PHOTOCATALYTIC DEGRADATION OF VOCS, TOXICS AND ODORS FROM AIR EMISSIONS OF WASTEWATER TREATMENT PLANTS AND MUNICIPAL SOLID WASTE LANDFILLS

by

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ABSTRACT

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The 1990 Clean Air Act Amendments (CAAA) require more stringent controls of sources of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Air quality managers at the state level are responsible for developing State Implementation Plans (SIPs) to improve regional air quality. Both wastewater treatment and landfills facilities are sources of VOCs, HAPs and odors.

This research examines the effectiveness of photocatalytic oxidation (PCO) in treating emissions from wastewater and landfill facilities. PCO rate constants of compounds such as methane, o-xylene, m-xylene, p-xylene and carbonyl sulfide are determined over titanium dioxide (TiO_2) catalyst in a continuous mixed-batch reactor.

The PCO destruction rates indicated first order decay. Destruction rate was higher for smaller molecules like methane and carbonyl sulfide and lower for complex molecules like xylenes. The destruction rate also depended on humidity. Research concludes that PCO is a promising method to treat emissions from smaller sources.

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CHAPTER 1

INTRODUCTION

1.1 Background

The 1990 Clean Air Act Amendments (CAAA) require stringent controls of sources of volatile organic compounds (VOCs) which are precursors to tropospheric ozone smog formation and hazardous air pollutants (HAPs) that are toxic for human health. Many control technologies have been successfully developed and utilized for larger sources of VOCs and HAPs, but they have not been found economical and effective for smaller sources. Photocatalytic oxidation is a relatively new technology which is found to be promising for smaller emission sources (Sattler and Liljestrand, 2003).

Photocatalytic oxidation converts the hydrocarbons to harmless gases like water and carbon dioxide in the presence of ultraviolet light (350 – 400 nm) and a catalyst such as titanium dioxide. Photocatalytic oxidation utilizes ultraviolet radiation to promote electrons from the valence band to the conduction band of the titanium dioxide semiconductor. As the electrons get promoted to the conduction band, corresponding holes are created in the valence band. The electrons act as reducing species and the holes act as oxidizing species. The hydrocarbons are oxidized and subsequently destroyed (Sattler and Liljestrand, 1996; Stevens et al., 1998; Zhao and Yang, 2002).

1.2 Research Objective

The overall objective of this research was to determine the effectiveness of using photocatalytic oxidation to treat gaseous emissions from wastewater treatment plants and municipal landfills. To determine the effectiveness of the process, it is necessary to determine the photocatalytic oxidation destruction rates of various VOCs and HAPs species associated with them. The destruction rates and other data obtained from such kinetic experiments aid optimal reactor design (Zhao and Yang, 2002). Reaction rates are important in reactor design because they determine the length of time the gas stream will need to reside in the reactor to achieve the desired level of destruction. If the gas flow is fixed, the required gas residence time determines the necessary reactor volume: for a slower reaction, a longer residence time and a larger reactor will be required and vice versa. Thus, to size a photocatalytic reactor, destruction rates for HAPs and VOCs are needed (Sattler and Liljestrand, 2003).

The objective of this research was to determine the destruction rate constants for various VOCs, HAPs and odors associated with wastewater treatment plants and municipal landfill emissions.

1.3 Research Rationale

The 1990 Clean Air Act Amendments (CAAA) requires the states to meet higher standards of air quality; this has lead to many regions of the states becoming non-attainment zones. Under CAAA, states are required to adopt a State Implementation Plan (SIP) to regulate pollutant emissions from mobile sources, power plants and other significant pollutant emitting works to meet National Ambient Air

Quality Standards (NAAQS). Two of the numerous pollutant emitting sources are wastewater treatment plants and municipal solid waste landfills. These were not considered substantial pollutant emitting sources for a long time, but as the air pollution regulations became more stringent, they are now being considered as potential pollutant emitting sources. The nature and amount of pollutants emitted depends on the size and configuration of the wastewater treatment plant or municipal landfill and the nature of waste being treated (industrial or municipal).

The major pollutants associated with the wastewater treatment plants and solid waste landfills are volatile organic compounds (VOCs). Some areas are required to limit VOC emissions to comply with ozone standards, since many VOCs are precursors to ozone formation. In addition, wastewater treatment plants and municipal landfills also emit CO_2, CO, NOx, SOx and particulate matter (PM) in small quantities. Some of the pollutants not only violate the air quality regulations, but are highly odorous and toxic, causing nuisance to the local community in the vicinity of the treatment plant, and posing a danger to the general public. These facts make it necessary to look into the nature and amount of the various pollutants released from the wastewater treatment plants and landfills and try to develop appropriate control technologies.

Some of the widely used gaseous pollutant removal techniques are absorption, adsorption, incineration, condensation, biofiltration and photocatalytic oxidation (Sattler and Liljestrand, 2003). Each technique is suited to a gas stream under certain conditions. Overall comparison of different techniques show that adsorption and absorption do not destroy the VOCs but simply transfer them from one medium to another, biofiltration is not suited to treat chlorinated hydrocarbons and toxic pollutant streams, and incineration is energy intensive and suitable only for high to moderate concentration VOC streams. Photocatalytic oxidation has none of these disadvantages and hence it is a promising gaseous pollutant removal technique and requires further research to determine its applicability and effectiveness (Sattler and Lijestrand, 2003; Zhao and Yang, 2002; Sun et al., 2005)

1.4 Research Scope

All experiment runs were performed in a continuous mix batch reactor photocatalytic oxidation system. Tests were limited to following pollutant species:

- For municipal landfill emissions, methane was tested.
- For wastewater treatment plants, o-xylene, p-xylene, m-xylene and carbonyl sulfide were tested.

The rate constants developed during the experiments may not be directly applicable to another system, since they depend on various parameters like ultraviolet light intensity, reactor configuration, and catalyst characteristics which are specific to any given system (Sattler and Liljestrand, 2003, Zhao and Yang, 2002, Gogate and Pandit, 2003). However, since rate constants would be simple function of these parameters, they can be easily scaled and applied to another system.

1.5 Research Organization

Table 1.1 discusses the research organization and presentation.

Table 1.1 Research Organization

Chapter	Content
2	This chapter contains a literature review of similar studies done using photocatalytic oxidation technique.
3	This chapter deals with the methodology that was employed in conducting experiments.
4	This chapter includes the results and analysis of the data obtained from experiments.
5	This chapter discusses the conclusions drawn from the analysis of the data.
6	This chapter lists the recommendations and further scope of research.

CHAPTER 2

LITERATURE REVIEW

<u>2.1 Air Quality Regulations</u>

2.1.1. Background

The 1990 amendments to the Clean Air Act (CAA) of 1970 renewed and intensified national efforts to reduce air pollution in the United States. The primary purposes of the actions mandated by the CAA were to improve public health, preserve property, and protect the environment (National Safety Council, 2006). The CAA identifies air pollutants and sets primary and secondary standards for each, called the National Ambient Air Quality Standards (NAAQS). The criteria air pollutants covered by the CAA are ozone (O_3), sulfur dioxide (SO_2), particulate matter (PM), lead (Pb), nitrogen oxides (NO_x), and carbon monoxide (CO). An area that meets or exceeds the National Ambient Air Quality Standards (NAAQS) is called an attainment area; an area that does not meet the primary standard is called a non-attainment area (National Safety Council, 2006; EPA: CAAA, 2006). Additionally, the Clean Air Act (CAA) requires EPA to regulate emissions of toxic air pollutants or hazardous air pollutants (HAPs) which are known to cause serious health and environmental effects. Due to the stringent air quality requirements by the regulations, many cities/regions are currently in violation of NAAQS (National Safety Council, 2006). Such a situation calls for intensive control measures for major as well as minor air pollutant sources.

Both wastewater treatment plants and municipal solid waste landfills are potential sources of volatile organic compounds (VOCs). Volatile organic compounds are precursors to ‘smog’, or troposheric ozone, which is known to be hazardous to human health and environment and it, also contributes to ‘haze’ along with particulate matter (EPA: “The Plain English Guide to Clean Air Act”, 2006). Beside the emissions of volatile organic compounds (VOCs), wastewater treatment and landfill facilities may potentially cause odors or toxicity to facility operators and downwind receptors. Hence it becomes imperative to develop effective control technology for such sources.

2.1.2. Air Quality Regulations and VOCs

As per EPA’s study, motor vehicles (mobile sources) are responsible for up to half of the smog-forming volatile organic compounds (VOCs) (EPA: The Plain English Guide to Clean Air Act, 2006). The balance is contributed by point sources such as chemical plants, cement manufacturers, steel mills, power plants, surface coating operations, printing operations and area sources such as wastewater treatment plants, municipal solid waste landfills, printing shops, auto body collision repair shops, gas stations, and indoor activities. VOCs emitted from wastewater treatment plant and solid waste landfills are of concern, as some of them are potential source of odors causing nuisance to the neighboring communities, and some of the VOCs are known toxics and detrimental to human health and the environment. VOCs are not directly regulated through National Ambient Air Quality Standards (NAAQS), but are indirectly regulated under ozone standards, and many are regulated as Hazardous Air Pollutants (HAPs).

2.1.3. Air Quality Regulations and Toxics

Toxic air contaminants (TACs), also known as hazardous air pollutants (HAPs), are regulated at both federal and state levels. Title III of 1990 CAAA establishes a list of 188 hazardous air pollutants. These include o-xylene, m-xylene, p-xylene, and carbonyl sulfide, which are being tested in this research. Title III specifically directs EPA to promulgate maximum achievable control technology (MACT) standards for publicly owned treatment works (POTWs) and municipal solid waste landfills.

2.1.4. Air Quality Regulations and Odors

CAAA of 1990 does not include regulations for odor-causing pollutants. However, an important odorous compound, carbonyl sulfide, is included the in list of 188 hazardous air pollutants established by CAAA. Even though the regulations so far have not addressed the nuisance of odorous air pollutants, it is still a grave problem associated with wastewater treatment plants and municipal solid waste landfills and needs to be addressed by facility planners, designers, engineers and operators.

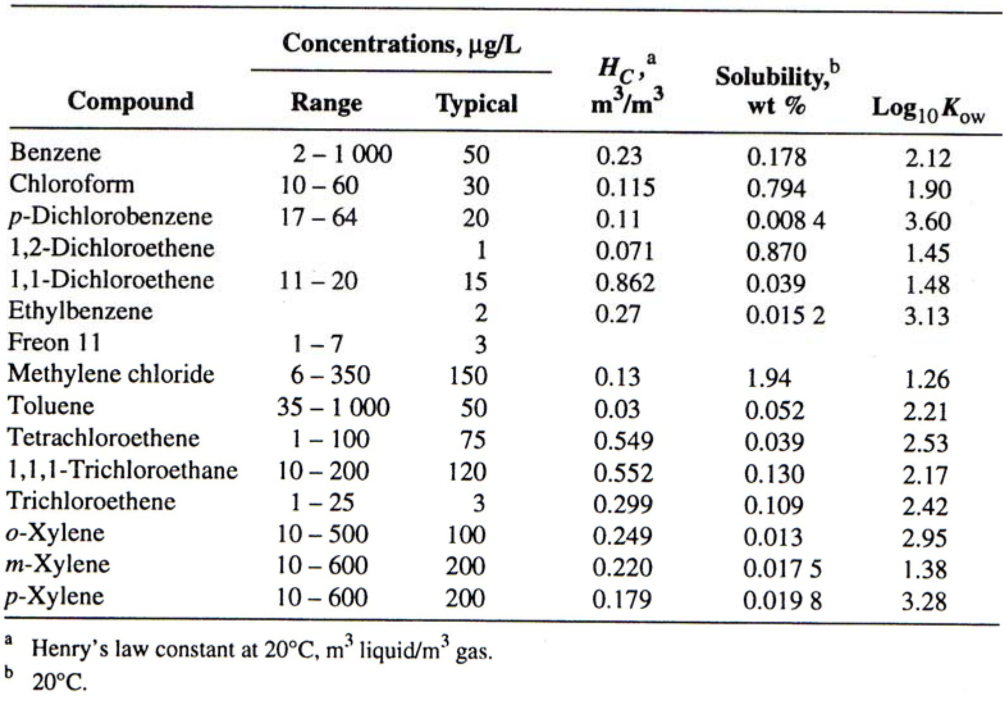
2.2 Emissions from Wastewater Treatment Plants and Municipal Solid Waste Landfills

2.2.1. Emissions – Wastewater Treatment Plants

Emissions can occur through diffusive or convective mechanisms, or both. Diffusion occurs when organic concentrations at the water surface are much higher than ambient concentrations. The organics volatilize or diffuse into the air in an attempt to reach equilibrium between aqueous and vapor phases. Convection occurs when air flows over the water surface, thereby sweeping organic vapors from the surface into the air. Some of the emissions are due to turbulence. The rate of volatilization is directly related to the speed of the airflow over the water surface. At the intake end of the treatment plant, the wastewater stream is turbulent and open to air; this condition leads to a lot of rapid volatilization of the pollutants. The rate of volatilization is directly related to the speed of the airflow over the water surface (EPA: AP 42, Wastewater Collection Systems, Treatment and Storage, 1998).

Other factors that can affect the rate of volatilization include wastewater surface area, temperature, and turbulence; wastewater retention time in the system(s); the depth of the wastewater in the system(s); the concentration of organic compounds in the waste water and their physical properties, such as volatility and diffusivity in water; the presence of a mechanism that inhibits volatilization, such as an oil film; or a competing mechanism, such as biodegradation (EPA: AP42, Wastewater Collection Systems, Treatment and Storage, 1998). Table 2.1 lists the VOCs, Table 2.2 lists the odorous compounds and Table 2.3 lists the HAPs emitted by wastewater treatment plants.

Table 2.1 Volatile Organic Compounds Found in Municipal Wastewater (ASCE, 1995)



Compound	Concentrations, μg/L		H_C,[a] m^3/m^3	Solubility,[b] wt %	$Log_{10} K_{ow}$
	Range	Typical			
Benzene	2 – 1 000	50	0.23	0.178	2.12
Chloroform	10 – 60	30	0.115	0.794	1.90
p-Dichlorobenzene	17 – 64	20	0.11	0.008 4	3.60
1,2-Dichloroethene		1	0.071	0.870	1.45
1,1-Dichloroethene	11 – 20	15	0.862	0.039	1.48
Ethylbenzene		2	0.27	0.015 2	3.13
Freon 11	1 – 7	3			
Methylene chloride	6 – 350	150	0.13	1.94	1.26
Toluene	35 – 1 000	50	0.03	0.052	2.21
Tetrachloroethene	1 – 100	75	0.549	0.039	2.53
1,1,1-Trichloroethane	10 – 200	120	0.552	0.130	2.17
Trichloroethene	1 – 25	3	0.299	0.109	2.42
o-Xylene	10 – 500	100	0.249	0.013	2.95
m-Xylene	10 – 600	200	0.220	0.017 5	1.38
p-Xylene	10 – 600	200	0.179	0.019 8	3.28

[a] Henry's law constant at 20°C, m^3 liquid/m^3 gas.

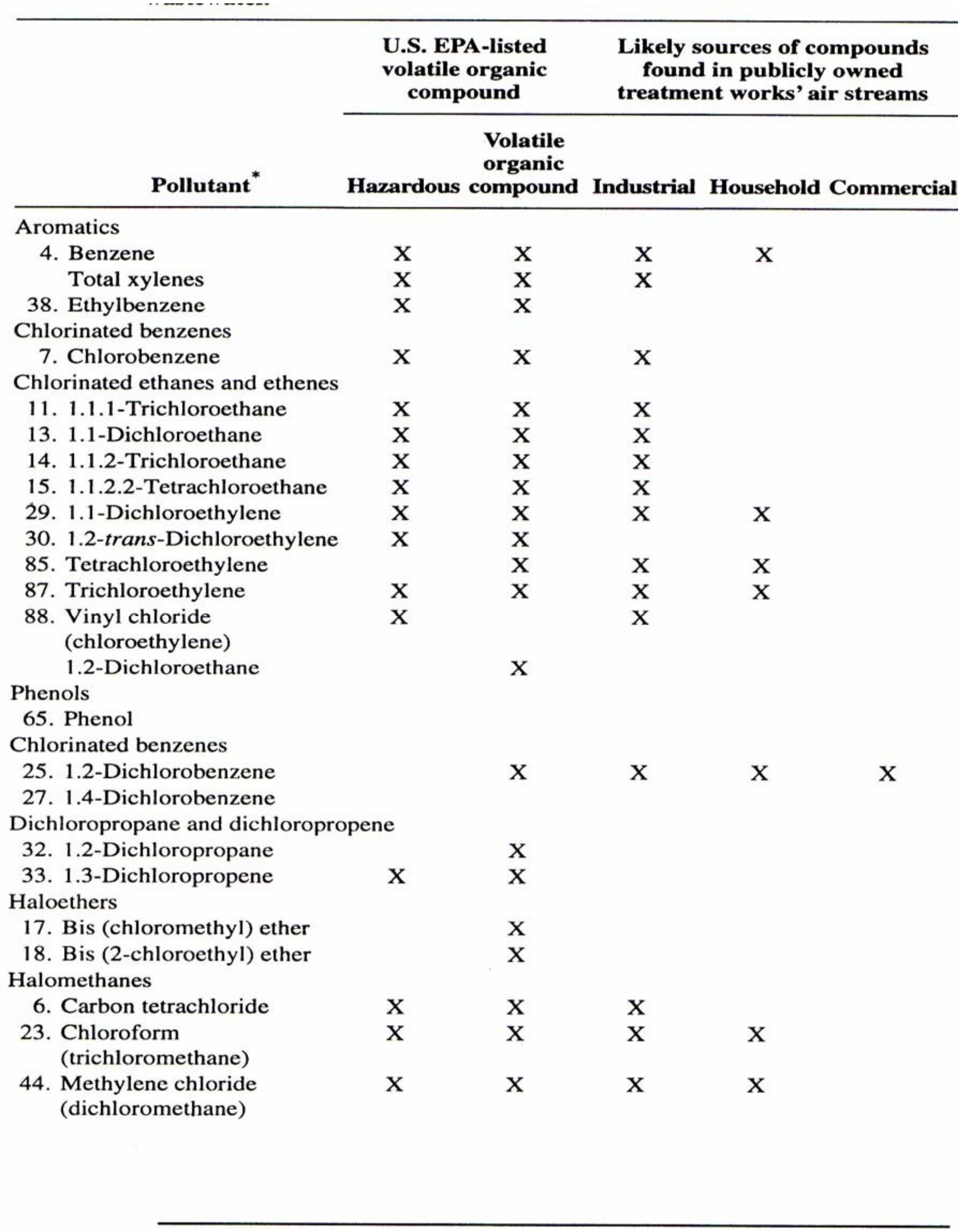
[b] 20°C.

Table 2.2 Odorous Emissions from Wastewater Plants (Water Environment Federation, 1995)

Compound name	Formula	Molecular weight	Volatility at 25 °C, ppm (v/v)	Detection threshold, ppm (v/v)	Recognition threshold, ppm (v/v)	Odor description
Acetaldehyde	CH_3CHO	44	Gas	0.067	0.21	Pungent, fruity
Allyl mercaptan	$CH_2{:}CHCH_2SH$	74		0.000 1	0.001 5	Disagreeable, garlic
Ammonia	NH_3	17	Gas	17	37	Pungent, irritating
Amyl mercaptan	$CH_3(CH_2)_4SH$	104		0.000 3	—	Unpleasant, putrid
Benzyl mercaptan	$C_6H_5CH_2SH$	124		0.000 2	0.002 6	Unpleasant, strong
n-Butyl amine	$CH_3(CH_2)NH_2$	73	93 000	0.080	1.8	Sour, ammonia
Chlorine	Cl_2	71	Gas	0.080	0.31	Pungent, suffocating
Dibutyl amine	$(C_4H_9)_2NH$	129	8 000	0.016	—	Fishy
Diisopropyl amine	$(C_3H_7)_2NH$	101		0.13	0.38	Fishy
Dimethyl amine	$(CH_3)_2NH$	45	Gas	0.34	—	Putrid, fishy
Dimethyl sulfide	$(CH_3)_2S$	62	830 000	0.001	0.001	Decayed cabbage
Diphenyl sulfide	$(C_6H_5)_2S$	186	100	0.000 1	0.002 1	Unpleasant
Ethyl amine	$C_2H_5NH_2$	45	Gas	0.27	1.7	Ammonialike
Ethyl mercaptan	C_2H_5SH	62	710 000	0.000 3	0.001	Decayed cabbage
Hydrogen sulfide	H_2S	34	Gas	0.000 5	0.004 7	Rotten eggs
Indole	$C_6H_4(CH)_2NH$	117	360	0.000 1	—	Fecal, nauseating
Methyl amine	CH_3NH_2	31	Gas	4.7	—	Putrid, fishy
Methyl mercaptan	CH_3SH	48	Gas	0.000 5	0.001 0	Rotten cabbage
Ozone	O_3	48	Gas	0.5	—	Pungent, irritating
Phenyl mercaptan	C_6H_5SH	110	2 000	0.000 3	0.001 5	Putrid, garlic
Propyl mercaptan	C_3H_7SH	76	220 000	0.000 5	0.020	Unpleasant
Pyridine	C_5H_5N	79	27 000	0.66	0.74	Pungent, irritating
Skatole	C_9H_9N	131	200	0.001	0.050	Fecal, nauseating
Sulfur dioxide	SO_2	64	Gas	2.7	4.4	Pungent, irritating
Thiocresol	$CH_3C_6H_4SH$	124		0.000 1	—	Skunky, irritating
Trimethyl amine	$(CH_3)_3N$	59	Gas	0.000 4	—	Pungent, fishy

[a] It should be noted that different sources report a range of values for odor detection or recognition thresholds, particularly for compounds such as hydrogen sulfide or ammonia. The range of values used for hydrogen sulfide generally varies from 0.47 to 9 ppb. Odor thresholds mentioned in this manual may vary and are not intended to be definitive because of the lack of agreement among experts. The odor thresholds are included to give the reader a sense of what odor levels are potentially an issue relative to the particular chapter of this manual in which they are included.

Table 2.3 Air Toxics in Wastewater (Water Environment Federation, 2004)



	U.S. EPA-listed volatile organic compound		Likely sources of compounds found in publicly owned treatment works' air streams		
Pollutant*	Hazardous	Volatile organic compound	Industrial	Household	Commercial
Aromatics					
4. Benzene	X	X	X	X	
Total xylenes	X	X	X		
38. Ethylbenzene	X	X			
Chlorinated benzenes					
7. Chlorobenzene	X	X	X		
Chlorinated ethanes and ethenes					
11. 1.1.1-Trichloroethane	X	X	X		
13. 1.1-Dichloroethane	X	X	X		
14. 1.1.2-Trichloroethane	X	X	X		
15. 1.1.2.2-Tetrachloroethane	X	X	X		
29. 1.1-Dichloroethylene	X	X	X	X	
30. 1.2-*trans*-Dichloroethylene	X	X			
85. Tetrachloroethylene		X	X	X	
87. Trichloroethylene	X	X	X	X	
88. Vinyl chloride (chloroethylene)	X		X		
1.2-Dichloroethane		X			
Phenols					
65. Phenol					
Chlorinated benzenes					
25. 1.2-Dichlorobenzene		X	X	X	X
27. 1.4-Dichlorobenzene					
Dichloropropane and dichloropropene					
32. 1.2-Dichloropropane		X			
33. 1.3-Dichloropropene	X	X			
Haloethers					
17. Bis (chloromethyl) ether		X			
18. Bis (2-chloroethyl) ether		X			
Halomethanes					
6. Carbon tetrachloride	X	X	X		
23. Chloroform (trichloromethane)	X	X	X	X	
44. Methylene chloride (dichloromethane)	X	X	X	X	

2.2.2. Emissions – Municipal Solid Waste Landfills

Municipal solid waste (MSW) landfills typically generate significant volumes of various gases during their active life and for a period of time after closure. Most of the gas generated is methane and carbon dioxide, with smaller amounts of volatile organic compounds (VOCs). The gas is emitted into the atmosphere and can travel long distances in the soil. Landfill gases, VOCs in particular, contribute to air pollution and the formation of ground-level ozone. Methane, a colorless and odorless gas, is highly explosive at a concentration of 5% to 15% in air and can accumulate to dangerous levels virtually undetected. Although methane is not highly reactive in terms of ozone formation, it is a significant greenhouse gas. Therefore, at municipal solid waste landfills it is necessary to control the landfill gas for either safety reasons or to abate air pollution.

Along with methane and carbon dioxide, certain other gases too are emitted in trace amounts, as indicated in Table 2.4 and 2.5.

Table 2.4: Typical Constituents Found in Municipal Solid Waste Landfill Gas (Tchobanoglous, 1993)

Component	Percent (dry volume basis)
Methane	40-60%
Carbon Dioxide	40-60%
Nitrogen	2-5%
Oxygen	0.1-1.0%
Ammonia	0.1-1.0%
Sulfides, disulfides, mercaptans,etc.	0-0.2%
Hydrogen	0-0.2%
Carbon Monoxide	0-0.2%
Trace Constituents	0.01-0.6%

Table 2.5: Typical Concentrations of Some Trace Compounds Found in Landfill Gas (Wilcos and W.Clister, 1996)

Component	Mean Concentration (in ppb by volume)
Toluene	34,907
Dichloromethane	25,694
Ethyl Benzene	7,334
Acetone	6,838
Vinyl Acetate	5,663
Tetrachloroethylene	5,244
Vinyl Chloride	3,508
Methyl Ethyl Ketone	3,092
Xylenes	2,651
1,1- Dichloroethane	2,801
Trichloroethylene	2,079
Benzene	2,057

2.2.3. Selection of Compounds for This Study

The objective of this study was to determine the effectiveness of photocatalytic oxidation technique to destroy VOCs, toxics and odors emitted by wastewater treatment plants and municipal landfills. Beside the cost and availability of the compounds, there were other factors that affected the selection of the compounds to be tested.

According to the information presented in Table 2.1, of all the VOCs emitted from the wastewater treatment plants, xylenes are present in the highest concentration in wastewater. Table 2.3 shows that xylenes are hazardous VOCs emitted by wastewater treatment plants. Xylenes are also emitted by landfills, although in small amounts as trace gas, according to Table 2.5. Moreover, the literature review done for this study indicated that not much research has been done to treat xylenes in the air stream via photocatalytic oxidation. The only previous study of xylenes in air tested initial concentration of 14-22 ppb, typical of indoor air, and much lower than concentrations released from wastewater treatment plants or landfills (Disdier et al., 2005). Hence, all three xylenes are selected for this study.

Carbonyl sulfide is known odor sources in air emissions from wastewater treatment plants. Methane is a prime component of landfill gas. It comprises about 50% (by dry volume) of the total landfill emissions according to the Table 2.4. As discussed in an earlier section, methane is undetectable and highly explosive at small concentrations, hence it poses a danger to the operators of the plant and public residing near the landfill site. Hence its control is necessary, thus methane was selected for this study.

All the selected compounds were tested with their concentration equivalent to the concentrations at which they are emitted. The Table 2.6 lists the selected compounds and the concentration at which they were tested. During the experiments, the initial concentration varied slightly from the listed values since it was difficult to inject exact the same concentration in the photocatalytic oxidation system for every experimental run. In some cases, the initial concentration had to be increased slightly due to sensor limitations.

Table 2.6 Selected Compounds and Respective Concentrations

Compounds	Concentration (ppm)
O-Xylene	100
M-Xylene	200
P-Xylene	200
Carbonyl Sulfide	30
Hydrogen Sulfide	30
Methane	300,000

2.3 Comparison of Various Control Technologies

2.3.1. Background – Control Technologies

Control of gaseous pollutants can be carried out in several ways. The first consideration would be elimination of the source of pollution; however, this is not possible in all cases and hence end of the pipe control measure are required. Commonly applied technologies for treating gaseous pollutants are:

- Absorption towers
- Adsorption beds
- Incineration
- Condensation

Relatively newer technologies for the control of gaseous pollutants are:

- Biofiltration

- Photocatalytic oxidation

A brief discussion of each technology, its applications, advantages and disadvantages follows. Information presented below has been adapted from EPA: Air Pollutants and Control Techniques, 2006; EPA: MACT, and Meridian Engineering and Technology, 1997.

2.3.2. Absorption

In absorption processes, gaseous contaminants are removed from a gas stream by transferring them to a liquid. That liquid is usually water or an aqueous solution that contains chemicals selected to react with the absorbed contaminants.

➢ **Application**

- Used for compounds with high solubility.

➢ **Advantages**

- Few internal moving parts, lower maintenance.
- Fuel ignition as in incineration not required, hence no fuel cost.
- Can recover contaminant for reuse.

➢ **Disadvantages**

- Applicability limited to compounds with higher solubility.
- High pressure drops required.
- Internal plugging, corrosion, erosion problems.
- Increased need for internal inspection.
- Formation / precipitation of solids.

The major drawback of this system is that the pollutants are not destroyed, but rather transferred from the gas phase to the liquid the phase. Further treatment of the absorbing media is required.

2.3.3. Adsorption

In adsorption processes, gaseous contaminants are removed from a gas stream by transferring them to the surface of a solid adsorbent. These adsorbent materials include silica gel, activated alumina, molecular sieves, polymers and activated carbon. The most common material for the adsorption of organic pollutants is activated carbon. A typical adsorption system is show in Figure 2.1.

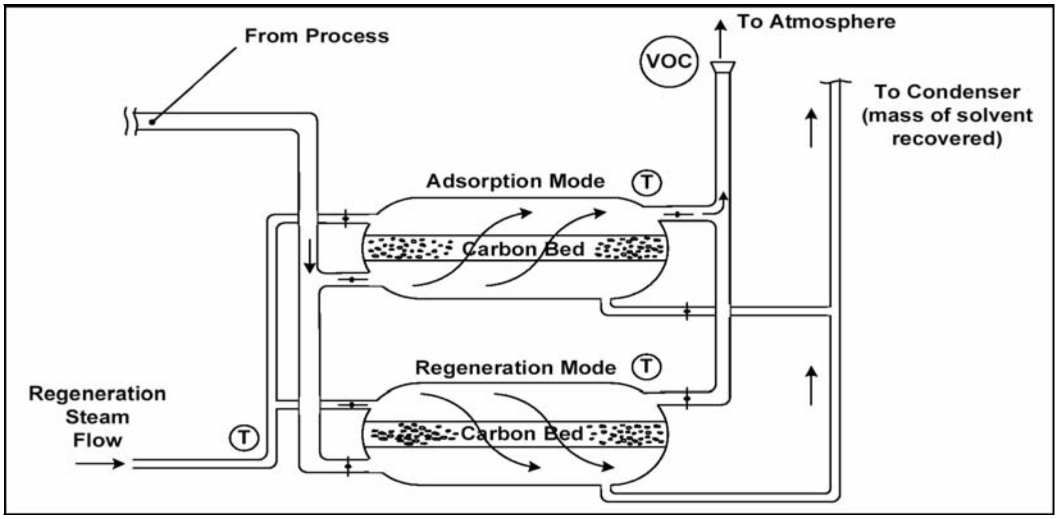


Figure 2.1 Adsorption System (EPA).

- **Application**

- Limited to VOCs having a molecular weight between 50 and 200 (EPA: Air Pollutants and Control Techniques, 2006).

- Can be used for a wide range of VOC concentrations from less than 10 ppm to approximately 10,000 ppm (EPA: Air Pollutants and Control Techniques, 2006).

➢ **Advantages**

- Can recover contaminant for reuse.
- Normal operation at ambient temperature.

➢ **Disadvantages**

- May require multiple units; one in service, one in recycle mode.
- Bed material (activated carbon) regeneration required from time to time.
- Higher moisture content can reduce efficiency.

The major disadvantage of this system is that the pollutants are not destroyed, but rather transferred from the gas phase to the solid phase. Regeneration of the adsorption bed is required at regular intervals.

2.3.4. Incineration

In vapor incineration processes, organic contaminants are removed from a gas stream by oxidizing them to other compounds. If the organic compounds are composed of carbon and hydrogen, then the products of that oxidation are carbon dioxide and water vapor. However, if the organic materials contain chlorine, fluorine or sulfur, then hydrochloric acid vapor, hydrofluoric acid vapor, sulfur dioxide, or other compounds may be formed. Figure 2.2 shows a typical incineration system.

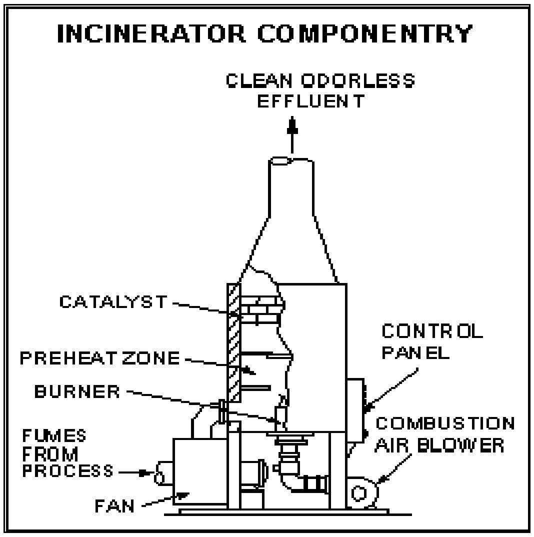


Figure 2.2 Incinerator System (Meridian Engineering and Technology, 1997)

- **Application**

- Broadest applicability of all the VOC control devices.
- Used for almost any VOC compound.
- Can be used for gas streams having VOC concentrations at the very low concentration range of less than 10 ppm up to the very high concentrations approaching 10,000 ppm (EPA: Air Pollutants and Control Techniques, 2006).

- **Advantages**

- High destruction efficiencies possible.
- Complete destruction of pollutants possible, hence no post treatment required.

- **Disadvantages**

- High cost of supplementary fuel.
- High temperatures require good thermal loss control.
- Hot surfaces, flashback, and explosive conditions.

2.3.5. Condensation

In condensation processes, gaseous contaminants are removed from a gas stream by causing them to change to a liquid. In general, this can be accomplished by increasing the pressure or reducing the temperature or by a combination of both. However, because of the cost of operating and maintaining compression equipment, most condensers for air pollution control use temperature reduction.

- **Application**

- Used for gas streams those contain only VOC compounds.
- Used for high concentration, low gas flow rate sources.

- **Advantages**

- High efficiencies possible.
- Direct contact condensers are relatively simple in operation and low in cost.

- **Disadvantages**

- Increases the wastewater treatment or recovery cost.
- Cost of refrigeration is high.
- Cost of refrigeration increases if the inlet air temperature is high.

2.3.6. Biofiltration

Biofiltration is a relatively new pollution control technology. It is an effective technique for the elimination of malodorous gas emissions and of low concentrations of volatile organic compounds (VOCs). Biological purification of gases involves passing the gas through a filter medium on which micro-organisms have been implanted. Gases are treated by biodegradation, sorption and filtration.

- **Application**

- Used primarily for very low concentration VOC-laden streams.
- Not useful for toxic pollutant streams.
- Not applicable for air streams at very high temperatures.

- **Advantages**

- Low capital and operating costs.
- Low energy requirements.
- Absence of byproducts or end products requiring further treatment or disposal.

- **Disadvantages**

- The microbial process can be upset, resulting in periods of lower performance so that there is lower reliability.
- Cannot handle high VOC concentrations or high flow rates.
- Cannot be used with toxics, as they can adversely affect the microbial performance.

2.4 Photocatalytic Oxidation

2.4.1. Introduction

Photocatalytic oxidation is a relatively new technology which shows promise for economically controlling HAPs and VOCs from smaller sources such as wastewater treatment plants, dry-cleaning facilities, painting facilities, carbon regeneration plants, air stripping towers, soil venting processes, hazardous waste incinerators, and municipal landfills (Sattler, 2003). Further discussion regarding the mechanism of photocatalysis and VOC removal, photocatalytic rate constant derivation, applications, advantages and limitations of the technique are discussed in the following section. Figure 2.3 shows commercially available photocatalytic oxidation system.

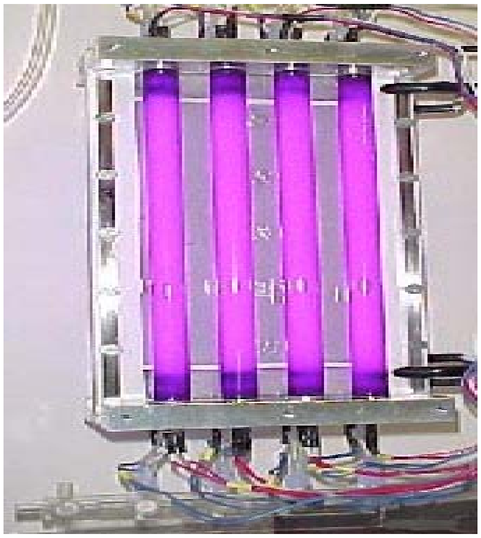


Figure 2.3 Photocatalytic Oxidation System (Lynntech, Inc.)

2.4.2. Mechanism of TiO_2 Photocatalysis and VOC removal

2.4.2.1. Reaction Mechanism

Photocatalytic oxidation utilizes ultraviolet or near-ultraviolet (< 385 nm) radiation to promote electrons from the valence band into the conduction band of a titanium dioxide semiconductor. Destruction of organic compounds takes place through reactions with molecular oxygen or through reactions with hydroxyl radicals and super-oxide ions formed after the initial production of highly reactive electron and hole pairs. The oxidation reaction with VOCs is heterogeneous catalysis, commonly referred to as photocatalytic oxidation (Stevens, et al., 1998).

The activation of TiO_2 by UV light can be written as:

$$\mathrm{TiO2} + h\upsilon \rightarrow h^{+} + e^{-} \tag{2.1}$$

When water is present in the air stream, it adsorbs onto the catalyst and its dissociation can be written as:

$$H_2O \leftrightarrow H^{+} + OH^{-} \tag{2.2}$$

The formation of the OH° can be written as:

$$OH^{-} + h^{+} \rightarrow OH^{\circ} \tag{2.3}$$

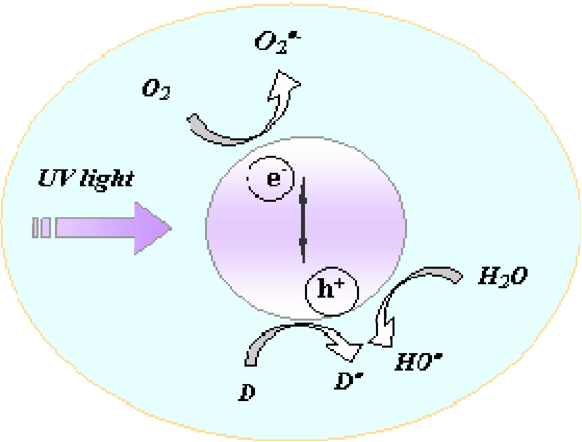


Figure 2.4 Photocatalysis (http://www.ntu.edu.sg/cwp/pco/)

The process generates hydroxyl radicals (OH°), which are very reactive free radicals and strong oxidants that degrade volatile organic compounds. Under proper conditions, organic contaminants in an air stream can be mineralized to CO_2 and water (Lynntech Products, Sattler and Liljestrand, 2003).

The overall photocatalytic oxidation reaction can be written as:

$OH^{\circ} + VOC + O_2 \rightarrow$ Products (CO_2, H_2O, byproducts in case of incomplete oxidation) (Zhao and Yang, 2002).

2.4.2.2. Photocatalyst

Several semiconductors and materials have band-gap energies sufficient for promoting photocatalytic activities. A few examples include WO_3, Fe_2O_3, $SrTiO_3$, ZnO, ZnS. However, TiO_2 is the most effective and widely used photocatalyst (Lynntech Products). Its superior characteristics include:

- Inexpensive, safe and very stable, showing high photocatalytic efficiency (Zhao and Yang, 2002; Zorn, 2003).
- It promotes ambient temperature oxidation of the major classes of indoor air pollutants (Zhao and Yang, 2002).
- Complete degradation of a broad range of pollutants can be achieved under certain operating conditions (Zhao and Yang, 2002, Sun et al., 2005).
- No chemical additives required (Zhao and Yang, 2002).
- Corrosion resistant (Zorn, 2003).

2.4.2.3. Reaction Rate and Influencing Factors

The reaction rate of PCO is a very important kinetic factor because it represents the efficiency of the photo-oxidation process. Theoretically, the reaction rate can be simply expressed as the decreasing rate of any reactant or the increasing rate of the products. In the unimolecular decomposition reaction,

$$A \rightarrow B + C$$

$$\text{Rate of reaction} = -d\,[A]/dt = d\,[B]/dt = d\,[C]/dt$$

Reaction rate can be expressed by the use of power law:

$$\text{Rate of reaction} = -d\,[A]/dt = k[A]^n$$

where, [A] = concentration of A, k = rate constant and n = order of the reaction.

Previous researches (Disdier et al., 2005) suggest that generally a first order reaction is applicable to photocatalytic oxidation systems.

In a first order reaction, the reaction rate depends on the concentration of the reactants and the rate constant has the unit of 1/time. The general form is:

Rate of reaction = $-d[A]/dt = k[A]$

Variable separation and integration would result in:

$[A] / [A]_0 = \exp(-kt)$

where, $[A]_0$ = initial concentration of A. (Metcalf & Eddy, 2003; Zhao and Yang, 2002).

Data of [A] vs. time can be fit in the reaction to arrive at the value of the reaction rate constant.

The photocatalytic destruction rate depends on numerous factors:

- Temperature
- Light intensity
- Reactor configuration
- Catalyst
- Humidity
- Oxygen concentration
- Contaminant concentration

(Sattler and Liljestrand, 2003, Zhao and Yang, 2002)

2.4.3. Applications

Photocatalytic oxidation has wide range of applications. Some of its applications are listed below:

- Portable indoor air cleaners for indoor gaseous pollutant removal (Stevens et al., 1998; Disdier et al., 2005).
- Preparation of high purity water for medical applications (Lynntech, Inc.).
- Detoxification of drinking water (Lynntech, Inc.).
- Preparation of high purity industrial water for electronics manufactures (Lynntech, Inc.).
- Polishing waste water effluent stream, PCO is effective in removal of BOD, COD, TOC, taste and odor components (Gogate and Pandit, 2003).
- TiO_2 application on window panes turn them to self cleaning panes, on bulbs and tube lights can help treat indoor air, on roadways and sidewalks can help reduce VOCs.

Research so far has shown that the scope of applications of PCO is immense. PCO technique is used equally and successfully for both water and air purifications and for indoor and outdoor air quality.

2.4.4. Advantages

In comparison with other techniques for gaseous pollutant removal from an air stream, PCO has numerous advantages, which are listed as:

- There is no consumption of expensive oxidizing chemicals; the oxidant is atmospheric oxygen and the catalyst is non-hazardous (IUPAC, 1992).

- The light required to activate the catalyst may be long wavelength UV transmitted by glass (IUPAC, 1992).
- The photocatalytic reaction may be driven by the natural UV component of sunlight (IUPAC, 1992).
- High destruction efficiencies at room temperature.
- No chemical additives, such as auxiliary fuel, are required.
- High quantum yields for gas phase reactants (low-intensity UV lamps).
- Complete oxidation of organics to CO_2 and H_2O is possible.
- Inexpensive catalyst (titanium dioxide).
- Applicable to a large number of organics.
- Effective for low concentrations of pollutants.
- Works in humid conditions.
- Activity of catalyst not destroyed by chlorinated organics.

The wide range of applications and numerous advantages of the PCO process is a convincing reason to carry out further research and assess its applicability to the treatment of emissions from the wastewater treatment plant and landfills.

2.5 Literature Review

Many studies have been conducted using photocatalytic oxidation to destroy VOCs, focusing on various parameters. Also, these researches apply photocatalytic oxidation process to numerous applications. A number of ongoing and previous researches are listed in Table 2.7, which aim to measure photocatalytic destruction rates and consider various factors affecting the rates. The studies are then discussed in greater detail at the end of the chapter.

Table 2.7 Literature Review

	Author	**Agency**	**Application**	**Parameter(s) measured**	**Result**
1	Sattler, M; Liljestrand, H.	University of Texas, Arlington and University of Texas, Austin, 2003.	To establish a relation between the PCO rate constants and physical-chemical characteristics of compounds.	PCO rate constants of alkanes and alkenes in air stream.	PCO rates constants of alkanes and alkenes vary linearly with ionization potential and with OH^{o} reaction rate constant for each class of compounds.
2	Sun, Liu, et al.	Nanyang Technological University, Singapore, 2005.	Purification of water and saline water.	PCO rate constants of o-xylene in water and saline water.	Removal efficiency of o-xylene in water and saline water at 50 min. retention time were 87% and 91%, respectively.

Table 2.7 - continued

3	Stevens, Lannings, et al.	University of Colorado at Denver and NREL, 1998.	Indoor air purification.	PCO destruction of carbonyl compounds in indoor air.	100% destruction of the carbonyl compounds.
4	Zorn, M.	University of Wisconsin, Green Bay, 2003.	Space shuttle cabins and space centre indoor air purification.	PCO destruction rates for multiple reactive compound system containing, propane, propene, acetone and propanal.	The relative time required for degradation of the compounds was directly dependent upon the predicted affinity for the catalyst surface.

Table 2.7 - continued

5	Zuo, et al.	Institute of Chemical Defence, Beijing, China, 2005.	Comparative study between destruction rates of photocatalysis (UV and TiO_2) and photolysis (only UV) for aromatics and chlorohydrocarbons in air.	Photocatalytic and photolytic destruction rates for trichloroethylene, dichloromethane, chloroform, toluene, benzene and carbon tetrachloride.	Chlorocarbons except for carbon tetrachloride could be degraded through either photolysis or photocatalysis. Elimination of chlorohydrocarbons through photolysis was quicker than photocatalysis. Aromatics were degraded faster by photocatalysis.

Table 2.7 - continued

6	Kim, et al.	Korea University and Kyonggi University, South Korea, 2001	Examination of kinetics of photocatalytic degradation of VOCs in air stream.	PCO destruction rates for trichloroethylene, acetone, methanol and toluene. Variable parameters were initial concentration, humidity and photon flux.	PCO degradation rate increased with increase in initial concentration up to a point and then remained constant. There was an optimum concentration of humidity for TCE and methanol. Humidity enhanced the degradation of toluene and inhibited that of acetone. Photocatalytic oxidation occurs in two regimes with respect to photon flux.

Table 2.7 - continued

7	Zhao, et al.	University of Miami, Florida, 2003.	Indoor air purification.	Through kinetic experiments, the dependence of reaction rate on moisture, light intensity and initial contaminant concentration are found.	Influence of water vapor is different on the degradation rates of different compounds. Destruction rate constant increases with increase in initial contaminant concentration and then remains constant (decreases for some compounds). Destruction rate improved with increase in UV intensity.

Table 2.7 - continued

8	Gogate and Pandit.	Mumbai University Institute of Chemical Technology, India, 2003.	Wastewater effluent polishing (getting rid of microorganisms).	Comparing destruction efficiencies of	Photocatalytic oxidation found to be the most suitable and efficient method among all the method researched.
9	Turchi, et al.	SEMATECH, 1995.	Treating VOC emissions from semiconductor plant.	PCO destruction rates for isopropanol, acetone and methanol.	Greater than 95% of destruction of contaminants to carbon dioxide and water.

2.5.1. Method for Predicting Photocatalytic Oxidation Rates of Organic Compounds

In designing a PCO system for a given air pollution source, destruction rates for VOCs are required. This research deals with development of a systematic method to predict PCO rate constants by correlating them with physical chemical characteristics of the pollutants. Tests were carried out in the presence of Degussa's P-25 grade TiO_2 and UV source at a wavelength of 366nm. A correlation was proposed between PCO rates and ionization potential (IP) of the compounds. Ionization potential was chosen as a measure of compound structure likely to correlate with PCO rate constants because IP has been shown to correlate with gas phase OH^o reaction rate constants (k_{OH}) and PCO proceeds primarily via OH^o attack (in presence of moisture in the air stream). The research demonstrated that PCO rate constants of alkanes and alkenes vary linearly with IP and with OH^o reaction rate constant for each class of compounds. The correlations allow the rates of destruction of compounds not tested in this research to be predicted based on physical chemical characteristics.

2.5.2. Photocatalytic Degradation of O-Xylene in Water

This study researched the possibility of utilizing PCO technique as pretreatment for the removal of oil compounds prior to membrane processes. O-xylene as a model oil pollutant was selected for this investigation. An UV bubble reactor was developed for the PCO process using suspended TiO_2 catalyst. It was found from the experiments that the PCO reactor system could effectively degrade the o-xylene in both fresh water and saline water. The removal efficiency at HRT 50 min. in water and saline water was 87% and 91%, respectively. The experiments came up with interesting results: it was discovered that the pH and temperature did not have much influence on PCO degradation of o-xylene in water. However, dissolved oxygen (DO) played an important role on PCO degradation of o-xylene. The degradation was almost quenched in the absence of DO, but increased with the increase of DO, then almost kept constant when the partial pressure of oxygen (P_{O2}) was beyond 0.8 atm.

2.5.3. Investigation of the Photocatalytic Oxidation of Low-Level Carbonyl Compounds

This paper does some interesting work in applying the PCO technique to treat very low concentration of VOCs, in the range of parts per billions (ppb), since that is more typical to indoor air quality issues. The research also examines operational characteristics of four PCO reactor designs: coated wall annular, packed bed annular, box and flat bed. The researchers examined destruction of formaldehyde, acetaldehyde and acetone. Intrinsic photocatalytic reaction rates could not be calculated for this project because of the nearly complete conversion of carbonyl compounds. The results demonstrated that the destruction of low molecular weight carbonyl compounds at concentrations associated with indoor air quality issues is nearly 100% using the PCO technique. Additionally, they concluded that the destruction of carbonyl compounds was independent of reactor design, residence time (flow rate), and light intensity, and the box reactor shows the greatest destruction efficiency for TCE. These results contradict the finding of the other studies which show that reaction rate constant depends on the light intensity and the reactor configuration. It also contradicts the fact that the extent of destruction of compounds is dependent on the residence time. Thus further investigation is required to determine the relationship between the reaction rate constant and photocatalytic system parameters.

2.5.4. Photocatalytic Oxidation of Gas-Phase Compounds in Confined Areas: Investigation of Multiple Component Systems

The results suggests that the presence of the four compounds in a single test environment would result in a competitive disadvantage for the slower reacting compounds (i.e., propane and propene) and a competitive advantage for the faster reacting compounds (i.e., acetone and propanol).

2.5.5. Study on Photocatalytic Degradation of Several Volatile Organic Compounds

This study focuses on comparison of two different VOC removal technologies, photolysis and photocatalysis. It was found that chlorohydrocarbons can be effectively degraded by photolysis and aromatics are degraded better by photocatalysis.

2.5.6. Kinetic Study for Photocatalytic Degradation of Volatile Organic Compounds in Air Using Thin Film TiO_2 Photocatalyst

This study states that photocatalytic destruction rate increases with UV light intensity, and increases with increasing initial concentration of VOCs but is maintained almost constant beyond a certain concentration. The presence of water vapor enhances the degradation rate of toluene, whereas it inhibited that of acetone. Sattler and Liljestrand (2003) found that the rate constant increased as the initial concentration decreased. Hence, further investigation is required to ascertain the relationship between the initial concentration of the compound and its photocatalytic reaction rate constant.

2.5.7. Photocatalytic Oxidation for Indoor Air Purification: A Literature Review

This research reviews work done in past to determine the dependence of reaction rate on some key influencing factors (moisture, light intensity and initial contaminant concentration). Their findings include: influence of water vapor is different on the degradation rates of different compounds, destruction rate constant increases with increase in initial contaminant concentration and then remains constant or decreases, and destruction rate improved with increase in UV light intensity.

2.5.8. A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions

Comparisons of the techniques of cavitation, photocatalytic oxidation, ozonation, Fenton's chemistry and use of hydrogen peroxide suggest that photocatalytic oxidation is the best technology for polishing of wastewater effluent (removal of microorganisms).

2.5.9. Destruction of VOC Emissions by Photocatalytic Oxidation (PCO)

The research shows that photocatalytic oxidation is effective for treatment of air emissions from a semiconductor plant, which include isopropanol, acetone and methanol. The paper also proposes the optimization of the process and its cost analysis.

2.6 Research Objectives

The literature review shows that photocatalytic oxidation is a promising technique to treat VOC laden air streams. However, there is not much research done for the applications to treat HAPs and odors. Also, the literature reviews shows that there is still uncertainty about the effect of factors such as temperature, humidity and initial concentration on the reaction rate constant. This research thus aims to test photocatalytic oxidation for HAPs, odors, and VOCs originating from wastewater treatment plants and landfills by determining the photocatalytic oxidation reaction rate constants for each compound listed in the earlier chapter.

CHAPTER 3

INTRODUCTION

3.1 Experimental Apparatus

This section describes the experimental apparatus, including photocatalytic oxidation system, photocatalyst, gas chromatographs, sensors and chemicals used in this research. The experimental setup and procedure were similar to the research done by Sattler and Liljestrand; hence, the following discussion is adapted from their work.

3.1.1. Photocatalytic Oxidation System

The photocatalytic oxidation system was a closed loop batch reactor comprised of a photocatalytic oxidation reactor, a pump, a DC supply double output system, injection/sampling port and Teflon tubing. Figures 3.1 and 3.2 show the layout of the system.

A glass column, 30 cm in length and 3 cm in diameter, placed horizontally served as the photocatalytic oxidation chamber, as shown in Figures 3.3 and 3.4. A 2.5x30 cm titanium dioxide-coated glass plate described in the following section was placed in the column. However, only 23.6 cm of the length of the slide were directly exposed to the light due to the fact that the transparent portion of the chamber was only 23.6 cm.

A lamp with two 15 watt cylindrical bulbs (NIS F15 T8BLB 15W black light blue), 2.6 cm in diameter set 2.6 cm apart, was set at 4.35 cm above the glass slide.

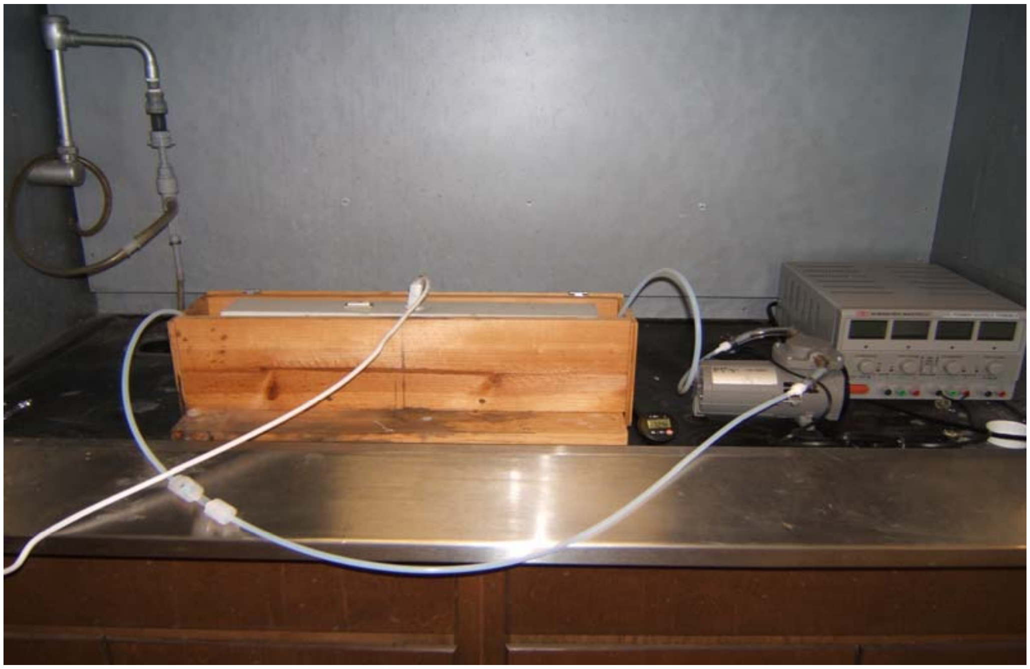


Figure 3.1 Photocatalytic System

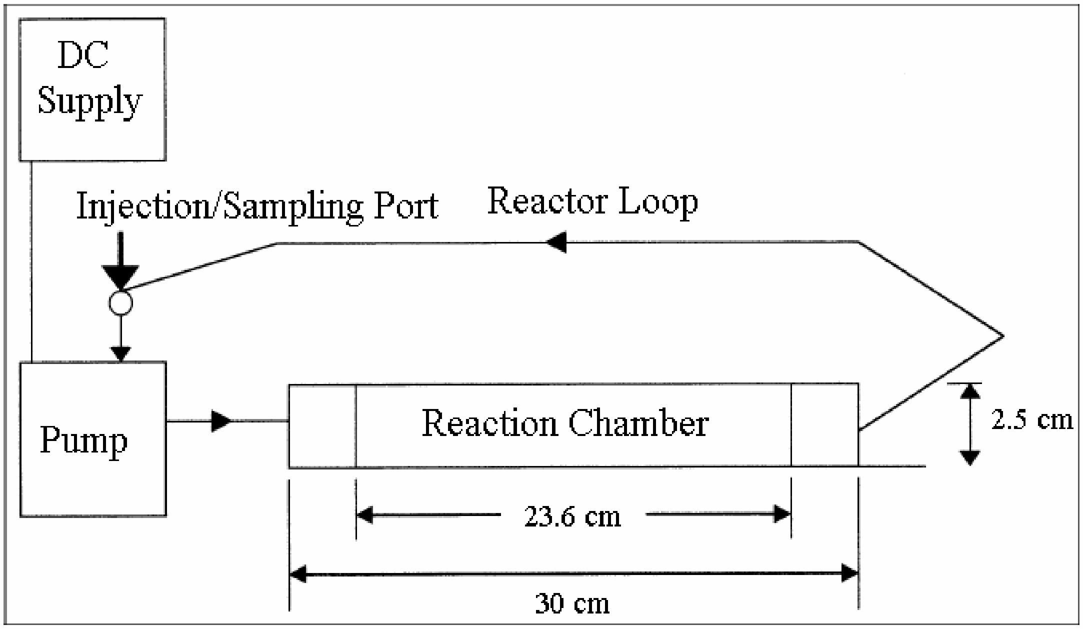


Figure 3.2 Photacatalytic Oxidation System Schematic (Adapted from Sattler and Liljestrand, 2003)

It provided illumination at a wavelength of 366 nm. A diaphragm pump (Cole-Parmer Model No. L – 79200-10) set at maximum pressure of 20 psi provided circulation through the loop. A DC supply double output system from Shenzhen Mastech connected to the pump was set at 15 volts, which reduced the voltage reaching the pump from its normal value of 110 volts and thus reduced the pump speed by a corresponding amount. The contaminated air stream circulates in the entire system via Teflon tubing. All the components of the system are made up of either glass or Teflon, neither of which should react with organics.

Contaminants are injected using a 1 ml syringe into the injection port and are allowed to mix uniformly inside the system before the UV light is turned on. The compounds are injected as pure chemicals straight out of the bottle or first transferred to a smaller container for ease of handling and to avoid contamination to the main stock. Since the applicability of the photocatalytic oxidation system needs to be assessed at ambient conditions, all the tests were carried out at room temperature which was 72 ± 1° F, pressure and relative humidity 50 ± 10 %.

3.1.2. Photocatalyst

As discussed in the literature review, TiO_2 is the most effective of all the semiconductor photocatalysts available; hence, all the experiments were performed in the presence of TiO_2. Degussa's P-25 grade TiO_2 was used as a photocatalyst. P-25 particles have an average surface area of 50 + 15 m^2/g and an average diameter of 21 nm based on number count and 32 nm based on surface area measurement (Sattler and

Liljestrand, 200x). P-25 contains a mixture of 70-80% anatase and 20-30% rutile (Sattler and Liljestrand, 2003).

The titanium dioxide was deposited onto the glass plate by immersing the plates in a suspension of titanium dioxide in distilled water and allowing the water to evaporate, leaving behind a titanium dioxide coating on the plate surface. This procedure appeared by visual inspection to give a fairly uniform TiO_2 coating, indicating that the coating was thick enough for all the light from the UV would be absorbed.

3.1.3. Gas Chromatograph

The gas chromatograph used for measuring destruction of VOCs was a SRI Instrument, model 8610C, with flame ionization detector (FID). Methane destruction was detected by a Haysep D packed column, and xylene destruction was detected by a packed column, from Restek, 2 m in length, which had the capability to detect BTEX compounds (benzene, toluene, ethyl benzene and xylene). Helium (from Matheson) was used as the carrier gas. Windows based Peak Simple software regulated the carrier gas flow, temperature and other GC parameters. The software also displayed detector parameters and results. Figure 3.3 shows the GC model used for this study.

3.1.4. Carbonyl Sulfide Sensor

The carbonyl sulfide sensor was an International Sensor Technology, model IQ-350 with a solid state sensor. It was configured to measure carbonyl sulfide concentration within the range of 0 to 50 ppm. A power supply and charger unit provided a voltage of 6 volts to the sensor. An in-built pump, pumps the contaminated air stream through the sensor and a digital display indicates the gas concentration. Figure 3.4 shows the sensor model utilized in this study.

3.1.5. Chemicals

The research attempts to evaluate the application of photocatalytic oxidation to VOCs, HAPs and odors from wastewater treatment plant and solid waste landfills. The compounds/chemicals utilized in this study are presented in Table 3.1.

Table 3.1 Chemicals Used for Experiments

Compound	**Manufacturer**	**Purity**
Methane	Matheson	99%
O-xylene	Cole & Parmer	99%
M-xylene	Cole & Parmer	99%
P-xylene	Cole & Parmer	99%
Carbonyl Sulfide	Matheson	3% carbonyl sulfide and balance is nitrogen.

Figure 3.3 Gas Chromatograph (SRI, Model – 8610C)

Figure 3.4 Carbonyl Sulfide Sensor (International Sensor Technology, Model – IQ – 350)

3.2 Experimental Methodology

3.2.1. Method for Operating Gas Chromatograph

Temperature control parameters such as initial, hold, ramp and final temperature vary with compounds. There values were predetermined and provided by SRI. Before beginning an experiment, the temperatures were set according to the type of compound being evaluated, and the integration based approach was selected to compute the area below the peak. For rest of the settings, the default setting was maintained.

3.2.2. Method for Operating Carbonyl Sulfide Sensors

Before starting the experimental run, the sensor was incorporated into the photocatalytic system by connecting the input and output (sensor) ends of the sensor to the photocatalytic system to form a closed loop batch reactor. This was possible since the sensor was non destructive. During the experiments, the photocatalytic system DC supply double output unit and pump were turned off. The steps involved in conducting carbonyl sulfide sensor run are listed below:

1. Initially the power supply to the sensor and the sensor pump were turned on. A sample of carbonyl sulfide was injected into the system via the injection/sampling port, using a gas tight 1 ml syringe.
2. The system was allowed to stabilize until a constant concentration value was displayed by the sensor's digital display, after which, the UV bulbs were turned on.
3. The carbonyl sulfide destruction rate was measured by observing the time elapsed and concentration values at regular intervals.

4. The experimental run was carried on until carbonyl sulfide was completely destroyed. After the completion of the test, the system was opened to release the byproducts and ensure ambient conditions inside the system for the following run.

3.2.3. Method for Conducting Photocatalytic Oxidation Experiments

Before starting the experimental run, dark tests were carried out to ensure that there was no leakage in the system, the system was well mixed and no photocatalytic oxidation destruction occurred without the UV lights turned on. It was observed that in the absence of ultraviolet light, the contaminant concentration remained constant.

Gas chromatograph 8610C with FID was used to measure VOC concentration after it was calibrated for that VOC. Calibration was done by injecting two 1 ml volumes of the compound of known concentrations into the GC. The peak simple program calibrated the compound based on the known concentrations values. The calibration file was saved and used during the experimental run.

The steps involved in conducting photocatalytic oxidation experiment are outlined below:

1. The system was left open to the atmosphere before starting the experiments so that the ambient conditions like temperature, pressure and humidity were maintained inside the system. During the experimental runs, ambient temperature and pressure were measured and noted. Before starting the experimental run, the system was closed and the DC supply and the pump were turned on.
2. After the pump was turned on, the compound to be destroyed was slowly injected into the PCO system through the injection/sampling port. A gas-tight syringe was

used for gaseous compounds (methane, ammonia, hydrogen sulfide and carbonyl sulfide) and a regular syringe was used for liquid compounds (xylenes). The syringe was cleaned by flushing two volumes of air for gas-tight syringe and two volumes of clean water after every run to get rid of any residue which might be left behind.

3. The system was allowed to mix for 6 minutes, and during that time after every two minutes dark test (with UV lights turned off) samples were taken and analyzed by the GC to ensure thorough mixing and no destruction in the absence of UV light.
4. Next, a sample of initial concentration of the compound in the system was collected and injected into the GC for analysis.
5. During the experiments, the UV light was turned on to initiate PCO. The placing of UV bulbs and the photocatalyst was not disturbed. The GC settings were maintained constant during the experiment. The same volume of samples was collected from the system. The samples were collected at intervals ranging from 2 minutes or more depending on the destruction rate of the compound.
6. Each sample was injected into the GC for analysis. The syringe was held at the GC injection port for 10 seconds following injection to assure that none of the sample was expelled through the injection port.
7. Between collections of each sample, several volumes of air were drawn into and expelled to ensure complete cleaning of the syringe before drawing another sample.

8. After completion of the experimental run, the system was opened to atmosphere with the pump turned on. This ensured proper cleaning of the system before another run was carried out.
9. Each experimental test was continued until the compound was destroyed at least 95% of the initial concentration was destroyed or until the compound concentration was below the detection threshold of the sensor.

CHAPTER 4

4.1 Introduction

This chapter discusses the results of experiments conducted according to the methods discussed in the previous chapter. First, the applicability of the first order decay is discussed, followed by the reaction rate constants measured for various contaminants tested.

4.2 First Order Decay

Rate constants were determined for the destruction of several VOCs, HAPs and odorous compounds associated with wastewater and solid waste landfills. The photocatalytic oxidation system is assumed to be uniformly mixed and is analyzed as a batch reactor. The rate constants found from the experiments can be applied to other types of reactors using appropriate mass balance equations.

Figure 4.1, which shows the destruction of methane, is best described as exponential, indicating that the destruction is first order with respect to concentration. The results agree with the hypothesis based on the previous researches that the destruction rates of VOCs over the TiO_2 in presence of UV light are in most cases first order reactions.

$$\text{Rate of reaction} = dC/dt = -kC \qquad (4.1)$$

The integrated form of Eq. (1) is:

$$C = Co * \exp(-kt) \quad (4.2)$$

or

$$\ln (C/Co) = -kt$$

The rate constant k can be found by plotting ln (C/Co) vs. t. Tables 4.1 through 4.7 present rate constants thus obtained for methane, o-xylene, m-xylene, p-xylene, ammonia, carbonyl sulfide, hydrogen sulfide, respectively. All the calculations, graphs and curve fits were performed using MS Excel.

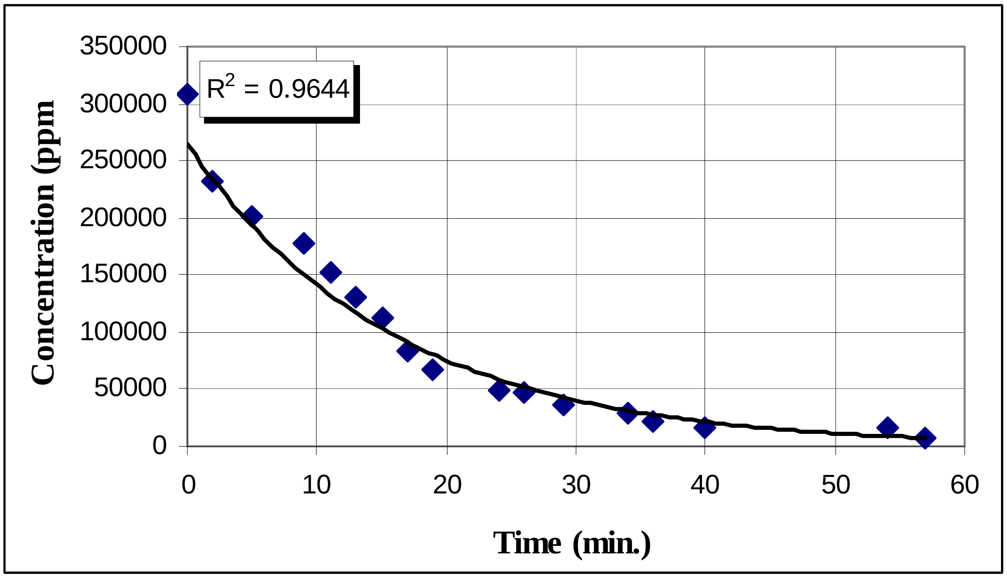


Figure 4.1 Destruction Rate of Methane

4.3 Results and Discussion – Methane

Initially only two runs were carried out, but due to significant differences between the rate constant values, an additional two runs were conducted. All runs were carried out at ambient temperature, pressure and humidity conditions. The results for methane runs are presented in Table 4.1. Figures 4.2 through 4.5 shows the graphs of –

ln(C/Co) vs. time, where the slope is equal to the first order rate constant. Appendix A shows the test data and the calculations.

Table 4.1 Summary of Rate Constants for Methane for First -Order Decay

Run No.	Initial Concentration (Co, ppm)	Average Temperature (°F)	Average Relative Humidity (%)	k (first order rate constant) (min^-1)	R^2 Value
1	277827	72.1	60.1	0.151	0.81
2	307390	72.4	49.3	0.064	0.99
3	319872	70.5	54.3	0.079	0.84
4	302980	72.0	56.4	0.090	0.89

The overall average of k is 0.096 min^{-1}. There is a significant variation in all the four values of k. Rate constants are known to depend on parameters such as initial concentration, temperature, humidity, UV intensity, type of catalyst, reactor configuration and oxygen concentration. All tests were performed with the same experimental setup so the type of catalyst, reactor configuration and the UV light intensity remained same. Oxygen concentration can be assumed to be constant with time. Initial concentration and temperature were nearly same and hence their effect on the rate constant can be neglected. Hence the only parameter that is variable and can affect the rate constant is humidity. As per the discussion in the literature review section, it is very well established that the photocatalytic oxidation destruction occurs basically due to the presence of OH° radicals which come from the water molecules in the air stream.

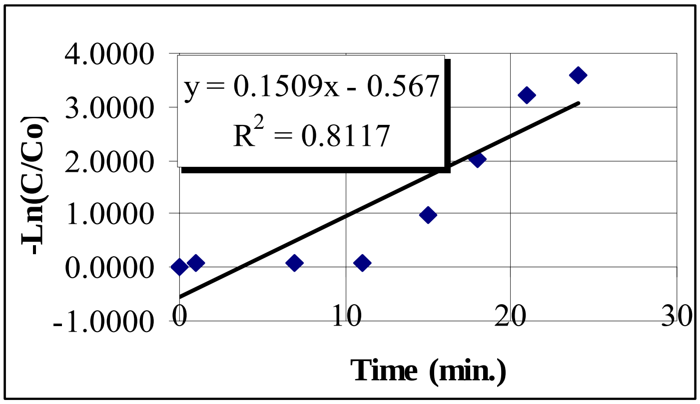


Figure 4.2 Methane Test Run 1

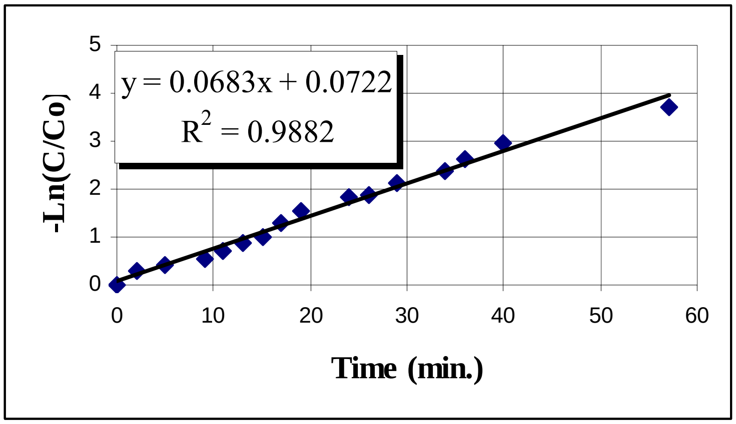


Figure 4.3 Methane Test Run 2

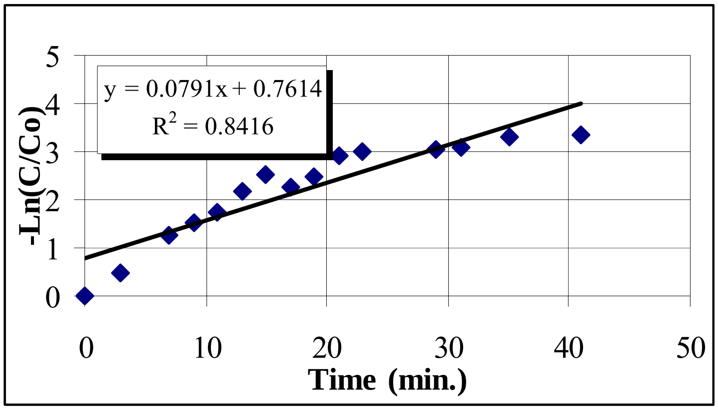


Figure 4.4 Methane Test Run 3

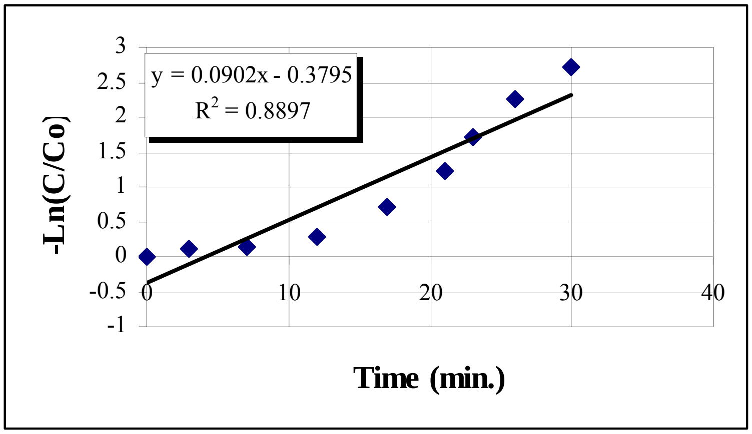


Figure 4.5 Methane Test Run 4

Study was also done to understand the relationship between the reaction rate constant for methane and relative humidity in the inlet stream. Figure 4.6 presents the result. In the relative humidity range of 49.3% - 60.1%, the rate constant increases with the increase in the relative humidity. It was found that an exponential curve best describes the relationship. Further research is recommended to verify this relationship.

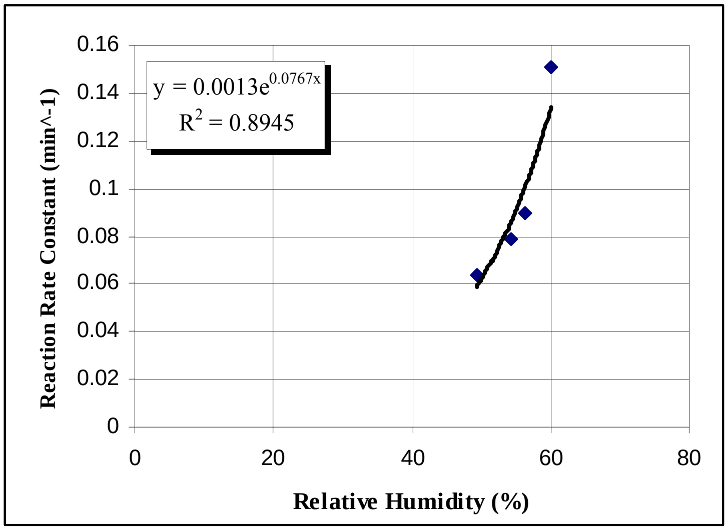


Figure 4.6 Relationship between Reaction Rate Constant for Methane and Humidity in the Humidity Range of 49.3 – 60.1%

4.4 Results and Discussion – O-Xylene

The results for the tests carried out for o-xylene are summarized in Table 4.2.

Table 4.2 Summary of Rate Constants for O-Xylene for First-Order Decay

Run No.	Initial Concentration (Co, ppm)	Average Temperature (°F)	Average Relative Humidity (%)	k (first order rate constant) (min^-1)	R^2 Value
1	207	71.5	44.5	0.028	0.89
2	305	74.5	46.8	0.027	0.83

Two experimental runs were carried out for o-xylene. The results for both the runs are presented in Figures 4.2 and 4.3. The average reaction rate constant value was 0.0275 min^{-1}. The results indicate that the reaction rate constant value for o-xylene is lower compared to that of methane. This could have been because of several reasons: xylene structure, humidity or initial concentration. Xylene molecule is a bigger molecule and it has a complex structure as compared with methane molecule; hence, xylene photocatalytic destruction rate would be lower as compared with methane destruction rate. Secondly, low humidity (44.5 to 46.8%) during the o-xylene experiments could have affected the reaction rate. Also, initial concentration could have affected the reaction rate constant.

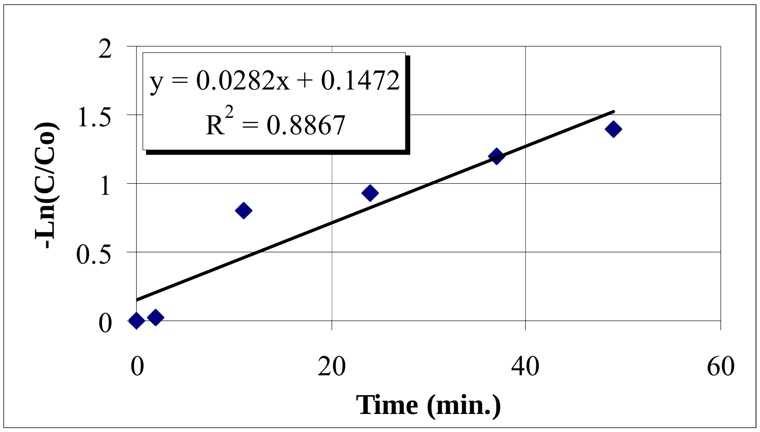


Figure 4.7 O-Xylene Test Run 1

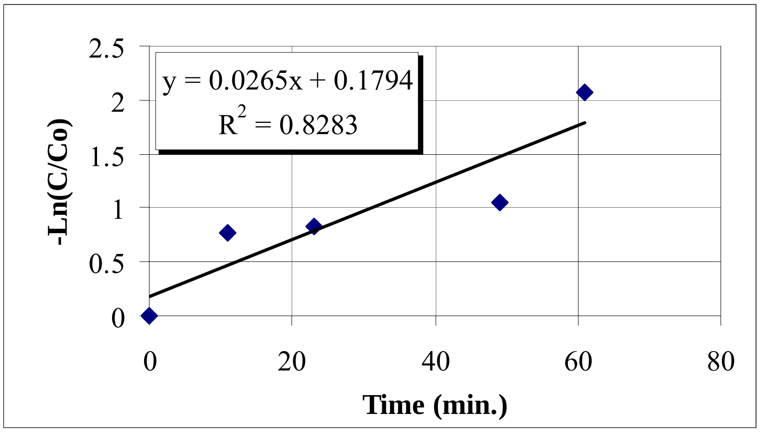


Figure 4.8 O-Xylene Test Run 2

4.5 Results and Discussion – M-Xylene

The summary of the results for the m-xylene runs is presented in Table 4.3.

Table 4.3 Summary of Rate Constants for M-Xylene for First-Order Decay

Run No.	Initial Concentration (Co, ppm)	Average Temperature (°F)	Average Relative Humidity (%)	k (first order rate constant) (min^-1)	R^2 Value
1	262	71.6	43.1	0.040	0.82
2	211	72.3	47.5	0.010	0.71

Similar to o-xylene, two experimental runs were carried out for m-xylene. The average reaction rate constant value for p-xylene was 0.025 min^{-1}. The reaction rate constant value was low, which agrees with the theory that xylene being a bigger and complex molecule would be difficult to break. The smaller value of the reaction rate constant suggests that for similar photocatalytic oxidation reactor parameters, xylene would have to reside in the system longer compared to methane to be completely destroyed. Besides, for both the experimental runs for m-xylene, the humidity was low (43.1 – 47.5%). The individual experimental run results are presented in Figures 4.4 and 4.5.

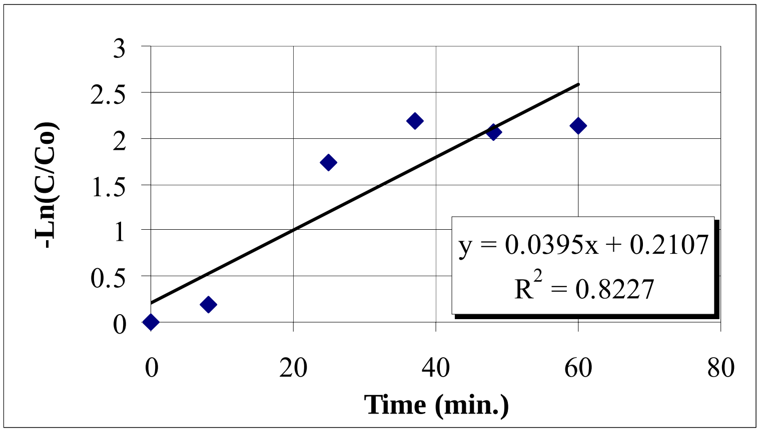


Figure 4.9 M-Xylene Test Run 1

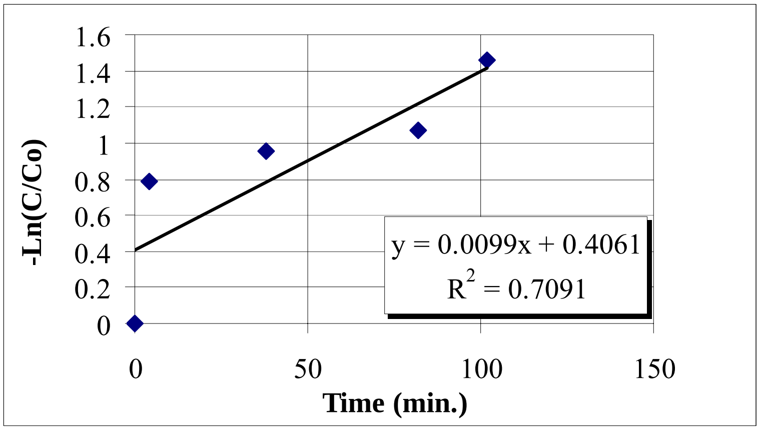


Figure 4.10 M-Xylene Test Run 2

4.6 Results and Discussion – P-Xylene

P-xylene test results are presented in Table 4.4. The average reaction rate constant value for p-xylene is 0.0125 min^{-1}. Once again, the results indicate that the reaction rate constant value for p-xylene is low. The same theory of xylene being a bigger and a complex molecule applies to p-xylene run results. Secondly, low humidity (45.7 to 55%) during the p-xylene experiments could have affected the reaction rate.

Also, initial concentration could have affected the reaction rate constant. The experimental test run details for each run is presented in Figures 4.6 and 4.7.

Table 4.4 Summary of Rate Constants for P-Xylene for First-Order Decay

Run No.	Initial Concentration (Co, ppm)	Average Temperature (°F)	Average Relative Humidity (%)	k (first order rate constant) (min^-1)	R^2 Value
1	401	72.1	55	0.012	0.74
2	355	70.6	45.7	0.013	0.74

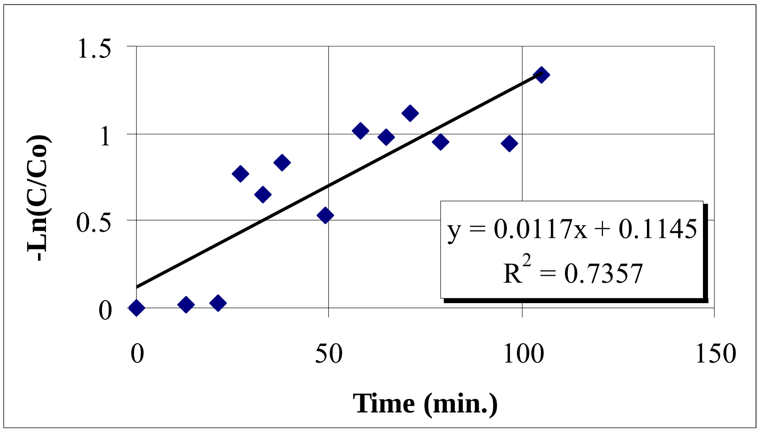


Figure 4.11 P-Xylene Test Run 1

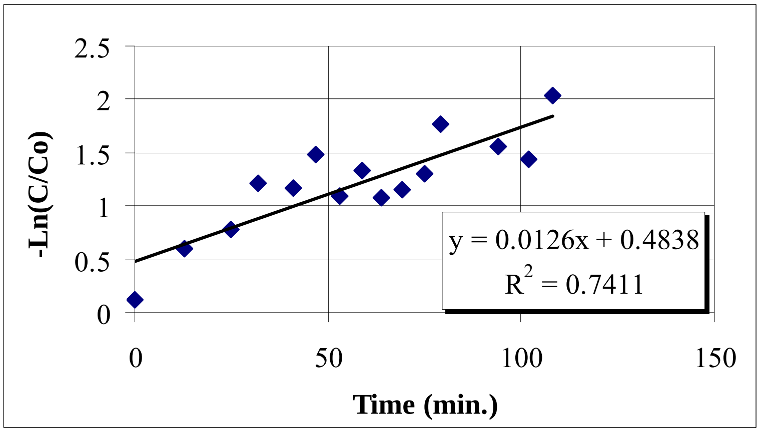


Figure 4.12 P-Xylene Test Run 2

4.7 Results and Discussion – Carbonyl Sulfide

Two runs with an initial concentration of 30 ppm were carried out to determine the rate constant for carbonyl sulfide. The result summary is presented in Table 4.5. The average reaction rate constant value is 1.13 min^{-1}.

Table 4.5 Summary of Rate Constants for Carbonyl Sulfide for First-Order Decay

Run No.	Initial Concentration (Co, ppm)	Average Temperature (°F)	Average Relative Humidity (%)	k (first order rate constant) (min^-1)	R^2 Value
1	30	71.5	61.1	1.11	0.95
2	30	71.5	63.1	1.15	0.90

During this study, the initial concentration, photocatalytic system parameters and temperature remained constant. Hence the reaction rate constant values for both experimental runs were close to each other. The reaction rate constant values for carbonyl sulfide are high. This could be because, similar to methane, carbonyl sulfide is a small and less complex molecule and hence its destruction rate is fast. Besides, carbonyl sulfide molecule has a double bond which is relatively easy to break, since it has a high electron density to which OH° is attracted. Additionally, the humidity level was high (61.1 – 63.1%) which could have promoted the destruction process and led to a higher value of reaction rate constant.

There was a slight variation in the humidity level; the results show that with a slight increase in the humidity, there was a slight increase in the value of the rate constant. The humidity and the reaction rate constant relation follow the same trend as seen in the methane experiments. The individual carbonyl sulfide run details are shown below in Figures 4.8 and 4.9.

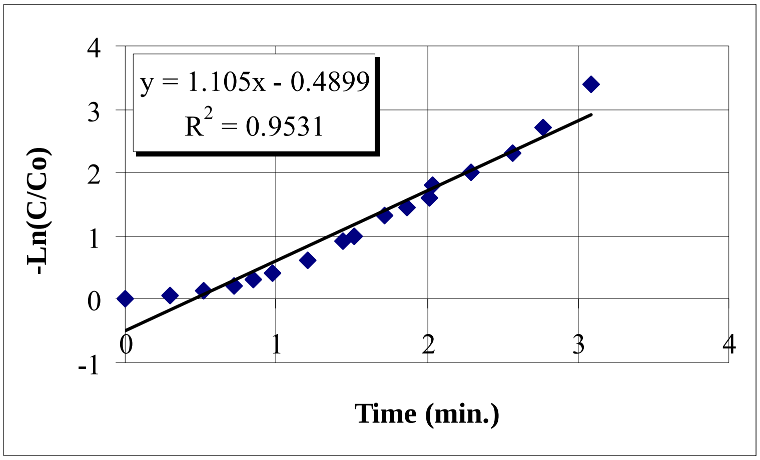


Figure 4.13 Carbonyl Sulfide Test Run 1

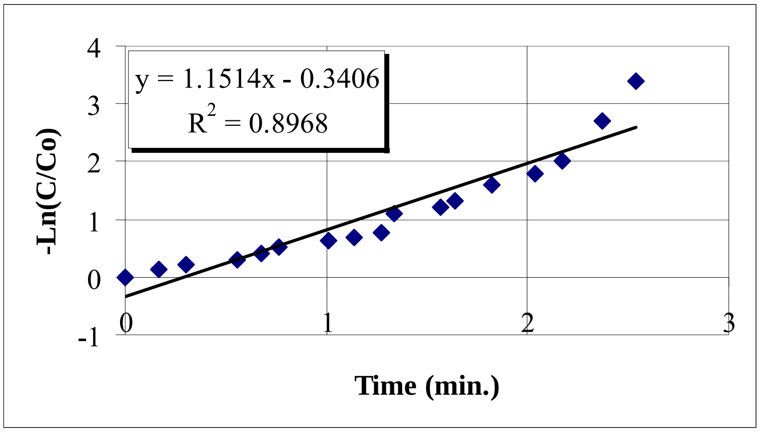


Figure 4.14 Carbonyl Sulfide Test Run 2

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research was aimed at evaluating the effectiveness of photocatalytic oxidation systems in treating emissions from wastewater and landfill facilities such as methane, xylenes and carbonyl sulfide. Analysis of each of the compound and its reaction rate constant leads to following conclusions:

- A summary of the reaction rate constant comparison of all the compounds tested is presented in Table 5.1.

Table 5.1 Summary of Reaction Rate Constant Comparison of Compounds Tested

Compound	**Avg. Initial Concentration C, ppm**	**Avg. Temperature °F**	**Avg. Relative Humidity %**	**Avg. Rate Constant k, min^-1**	**Avg. R^2 Value**
Methane	30,2017	71.8	55	0.096	0.883
O-Xylene	256	73	45.7	0.0275	0.860
M-Xylene	237	71.9	45.3	0.025	0.765
P-Xylene	378	71.4	50.1	0.0125	0.740
Carbonyl Sulfide	30	71.5	62.1	1.13	0.925

- Reaction rate constants for methane and carbonyl sulfide are higher compared to that of the xylenes. A smaller and simpler molecule like methane or carbonyl sulfide would be anticipated to break easily and quickly compared to a bigger and more complex molecule like xylene. This suggests that to achieve the same amount of destruction, xylenes would have to reside inside the photocatalytic oxidation reactor longer than methane and carbonyl sulfide. In other words, to achieve same amount of destruction for a constant flow rate of air stream, xylenes would require a larger reactor as compared to methane and carbonyl sulfide. Thus, this research can aid in the process of reactor design.

- It was also seen that the reaction rate constant depended on parameter such as humidity. Additional research done to evaluate the relationship between the reaction rate constant of methane and relative humidity indicates an exponential relationship. From past research it is also known that parameters such as relative humidity, temperature and initial concentration have different effects on different contaminants. Hence, to achieve maximum destruction, it is important to study the effect of humidity on individual contaminants and optimum values needs to be found for humidity for each contaminant being treated.

5.2 Recommendations

The following recommendations are suggested for future research using photocatalytic oxidation system:

- This research determined the reaction rate constants of only a few of the many constituents of emissions from wastewater treatment and landfill facilities. Further research for determining the reaction rate constants of other constituents could be added to this research to get a better understanding of effectiveness of using photocatalytic oxidation system in treating emissions.
- Parameters such as UV light intensity and reactor configuration which were fixed in this study should also be studied since they too play an important role by affecting destruction efficiency of the photocatalytic system.
- This research indicates that the humidity affects the reaction rates the most. Hence further research should be done to understand the affect of humidity on reaction rate constants of different contaminants.

- During this research, relative humidity was measured only once, at the beginning of each experiment run. Continuous monitoring of the humidity is required to account for the humidity added during the photocatalysis process.
- In this research, the destruction rate of each contaminant was measured individually. In real world situation, photocatalytic reactor system would be anticipated to treat a mixture of contaminants; hence, mix stream destruction evaluation is required, in order to get a correct sense of the effectiveness of photocatalytic oxidation in treating the emissions from wastewater treatment plants and solid waste landfills.

APPENDIX A

METHANE TEST DATA

A-1 Methane Test Run 1 Data and Calculations

Average Temperature = 72.1 F			
Relative Humidity = 60.1 %			
Initial Concentration = 277827 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
277827	0	1	0
252560	1	0.909	0.0953
259667	7	0.935	0.0676
251580	11	0.906	0.0992
104220	15	0.375	0.980
36403	18	0.131	2.03
11050	21	0.0398	3.22
7569	24	0.0272	3.60
0	30	0	-

A-2 Methane Test Run 2 Data and Calculations

Average Temperature = 72.4 F			
Relative Humidity = 49.3 %			
Initial Concentration = 307390 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
307390	0	1	0
231953	2	0.755	0.282
201290	5	0.655	0.423
177108	9	0.576	0.551
151716	11	0.494	0.706
130216	13	0.424	0.859
112181	15	0.365	1.008
83664	17	0.272	1.30
66331	19	0.216	1.53
49352	24	0.161	1.83
48051	26	0.156	1.86
35979	29	0.117	2.15
28347	34	0.0922	2.38
22374	36	0.0728	2.62
16182	40	0.0526	2.94
7389	57	0.0240	3.73

A-3 Methane Test Run 3 Data and Calculations

Average Temperature = 70.5 F			
Relative Humidity = 54.3 %			
Initial Concentration = 319872 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
319872	0	1	0
198226	3	0.620	0.479
89747	7	0.281	1.271
70456	9	0.220	1.51
56399	11	0.176	1.74
36258	13	0.113	2.18
26042	15	0.0814	2.51
33692	17	0.105	2.25
27160	19	0.0850	2.47
17169	21	0.0537	2.92
16117	23	0.0504	2.99
15476	29	0.0484	3.03
14570	31	0.0455	3.09
11495	35	0.0359	3.33
11491	41	0.0359	3.33

A-4 Methane Test Run 4 Data and Calculations

Average Temperature = 72.0 F			
Relative Humidity = 56.4%			
Initial Concentration = 302980 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
302980	0	1	0
270520	3	0.893	0.113
261906	7	0.864	0.146
230015	12	0.759	0.276
150205	17	0.496	0.702
89050	21	0.294	1.22
54890	23	0.181	1.71
32020	26	0.106	2.25
20300	30	0.067	2.70

APPENDIX B

XYLENES TEST DATA

B-1 O-Xylene Test Run 1 Data and Calculations

Average Temperature = 71.5 F			
Relative Humidity = 44.5%			
Initial Concentration = 207 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
207	0	1.000	0.000
202	2	0.977	0.023
93	11	0.450	0.798
82	24	0.396	0.927
62	37	0.300	1.20
51	49	0.247	1.40

B-2 O-Xylene Test Run 2 Data and Calculations

Average Temperature = 74.5 F			
Relative Humidity = 46.8%			
Initial Concentration = 305 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
305	0	1.000	0.000
142	11	0.466	0.764
133	23	0.438	0.826
107	49	0.351	1.05
38	61	0.126	2.07

B-3 M-Xylene Test Run 1 Data and Calculations

Average Temperature = 71.6 F			
Relative Humidity = 43.1%			
Initial Concentration = 262 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
262	0	1.000	0.000
215	8	0.820	0.198
47	25	0.177	1.73
30	37	0.113	2.18
33	48	0.127	2.06
31	60	0.119	2.13

B-4 M-Xylene Test Run 2 Data and Calculations

Average Temperature = 72.3 F			
Relative Humidity = 47.5%			
Initial Concentration = 211 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
211	0	1.000	0.000
96	4	0.454	0.789
81	38	0.386	0.952
73	82	0.345	1.07
49	102	0.232	1.46

B-5 P-Xylene Test Run 1 Data and Calculations

Average Temperature = 72.1 F			
Relative Humidity = 55.0%			
Initial Concentration = 401 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
401	0	1.000	0.000
394	13	0.982	0.018
389	21	0.969	0.031
185	27	0.462	0.771
209	33	0.521	0.652
174	38	0.433	0.836
236	49	0.588	0.532
145	58	0.362	1.02
150	65	0.374	0.98
132	71	0.329	1.11
155	79	0.386	0.953
157	97	0.391	0.940
106	105	0.263	1.34

B-6 P-Xylene Test Run 2 Data and Calculations

Average Temperature = 70.6 F			
Relative Humidity = 45.7%			
Initial Concentration = 355 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
355	0	1.000	0.000
220	13	0.619	0.479
185	25	0.521	0.653
120	32	0.337	1.09
125	41	0.353	1.04
91	47	0.258	1.36
135	53	0.382	0.96
105	59	0.297	1.22
136	64	0.384	0.957
127	69	0.358	1.03
109	75	0.308	1.18
69	79	0.194	1.64
84	94	0.238	1.44
96	102	0.269	1.31
52	108	0.148	1.91

APPENDIX C

CARBONYL SULFIDE TEST DATA

C-1 Carbonyl Sulfide Test Run 1 Data and Calculations

Average Temperature = 71.5 F			
Relative Humidity = 61.1%			
Initial Concentration = 30 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
30	0	1.000	0.000
28	0.3	0.933	0.069
26	0.52	0.867	0.143
24	0.72	0.800	0.223
22	0.85	0.733	0.310
20	0.98	0.667	0.405
16	1.21	0.533	0.629
12	1.44	0.400	0.916
11	1.52	0.367	1.00
8	1.72	0.267	1.32
7	1.87	0.233	1.46
6	2.02	0.200	1.61
5	2.04	0.167	1.79
4	2.29	0.133	2.02
3	2.57	0.100	2.30
2	2.77	0.067	2.71
1	3.09	0.033	3.40

C-2 Carbonyl Sulfide Test Run 2 Data and Calculations

Average Temperature = 71.5 F			
Relative Humidity = 63.1%			
Initial Concentration = 30 ppm			
Concentration C, ppm	**Time t, min**	**C/Co**	**Neg ln(C/Co)**
30	0	1.000	0.000
26	0.17	0.867	0.143
24	0.3	0.800	0.223
22	0.56	0.733	0.310
20	0.68	0.667	0.405
18	0.76	0.600	0.511
16	1.01	0.533	0.629
15	1.14	0.500	0.693
14	1.27	0.467	0.762
10	1.34	0.333	1.10
9	1.57	0.300	1.20
8	1.64	0.267	1.32
6	1.82	0.200	1.61
5	2.04	0.167	1.79
4	2.17	0.133	2.02
2	2.37	0.067	2.71
1	2.54	0.033	3.40

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BIOGRAPHICAL INFORMATION

Born on March 30th 1980, Mita Suresh Upadhyay earned her Bachelor of Civil Engineering from Birla Vishwakarma Mahavidhyalay Engineering College, Sardar Patel University, India in August of 2002.

The author has earned her Masters of Science in Environmental Engineering from The University of Texas at Arlington. During her graduate studies, she was appointed as a teaching assistant by the Civil & Environmental Department to assist professors in teaching various courses such as Air Pollution Chemistry and Meteorology (Spring 2005), Fluid Mechanics (Summer and Fall, 2005) and Principles of Environmental Engineering (Spring 2006). During the course of her graduate studies, she also served as research assistant to Dr. Melanie L. Sattler. Her master's research was focused on the "Photocatalytic Degradation of VOCS, Toxics and Odors from Air Emissions of Wastewater Treatment Plants and Municipal Solid Waste Landfills". The study dealt with determining the effectiveness of using photocatalytic oxidation technology in treating the emissions from wastewater and landfill facilities. She showed through her thesis that photocatalytic oxidation system is a promising method of treatment for smaller pollution sources.

Presently, she is working as an air quality consultant with Trinity Consultants and is based in Corpus Christi.