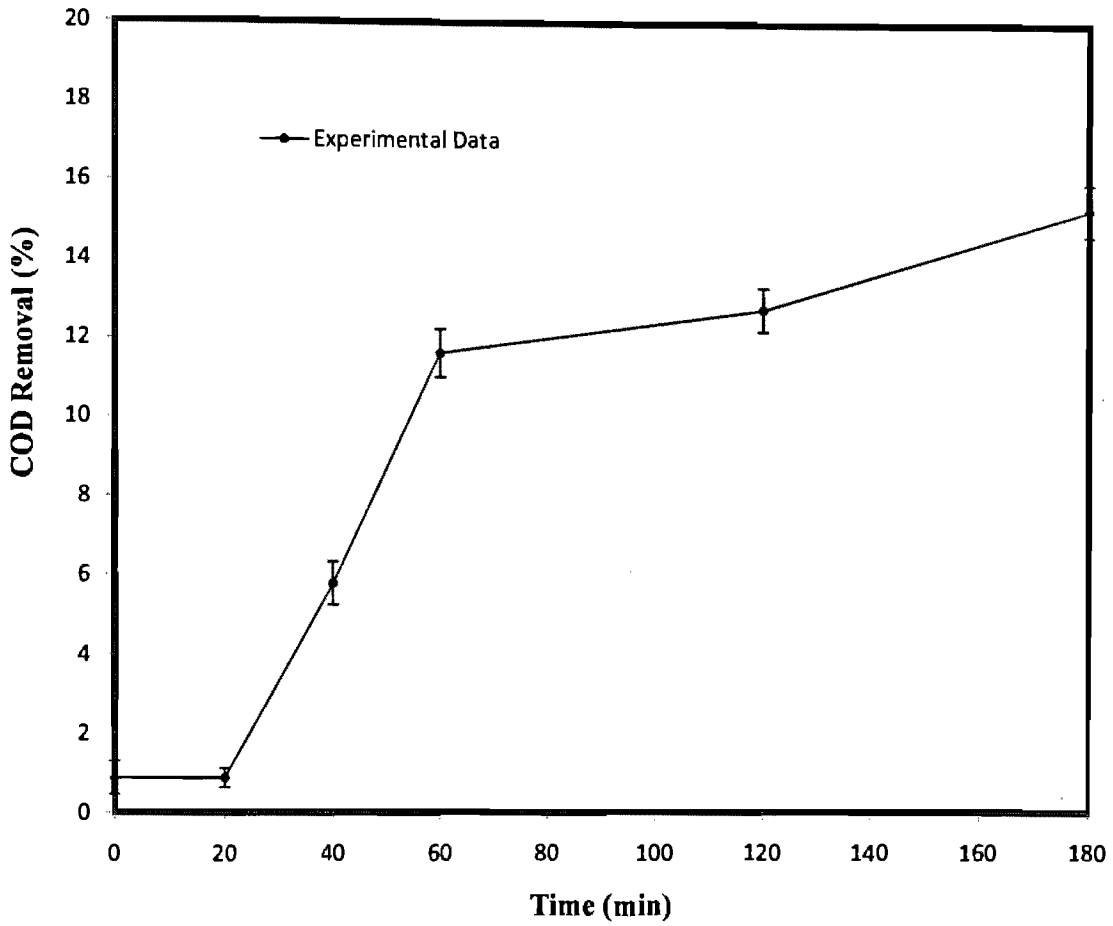


Figure 4.7: COD removal of BTEX by H_2O_2 alone with no UV-light in a closed stirred batch reactor.

COD value should have decreased to zero.

As illustrated in Figure 4.8, the COD removal at the end of the stirred batch experiment with UV-254 nm and H_2O_2 was 22.5%. This COD removal value is not 100% due to the incomplete mineralization of the BTEX but also it demonstrates the interference of H_2O_2 with the COD measurement (Kang et al., 1998). In addition, the theoretical COD of 43 mg/L of BTEX in the mass ratio of 11:26:11:52 is 122 mg/L, while the experimental value measured was 148.8 mg/L. This difference in the theoretical and experimental COD values clearly demonstrated the interference of H_2O_2.

When hydrogen peroxide is added to potassium dichromate acidified by sulfuric acid, the colour of the solution turns green. This is due to the formation of Cr_3^+ ions from the reduction of potassium dichromate (Reaction 4.2). Also due to its reductive ability, H_2O_2 is able to reduce potassium dichromate and thus interferes with the COD analysis (Kang et al., 1998):

$$Kr_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \quad (4.2)$$

Kang et al. (1998) analyzed their experimental values by the least square method using a second order linear equation, producing the following equation:

$$COD_{H_2O_2} = 0.4591[H_2O_2] - 3.24 \times 10^{-5}[H_2O_2]^2 \quad (4.3)$$

Where

$[H_2O_2]$ = the concentration of hydrogen peroxide in mg/L

The interference of H_2O_2 with the COD values were calculated and are presented in Appendix D. There was a 16.1% difference between the theoretical COD of BTEX and the measured COD subtracted the H_2O_2 interference.

Even though hydrogen peroxide is a powerful oxidizing agent, it acts as a

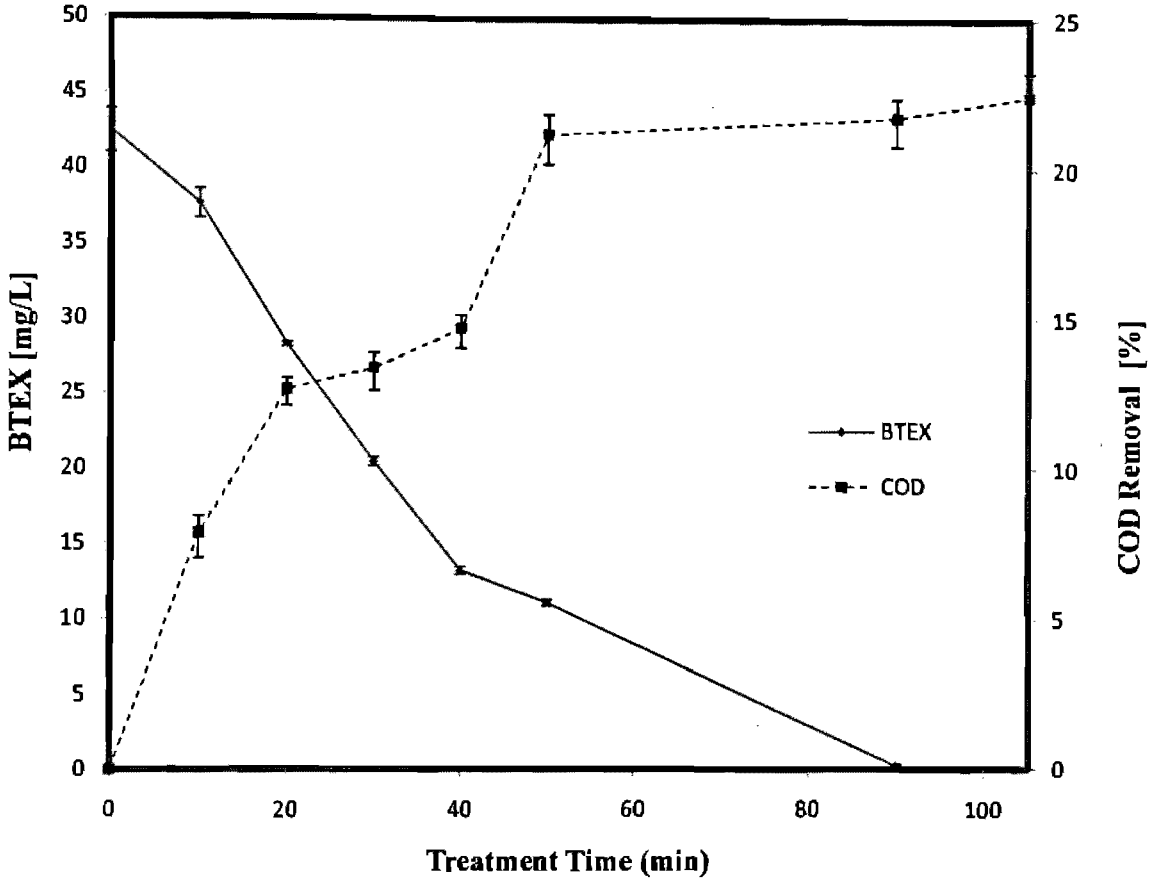


Figure 4.8: Comparison between the concentration of BTEX and its COD removal during irradiation under UV-254 nm in a stirred closed batch system. The H_2O_2 concentration was 315mg/L.

reducing agent when reacting with stronger oxidizing agents such as chlorine, potassium permanganate, and potassium dichromate (Kang et al., 1999).

Figure 4.9 demonstrates that H_2O_2 was reduced by dichromate ion in acidic conditions under the irradiation of UV-254 nm. Therefore, H_2O_2 would interfere with the COD measurement of any organic compound. Due to H_2O_2 interference with the COD value of BTEX, the use of COD analysis in this project was limited. The rest of the experiments were analyzed using TOC and BOD.

4.1.4. Recommended Value of H_2O_2 for the Degradation of BTEX

Considering the fact that the slow rate (10-25% removal in 3 h) of degradation of BTEX with H_2O_2, UV alone, and the photoactivity of H_2O_2 at 185-400 nm, it can be concluded that the degradation process must occur by direct photolysis of H_2O_2.

In this section, several experiments were performed using different H_2O_2 concentrations with 100 mg/L TOC of BTEX to determine the optimal concentration of H_2O_2 for the degradation of BTEX.

In order to accelerate the degradation of BTEX, sufficient amounts o f H_2O_2 are required to absorb UV light and generate enough hydroxyl radicals. Different concentrations of H_2O_2 were added to 100 mg/L TOC of BTEX under the irradiation of UV-254 nm in the batch reactor. In addition, different concentrations of H_2O_2 were added to the continuous reactor under the irradiation of UV-185 and UV-254 nm to determine its effect on the degradation of BTEX. It was determined that an increase in the concentration of H_2O_2 in the reactor led to an increase in the TOC removal of BTEX. As shown in Figure 4.10, it was observed that the rate of removal of BTEX was increased by increasing the H_2O_2 concentration in the batch reactor with UV-254 nm irradiation. For example, after an hour of treatment with UV-254 nm, the difference in removal of BTEX between the batch reactor

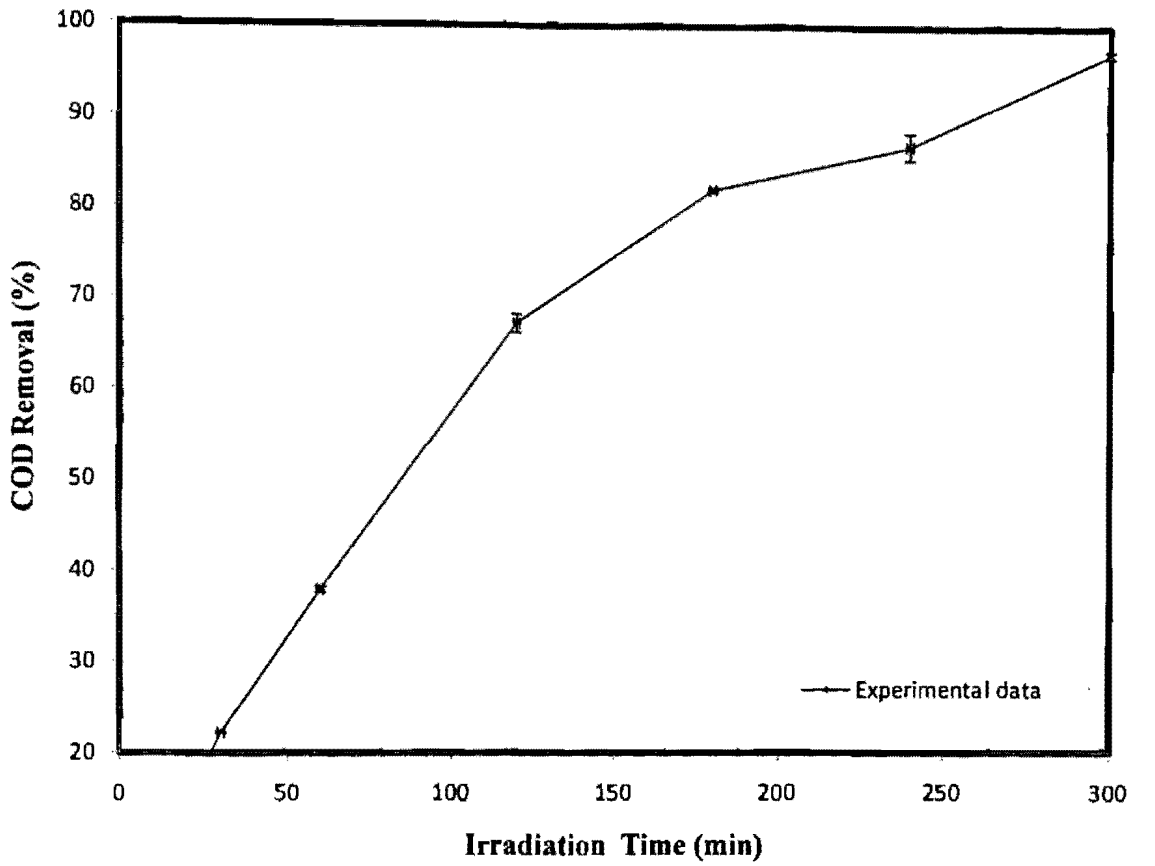


Figure 4.9: COD removal of H_2O_2 under the irradiation with UV-254 nm in a closed batch reactor system. The initial concentration of H_2O_2 was 350 mg/L.

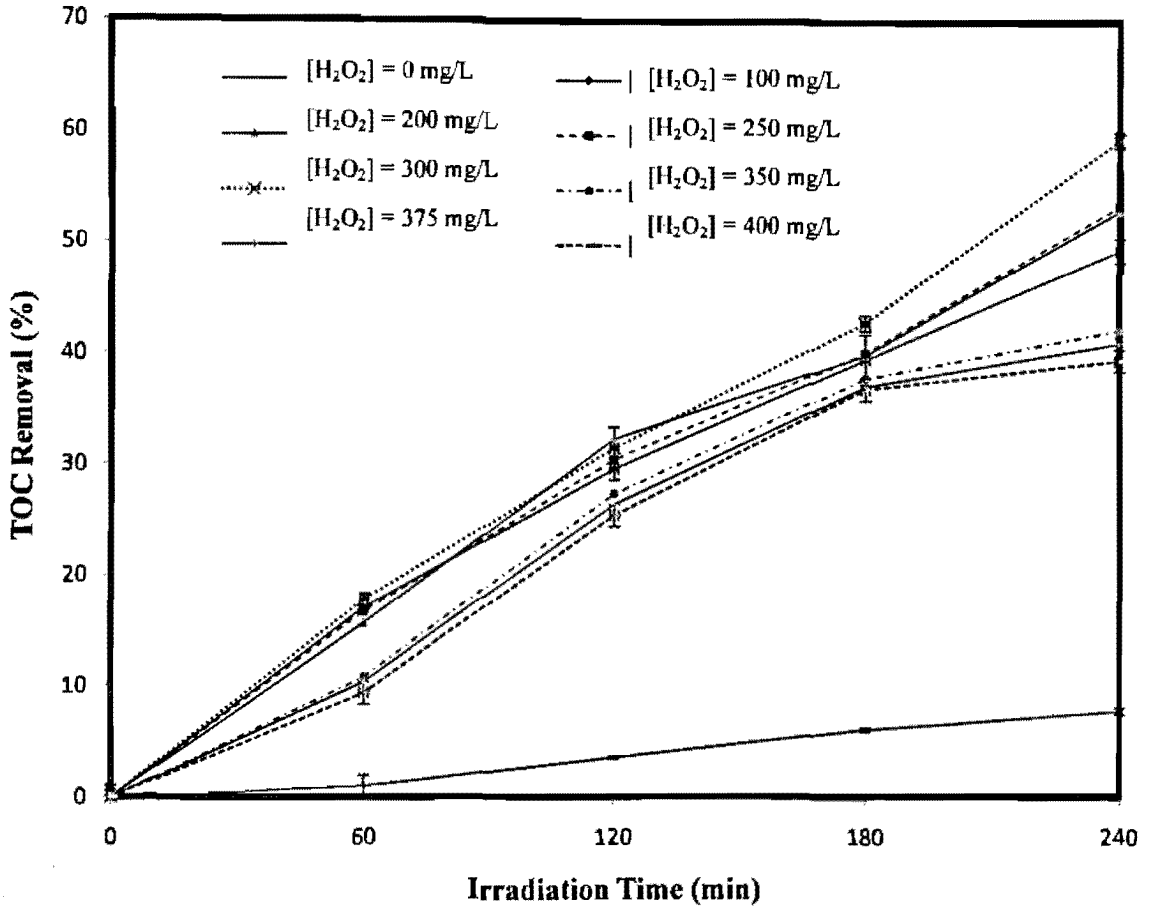


Figure 4.10: The effect of addition of H_2O_2 on the degradation of 100 mgTOC/L of BTEX in a batch reactor under UV-254 nm.

with no H_2O_2 and the batch reactor with 100 mg/L H_2O_2 was 16%.

To illustrate the optimal concentration of H_2O_2 for the removal of BTEX with UV-254 nm irradiation, and H_2O_2 in the batch reactor, the TOC removal of BTEX was plotted against the concentration of H_2O_2 used. Figure 4.11 demonstrates that the optimal H_2O_2 concentration to degrade 100 mgTOC/L of BTEX was 300 mg/L.

As shown in Figure 4.12, the difference between the removal of 100 mgTOC/L of BTEX by 0 mg/L and 100 mg/L of H_2O_2 after an hour irradiation under UV-185 was 23.3%. The TOC removal (%) of BTEX for the same residence time was increased by increasing the concentration of H_2O_2 until the H_2O_2 concentration was 250 mg/L. With 300 mg/L of H_2O_2, the TOC removal (%) was decreased (0.5-8% TOC removal) at all residence times and with 350 mg/L H_2O_2, the TOC removal (%) was decreased even further (1.1-16.9% TOC removal) The removal of BTEX at 250 mg/L of H_2O_2 for 1 and 4 h of residence was 36.6% and 68.8%, respectively.

On the other hand, at 1 and 4 h residence time, the TOC removal (%) with 300 mg/L of H_2O_2 was 37.1% and 52.6 %, respectively. Considering the results of these experiments, it was concluded that under the irradiation of UV-185 nm at any residence time, the maximum percentage removal (of 100 mgTOC/L of BTEX) occurred at 250 mg/L of H_2O_2. To illustrate the optimal concentration of H_2O_2 with UV-185 for the degradation of 100 mgTOC/L of BTEX, the TOC removal (%) was graphed against the ratio of H_2O_2 and TOC (Figure 4.13).

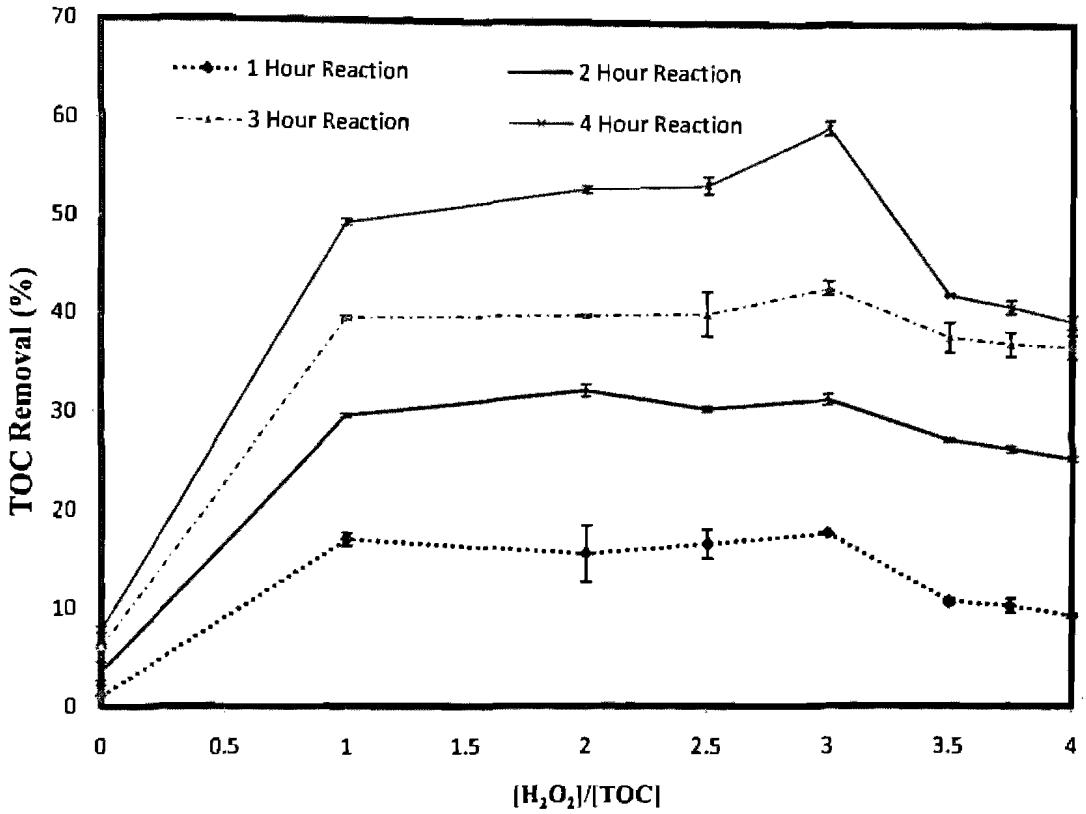


Figure 4.11: The optimal quantity of H_2O_2 required to degrade 100 mgTOC/L BTEX in water in a batch reactor with UV-254 nm.

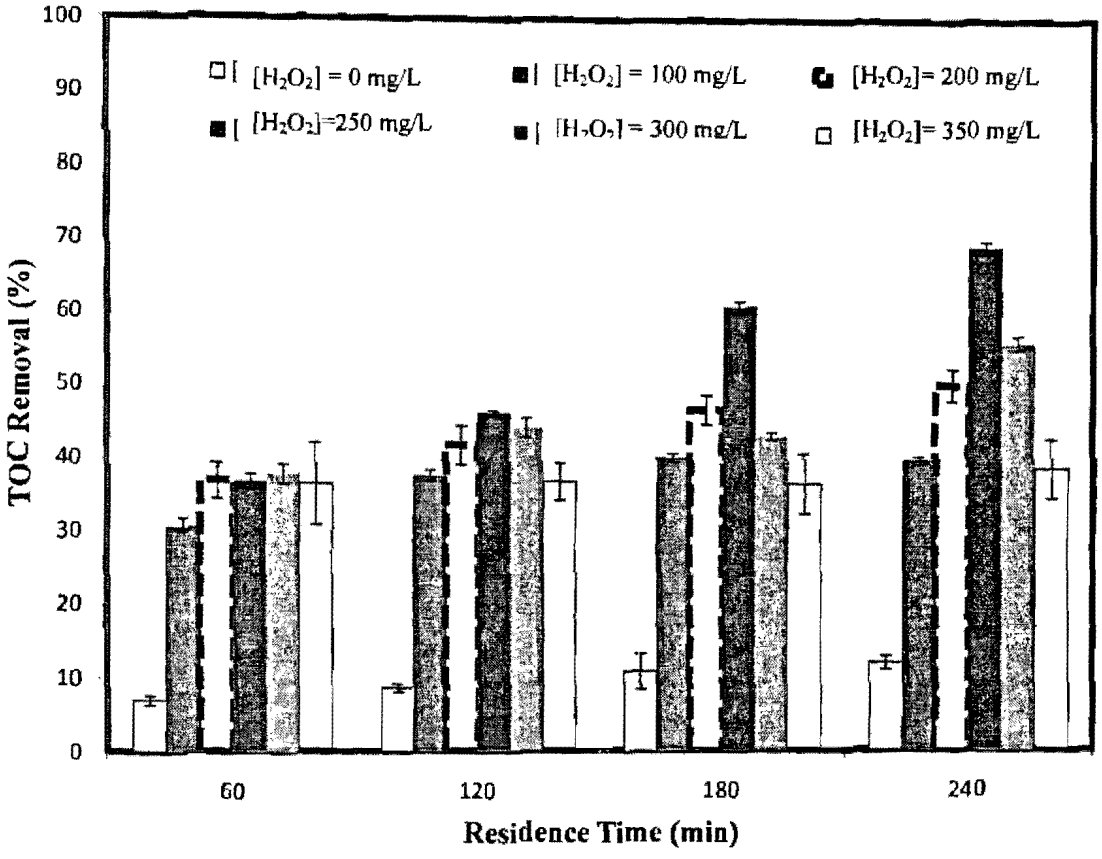


Figure 4.12: The effect of the addition of H_2O_2 on the photolytic degradation of 100 mgTOC/L of BTEX in a continuous flow photoreactor. The irradiation source was UV-185 nm.

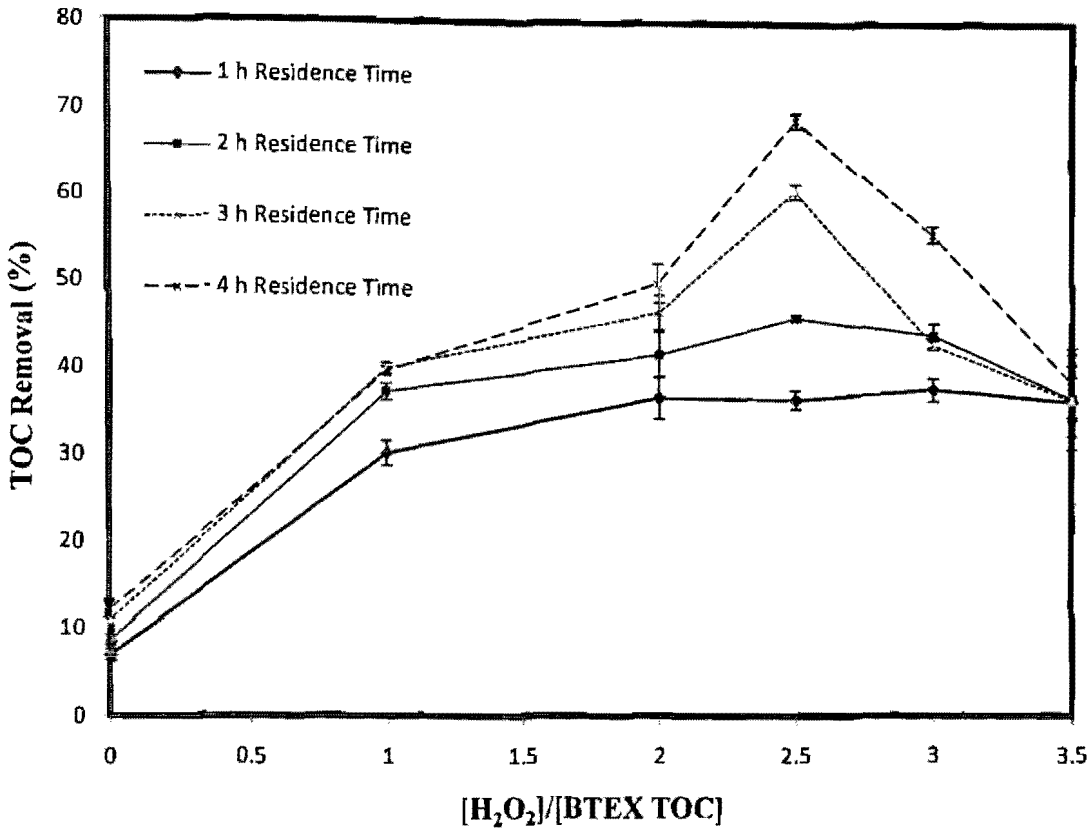


Figure 4.13: The optimal quantity of H_2O_2 required to degrade 100 mgTOC/L BTEX in water in a continuous flow reactor with UV-185nm.

Similar to the irradiation of UV-185 nm, the TOC removal (%) of BTEX increased with an increase in H_2O_2 concentration under the irradiation of UV-254 nm in the continuous flow photoreactor (Figure 4.14). The difference in the TOC removal (%) of 100 mgTOC/L of BTEX by 0 mg/L and 100 mg/L of H_2O_2 at any residence time was 24-28%. The TOC removal (%) of BTEX for the same residence time increased with an increase in the concentration of H_2O_2 until H_2O_2 concentration was 300 mg/L. At 350 mg/L of H_2O_2, the percentage removal decreased (19-23%) at all residence times compared to the percentage removal with 300 mg/L of H_2O_2. The TOC removal (%) of BTEX at 300 mg/L of H_2O_2 for 1 and 4 h residence time was 51.2% and 59.9%, respectively. Alternatively, at 1 and 4 h residence time, the percentage removal with 350 mg/L of H_2O_2 was 36.2% and 38.4 %, respectively. Considering the results of these experiments, it was concluded that under the irradiation of UV-254 nm at any residence time, the maximum percentage removal of 100 mgTOC/L of BTEX occurred with 300 mg/L of H_2O_2.

It was observed that when lower concentration of H_2O_2 was used, the percentage removal of BTEX TOC was low. The low percentage removal of TOC was due to the smaller fraction of adsorbed incident light, leading to a decrease in the rate of formation of ·OH radicals. Increasing the concentration of H_2O_2 beyond the optimum had a negative impact (decreasing the TOC percentage removal by 28.9% in batch). This negative impact is due to the extra H_2O_2 that competed with BTEX for hydroxyl radical and acting as scavenger for the hydroxyl radical as described by the following reaction (Buxton et al., 1988):

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad (4.4)$$

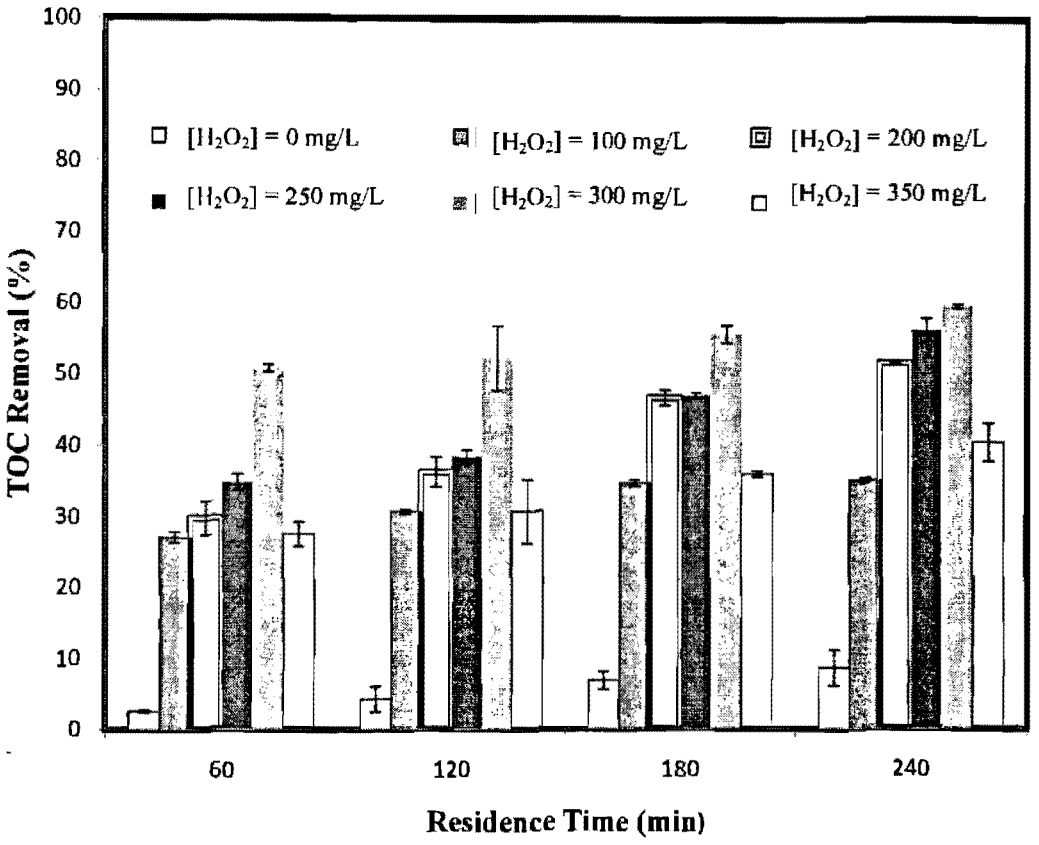


Figure 4.14: The effect of addition of H_2O_2 on the photolytic degradation of 100 mgTOC/L of BTEX in continuous flow photoreactor. The irradiation source was UV-254 nm in continuous photo-reactor.

For comparison purposes, the results of the experiments for the optimum H_2O_2 for UV-185and UV-254 nm were plotted in Figure 4.15. The results in these experiments showed that the percentage removal of TOC by UV-185/H_2O_2 increased with time (by 32% TOC removal comparing 1 h to 4 h of residence time). On the other hand, the TOC removal of UV-254/ H_2O_2 did not increase at the same rate as for UV-185 (comparing the 1 h to 4 h of residence, the removal increase was 8.8%).

The experimental optimum value for the degradation of 100 mg/L TOC of BTEX by UV-254 was 300 mg/L H_2O_2. The theoretical oxygen demand of 100 mgTOC/L of BTEX is 286 mg/L, which demonstrates the accuracy of the experimental optimal value obtained. The difference between the theoretical oxygen demand and the experimental is 4.7%.

The experimental optimum value for the degradation of BTEX by UV-185 nm was 250 mg/L, which was off by 12.6% from the theoretical value. This optimum value is lower because UV-185 nm has the energy to break the covalent bond of water decomposing it into hydroxyl radicals. Therefore, it is concluded that the remainder of hydroxyl radicals were supplied by the breakdown of water with UV-185 nm.

For comparison purposes, the results of TOC removal by UV-254 in a batch reactor and continuous flow reactor with 300 mg of H_2O_2 are plotted in Figure 4.16. It can be observed that the degradation of BTEX by the flow reactor is higher than in the batch reactor, this is due to two reasons. The flow reactor is made of electro polished 316L stainless steel, which was designed for the efficient transfer of radiation into water. On the other hand the batch reactor was glass wrapped with aluminum foil, which as demonstrated was not as effective as reactor made out of stainless steel. The other reason for the higher removal of TOC by the continuous flow reactor, the power of the lamp was 17 watts while the lamp used for batch reactor was 9 W. A suitable comparison can be performed if both batch and

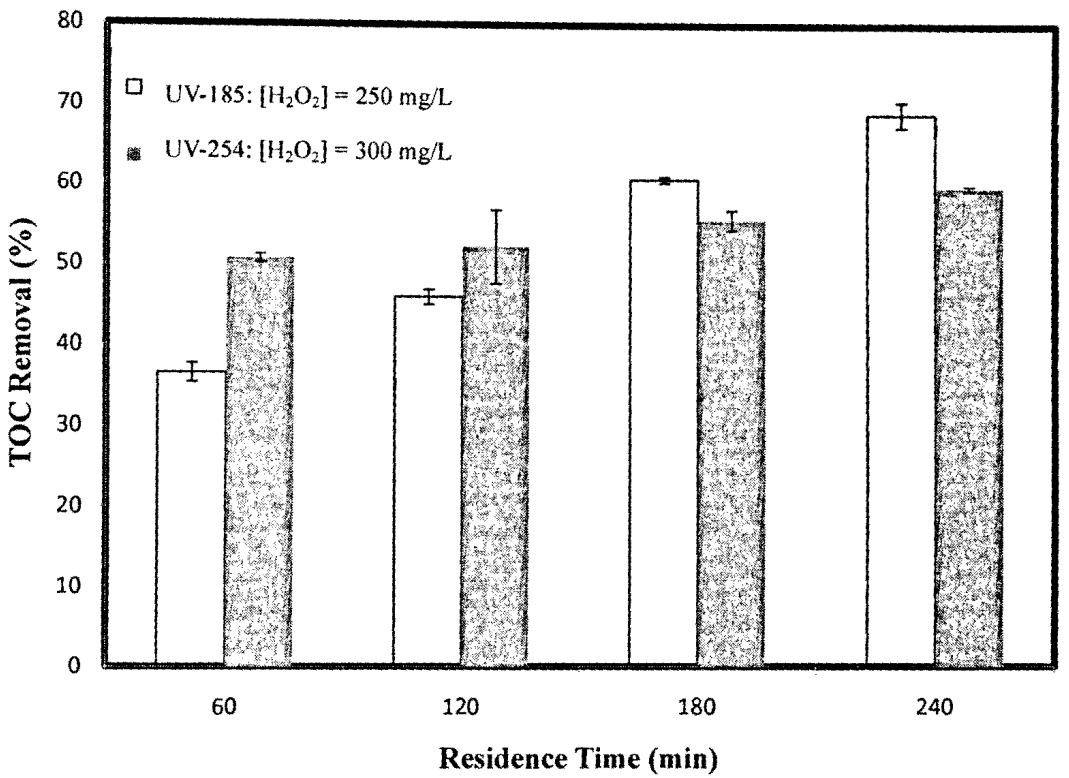


Figure 4.15: TOC removal (%) of BTEX in a continuous flow photoreactor with UV-185 nm and UV-254 nm. The inlet concentration of BTEX was 100 mgTOC/L.

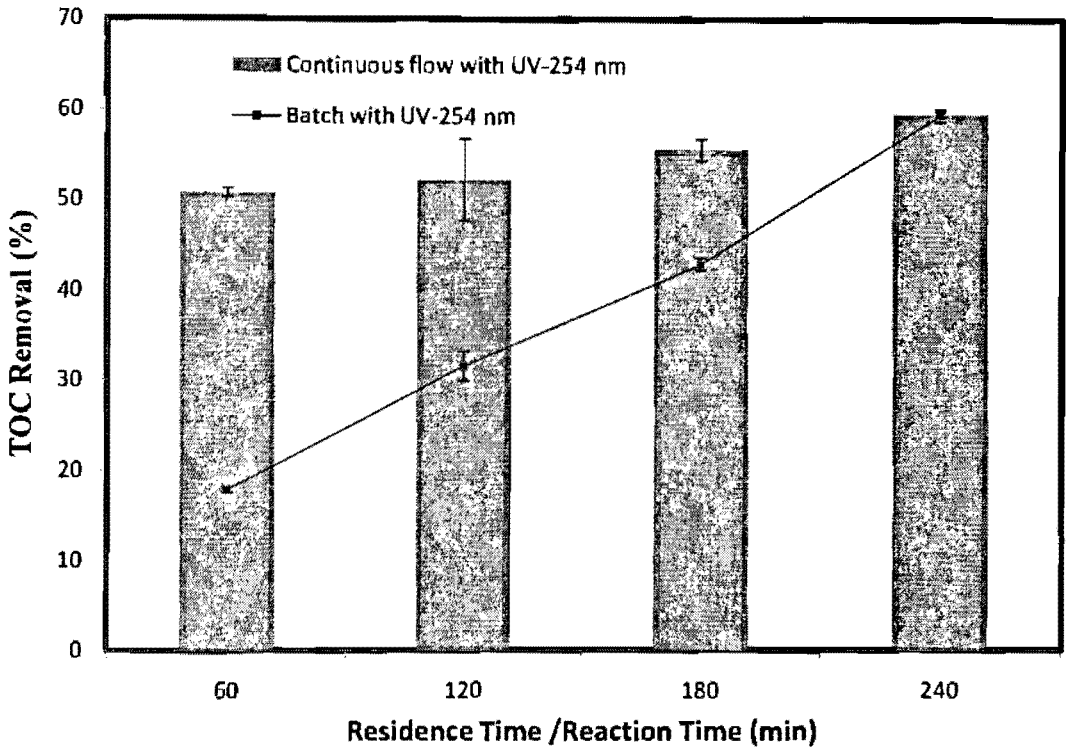


Figure 4.16: TOC removal (%) of 100 mgTOC/L of BTEX by UV-254 in a batch reactor and a continuous flow reactor with the concentration of H_2O_2 of 300 mg/L

continuous flow reactor were made of same material of construction and the power of the lamps was the same. As stated by Equation (2.22), the rate of reaction is dependent on the power of the lamp and the AOP constant, ξ, which were the two items not comparable the batch and continuous setups.

4.1.5. Acidic, basic, and unadjusted pH

The pH was monitored for all experiments. By increasing the residence time, the pH of the samples decreased. The pH value of BTEX solutions was dropped to 3.0-3.3 under the irradiation of UV-254 (Figure 4.17) in both the batch and continuous flow photoreactor. Considering that the solution becomes acidic (pH≈3), experiments were performed to evaluate the effect of inlet pH on the removal of BTEX. The pH becomes acidic, due to the formation of carbon dioxide, which dissolves in water producing carbonic acid (H_2CO_3) (Crittenden et al., 1999).

Once the recommended concentration of H_2O_2 was determined, a series of experiments were performed under: acidic conditions pH 3, basic pH 11.5 and unadjusted pH. With hydrogen peroxide at its recommended concentration of 300 mg/L and 250 mg/L for UV-254 nm and UV-185 nm, respectively, the TOC removal was higher by 15-25% under the acidic condition compared to basic and unadjusted pH (Figure 4.18 and Figure 4.19). With the inlet adjusted pH of 3, UV-185 nm with 250 mg/L H_2O_2 had 14.8% TOC removed more than by UV-254 nm with 300 mg/L H_2O_2 in the continuous flow photoreactor at 3 h residence. By lowering the pH of the solution to 3, the production of hydroxyl radical is optimized (Daifullah and Mohamed, 2004). In addition, the dissociated form of hydrogen peroxide (HO_2^-), in alkaline solution reacts with hydroxyl radicals more than two orders of magnitude faster than hydrogen hydroxyl radicals, refer to Reaction 2.15 and 2.16. The reaction rate constant for the HO_2^- with hydroxyl is higher (7.5×10^9 $M^{-1}s^{-1}$) compared to the

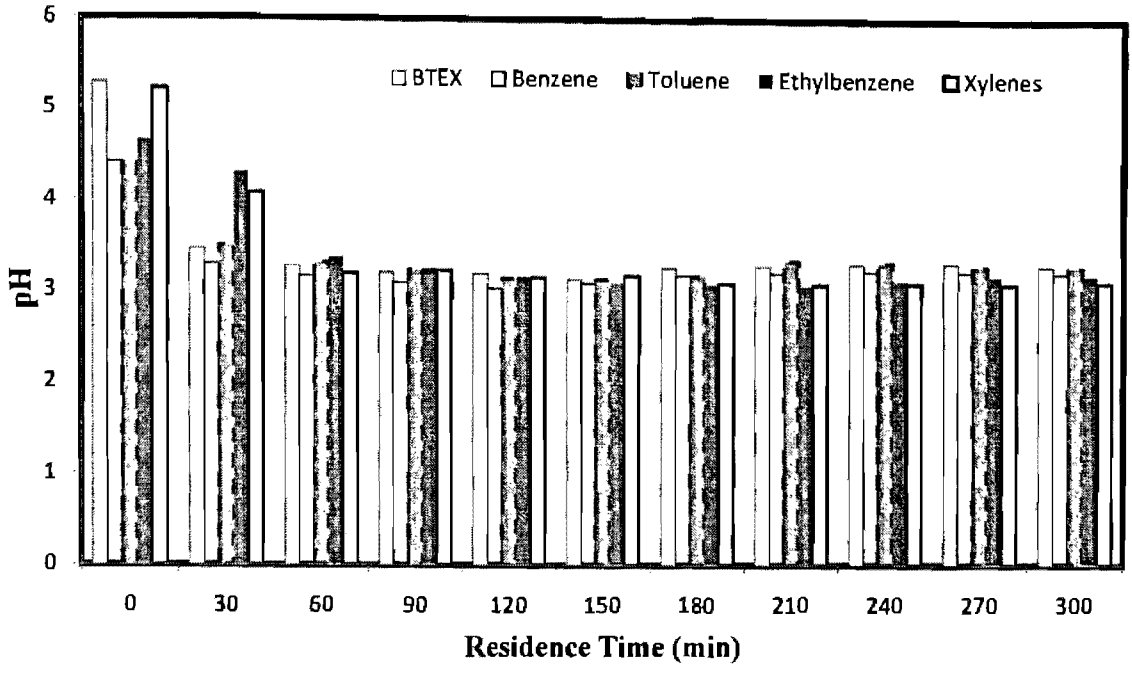


Figure 4.17: The pH values of benzene, toluene, ethylbenzene, xylenes and BTEX under the irradiation of UV-254/H_2O_2 in a continuous flow photoreactor. The inlet concentration of H_2O_2 was 300 mg/L. The concentration of all pollutants for each experiment was 100 mgTOC/L.

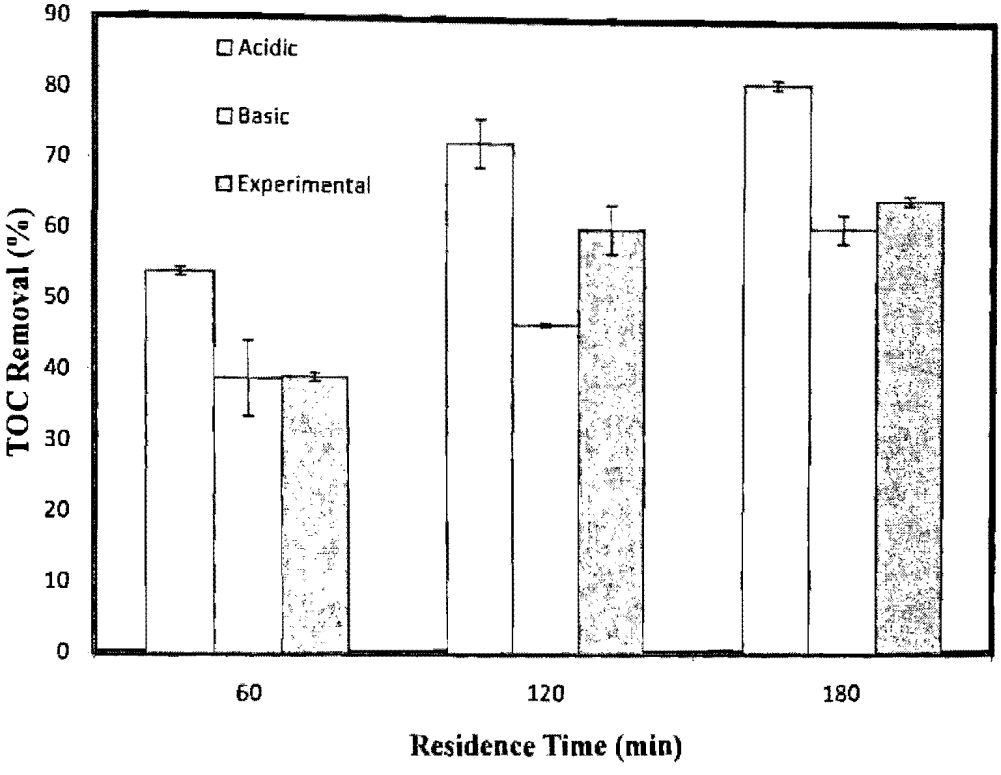


Figure 4.18: Degradation of BTEX with H_2O_2 and UV-185 nm with acidic, basic and unad justed pH. The inlet TOC of BTEX was 100 mg/L and the concentration of H_2O_2 was 250 mg/L.

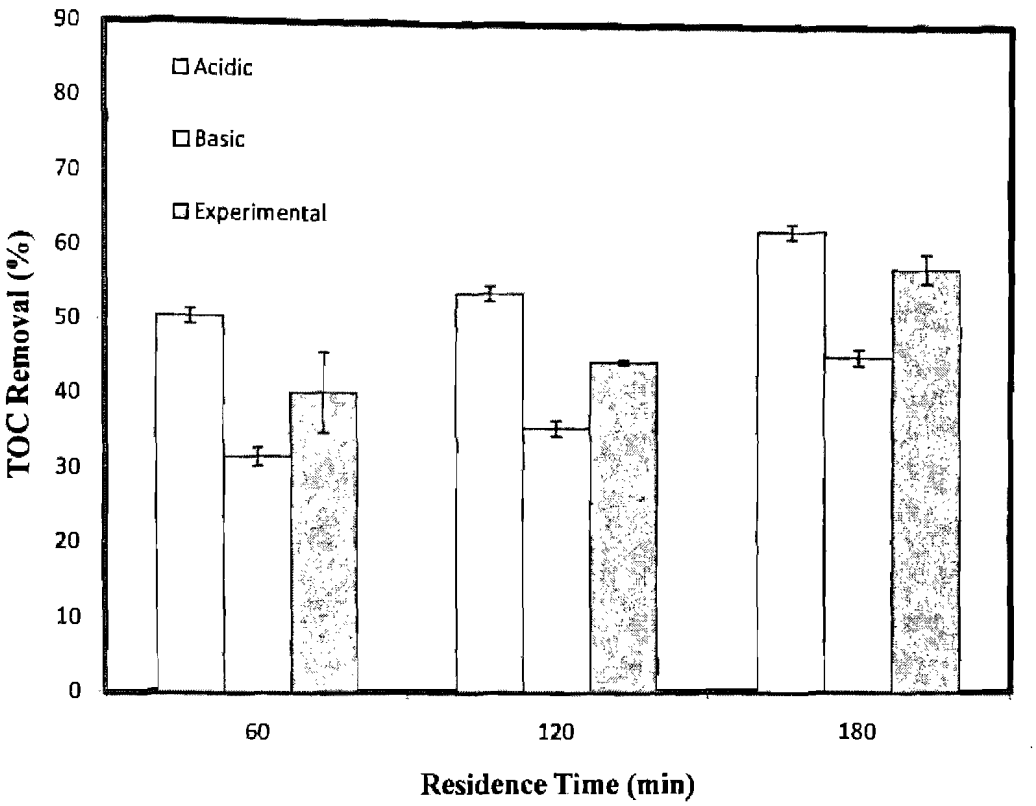


Figure 4.19: Degradation of BTEX with H_2O_2 and UV-254 nm with acidic, basic and unadjusted pH. The inlet TOC of BTEX was 100 mg/L and the concentration of H_2O_2 was 300 mg/L.

reaction rate constant ($2.7 \times 10^7 M^{-1}s^{-1}$) for hydrogen peroxide with hydroxyl radical.

However, the lower pH may cause a discharge issue. The discharge of industrial wastewater to the environment must have a pH falling in the range of 6-9 (Correctional Service Canada, 2003). In addition, high pH causes corrosion and safety problems. In the event if UV/H_2O_2 is used as a treatment method, prior to discharge of treated water, it has to be neutralized in order to be complaint with regulations and to protect the environment.

4.1.7. Experiments with Acidic pH and Optimal H_2O_2

A series of experiments were performed under acidic conditions (pH 3) and with the recommended H_2O_2 concentrations (300 mg/L with UV-254 nm and 250 mg/L with UV-185 nm). It was observed that after 6 h irradiation under UV-185 nm, 91.5% TOC was removed from the solution, while with UV-254 78.1% TOC was removed. This illustrated that for TOC percentage removal, UV-185 nm performed 14.6% better than UV-254 nm under their respective optimal conditions (Figure 4.20).

4.1.8. Use of UV-185 nm and UV-254 nm in Series

Experiments were performed to see the effect of UV-lights in series. 100 mgTOC/L of BTEX solutions were prepared and 300 mg/L of H_2O_2 was added to the solutions (acidic condition, pH = 3). The BTEX solution was fed to the UV-185 nm, such that the residence time was 1 h. The same procedure was repeated, except the residence time in UV-254 nm photoreactor was increased by increments of 1 h. A total of 4 experiments were performed with the initial residence time of 1 h in the photoreactor with UV-185 nm followed with 1, 2, 3 and 4 h of residence in the photoreactor with UV-254 nm. The results are plotted in Figure 4.21.

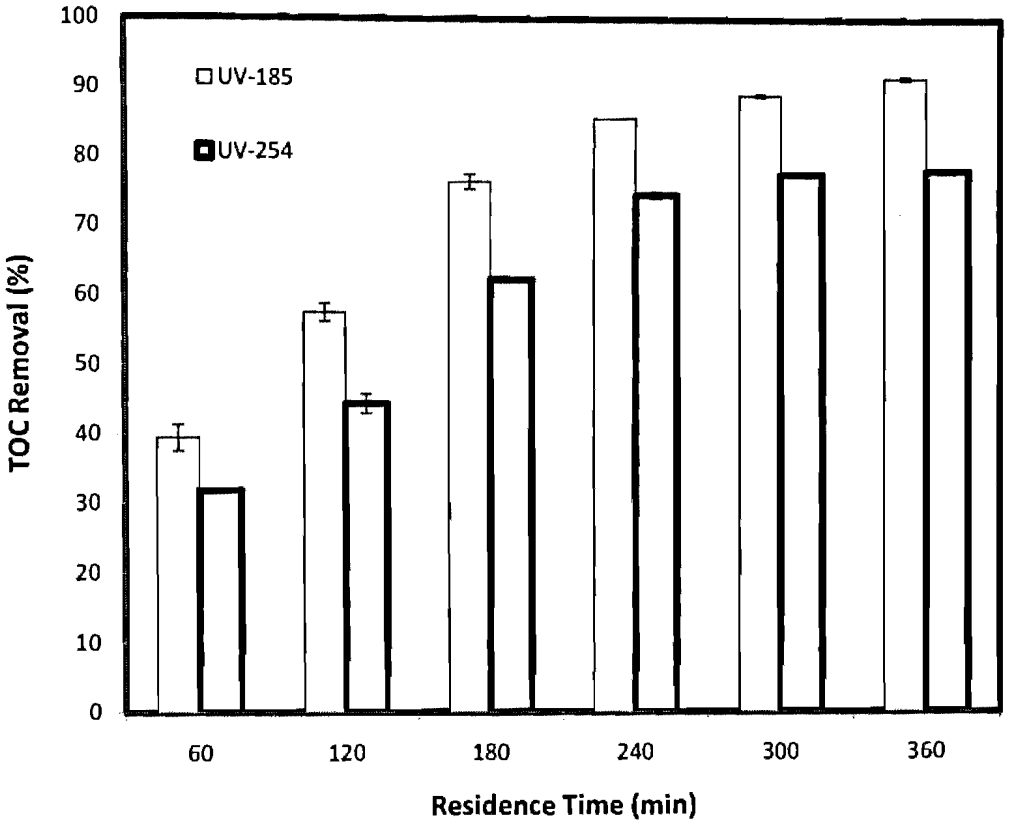


Figure 4.20: TOC removal (%) of BTEX water treated under acidic condition, pH 3. The inlet TOC of BTEX was 100 mg/L. The error bars are the standard deviations of triplicates samples at each time.

Similar experiments were performed in the photoreactor with UV-254 nm followed by the photoreactor with UV-185 nm. The results are shown in Figure 4.21. It was observed that after 4 h irradiation in either of the arrangements, the TOC percentage removal was the same, 47% was removed. However, at 2 h irradiation, the TOC percentage removal by UV-254 followed by UV-185 is 2-5% higher than UV-185 nm followed by UV-254 nm.

In Figure 4.22, the results of UV-lights in series and UV-lights alone are shown. It was observed that the use of light in series did not improve the TOC removal of BTEX. The TOC removal efficiency was as follows: UV-185 > UV-254 > UV-lights in series.

4.2. Biological Oxygen Demand (BOD)

The BOD of BTEX, under the irradiation of UV-254 nm in a batch stirred reactor was measured. The ratio of BOD/COD indicates whether a chemical is readily biodegradable or not. If BOD/COD is less than 0.3, then the solution is not readily biodegradable. As illustrated in Figure 4.23 b, the BOD/COD ratio is 0.34 initially, but it was decreased (from 0.34 to 0.24) with an increase in the irradiation time. The BOD/COD ratio was 0.24 after 140 min irradiation. Due to the interference of H_2O_2 with the COD value of the BTEX, no conclusion can be drawn from the BOD/COD ratio.

The BOD analysis was performed on the BTEX solutions, under the irradiation of UV-254 nm and UV-185 nm. As illustrated in Figure 4.24, the BOD decreased (from 57 mg/L to 30 mg/L) as residence time in the photoreactor increased (0-140 min). For example, the inlet BOD of solution of BTEX (100 mgTOC/L) was 57 mg/L. After 2 h irradiation, the BOD was 26 mg/L. The pattern for water treated with UV-185 nm and UV-254 nm was similar. In Figure 4.25, the BOD/TOC results show that biodegradability of BTEX treated with UV-254 and UV-185 is not enhanced. The BOD/TOC ratio for UV-254 decreased by 32% and for UV-

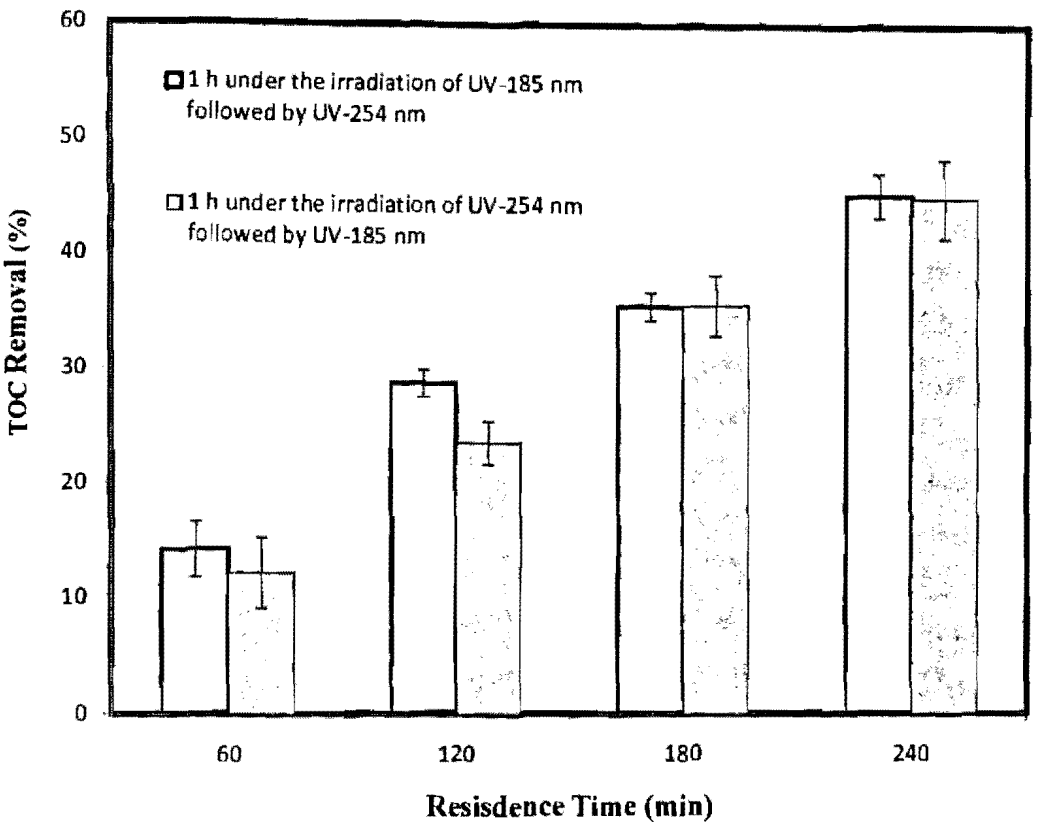


Figure 4.21: Effect of using UV-185 and UV-254 nm in series in a continuous photoreactor with inlet BTEX TOC of 100 mg/L and 300 mg/L H_2O_2 in acidic condition (pH = 3).

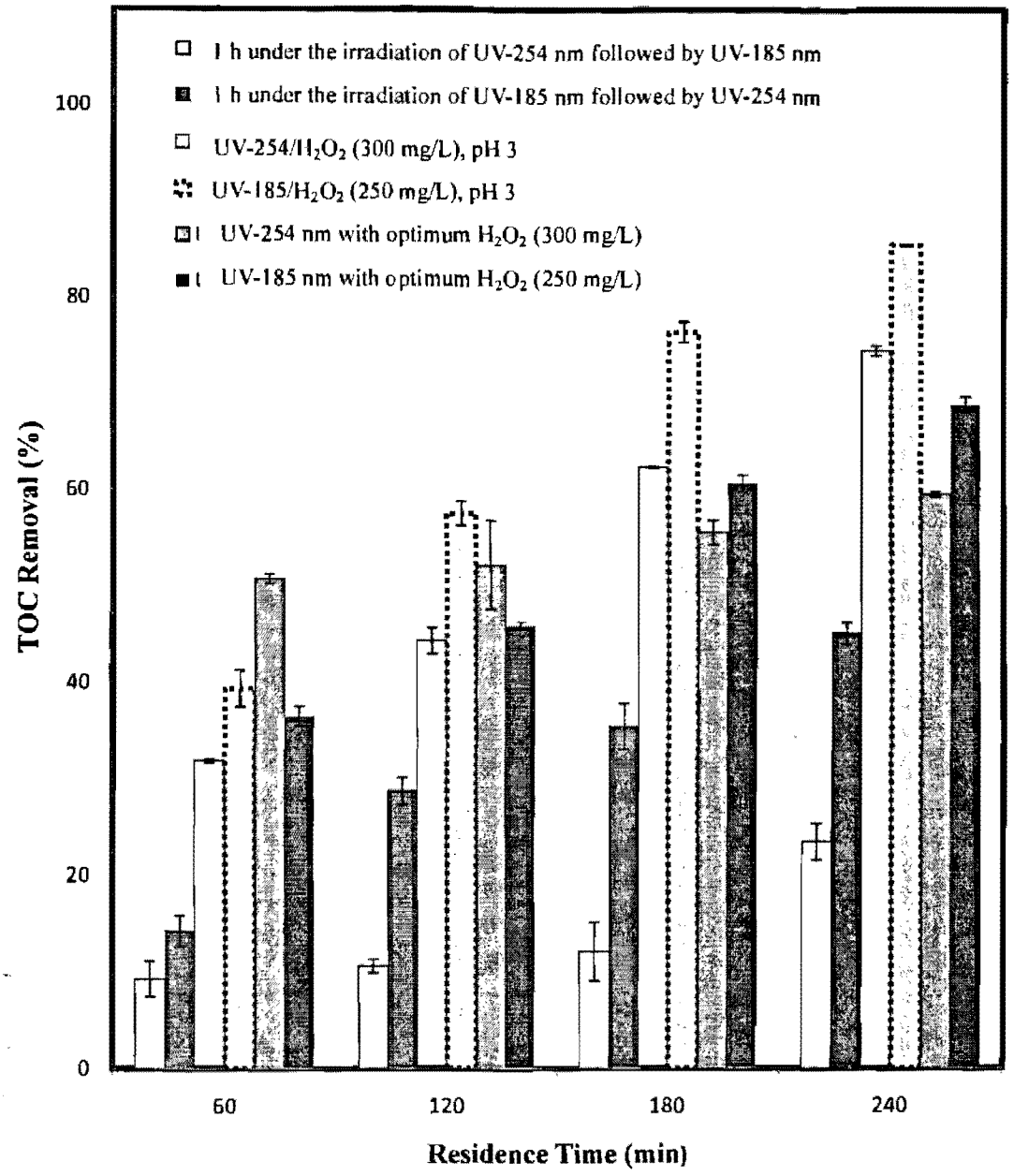
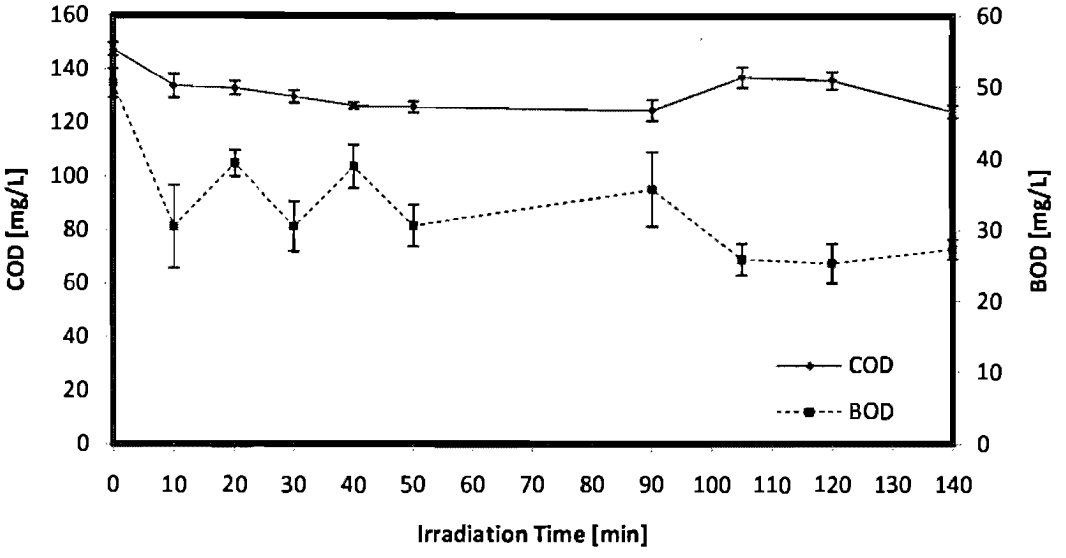
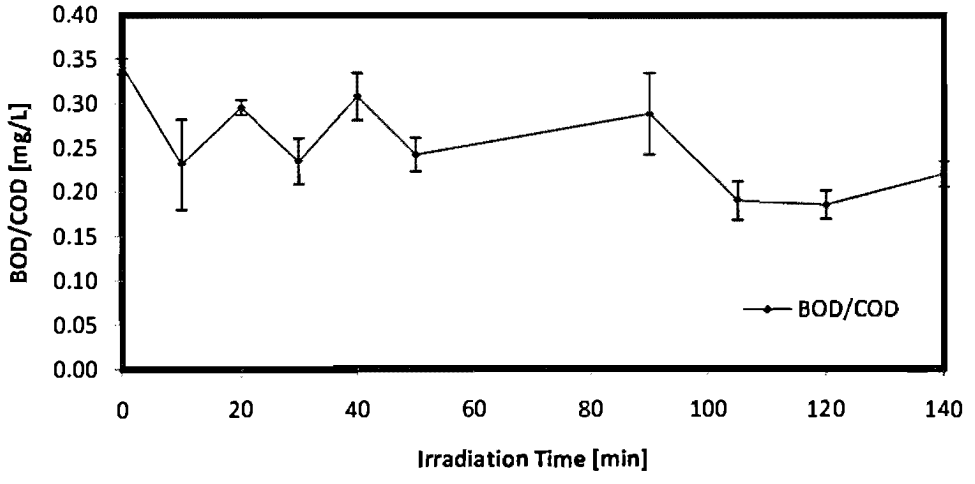


Figure 4.22: Comparison of UV-185 and UV-254 nm in series and UV-185 and UV-254 alone in a continuous photoreactor with inlet BTEX TOC of 100 mg/L and 300 mg/L H_2O_2.



(a)



(b)

Figure 4.23: (a): Degradation of BTEX with initial concentration of 43 mg/L in a closed batch reactor under the irradiation of UV-254 nm. (b) Ratio of BOD to COD for BTEX.

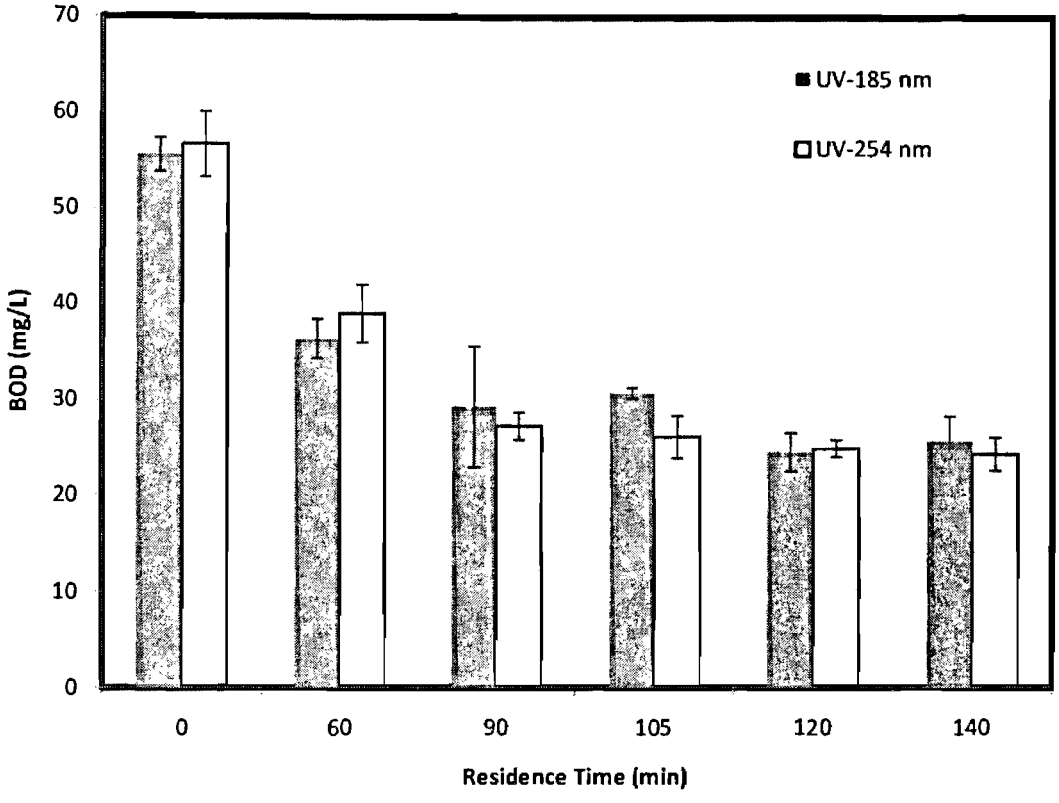


Figure 4.24: Determination of BOD of BTEX during irradiation under UV-185 nm and UV-254 nm in continuous photoreactor. The inlet concentration of BTEX was 100 ± 10 mgTOC/L. The H_2O_2 concentrations were 250 mg/L and 300 mg/L for experiments with UV-185 nm and UV-254 nm, respectively.

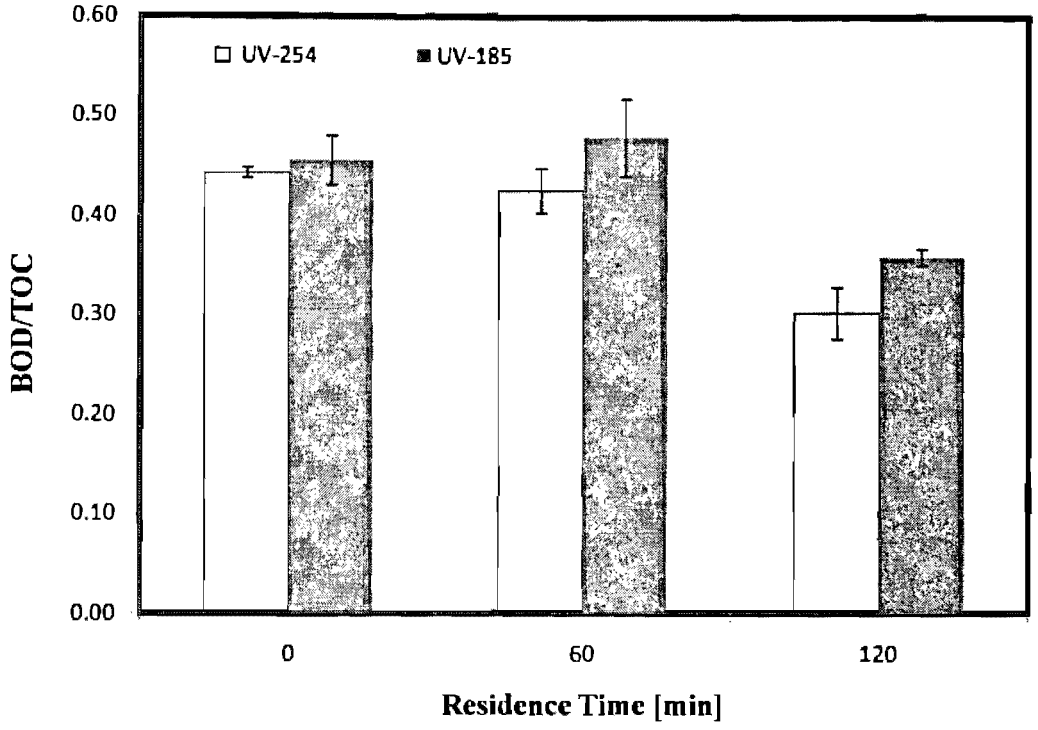


Figure 4.25: Determination of BOD/TOC ratio of BTEX during irradiation under UV-185 nm and UV-254 nm in continuous photoreactor. The inlet concentration of BTEX was 100 mgTOC/L. The H_2O_2 concentrations were 250 mg/L and 300 mg/L for experiments with UV-185 nm and UV-254 nm, respectively.

185 it decreased by 21% after 2 h irradiation. Based on BOD/TOC ratio, it is concluded that biodegradability of BTEX under the irradiation of UV-185 and UV-254 is not enhanced.

4.3. Anaerobic Baffled Reactor (ABR) Experiments

Biodegradation experiments were performed using anaerobic baffled reactor, which was acclimated to slaughter house waste water from a previous study. BTEX (10 mg/L) was introduced to the ABR with slaughter house waste water. For over a month, the sludge was fed with 10 mg/L of BTEX and slaughter house waste. The initial concentration of slaughter house waste was 900 mgTOC/L. Gradually, the concentration of slaughter house waste was reduced to 0 mgTOC/L. The concentration of BTEX was kept at 10 mg/L. The flow rate was adjusted to 0.63 L/h (the hydraulic retention time (HRT) was 2.2 days). During the experiments, sludge washout was observed. There was occurrence of sludge bulking (usually occurs when the sludge fails to separate out from the wastewater).

The data for volatile suspended solid (Figure 4.26) demonstrated the bulking of sludge. The TOC in the different compartments during the acclimation period was measured and are plotted in Figure 4.27.

The sludge was settling as the concentration of slaughter house was decreased. This could have been due two factors, the hazardous nature of BTEX affecting the health of the sludge, and also due to less TOC available for consumption. The sludge did not seem healthy and the samples collected were bulking. Based on the data obtained, one cannot conclude the performance of ABR for BTEX, therefore the experiment was stop.

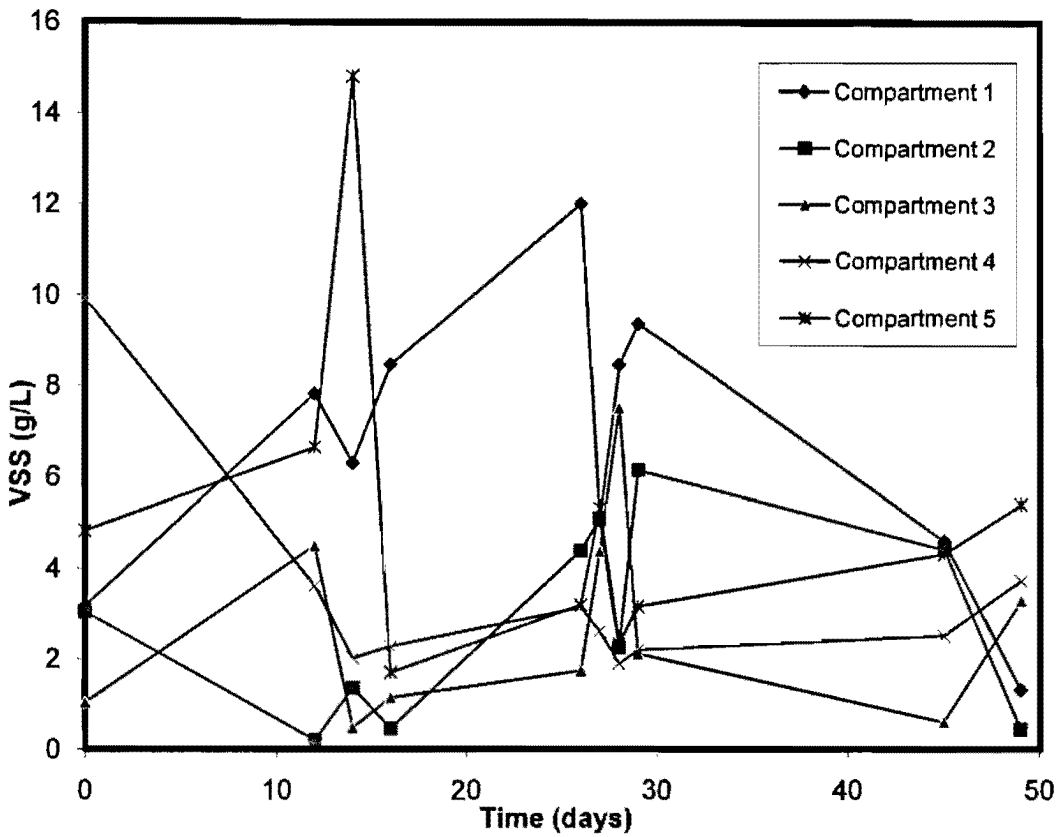


Figure 4.26 : The Volatile suspended solids during the acclimation of anaerobic sludge to BTEX.

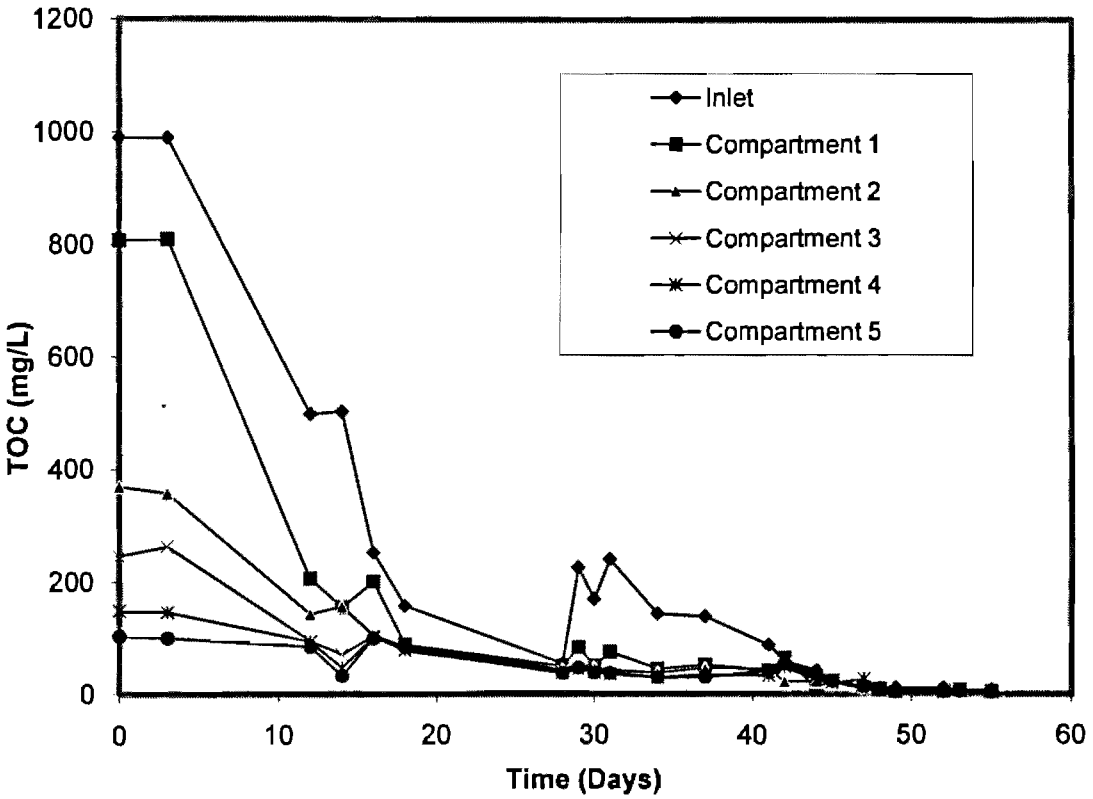


Figure 4.27 : Concentration (mgTOC/L) of chemicals in different compartments of the ABR during the acclimation period.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from this thesis:

5.1. Conclusions

1. The UV/H_2O_2 contributed to the degradation of BTEX; however, this process was slow. Under the irradiation of UV-254 nm in the batch photoreactor, the change in COD of BTEX was 27%, while the change in TOC was less than 10% in the continuous photoreactor.
2. The recommended concentration of H_2O_2 to degrade 100 mgTOC/L of BTEX is 300 mg/L under the irradiation of UV-254 nm.
3. The experimental results demonstrated that maximum removal (68%) of BTEX TOC occurred with 250 mg/L of H_2O_2 under the irradiation UV-185 in continuous flow photoreactor at flow rate of 0.45 L/h (3 h residence time).
4. The continuous flow photodegradation of BTEX were performed in three pH conditions; it was observed that the TOC percentage removal was the highest with pH 3.With the recommended quantity of H_2O_2 (300 mg/L and 250 mg/L) and acidic pH, the maximum mineralization was 80% and 90% for UV-254 and UV-185 nm, respectively. However, the lower pH may cause discharge environmental issues. The

discharge of industrial wastewater to the environment must have a pH in the range of 6-9.

5. During the batch UV-H_2O_2, the concentration of BTEX was zero after 90 min irradiation under UV-254, however the COD was 116 mg/L. This COD value leads to conclude that the BTEX have been transformed into its intermediates.
6. Using UV-185 and UV-254 nm in series did not improve the TOC removal, after 4 h of exposure; its TOC removal was 47%; while the TOC removal by UV-185 and UV-254 alone were 68% and 60%, respectively.
7. The photochemical degradation of BTEX produced intermediates, which did not improve its biodegradability. The BOD of BTEX decreased as the irradiation time increased. In addition the BOD/TOC ratio of BTEX under the irradiation of UV-185 and UV-254 and optimum quantity of H_2O_2 decreased by 21% and 32%, respectively.

5.2. Recommendations

1. Due to the volatile nature of BTEX, further experiments should be performed to investigate the effect of volatility on the photodegradation results of BTEX.
2. Water from nature that is contaminated with gasoline that has other chemicals present in it, therefore the interference of other chemicals on the degradation of BTEX should be taken into account in future studies.
3. Further studies should be performed to identify the by-products that are produced during the photodegradation of BTEX.
4. Kinetics studies should be performed for UV-185/H_2O_2 to demonstrate the pseudo first order reaction.
5. Further studies should be performed under the entire pH range. In addition, cost optimization may be considered when treating the waste under extreme acidic or basic

conditions (not within the discharge limits: pH 6 -9). Neutralizing waste prior to discharge would be an additional cost.

6. Photodegradation experiments may be performed on post biodegradation of BTEX contaminated water.
7. Actual petroleum contaminated wastewater, from contaminated site or from a spillage site, could be used in the UV/H_2O_2 process to evaluate its experimental findings and the possibility of application in practice. The contaminated water from site would have sludge and particulates, which will reduce the intensity of light. To avoid reducing intensity of light, filtering of water may be performed.

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APPENDICES

A. Determination of BOD

The BOD of samples was calculated using the following equation:

$$BOD = \frac{(D_1 - D_2) - SCF}{P} \tag{3.3}$$

$$SCF = (B_1 - B_2) f \tag{3.4}$$

For example, for the determination of the initial BOD_5 of BTEX, each of 300 ml BOD bottle contained 20 mL initial wastewater (P=20/300), and the volume of seed solution used in glucose, glutamic acid (GGA) test was 4 mL. The volume of the seed solution used in seed control was 10, 15, 20 mL, respectively. The average initial BOD_5 was measured to be 57.02 mg/L. The calculation of SCF was shown in Table A.1. All details for BOD test are in Section 3.2.6.

Table A.1: Seed Correction Factor (SCF) Calculation

Sample ID	B_1 [mg/L]	B_2 [mg/L]	B_1-B_2 [mg/L]	SCF :$(B_1-B_2)f$; must be between 0.6-1.0	f = volume of GGA / Volume of Polyseed in Seed control
Seed Control 1	8.9	6.7	2.2	0.88	0.40
Seed Control 2	8.7	5	3.7	0.99	0.27
Seed Control 3	8.9	4.8	4.1	0.82	0.20
	Average			0.90	0.29

Table A.2: BOD Calculation for the Initial Solution of BTEX (100 mgTOC/L)

Sample	D_1 [mg/L]	D_2 [mg/L]	D_1-D_2 [mg/L]	Sample BOD [mg/L]: $[(D_1-D_2)-(B_1-B_2)f] / P$
BTEX1	8.7	3.9	4.8	58.8
BTEX2	8.7	4	4.7	55.7
BTEX3	8.7	4.1	4.6	56.7
	Average			57.07

The average inlet BOD_5 of BTEX (100 mgTOC/L) was determined to be 57.02 mg/L.

B. Standard Error Calculation

The standard error of the mean was used as the error bar in this study. It is defined as the standard deviation divided by the square root of number of samples as follows (Skoog et al., 1998)

$$\text{Standard Error} = \frac{s}{\sqrt{N}} \qquad \text{(B.1)}$$

Where s = the standard deviation

N = the number of samples

Sample standard deviation is used to analyze the accuracy of an experimental measurement for a finite set of experimental data. Sample mean (x) and sample standard deviation (s) are determined as follows (Skoog *et al.*, 1998).

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - x)}{N-1}} \qquad \text{(B.2)}$$

Where s is the standard deviation and N is the number of samples, x_i is the i^{th} sample value and x is the average of samples.

Between +1 and -1 standard error is the range in which there is a 68% probability that the true mean value was measured. For a stronger probability, the limits were extended to +2 and -2 times the standard error and, therefore, provided 95% confidence.

Excel files were programmed to calculate the standard deviation and the standard error. For example, in Figure 4.6, the error bar for UV-185 nm at 180 min was calculated to be 3.17.

Table B.1 lists the experimental data and calculated data for degradation of BTEX in continuous flow photoreactor with no hydrogen peroxide under the irradiation of UV-185 nm.

Table B.1: TOC Data for the Standard Error Calculations

Time (min)	0	180
Sample 1 (mgTOC/L)	101.34	91.81
Sample 2 (mgTOC/L)	98.35	89.13
Sample 3 (mgTOC/L)	99.70	86.32
Mean: x	99.80	89.09
Standard Deviation: s	1.50	2.75
Standard Error	1.73	3.17
Percentage Removal (%)	0.00	10.73

$$x = \frac{91.81 + 89.13 + 86.32}{3} = 89.09$$

$$s = \sqrt{\frac{[(91.81 - 89.09)^2 + (89.13 - 89.09)^2 + (86.32 - 89.09)^2]}{3 - 1}} = 2.75$$

In order to be in the 95% confidence, the standard was calculated as follows

$$\text{Standard Error} = \pm 2 \times \frac{2.75}{\sqrt{3}} = \pm 3.17$$

C. Percentage Removal/ Removal Efficiency

The percentage removal (removal efficiency) of COD and TOC can be was calculated using equations 3.7 and 3.8, respectively. As a sample calculation, the TOC removal is shown using Equation 3.8 as follows:

$$TOC\% = \left(\frac{TOC_i - TOC_f}{TOC_i} \right) \times 100\% \tag{3.8}$$

Where TOC_i=the initial or inlet concentration

TOC_f = the final concentration.

For example, the TOC percentage removal of BTEX in continuous flow photoreactor with no hydrogen peroxide under the irradiation of UV-185 nm after 180 min was (see Table B.1 for inlet and final values)

$$\text{Removal}(\%) = \frac{99.8 - 89.09}{99.8} \times 100\% = 10.73\%$$

D. H_2O_2 Calculations

The initial COD for hydrogen peroxide can be calculated using Equation (4.3) as follows:

$$COD_{H_2O_2} = 0.4591[H_2O_2] - 3.24 \times 10^{-5}[H_2O_2]^2 \tag{4.3}$$

The hydrogen peroxide values were measured prior to the BOD test. The results for the

experiment with 43 mg/L BTEX (with theoretical COD of 122 mg/L) in the batch setup with UV-254 nm are tabulated below (Table D.1). The concentration of H_2O_2 added to the solution was 100 mg/L. Equation 4.3 was used to calculate the COD of H_2O_2 as follows:

$$COD_{H_2O_2} = 0.4591[100] - 3.24 \times 10^{-5}[100]^2 = 45.586\, mg/L$$

Table D.1: Calculated COD values for H_2O_2

Irradiation Time (min)	COD of BTEX Solution with H_2O_2 [mg/]	Hydrogen peroxide Lovibond CHECKIT		Calculated COD of H_2O_2 [mg/L] (using Equation 4.3)
		Colour reading of BTEX-H_2O_2 solution	Corresponding H_2O_2 range [mg/L]	
0	148.81	Dark Orange	10-100	4.56-45.59
10	135.05	Dark Orange	10-100	4.56-45.59
20	132.15	Dark Orange	10-100	4.56-45.59
30	128.09	Dark Orange	10-100	4.56-45.59
40	126.24	Dark Orange	10-100	4.56-45.59
50	126.34	Dark Orange	10-100	4.56-45.586
90	117.00	Orange	10-100	4.56-45.59
105	137.00	Orange	10-100	4.56-45.59
120	135.39	Pink	0.2-2	0.092-0.92
140	124.22	Pink	0.2-2	0.092-0.92

Given that the hydrogen peroxide Lovibond CHECKIT gives a range for the concentration of H_2O_2 therefore the corresponding calculated COD value is also a range. Given that the theoretical COD of BTEX was 122 mg/L and the measured COD was 148.81 mg/L, the higher value indicates the interference of H_2O_2. According to Kang et al., (1998), the calculated value of H_2O_2 must be subtracted from the measured COD value to eliminate the

interference of H_2O_2. Hence the corrected initial COD value of BTEX in the solution based on Kang et al., (1998) would be 102.414, which is off by 16.1% from the theoretical value of 122.

E. Anaerobic Baffled Reactor Data

Table E.1 shows the TOC for the different compartments during the last 10 days of the experimental study period.

Table E.1: TOC Concentration (mg/L) in Each of the Compartments of the ABR

Day	45th	47th	48th	49th	52nd	53rd	55th
Inlet (mgTOC/L)	24.38	10.06	15.85	10.9534	11.0476	6.1406	7.512
Compartment 1 (mgTOC/L)	24.07	11.42	8.74	3.7917	5.8502	7.1278	4.1493
Compartment 2 (mgTOC/L)	24.96	10.45	7.23	4.0269	4.1719	5.5137	4.5072
Compartment 3 (mgTOC/L)	20.63	9.15	8.66	4.6067	5.127	6.2114	2.6819
Compartment 4 (mgTOC/L)	19.61	26.30	6.59	3.7478	3.5564	5.4676	5.0377
Compartment 5 (mgTOC/L)	22.69	13.79	6.95	4.1829	4.744	5.6123	3.6733

F. Volatile Suspended Solids (VSS) Calculations

The TSS and VSS were determined by Equations (3.3) and (3.4) based on Standard Methods (APHA, 1998). Table D.2 lists all the values for the calculation of TSS and VSS.

$$TSS\,(mg/L) = \frac{W_1 - W_2 - W_3}{V} \qquad \text{(D.1)}$$

$$VSS\ (mg/L) = \frac{W_1 - W_2 - W_3 - (W_4 - W_3)}{V} = \frac{TSS - (W_4 - W_3)}{V} \quad (D.2)$$

Where

W_1 = the sum of the weights of the dried filter paper, dish, and solids of sample, mg

W_2 = the weight of dried filter paper, mg

W_3 = the weight of dried dish, mg

V = the volume of sample, mL

W_4 = the sum of the weights of solids of sample and dish after burning (the filter paper was burned in the furnace), mg

Table F.1: Calculation for TSS and VSS of the Sludge in Each of the Compartments of the ABR

Item	Parameter	Value
(1)	Volume of sludge (mL)	5.0
(2)	Weight of filter (g)	0.9283
(3)	Weight of aluminum weighting dish (g)	1.3025
(4)	Total weight of filter and aluminum dish after 1 h heating in the oven at 104°C (g)	2.252
(5)	Total weight of filter and aluminum dish after 15 min igniting in the furnace at 550°C (g)	1.3078
(6)	TSS = (4)-(3)-(2) (g)	0.00424
(7)	VSS = (4)-(5)-(2) (g)	0.00318
(8)	Concentration of TSS in sludge =(6)/(1)×1000 (g/L)	4.24
(9)	Concentration of VSS in sludge =(7)/(1)×1000 (g/L)	3.18