THE USE OF OZONE FOR THE REMOVAL OF ODOR FROM SWINE MANURE

By

Jiunn-Jer (Jerry) Wu

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ABSRTACT

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The ozonation of swine manure was investigated. Malodorous chemicals including phenol, *p*-cresol, *p*-ethylphenol, indole, skatole, volatile fatty acids, ammonia, and hydrogen sulfides were monitored during ozonation of swine manure. To characterize the generation of these malodorous chemicals during manure storage, the freshly collected manure was stored in a fermentation tank for 12 weeks. During this time the concentrations of the target malodorous compounds along with odor and the number of microorganisms were monitored. As part of this study, swine manure was treated in lab-scale and pilot-scale reactors to investigate the ozonolysis of malodorous compounds, to determine the operational parameters for reactor design, to understand the physical and chemical factors affecting the ozonation of these target compounds, and to predict the degradation of odorous substances during ozonation by using a mathematical model.

Malodorous compounds accumulated rapidly in manure during storage. The odor of both the fresh and stored (up to 12 weeks) manure was reduced to an acceptable level after ozonation at a dosage of 1 g/L. The odor of ozone-treated manure did not recur during subsequent storage, even after several months. The concentrations of the phenolic

and indolic compounds were reduced to nondetectable levels. The populations of anaerobic and aerobic microorganisms were found to be slightly reduced after ozonation at a dosage of 1 g/L. However, *E. coli* and total coliform were almost eliminated by ozone. In the pilot study, a reactor having a capacity of 3 gallons was constructed to treat swine manure. Using this design, the applied ozone dosage can be reduced to 0.5 g/L and still reduce the odor to an acceptable level as determined by the olfactometry test. The pilot-scale reactor has the advantages of a venturi injector which generates fine bubbles and deep-reactor which increases the liquid-gas contact time. Also, a stirrer provides more hydrodynamic mixing. This ensures almost complete absorption of ozone by the manure slurry and serves to effectively reduce the concentrations of malodorous compounds.

A mass-transfer model for ozone was developed to estimate the mass-transfer coefficient and partition coefficient for a semi-batch reactor. A plug-flow pattern described the rise of ozone bubbles from the bottom to the top of the reactor. In the kinetic study, stoichiometric factors and rate constants for the reaction of ozone with phenolic and indolic compounds were determined. Increases in the pH of the aqueous solution resulted in a significant increase in the reaction rate constants of the phenolic and indolic compounds. In a semi-batch experiment, it was shown that the applied ozone dosage is a reliable operational parameter that can be used to describe the removal of malodorous compounds. An oxidation model that combines mass transfer and chemical oxidation has been developed to predict the degradation of malodorous compounds during ozonation of either artificial or real swine manure.

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Chapter 1

INTRODUCTION

1.1 Environmental Significance

Environmental pollution by livestock waste is a major nationwide concern of the animal agriculture industry. As livestock production has moved to larger and more intense production units, odor complaints have increased from the residents of surrounding communities (Ritter, 1989). There is a growing public intolerance of odors that result from modern farming practices. The increase in the size of livestock enterprises and the increasing number of people living in rural areas will result in pressure on livestock producers to take positive actions to reduce this odor. Therefore, the problem of handling the large amounts of animal wastes generated on farms is a formidable task and is of significant concern to agricultural community.

An increasing number of civil litigations, more restrictive township ordinances, demands for the protection of public health and new Federal and State regulations governing surface run-off and groundwater contamination necessitate that the livestock industry take actions to control the environmental problems associated with livestock operations. George et al. (1985) summarized the US Midwest odor litigations and decisions. They recommended that odor concerns should be addressed during initial planning, site selection and design. They also concluded that day-to-day management

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actions and public relations might be the most significant determinants as to the development and outcome of any conflict or litigation regarding an odor problem.

The application of animal wastes to agricultural lands poses significant problems to the agricultural industry, despite all of the benefits of waste application in terms of nutrient addition. Since animal wastes contain very high phosphorus and nitrogen concentrations, the application of wastes can cause excessively high nutrient loadings to the soil. The problem is exacerbated by the use of manure injection techniques which can inject the manure below the plant root zone, thus, increasing potential nutrient migration to the groundwater. Odors emanating from livestock wastes can also exacerbate the problem as farmers are not necessarily able to apply manure to the land when the soil conditions are optimal because of such constraints as wind direction. Innovative methods to control, reduce or eliminate odors associated with livestock wastes would mean that the less malodorous wastes (1) would not need to be injected and could be surface-applied; as such, the nutrients would be available to the plant roots for a longer period of time; and (2) could be applied to the soil at the time of optimal soil conditions, rather than at times such as optimal weather conditions.

1.2 Original and Identification of Malodorous Substances in Livestock Waste

Odors from swine farms emanate from the ventilation air from the buildings, the odors from the slurry handling near the piggery and in the storage pits, and from spreading slurry on land. (Sneath et al., 1992). Generally odors from the livestock wastes are a result of anaerobic microbial decomposition. Mackie (1994) indicated that four classes of odorous components, including volatile fatty acids (VFA), phenols and indoles,

ammonia and volatile amines, and volatile sulfur-containing compounds, are the normal bacterial metabolic end-products from the breakdown of amino acids. Welsh et al. (1977) reported the anaerobic degradation of cellulose, lipids, proteins, and other complex organic materials results in intermediate fermentation products which are responsible for most odors in anaerobic storage of manure. Many researchers have identified specific odorous compounds of livestock waste odors. Barth et al. (1984) reported that more than 75 specific odorous compounds have been identified in livestock waste. O'Neill and Phillips (1992) reported that 168 odorous compounds are present in livestock waste and in the air surrounding these operations. Odor producing compounds have been measured by gas chromatography, wet chemistry and organoleptic tests (Ritter, 1989). These compounds are end products or intermediate products of biological reactions and include: volatile organic acids, alcohol, aldehydes, fixed gases, carbonyls, esters, amines, sulfides, mercaptans, and nitrogen heterocycles. Some of the specific compounds identified in swine waste are listed in Table 1.1.

1.3 Odor Measurement

There are five basic approaches to odor detection and measurement. All are based on the nose, wet chemistry and gas chromatography (Ritter, 1989). These methods are:

(a) identification of odor gases;

(b) measurement of odorant concentration;

(c) measurement of odor intensity by vapor dilution;

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Table 1.1 Identified Odorous Compounds in Livestock Waste

Nitrogen Compounds	Volatile Fatty Acids	Sulfur Compounds
Ammonia	Methanoic acid	Carbonylsulfide
Methylamine	Ethanoic acid	Hydrogen sulfide
Ethylamine	propanoic acid	Methanethiol
Trimethylamine	Butanoic acid	Dimethylsulfide
Triethylamine	2-Methylpropanoic acid	Dimethyldisulfide
	Pentanoic acid	Dimethyltrisulfide
Alcohols	3-Methylbutanoic acid	Diethyldisulfide
Methanol	Hexanoic acid	Propanethiol
Ethanol	4-Methylpentanoic acid	Butanethiol
1-Propanol	Heptanoic acid	Dipropldisulfide
2-Propanol	Octanoic acid	2-Methylthiophene
1-Butanol	Nonanoic acid	Propylprop-1-ethyldisulfide
2-Butanol	Phenylacetic acid	2,4-Dimethylthiophene
2-Methyl-1-Propanol	2-Phenylpropanoic acid	2-Methylfuran
3-Methyl-1-butanol		
2-Ethoxy-1-propanol	**Aromatics**	
2-Methyl-2-pentanol	Phenol	
2,3-Butanediol	4-Methylphenol	
	4-Ethylphenol	
Aldehydes	Toluene	
Methanal	Xylene	
Ethanal	Indole	
Propanal	Benzaldehyde	
Butanal	Benzoic acid	
Pentanal	Methylphthalene	
Hexanal	Skatole	
Octanal	Acetophenone	
Decanal	o-Aminoacetophenone	
2-Methyl-1-Propanal	Aneline	

(d) measurement of odor intensity by liquid dilution; and

(e) ranking of odor intensities by arbitrary scales based upon the offensiveness of the odor.

Elliott et al. (1978) reviewed the analytical methods for detecting odors. They concluded that quick and economical means of measuring odors from waste management systems are needed in order to develop odor control technology. Although the nose can be used to measure odor intensity, vapor and liquid dilution are more popular methods for measuring odor intensity. However, vapor dilution methods are probably more popular than liquid dilution techniques because they are easier tests and can be done both in the laboratory and field (Ritter, 1989). A dynamic dilution binary scale olfactometer using air/odorant vapor mixtures at 8 different concentrations has been developed by IIT Research Institute to measure the odor intensity (Dravnieks, 1974). The liquid dilution technique involves mixing odor-containing material with odor-free water. Several dilutions are generally made and then the odorous dilution samples along with odor-free samples are evaluated by a panel of observers. The odor intensity can be determined by using odor intensity index which depends on the dilution ratio of odor-free water to sample used. Sobel (1972) evaluated odor quality with a panel ranking the offensiveness of the odor on a scale from 0 (non-offensiveness) to 10 (very strong offensiveness). Williams (1984) indicated that odor offensiveness should be used rather than intensity to evaluate the change of odors. In recent years, an electronic nose has been commercially developed in the food and flavor industry for quality control. Gardner and Bartlett (1994) defined an electronic nose system as an instrument which consists of an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition

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system capable of recognizing simple or complex odors. They list a range of active materials which have been used in sensor arrays, including sintered metal oxide, catalytic metals, lipid layers, phthalocyanins, conducting polymers and organic semi-conductors. Persaud et al. (1996) have been developing an instrument (the Odormapper) with sensor arrays based on conducting polymers which have been shown to respond well to the volatile compounds found in the headspace above pig slurries and give reproducible results over a three month period. Hobbs et al. (1995), using an earlier version of the Odormapper, demonstrated its ability to discriminate between odors from pig and chicken slurries, but reported low sensitivity of the instrument when compared with olfactometry for measuring odor concentration. Recent development in the electronic nose technique has led to new applications in the assessment of odor from livestock waste. It is expected, eventually, that the electronic nose will be favored over traditional olfactometry, as it can avoid the subjectivity associated with the human nose and perception.

1.4 Current Technologies to Control Odor

A wide variety of biochemical and chemical products are being sold to treat and prevent odors in feedlots, liquid waste storage tanks and lagoons. There are six categories of odor controlling agents:

(1) masking agents, which are mixtures of aromatic oils that have a strong particular odor of their own and are designed to cover up the waste odor with a more desirable one;

(2) counteractants, which are mixtures of aromatic oils that cancel or neutralize the waste odor so that the intensity of the mixture is less than that of the constituents;

(3) digestive deodorants, which contain bacteria or enzymes that eliminate odors through modifications in biochemical digestive processes;

(4) adsorbents, which are products having a large surface area that may be used to adsorb the odors before they are released to the environment;

(5) feed additives, which are compounds added to feed to improve animal performance and reduce odors;

(6) chemical deodorants, which are strong oxidizing or germicidal agents that alter or eliminate the bacteria responsible for odor production or chemically oxidize odorous compounds.

A variety of masking agents and counteractants are available for odor control. Burnett and Dondero (1970) evaluated 38 masking agents and counteractants on poultry waste along with several digestive deodorants and chemical deodorants. The results indicated that, in general, masking agents and counter agents are the most effective, while chemical deodorants are moderately effective and digestive deodorants least effective. Despite research data to indicate the limited success of digestive deodorants, digestive deodorants are the most popular of the proprietary chemicals sold for odor control because of aggressive marketing by some companies (Ritter, 1989). Williams and Schiffman (1995) indicated that chemical deodorants did not significantly improve the odor. Powers et al. (1995) also suggested that the odor of liquid dairy manure was not improved after the use of commercial additives. Chemical deodorants are either oxidizing agents or disinfectants. Oxidizing agents transform odorous compounds into

less offensive ones by chemical oxidation. Disinfectants alter or eliminate the bacterial action that is responsible for odor production. Strong oxidizing agents also act as disinfectants via their ability to degrade oxidatively enzymatic proteins (Ritter, 1989).

In addition to methods of controlling odor, two biological processes, anaerobic digestion and aerobic lagoon, have been developed for manure management and odor removal (Powers et al., 1995; Burton, 1992; Sneath et al., 1992; Williams et al., 1984; Evans et al., 1983; Welsh et al., 1977). Although anaerobic digestion provides some benefits including energy production, odor control, waste stabilization, and digester residual as a feed component, there are very few farm digesters in operation in North America. Major problems with the digester include waste handling, gas leakage, and pipe and valve corrosion (Ritter, 1989). Although anaerobic digestion reduces odors, the digested effluent is still a source of odor when it is spread on land (Voermans, 1986). Aerobic treatment of animal slurries represents an increasingly popular option for producers in the management of animal waste (Burton, 1992). Odors will not be problematic if aerobic conditions are maintained. However, when malfunctions or other circumstances cause aerobic systems to go anaerobic, odors will be released. As lagoons or oxidation ponds require large land areas and the mechanically aerated systems used have high energy requirements, aerobic systems are expensive to operate (Ritter, 1989).

1.5 Background of Using Ozone Treatment

Ozone, the triatomic allotrope of oxygen, has the formula O_3 and generally exists as a relatively unstable, reactive gas. Commercially, large quantities of ozone are produced in specially engineered corona discharges (Carlins and Clark, 1982). Ozone is a very

powerful oxidant (E^o = 2.07 volts), which is capable of reacting with numerous of organic chemicals. It is more powerful than most of the other oxidants currently used in water treatment (Rice and Browning, 1981) (see Table 1.2).

Table 1.2 Oxidation-reduction Potentials for Water Treatment Agents

Reactions	Potential in Volts (E^o) at 25 °C
$F_2 + 2e^- = 2F^-$	2.87
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$ (acid)	1.76
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.68
$HClO_2 + 3H^+ + 4e^- = Cl^- + H_2O$	1.57
$HOCl + H^+ + 2e^- = Cl^- + H_2O$	1.49
$Cl_2 + 2e^- = 2Cl^-$	1.36
$HOBr + H^+ + 2e^- = Br^- + H2O$	1.33
$Br_2 + 2e^- = 2Br^-$	1.07
$ClO_{2(aq)} + e^- = ClO_2^-$	0.95
$H_2O_2 + 2H_3O+ + 2e^- = 4H_2O$ (base)	0.87

In an aqueous solution, ozone may react with compounds (M) either:

- by direct reactions with molecular ozone, or
- by indirect reactions with the radical species that are formed when ozone decomposes in water.

The resonance structures of the ozone molecule make it as a dipole, an electrophile, and a nucleophile. Therefore, the direct reactions include three kinds of elementary reactions, namely such as cyclo addition, electrophilic reaction, and nucleophilic reaction (Langlais et al., 1990). Ozone can react with aromatic compounds directly or indirectly. The direct reaction is selective, favoring compounds with electron donating groups (e.g.,

OH and NH_2). Compounds with electron withdrawing groups (e.g., NO_2 and Cl) are not easily oxidized by ozone. However, these compounds can be oxidized with ozone indirectly using OH radicals.

Figure 1.1 illustrates the reaction of aqueous ozone in water (Masten and Davies, 1994). Hydroxide ions initiate ozone decomposition by reacting with ozone, producing superoxide anions (O_2^-). Ozone then reacts with the superoxide anion to form ozonide radical ions and oxygen. The protonated ozonide ion rapidly decomposes to produce oxygen and hydroxyl radicals. The hydroxyl radicals decompose ozone further, producing more superoxide ions, which enter into the cyclic reaction. The stability of dissolved ozone is affected by pH, ultraviolet (UV) light, ozone concentration, and the concentration of radical scavengers.

Ozone is recognized as an effective means for the treatment of water, industrial effluents and sewage. Ozonation is used extensively in Europe for drinking water treatment; there are well over 1000 drinking water treatment plants using ozone in Europe. More than 200 drinking water treatment plants in North America presently use ozone (IOA News, 1997; Debevec, 1990; Fressonet-Chambarlhac et al., 1983; Glaze, 1987). Ozonation is used in over 40 wastewater treatment plants in the United States (Masten and Davies, 1994). While ozone has been used for odor removal in municipal wastewater treatment plants, it has not, to our knowledge, been used for odor control for stored livestock waste facilities. Ozonation has the potential to reduce odors in stored livestock waste by (1) controlling the rate of production of odorous metabolites by killing the odor-causing bacteria and (2) oxidizing odorous metabolites produced as a result of fermentation. The ozonation of agricultural wastes could, potentially, reduce the

likelihood of contamination of groundwater and surface run-off by pathogenic bacteria and viruses that are often found in agricultural wastes. As ozone is a very strong oxidant which attacks the cell wall and the cytoplasmic membrane of the cell, pathogens can be inactivated. Thus, ozone can be used not only to reduce the concentration of odor-causing chemicals, some of which are harmful to the animals, but also to reduce the numbers of pathogens present in the water.

1.6 Research Hypotheses

In this research we evaluated, in a bench-scale and pilot-scale systems, the effectiveness of ozone for the treatment of swine manure slurry. The following hypotheses were tested:

1. The fermentation of manure slurries during storage results in an increase in the odor emanating from swine waste.
2. Odorous gases, such as ammonia and hydrogen sulfide, are expected to be released from stored manure waste.
3. Ozone, with its strong oxidation power, is very effective in removing malodorous chemical compounds from fresh or stored manure waste, and the ozone-treated manure waste will no longer be malodorous.
4. Ozone can effectively kill the bacteria and pathogens that normally exist in untreated swine waste.
5. The mass transfer or absorption of ozone in the liquid slurry can be enhanced by the proper design of the pilot treatment system. In other words, the applied ozone dosage can be specified that will treat manure waste to an acceptable level.

6. Temperature affects the rate of the reaction between ozone and malodorous components. Thus, adjusting ozone dosages will be necessary to remove the odor at different temperatures.
7. The combination of hydrogen peroxide with ozone (advanced oxidation process), thus generating more reactive radicals, will remove odorous compounds more efficiently than the ozonation process alone.
8. A model including mass transfer and oxidation kinetics can be developed and used to predict the disappearance of malodorous compounds in the swine manure. The concentration of COD (Chemical Oxygen Demand) can be an indicative parameter of the consumption of ozone in the treatment system.

1.7 Research Objective

This study was conducted in four phases. The first phase focused on laboratory studies to investigate the effect of ozonation on the physical, chemical, biological and odor characteristics of the swine waste slurry. Changes in the characteristics of the untreated manure waste during storage were studied. In the second phase, we designed and constructed a pilot-scale ozonation system and tested it in a field situation to develop and demonstrate the technology that is appropriate for commercial swine operation. In the third phase, mass transfer theory was explored to develop the model that could be used to describe the transport of ozone in the semi-batch reactor. In the fourth phase, the kinetics and the reactions of ozone with five malodorous compounds that exist in the swine manure (phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole) were investigated. In addition, the effect of physical and chemical parameters on ozonation process was

determined at this phase. Finally, a model combining mass transfer and oxidation kinetics was developed to predict the fate of phenolic and indolic compounds during ozone treatment in a semi-batch reactor.

1.7.1 Specific Aims: Phase I

(1) To characterize changes in the characteristics of the manure slurry that occurs during the fermentation in the slurry storage pit. Changes in the number of microorganisms, including aerobes, anaerobes, coliforms, *E. coli.* and coliphage, and in the physicochemical characteristics of the stored manure slurry were investigated.

(2) To study the effect that storage of the wastes (prior to treatment) has on the odor of the waste and how length of storage affects the efficacy of ozonation.

(3) To determine the effect of ozone (applied dosage of 1 g ozone per liter waste) on the physicochemical and biological characteristics and the odor of the swine waste.

(4) To determine if the malodor reoccurs upon storage of the ozone-treated swine manure.

1.7.2. Specific Aims: Phase II

(1) To design, construct and test the pilot-scale ozonation system. The mass-transfer experiment was conduct to determine the mass transfer of ozone into the liquid.

(2) To evaluate the effect of ozonation on the physicochemical and biological characteristics of fresh and stored swine manure waste using the pilot-scale system.

(3) To determine the minimum dosage of ozone required to achieve an acceptable level of odor reduction.

(4) To compare the efficiency of using advanced oxidation process, such as combined treatment of hydrogen peroxide and ozone, and ozonation process alone. The optimal ratio of applied dosage between hydrogen peroxide and ozone was also determined by observing the reduction of odor, concentrations of phenolic and indolic metabolites, and numbers of microorganisms.

(5) To determine the effect of water temperature on the ozonation process.

(6) To conduct an economic evaluation of the treatment process.

1.7.3 Specific Aims: Phase III

(1) To develop a mass-transfer model that can predict the mass-transfer coefficient and partition coefficient of ozone in a semi-batch reactor.

(2) To determine the effect of temperature, flowrate, pH, and ionic strength on the mass-transfer coefficient and partition coefficient.

1.7.4 Specific Aims: Phase IV

(1) To determine the stoichiometric factor and reaction rate constants for the reactions of ozone with five target compounds, including phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole, at different pH values.

(2) To understand the effect that competition for ozone has on the reactivity of these compounds.

(3) To investigate the effect of other substances that are naturally present in the swine manure, and which have a low reactivity with ozone, on the oxidation of the target compounds. These substances include ammonia and VFAs.

(4) To formulate a kinetic model for predicting the removal of target compounds in synthetic and real manure.

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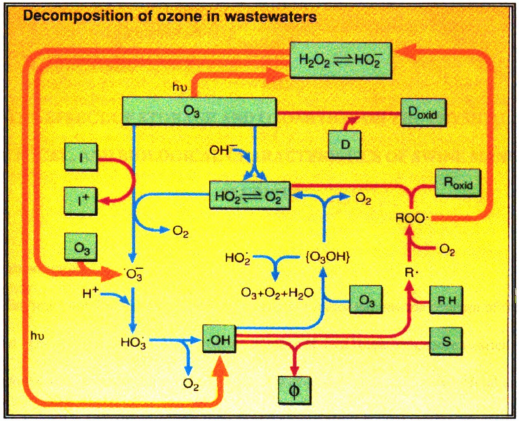

The dark reactions that occur in "pure" water are shown in blue. The additional dark reactions that may occur when reactive solutes are present are shown in red. D is a compound that, when it reacts with ozone directly with ozone; I is a compound that, when it reacts with ozone via an electron transfer reaction, produces the ozonide radical ion (i.e., it is an initiator of ozone decomposition); RH is a promoter of ozone decomposition; and S is an ·OH scavenger. Propagation of the chain reaction may occur by the reaction of RH with ·OH to from an organoperoxide radical, ROO·. Termination of the chain reaction may occur via reaction of S with ·OH to form a secondary radical ϕ, which does not participate in the chain reaction. Additional reactions that occur in O_3/H_2O_2 and/or O_3/UV system are shown in yellow.

Figure 1.1 Decompostion of Ozone in Wastewaters

Chapter 2

THE EFFECT OF STORAGE AND OZONATION ON THE PHYSICAL, CHEMICAL, AND BIOLOGICAL CHARACTERISTICS OF SWINE MANURE SLURRIES

2.1 Introduction

Environmental pollution by livestock waste is a major nationwide concern of the animal agriculture industry. An increasing number of civil litigations, more restrictive township ordinances, demands for the protection of public health and new Federal and State regulations governing surface run-off and groundwater contamination necessitate that the livestock industry take action to control the environmental problems associated with livestock operations.

Odors emanating from livestock operations are the major source of complaints against livestock farms. As livestock production has moved to larger and more intensive production units, odor complaints from residents of surrounding communities have increased (Ritter, 1989). Innovative methods to control, reduce or eliminate odors associated with livestock operations must be developed and employed to ensure the future viability of the industry.

Ozonation has the potential to reduce odors in stored livestock waste by (1) controlling the rate of production of odorous metabolites by killing the odor-causing bacteria and (2) chemically oxidizing of odorous metabolites produced during fermentation. As ozone is a very strong oxidant that attacks the cell wall and the cytoplasmic membrane of the cell to inactivate the organism, ozone can also be used to reduce the concentration of odor-causing chemicals and to reduce the numbers of pathogens present in the waste water, making it safer for reuse. The ozonation of agricultural wastes has the potential to reduce the likelihood of contamination of groundwater and surface run-off by pathogenic bacteria and viruses that are ubiquitous in agricultural wastes.

In the study presented in this chapter no attempt was made to optimize the mass transfer of ozone into the reactor. As such, a significant fraction of the applied ozone dosage may be wasted. Manure slurries were stored anaerobically for 12 weeks. Over these weeks the changes were measured in physical, chemical and biological characteristics of the swine manure slurry. Each week a portion of the manure slurry was ozonated and the effect of ozonation was evaluated. Since swine manure slurry is typically held (prior to land application) for approximately 3-12 months, it was imperative that we determine if ozonation could be applied anytime during storage and how long odors remain surpressed during storage at the ozone treated swine manure slurry.

2.2 Materials and Methods

2.2.1 Manure Collection and Storage Test

Fresh swine manure slurry was collected from the Michigan State University Swine Research and Teaching Farm, East Lansing, MI. Four 100-kg finishing pigs, which were fed a standard corn-soybean finishing ration, were placed in a crate with a slotted floor, which allowed for the collection of fresh manure. The manure was collected over a five-day period by flushing a small amount of water to wash the manure, which had adhered to the slotted floor into a collection tray. Upon collection, the manure was stored at 4 ^{o}C to minimize any changes that might occur in its physicochemical and biological properties. Approximately 150 liters of manure slurry was collected.

A tank was used to simulate the processes that occur during storage of the slurry in the storage pits. The tank was constructed of PVC and had a capacity of forty gallons (Figures 2.1 and 2.2). Four sampling ports were located along the side of the tank at intervals of 21 cm, dividing the 90 cm-deep tank into 4 zones (with zone 1 being the uppermost region and zone 4 the bottom). This allowed for the investigation of the effect of the length of storage and tank depth on the physical, chemical and microbiological properties of the waste. During storage in this tank the manure was maintained at 20-25 ^{o}C. The manure was stored for a period of 3 months and sampled once per week for BOD, COD, phosphates, sulfides, sulfates, odor, solids, phenolic and indolic metabolites, volatile fatty acid concentrations, total aerobic and anaerobic bacterial numbers, total coliforms, and total coliphage numbers. To capture the ammonia and hydrogen sulfide as it volatilized from the slurry, cylinder air was continually passed across the headspace of the tank at a flow rate of 10-15 mL/min. The effluent air was then passed into solutions

of boric acid and zinc acetate to trap the ammonia and hydrogen sulfide from the air stream.

2.2.2 Ozone and Ozonation Test

Ozone was generated from dried pure oxygen by corona discharge using an ozone generator (Model T-408, Polymetrics Inc., San Jose, CA), which produced an ozone concentration of 1.3% (by volume) in the oxygen gas stream. The oxygen was dried using a molecular sieve (S/P Brand #G5301-21). A 500 mL gas-washing bottle was used as the ozonation reactor (Figure 2.3). Ozone was bubbled through a porous diffuser into 300 mL of the manure slurry. The manure slurry was treated for approximately 25 minutes at a flowrate of 150 mL/min until an ozone dosage of 1 g ozone/L of manure was achieved. The gaseous ozone concentration in the inlet stream was determined spectrophotometrically. The absorbance of ozone was measured in a 2-mm flow-through quartz cuvette at the wavelength 258 nm. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ was used to convert absorbances to concentration units (Nowell and Hoigné, 1988). To reduce foaming caused by the bubbling of ozone into the slurry, 1 mL of anti-foaming agent, Anti-foam 289 (Sigma Co., St. Louis, MO) was added to the slurry prior to ozonation. Between ozonation experiments the porous diffuser was cleaned by purging nitrogen through the frit, which was submerged in a mixture of water and hydrogen peroxide (85:15).

2.2.3 Odor Evaluation – Olfactometry

A dynamic dilution binary scale olfactometer (ASTM E544-75, IIT Research Center, Chicago, Illinois), which employs 1-butanol as the standard odorant, was utilized to quantify the odor intensity from untreated or ozonated manure samples (see Figure 2.4). Six participants were asked to smell the samples, presented in a random order, and match the intensity of the odor of the samples with that coming from sensory ports that discharged 1-butanol vapor at various concentrations.

2.2.4 Chemical Analysis

Chemical oxygen demand (COD) determinations were made using prepackaged Hach vials (0-15,000 mg/L). Total solids and biological oxygen demand (BOD) determinations were made according to *Standard Methods for the Examination of Water and Wastewater* (1992). Phosphate and sulfate were determined using ion chromatography. Samples were pretreated by centrifugation at 6,0000 G for 20 minutes and filtration through a 0.22 μm glass filter to remove the solid material, thereby reducing the possibility of clogging the ion chromatographic columns. Ammonia was measured with an ammonium electrode connected to a pH meter. Quantification was accomplished using the method of known addition. Sulfides were measured using a purge and trap method (Barth and Polkowski, 1974), employing nitrogen gas to purge hydrogen sulfide out of the solution. All sulfide species were first converted to hydrogen sulfide by the addition of 10 mL concentrated sulfuric acid to lower the pH of the samples to 2. The trap solution was prepared by adding 15 mL of zinc acetate (2N) to 135 mL deionized water. After trapping, the sulfides were determined according to Standard Methods for

the Examination of Water and Wastewater (1992). The concentrations of volatile fatty acids (namely acetate, propionate, butyrate, iso-butyrate, valerate, iso-valerate) were determined by gas-liquid chromatography (Model 5840A, Hewlett-Packard Inc., Avondale, PA). One mL of concentrated hydrochloric acid was added to 10 ml of slurry sample. After the mixture was agitated in a vortex mixer, it was centrifuged at 11,950 G for 10 minutes to remove all particulate matter. The supernatant was injected directly into a glass column packed with Supelco GP 10% SP-1000/1% H_3PO_4 on 100/120 Chromosorb W AW. Nitrogen was used as a carrier gas at a flow rate of 50 mL/min. The initial injection temperature was held 110 °C for 3 minutes; the temperature was ramped at 5 °C/min to 170 °C for 30 minutes.

The bacterial degradation of tyrosine and tryptophan in the intestinal tract and during storage of swine manure results in the production of several odorous volatile phenolic and indolic metabolites. These include phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole (see Table 2.1). The concentrations of these metabolites were quantitatively determined in the swine waste slurry by gas-liquid chromatography (Yokoyama et. al, 1982). Samples (10 mL) were adjusted to pH 4.0 with concentrated sulfuric acid and extracted twice with 30 mL of methylene chloride. The extract was evaporated down to a volume of approximately 1 mL using a rotary evaporator, transferred to a screw cap vial, and made up to 4.0 mL with methylene chloride. Two µL were analyzed directly by GC-FID, using a stainless steel column (2 m×2 mm) packed with 21% Carbowax 4000 and WAW-DMCS (60/80 mesh). The oven temperature was programmed as follows: held at 100 °C

Table 2.1 The Structure of the Phenolic and Indolic Compounds

1. Phenol

2. *p*-Cresol

3. *p*-Ethylphenol

4. Indole

5. Skatole

for the first 1 min after injection, ramped at 10 °C/min to 125 °C and held for 8 min, then ramped at 2 °C/min to 155 °C. The total run for each sample was 26.5 min. The Injection port and detector temperatures were maintained at 200 and 250 °C, respectively.

2.2.5 Microbiological Analysis

Total aerobic bacterial numbers were determined by the pour plate method using Sterile Nutrient Agar. Manure samples were serially diluted in sterile 0.1% peptone water and 0.1 ml of each dilution was inoculated on agar pour plates. Plates were incubated at 39 °C for 48 hrs, then enumerated for emergent colonies. Total anaerobic bacterial numbers were determined by the anaerobic roll tube technique of Hungate (1950). A prereduced medium of GCSX (glucose, cellobiose, starch, and xylose) plus clarified ruminal fluid (20%) was prepared with 1.8% agar and autoclaved. Nine mL of the media were added to the tubes and the sterile media was stored at 45-50 °C until it was used. Samples were serially diluted in anaerobic dilution media (mineral solution I, 11.2 mL; mineral solution II 11.2 mL; resazurin, 0.3 mL; distilled water, 256.3 mL). Dilutions were inoculated into the tubed GCSX medium, immediately rolled under cold water to solidify the agar, and allowed to set for 10 min. After the rolled agar tubes were incubated at 39 °C for 48 hrs, the emergent colonies were enumerated.

Total coliforms and *Escherichia coli* were determined by the Most Probable Numbers Method (Hungate and Fletcher, 1957). Slurry samples were serially diluted in EC broth medium, containing fermentation gas tubes, and incubated at either room temperature or in a 45 °C water bath. Growth in the highest dilution of the EC broth

medium (4 replicates) at room temperature was used to estimate total coliform numbers. Growth at 45 ^{o}C with gas production was used as an estimate of *E. coli* numbers.

Coliphage determinations were made by the IPTG/X-gal method (Ijzerman and Hagedorn, 1992), which involved the use of *E. coli* C inoculated from ATCC strain 13706 into 10 mL sterile LB broth containing glycerol (10%) and incubated at 37 ^{o}C until an O.D. (at 520 nm) of 0.35 was obtained. One and one-half mL of *E. coli* culture was added to 18 mL of modified LB agar at 50 ^{o}C (modified by adding ammonium nitrate, NH_4NO_3, 1.6g/L; strontium nitrate, $Sr(NO_3)_2$, 1.21g/L; and agar, 15g/L). The manure sample (8 mL) was centrifuged at 2400 rpm for 80 min, and the supernatant obtained was filtered twice by using 0.45 μm and 0.22 μm syringe filters. One mL of filtered sample was then serially diluted into 9 mL SM buffer. Three mL of the filtered and diluted sample containing bacteriophage were added along with 66 μL isopropyl-β-D-thiogalactoside (IPTG) (200 mg/mL) and 360 μL 5-bromo-4-chloro-3-indolyl-β-D-galactopyranoside (X-gal) (10 mg/mL) dissolved in dimethylformamide. The solution was swirled to mix the components and evenly distributed onto two 100×15mm Petri dishes. After the agar had hardened, the plates were inverted and incubated at 37 ^{o}C. Pale blue plaques appeared after 4 hrs and the color intensified as the plaques developed (after 7 to 8 hrs). Each plaque produced was assumed to have initiated from a single baceriophage. The plaque numbers were enumerated after 16 hrs of incubation.

2.3 Results and Discussion

The storage of the swine manure slurry was followed over a three-month period from June 12 through September 4, 1995. The experimental studies were divided into two parts: those pertaining to storage and those on the ozonation of the manure slurry.

2.3.1 Storage Experiment

Gas phase analysis: The release of ammonia and hydrogen sulfide from the surface of the stored manure is summarized in Figure 2.5. The concentration of ammonia reached its maximum concentration in the 4th week then dropped off to a lower and more constant level for the remaining test period. The concentration of hydrogen sulfide was erratic during the first seven weeks, but then increased steadily during the last four weeks of the experiment. The final discharge achieved was 63 mg. The total mass of ammonia released during 12-week storage (ca. 30 mg) was much less the total mass of hydrogen sulfide emitted (ca. 360 mg).

Liquid phase analysis: The pH of the fresh manure was initially 8.8. After 2 weeks of storage the pH of the slurry decreased to about 7.2 and then remained relatively constant for the remaining 10 weeks (Figure 2.6). There was little variation in the pH of the manure slurry in each of the four zones during the entire storage period. The production and accumulation of acidic intermediates as a result of the decomposition of organic compounds is probably the major reason for the initial decrease in pH. This is consistent with our observation that the concentrations of volatile fatty acids increase during storage. Sufficient buffering capacity may have prevented any further decrease in pH. The

buffering capacity may, in part, originate from alkaline metabolites produced from the metabolism of proteins.

The concentration of ammonia nitrogen in the swine manure steadily increased in all of the four zones during the first seven weeks of storage (Figure 2.7). The initial concentration of ammonia nitrogen ranged from 3300-3400 mg/L (week 0) to 3600-3800 mg/L (week 7). The ammonia concentration was consistently higher in zone 4 than in the other zones. This increase is presumed to be the result of the production of ammonia nitrogen from the microbial degradation of nitrogenous organic compounds. After week 7, the ammonia concentrations in all 4 zones remained essentially constant at approximately 3600-3700 mg/L.

The concentration ranges of BOD_5, COD and total solids of the stored manure slurry were respectively 8,000-26,000 mg/L, 18,000-58,000 mg/L, and 7,000-35,000 mg/L (Figures 2.8-2.10). The solids contribute most of the organic material to the slurries. Therefore, the concentrations of organic material (BOD_5 and COD) were normalized using the solid concentrations. The ratio of COD to total solids was essentially unchanged over 12 weeks of storage and within the range of 2 ± 0.5. Evans et al. (1979) reported a COD/TS ratio for untreated slurry of 1.3. The ratio of BOD_5 to COD observed in the upper three zones increased during the first four weeks of storage from 0.45 to 0.6 (Figure 2.11), substantiating the conclusion that during this initial period there is a conversion of organic material to a more biodegradable form. This observation is also substantiated by the work of Williams and Evans (1981), which showed that an increase on BOD_5 was due to the production of more biodegradable soluble intermediates from

the degradation of higher molecular weight components such as fiber and protein. The values of BOD_5 to COD observed in zone 4 appeared to be almost random.

Manure slurry is commonly recycled as fertilizer because of its high nutrient content. These nutrients include phosphate and nitrogen. The concentrations of nitrate could not be accurately measured due to the presence of interfering substances in the manure slurry. The effect of storage on the phosphate concentration was quantified. The concentration of soluble phosphate in the upper three zones remained essentially constant over the course of the experiment, suggesting that phosphate was not being released during the storage process (Figure 2.12). The concentration of soluble phosphate in the bottom (zone 4) increased from 520 mg/L to 1,100 mg/L during the first six weeks, then subsequently decreased to 590 mg/L. The initial increase is thought to be due to the release of soluble phosphate from the solid material. The latter decrease may be due to further settling of the solid material below the sampling port and insufficient mixing of any phosphate released from those solids. Alternatively, it could be due to a decrease in metabolic activity or a change in the rate at which phosphate was released from the solids (possibly due to the early release of the more easily metabolized fraction, with what remained being much more difficult to metabolize).

The concentration of sulfate was also monitored in the storage tank. It was found that the concentration of sulfate remained relatively constant at approximately 500 mg/L for the first 8 weeks, then decreased to < 100 mg/L by the 12^{th} week (Figure 2.13). Concurrently, in the last 4 weeks, there appeared to be an increase in the ratio of sulfide concentration to the total solid concentration (Figure 2.14). This is thought to be due to

the utilization and transformation of sulfide by the sulfur-reducing bacteria that likely began to proliferate after the 8th week.

Volatile fatty acid (VFA) concentrations were determined from a composite sample taken from the four zones. Acetate was found to be the predominant VFA, followed in decreasing order by propionate, butyrate, iso-butyrate, iso-valerate, and valerate (Table 2.2). This is consistent with the observation of Cooper and Cornforth (1978). Total VFA concentrations peaked around the 10th week (Figure 2.15). Based upon the work of Spoelstra (1979), VFA accumulation is likely to be due to the production of VFAs during the anaerobic degradation of fiber (mainly cellulose and hemicellulose) and protein. The subsequent decrease is thought to be due to the consumption of VFAs by methanogenic bacteria. This result was verified by the observation of lots of gaseous bubbles accumulated at the upper zone of the storage tank.

Phenols (phenol, *p*-cresol, and *p*-ethylphenol) and indoles (indole and skatole) are regarded as important malodorous components in swine waste slurry (Schaefer, 1977; Spoelstra, 1977; Williams and Evans, 1981; Williams, 1983). The concentrations of phenolic and indolic metabolites were analyzed from composite samples from the 4 zones of the fermentation reactor. In the raw manure, *p*-cresol predominated, followed in decreasing order by phenol, *p*-ethylphenol, and skatole (Figure 2.16). The concentration of *p*-cresol peaked around the 6th week of storage. The concentration of phenol did not change during storage. The concentration of *p*-ethylphenol increased rapidly during the first week storage then remained constant. The concentration of indole was below detection limits. The concentration of skatole rose until the fourth week, then gradually reduced to non-detectable levels after 10 weeks storage.

Table 2.2 The Concentrations of Each Volatile Fatty Acid during 12 Weeks of Storage Period

Time (weeks)	Acetate (mg/L)	Propionate (mg/L)	Butyrate (mg/L)	i-Butyrate (mg/L)	Valerate (mg/L)	i-Valerate (mg/L)
0	10060	2170	1070	240	290	300
1	10410	2310	1320	260	240	290
2	10380	2240	1320	270	240	300
3	10500	2250	1350	280	240	300
4	10600	2240	1360	310	260	310
5	10270	2300	1340	320	250	320
6	10280	2290	1310	330	240	320
7	10310	2320	1280	340	240	330
8	10730	2310	1120	340	240	330
9	12000	2510	390	360	240	350
10	11990	2520	300	370	250	360
11	10600	2480	260	380	250	370
12	10820	1350	230	360	230	360

As shown in Figure 2.17, the odor intensity of the swine manure tended to increase with storage time (although the variations in intensity for any specific time were large). The intensity of the odor was also found to increase with tank depth (over the entire course of the experiment). As such, it is apparent that anaerobic storage results in an increase in odor intensity, most likely due to the formation of odorous chemical compounds resulting from microbiological reactions.

Numberous attempts have been made to relate the odor intensity to the specific chemical characteristics of manure slurries. Barth et al. (1974), Williams (1984), Carney and Dod (1989), and Misselbrook et al. (1993) related the concentrations of specific malodorous compounds (along with other chemical compponents) to the odor intensity by using category scaling and ratio scaling:

where k_1, k_2, a, and b are empirically determinant constants. Although the concentration of ammonia nitrogen in the stored swine manure slurry increased with the storage time, the odor intensity determined by olfactometry test was found to have a low correlation with ammonia nitrogen for stored swine manure slurry (Figure 2.18). The regression coefficients, R, for category and ratio scalings were found to be 0.34 and 0.41, respectively. However, the ratio of sulfide to total solids concentration seemed to be a better indicator of odor intensity than ammonia nitrogen (Figure 2.19), with regression coefficients for category and ratio scaling of 0.64 and 0.61, respectively. The mathematical expressions for these relationships can be written as:

$$\text{Odor intensity (ppm of 1-butanol)} = 262.82 \ln(\text{Sulfides/TS}) + 2909$$

$$\text{Odor intensity (ppm of 1-butanol)} = 7129.5(\text{Sulfides/TS})^{0.28}$$

2.3.2 Ozonation Experiment

For the ozonation experiments, equal volumes of manure slurry were taken from each of the four zones of the fermentation reactor and mixed. The composite sample was then ozonated at a dosage of 1 g ozone per liter slurry. Following ozonation, the original (control) and ozonation samples were analyzed to evaluate the efficacy of ozone for the reduction of odor along with evaluating the changes in the physical, chemical, and microbiological properties of the slurry.

Ozonation resulted in an increase in the pH of the swine manure slurry (Figure 2.20). Similar results were obtained by Watkins et al. (1997). After bubbling oxygen into the

swine manure (pH=6.5), Watkins et al. (1997) found that the pH increased to 7.1. In our study, sparging with helium resulted in an increase in the pH of the manure slurry from 7.6 to 8.7. Ozonation resulted in an increase from 7.6 to 8.1. The increase in pH upon sparging with oxygen or helium is thought to be due to the volatilization of VFAs. However, during ozonation, both the VFA volatilization and VFA generation by oxidization of its precursors are likely to occur. Apparently, the formation of VFAs is significant as the concentration of total VFAs was observed to increase upon ozonation (Figure 2.21) and the pH that is observed after ozonation is lower than that observed when sparging with helium was used (8.1 vs. 8.7). Additionally, when the slurry that had previously been sparged with helium (pH=8.7) was ozonated the pH was 8.4 (rather than 8.1 without sparging as a pretreatment method).

The concentration of sulfide decreased as a result of ozonation (Figure 2.22), whereas the concentration of sulfate increased (Figure 2.23). This phenomenon indicates that the sulfides are easily oxidized by ozone and transformed into sulfate. A mass balance approach was used to try to relate the conversion of sulfide to sulfate. However, the increase in mass of sulfate exceeded, in most cases, the mass of sulfides removed from the system by ozonation. Thus, there appears to be an additional source of sulfate beyond the oxidation of sulfides by ozone. The additional sulfate formed may be due to the oxidation of sulfur-containing metabolites.

A comparison of the odor intensity of the untreated and ozonated samples demonstrated the ability of ozone to significantly reduce the odor of the swine manure slurry (Figure 2.24). The odor intensities of the slurries were all reduced to approximately the same level, irrespective of the initial odor intensity of the untreated

samples. There was also less variation in the measurements of odor intensity of the ozonated samples (as compared to the raw samples), suggesting that the perception of reduced intensity was much more consistent among the six panelists. Based upon these results, the efficacy of ozonation is independent of the initial odor intensity of the stored manure. The reoccurrence of odor was also assessed by storing the ozonated samples, which were open to the atmosphere, in a hood at room temperature. Although the odor intensity of these samples was found to increase gradually with time (Figure 2.25), the odor of these stored ozonated samples was much less offensive than that of the original raw manure slurry.

Ozonation of the swine manure slurry did not significantly modify the BOD_5, COD, solids, ammonia, and phosphate concentrations of the slurry (Figures 2.26-2.30). These results indicate that ozonation preserves both the organic concentration and the nutrient content of the manure slurry, the nutrient content is preserved. Ozonation did not significantly change the concentrations of the individual VFAs (Table 2.3).

The phenolic and indolic metabolites in the stored slurry samples were completely degraded by ozone a dosage of 1 g/L. It is thought that the change in the odor upon ozonation is likely to be due to the rapid oxidation of these simple aromatic compounds.

The effect of ozonation on the microbiological characteristics (e.g., aerobic and anaerobic bacterial numbers, total coliforms, total *E. coli* and total coliphage) of the slurry were evaluated. The numbers of total aerobes in the raw slurry (zero week) decreased by almost 50% after ozonation, while the numbers of total anaerobes decreased by about 25% (Figure 2.31). In the last 5 weeks of storage, ozone appeared to be less effective at reducing the numbers of total aerobes than in the early weeks of storage. The

Table 2.

Storage

Table 2.3 The Concentrations of Each Volatile Fatty Acid for Stored and Ozonated Swine Manure Slurry

Storage Weeks	(mg/L)	C_2	C_3	C_4	*i*-C_4	C_5	*i*-C_5
0	Raw	10,060	2,170	1,070	240	290	300
	Ozonated	10,500	2,260	1,190	230	230	280
1	Raw	10,410	2,310	1,320	260	240	290
	Ozonated	11,290	2,370	1,280	250	210	270
2	Raw	10,380	2,240	1,320	270	240	300
	Ozonated	10,920	2,230	1,260	270	210	260
3	Raw	10,500	2,250	1,350	280	240	300
	Ozonated	11,510	2,350	1,310	280	220	280
4	Raw	10,600	2,240	1,360	310	260	310
	Ozonated	10,740	2,240	1,270	280	220	280
5	Raw	10,270	2,300	1,340	320	250	320
	Ozonated	10,890	2,290	1,240	300	210	290
6	Raw	10,280	2,290	1,310	330	240	320
	Ozonated	11,360	2,410	1,290	330	210	310
7	Raw	10,310	2,320	1,280	340	240	330
	Ozonated	10,920	2,320	1,210	320	210	300
8	Raw	10,730	2,310	1,120	340	240	330
	Ozonated	11,150	2,350	1,070	340	210	310
9	Raw	12,000	2,510	390	360	240	350
	Ozonated	12,690	2,400	390	350	210	320
10	Raw	11,990	2,520	300	370	250	360
	Ozonated	12,650	2,520	280	350	210	320
11	Raw	10,600	2,480	260	380	250	370
	Ozonated	9,850	2,540	260	380	210	350
12	Raw	10,820	1,350	230	360	230	360
	Ozonated	9,810	1,610	240	380	210	350

total aerobes and aerobes in the raw, untreated swine manure slurry gradually decreased with time of storage, indicating unfavorable conditions for the growth of total aerobes and anaerobes in the storage system. Nevertheless, it is thought that some species of anaerobes such as sulfur-reducing bacteria proliferate during storage. After 7 weeks of storage, ozone became ineffective at reducing the number of total anaerobes. One explanation might be that unfavorable conditions in the reactor resulted in the sporulation of vegetative cells. These spores would be expected to be more resistant to ozone than the vegetative cells. The number of coliforms decreased with ozonation of swine manure slurry by a factor of 10-1000 (Figure 2.32). The number of *E. coli* decreased in the fresh manure substantially upon ozonation (from 50,000 to 0). However, the number of *E. coli* in untreated swine manure slurry declined to zero after 3 weeks of storage, so that by week 3 there was no difference in the numbers of *E. coli* in the untreated and ozonated slurries (Figure 2.33). Coliphage plaque numbers, which indicate of the presence of viruses, decreased significantly after ozonation (Figure 2.34).

2.4 Conclusions

In general, the production of malodors from swine waste manure is the combined effect of odorous compounds that are present in the fresh manure and those that accumulate due to the degradation of organic matter by anaerobic microorganisms during storage.

1. The storage of manure slurry resulted in (a) an increase in the concentration of sulfides per unit of total solids due to sulfate reduction by sulfur-reducing bacteria and

(b) an increase in the concentrations of ammonia nitrogen due to the mineralization of organic nitrogen.

2. The storage of manure slurry resulted in the accumulation of total volatile fatty acids during the first ten weeks of storage. The subsequent reduction in the concentration of VFAs during the final two weeks of storage was ascribed to the decomposition of acetate into methane and carbon dioxide by methanogenic bacteria.
3. Microbial populations of aerobes, anaerobes, and *E. coli* were found to decrease during storage, suggesting an unfavorable environment for these bacteria compared with that of the host. *E. coli* was undectable after 4 weeks of storage.
4. Ozonation (at a dosage of 1 g/L) is effective in reducing the concentrations of sulfides, phenol, *p*-presol, *p*-ethylphenol, and skatole in swine manure.
5. The soluble phosphate concentration did not change through ozonation, indicating the preservation of nutrient content.
6. The ozonation at a dosage of 1 g/L of fresh or stored swine manure reduced the odors to acceptable levels.
7. As the concentrations of total VFAs increased and ammonia remained unchanged upon ozonation, while the malodor was significantly reduced, it appears that neither VFAs nor ammonia contribute extensively to the malodor of the manure.
8. Ozonation is able to kill some of the indicator microorganisms such as coliforms, *E. coli* and coliphage. However, it does not provide a significant benefit in reducing the organic loading (as measured by BOD_5, COD, and VFAs).

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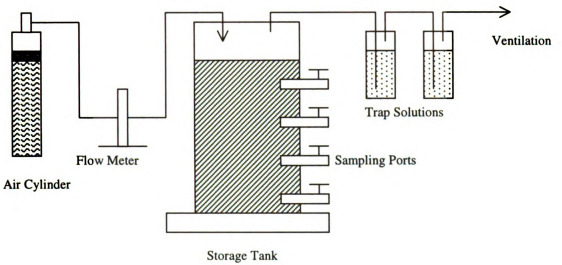


Figure 2.1 System Setup for the Storage Experiment

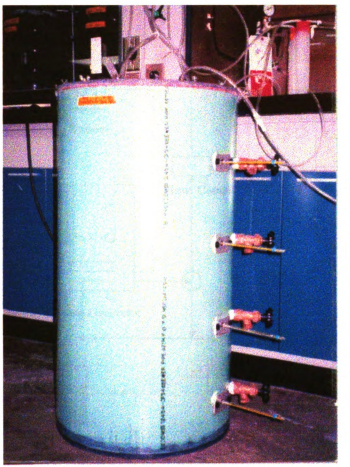


Figure 2.2 The photo of the Fermentation Tank for Storage Experiment

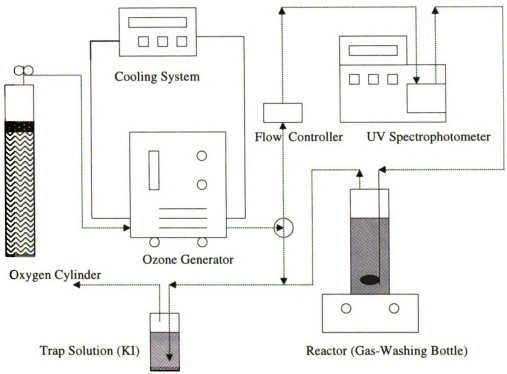


Figure 2.3 System Setup for the Ozonation Experiment

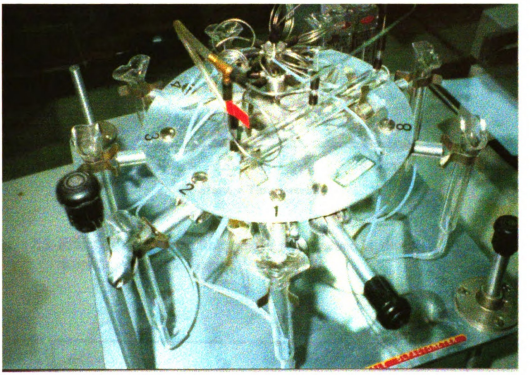


Figure 2.4 The Photo of the Dynamic Dilution Binary Scale Olfactometer

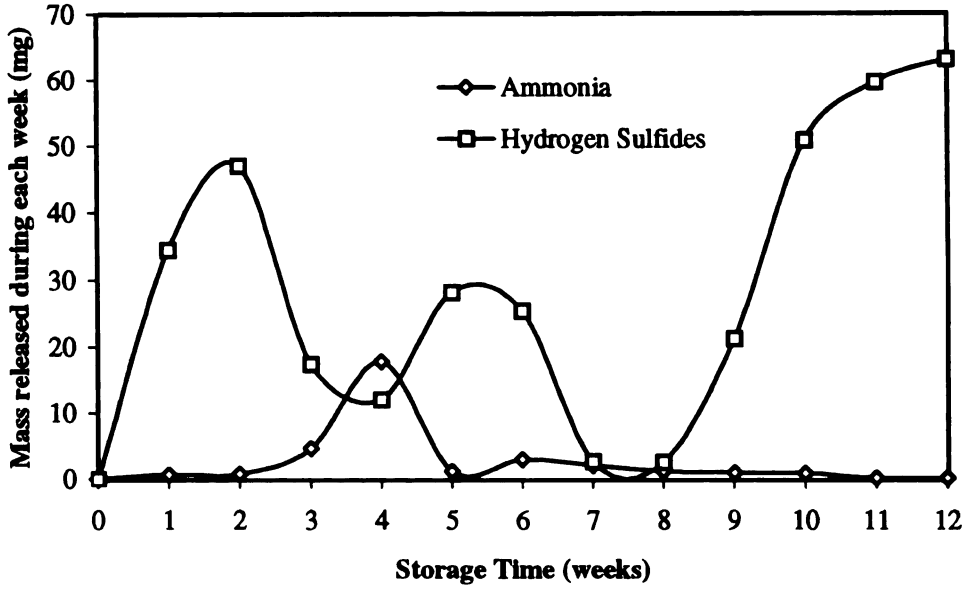


Figure 2.5 Effect of Time on the Release of Ammonia and Hydrogen Sulfide from Stored Swine Manure

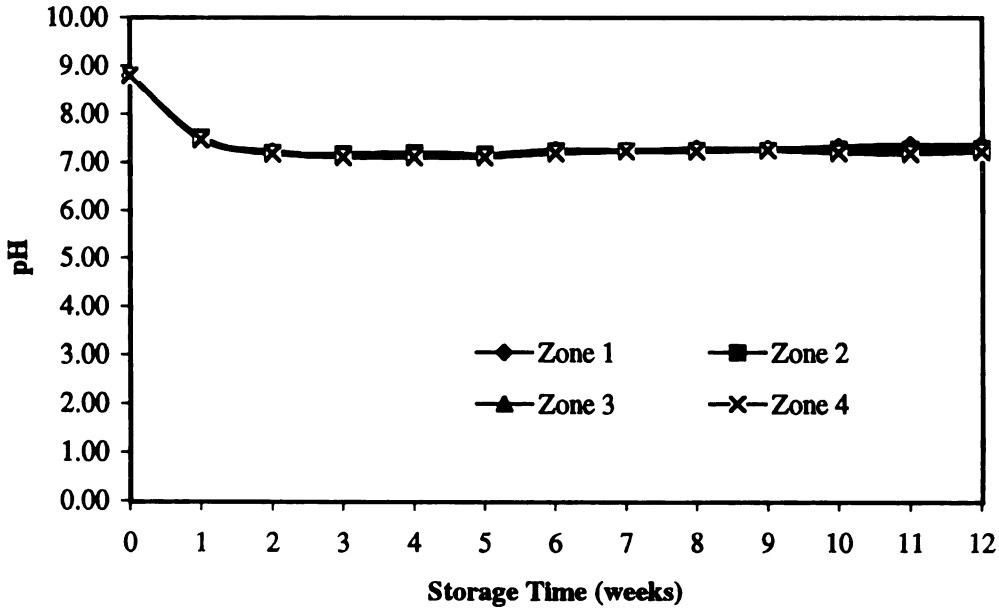


Figure 2.6 Effect of Time on the pH in Stored Swine Manure Slurry

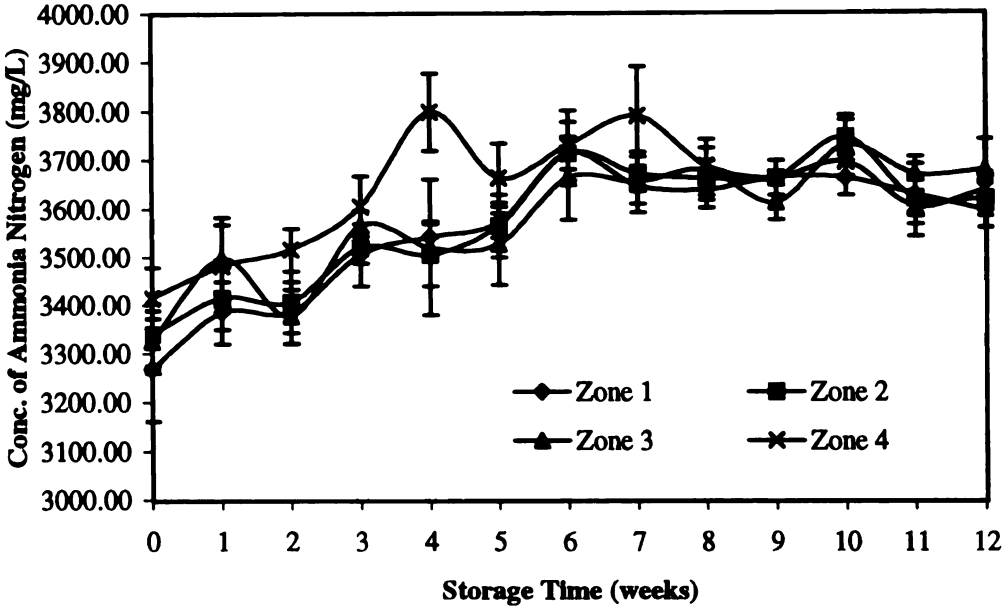


Figure 2.7 Effect of Time on the Concentrations of Ammonia Nitrogen in Stored Swine Manure Slurry

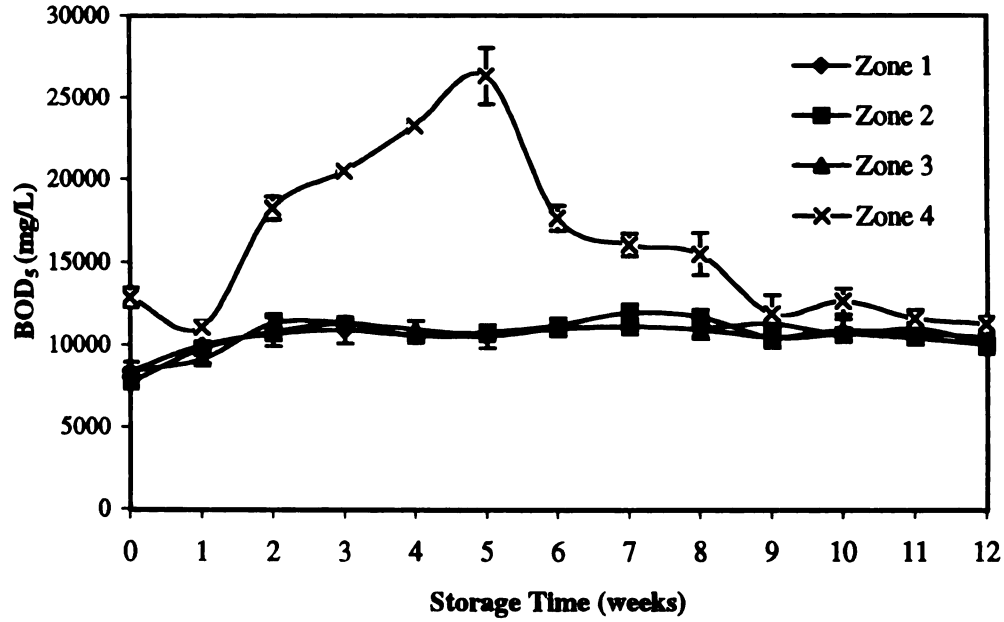


Figure 2.8 Effect of Time on the Concentrations of BOD_5 in Stored Swine Manure Slurry

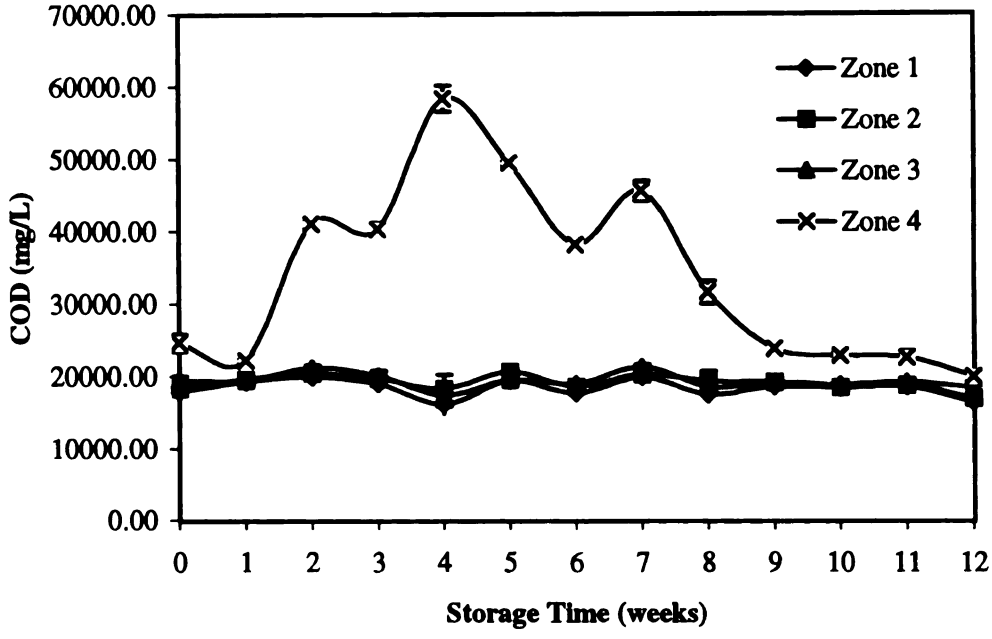


Figure 2.9 Effect of Time on the Concentrations of COD in Stored Swine Manure Slurry

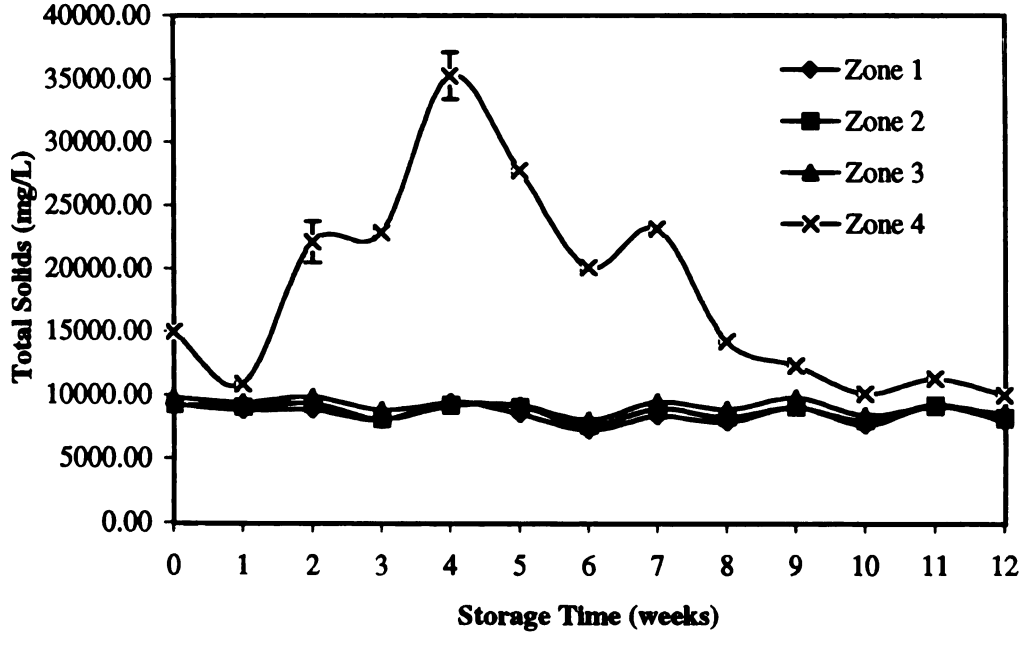


Figure 2.10 Effect of Time on the Concentrations of Total Solids in Stored Swine Manure Slurry

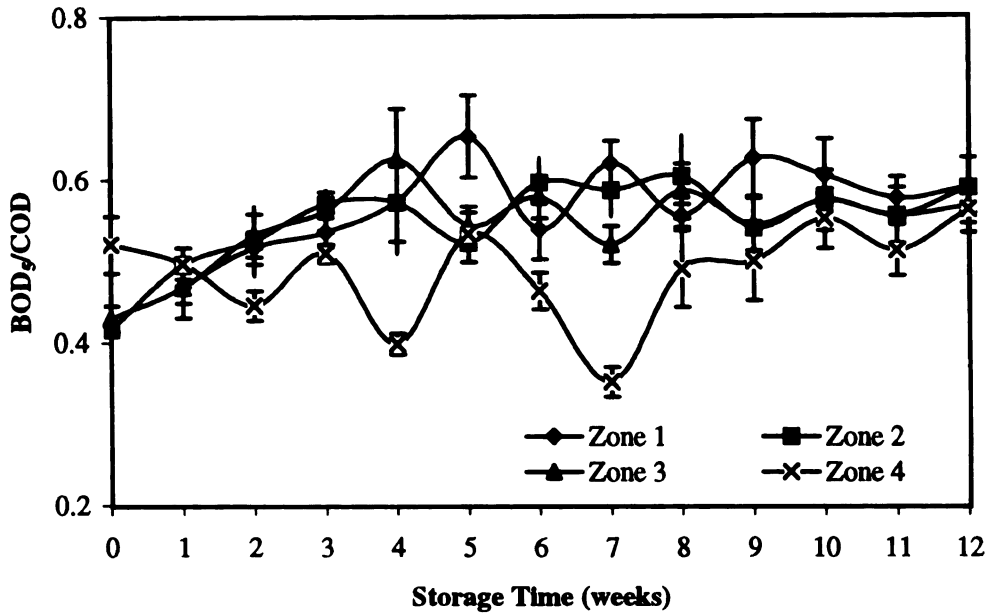


Figure 2.11 Effect of Time on the Ratios of BOD_5 to COD in Stored Swine Manure Slurry

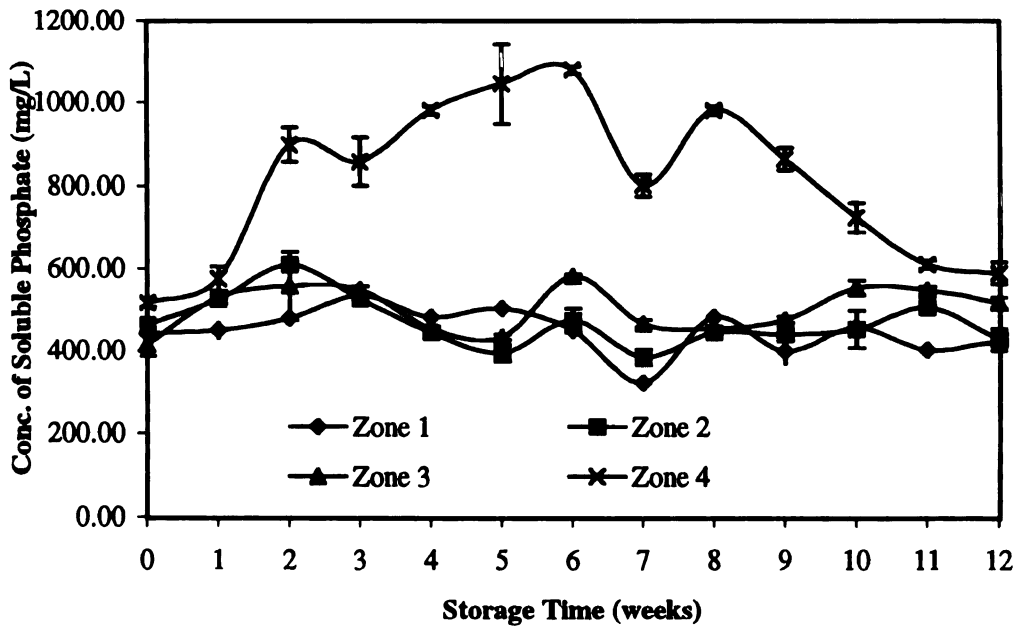


Figure 2.12 Effect of Time on the Concentrations of Soluble Phosphate in Stored Swine Manure Slurry

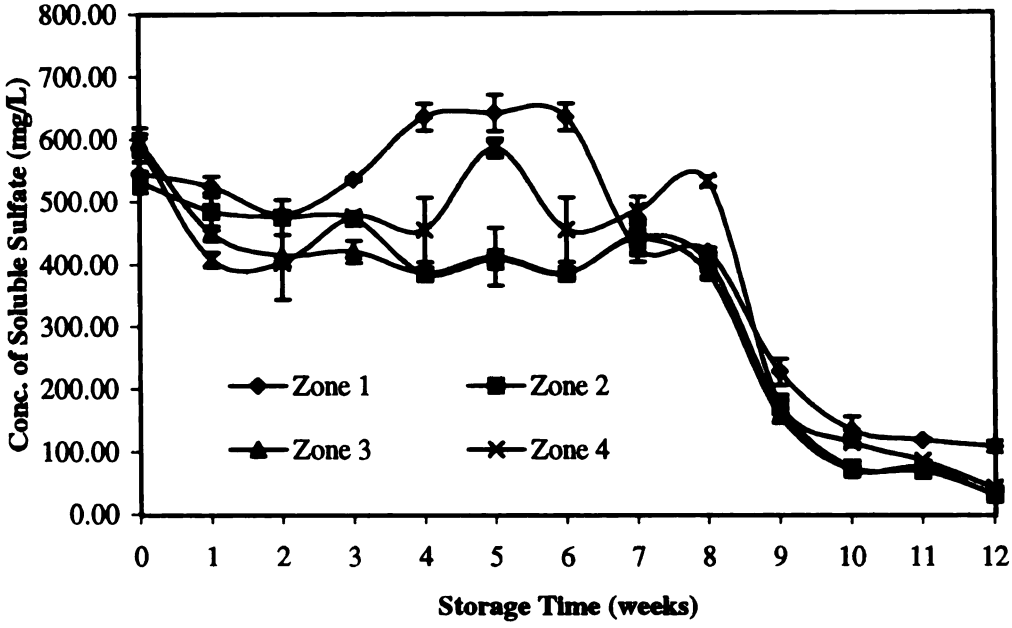


Figure 2.13 Effect of Time on the Concentrations of Soluble Sulfate in Stored Swine Manure Slurry

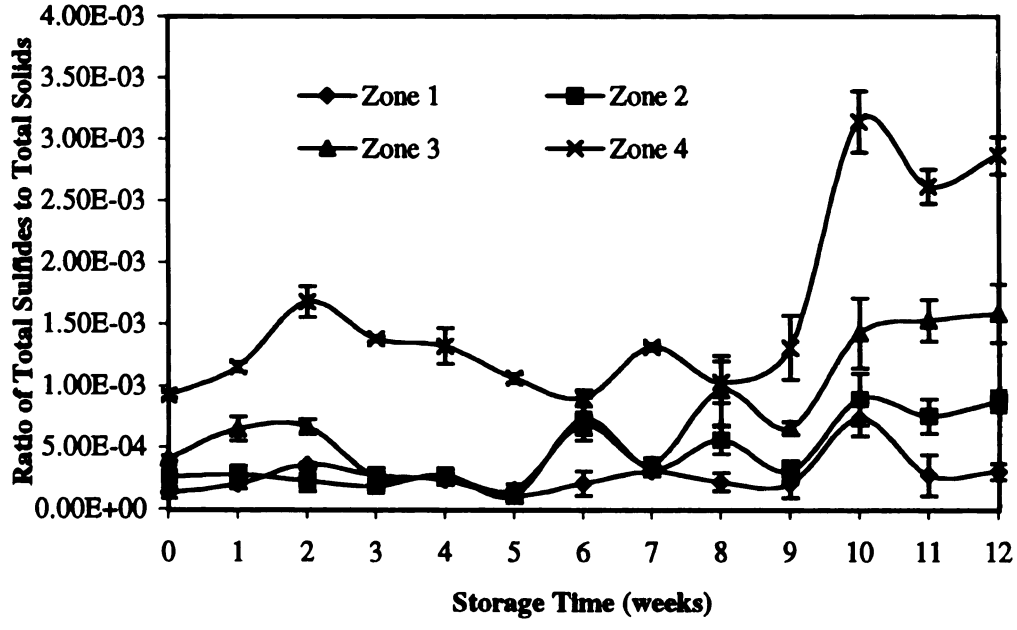
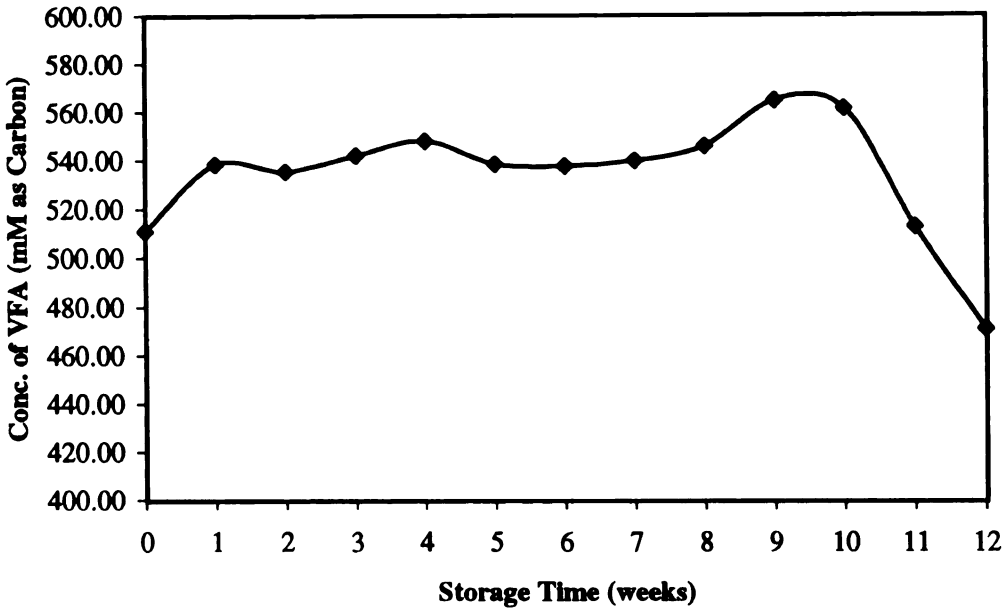


Figure 2.14 Effect of Time on the Ratios of Total Sulfides to Total Solids in Stored Swine Manure Slurry



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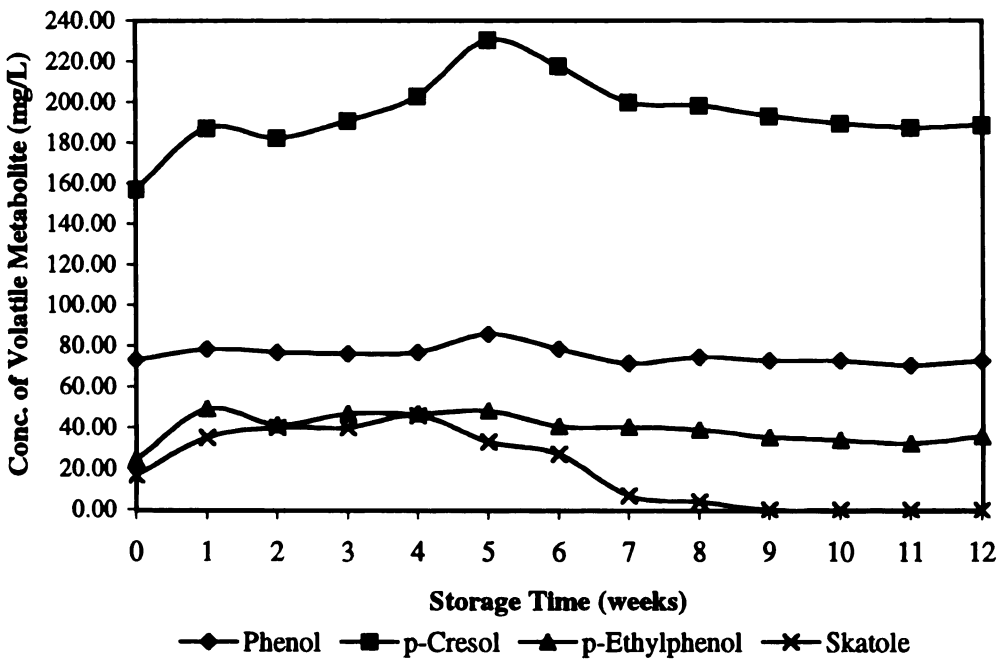

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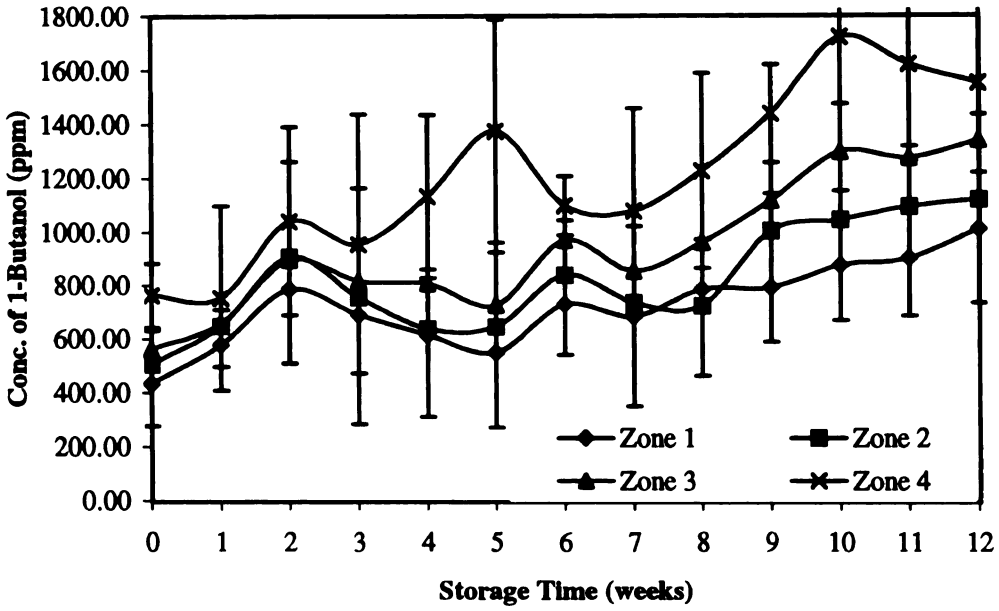
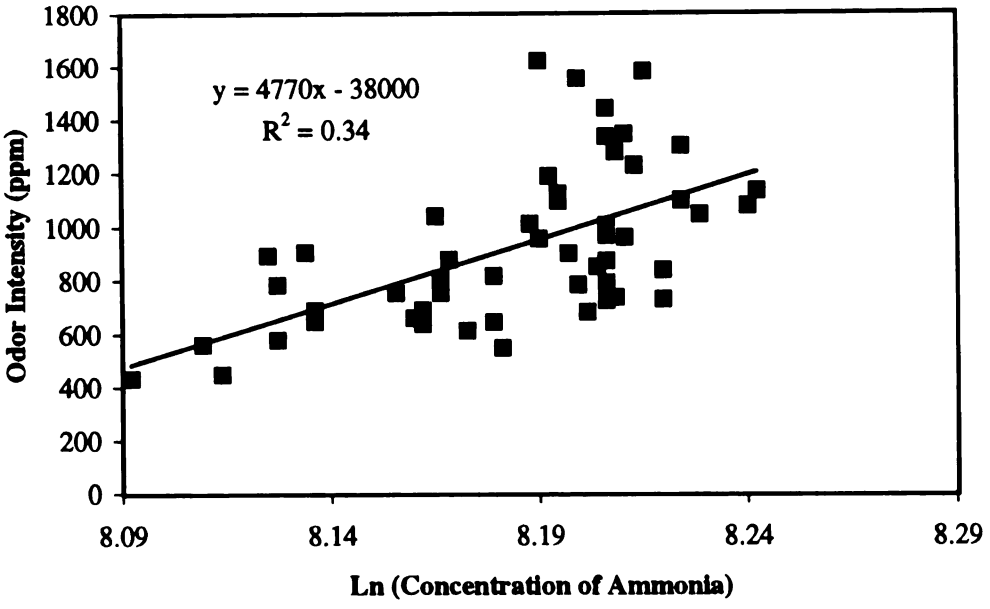


Figure 2.17 Effect of Time on the Odor Intensity in Stored Swine Manure Slurry



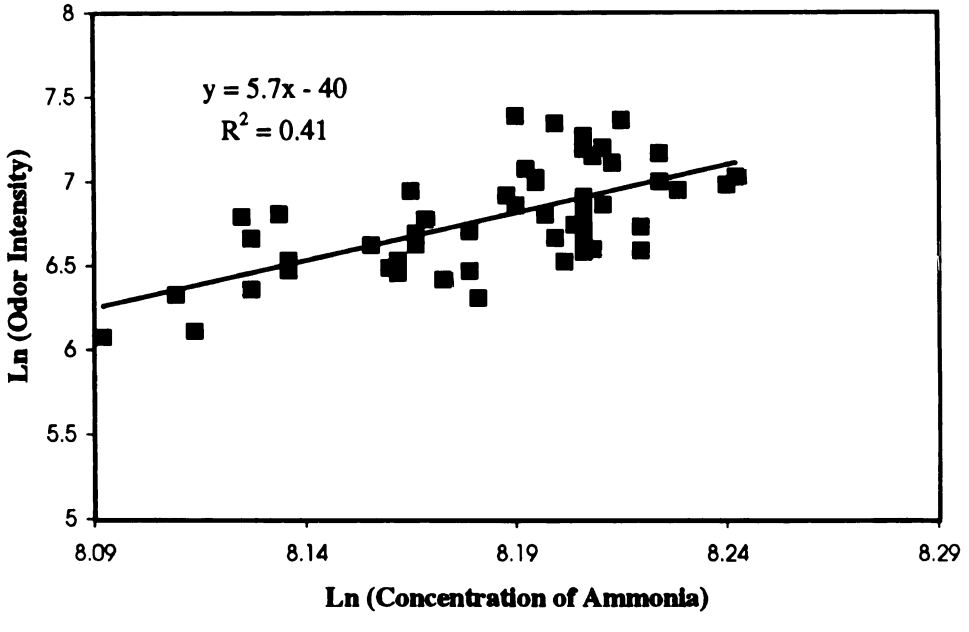
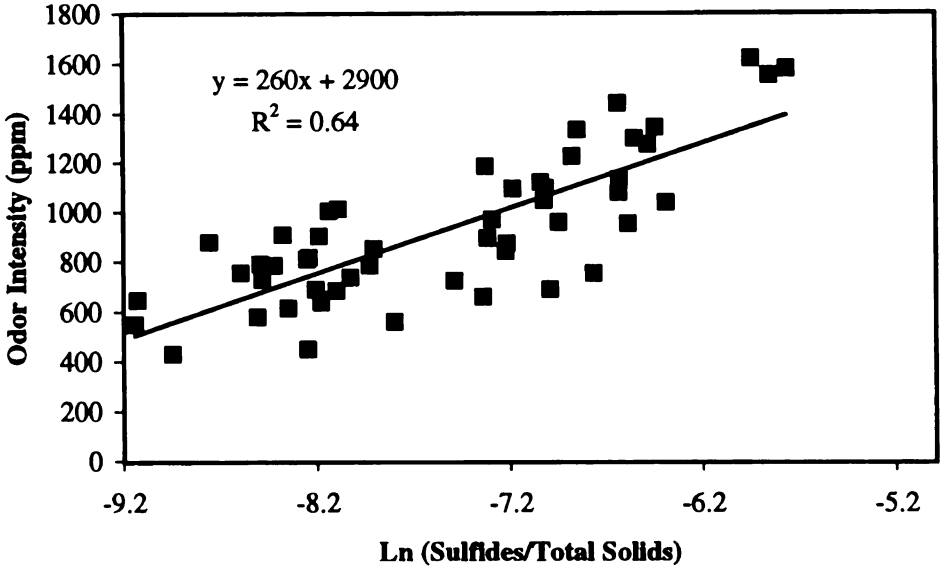


Figure 2.18 Relationships between Odor Intensity and Concentrations of Ammonia Nitrogen in Stored Swine Manure Slurry



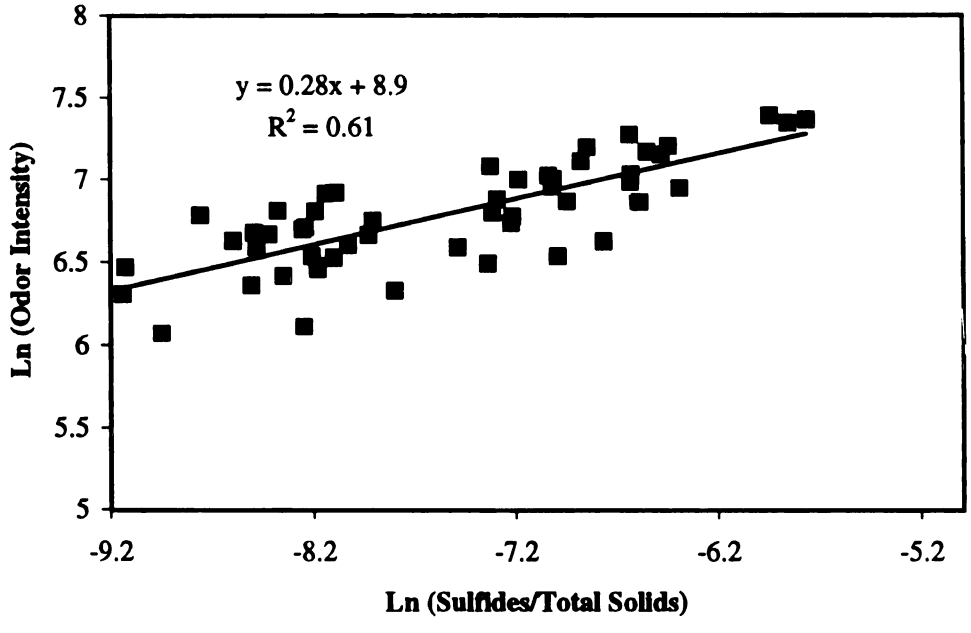


Figure 2.19 Relationships between Odor Intensity and Concentrations of Sulfides/Total Solids in Stored Swine Manure Slurry

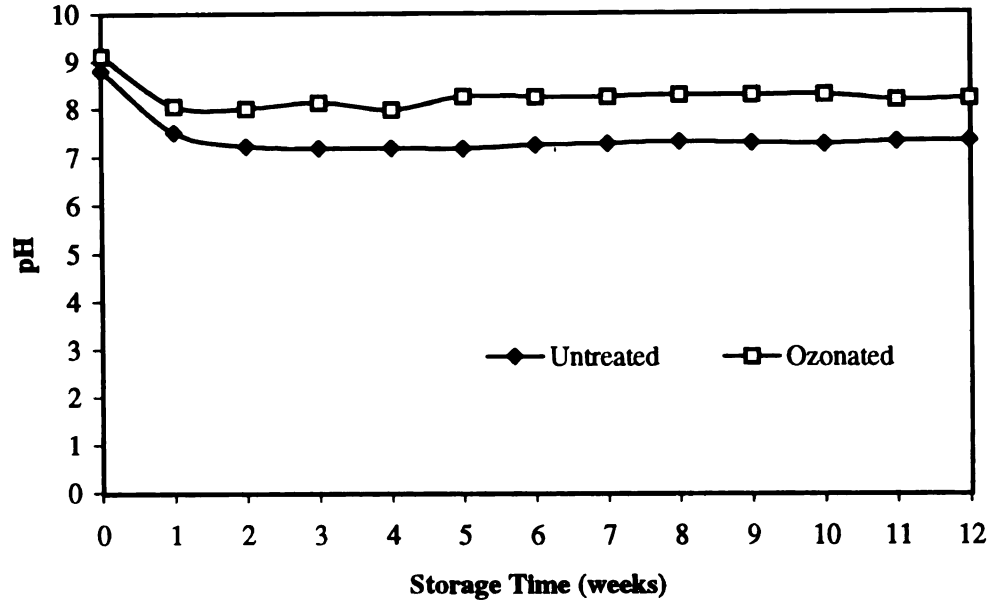
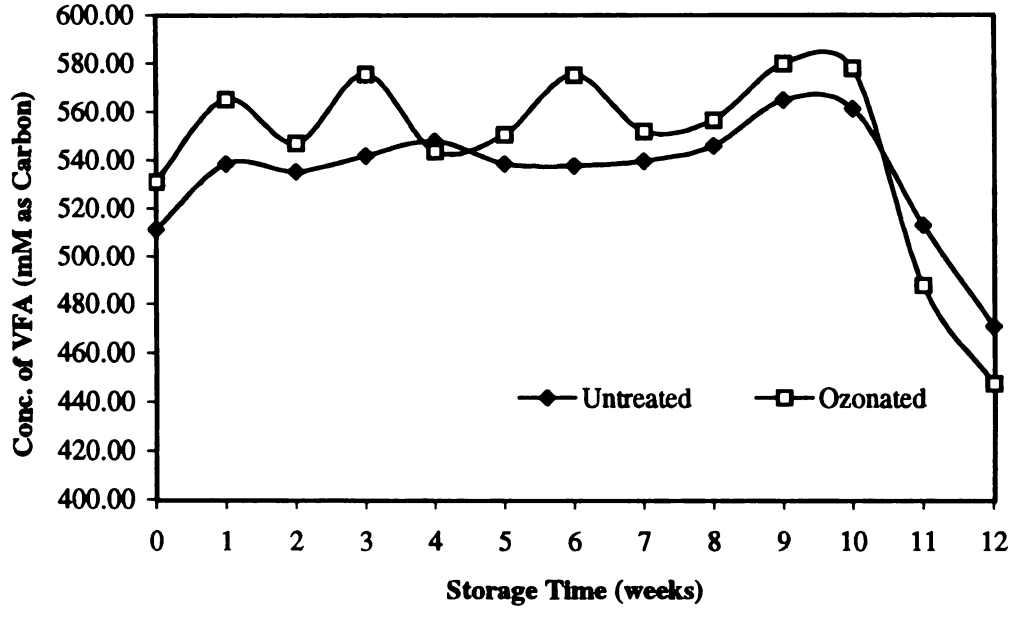


Figure 2.20 Effect of Time and Ozonation on the pHs in Stored Swine Manure Slurry



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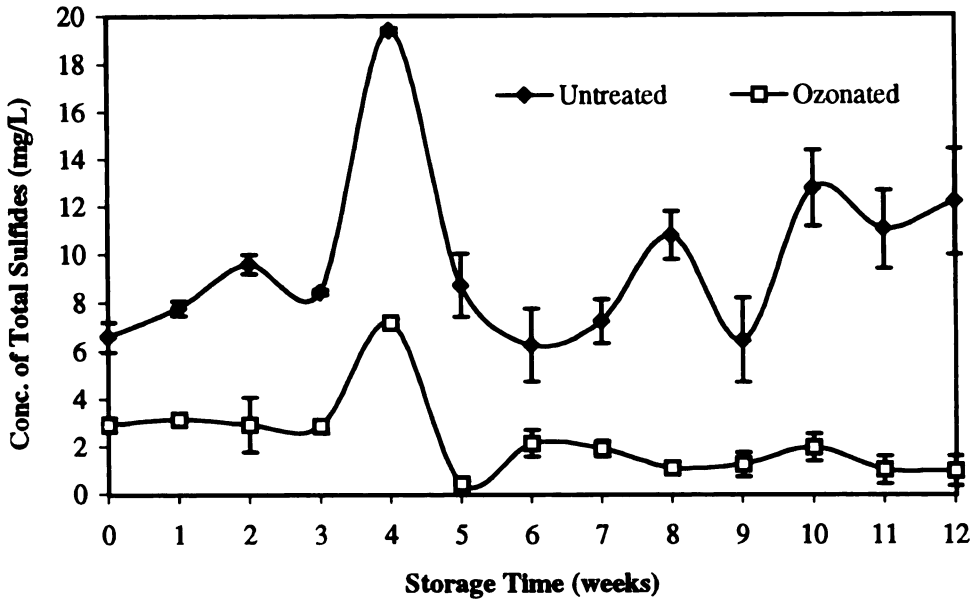

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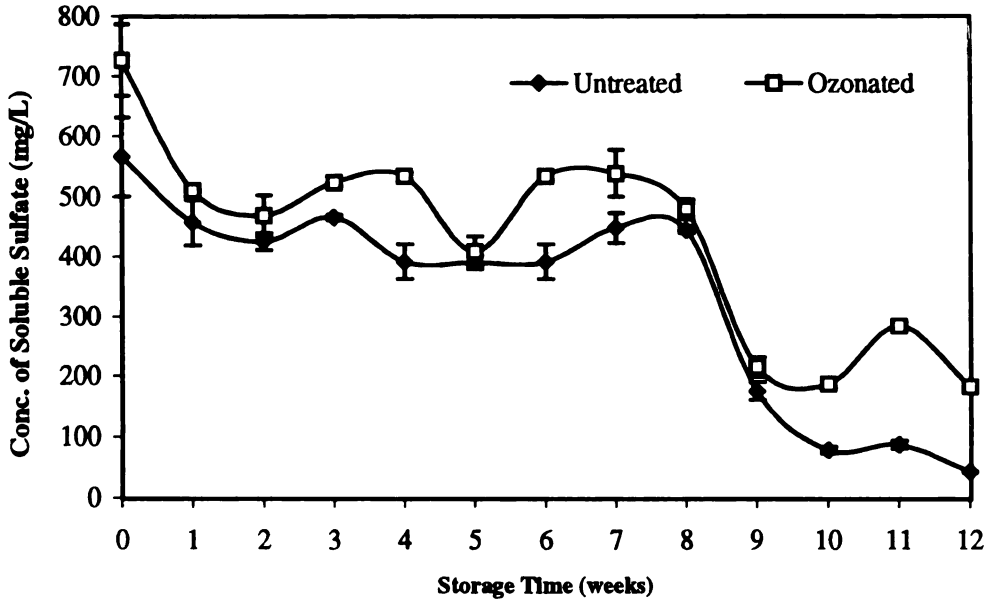

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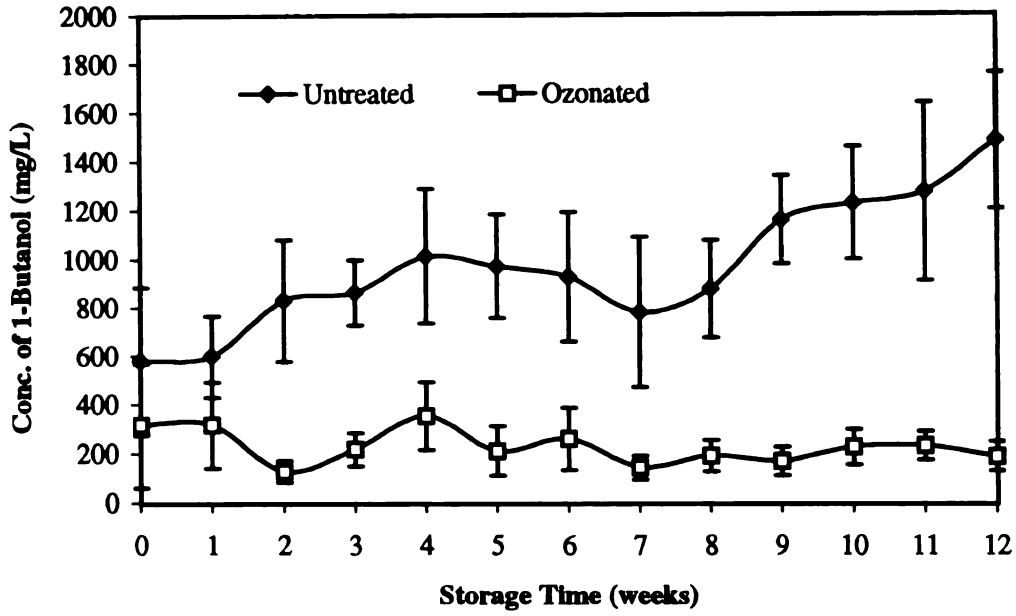


Figure 2.24 Effect of Time and Ozonation on the Odor Intensity of Stored Swine Manure Slurry

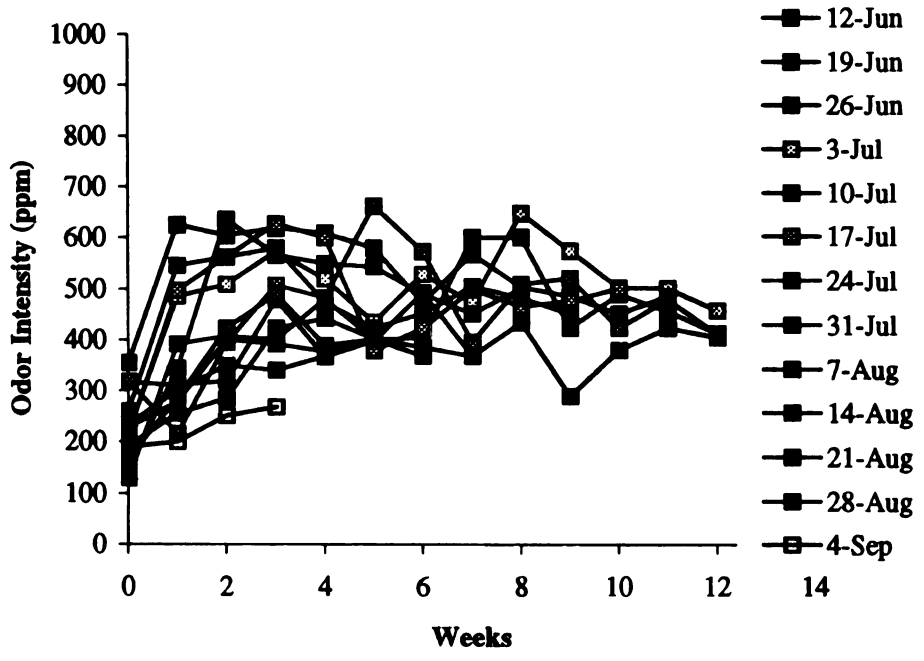
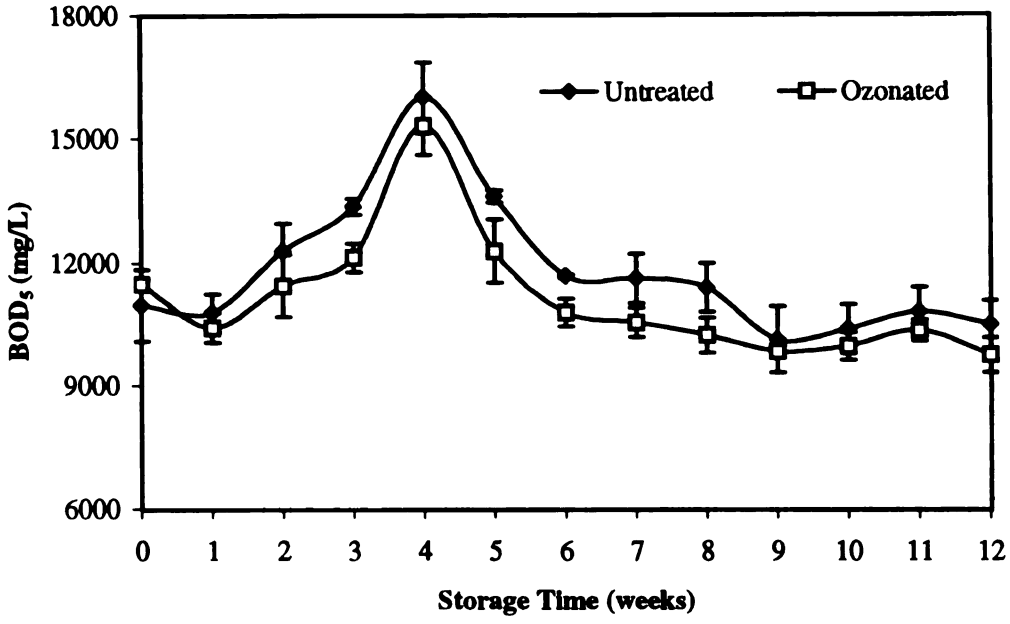


Figure 2.25 Effect of Subsequent Storage on the Odor Intensity of Ozonated Swine Manure Slurry



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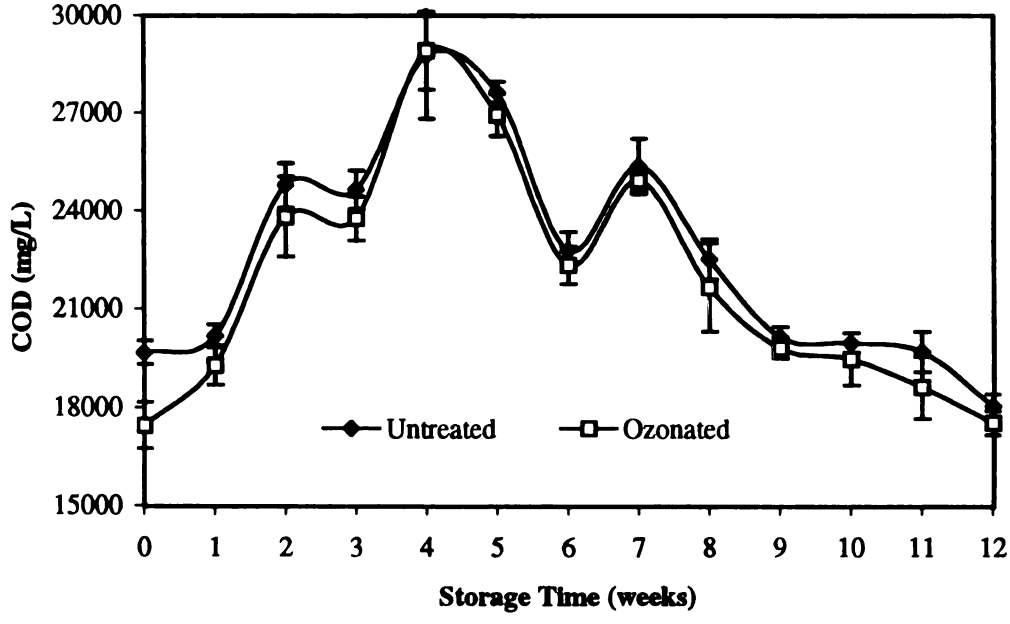

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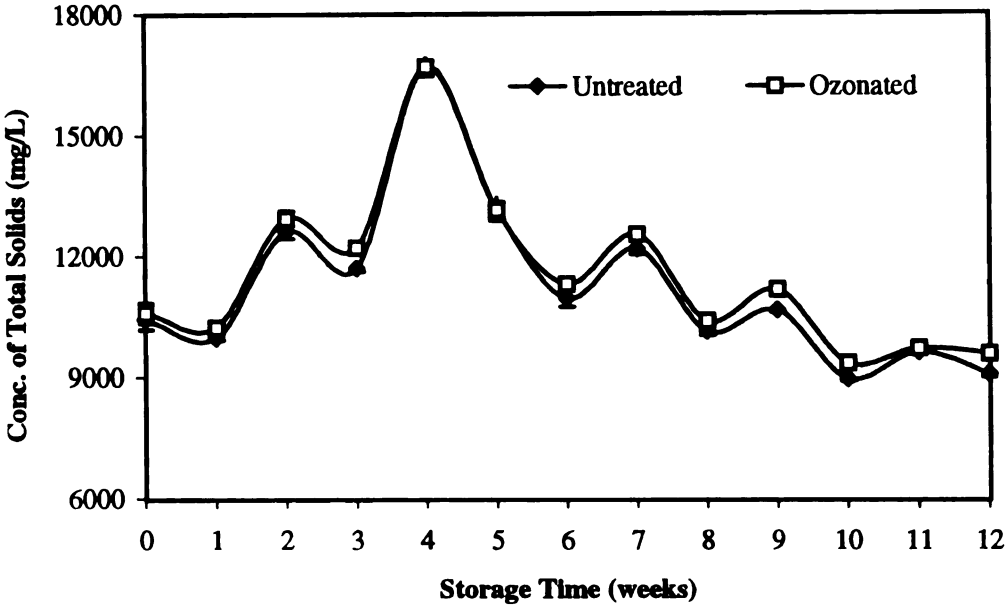
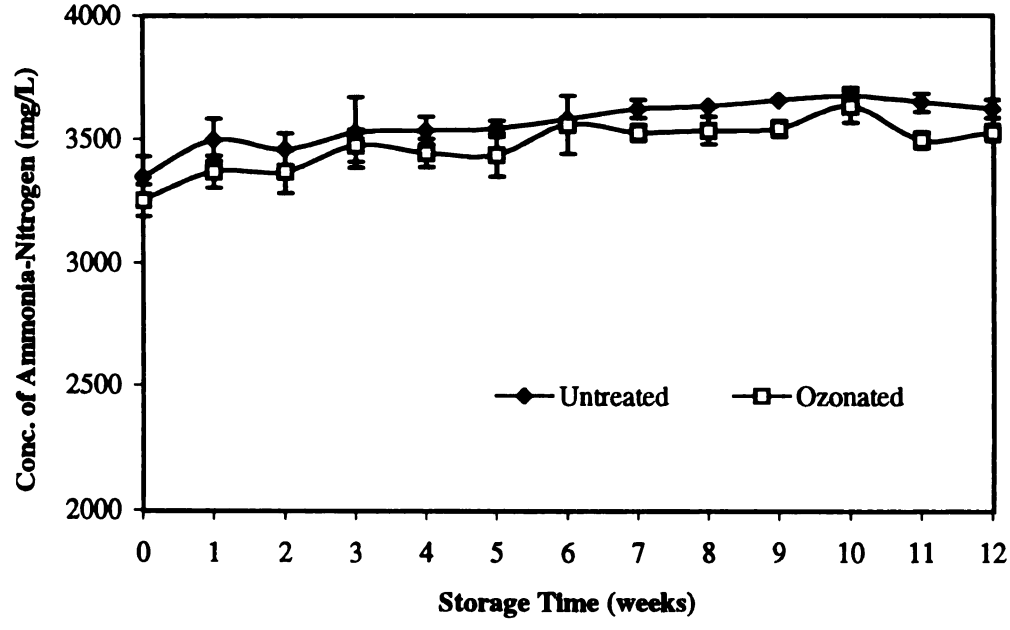


Figure 2.28 Effect of Time and Ozonation on the Concentrations of Total Solids in Stored Swine Manure Slurry



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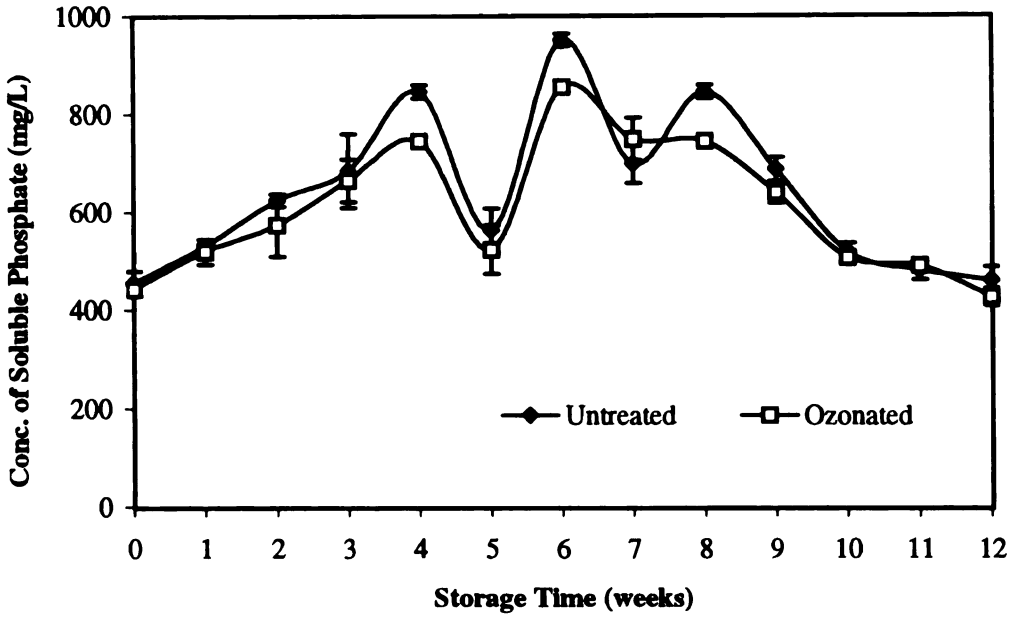

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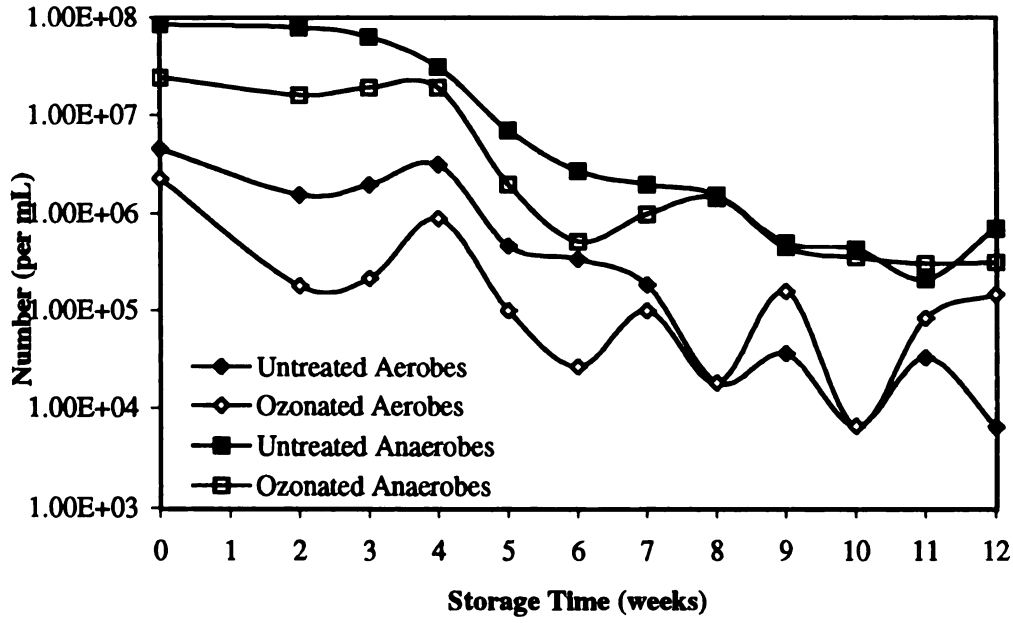

Figure 2.31 Effect of Time and Ozonation on Aerobes and Anaerobes in Stored Swine Manure Slurry

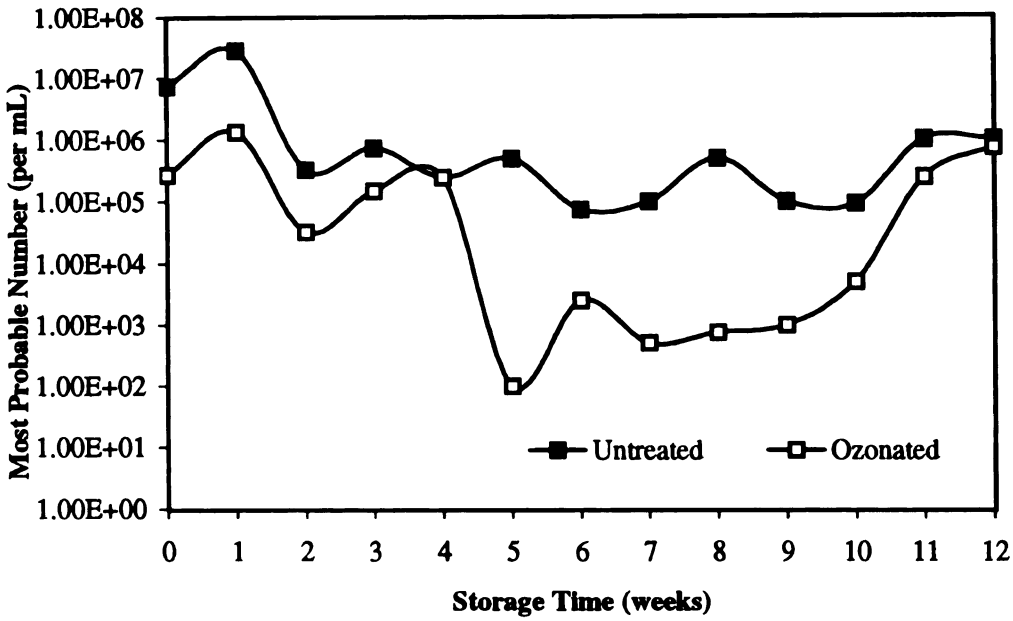

Figure 2.32 Effect of Time and Ozonation on Total Coliforms in Stored Swine Manure Slurry

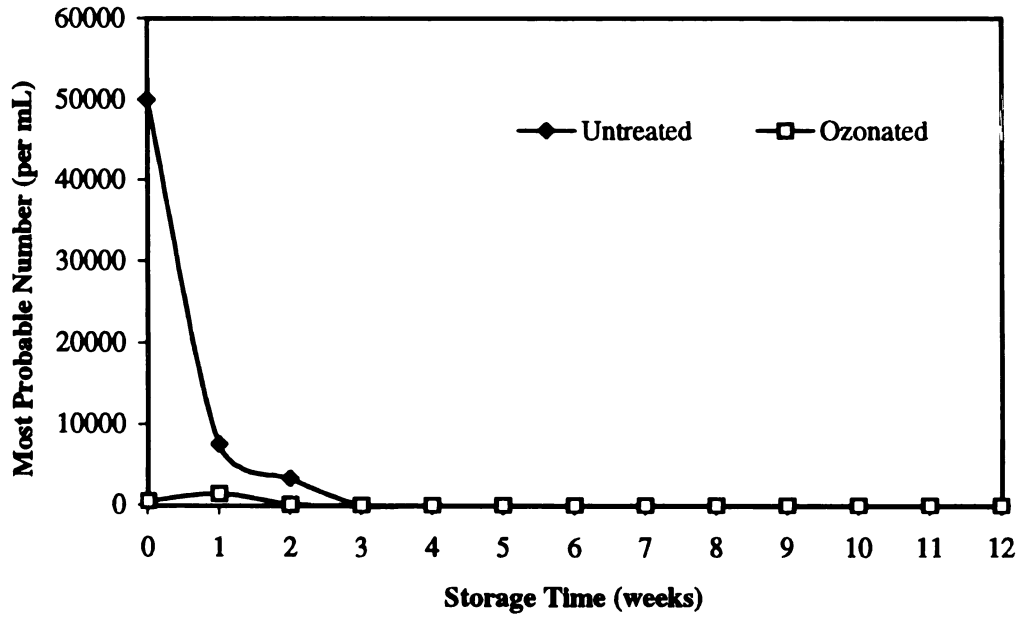

Figure 2.33 Effect of Time and Ozonation on *E. Coli* in Stored Swine Manure Slurry

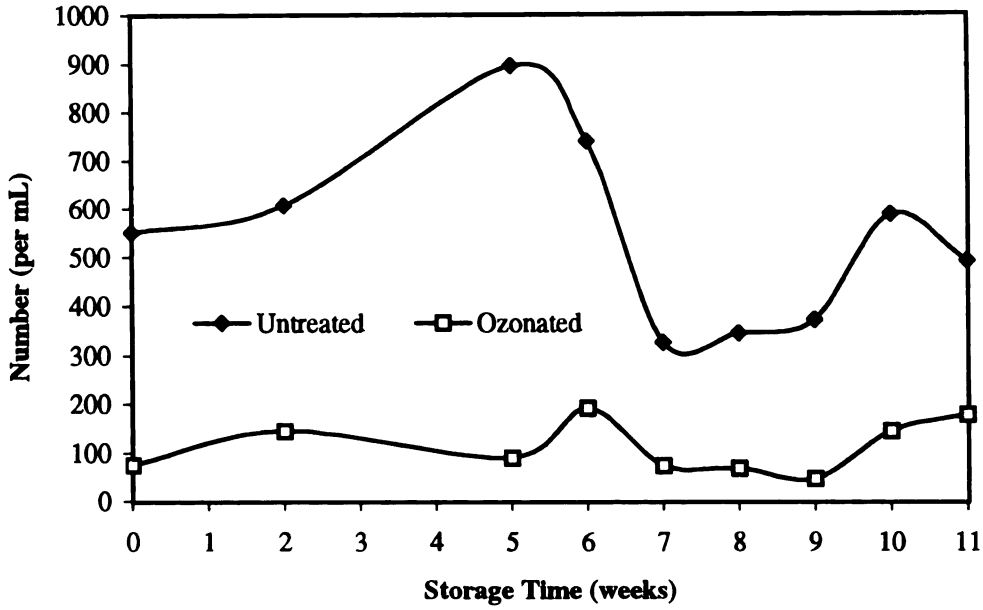

Figure 2.34 Effect of Time and Ozonation on Coliphage Plaques Produced on *E. Coli* in Stored Swine Manure Slurry

Chapter 3

THE USE OF OZONE TO REDUCE THE CONCENTRATION OF MALODOROUS METABOLITES IN SWINE MANURE SLURRY BY USING A PILOT-SCALE SYSTEM

3.1 Introduction

Environmental pollution by livestock waste is a major nation-wide concern of the animal agriculture industry. An increasing number of civil litigations, more restrictive township ordinances, demands for the protection of public health and new Federal and State regulations governing surface run-off and ground water contamination necessitate that the livestock industry take action to control the environmental problems associated with livestock production.

Malodors emanating from livestock production are the major source of complaints against livestock farms. As livestock farms have moved to larger and more intensive production units, odor complaints from nearby residents have correspondingly increased (Ritter, 1989). Innovative methods to control, reduce or eliminate malodors associated with livestock farms must be developed and employed to ensure the future viability of the industry.

More than 160 odorous compounds have been identified in livestock wastes (O'Neill and Phillips, 1992). Among these compounds, the volatile phenolic and indolic metabolites are among the most malodorous of the compounds found in swine manure slurry (Spoelstra, 1977). These compounds are formed from the bacterial degradation of tyrosine and tryptophan in the intestinal tract and during storage of swine waste (Yokoyama et al., 1982). Other volatile components that have been identified in swine are the C_2 to C_5 carboxylic acids (Schaefer, 1977), aromatic carboxylic acids, alcohols, carbonyl compounds, and sulfur-containing compounds (Yasuhara et al., 1984). Williams and Evans (1981) indicated that during storage the odor offensiveness increased, as did the concentration of malodorous compounds including phenol, *p*-cresol, skatole and volatile fatty acids (VFAs).

Ozonation is recognized as an environmentally safe and effective process for the treatment of industrial effluents, drinking water and sewage (Masten and Davies, 1994). Ozonation has the potential to reduce the malodorous metabolites produced during anaerobic storage of livestock waste by chemically oxidizing these compounds. Ozone is a very strong oxidant that attacks the cell wall and the cytoplasmic membrane of the cell (Block, 1982), thereby inactivating the organism. As such, ozone has the potential to reduce the number of micro-organisms present in waste, and thereby control the rate of production of these malodorous metabolites. Previous researches (Wu et al., 1998; Watkins et al., 1997) indicate that ozone preferentially oxidizes odor producing metabolites, reduces odor intensity and inactivates micro-organisms.

Scale-up of ozone reactors typically occurs after bench-scale and pilot-scale experiments have been conducted (Finch and Smith, 1990). In the previous chapter, it

was reported that an ozone dosage of 1 g/L was found to be effective in controlling the malodor of fresh and stored swine manure slurry using a lab-scale reactor. However, it is also imperative to test the ozonation process using a pilot-scale reactor prior to the installation of a full-scale ozonation system. This will allow us to determine the effect of the operational parameters on the removal of malodors in the swine manure. As the reaction rate of those major malodorants including phenolic and indolic compounds were found to be very fast (Hoigné and Bader, 1983), the efficiency of mass transfer becomes the main controlling factor in ozonating swine manure. Therefore, an attempt should be made to enhance the mass transfer of ozone during the treatment. Based upon this, the pilot-scale system will be designed to optimize the mixing of the liquid and gaseous ozone. A cost analysis will also be done to evaluate the capital and operational costs of the pilot-scale system. These costs will be related to the full-scale system.

3.2 Materials and Methods

3.2.1 Manure Collection and Storage

Fresh swine manure was collected from the Michigan State University Swine Research and Teaching Farm (Figures 3.1-3.2). Four 115 kg finishing pigs were placed in a metabolism crate and fed a standard corn-soy diet. The crate had a slotted floor, which allowed for the collection of the liquid fraction of the manure slurry (hereafter, referred to as the manure slurry). Each day's manure slurry was stored at 4 ^{o}C to minimize changes that might have occurred in its physicochemical and biological properties. After collection over a 5-day period, the manure slurry was decanted into a 150 liter storage tank. During three weeks of storage the manure was maintained at 18 ^{o}C. It was stirred

and sampled once per week to determine the concentrations of COD, phosphates, sulfides, sulfates, phenolic and indolic metabolites, and volatile fatty acids.

3.2.2 Ozone and Ozonation Reactor

A semi-continuous pilot-scale ozonation system (Figures 3.3-3.4) was constructed and used for treating the manure slurry. The 3.5-gallon reactor was equipped with four baffles, each with 1/10 of the width of the reactor diameter, located on the wall of the reactor and a multiple-stage mixer consisting of Rushton disc turbines with the ratio of 1/3 of the turbine size to the reactor size, which was demonstrated to be the optimum ratio in maintaining the effective mixing with the minimum power needed (Oldshue, 1983). Using this design, the formation of central vortex or swirling would be avoided (McCabe et al., 1985; Tatterson, 1994) and complete mixing of liquid along the horizontal and vertical paths would be produced in the tall reactor (Oldshue, 1983). To maintain the desired temperature during treatment (14 °C, 18 °C, 25 °C), a water bath was used to circulate water around the jacket of the reactor.

Ozone was generated from pure oxygen by corona discharge using Ozonia® Model No. GTC-0.5C ozone generator (Ozonia Corp., Lodi, NJ). A Venturi in-line injector (Mazzei Injector Corp., Bakersfield, CA) was installed at the inlet of the ozone stream. A circulator pump (Grundfos Pumps Corp., Clovis, CA) was used to circulate the liquid through the venturi. This system resulted in the generation of very small bubbles (< 1 mm diameter) of ozone-enriched oxygen. The inlet stream of ozone flowed at 1.8 L/min and had a concentration of 153 mg of ozone per liter of gas. Detention times of 10, 20, 30, and 40 minutes provided ozone dosages of 0.25, 0.5, 0.75, and 1 g/L, respectively. To

reduce foaming caused by the bubbling of ozone into the manure slurry, 10 mL of an anti-foaming agent (Anti-foam 289, Sigma Co., St. Louis, MO), were added to the slurry just prior to ozonation.

At weekly intervals during the three weeks of storage, 3-gallon aliquots including fresh and stored manure slurry were ozonated. In addition, the last aliquot of ozonated manure slurry was stored for an additional four weeks to determine if the malodors reoccurred.

3.2.3 Odor Evaluation

A odor panel, consisting of five untrained graduate students in the Department of Civil and Environmental Engineering at Michigan State University, was asked to evaluate the odor of the raw and ozonated manure slurry samples. Each individual in the panel ranked the samples in order of worst to best odor and classified the odor of each sample as acceptable, unacceptable, or extremely unacceptable. The classifications of acceptable, unacceptable, and extremely unacceptable were ranked as 1, 2, and 3 respectively. A repeat measure analysis of variance was used to explain the subjectively determined measure of odor at weeks 0, 1, 2, and 3 (The SAS System for Information Delivery, Version 6.12., SAS Institute, Inc., Cary, NC). Independent variables were the panelists and ozone dosages. The orthogonal test for sphericity was P=0.99, indicating that use of the major assumptions for this procedure were not violated and the univariate tests were valid. Specific contrasts were performed between ozone dosage levels.

3.2.4 Chemical Analysis

The aqueous ozone concentration was quantified using an ozone monitor (Exidyne Instrumentation Technologies Inc., Exton, PA) through which a small amount of liquid was passed across a detection probe. The gaseous ozone concentrations in the inlet and outlet streams were determined spectrophotometrically. The absorbance of the ozone solution was measured in a 2-mm flow-through UV cell at a wavelength of 258 nm. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ was used to convert absorbance to concentration (Nowell and Hoigné, 1988).

Chemical oxygen demand (COD) was determined using pre-packaged Hach vials (0-1,500 mg/L) (Hach Company, Loveland, CO). Phosphate and sulfate were determined using ion chromatography (Method 4110, Standard Methods for the Examination of Water and Wastewater). Ammonia was measured with an ammonium electrode connected to a pH meter and quantification was accomplished using the method of known addition (Method 4500-NH_3, Standard Methods for the Examination of Water and Wastewater 1995). Sulfides were measured using a purge and trap method (Barth and Polkowski, 1974), employing nitrogen gas to purge hydrogen sulfide from the solution. All sulfide species were first converted to hydrogen sulfide by the addition of 10 mL of concentrated sulfuric acid to lower the pH of the samples to 2. The trap solution was prepared by adding 15 mL of zinc acetate (2N) to 135 mL deionized water. After trapping, the sulfides were determined according to Method 4500-S^{2-} (Standard Methods for the Examination of Water and Wastewater, 1995). Aldehydes were determined by the formation of 2,4-dinitrophenylhydrazones (DNPH) using solid-phase extraction and high performance liquid chromatography (HPLC). 15 mL of DNP reagent (0.25 g 2,4-

dinitrophenylhydrazine were dissolved in 100 mL of 6 M hydrochloric acid) were added into 100 mL of aqueous sample. The mixture was stirred for 5 minutes and then passed through a C18 bonded cartridge that has been previously conditioned with methanol. The cartridge, which contains the DNPH derivative, was washed with DI water and eluted with two 500 μL aliquots of methylene chloride directly into a 1 mL volumetric flask. The concentrated extract was injected into a HPLC equipped with C18 column and an ultraviolet (UV) absorbance detector whose wavelength was set to 365 nm. The mobile phase was used a binary mixture consisting of 80% acetonitrile and 20% DDI. The flow rate was operated at 1 mL/min.

The concentrations of volatile fatty acids (including acetate, propionate, butyrate, isobutyrate, valerate, isovalerate) were determined using a HP 5890 gas-liquid chromatograph (Hewlett-Packard Inc., Avondale, PA) with a flame ionization detector (FID). One mL of concentrated hydrochloric acid was added to 10 mL of manure slurry sample. After the mixture was agitated in a vortex mixer, it was centrifuged at 12,000 G for 10 minutes to remove particulate matter. The supernatant (3 μL) was injected directly into a 900 mm x 6 mm glass column packed with Supelco GP 10% SP-2100 on 100/120 Chromosorb W AW (Supelco Inc., Bellefonte, PA). The carrier gas was nitrogen flowing at 25 mL/min. The column temperature was held at 110 ^{o}C for the first three minutes after injection; the temperature was ramped at 5 ^{o}C/min to 170 ^{o}C and held for fifteen minutes. Injection port and FID temperatures were maintained at 150 and 200°C, respectively.

The concentrations of phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole were quantitatively determined in the swine manure slurry by gas-liquid chromatography

(Yokoyama et al., 1982). The pH of each sample (10 mL) was adjusted to 4.0 with concentrated sulfuric acid. The analytes were extracted from the acidified samples twice with 30 mL of methylene chloride. The extract was evaporated down to a volume of approximately 1 mL using a rotary evaporator, transferred to a screw cap vial, and made up to 4.0 mL with methylene chloride. Samples (2 μL) were analysed directly by GC-FID (HP 5890), using a stainless steel column (2 m x 2 mm) packed with 4% Carbowax 80/120 Carbopack (Supelco, Bellefonte, PA). The oven temperature was programmed to increase from 100 °C to 175 °C at a ramping rate of 8 °C/min. Injection port and FID temperatures were maintained at 200 °C. The efficiency of recovery of the volatile phenolic and indolic metabolites was determined to be greater than 95% (Yokoyama et al., 1982).

3.3 Results and Discussion

3.3.1 Effect of Storage and Ozonation

The stored manure slurry was analyzed weekly for its chemical characteristics and odor. After three weeks of storage, the pH of the swine manure slurry decreased from 8.9 to 7.9. During storage, the VFA concentration increased from 62 to 240 mM. The concentrations of other chemical analytes (e.g., ammonia-nitrogen, sulfides, phenolic metabolites, phosphate and sulfate) also increased (Table 3.1). The chemical oxygen demand (COD) of the manure remained constant, around 14,000 mg/L, during the storage period. The concentrations of all aldehydes, including formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, and hexaldehyde, in the all fresh and stored manure samples were below the detection limits (1 ppb). Acetate was the

predominant VFA, followed in decreasing order of concentration by propionate, butyrate, isovalerate, isobutyrate, and valerate. This is consistent with the observation of Cooper and Cornforth (1978). The concentrations of all VFAs were observed to increase during storage. The odors (Table 3.2) of the fresh and one-week-storage samples were classified as unacceptable and the odors of the samples held for longer storage times were deemed as extremely unacceptable.

The ozonation of the fresh and stored manure slurries was evaluated at different dosages of ozone to determine the minimal dose for effective odor reduction (Table 3.2). The program used in SAS is provided in the Appendix. The effect of overall treatment was highly significant at $P=0.0001$, while the effect of the panelists was not significant at $P=0.34$. The effect of storage time was significant at $P=0.0047$. At all four weeks, the negative control treatment (0 g/L ozone dosage) differed at $P< 0.05$ from all dosages greater than 0.25 g/L; the 0.25 g/L dosage differed from all higher dosages at $P<0.05$, and the 0.5 g/L dosages did not differ from higher dosages at $P>0.13$. These results indicate that no significant additional beneficial effect was realized at ozone dosages greater than 0.5 g/L. Therefore, the results from the odor panel indicateded that ozone is effective in reducing malodor to an acceptable level at a dosage of 0.5 g/L.

Sulfides were observed to be removed rapidly from either fresh or stored manure slurries using ozone dosages greater than 0.25 g/L. The concentration of phenol (Figure 3.5) in the manure slurry that had been stored for more than 2 weeks was observed to

Table 3.1 The Characteristics of Fresh and Stored Swine Manure

	Fresh Manure	1st Week Storage	2nd Week Storage	3rd Week Storage
pH	8.9	8.7	8.1	7.9
NH3-N (mg/L)	2960	3400	4000	4930
Sulfides (mg/L)	1.6	8.0	12.0	8.0
COD (mg/L)	13500	13500	13500	13500
Phenol (mg/L)	15.8	13.6	52.0	61.4
p-Cresol (mg/L)	2.0	22.5	133.8	167.5
p-Ethylphenol (mg/L)	0.6	4.8	3.6	5.4
Indole (mg/L)	ND	ND	ND	ND
Skatole (mg/L)	ND	4.4	2.5	2.0
Dissolved phosphate (mg/L)	ND	200	1550	2150
Dissolved sulfate (mg/L)	1660	4120	6030	4000
Acetate (mM)	22.1	29.1	48.0	93.1
Propionate (mM)	2.8	2.5	3.9	8.2
Butyrate (mM)	1.2	1.3	2.9	5.1
Isobutyrate (mM)	0.1	0.2	0.5	0.9
Valerate (mM)	0.2	0.2	0.2	0.3
Isovalerate (mM)	0.3	0.4	0.6	1.1
Total VFAs (mM as carbon)	60.7	74.8	125.3	241.3

ND = Not Detectable

Table 3.2 Evaluation of the Odor of Fresh and Stored Manure before and after Ozonation

Panelist	Fresh Manure	0.25 g/L Ozone	0.5 g/L ozone	0.75 g/L Ozone	1 g/L Ozone
V	2	2	1	1	1
W	2	3	1	1	1
X	1	1	1	1	1
Y	2	2	2	1	1
Z	2	1	1	1	1
Panelist	1st Week Storage	0.25 g/L Ozone	0.5 g/L Ozone	0.75 g/L Ozone	1 g/L Ozone
V	2	2	2	2	1
W	2	2	1	1	1
X	3	2	1	1	1
Y	3	3	2	1	1
Z	2	2	1	1	1
Panelist	2nd Week Storage	0.25 g/L Ozone	0.5 g/L Ozone	0.75 g/L Ozone	1 g/L Ozone
V	3	3	2	1	1
W	3	2	1	1	1
X	2	3	2	1	1
Y	3	3	1	1	1
Z	3	2	1	1	1
Panelist	3rd Week Storage	0.25 g/L Ozone	0.5 g/L Ozone	0.75 g/L Ozone	1 g/L Ozone
V	3	2	1	2	1
W	2	3	2	1	1
X	3	3	2	1	1
Y	3	2	1	1	1
Z	3	2	1	1	2

1: acceptable; 2: unacceptable; 3: extremely unacceptable

decrease with increasing ozone dosage. In the fresh manure slurry and the manure slurry that had been stored for only one week, the concentration of phenol did not follow a consistent pattern, although a substantially lower phenol concentration was measured after ozonation at a dose of 1 g/L (Figure 3.5). Similar trends for the decrease in the concentration of *p*-cresol (as compared to phenol) were observed except that the concentration of *p*-cresol in the fresh slurry did not decrease until 1 g/L of ozone had been applied (Figure 3.6). The concentrations of *p*-ethylphenol (Figure 3.7) and skatole (Figure 3.8) were also observed to decrease significantly. The concentrations of other analytes, such as ammonia nitrogen, phosphate, sulfate, COD, and VFAs, were not affected by the ozonation treatment.

Phenol, *p*-cresol, *p*-ethylphenol, indole, skatole, hydrogen sulfide, and VFAs are thought to be the major malodorous compounds contributing to the odor problem of swine manure slurry (Spoelstra, 1977, 1979, 1980; Williams and Evans, 1981; Williams' 1984). Storage of manure results in the formation and accumulation of these malodorous compounds through anaerobic microbial activity and fermentation (Welsh et al., 1977). The results of this study confirm the finding of Welsh et al. (1977) as the rapid accumulation of malodorous compounds during the three weeks of storage correlated with an increase in odor intensity. Among the malodorous compounds, the concentration of *p*-cresol was observed to increase the most significantly. It is thought that *p*-cresol contributes most directly to the odor of swine manure slurry. Ozone dosages greater than 0.5 g/L resulted in a substantial decrease in the concentration of this compound. This result did not depend on the length of storage.

The concentrations of VFAs did not decrease even after ozone treatment at a dosage of 1 g/L, although a marked improvement in odor was evident. Therefore, at the pH of the manure slurry (7 to 9), VFAs do not appear to be a suitable indicator of odor intensity. VFA apparently play a minor role in contributing to the odor characteristics of the manure slurry (as compared with the phenolic and indolic metabolites).

The microbiological data, including numbers of aerobes, anaerobes and coliphage, were also analyzed. The number of total aerobes decreased significantly during 3-week storage and decreased to a lesser extent upon ozonation (Figure 3.9). The number of total anaerobes decreased slightly during 3-week storage and upon ozonation (Figure 3.10). It is thought that the conditions under which the liquid manure slurry is stored are unfavored to the growth of these microorganisms, especially to the aerobes. Ozone dosed from 0.25 to 1 g/L was found to deactivate and kill some of the aerobes and anaerobes. This result is consistent with that presented in Chapter 2. The number of coliphage was found to increase after ozonation at lower dosages, whereas, its numbers decreased at the higher ozone dosage (Figure 3.11). These results indicated that ozone can induce the release of coliphage while killing its host, *E.coli*. When the ozone dosage was increased, ozonation resulted in a decrease in the number of coliphage. In earlier work (see Chapter 2), only an ozone dosage (1 g/L) was used. As such, the numbers of coliphage were observed to decrease.

The utilization of ozone in the pilot-scale system was evaluated using three different parameters: ozone utilized, transfer efficiency, and transferred mass. These are defined as (Chrostowski et al., 198; Langlais et al., 1990):

$$\text{OU (Ozone Utilized, mg/L)} = \frac{(C_{in} - C_{out}) \times V_g}{V_l} - C_{res}$$

$$\text{TE (Transfer Efficiency, percent)} = \frac{(C_{in} - C_{out})}{C_{in}} \times 100$$

$$\text{TM (Transferred Mass, mg/min)} = TE \times C_{in} \times Q$$

where, C_{in} = ozone concentration in the feed gas (mg/L); C_{out} = ozone concentration in the effluent gas (mg/L); V_g = volume of applied ozone (L); V_l = volume of liquid treated (L); C_{res} = aqueous ozone residual in the reactor (mg/L); Q = applied flowrate of ozone (L/min). The experimental results are summarized in Table 3.3. The applied ozone was fully consumed by the manure slurry using this pilot-scale ozonation system. Therefore, almost no wasted ozone can be seen in the off-gas when the pilot-scale system was used to treat the fresh and stored swine manure.

Table 3.3 The Systematic Parameters of Ozonating Stored Manure

Time (min)	Applied Dosage (mg/L)	C_{in} (mg/L)	C_{out} (mg/L)	C_{res} (mg/L)	OU (mg/L)	TE (%)	TM (mg/min)
0	0	0	0	0	0	0	0
10	250	153	0	0	250	100	275
20	500	153	1	0	498	99.4	273
30	750	153	2.5	0	744	98.4	271
40	1000	153	4	0	988	97.4	268

C_{in} = Ozone concentration in the feed gas (mg/L)
C_{out} = Ozone concentration in the effluent gas (mg/L)
C_{res} = Aqueous ozone residual in the reactor (mg/L)
OU = Ozone Utilized (mg/L)
TE = Transfer Efficiency (percent)
TM = Transferred Mass (mg/min)

3.3.2 Comparison of Stripping, Oxygenation, and Ozonation

To compare the effects of stripping with nitrogen, oxidation by oxygen, and oxidation by ozone, we treated the manure slurry with nitrogen, oxygen, and ozone-enriched oxygen (Figures 3.12 to 3.15). A flowrate of 1.8 L/min and treatment time of 40 minutes were used in all experiments. The percentage removals reported are calculated for the individual processes. For example, if the concentration of a compound were to be reduced by 10% during stripping, 25% during oxygenation and 100% during ozonation, the percent removals for volatilization (stripping), aerobic degradation and reaction with ozone are reported as 10, 15 and 75%. Our experiments showed that less than 20% of the phenol was removed by nitrogen and oxygen. In contrast, approximately 80% of the phenol was removed by its reaction with ozone at a dosage of 1 g/L. The stripping of *p*-cresol by nitrogen appears to be insignificant (less than 10%) compared with that removed by the oxidation of oxygen (40%) and ozone (50%). Approximately 15% of the *p*-ethylphenol was removed by stripping, whereas 30% was removed by oxygenation and 55% by ozone. Approximately 30% of skatole was removed by stripping, whereas only 15% was removed by oxygenation and 55% by ozonation. The use of nitrogen and oxygen to compare the efficiency of ozone in removing the odorous compounds demonstrates that the reaction of these compounds with ozone is the predominant mechanism resulting in the reduction in the odor of the manure slurry. Stripping had a greater effect on the removal of skatole and *p*-ethylphenol as compared to *p*-cresol and phenol, most likely because the first two compounds are more hydrophobic than the latter two. About 50% of the *p*-cresol was removed during oxygenation (for 40 minutes), which would have resulted both in the stripping of *p*-cresol and in an enhancement of

activity of aerobic microorganisms. It appears that *p*-cresol is biodegraded more easily than the other phenolic and indolic compounds, since the enhancement in the efficiency at which *p*-cresol was removed during treatment with oxygen (as compared to that with nitrogen) significantly greater than that observed for the other compounds.

3.3.3 Comparison of Varying Temperature and Using Hydrogen Peroxide

To determine the effect of temperature (14-25 °C) on the efficiency of the treatment of the swine manure slurry, samples which had been stored for one month were ozonated at different temperatures using an ozone dosage of 1 g/L. Temperature did not have a significant effect (at the 95% confidence interval) on the removal of either the phenolic or the indolic compounds (Figures 3.16-3.19). The aqueous solubility of ozone decreases with increasing temperature, whereas the reaction rate of ozone with organic compounds increases with increasing temperature. In the swine manure slurry, which is a very complex mixture, these two factors appear to counter-balance each other over the temperature range studied (14-25 °C). This result would indicate that, for this temperature range, the design of an ozonation process will not be affected by seasonal variations in the temperature of the manure slurry.

The effect of ozone combined with hydrogen peroxide on the removal of the phenolic and indolic compounds was also evaluated. Hydrogen peroxide to ozone ratios of 0, 0.51, 0.84, 1.4 g/g were used. No significant benefit (at the 95% confidence interval) from the addition of hydrogen peroxide was obtained (Figures 3.20-3.23). Although advanced oxidation processes (AOPs) have been used to improve the efficiency of ozonation of water and wastewater (Brunet et al., 1985; Glaze et al., 1987; Preis et al.,

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1995; Roche and Prados, 1986), it has been reported that AOPs are not advantageous for the oxidation of specific organic compounds which are highly reactive with molecular ozone (Masten and Butler, 1986; Trapido et al., 1994; Beltrán et al., 1996). Our studies, similarly, indicate that the addition of hydrogen peroxide (at the ratios from 0 - 1.4 g/g) had no beneficial effect for the oxidation of the phenolic and indolic compounds. This may have been due to: (1) the rapid consumption of the free radicals generated during the decomposition of ozone by other non-target compounds in such a complicated matrix, or (2) the design of the reactor in which hydrogen peroxide was added at the top of the reactor and ozone at the bottom. Had all of the ozone reacted before it could have come in contact with the hydrogen peroxide, free radicals could not have formed. As such, the odorous metabolites in the manure slurry could be oxidized only by ozone.

3.3.4 Effect of Subsequent Storage of Manure Slurry after Ozone Treatment

To determine the extent to which the malodor would reoccur after ozone treatment, the ozonated manure slurry was stored at room temperature (18 °C) and analyzed each week for one month. Results indicate that the concentrations of the phenolic and indolic compounds decreased to a level that was less than that observed in the manure slurry immediately after ozonation (Table 3.4). The odor intensity remained at the same level as that observed in the freshly ozonated manure slurry. In addition, the concentrations of the

Table 3.4 Analysis of Stored Ozonated Manure (1 g/L) over a Period of Four Weeks

Storage Time (week)	*0*	*1*	*2*	*3*	*4*
Phenol (mg/L)	15.1	23.3	6.4	1.5	1.7
p-Cresol (mg/L)	ND	5.2	ND	ND	ND
p-Ethylphenol (mg/L)	2.6	7.2	5.9	1.8	1.4
Indole (mg/L)	ND	ND	ND	ND	ND
Skatole (mg/L)	ND	2.0	2.2	ND	ND
Acetate (mM)	92.1	77.2	29.2	5.0	4.6
Propionate(mM)	7.7	7.1	3.0	0.9	1.0
Butyrate (mM)	2.0	1.9	1.5	0.6	0.4
Isobutyrate (mM)	4.2	4.1	3.6	2.3	1.0
Valerate (mM)	1.0	1.0	0.6	0.3	0.3
Isovalerate (mM)	2.4	2.2	2.3	1.8	0.7
VFAs (mM as Carbon)	249	216	102	34	23

0: Freshly Ozonated Manure Slurry
1: One Week of Subsequent Storage after Ozonation
2: Two Weeks of Subsequent Storage after Ozonation
3: Three Weeks of Subsequent Storage after Ozonation
4: Four Weeks of Subsequent Storage after Ozonation
ND: Not Detectable

VFAs were observed to decrease significantly (from 250 mM to 20 mM) during one-month of storage. The major malodorous metabolites (phenolic and indolic compounds) were eliminated during ozonation and were not regenerated during subsequent storage. It is possible that these metabolites were not regenerated during storage because (1) ozone degraded the tryptophan and tyrosine, the precursors of the phenolic and indolic compounds, or (2) ozone inactivated the class of malodor-causing bacteria that degrade tryptophan and tyrosine into the phenolic and indolic compounds. On the other hand, the concentrations of VFAs were found to decrease during storage (post-ozonation). Since a wide class of bacteria would be able to use the VFAs as a growth substrate, it is thought

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that ozonation is ineffective at reducing the number of these microorganisms responsible to impede methanogenesis. This phenomenum was verified by observing the rising and accumulating of gaseous bubbles on the surface of storage tank probably due to the generation of carbon dioxide and methane. Because it was observed that the ozonation process effectively removes odorous metabolites and inhibits their formation for at least four weeks following treatment, the ozonated manure slurry could be potentially stored for at least four weeks prior to land application without encountering the problems associated with malodors.

3.3.5 Economic Analysis of Pilot-scale Ozonation System

An economic analysis of the pilot-scale system, including construction and operational costs, is summarized in Tables 3.5 and 3.6. The capital costs include the cost of materials, equipment, and construction. The operational cost includes the supply of oxygen gas and electric consumption when operating the ozonation system. Considering the current electricity rate in Michigan ($0.07/kW-hr) and 40 minutes ozone treatment (at 1 g/L ozone dosage), the operational cost was estimated to be approximately $2.00 for treating 100 gallons of swine manure. When using a detention time of 20 minutes, corresponding to an ozone dosage of 0.5 g/L, the operational cost would be reduced to half ($1.00/100 gallons). At this dosage, a maximum capacity of 144 gallons of liquid manure per day can be obtained using a treatment cycle of 30 minutes including 5 minutes for filling, 20 minutes of treatment, and 5 minutes for flushing. Thus, the operational cost can be estimated to be about $500 per year. The unit cost including capital and operational costs to treat the liquid manure is $0.024 dollar/gallon manure as

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calculated in Table 3.7. If this rate is applicable to the full-scale system used to treat the liquid discharge of MSU Swine Farm (about 1,600 gallons per day), the total operational cost will be $38 per day. On average, 10 pigs (at 220 lbs) are sent to the market per day from MSU Swine Farm (Tengman, 1995). Thus, the profits on each pig (within the range of $11.00 – 19.00 for 1993-1996 reported by Iowa State University) will be reduced by $3.80 if the ozonation system is used to treat the manure waste.

Table 3.5 The Capital Cost for the Pilot-scale Ozonation System

Items	Capital Cost (US dollars)
Ozone generator	5,000
Pilot-scale reactor	1,000
Venturi injector	100
Circulation pump	200
Ozone monitor	3,000
Agitation facility	2,000
Temperature-control system	1,000
Flowmeter	1,200
Tubing and fitting	500
Total	**14,000**

Table 3.6 The Operational Cost for the Pilot-scale System (Based on the calculation at 0.5 g/L ozone dosage)

Items	Power Consumption (watt)	Cost ($)/100 Gallons Treated
Ozone generator	115	0.18
Circulation pump	85	0.13
Agitator Facility	50	0.08
Temperature-control System	60	0.10
Oxygen supply		0.50
Total		**0.99**

Table 3.7 The Calculation of Total Cost for the Pilot-scale System

Initial cost: $ 14,000
Initial annual operating cost: $ 500, and increasing cost per year (3%): $ 15
Estimated salvage value: $ 500
Life expectancy: 15 years
Interest factor: 8 %

The total cost (present worth)= Initial cost + Annual operating cost + Increasing operating cost – Salvage value

$$= 14{,}000 + 500\left[\frac{(1+0.08)^{15}-1}{0.08(1+0.08)^{15}}\right] + \frac{15}{0.08}\left[\frac{(1+0.08)^{14}-1}{0.08} - 14\right]\left[\frac{1}{(1+0.08)^{14}}\right] - 500(1+0.08)^{-15}$$

=14,000+4300+650-160

=18790

The total volume of swine manure during 15 years: 144 (gal/day) × 365 (day/year) × 15 (year)=788,400 (gallon)

Therefore, 18790 (dollar)/788400 (gallon)= $ 0.024 dollar/gallon

3.4 Conclusions

Although ozonation has been extensively used in water and wastewater treatment, the application of ozone has not been used in the field to remove malodors from swine manure slurry. Based on the pilot-scale study, ozone treatment is a quick and effective method for removing the malodorous components from swine manure slurry. The design of an ozone facility to treat swine manure slurry will need to consider neither temperature variations nor the length of storage (up to 4 weeks) prior to treatment. A minimum dosage of ozone, 0.5 g/L, has been established to reduce the odor intensity of fresh and stored manure slurry to an acceptable level. The results of this study have encouraged us to install a full-scale ozonation system on a 2000-swine operation to investigate the feasibility of odor-control in a full-scale environment. To protect groundwater, the quality of which can be degraded by the migration of contaminants from the land discharged slurry, the treatment of the manure slurry using a lagoon or other biological treatment after ozone treatment is strongly recommended in order to diminish such components as ammonia-nitrogen, VFAs, and COD. Direct land application of ozone-treated swine manure slurry should been evaluated to determine the impact of high organic loading on the environment and ecology of soils and plants, even though the odorous substances have been substantially removed.

In the economic analysis, the operational cost when using 0.5 g/L ozone dosage was about $1.00 per100 gallons of liquid swine manure. The capital costs were $14,000. When amortizing the capital and operational costs over 15 years, it was determined that the profits from the swine operation would be reduced by $3.80 per pig marketed. This

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cost is excessive and modifications will be necessary if ozonation is to be implemented on a large scale by swine producers. Future work will focus on these modifications.

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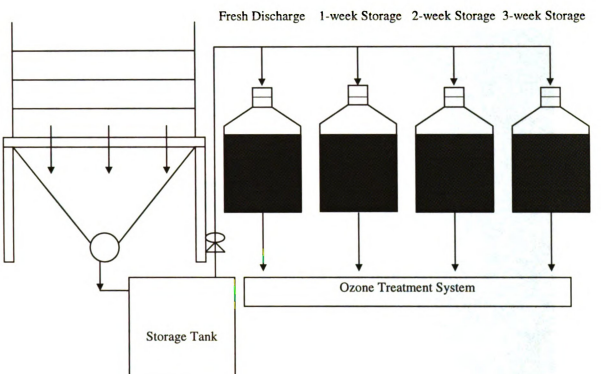


Figure 3.1 The Collection System for the Swine Manure

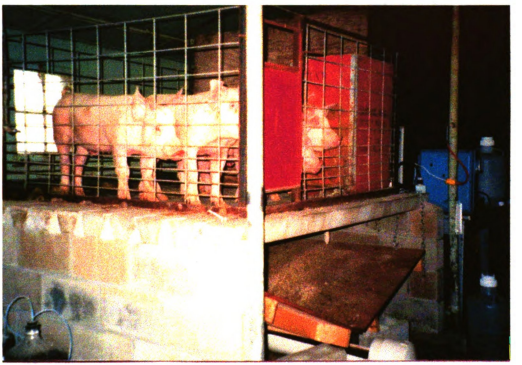
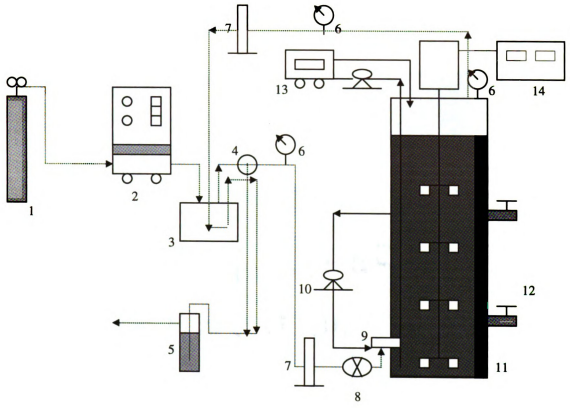


Figure 3.2 The Photo of the Manure Collection System



1: Oxygen Cylinder
2: Ozone Generator
3: UV Spectrophotometer
4: Three Way Valve
5: KI Solution
6: Pressure Gauge
7: Flow Meter
8: Flow Rate Controller
9: Venturi Injector
10: Circulation Pump
11: Ozonation Contactor
12: Sampling Ports
13: Dissolved Ozone Monitor
14: Agitator Controller

Figure 3.3 The Configuration of Pilot-Scale System for Ozone Treatment

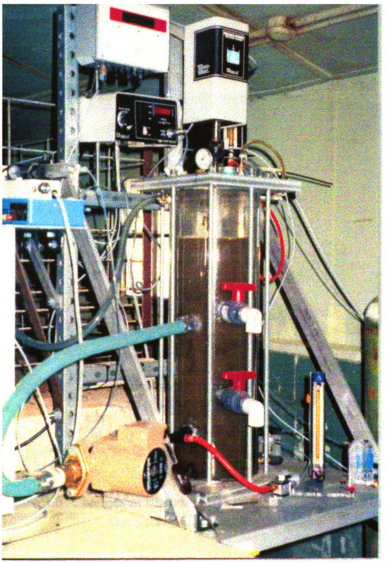


Figure 3.4 The Photo of Pilot-Scale System for Ozone Treatment

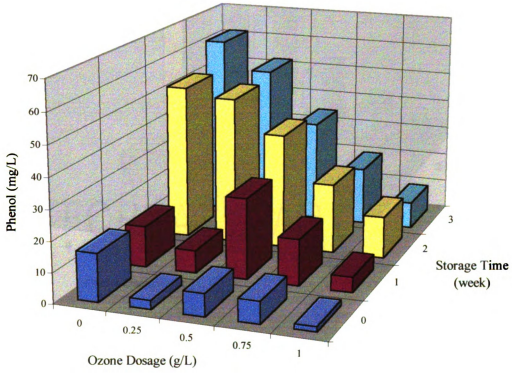


Figure 3.5 Changes in Phenol Concentration during the Storage and Ozonation of Swine Waste Slurry

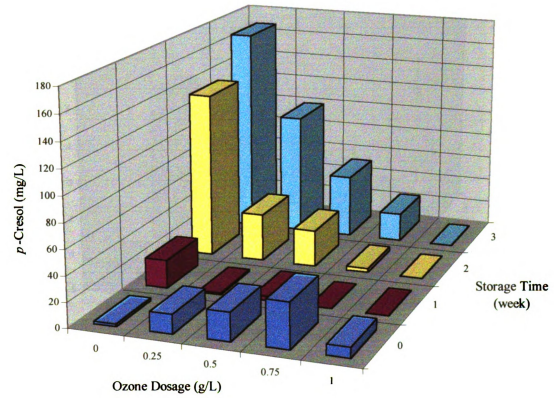


Figure 3.6 Changes in *p*-Cresol Concentration during the Storage and Ozonation of Swine Waste Slurry

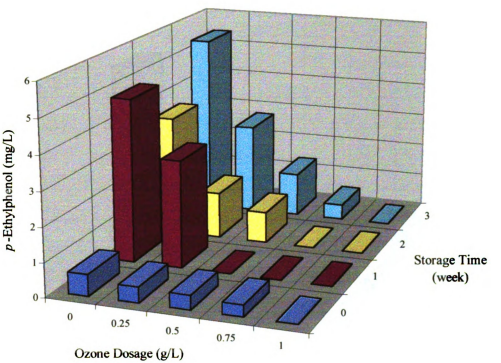


Figure 3.7 Changes in p-Ethylphenol Concentration during the Storage and Ozonation of Swine Waste Slurry

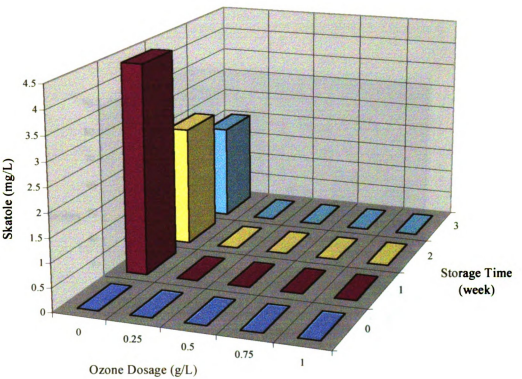


Figure 3.8 Changes in Skatole (3-methyl-indole) Concentration during the Storage and Ozonation of Swine Waste Slurry

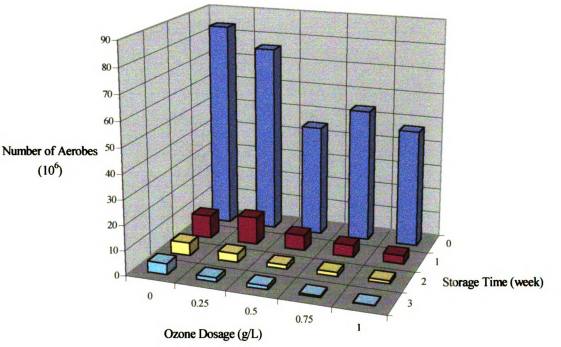


Figure 3.9 Changes in Number of Total Aerobes during the Storage and Ozonation of Swine Manure Slurry

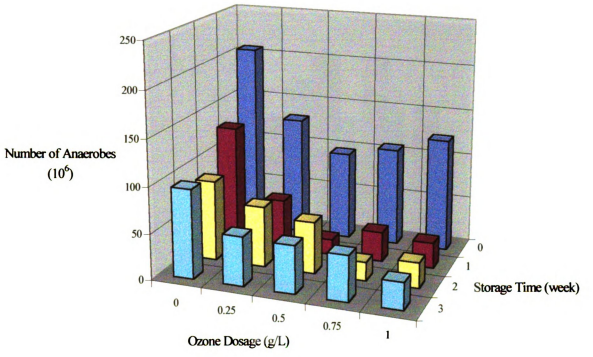


Figure 3.10 Changes in Number of Total Anaerobes during the Storage and Ozonation of Swine Manure Slurry

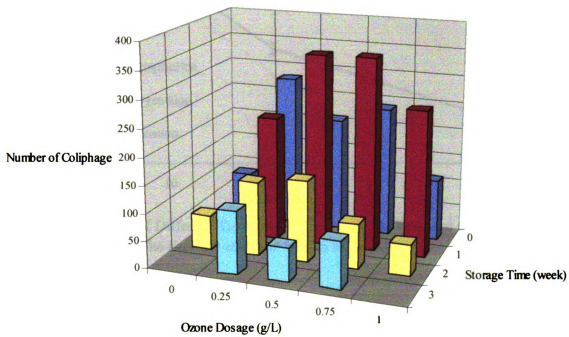


Figure 3.11 Changes in Number of Coliphage during the Storage and Ozonation of Swine Manure Slurry

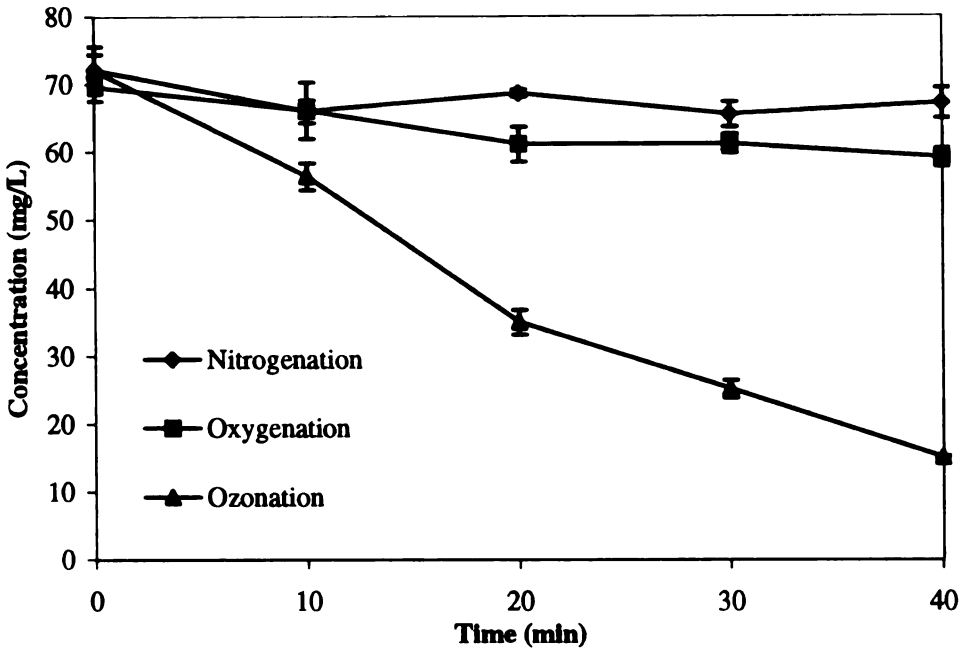


Figure 3.12 Effect of Different Treatment Processes on the Removal of Phenol (The flowrate of ozone was 25 mg/L-min)

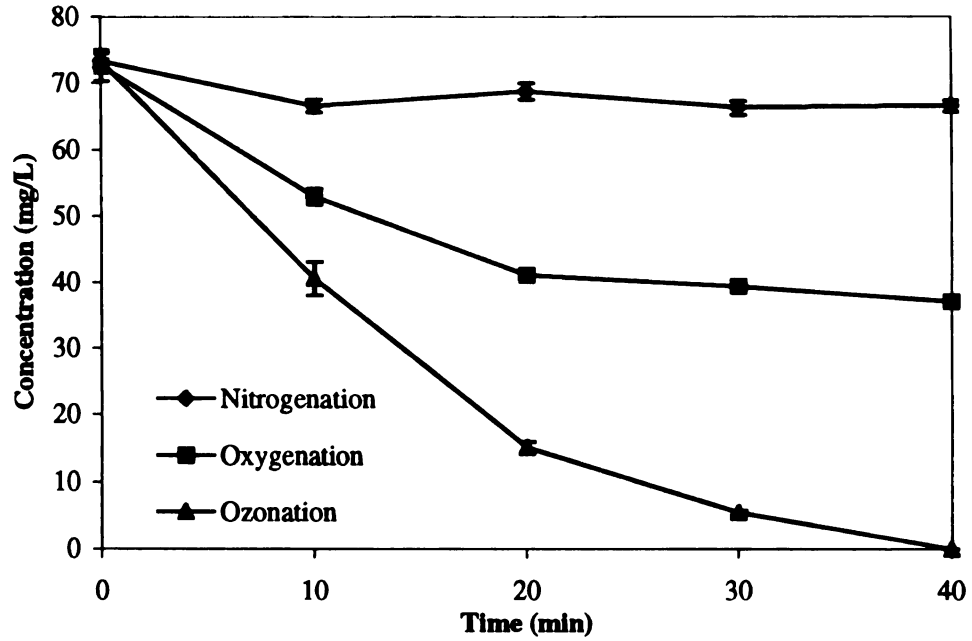


Figure 3.13 Effect of Different Treatment Processes on the Removal of *p*-Cresol (The flowrate of ozone was 25 mg/L-min)

Concentration (mg/L)

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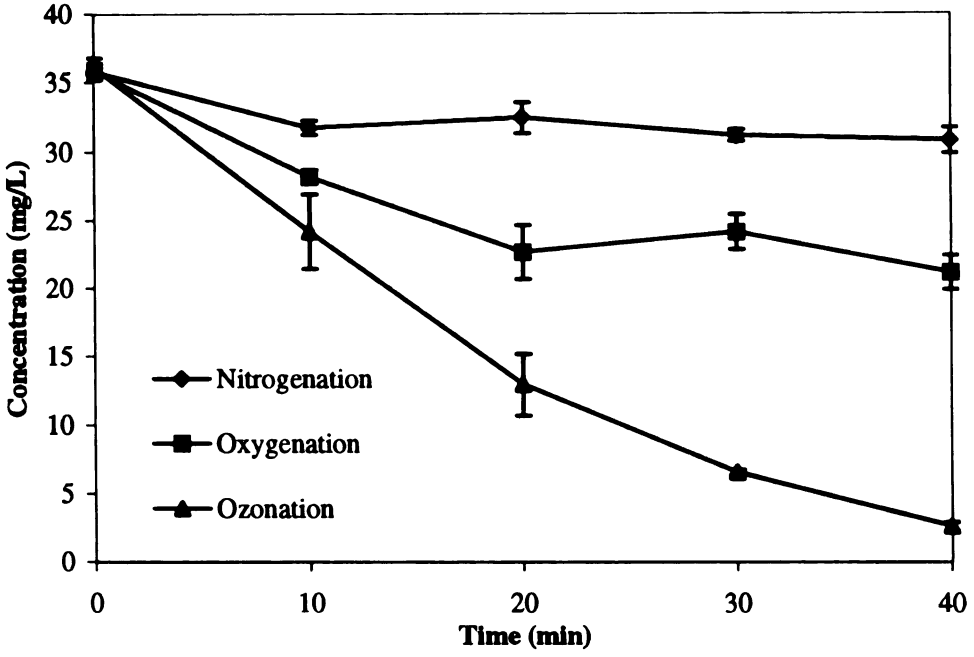

Figure 3.14 Effect of Different Treatment Processes on the Removal of *p* -Ethylphenol (The flowrate of ozone was 25 mg/L-min)

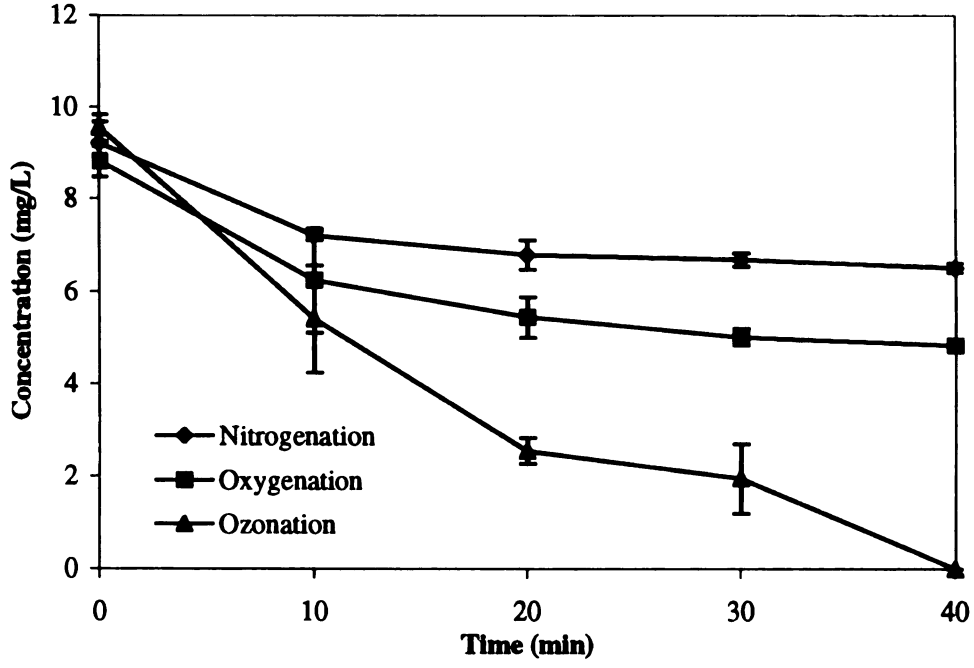

Figure 3.15 Effect of Different Treatment Processes on the Removal of Skatole (The flowrate of ozone was 25 mg/L-min)

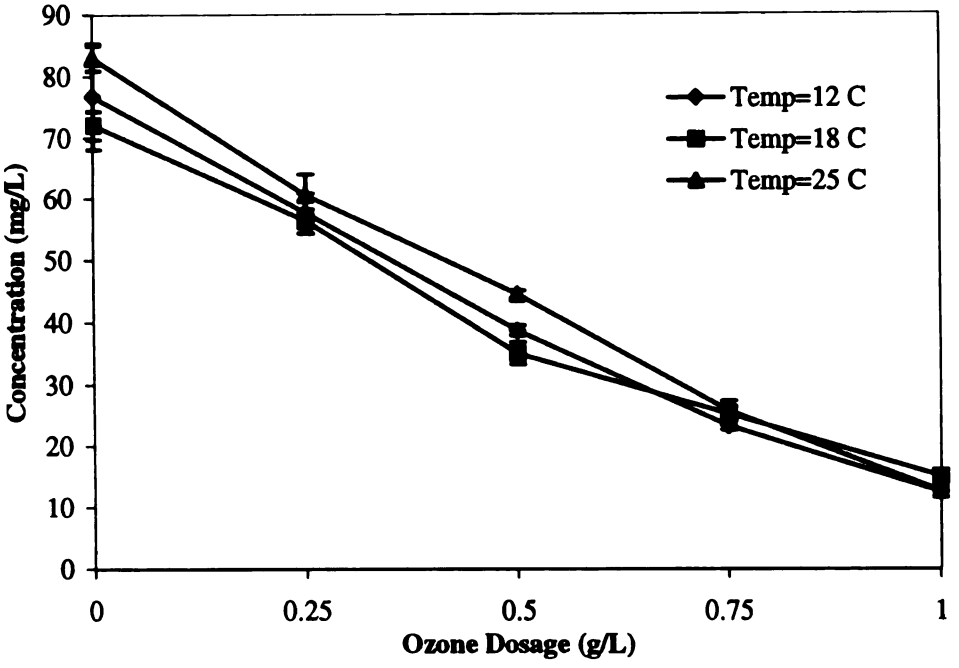

Figure 3.16 Effect of Temperature on the Removal of Phenol

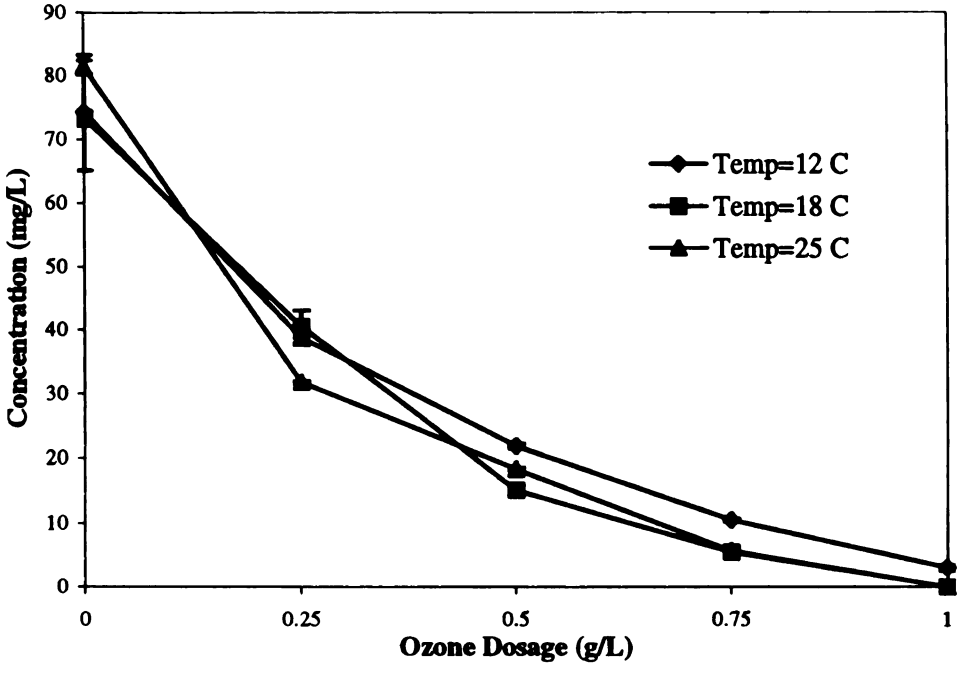

Figure 3.17 Effect of Temperature on the Removal of *p* -Cresol

Concentration (mg/L)

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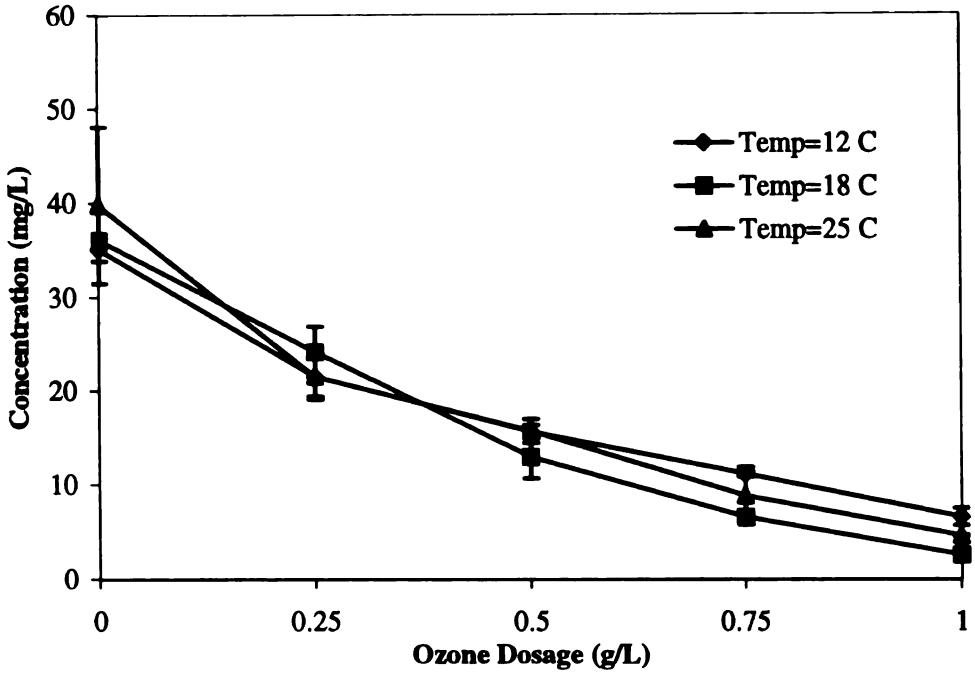

Figure 3.18 Effect of Temperature on the Removal of *p* -Ethylphenol

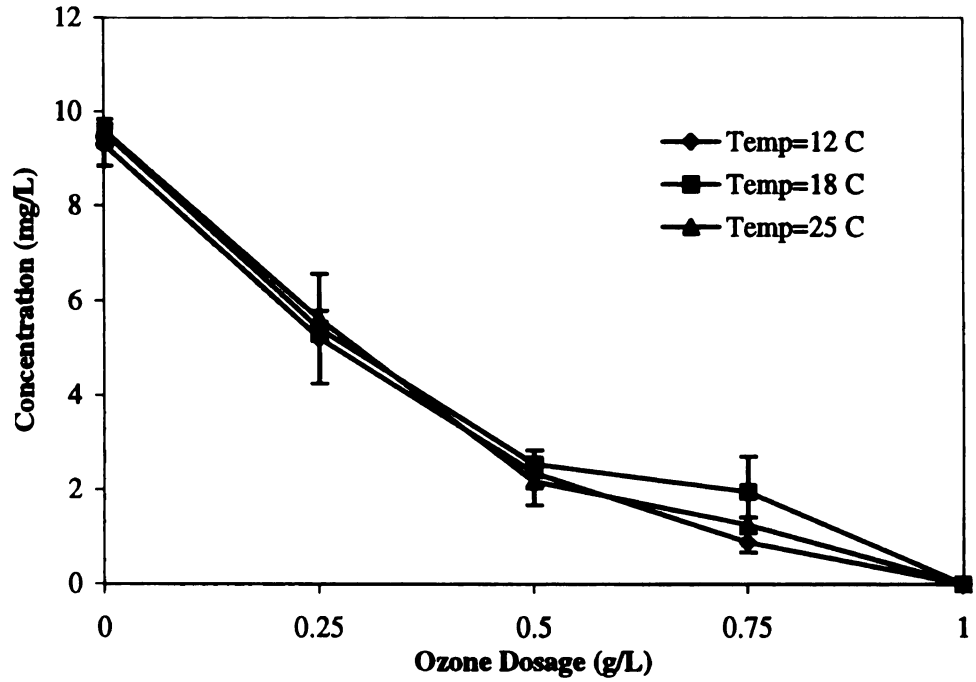

Figure 3.19 Effect of Temperature on the Removal of Skatole

Concentration (mg/L)

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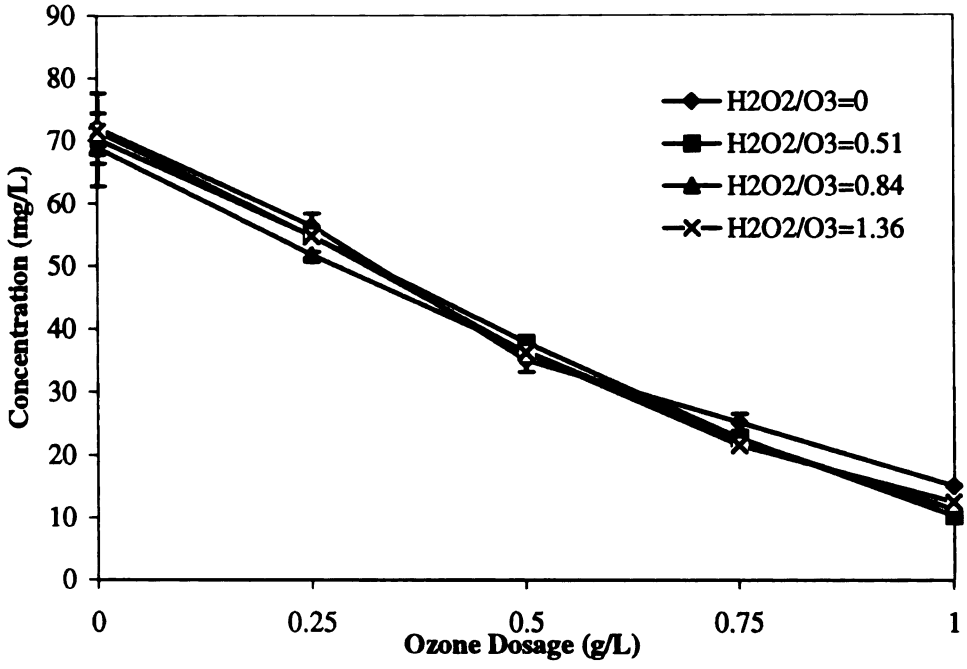

Figure 3.20 Effect of the Ratio of Hydrogen Peroxide to Ozone on the Removal of Phenol

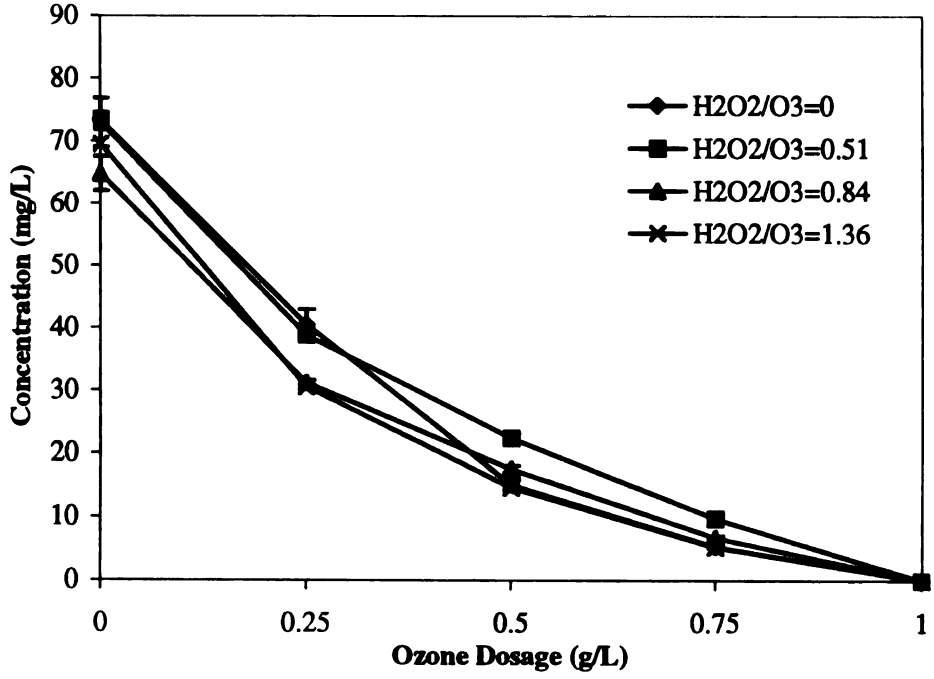

Figure 3.21 Effect of the Ratio of Hydrogen Peroxide to Ozone on the Removal of *p* -Cresol

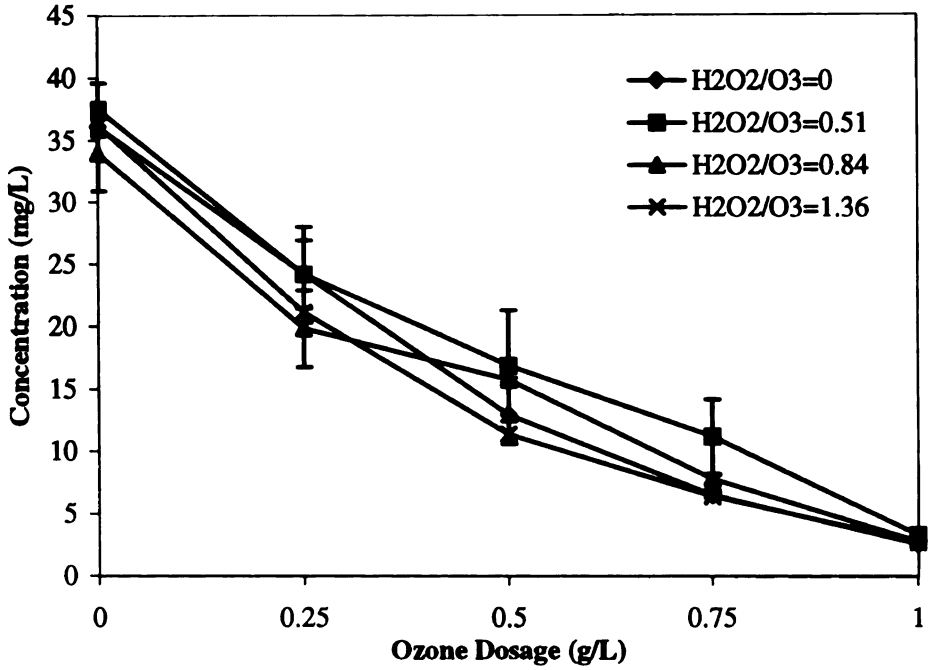

Figure 3.22 Effect of the Ratio of Hydrogen Peroxide to Ozone on the Removal of *p* -Ethylphenol

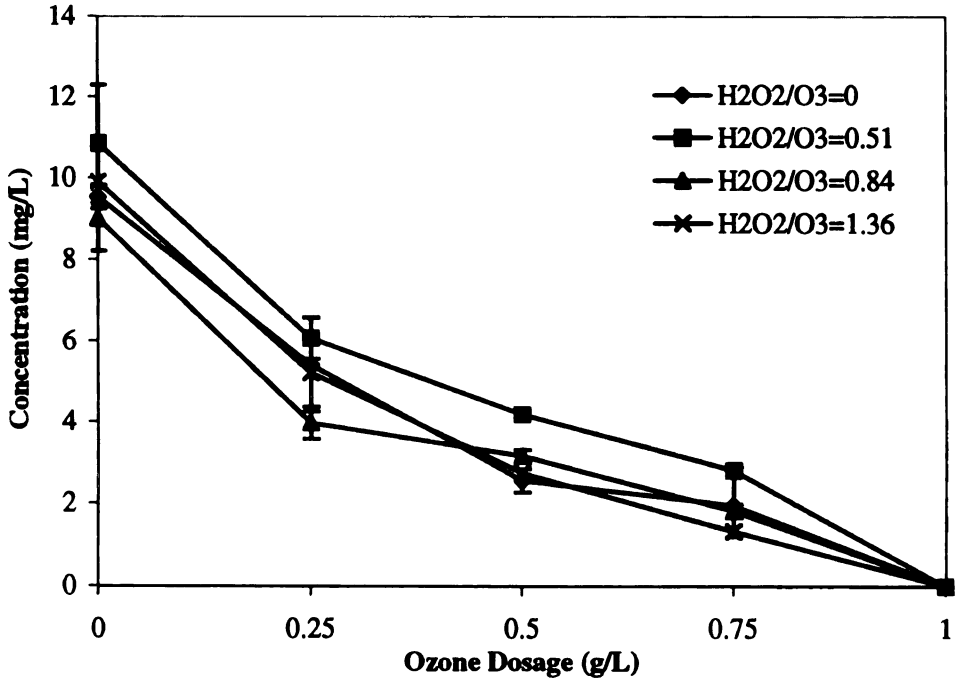

Figure 3.23 Effect of the Ratio of Hydrogen Peroxide to Ozone on the Removal of Skatole

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Chapter 4

MASS TRANSFER OF OZONE IN A SEMI-BATCH STIRRED REACTOR

4.1 Introduction

The increasing demand for high quality water has accelerated the use of ozone in water and wastewater treatment. With its powerful oxidation potential, ozone reacts rapidly with many organic and inorganic compounds (Hoigné and Bader, 1983[a], 1983[b], 1985). Thus, the reaction rate for many ozonation processes is limited by mass-transfer. Traditionally, the ozonation of the most environmental contaminants is accomplished using a semi-batch or continuous system in which the gaseous ozone is passed through the liquid phase. Before ozone can react with any substance in the liquid phase, it must pass across an interface between gaseous ozone and liquid. As ozone is a sparingly soluble gas, its transfer efficiency is controlled by such physical parameters as temperature, gaseous flowrate, mixing speed, type of diffusers, and reactor geometry, and such chemical parameters as pH, ionic strength, and composition of the aqueous solution. Since the transfer efficiency of mass transfer of ozone into the aqueous phase can be described by two variables, mass-transfer and partition coefficients, the effect of these systematic parameters on the mass-transfer and partition coefficients will be the focus of

this study. A mass-transfer model will be developed and used to predict the ozone concentration profile during the period of mass-transfer.

4.2 Materials and Methods

A semi-batch stirred reactor (Figures 4.1-4.2) made of pyrex glass with a capacity of 1.5 L was utilized to investigate the mass transfer of ozone. To prevent any interference from impurities, deionized distilled water (DDI) was used. Ozone was generated from pure oxygen by corona discharge using an ozone generator (Model T-408, Polymetrics Inc., San Jose, CA), which produced an ozone concentration of ca. 1.3 % (by volume) in the oxygen gas stream. The oxygen stream was dried using a molecular sieve trap (S/P Brand #G5301-21) prior to ozone generation. In this reactor, a fritted glass diffuser that is able to generate fine bubbles (bubble diameter < 1 mm) was located near the bottom of the reactor and a magnetic stirrer bar was placed under the diffuser to achieve complete mixing throughout the liquid. In addition, a water jacket around the reactor maintained the desired temperature with water circulated from a water bath.

The concentrations of gaseous ozone were monitored using an UV spectrophotometer (UV 1201, Shimadzu, Japan) by passing ozone gas, from both the inlet and outlet, through two 2-mm flow cells. The concentration of aqueous ozone was also determined spectrophotometrically. In this case, the liquid was pumped through a 1-cm flow cell. The absorbance of the ozone was monitored at the wavelength 258 nm. An extinction coefficient of 3000 $M^{-1}cm^{-1}$ was used to convert absorbances to concentration units (Nowell and Hoigné, 1988).

Before initiating each experiment, a three-way valve was used to bypass the inlet ozone into a potassium iodine solution (trap) until it was observed that the inlet concentration was constant. When a desired concentration of inlet ozone was obtained, the run was started by rotating this valve and admitting ozone in oxygen into the reactor. During the run, the ozone absorbances in the inlet and outlet gas streams and in the liquid stream were monitored at five-minute intervals by using a kinetic diskette in the UV spectrophotometer. When all absorbances became stable, the experiment was stopped. The rate of ozone decomposition was determined by monitoring the decrease of concentration with time after the introduction of gaseous ozone was ceased. The systematic parameters that were varied are summarized below:

- Temperature: 14, 22, 30 °C
- Inlet concentration: 5.4, 22.4, 44.3, 62.4 mg/L
- Inlet flowrate: 100, 200, 300, 400, 500 mL/min
- pH: 6.0-6.5 (unbuffered distilled deionized water), 2.1 (acidified by adding 50 mL of a solution which was made by the addition of 8 mL concentrated H_2SO_4 and 120.7 g Na_2SO_4 to 0.5 liter DDI water), 6.7 (buffered by adding 50 mL of phosphate solution which was made by the addition of 92.84 g Na_2HPO_4 and 141.13 g KH_2PO_4 to 1 liter DDI water)
- Ionic Strength: 0.1, 0.2, 0.3, 0.4, 0.5 (M)

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4.3 Model Development

A mathematical model of the mass transport of ozone from the gas into the bulk liquid in a semi-batch reactor needs to be developed to determine the mass-transfer coefficient, which is relatively important when the reaction of ozone and target compounds is controlled by the rate of mass transfer instead of by the chemical reaction rate. Approaches to developing the mass-transfer model have been proposed by many investigators (Kuo et al., 1976, Yocum, 1979, Roth and Sullivan, 1981, Shaffer and Esterson, 1982, Anselmi et al., 1984, Roustan et al., 1987, Sotelo et al., 1989). However, among these models, only the model proposed by Anselmi et al. (1984) considered the effect of head space above the liquid on the concentration of ozone in the gas phase. Nevertheless, this model still neglects the effect of ozone self-decomposition in the aqueous and gas phases. As such, Anselmi's model is inappropriate for ozone solutions having a pH>6 and for low flowrate systems, in which the self-decomposition of moisturized ozone gas may be significant due to longer detention times in the system. To develop a general model which can be used in any situation, the effect of ozone self-decomposition was taken into consideration although this resulted in more complicated mathematical computations. Fortunately, Laplace operators can be employed as a mathematical tool to determine the analytical solutions. In this first model, the overall mass balance between the aqueous phase and gas phase, including the gas bubble and headspace have been examined thoroughly. It is also assumed that the gas flow is completely mixed. As there is some dispute whether the flow pattern of gas is completely mixed or plug flow (Nishikawa et al., 1981), a second model was developed in which it was assumed that the flow of the bubbles in the system could be modeled as

plug flow. In order to simulate a plug flow system, the reactor is divided into 10 sections, each completely mixed. As a result, in the second model there are eleven ordinary differential equations that could be solved only by using numerical methods.

4.3.1 Mixed-Flow Model

The following assumptions were made:

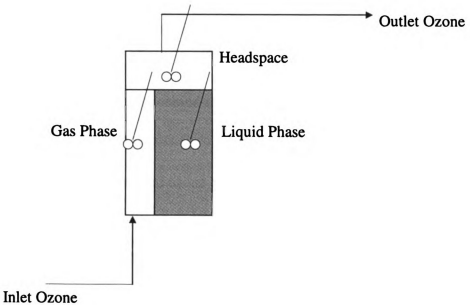
(1) complete mixing of all liquid and gas phases;

(2) constant temperature and pressure;

(3) constant liquid volume;

(4) first order self-decomposition of ozone in both gas and liquid phases;

(5) two-film model to describe the liquid side resistance (neglecting the gas phase resistance) since ozone is sparingly soluble in water.



The mass balance of ozone in all liquid and gas phases can be expressed as:

$$V \times \frac{dC_L}{dt} = K_{La} \times V \times (C_L^* - C_L) - k \times V \times C_L = K_{La} \times V \times (\alpha C_g' - C_L) - k \times V \times C_L \quad (4.1)$$

$$H_0 \times \frac{dC_g'}{dt} = Q \times (C_g^{in} - C_g') - K_{La} \times V \times (\alpha C_g' - C_L) \quad (4.2)$$

$$V \times \frac{dC_g^e}{dt} = Q \times (C_g' - C_g^e) - k' \times V' \times C_g^e \quad (4.3)$$

where the initial conditions are:

(1) t=0, $C_L(0) = 0$

(2) t=0, $C_g'(0) = 0$

(3) t=0, $C_g^e(0) = 0$

and the terms are defined as:

V : volume of the liquid phase reactor (L)

K_{La} : mass transfer coefficient in the liquid phase (1/min)

k : first order decomposition rate constant for dissolved ozone in the liquid phase (1/min)

k' : first order decomposition rate constant for moisturized gaseous ozone (1/min)

C_L : dissolved ozone concentration in the liquid phase (mg/L)

C_L^* : saturated dissolved ozone concentration in the liquid phase which is equilibrium with the gas phase (mg/L)

α : partition coefficient for ozone

H_0 : gas hold up (total volume of bubbles) in the reactor (L)

V' : volume of the reactor headspace (L)

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C_g' : ozone concentration leaving the reactor or inlet ozone concentration to the headspace(mg/L)

C_g^{in} : inlet ozone concentration to the gas phase (bubbles) (mg/L)

C_g^e : outlet ozone concentration leaving the headspace (mg/L)

Q : ozone flow rate (L/min)

Taking the Laplace transformation of each the mass balance equations yields:

$$V \times (S\hat{C}_L(S) - C_L(0)) = K_{La}V(\alpha\hat{C}_g'(S) - \hat{C}_L(S)) - kV\hat{C}_L(S) \tag{4.4}$$

$$H_0 \times (S\hat{C}_g'(S) - C_g'(0)) = \frac{QC_g^{in}}{S} - Q\hat{C}_g'(S) - K_{La}V(\alpha\hat{C}_g'(S) - \hat{C}_L(S)) \tag{4.5}$$

$$V' \times (S\hat{C}_g^e(S) - C_g^e(0)) = Q(\hat{C}_g'(S) - \hat{C}_g^e(S)) - k'V'\hat{C}_g^e(S) \tag{4.6}$$

According to the initial conditions:

$$\hat{C}_L(S) = (\frac{\alpha K_{La}V}{VS + K_{La}V + kV})\hat{C}_g'(S) = (\frac{\alpha K_{La}}{S + K_{La} + k})\hat{C}_g'(S) \tag{4.7}$$

After substitution, we can write that:

$$\hat{C}_g'(S) = \frac{\frac{1}{S} \times Q \times C_g^{in}}{H_0 S + Q + \alpha K_{La}V - \frac{\alpha K_{La}{}^2 V}{S + K_{La} + k}} \tag{4.8}$$

$$= \frac{(S + K_{La} + k)QC_g^{in}}{S[H_0 S^2 + (H_0 K_{La} + H_0 k + Q + \alpha K_{La}V)S + (QK_{La} + Qk + \alpha k K_{La}V)]} \tag{4.9}$$

If we let $\lambda_1 = H_0 K_{La} + H_0 k + Q + \alpha K_{La}V$
$\lambda_2 = QK_{La} + Qk + \alpha k K_{La}V$

then,

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$$\hat{C}_g^{'}(S) = \frac{(S + K_{La} + k)QC_g^{in}}{S(H_0 S^2 + \lambda_1 S + \lambda_2)} \tag{4.10}$$

$$= \frac{(S + K_{La} + k)QC_g^{in}}{H_0 S(S - \frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0})(S - \frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0})} \tag{4.11}$$

$$\lambda_1^2 - 4H_0\lambda_2 = (H_0 K_{La} + H_0 k - Q - \alpha K_{La} V)^2 + 4H_0 \alpha K_{La}^2 V > 0$$

$$\hat{C}_g^{'}(S) = \frac{A}{S} + \frac{B}{S - \frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0}} + \frac{C}{S - \frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0}} \tag{4.12}$$

$$A = \frac{(K_{La} + k)QC_g^{in}}{\lambda_2}$$

where, $B = \dfrac{QC_g^{in}(-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2} + 2H_0 K_{La} + 2H_0 k)}{\lambda_1^2 - \lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2} - 4H_0\lambda_2}$

$$C = \frac{QC_g^{in}(-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2} + 2H_0 K_{La} + 2H_0 k)}{\lambda_1^2 + \lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2} - 4H_0\lambda_2}$$

Taking the reverse Laplace transformation yields:

$$C_g^{'}(t) = A + B \times Exp(\frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} t) + C \times Exp(\frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} t) \tag{4.13}$$

In the same way, the ozone concentration in liquid phase can be found as:

$$C_L(t) = D + E \times Exp(\frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0 V\lambda_2}}{2H_0 V} t) + F \times Exp(\frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0 V\lambda_2}}{2H_0 V} t) \tag{4.14}$$

$$D = \frac{\alpha K_{La} Q C_g^{in}}{\lambda_2}$$

$$E = \frac{2\alpha H_o K_{La} Q C_g^{in}}{\lambda_1^2 - 4H_0\lambda_2 - \lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2}}$$

$$F = \frac{2\alpha H_o K_{La} Q C_g^{in}}{\lambda_1^2 - 4H_0\lambda_2 + \lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2}}$$

Then, the outlet ozone concentration from the second gas phase can also be obtained as:

$$\therefore C_g^e(t) = W + X \times Exp[(-\frac{Q}{V'} - k')t] + Y \times Exp(\frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} t) + Z \times Exp(\frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} t) \quad (4.15)$$

$$W = \frac{(K_{La} + k) Q C_g^{in}}{\lambda_2 (1 + k'(\frac{V'}{Q}))}$$

$$X = \frac{\frac{Q}{V'}(-\frac{Q}{V'} - k' + K_{La} + k) Q C_g^{in}}{(-\frac{Q}{V'} - k')[H_0(-\frac{Q}{V'} - k')^2 + \lambda_1(-\frac{Q}{V'} - k') + \lambda_2]}$$

$$Y = \frac{Q(-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2} + 2H_0 K_{La} + 2kH_0)(\frac{Q}{V'}) C_g^{in}}{(-\lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2} + \lambda_1^2 - 4H_0\lambda_2)(\frac{-\lambda_1 + \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} + \frac{Q}{V'} + k')}$$

$$Z = \frac{Q(-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2} + 2H_0 K_{La} + 2kH_0)(\frac{Q}{V'}) C_g^{in}}{(\lambda_1\sqrt{\lambda_1^2 - 4H_0\lambda_2} + \lambda_1^2 - 4H_0\lambda_2)(\frac{-\lambda_1 - \sqrt{\lambda_1^2 - 4H_0\lambda_2}}{2H_0} + \frac{Q}{V'} + k')}$$

4.3.2 Plug-Flow Model

The following assumptions were made:

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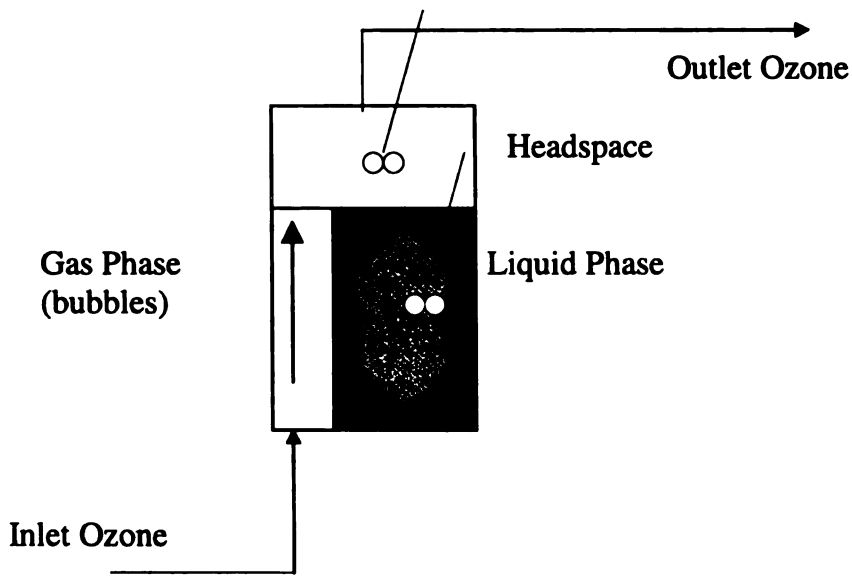
(1) the liquid in the reactor and the gas in headspace are both completely mixed. The flux of gas in the reactor can be described as plug flow;

(2) constant temperature and pressure;

(3) constant liquid volume;

(4) first order self-decomposition of ozone at both gas and liquid phase;

(5) two-film model to describe the liquid side resistance (neglecting the gas phase resistance) as ozone is sparingly in water.



The plug flow region in portion of the reactor containing the gas phase (bubbles) can be divided into 10 small sections, each of which is assumed to be completely mixed.

Mass balance equations of ozone at all liquid and gas phases:

$$10\times\frac{dX(t)}{dt}=K_{La}(\alpha\times(Y_1(t)+Y\ (t)+Y_3(t)+Y_4(t)+Y_5(t)+Y_6(t)+Y_7(t)+Y_8(t)+Y_9(t)+Y_{10}(t))-10\times X(t))-10\times k_1\times X(t) \quad (4.16)$$

$$H_0\times\frac{dY_1(t)}{dt}=10\times Q\times(C_g^{in}-Y_1(t))-k_2\times H_0\times Y_1(t)-K_{La}\times V\times(\alpha\times Y_1(t)-X(t)) \quad (4.17)$$

$$H_0 \times \frac{dY_2(t)}{dt} = 10 \times Q \times (Y_1(t) - Y_2(t)) - k_2 \times H_0 \times Y_2(t) - K_{La} \times V \times (\alpha \times Y_2(t) - X(t)) \quad (4.18)$$

$$H_0 \times \frac{dY_3(t)}{dt} = 10 \times Q \times (Y_2(t) - Y_3(t)) - k_2 \times H_0 \times Y_3(t) - K_{La} \times V \times (\alpha \times Y_3(t) - X(t)) \quad (4.19)$$

$$H_0 \times \frac{dY_4(t)}{dt} = 10 \times Q \times (Y_3(t) - Y_4(t)) - k_2 \times H_0 \times Y_4(t) - K_{La} \times V \times (\alpha \times Y_4(t) - X(t)) \quad (4.20)$$

$$H_0 \times \frac{dY_5(t)}{dt} = 10 \times Q \times (Y_4(t) - Y_5(t)) - k_2 \times H_0 \times Y_5(t) - K_{La} \times V \times (\alpha \times Y_5(t) - X(t)) \quad (4.21)$$

$$H_0 \times \frac{dY_6(t)}{dt} = 10 \times Q \times (Y_5(t) - Y_6(t)) - k_2 \times H_0 \times Y_6(t) - K_{La} \times V \times (\alpha \times Y_6(t) - X(t)) \quad (4.22)$$

$$H_0 \times \frac{dY_7(t)}{dt} = 10 \times Q \times (Y_6(t) - Y_7(t)) - k_2 \times H_0 \times Y_7(t) - K_{La} \times V \times (\alpha \times Y_7(t) - X(t)) \quad (4.23)$$

$$H_0 \times \frac{dY_8(t)}{dt} = 10 \times Q \times (Y_7(t) - Y_8(t)) - k_2 \times H_0 \times Y_8(t) - K_{la} \times V \times (\alpha \times Y_8(t) - X(t)) \quad (4.24)$$

$$H_0 \times \frac{dY_9(t)}{dt} = 10 \times Q \times (Y_8(t) - Y_9(t)) - k_2 \times H_0 \times Y_9(t) - K_{la} \times V \times (\alpha \times Y_9(t) - X(t)) \quad (4.25)$$

$$H_0 \times \frac{dY_{10}(t)}{dt} = 10 \times Q \times (Y_9(t) - Y_{10}(t)) - k_2 \times H_0 \times Y_{10}(t) - K_{la} \times V \times (\alpha \times Y_{10}(t) - X(t)) \quad (4.26)$$

$$V_1 \times \frac{dZ(t)}{dt} = Q \times (Y_{10}(t) - Z(t)) - k_2 \times V_1 \times Z(t) \quad (4.27)$$

The initial conditions are:

$$X(0) = 0, Y_1(0) = 0, Y_2(0) = 0, Y_3(0) = 0, Y_4(0) = 0, Y_5(0) = 0, Y_6(0) = 0, Y_7(0) = 0, Y_8(0) = 0,$$
$$Y_9(0) = 0, Y_{10}(0) = 0, Z(0) = 0$$

The terms used in the above equations are defined as:

X(t): dissolved ozone concentration in the liquid phase;

$Y_j(t)$: gaseous ozone concentration in the j^{th} section of the bubble phase, j is the number of the section;

Z(t): gaseous ozone concentration in the headspace.

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This system of equations was solved numerically by using the mathematical computer software, MAPLE V (Release 4.0, Waterloo Maple Inc., Waterloo, Ontario)

4.4 Results and Discussion

4.4.1 Self-decomposition of Ozone in Water and Headspace

The order and rate of the decomposition of dissolved ozone were determined by observing the reduction in the ozone concentration under different temperatures in unbuffered DDI water and buffered DDI water at pH of 6.7. Results (Table 4.1) indicate that the rate of ozone decomposition in unbuffered DDI water occurs via a first order reaction (Figure 4.3), while in buffered DDI water (pH=6.7) ozone decomposition follows second order reaction (Figure 4.4). According to the results of many researchers and summarized by Sugimitsu et al. (1989), the decomposition of ozone has a reaction order of 1, 1.5, or 2. Gurol and Singer (1982) concluded that the major differences are due to (a) the use of different analytical techniques to measure the concentration of dissolved ozone, (b) uncertainties in the data analysis and data interpretation, (c) the effect of solution composition, (d) the possible presence of impurities in the reagents used. Therefore, in our studies, the discrepancy in the reaction order for the unbuffered and buffered DDI water can be explained as the effect of solution composition.

The rate of ozone decomposition was also determined at pH 2.1. At this pH, the concentration of dissolved ozone decreased quite slowly. As such, the decomposition rate can be said to be negligible compared with that obtained under higher pH conditions. This is consistent with the observation of other researchers (Gurol and Singer, 1982; Sugimitsu et al., 1989). Increasing the temperature is also expected to increase the rate of

self-decomposition of dissolved ozone in water. The enhancement of self-decomposition of ozone in water can be demonstrated by the relationship derived from the Arrhenius equation (Kuo et al., 1976, Ghaieb and Bes, 1989):

$$k_d = k_0[OH^-]^m \exp(-E/RT) \qquad (4.28)$$

where k_d is the decomposition rate constant, k_0 is the frequency factor, $[OH^-]$ is the concentration of hydroxide ion (mole/L), m is the reaction order, E is the activation energy (kcal/mole), R is the gas constant (kcal/K-mole), and T is temperature (K). The effect of temperature (over the range from 14 °C to 30 °C) on the decomposition rate of ozone was more significant for the buffered DDI water. The decomposition rate constant increased by ca. 140%. On the other hand, over a temperature ranged from 14 °C to 30 °C the ozone decomposition rate constant in unbuffered DDI water increased by only ca. 10%. Using equation 4.25, the activated energies were calculated to be 1.4 and 9.6 Kcal/mole, respectively, for the unbuffered and buffered DDI water. This result implies that the decomposition rate constant of ozone in buffered DDI water is much more sensitive to the change in temperatures than it is in unbuffered DDI water.

The rate of decomposition of ozone in the moisturized gas in the headspace of the reactor was estimated (Figure 4.5). The concentrations of ozone at the entrance and exit of the headspace were unchanged at different flowrates. Therefore, the self-decomposition of moisturized gaseous ozone can be neglected.

Table 4.1 Self-decomposition of Dissolved Ozone in DDI Water under Different Temperature

Mathematical Expression of Ozone Decomposition : $-d[O_3]/dt = k_d[O_3]^m$				
	DDI without buffer		DDI buffered at pH=6.7	
Temperature (°C)	m	k_d	m	k_d
14	1	0.0201	2	0.00284
22	1	0.0215	2	0.00402
30	1	0.0229	2	0.00691

4.4.2 Transfer of Ozone in DDI Water (without pH buffer)

The mass transfer of ozone in DDI water was determined by changing the various concentrations of inlet ozone, system temperature, and ozone flow rate. To measure the mass-transfer coefficient, K_La, and the partition coefficient, α, the experimentally determined concentrations of outlet ozone and dissolved ozone were used in the two models. In the first model, it was assumed that the gas phase was completely mixed, while in the second phase it was assumed that the movement of gas bubbles in the gas phase followed plug-flow conditions. The logarithmic concentration of ozone in the bubbles (Beltrán et al., 1997) was used as the average driving force in plug-flow model. To validate these models, the concentration of inlet ozone was varied under the operational conditions of 14 °C and 400 mL/min flowrate. This data was used to calculate the mass-transfer and partition coefficients for ozone (Table 4.2). These results indicate that, by using these two parameters, the transfer of ozone can be modeled (Figure 4.6). For most experiments, the plug-flow model better simulated the data than did the mixed-flow model. This result supports the conclusion proposed by Nishikawa et al. (1981) that the movement of ozone bubbles in a semi-batch reactor is best represented by

a plug-flow model. Although the concentrations of inlet ozone differed, by an order of magnitude, there is little variation in the fitted values of the mass transfer and the partition coefficient.

Table 4.2 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Inlet Ozone Concentrations

14°C, Q=400 mL/min	Mixed-flow Model			Plug-flow Model		
Conc. of Inlet Ozone (mg/L)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
5.41	0.332	0.2245	0.961	0.339	0.1779	0.932
22.37	0.343	0.2249	0.969	0.344	0.1763	0.979
44.29	0.338	0.2236	0.975	0.342	0.1728	0.988
62.37	0.348	0.2273	0.962	0.353	0.1774	0.990

The effect of temperature on mass-transfer and partition coefficients of ozone indicates that as the temperature increases, the mass-transfer coefficient increases and the partition coefficient decreases (Table 4.3). Adams et al. (1981) indicated that temperature is one of the most significant factors to affect the mass transfer coefficient of oxygen, with relationship as below:

$$K_L a_{(T)} = K_L a_{(20°)} \theta^{(T-20)} \qquad (4.29)$$

The temperature factor, θ, for oxygen has been reported to vary from 1.016 to 1.037 (Adams et al., 1981). Our experimental results for ozone mass-transfer also show that a similar relationship may exist. Using the mass-transfer coefficient for ozone that was derived from the plug-flow model, the θ value can be estimated to be 1.031 (R^2=0.96). As such, the effect of temperature on the mass-transfer coefficient of ozone is similar to

that for oxygen. The partition coefficient for ozone was reported to be 0.34, 0.24, and 0.17 for temperatures of 12 °C, 21 °C, and 31 °C, respectively (Caprio et al., 1981). Thus, the partition coefficients we obtained agree satisfactorily with those of Caprio et al. (1981).

Table 4.3 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Temperatures in DDI Water

C=46mg/L, Q=400mL/min	Mixed-flow Model			Plug-flow Model		
Temperature (°C)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
14	0.355	0.2152	0.957	0.353	0.1723	0.989
22	0.253	0.2851	0.964	0.249	0.2397	0.970
30	0.178	0.3551	0.971	0.176	0.2800	0.971

The effect of flowrate on the mass-transfer coefficient in a semi-batch stirred reactor was also investigated (Table 4.4). The mass-transfer coefficient of ozone was found increase with increasing the gas flowrate. Yocum (1980) indicated that the effect of an increase in the gas feed rate was found to be similar to that of increasing the turbine speed. This was thought to be due to an increase in the absorption rate of ozone, because of the larger interfacial area created at the higher gas feed rates. The mathematical relationship between mass-transfer coefficient and superficial velocity, U_g (flowrate divided by section area of reactor), of oxygen (Figueiredo and Calserbank, 1979 and Nishikawa et al., 1981) and ozone (Yocum, 1980, Anselmi et al., 1984, Roustan et al., 1987, Stankovic, 1988, and Laplanche et al., 1991) is a power law ($K_La= aU_g^b$). From the data we obtained at 14 °C, the constants, a and b, were determined by plotting the

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relationship between mass-transfer coefficient and superficial velocity on a logarithmic scale. As shown in Figure 4.7, the equation:

$$K_L a = 0.091 U_g^{0.411} \qquad (4.30)$$

can be used to describe this relationship. The value of b obtained for our system falls within the values of 0.24 to 0.82 that have been determined by those investigators mentioned above. The variations in the values for b predominately depend on the geometry of the reactor, the range of superficial velocity covered, the experimental method used to measure the concentration of dissolved ozone, and the composition of solution used.

Table 4.4 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Flowrates in DDI Water

T=14°C, C=46 mg/L	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (mL/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.358	0.1717	0.909	0.367	0.0947	0.977
200	0.340	0.1647	0.939	0.326	0.1358	0.990
300	0.355	0.1727	0.982	0.349	0.1472	0.989
400	0.355	0.2152	0.957	0.353	0.1723	0.989
500	0.353	0.2582	0.963	0.369	0.1861	0.988

4.4.3 Transfer of Ozone in DDI Water (pH=2 acidified by sulfuric acid)

To prevent the self-decomposition of ozone, the experiments to determine the effect of ionic strength on mass transfer and partition coefficients were conducted at a pH of 2.1. This solution was prepared by adding sulfuric acid to adjust the pH. An appropriate amount of sodium sulfate was added to obtain the desired ionic strength. As shown in

Table 4.5, the partition coefficients were not affected by the ionic strength of the water. On the contrary, ionic strength was found to have a significant effect on the mass-transfer coefficient. As the ionic strength increased, the size of the bubbles emitted from the diffuser was observed to decrease significantly. This decrease in size may be due to the increase in surface tension as the ionic strength of the solution is increased. Therefore, ionic strength is an important criterion in any ozonation system design.

Table 4.5 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Ionic Strength in DDI Water (Acidified to pH=2)

22 °C, Q=400 mL/min	Mixed-flow Model			Plug-flow Model		
Ionic Strength (mole/L)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
0.1	0.208	0.4020	0.968	0.211	0.3033	0.994
0.2	0.214	1.0430	0.979	0.211	0.5701	0.997
0.3	0.210	2.2353	0.936	0.208	0.8910	0.983
0.4	0.211	2.2620	0.660	0.206	0.9805	0.955

The effect of temperature and flowrate on the mass-transfer and partition coefficients was studied using the acidified water (Table 4.6). Our results show that the plug-flow model yields a higher correlation for the fitted coefficients than did the mixed-flow model. The conclusion is consistent with that found in unbuffered DDI water. Within a temperature range of 14 – 30 °C, the θ value ranged from 1.020 to 1.025 for all five flowrates. Therefore, the effect of temperature on the mass-transfer coefficients is identical to that found in DDI water at the flowrate range of 100 – 500 mL/min. The power law was again used to examine the effect of flowrate on the mass-transfer coefficient under different temperatures. The relationships determined are given below:

$$\begin{aligned} &T = 14\,^{\circ}C, \quad K_L a = 0.115\,(U_g)^{0.483} \\ &T = 22\,^{\circ}C, \quad K_L a = 0.147\,(U_g)^{0.428} \\ &T = 30\,^{\circ}C, \quad K_L a = 0.170\,(U_g)^{0.459} \end{aligned} \tag{4.31}$$

The values of b in pH 2.1 water fall within the range of 0.42 to 0.49. As a comparison, the value obtained in unbuffered DDI water was 0.41.

4.4.4 Transfer of Ozone in DDI Water (pH=6.7 buffered by phosphate salt)

The transport of ozone in water (at circumneutral pH) was investigated. At circumneutral pH, the effect of self-decomposition of ozone is more significant than that observed at lower pH values. By using the mass-transfer model developed previously, the effect of temperature and flowrate on the mass-transfer and partition coefficients of ozone is shown in Table 4.7. The ionic strength of the solution was fixed at 0.1 M. The results show that the mass-transfer model of ozone remains applicable for this system and the plug-flow model is better than mixed-flow model for fitting the system parameters, although the correlation factors were lower than those obtained at pH 2.1. This may due to the errors associated with measuring dissolved ozone at higher pH as a result of the rapid decomposition of dissolved ozone. This also helps explain the greater variation in the partition coefficients. The temperature factor, θ, which ranged from 1.026 to 1.036, for different flowrates was also found to vary more at high pH than observed at lower pH. The power laws found for the different temperatures are given below:

$$\begin{aligned} &T = 14\,^{\circ}C, \quad K_L a = 0.103\,(U_g)^{0.629} \\ &T = 22\,^{\circ}C, \quad K_L a = 0.139\,(U_g)^{0.577} \\ &T = 30\,^{\circ}C, \quad K_L a = 0.161\,(U_g)^{0.655} \end{aligned} \tag{4.32}$$

The values of b, apparently, are larger than those obtained at pH 2.1. It also implies that at circumneutral pH, the effect of superficial velocity on mass-transfer coefficients is greater than observed in acidic pH water.

Table 4.6 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Temperatures and Flowrates in DDI Water (Acidified to pH=2)

T=14 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (ml/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.278	0.2386	0.822	0.278	0.1241	0.954
200	0.274	0.2506	0.966	0.266	0.1721	0.997
300	0.272	0.2949	0.967	0.271	0.2090	0.985
400	0.284	0.3239	0.968	0.282	0.2424	0.995
500	0.293	0.3589	0.951	0.291	0.2698	0.992
T=22 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (ml/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.224	0.2864	0.933	0.219	0.1574	0.975
200	0.215	0.3142	0.977	0.209	0.2122	0.962
300	0.224	0.3379	0.971	0.222	0.2357	0.979
400	0.232	0.3873	0.963	0.230	0.2843	0.992
500	0.238	0.4352	0.974	0.238	0.3188	0.996
T=30 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (ml/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.160	0.3554	0.818	0.158	0.1853	0.928
200	0.156	0.3722	0.985	0.156	0.2456	0.983
300	0.159	0.4102	0.961	0.159	0.2876	0.990
400	0.164	0.5073	0.979	0.164	0.3525	0.983
500	0.166	0.5080	0.978	0.164	0.3862	0.986

Tab

Table 4.7 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Temperatures and Flowrates in DDI Water (pH=6.7 Buffered by Phosphate System)

T=14 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (mL/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.305	0.2385	0.935	0.326	0.1125	0.986
200	0.292	0.3094	0.948	0.310	0.1735	0.988
300	0.304	0.3515	0.922	0.313	0.2268	0.986
400	0.303	0.4027	0.921	0.307	0.2771	0.971
500	0.332	0.4257	0.876	0.332	0.3027	0.967
T=22 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (mL/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.225	0.3029	0.743	0.232	0.1479	0.927
200	0.209	0.3899	0.980	0.210	0.2405	0.981
300	0.220	0.3673	0.958	0.222	0.2719	0.971
400	0.237	0.4116	0.884	0.233	0.3328	0.904
500	0.238	0.5618	0.967	0.240	0.3866	0.986
T=30 °C	Mixed-flow Model			Plug-flow Model		
Inlet Flowrate (mL/min)	α	K_La (min^{-1})	R^2	α	K_La (min^{-1})	R^2
100	0.168	0.3090	0.574	0.166	0.1709	0.841
200	0.158	0.4681	0.971	0.159	0.2808	0.965
300	0.158	0.6301	0.957	0.158	0.3982	0.956
400	0.172	0.5890	0.942	0.170	0.4318	0.966
500	0.173	0.7200	0.981	0.171	0.4798	0.987

The enhancement factor, E , which is due to a chemical reaction taking place in the liquid phase (Danckwerts, 1970), is defined as K_L(with reaction)/K_L(without reaction). In the absence of other reactive species at circumneutral or alkaline pH, the self-decomposition of ozone is the major reaction involving ozone. As such, the enhancement factor can be determined by dividing the mass-transfer coefficient found in water buffered at a pH of 6.7 by the mass-transfer coefficient in water having a pH of 2.1. The enhancement factors determined for the same ionic strength and temperature of the water are tabulated in Table 4.8. Except for the enhancement factors obtained for a flowrate of 100 mL/min, all enhancement factors were found to be slightly greater than 1. It is thought that the mass-transfer coefficients obtained at this lower flowrate are less reliable as the correlation factors obtained in fitting the mass-transfer model were poorer than those obtained for higher flowrate. These results indicate that the enhancement of mass-transfer coefficient by self-decomposition of ozone over this pH range is insignificant as compared with the enhancement obtained for the reactions of some organic compounds (Augugliaro and Lizzuti, 1978). Augugliaro and Lizzuti (1978) found that the enhancement factor was greater than 3 when ozonating wastewater containing high concentrations of phenol.

Table 4.8 Enhancement Factors for the DDI Water (pH=6.7) Buffered with Phosphate Solution

	Flowrate (mL/min)				
Temperature	100	200	300	400	500
14°C	0.91	1.01	1.09	1.14	1.12
22°C	0.94	1.13	1.15	1.17	1.21
30°C	0.92	1.14	1.38	1.22	1.24

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4.4.5 Comparison of Experimental Data and Model Prediction

In this section, the simulations obtained using mixed-flow and plug-flow mass-transfer models are compared with the experimental data. It should be noted that the mixed-flow model can be solved by either analytical or numerical methods. Figures 4.8 and 4.9 show the consistency of the solutions obtained using both the analytical and numerical methods. The concentration of ozone in the headspace (outlet concentration) and the experimentally determined dissolved ozone concentration are compared to the model prediction. To minimize the space requirements, this comparison is made only for flowrate and temperature of 400 mL/min and 22 °C (Figures 4.10 - 4.15), although similar results are obtained for the other flowrates and temperatures. The results indicate that both the concentrations of outlet and dissolved ozone predicted by either mixed-flow model or plug-flow model are slightly greater than the values observed experimentally. These variations may be due to the experimental errors, or some optimistic assumptions such as complete mixing in water and flow pattern of gas bubbles. The prediction obtained using the plug-flow model was close to the experimental data. Gas holdup, measured by monitoring the increase in height of water level while gas was sparged into water, was employed in computing the concentration of ozone in the mass-transfer models. Gas holdup was estimated to be 0.01425 L when the flowrate was 400 mL/min. The difference in the behavior of mixed-flow or plug-flow pattern for the gas bubbles might be insignificant due to such a small volume of gas bubbles in the reactor.

4.4.6 Sensitivity Analysis of Mass-Transfer Model of Ozone

Sensitivity analysis is usually used to determine the uncertainty of each parameter. The sensitivity of the mass-transfer model to each parameter was tested by changing each parameter over a range (±10 – 20%) of its value while the other parameters were held constant at their base values. The effects of mass-transfer coefficient, partition coefficient, self-decomposition coefficient, and gas holdup were determined on the profiles of dissolved ozone and outlet ozone concentrations (Figures 4.16-4.19). It is found that, of all the parameters tested, the partition coefficient (α) had the greatest effect on the dissolved ozone concentration. Following this, was the mass-transfer coefficient. However, the profile of the concentration of outlet ozone gas appeared to be insensitive to all parameters tested. Any change in the self-decomposition coefficient or the gas holdup did not have any effect on either concentration. Therefore, it is very important to accurately determine the value of the partition coefficient when using the ozone mass-transfer model to predict the concentrations of outlet ozone gas and dissolved ozone.

4.4.7 Application of Mass-transfer Model in a Pilot-scale System

Based on the successful use of mass-transfer model (plug-flow model) in a lab-scale reactor, this model was used to demonstrate its applicability for a pilot-scale reactor, which had been operated to treat the stored swine manure (see Chapter 3). The effect of temperature and agitation speed on the partition and mass-transfer coefficients for ozone in DDI water was investigated (see Table 4.9):

Table 4.9 Fitting Parameters Obtained from the Mass-transfer Equations. Effect of Changes in Temperatures and Agitation Speeds in DDI Water in a Pilot-scale Reactor

Q=443 mL/min, 200 rpm	α	K_La	R^2
T=15 °C	0.356	0.3671	0.971
T=20 °C	0.268	0.4327	0.980
T=30 °C	0.213	0.4764	0.957
Q=443 mL/min, T=20 °C	α	K_La	R^2
0 rpm	0.257	0.3590	0.988
200 rpm	0.268	0.4269	0.981
400 rpm	0.268	0.4327	0.980
600 rpm	0.278	0.4795	0.938

Similar effects of temperature on the mass-transfer and partition coefficient were observed in both the lab-scale and pilot-scale reactors (Table 4.9). An increase in temperature resulted in a decrease in the partition coefficient and an increase in the mass-transfer coefficient. Increases in agitation speed, while keeping other conditions constant, effectively enhanced the mass-transfer coefficient. It is thought that the larger the agitation intensity the bigger the contact area between gas bubbles and liquid. This would also increase the detention time of the gas bubbles in the reactor. In figures 4.20 and 4.21, the concentrations of dissolved ozone and outlet ozone obtained from experimental data and model predictions are compared. It appears that the plug-flow model can also be used to describe ozone mass transfer in the pilot-scale system.

4.5 Conclusions

From the results presented in this chapter, several conclusions can be drawn.

1. The self-decomposition of ozone in unbuffered DDI water follows a first order kinetic model. However, ozone decomposes by a second-order reaction in DDI water buffered with phosphate at pH of 6.7. Increasing the temperature of the solution accelerated the self-decomposition of aqueous ozone. However, the rate constant for the self-decomposition of moisturized gaseous ozone was found to be zero.
2. A mass-transfer model using plug-flow in the bubble phase was successfully used in the semi-batch laboratory scale reactor as well as in the pilot-scale reactor. Although other investigators have used the mixed-flow model more often than plug-flow model for the analysis of mass-transfer of ozone, our data show that use of plug-flow model yields higher correlation factors for mass-transfer and partition coefficients of ozone.
3. The mass-transfer coefficient increased with increasing flowrate, temperature, and ionic strength. The effect of flowrate on the mass-transfer coefficient can be described by using a power law. The effect of temperature can be corrected by a temperature coefficient (θ), which was estimated to fall within the same range as that observed for oxygen. In addition, it was noted that an increase in ionic strength resulted in smaller ozone bubbles. Therefore, while maximizing the mass-transfer efficiency of an ozone reactor, the chemical composition of liquid should be taken into consideration in the design of the reactor.
4. Of the factors tested, partition coefficient was found to be the only parameter that varied both with temperature and aqueous composition. However, temperature is still the major factor to affect the partition coefficient.
5. Any chemical reaction in the ozonation system including ozone self-decomposition and its reaction with organic and inorganic compounds will enhance the mass-transfer

coefficient of ozone. The enhancement factor for the ozone self-decomposition was observed to fall within the range of 0.9-1.4 (pH of 6.7 and flowrate ranging from 100 to 500 mL/min. Therefore, the enhancement factor caused by ozone self-decomposition at this pH tested is insignificant.

6. Using a sensitivity analysis, the partition coefficient (α) was found to be the most sensitive factor that affected the concentration profile of dissolved ozone. The mass-transfer coefficient had a minor effect on the dissolved ozone. The concentration of dissolved ozone was unaffected by the self-decomposition rate constant of ozone and gas-holdup. For the concentration profile of outlet ozone, all of these four parameters are insensitive.

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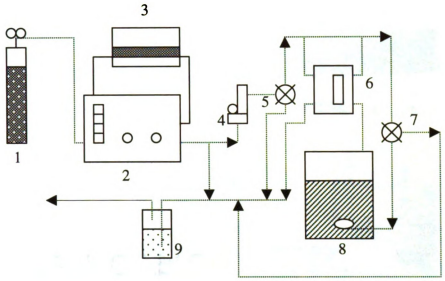


1: Oxygen Cylinder
2: Ozone Generator
3: Cooling System
4: Flow Controller
5: Three-way Valve
6: UV Spectrophotometer
7: Three-way Valve
8: Semi-batch Reactor
9: Trap Solution (KI)

Figure 4.1 The System Setup for the Semi-batch Ozonation Process

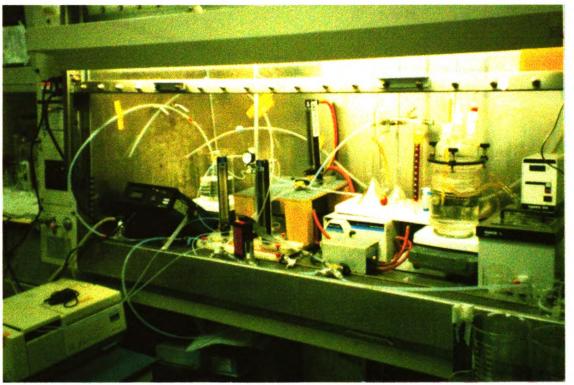
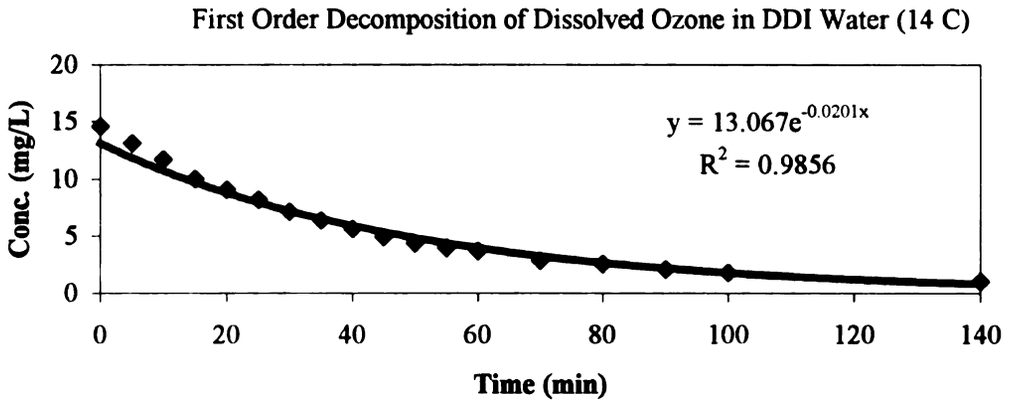
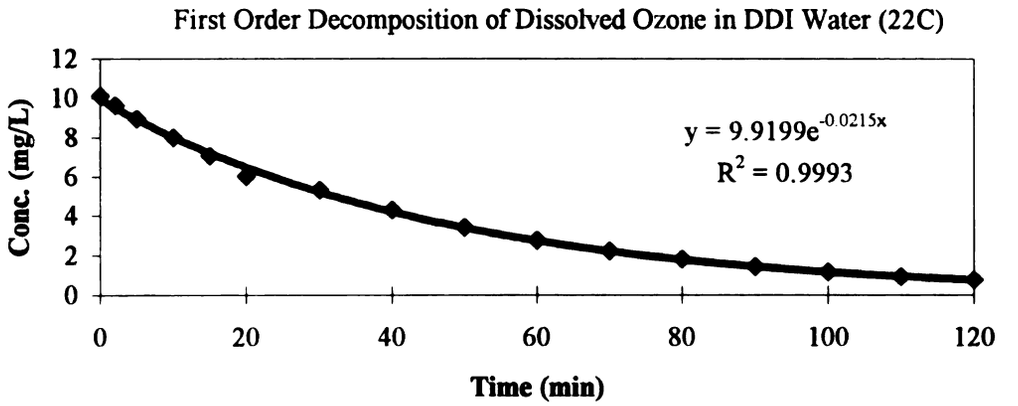


Figure 4.2 The Photo of the System Setup for the Semi-batch Ozonation Process





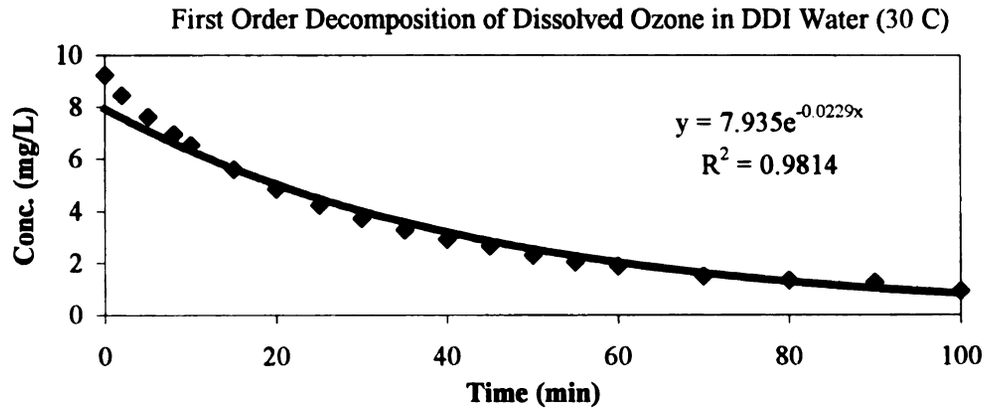
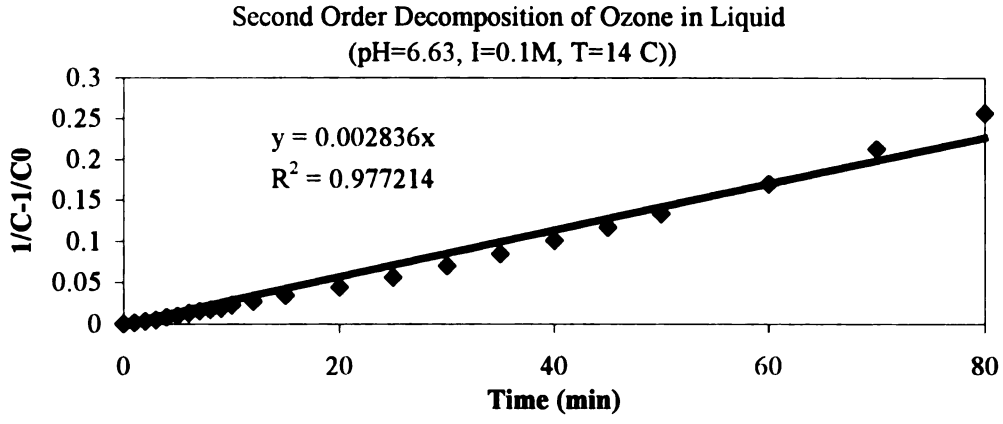
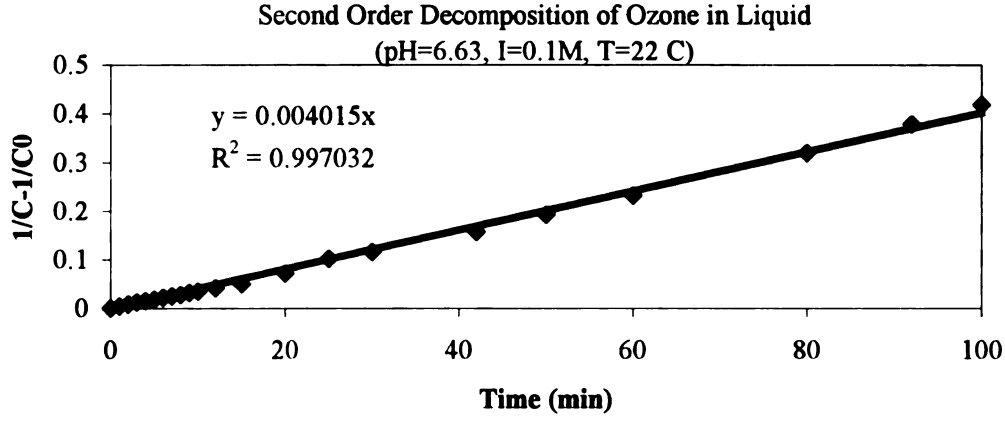


Figure 4.3 First-order Decomposition of Dissolved Ozone in DDI Water





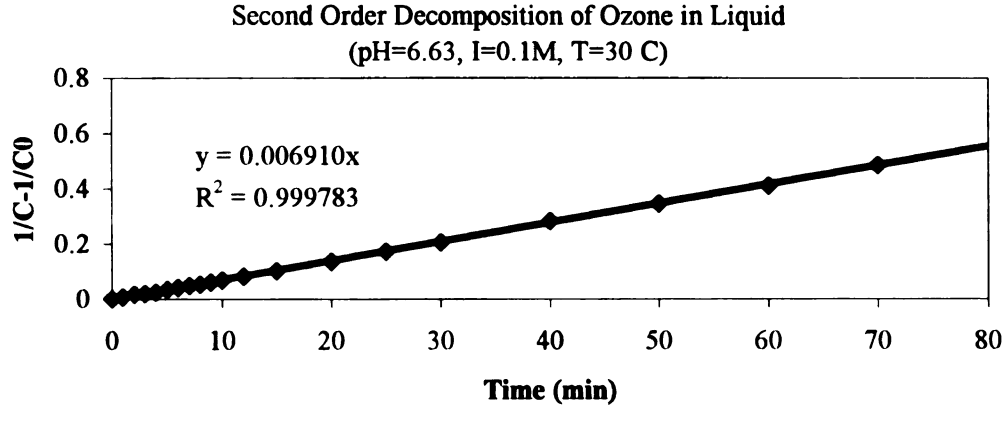
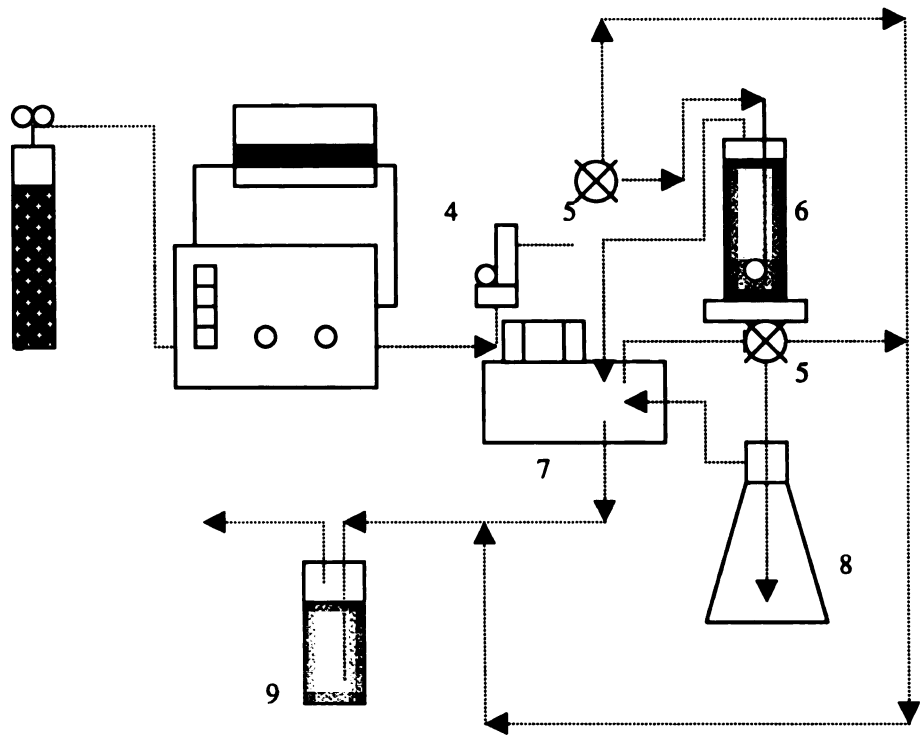


Figure 4.4 Second-order Decomposition of Dissolved Ozone in DDI Water (pH=6.7)



1: Oxygen Cylinder
2: Ozone Generator
3: Cooling System
4: Flow Controller
5: Three-way Valve
6: Gas Washing Bottle (To moisture the gaseous ozone before entering into headspace)
7: UV Spectrophotometer
8: Cone Beaker (2.0 L to simulate the headspace in a semi-batch reactor)
9: Trap Solution (KI)

Figure 4.5 System Setup for Determining the Self-decomposition rate of Moisturized Gaseous Ozone

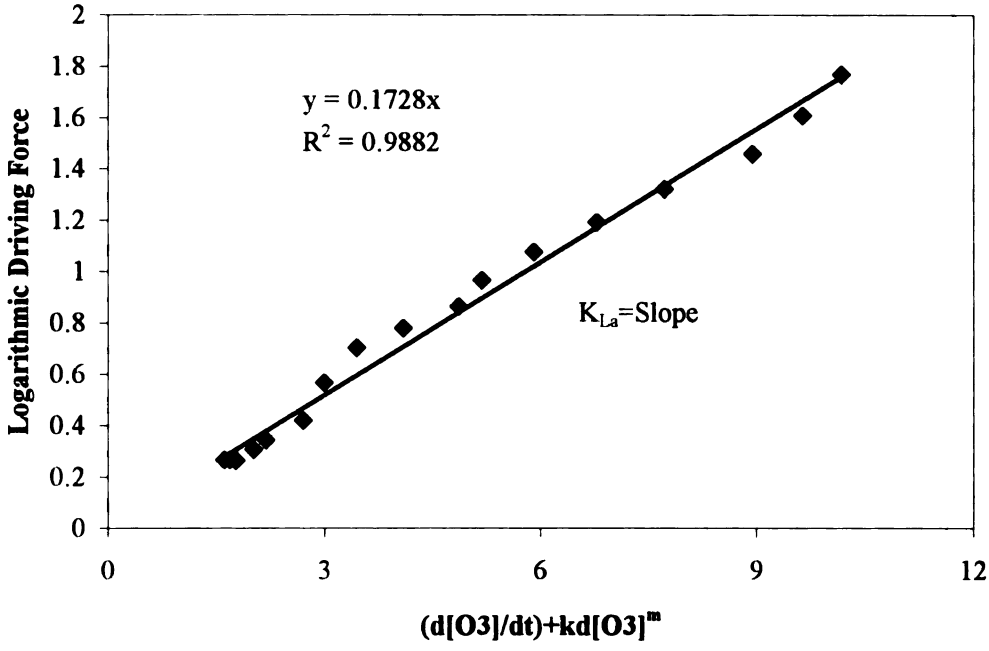


Figure 4.6 Method to Fit the Mass-transfer and Partition Coefficients by Linear Regression

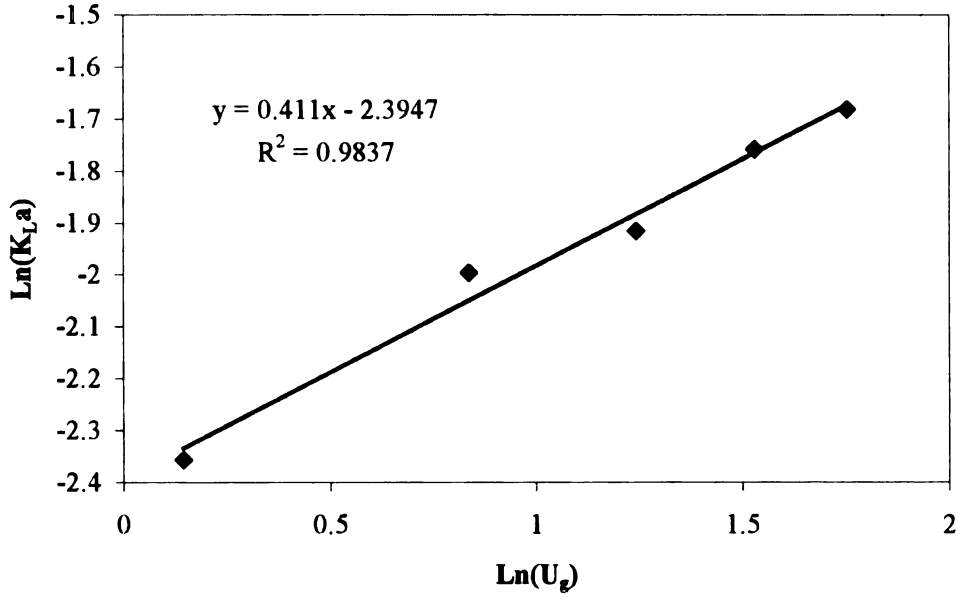


Figure 4.7 Relationship between Mass-transfer Coefficient of Ozone and Superficial Velocity

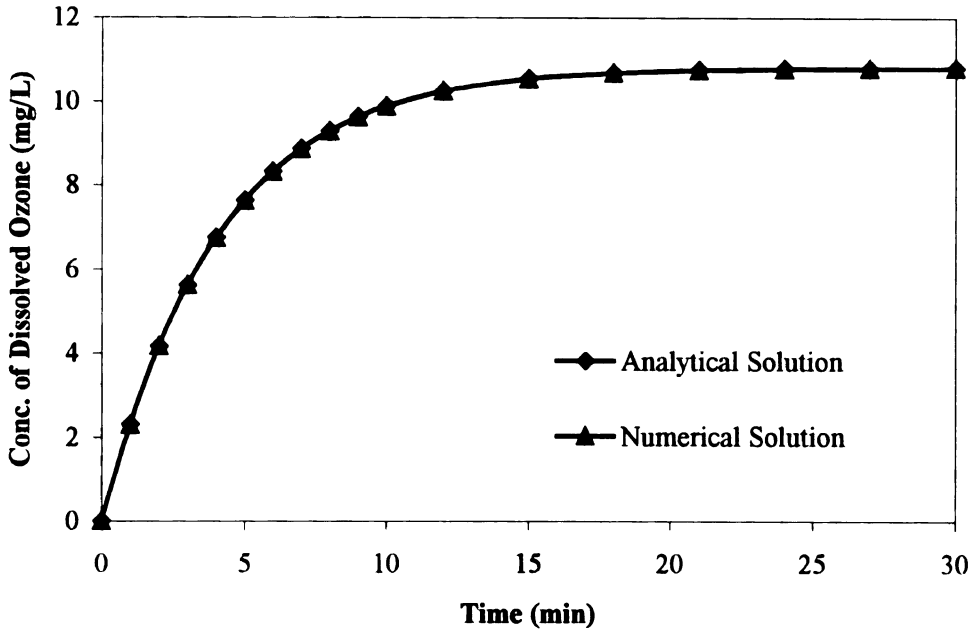


Figure 4.8 Comparison of Dissolved Ozone Concentration Calculated by Analytical and Numerical Solutions in Mixed-flow Model for DDI Water at Flowrate 400 mL/min and Temperature 22 C

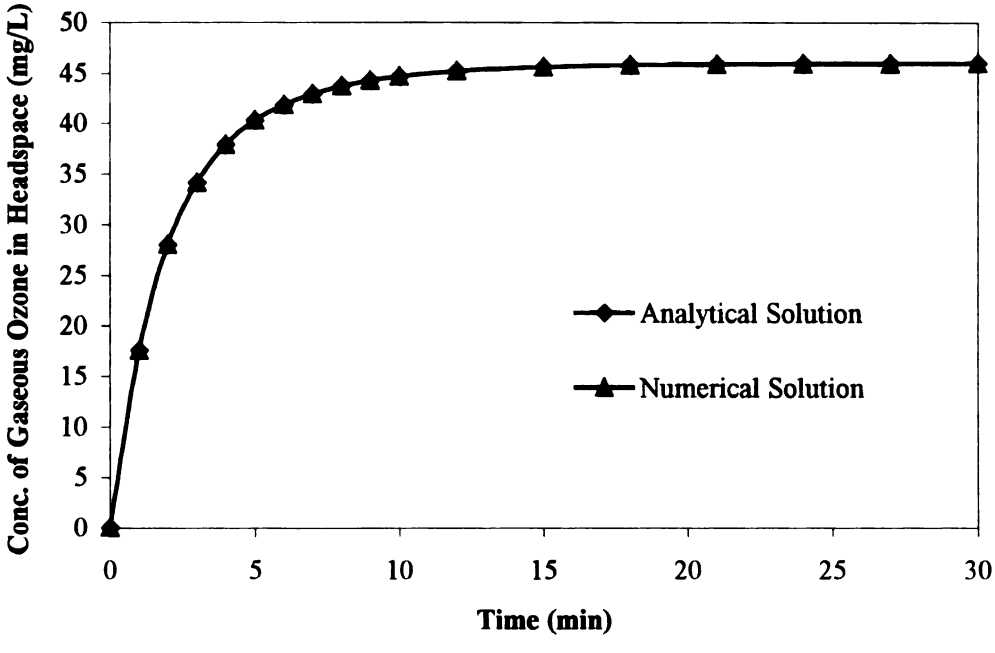


Figure 4.9 Comparison of Exit Ozone Concentration Calculated by Analytical and Numerical Solutions in Mixed-flow Model for DDI Water at Flowrate 400 mL/min and Temperature 22 C

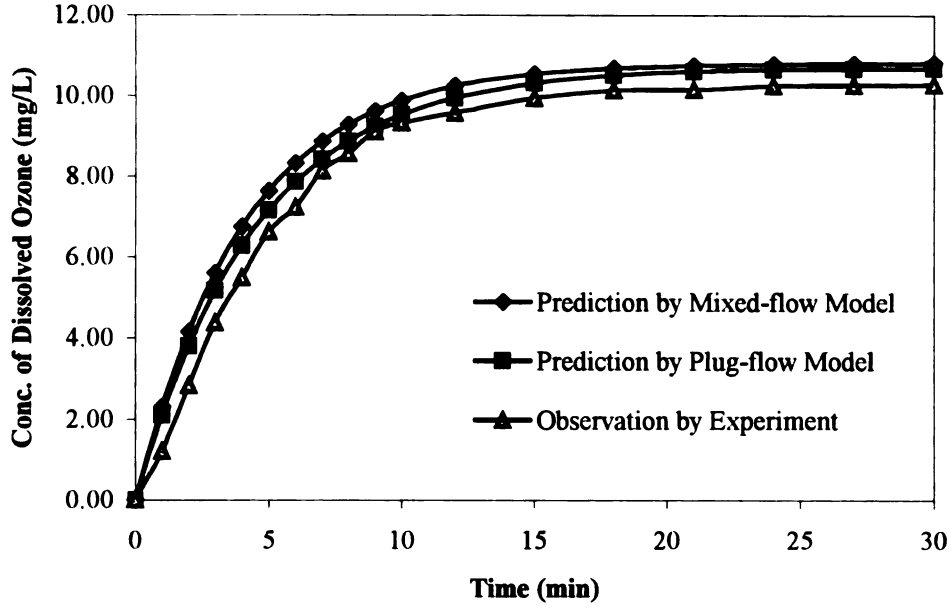


Figure 4.10 Comparison of Dissolved ozone Concentration in DDI Water Obtained Model Prediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C

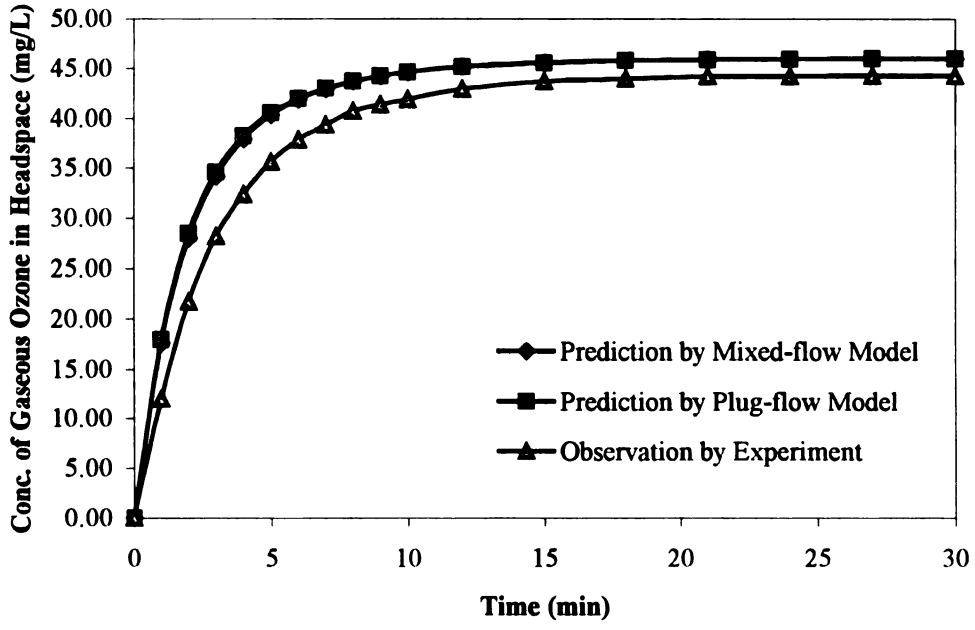


Figure 4.11 Comparison of Exit Ozone Concentration in DDI Water Obtained Model Prediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C

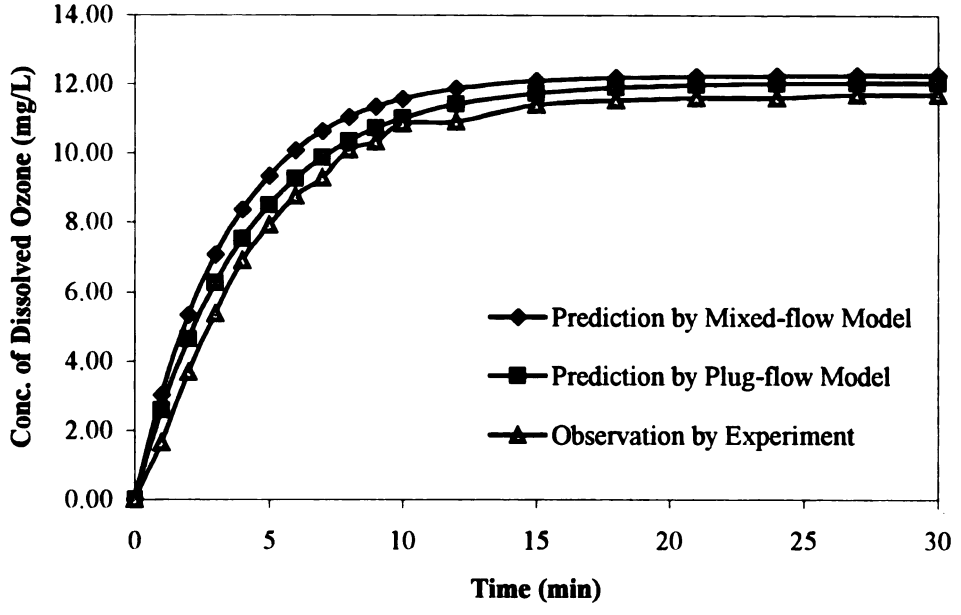


Figure 4.12 Comparison of Dissolved Ozone Concentration in DDI Water (pH 2.1) Obtained Model Prediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C

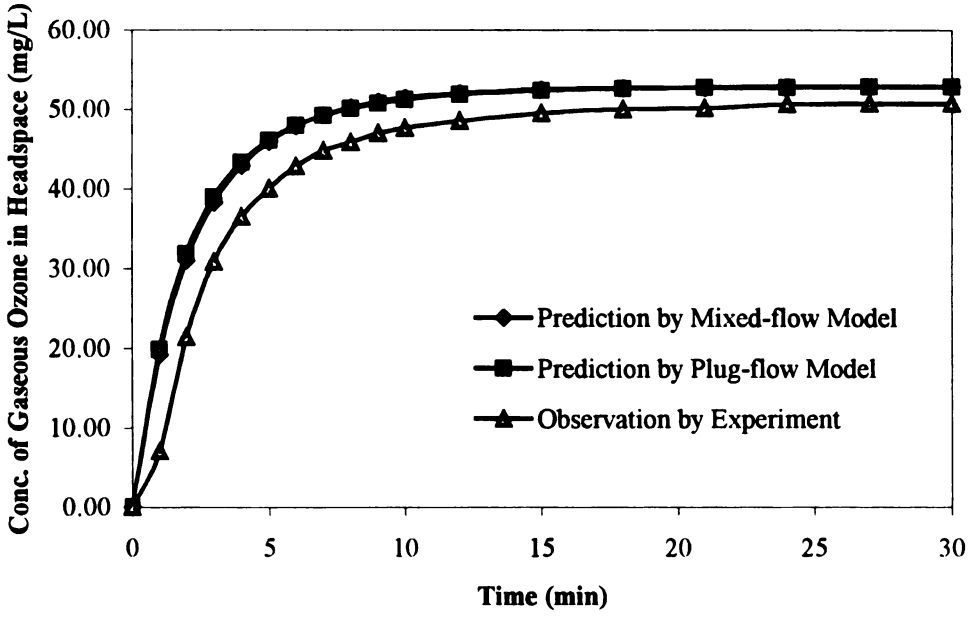


Figure 4.13 Comparison of Exit Ozone Concentration in DDI Water (pH=2.1) Obtained ModelPrediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C

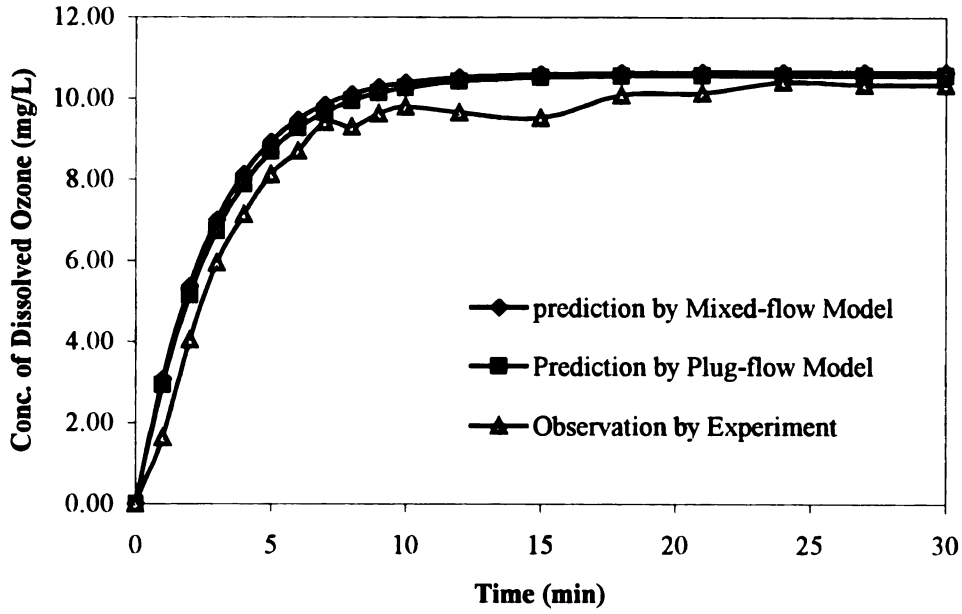


Figure 4.14 Comparison of Dissolved Ozone Concentration in DDI Water (pH 6.7) Obtained Model Prediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C

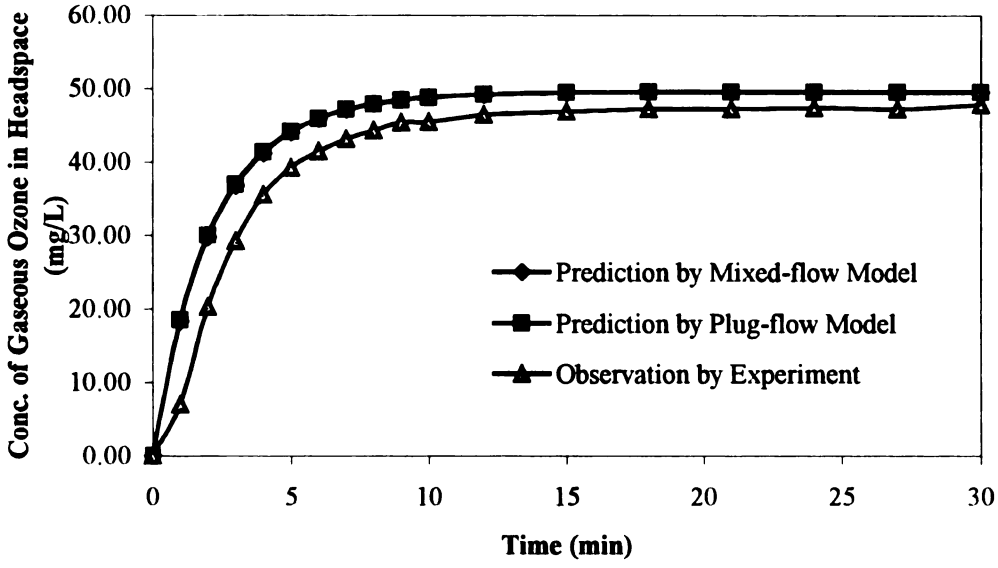
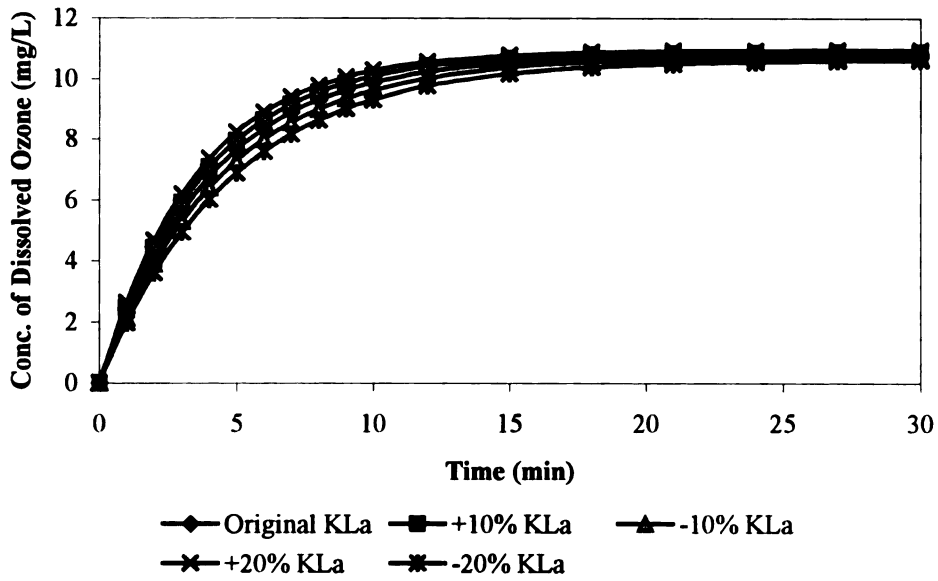


Figure 4.15 Comparison of Exit Ozone Concentration in DDI Water (pH=6.7) Obtained ModelPrediction with that Experimentally Determined at Flowrate 400 mL/min and Temperature 22 C



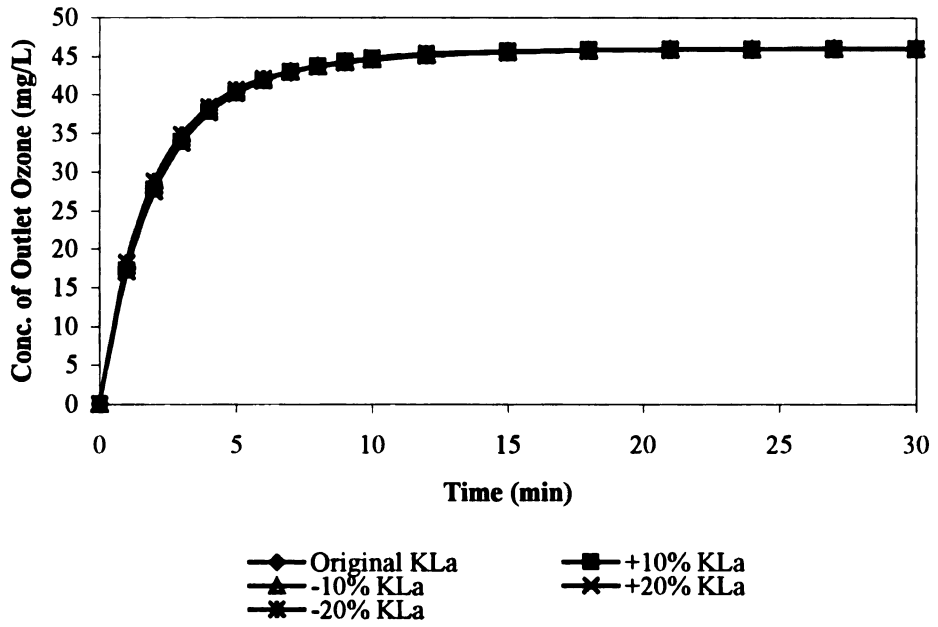
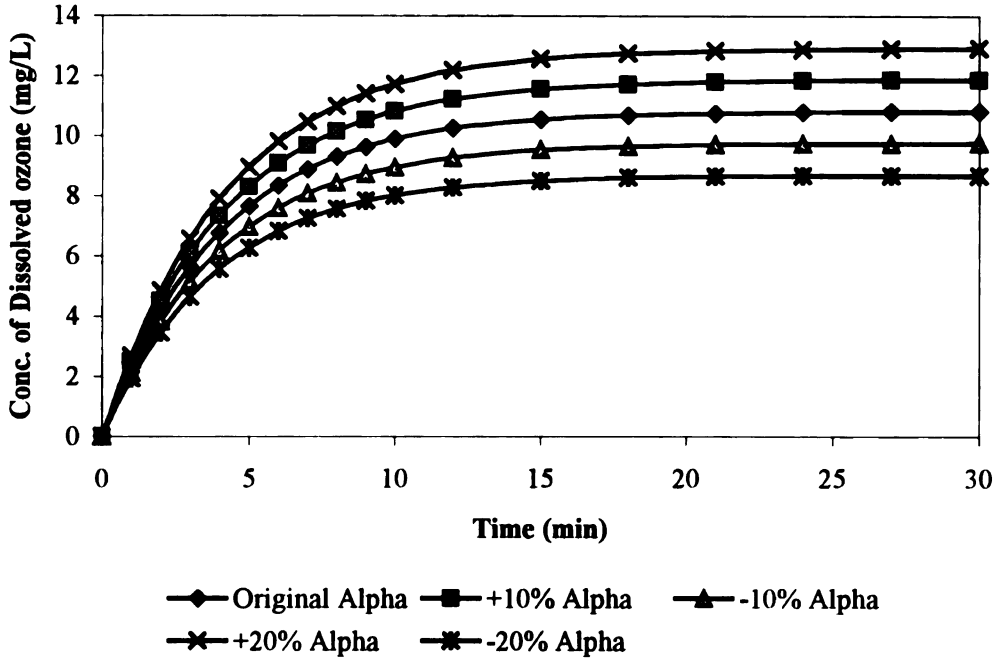


Figure 4.16 Sensitivity Profile of Dissolved and Exit Ozone Concentrations by Changing the Mass-transfer Coefficient in DDI Water



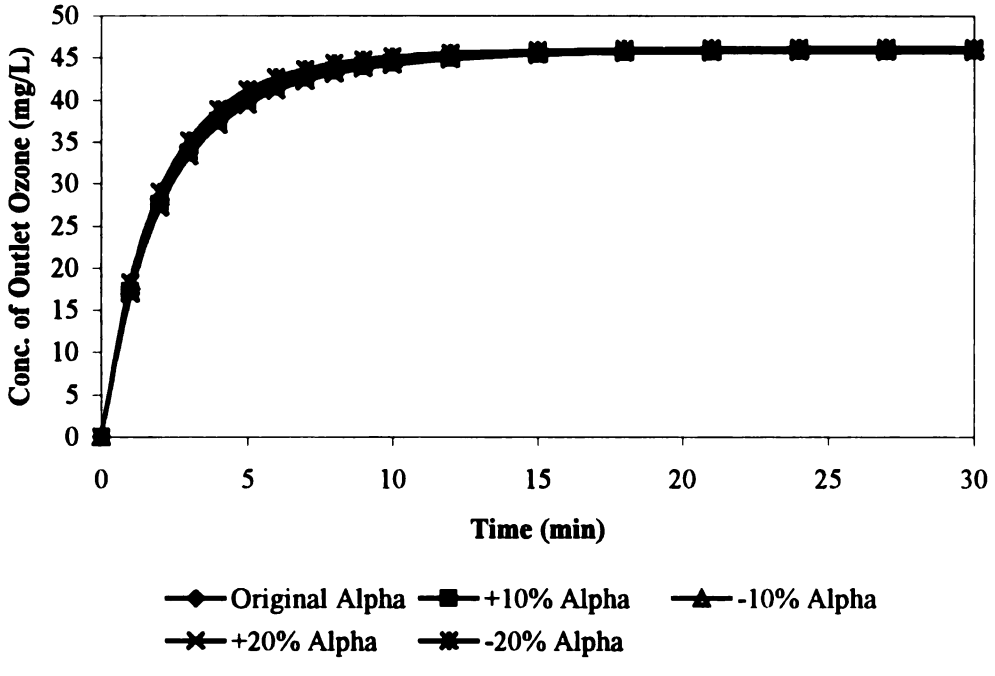
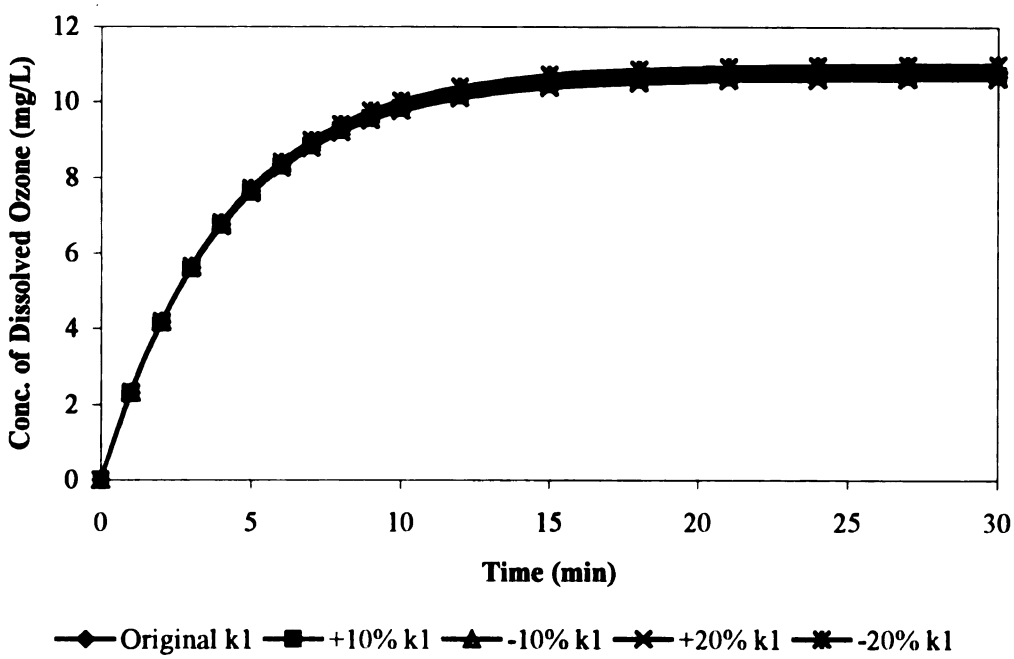


Figure 4.17 Sensitivity Profile of Dissolved and Exit Ozone Concentrations by Changing the Partition Coefficient Coefficient in DDI Water



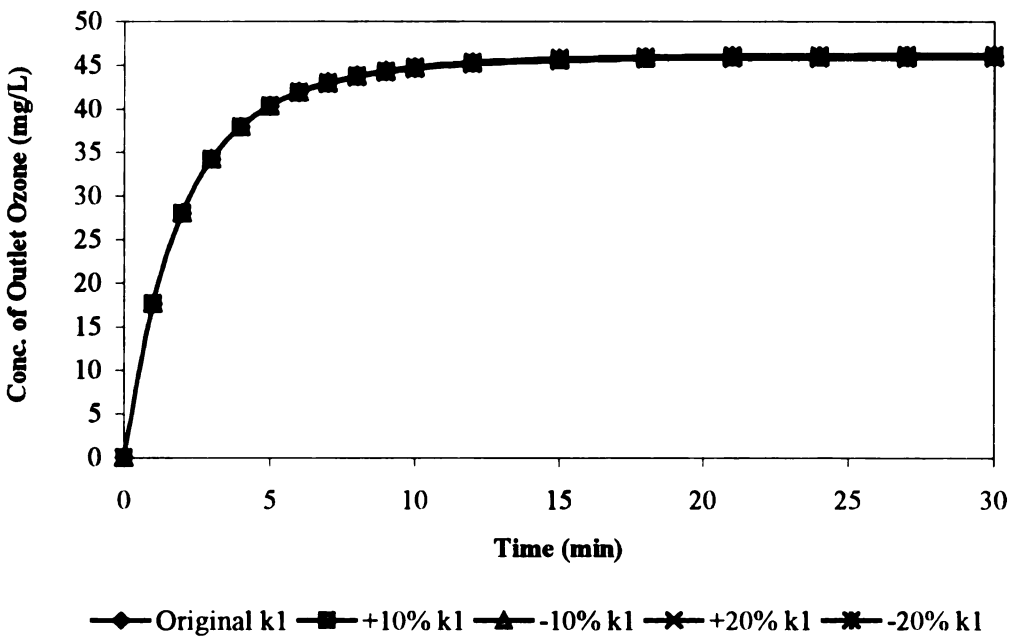
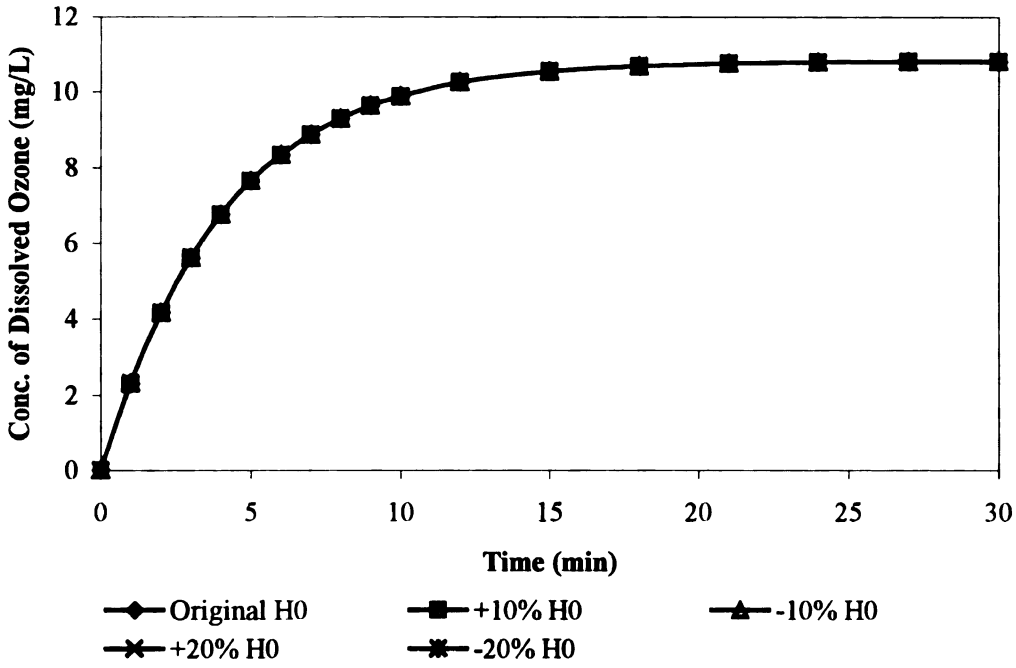


Figure 4.18 Sensitivity Profile of Dissolved and Exit Ozone Concentrations by Changing the Self-decomposition Coefficient Coefficient in DDI Water



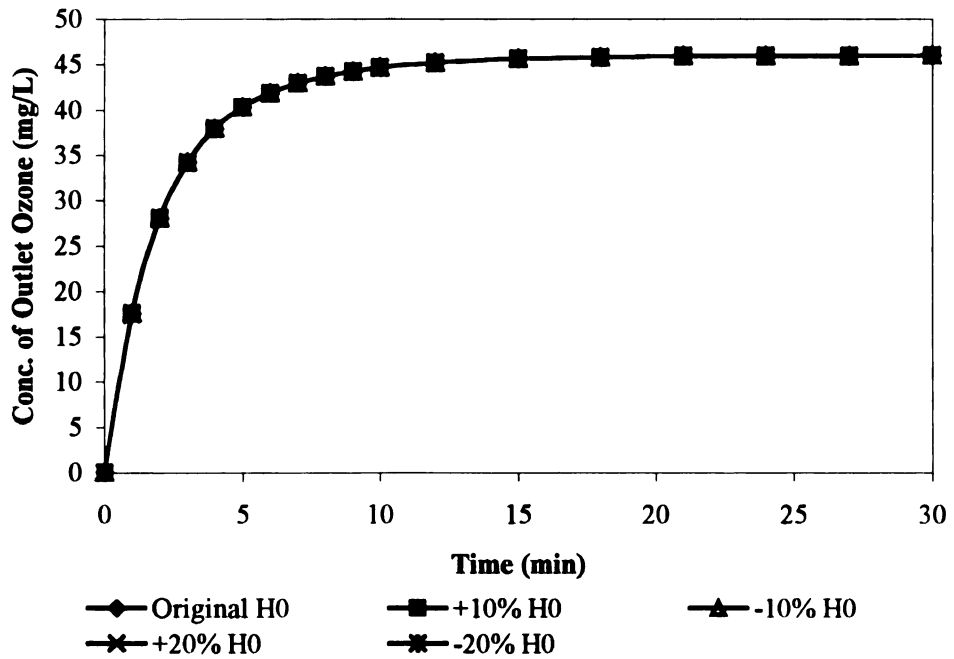


Figure 4.19 Sensitivity Profile of Dissolved and Exit Ozone Concentrations by Changing the Gas Hold-up in DDI Water

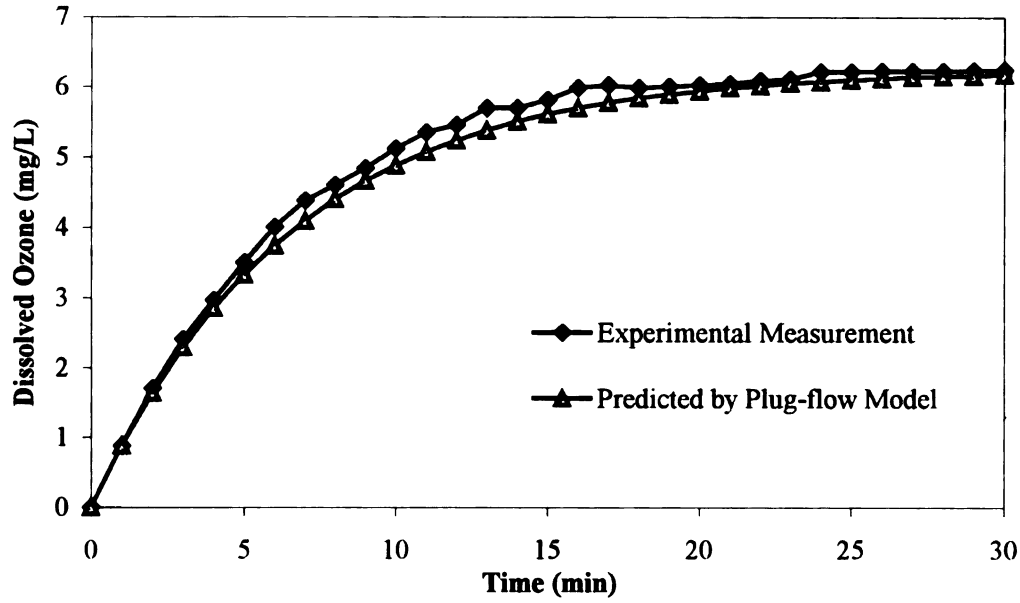


Figure 4.20 Comparison of Dissolved Ozone Concentration in DDI Water in Pilot-scale System Obtained by Model Prediction and Experimental Data at the Flowrate 443 mL/min and Temperature 22 C

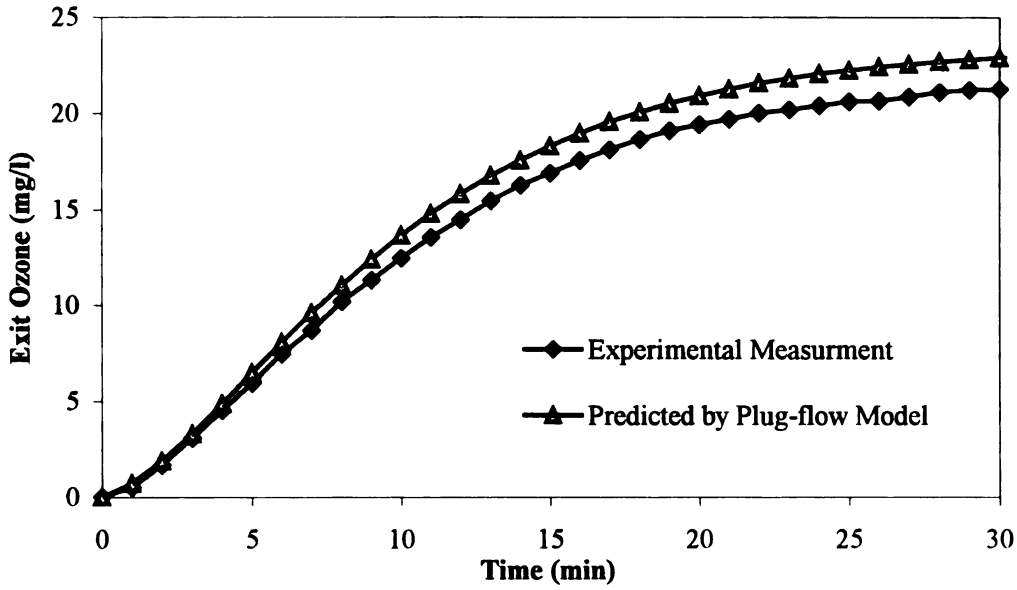


Figure 4.21 Comparison of Exit Ozone Concentration in DDI Water in Pilot-scale System Obtained by Model Prediction and Experimental Data at the Flowrate 443 mL/min and Temperature 22 C

Chapter 5

OXIDATION KINETICS OF PHENOLIC AND INDOLIC COMPOUNDS IN AQUEOUS ENVIRONMENT BY OZONE

5.1 Introduction

Phenolic (phenol, *p*-cresol, and *p*-ethylphenol) and indolic (indole and skatole) compounds are regarded as among the most malodorous compounds found in swine manure slurry (Spoelstra, 1977). Although many researchers have investigated the kinetics of the reaction of ozone with phenol and p-cresol (Gould and Weber, 1976; Augugliaro and Rizzuti, 1978; Hoigné and Bader, 1983; Singer and Gurol, 1983; Zheng et al., 1993), no effort has been made to investigate the kinetics of the reaction of these compounds in a complex matrix such as wastewater. Although, in full-scale contactors ozone gas is bubbled into the liquid being treated, few researchers have determined the kinetics of ozone in such heterogeneous systems. In a few cases, empirical kinetic models of ozonation have been proposed for heterogeneous systems in order to determine an apparent rate constant for the overall reaction as a function of both flow and chemical parameters (Roth et al., 1982), but these constants are only limited to the specific reactor type used.

The objectives of this study were to describe the kinetics of the oxidation of phenolic and indolic compounds by ozone in a semi-batch reactor, to determine the effect of such system parameters, such as flowrate, temperature, pH, and solution composition on the removal of these malodorous compounds, and to develop a mathematical model, which combines the mass transfer of ozone and ozonation kinetics, to predict the degradation of those compounds in synthetic and real swine manure.

5.2 Materials and Methods

5.2.1 Preparation of Buffer and Chemical Solutions

Stock buffer solutions for pH control were prepared according to Table 5.1. The ionic strength of stock buffer solutions was fixed at 3 M by adding a specific amount of sodium sulfate into each of the solutions. Malodorous chemicals such as phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole, respectively, were weighted and dissolved in DDI water. The phenolic and indolic compounds were placed in light-sensitive bottles and stored in the refrigerator for use. All chemicals were used within a week of preparation. Distilled deionized water (DDI water) was used to prepare all solutions. Aqueous ozone was prepared by continuously passing gaseous ozone from a fritted diffuser through DDI water to which had been added with 50 mL of a pH buffer to achieve the desired pH and ionic strength. The concentration of aqueous ozone achieved a stable level (ca. 16 mg/L at pH 2 and 11 mg/L at pH 6.7).

Table 5.1 The Composition of Stock Buffer Solution

pH	Reagents
2.1	8 mL concentrated H_2SO_4 + 120.7 g Na_2SO_4 in 500 mL DDI water
6.7	92.84 g Na_2HPO_4 + 141.13 g KH_2PO_4 in 1000 mL DDI water
9.9	74.2 g H_3BO_3 + 40 g NaOH + 95.14 g Na_2SO_4 in 1000 mL DDI water

5.2.2 Stoichiometric Factor and Reaction Rate Constant

This experiment was conducted in a series of 30 mL glass tubes into which were placed mini-stir bars to keep the solution completely mixed. The stoichiometric factor of the reactions was obtained by mixing aqueous target compound (phenol, *p*-cresol, *p*-ethylphenol, indole, or skatole) and ozone solutions of known concentrations. In order to avoid, as much as possible, the interference of other reactions (i.e., between ozone and byproducts), in all cases, the initial concentrations of target compounds were kept much higher than that of ozone so that the ozone could be consumed mainly by its reaction with parent compounds. Two concentrations of target compounds were used: 100 and 200 mg/L. An appropriate volume of the ozone solution was added to the tube to react with the target compounds. After the aqueous ozone was consumed, chemical analyses were done to determine the consumption of target compound. The stoichiometric factor was then computed as $\eta=\Delta[O3]/\Delta[M]$. All experiments were conducted in triplicate.

The concentrations of target compounds were determined using high-performance liquid chromatography (HPLC) (Perkin Elmer Corporation, Norwalk, CT). A platinum guard and analytical columns (EPS C18, Alltech Corporation, Deerfield, IL) were used. The HPLC was operated at the flowrate of 1 mL/min and the ratio of mobile phase 43:57

(acetonitrile:water). A wavelength in the UV diode array detector (Perkin Elmer Corporation, Norwalk, CT) of 255 nm was used.

The rate constants for the reaction of the target compounds and ozone were estimated using the method of competition kinetics (Xiong and Graham, 1992) and relative reaction-rate constants (Hoigné and Bader, 1983[a]). Considering a pair of organic compounds (M_1 and M_2) in aqueous solution, they will compete for ozone, as described below:

$$\frac{d[M_1]}{dt} = -k_{1,O_3}[M_1][O_3] \qquad (5.1)$$

$$\frac{d[M_2]}{dt} = -k_{1,O_3}[M_2][O_3] \qquad (5.2)$$

Thus,

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{1,O_3}[M_1]}{k_{2,O_3}[M_2]} \qquad (5.3)$$

$$k_{2,O_3} = k_{1,O_3}\frac{Log\left(\frac{[M_2]_t}{[M_2]_0}\right)}{Log\left(\frac{[M_1]_t}{[M_1]_0}\right)} \qquad (5.4)$$

p-Cresol was chosen as the reference compound as the reaction rate constant of ozone with *p*-cresol had been determined (Zheng et al., 1993). From this reaction rate constant, the reaction rate constant of the other target compounds could be calculated.

5.2.3 Factors Affecting the Removal of the Odorous Target Compounds by Ozone

A semi-batch reactor having a capacity of 1.5 L was used to observe the reduction of phenolic and indolic compounds by ozone in aqueous solution. In this phase, two aqueous solutions containing phenolic and indolic compounds, respectively, were utilized

to determine the effect of pH, flowrate, temperature, ammonia, COD, and VFA on the oxidation of the target compounds by ozone. The ozonation system was configured as shown in Figure 5.1 (the photo can be seen in Figure 4.2). In each experiment, pH, water temperature, ionic strength, and the concentrations of the target compounds were maintained at the desired levels. In addition, the gaseous concentration of inlet ozone was maintained at the desired value by adjusting the voltage valve on the panel of the ozone generator (Model T-408, Polymetrics Inc., San Jose, CA). When the experiment began, the kinetic program (Kinetic-2) in the UV spectrophotometer (UV 1201, Shimadzu Incorporation, Japan) was initiated to monitor and record the gaseous ozone concentration at both inlet and outlet lines at 5 minute intervals. In the meantime, the liquid samples were withdrawn from the reactor at regular intervals to measure the concentrations of target compounds by HPLC and dissolved ozone by the indigo method (Bader and Hoigné, 1982). The total liquid volume withdrawn for sampling purposes from the reactor was less than 7% of the initial volume in the reactor.

5.2.4 The Ozonation of Synthetic and Real Swine Manure in a Semi-batch Reactor

In order to better understand the reaction kinetics between ozone and the target malodorous components, a formulation of synthetic swine manure was at the concentrations of major malodorous composition reported by Wu et al. (1998) and Yasuhara (1980). The concentration of each compound is listed in Table 5.2. In these experiments, temperature (14, 22, 30 ^{o}C) and flowrate (100, 300, 500 mL/min) were varied to investigate their effect on the rate of ozonolysis of the target malodorous

Table 5.2 Concentrations of Malodors in the Synthetic Manure

Phenolic and Indolic Compounds	Concentration (mg/L)	Volatile Fatty Acids	Concentration (mg/L)
Phenol	28.1	Acetate	3000
p-Cresol	210	Propionate	170
p-Ethylphenol	3.5	*iso*-Butyrate	34.1
Indole	5.1	Butyrate	322
Skatole	12.8	*iso*-Valerate	128
		Valerate	83.2

compounds. The pH value of the synthetic manure was controlled using a phosphate buffer system (pH=6.7). The ionic strength of the synthetic manure was 0.1 M. A control experiment, in which the manure slurry was sparged with oxygen using the same flowrates as that used in the ozone experiments, was conducted to investigate the effect of stripping and oxygenation. Experimental procedures were the same as those documented in Section 5.2.3 except for the analytical methods used for the phenolic and indolic metabolites. Standards and samples of phenolic and indolic compounds were extracted by methylene chloride (1:1). Gas chromatography (HP 5890, Hewlett-Packard Inc., Avondale, PA) was employed to separate and quantify these compounds. Each sample (3 μL) was analyzed directly by GC-FID, using a stainless steel column (2 m×2 mm) packed with 21% Carbowax 4000 and WAW-DMCS (60/80 mesh). The column temperature was held at 100 ^{o}C for the first 1 min after injection; the temperature was ramped at 10 ^{o}C/min to 125 ^{o}C and held for 8 min, then ramped at 2 ^{o}C/min to 155 ^{o}C. The total run

for each sample was 26.5 min. Injection port and FID temperatures were maintained at 200 and 250°C, respectively.

The concentrations of volatile fatty acids (including acetate, propionate, butyrate, iso-butyrate, valerate, iso-valerate) were also determined by GC/FID. 0.5 mL of concentrated hydrochloric acid was added to 10 mL of manure slurry sample. After the mixture was agitated in a vortex mixer, it was centrifuged at 12,000 G for 10 min to remove particulate matter. An aliquot (3 μL) of the supernatant was injected directly into a 900 mm x 6 mm glass column packed with Supelco GP 10% SP-2100 on 100/120 Chromosorb W AW (Supelco Inc., Bellefonte, PA). The carrier gas was nitrogen flowing at 25 mL/min. The column temperature was held at 125 ^{o}C for the first 5 min after injection; the temperature was ramped at 4 ^{o}C/min to 175 ^{o}C and held for 25 min, then ramped at 5 ^{o}C/min to 200 ^{o}C and held for 15 min. The total run for each sample was 62.5 min. Injection port and FID temperatures were maintained at 150 and 200°C, respectively.

Real swine manure was collected from the storage pit of the one of the swine houses at MSU swine farm. After collection the manure was placed in a four-liter glass bottle for two weeks to allow fermentation to occur. Oxygenation and ozonation experiments were conducted at a temperature of 22 ^{o}C and a flowrate of 300 mL/min. Samples were taken at ozone dosages from 0 to 2 g/L at increments of 0.25 g/L. At the ozone dosage used, 19.3 min was needed for an incremental increase of 0.25 g/L ozone. The analytical methods for phenolic and indolic compounds were mentioned in the previous paragraph.

5.3 Model Development

A model combining mass transfer and chemical oxidation kinetics was developed to predict the accumulation of dissolved ozone concentration and the decrease in the concentrations of malodorous compounds in the synthetic and real swine manure during lab-scale ozonation. The mass-transfer model for ozone in DDI water was employed. Incorporated into this model were the concepts of enhancement factor and chemical kinetics. The following basic assumptions were made:

1. Liquid phase is completely mixed;
2. The flow pattern of gaseous ozone through the system is plug-flow;
3. Constant temperature and pressure are maintained during the experimental period.
4. Ozone is consumed mainly by malodorous parent compounds (phenol, *p*-cresol, *p*-ethylphenol, indole, and skatole); and
5. The enhancement factor is constant during the ozonation process.

Mass transfer and the ozonation reactions can be described mathematically by the following equations:

$$\frac{d[O_3]}{dt} = E \times K_{La}(\alpha C_g^{in} - [O_3]) - \sum \eta_i (k_i)[O_3][M]_i - k_f[O_3] - k_d[O_3]^m$$

$$-\frac{d[M]_i}{dt} = k_s[M]_i + (k_i)[O_3][M]_i$$

where:

$[O_3]$: Dissolved ozone concentration (mole/L)

E : Enhancement factor by chemical reaction

K_{La} : Mass - transfer coefficient of ozone in solution in the absence of ozone - reactive compounds (1/sec)

α : Partition Coefficient of ozone

C_g^{in} : Gaseous concentration of inlet ozone (mole/L)

η_i : Stoichiometric factor for malodorous compound, i

k_i : Re action rate constant for malodorous compound i with dissolved ozone (L/sec - mole)

$[M]_i$: Concentration of malodorous compound (mole/L)

k_f : Recation Coefficient by the byproducts or other compounds which also consume available ozone (1/sec)

k_d : Self - decomposition rate constant of dissolved ozone (1/sec for m equal to 1; L/sec - mole for m equal to 2)

m : Self - decomposition order of dissolved ozone

k_s : Coefficient for the removal of malodorous compound, i, by stripping and oxygenation

The number of system equations depended on the number of initial malodorous compounds in the ozonation reactor, e.g., if five malodorous compounds were selected, there would be six simultaneous equations in the model. Since the equations are non-linear, it is impossible to find an analytical solution for this model. Instead, numerical methods can be used to solve these non-linear simultaneous equations. Mathematica 3.0 (Wolfram Research Inc., Champaign, IL) provides a numerical package to obtain the solutions in the reaction system as long as we can estimate the values of some parameters. To distinguish the effect of the reaction between ozone and the intermediates formed from the oxidation of parent compounds, two models have been used. Model I assumes

that the reaction coefficient is zero. In Model II, the reaction coefficient is evaluated to fit the experimental data. It is especially important to determine the effects of side reactions on the degradation of target parent compound by ozone as the byproducts are also able to compete with their parent compounds for the available ozone.

5.4 Results and Discussion

5.4.1 Stoichiometric Factors and Rate Constants for Ozonation Reactions

The stoichiometric factors and rate constants for the reaction of ozone with phenolic and indolic compounds are summarized in Table 5.3. Results show that the stoichiometric factors for phenol are 1.81±0.16 and 1.86±0.16 at pH 2.1 and pH 6.7, respectively. Hoigné and Bader (1983) indicated that for the ozonation of phenol-like compounds, 2.5 moles of ozone are needed to consume 1 mole of phenol; Li et al. (1979) also reported that the stoichiometric factor is 2. However, Eisenhauer (1978), Gould and Weber (1976), and Roth et al. (1982) found that for the total destruction of phenol, between 4-6 moles of ozone are required to remove 1 mole of phenol. These values are higher than that found in this work because they did not distinguish between the amount of ozone that reacts with phenol and that which reacts with the ozonation byproducts. Since reaction conditions were such to favor the reaction of ozone with the target chemical over any other reaction, the stoichiometric factors found in this work seem to be reasonable. For *p*-cresol, the stoichiometric factors were found to be 1.00 ± 0.07 and 1.38 ± 0.11 at pH 2.1 and pH 6.7, respectively. The value reported by Zheng et al. (1993) for

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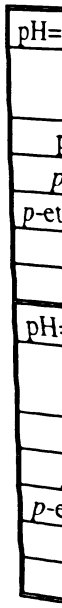

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Table 5.3 The Stoichiometric Factor and Rate Constants for the Reaction of Ozone with Phenolic and Indolic Compounds under Different pH Conditions (C.L.= Confidence Limits)

pH=2.1, I=0.1, T=22 °C				
	Stoichiometric factor	95% C.L.	Reaction rate constant ($M^{-1}sec^{-1}$)	95% C.L.
phenol	1.81	0.16	460	10
p-cresol	1.00	0.07	5,200	NR[a]
p-ethylphenol	1.13	0.05	1,650	280
indole	0.68	0.07	45,000	2,900
skatole	0.90	0.03	10,200	2,200
pH=6.7, I=0.1, T=22 °C				
	Stoichiometric factor	95% C.L.	Reaction rate constant ($M^{-1}sec^{-1}$)	95% C.L.
phenol	1.86	0.16	750,000	33,000
p-cresol	1.38	0.11	850,000	NR[a]
p-ethylphenol	1.29	0.11	990,000	110,000
indole	0.98	0.07	5,000,000	3,600,000
skatole	0.89	0.04	4,500,000	780,000

[a] Value was determined by Zheng et al. (1993) and C.L. were not reported

cresol isomers was 3; the value documented by Beltrán et al. (1990) for *o*-cresol was 2. Using the stoichiometric factor for *p*-cresol determined in this work, it appears that approximately 1 mole of ozone is consumed by 1 mole of *p*-cresol. Due to the lack of references relating to the ozonation kinetics of *p*-ethylphenol, indole, and skatole, no comparison could be made for the stoichiometric factors of these compounds. In our work, the stoichiometric factor of *p*-ethylphenol was found about 1.2 for the pH range we used. For indolic compounds, however, the stoichiometric factor at pH 6.7 was less than 1 (but close to 1). The only case is where the stoichiometric factor was less than one, occurred with indole. Its stoichiometric factor was 0.68 ± 0.07 at pH 2.1. One

explanation for this result is that one of the byproducts, which formed after ozone initially attacked indole, reacted with indole to further consume the parent compound.

The reaction rate constants for the phenolic and indolic compounds were found to increase significantly with increasing pH. This increase for phenolic compounds is thought to be due to greater reactivity of the phenolate ion as compared that of phenol. Augugliaro and Rizzuti (1978) and Hoigné and Bader (1983) both showed that the phenolate ion has a much larger rate constant towards ozone than that of phenol (10^9 $M^{-1}s^{-1}$ for phenolate ion and 500 $M^{-1}s^{-1}$ for phenol). Hoigné and Bader (1983) also demonstrated that the total reaction rate constants for phenolic compounds increase over a wide range of pH values by a factor of 10 per pH unit, corresponding to the incremental increase in the degree of dissociation. Although another explanation is that hydroxyl radicals cause the increase of the reaction rate with pH, Beltrán et al. (1992) negated this hypothesis when they found that the rate constants for the ozonation of *o*-cresol in aqueous solution with and without *tert*-butanol, a radical scavenger, were nearly identical. In our experiment, we used the phosphate buffer system to control the pH at 6.7. Masten et al. (1996) demonstrated that, at this pH, hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$) are the predominant OH radical scavengers in oxidizing trichlorobenzene by advanced oxidation process. Thus, the direct reactions between ozone and the target compounds predominate because any free radicals generated from the decomposition of ozone are likely to be scavenged by the phosphate species present in the buffer system we used.

The reaction rate constants determined at pH 2.1 were ranked, indole > skatole > *p*-cresol > *p*-ethylphenol > phenol. The electrophilic reaction is though to be the major

mechanism by which aromatic compounds react with ozone. This is especially true for aromatic compounds that have electron donating groups substituted at the ortho and para positions because of the high electron densities that result from this substitution. As a result of the high electron density, these compounds are very reactive with ozone. (Langlais et al., 1991). As *p*-cresol contains two electron donating groups, -OH and $-CH_3$ (Geissman, 1968), the reactivity of *p*-cresol by the initial attack of the ozone molecule is expected to be greater than that of phenol (with only a –OH group). The ethyl group ($-CH_2CH_3$) on *p*-ethylphenol is also electron donating group (Hart, 1991). The reactivity of *p*-ethylphenol is, therefore, expected to be greater than that of phenol. *p*-Cresol has a greater reaction rate constant than *p*-ethylphenol because the methyl group is a better electron donating group than is the ethyl group. In addition, it was reported by Geissman (1968) that indole and skatole are very reactive nucleophiles, and undergo electrophilic substitution reactions with ease. Nevertheless, no explanation can be offered at this point for why the reaction rate constants of indolic compounds are much faster than those of phenolic compounds because of structural differences in the two groups of compounds. A pH 6.7, the reaction rate constants for the three phenolic compounds are almost the same magnitude (close to 1×10^6 $M^{-1}s^{-1}$) and the rate constants of indole and skatole are 5×10^6 $M^{-1}s^{-1}$.

5.4.2 Factors Affecting the Oxidation of Phenolic and Indolic Compounds by Ozone

The effect of design parameters of ozonation system and physical and chemical characteristics of the swine manure on the reduction of the concentrations of phenolic and indolic compounds was determined. The physical parameters studied were flowrate and

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temperature; the chemical parameters were pH and other constitutional components in swine manure, such as VFAs, COD, ammonia, etc. By varying the flowrate (100-500 mL/min) the concentration of ozone in the inlet gas stream was maintained at 64.58 mg/L, it could be shown that the reduction in the concentrations of phenolic and indolic compounds increased as the flowrate also increased (Figures 5.2-5.6). If we consider the reduction in concentration as a function of ozone dosage rather than time, the reduction in concentrations appear to depend solely on ozone dosage and be independent of flowrate (Figures 5.7-5.11). As all of the ozone bubbled into the reactor was utilized and the concentration of dissolved ozone during the experiment was zero, all ozone dosed was consumed. Therefore, ozone dosage is thought to a valuable parameter in designing the ozonation system to treat the wastewater containing phenolic and indolic compounds.

pH has a significant effect on the reduction in the concentrations of phenolic and indolic compounds (Figures 5.12-5.16). At pH of 2.1, in a solution containing the three target phenolic compounds, *p*-cresol concentration was observed to rapidly decrease to below detection limits within 30 minutes. On the contrary, the reduction of phenol concentration was retarded during the initial twenty minutes, then began to accelerate after p-cresol was consumed. The *p*-ethylphenol concentration decreased to just between the concentrations of phenol and *p*-cresol. As mentioned in Section 5.4.1, the largest value for the reaction rates at pH 2.1 was that for *p*-cresol (5,200 $M^{-1}s^{-1}$), followed by *p*-ethylphenol (1650 $M^{-1}s^{-1}$), and then by phenol (460 $M^{-1}s^{-1}$). Based upon these rate constants, one would expect that, initially, the available ozone would be consumed mainly by *p*-cresol, and that phenol would not be oxidized until most of the *p*-cresol had disappeared. The results are consistent with the hypothesis. In studies conducted at pH

6.7 and 9.9, the rates of degradation of the three phenolic compounds, when present in a complex mixture, were not affected by increases in pH over this range. The reaction rate constants for these phenolic compounds are almost identical (at the same order) at the circumneutral and alkaline pH. Thus, the three components decreased according to the same pattern. It is worthy to note that in the presence of phenol and *p*-ethylphenol the concentration of *p*-cresol was significantly reduced at pH of 2.1 as the majority of ozone dosed into the system reacted with even though the reaction rate constant for *p*-cresol at pH 2.1 is much less than that in the solution having higher pHs. The effect of pH on the reduction in the concentrations of indolic compounds in a complex mixture solution was found to be insignificant, within the pH range of 2.1 to 9.9.

Temperature did not affect the rates of degradation of phenolic or indolic compounds when present in the complex mixture (Figures 5.17-5.21). This result is consistent with that found for pilot-scale studies and is thought to be due to the decrease in the solubility of ozone and the increase in reaction rate constant with increasing temperature. Over this temperature range (14 – 30 °C), these two factors appeared to counter-balance each other.

Dextran (M.W. ≅ 75,000), a type of starch, was used to simulate the complex organic constituents found in the swine manure. The COD in the phenolic or indolic solution containing dextran was 15,000 mg/L, which is the approximate concentration of the liquid part of swine manure. The results (Figures 5.22-5.24) indicate that dextran slightly retards the rate of oxidation of the phenolic compounds. This is thought to be because the dextran molecule is surface active and results in a resistance at the interface where available ozone can oxidize these chemicals. However, the effect of dextran on the

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rate of oxidation of indolic compounds is insignificant, apparently because the reaction rate constants of indolic compounds towards ozone are large enough to overcome any possible interference that might exist at the interface (Figures 5.25-5.26). Other factors, such as the presence of ammonia and volatile fatty acids, did not affect for the removal of the target odorous compounds (Figures 5.27-5.36).

To compare the effects of stripping and oxygenation on the removal of the phenolic and indolic compounds, oxygen was used to purge the solution. The maximum flowrate, 500 mL/min, was employed. Almost no change occurred in the concentration of any of the target compounds during a period of 80 minutes. This result differs from our previous experiment in which "real" swine manure was aerated using the pilot-scale system. In that study, the concentrations of the target compounds were decreased approximately by 15%, 50%, 40% and 45% for phenol, p-cresol, p-ethylphenol, and skatole, respectively, using oxygen. A flowrate of 1,800 mL/min and a treatment period of 40 minutes, respectively, were used. Therefore, it is hypothesized that microbiological metabolism, activated by oxygen, is the real mechanism by which the phenolic and indolic compounds disappear during aeration of the real swine manure.

5.4.3. Comparison between Experimental Result and Model Prediction

A model combining mass transfer and oxidation kinetics was employed to predict the concentration profiles of phenolic and indolic compounds in water under different pH values and flowates. Although, in previous experiments, the mass-transfer coefficients, partition coefficients, stoichiometric factors, and reaction rate constants have been determined, the enhancement factor and reaction factor (k_f) are still unknown. Once

those parameters are determined, the oxidation model can be used to simulate the ozonation process.

The enhancement factor is defined as the ratio between the actual and maximum physical absorption rates (Danckwerts, 1970; Charpentier, 1981):

$$E = \frac{N_{O_3}}{K_L a[O_3^*]} \tag{5.5}$$

$$N_{O_3} = \frac{m_i - m_o}{V} \tag{5.6}$$

where N_{O3} is determined from the difference between the molar flux of ozone at the reactor inlet and outlet, m_i and m_o, K_La is the liquid phase volumetric mass-transfer coefficient, $[O_3^*]$ is the dissolved ozone concentration at the water-gas interface, and V is the liquid volume in reactor. Until the phenolic or indolic compounds were removed from the reactor, the gaseous ozone concentration in the stream was not detectable. Thus, the enhancement factor is a constant during the reaction period. The E values at temperature of 22 °C were shown in Table 5.4 .

Table 5.4 The Enhancement Factor Calculated under Different Flowrates and pH Values

	pH=2.1	pH=6.7
Q=100 mL/min	1.9	2.0
Q=300 mL/min	3.8	3.2
Q=500 mL/min	4.4	3.8

Another important feature to be considered is the occurrence of competitive reactions involving ozone with the intermediates formed during the ozonation. Ozonation of phenolic compounds yields dihydroxybenzenes as the initial byproducts. These compounds are as reactive with ozone as the parent phenols (Gould and Weber, 1976; Singer and Gurol, 1983). These circumstances make kinetic studies more difficult to carry out especially for an initial reaction system with more than one parent compound. To overcome the difficulty in using the mathematical model, an overall reaction coefficient, k_f, was used to describe the consumption of ozone by all intermediates or impurities. The overall reaction coefficient could be estimated by fitting our experimental data to find a minimum residual, which is defined as below:

$$R = \sqrt{\frac{\sum_{j=1}^{N} \left(X_j - X_{Experiment}\right)^2}{N}} \qquad (5.7)$$

where X_j is the predicted concentration for the parent compounds in reactor, $X_{Experiment}$ is the observed concentration during the experiment, and N is the number of total observations.

Phenolic mixtures (phenol, *p*-cresol, *p*-ethylphenol) and indolic mixtures (indole and skatole) were ozonated respectively under the following conditions: pH 2.1, temperature of 22 °C, flowrate of 300 mL/min, and ionic strength of 0.1 M. In Figures 5.37-5.41, the experimental data and the predicted values determined using Models I and II are shown. The values for the minimum residuals used in Model II are 0.8 and 1.0 for the phenolic compounds and indolic compounds, respectively. When the reactions between intermediates and ozone were ignored, the predicted concentration profiles of those

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compounds decreased much faster than those determined experimentally. Therefore, for the oxidation of phenolic and indolic compounds, it is very important to consider the effect of side reactions during ozonation. At pH 6.7, the reaction coefficients were also compared. The reaction coefficients (k_f) are much larger than those found at pH 2.1. The fitted values for reaction coefficient are summarized in Table 5.5 and a comparison between experimental data and model predictions can be seen in Figures 5.42-5.56.

Table 5.5 The Reaction Coefficients for Phenols and Indoles under Different Flowrates at pH 6.7

	Phenols (s^{-1})	Indoles (s^{-1})
Q=100 mL/min	350	450
Q=300 mL/min	400	400
Q=500 mL/min	350	400

5.4.4 Oxidation of Synthetic Manure and Stored Swine manure by Ozone

Synthetic manure and stored swine manure were ozonated to investigate the oxidation of phenolic and indolic compounds in complex matrices. The synthetic manure was ozonated at different temperatures and flowrates. Changing the temperature from 14 – 30 °C had no effect on the removal of phenolic and indolic compounds (Figures 5.57-5.61). This is in agreement with our previous experiments in which individual phenolic or indolic compounds were ozonated. The effect of flowrate (100, 300, 500 mL/min) is shown in Figures 5.62-5.66. As observed previously, when plotting the concentration of compound as a function of ozone dosage, rather than time, the concentration profiles of

phenolic and indolic compounds appeared to be essentially independent of flowrate (Figures 5.67-5.71). Based upon the results presented in these figures, when the ozone dosage is greater than 0.5 g/L, phenol and *p*-cresol would be removed completely; when the ozone dosage is greater than 0.1 g/L, *p*-ethylphenol, indole, and skatole would also be removed. Therefore, an ozone dosage of 0.5 g/L can be established as that which will remove all of the malodorous components in the synthetic manure. It can be predicted that higher ozone dosage should be needed to treat the real swine manure when having the same original concentrations of phenolic and indolic compounds. In our pilot-scale study, although the ozone dosage of 0.5 g/L was established for the odor acceptability, 1 g/L ozone dosage was still needed to remove all of the phenolic and indolic compounds. For the engineering practical, however, the use of ozone dosage in designing the reaction system should adopt the one for the improvement of malodors to an acceptable level, instead of the complete removal of the malodorous substances.

The concentrations of VFAs were reduced by less than 10% during ozonation for 80 minutes (Figure 5.72). It is consistent with the finding in the chapter 2 and chapter 3 that the VFAs were not oxidized by ozone in the real manure. This can be explained by the very low rate constants of ozone with VFAs (Hoigné and Bader, 1983), which means that VFAs are not able to compete with the more readily oxidable substrates for ozone.

In the synthetic manure, stripping and oxygenation were ineffective at removing any of the phenolic or indolic compounds at the same hydrodynamic conditions as that used with ozone gas. As such, the losses of phenolic and indolic compounds from the synthetic manure appear to be due entirely to ozonation reactions. The oxidation model was used to predict and compare the decrease of those target compounds. Results show

that the prediction using Model I results in a much faster reduction than that observed experimentally. Thus, the reaction coefficient (k_f) should be used to take into account competing reactions. The reaction coefficients are summarized in Table 5.6 for the various flowrates. The fitted values of reaction coefficients are in the same range as that obtained when the individual phenolic or indolic compounds were ozonated. The comparisons of experimental observations and model predictions can be seen in Figures 5.73-5.87.

Table 5.6 The Reaction Coefficients for Synthetic Manure Determined at Different Flowrates

Flowrates	Reaction Coefficient (s^{-1})
Q=100 mL/min	300
Q=300 mL/min	400
Q=500 mL/min	600

The initial characteristics of the stored swine manure are given in Table 5.7. The manure was oxygenated and ozonated using a lab-scale reactor at a flowrate of 300 mL/min and temperature of 22 °C. Phenol, *p*-cresol, *p*-ethylphenol and skatole, were found to be reduced by about 10%, 30%, 20% and 25% after two and half hours of oxygenation (Figure 5.88). Although some attempts had been tried to fit the concentration curves, no satisfactory mathematical relationship could be obtained. Microbiological metabolism of the odorous compounds is thought to be the major removal mechanism when oxygen was provided, resulting in an increase in microbial activity. However, as the degradation rate of phenolic and indolic compounds in swine

Table 5.7 Chemical Characteristics of Real Swine Manure Taken from the Storage Pit

pH	7.5	Acetate (mM)	93.87
COD (mg/L)	30,000	Propionate (mM)	14.38
Phenol (mg/L)	75.2	*iso*-Butyrate (mM)	2.70
p-Cresol	186.6	Butyrate (mM)	9.66
p-Ethylphenol (mg/L)	20.9	*iso*-Valerate (mM)	2.17
Indole (mg/L)	ND	Valerate (mM)	1.58
Skatole (mg/L)	10.0	VFAs as Carbon (mM)	299.07

manure by microbial metabolism is slow, this removal mechanism can be ignored when compared with the removals obtained by ozone. During ozonation, all of these malodorous compounds were oxidized after 2 hours, i.e., at an ozone dosage of 1.5 g/L (Figure 5.89). The VFA concentrations did not change with either oxygenation or ozonation. The pH values increased from 7.5 to 8.4 after oxygenation and from 7.5 to 8.2 after ozonation for the period of two and half hours. As the initial pH was 7.5, the reaction rate constants were assumed to be 10 times greater than those obtained for a pH of 6.7. Thus, the rate constants used in the oxidation model are 10^7 $M^{-1}s^{-1}$ for the phenolic compounds and 5×10^7 $M^{-1}s^{-1}$ for skatole. A reaction coefficient of 40,000 s^{-1} was found to yield the minimum residual in fitting the experimental data (Figures 5.90-5.93). This value, which is much greater than that obtained for synthetic manure, is likely to be large because of impurities in real swine manure that can react with ozone.

The use of a model to predict the removals of odorous compounds in swine manure would be easier if the reaction coefficient could be determined from a "gross parameter" such as COD. As such, the relationship between k_f and COD was considered. We

assume that the mathematical relationship between COD and k_f can be expressed as $k_f=k_f'(COD)$, the intrinsic reaction coefficient, k_f', is calculated to be 1.33 for the real manure we tested. Similarly, k_f' is calculated as 0.125 for the synthetic manure, in which the COD is 3,200 mg/L. It should be noted that the pH of real manure is about a unit larger than that of synthetic manure. Therefore, the concentration of hydroxide ion in the real manure would be 10 times that in the synthetic manure. If the reaction rates of ozone with by-products or impurities would also increase for ten times by increasing the pH as suggested by Hoigné and Bader (1983), the mathematical expression in using COD would be valid for the two manures.

5.5 Conclusions

The combination of a mass transfer and kinetic study has led to the development of a model to predict the degradation of malodorous, phenolic and indolic compounds in a semi-batch ozonation reactor. For this study, several important conclusions can be drawn:

1. Reaction rate constants of the phenolic and indolic compounds increase with increasing pH.
2. No dissolved ozone and outlet gaseous ozone can be observed prior to the complete removal of the phenolic and indolic compounds. One hundred percent utilization of ozone was obtained under our experimental conditions. Therefore, ozone dosage becomes a very important and reliable parameter for the design of an ozone reactor to remove malodorous substances from the liquid manure slurry.

3. The effect of pH on the oxidation of phenolic and indolic compounds is predominately determined by their reaction rate constants and competition kinetics with ozone. For the solution containing phenolic compounds at lower pH values, the degradation of phenol is seriously retarded as its reaction rate is the smallest of the target compounds; the degradation of *p*-cresol is dramatically accelerated as it has the greatest reaction rate. As these reaction rates of phenolic compounds are identical at pH of 6.7, the degradation of these compounds follows similar patterns.
4. The reduction of phenolic and indolic compounds is unaffected by temperature and by the presence of other compounds, such VFAs and ammonia. Although COD, simulated by dextran, might cause a slight decrease in the rate of oxidation of these malodorous compounds by ozone, the effect is still small due to their fast reaction rates.
5. The removal of phenolic and indolic compounds by stripping and oxygenation was insignificant at the gas flowrates used. Therefore, the slight reduction of concentrations of these compounds in real swine manure is attributed to microbial degradation when ozone-enriched oxygen was used. The difference in the results obtained in pure water and synthetic manure is likely due to the large numbers of microorganisms in the real manure.
6. A model combining mass transfer and oxidation kinetics of ozone should include the effect of side reactions involving ozone and byproducts. Using Model I, which ignores the effect of side reactions, the predicted rates of the oxidation of these malodorous compounds are much greater than those observed experimentally. The reaction coefficients for artificial and real swine manure were estimated as 400

(s^{-1}) and 40,000 (s^{-1}), respectively. It is apparent that presence of ozonated reactive impurities results in a significant increase in the ozone dosage required to oxidize the target compounds.

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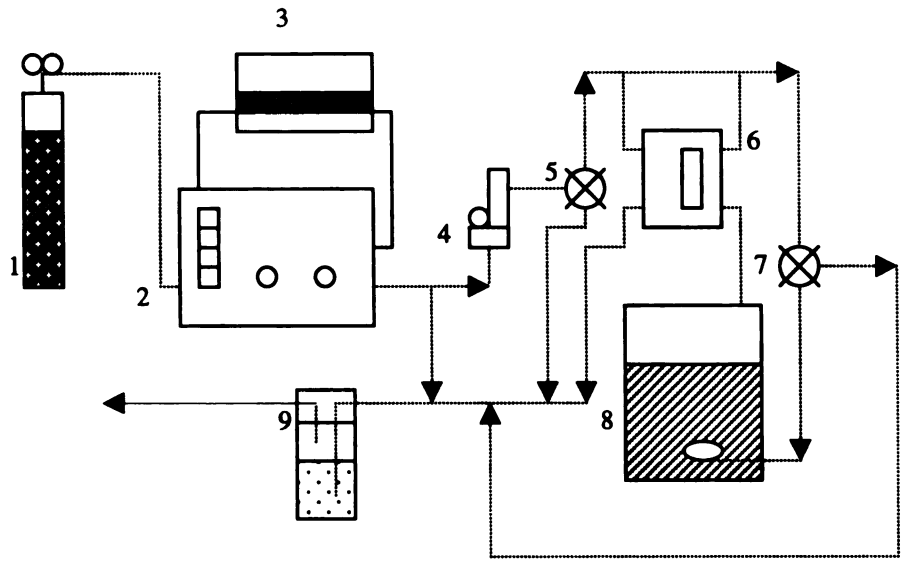

1: Oxygen Cylinder
2: Ozone Generator
3: Cooling System
4: Flow Controller
5: Three-way Valve
6: UV Spectrophotometer
7: Three-way Valve
8: Semi-batch Reactor
9: Trap Solution (KI)

Figure 5.1 The System Setup for the Semi-batch Ozonation Process

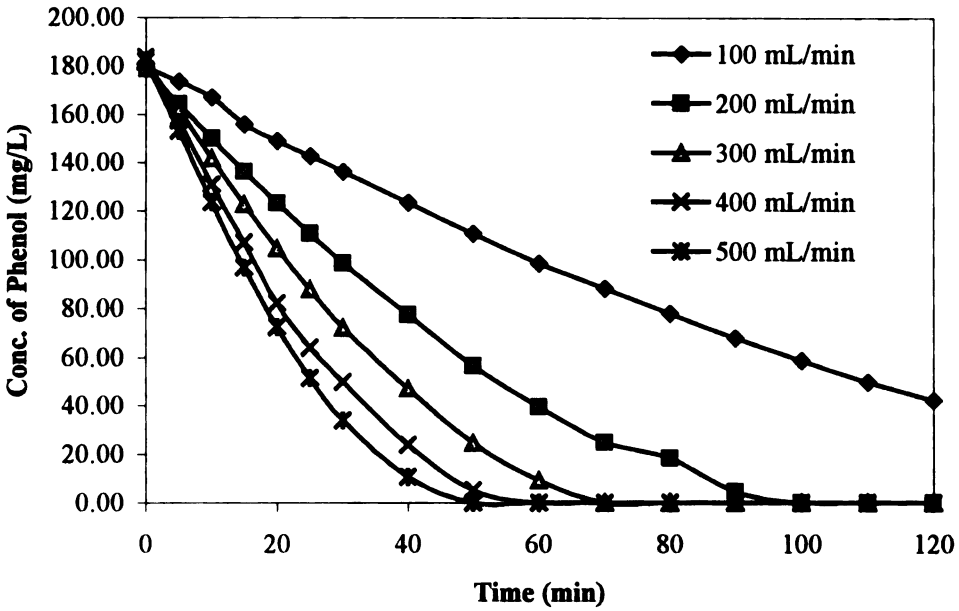

Figure 5.2 The Effect of Flowrate on the Oxidation of Phenol in the Mixture of Phenolic Compounds at pH 6.7 and Temperature 22 C

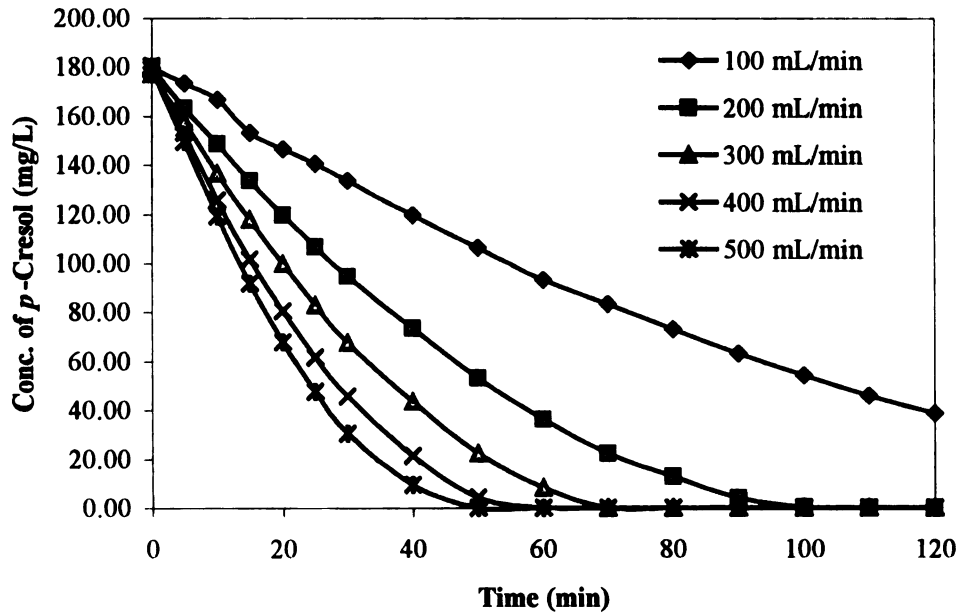

Figure 5.3 The Effect of Flowrate on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at pH 6.7 and Temperature 22 C

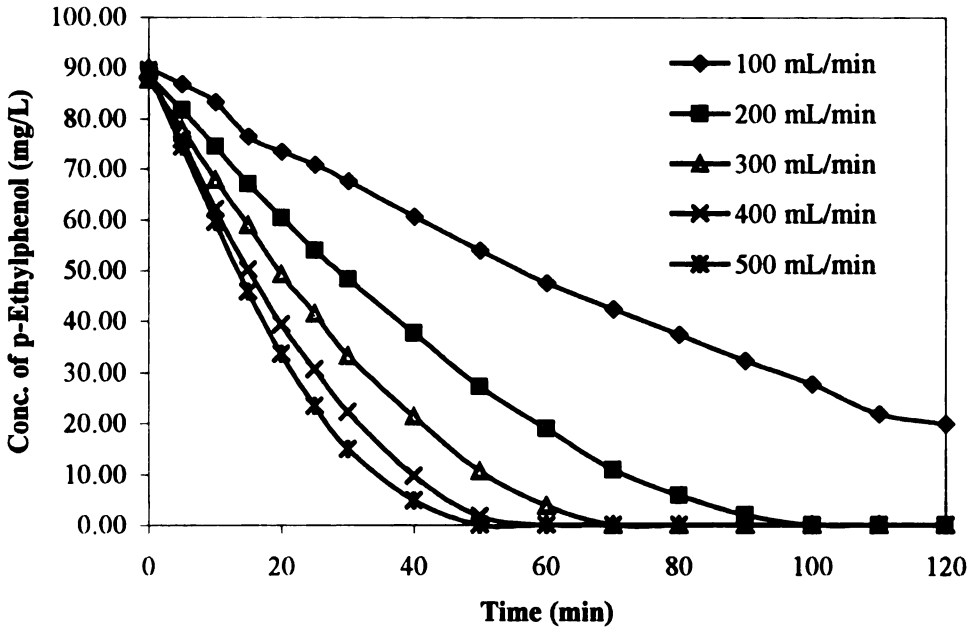

Figure 5.4 The Effect of Flowrate on the Oxidation of *p* -Ethylphenol in the Mixture of Phenolic Compounds at pH 6.7 and Temperature 22 C

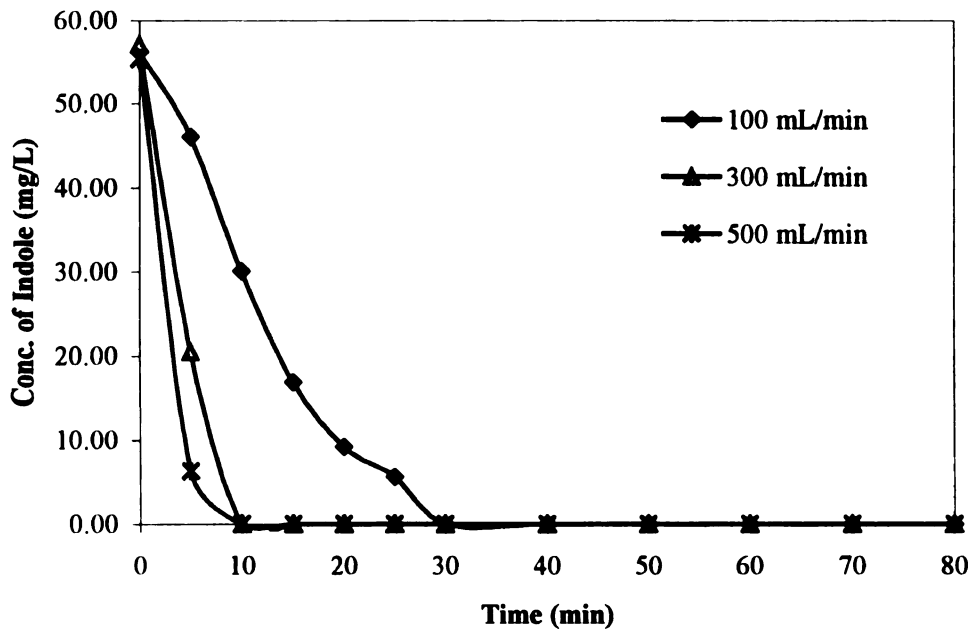

Figure 5.5 The Effect of Flowrate on the Oxidation of Indole in the Mixture of Indolic Compounds at pH 6.7 and Temperature 22 C

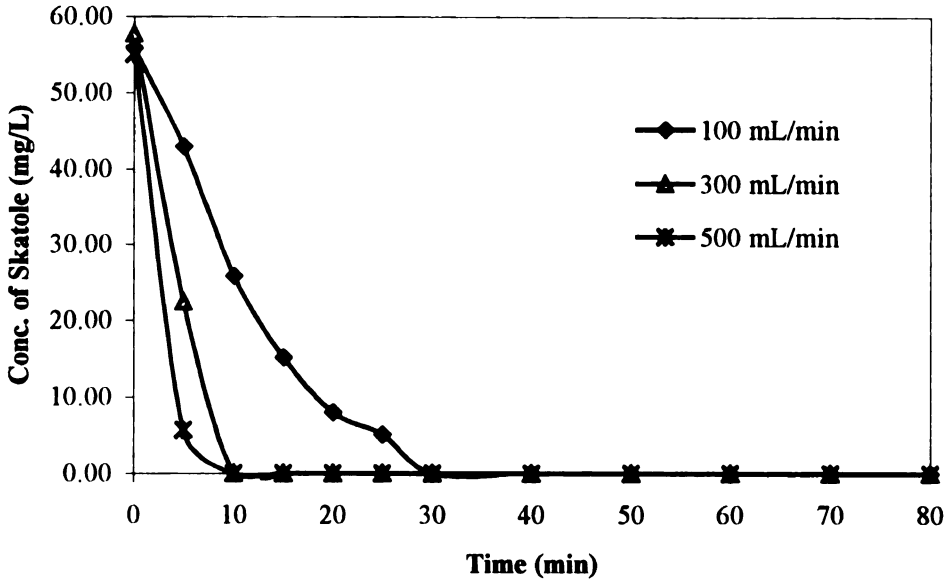

Figure 5.6 The Effect of Flowrate on the Oxidation of Skatole in the Mixture of Indolic Compounds at pH 6.7 and Temperature 22 C

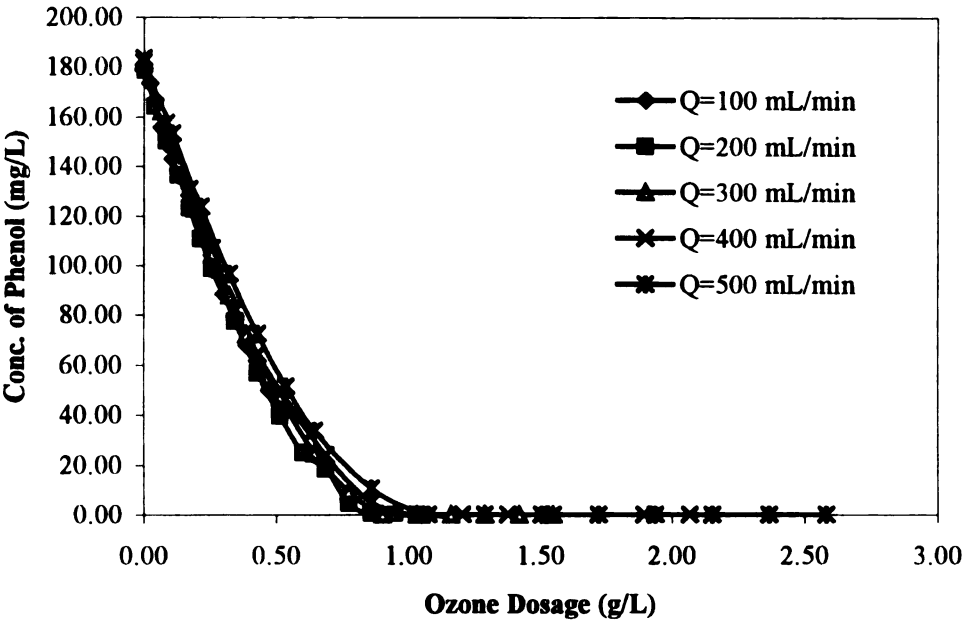

Figure 5.7 The Effect of Ozone Dosage on the Oxidation of Phenol in the Mixture of Phenolic Compounds by Different Flowrates at pH 6.7 and Temperature 22 C

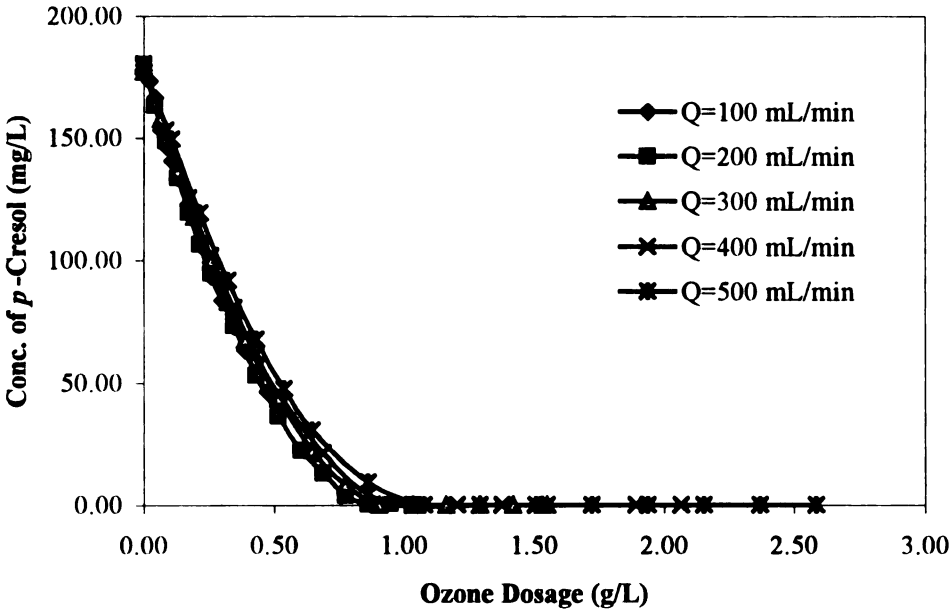

Figure 5.8 The Effect of Ozone Dosage on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds by Different Flowrates at pH 6.7 and Temperature 22 C

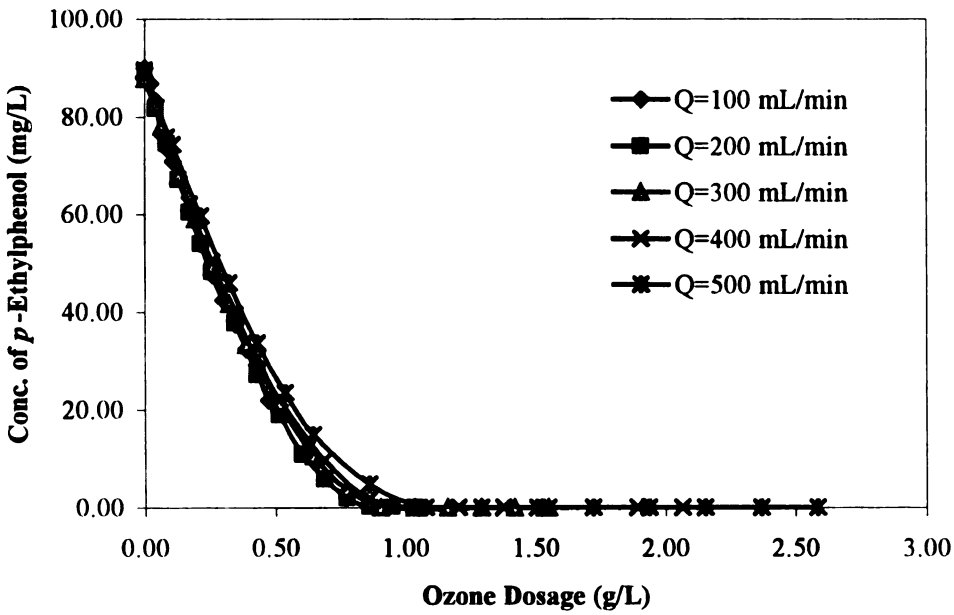

Figure 5.9 The Effect of Ozone Dosage on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds by Different Flowrates at pH 6.7 and Temperature 22 C

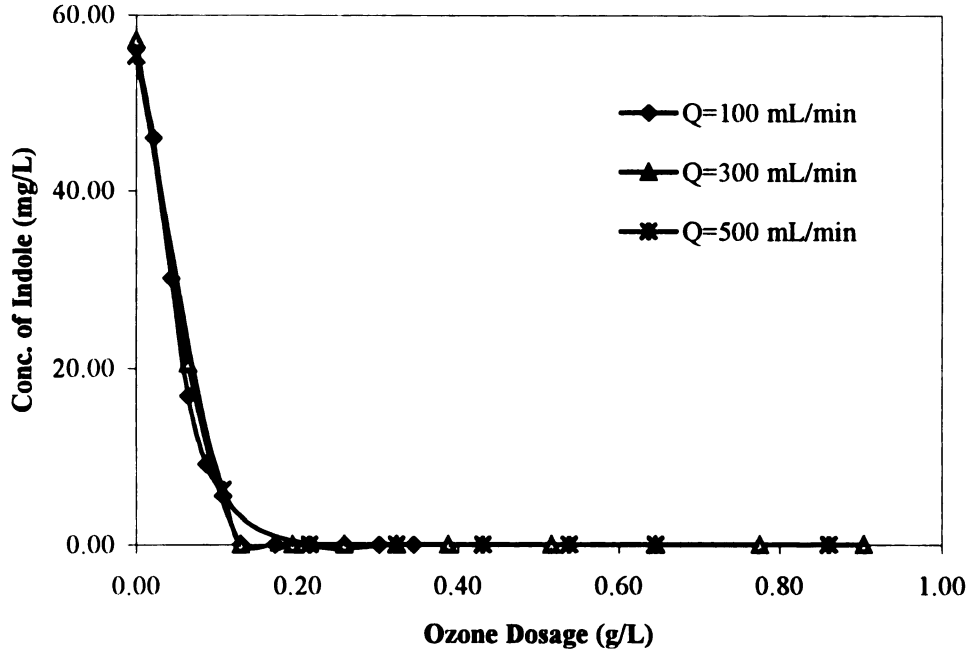

Figure 5.10 The Effect of Ozone Dosage on the Oxidation of Indole in the Mixture of Indolic Compounds by Different Flowrates at pH 6.7 and Temperature 22 C

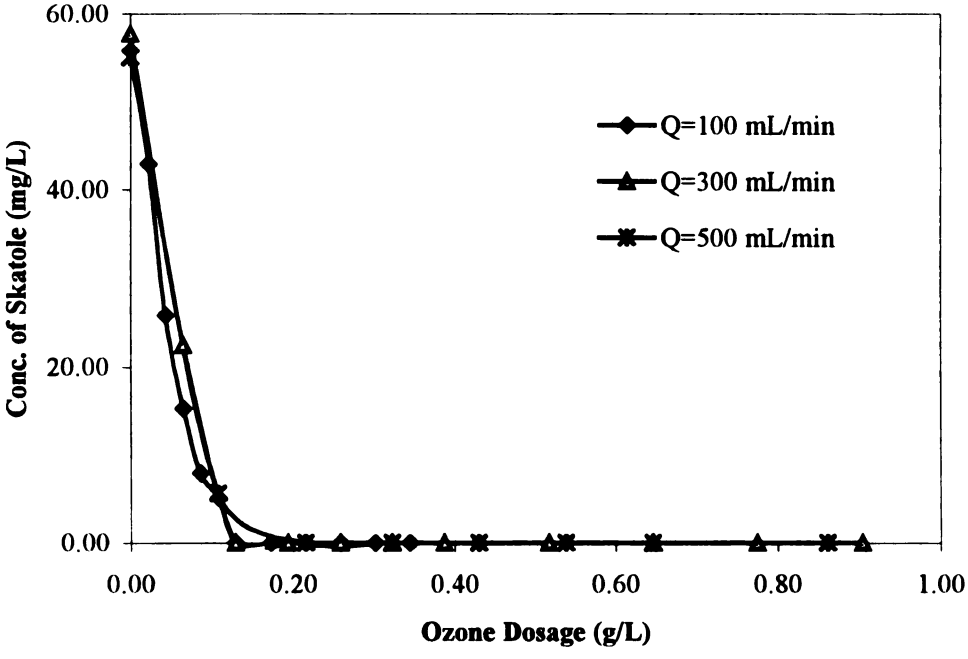

Figure 5.11 The Effect of Ozone Dosage on the Oxidation of Skatole in the Mixture of Indolic Compounds by Different Flowrates at pH 6.7 and Temperature 22 C

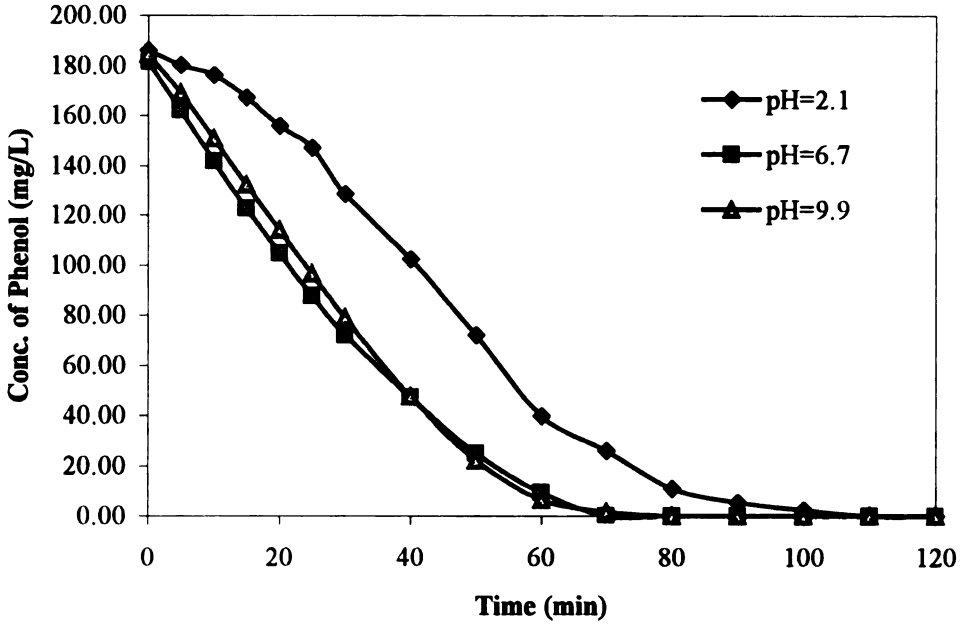

Figure 5.12 Effect of pH on the Oxidation of Phenol in the Mixture of Phenolic Compounds at Flowrate 300 mL/min and Temperature 22 C

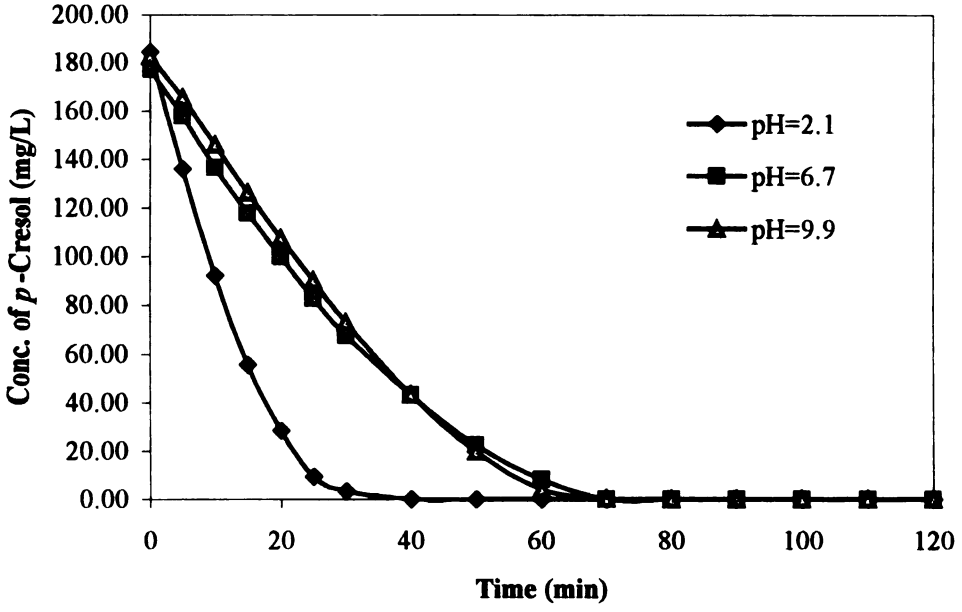

Figure 5.13 Effect of pH on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at Flowrate 300 mL/min and Temperature 22 C

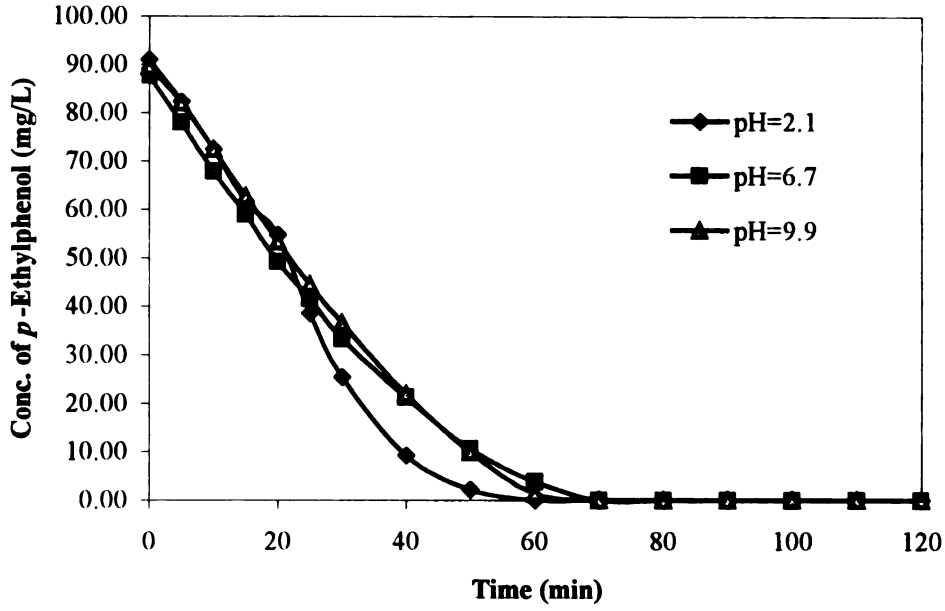

Figure 5.14 Effect of pH on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds at Flowrate 300 mL/min and Temperature 22 C

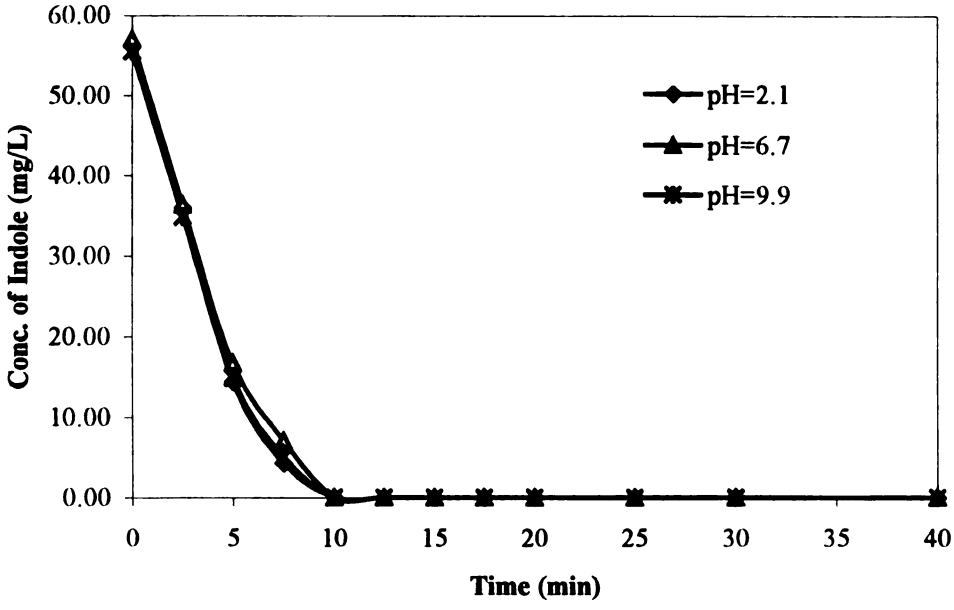

Figure 5.15 Effect of pH on the Oxidation of Indole in the Mixture of Indolic Compounds at Flowrate 300 mL/min and Temperature 22 C

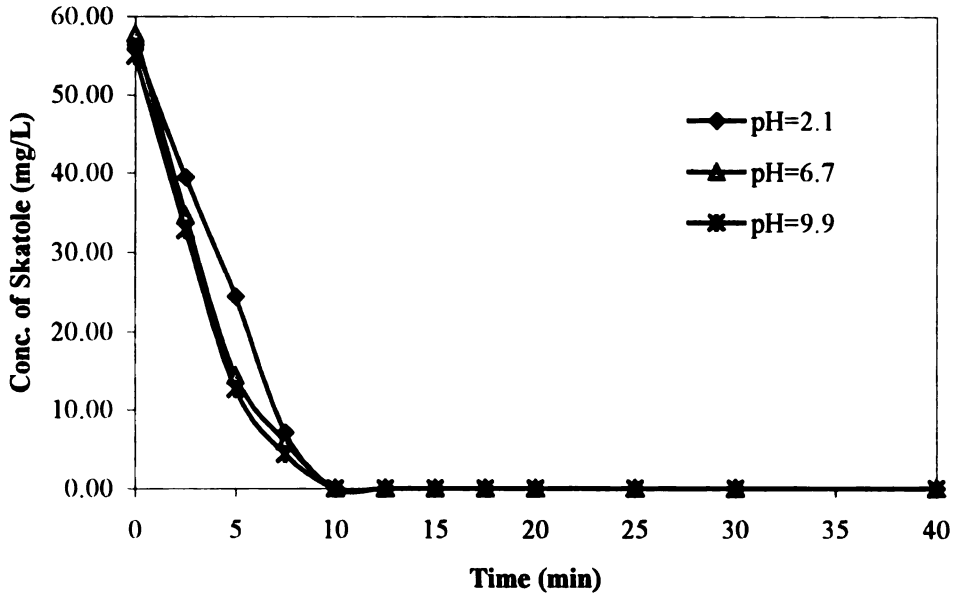

Figure 5.16 Effect of pH on the Oxidation of Skatole in the Mixture of Indolic Compounds at Flowrate 300 mL/min and Temperature 22 C

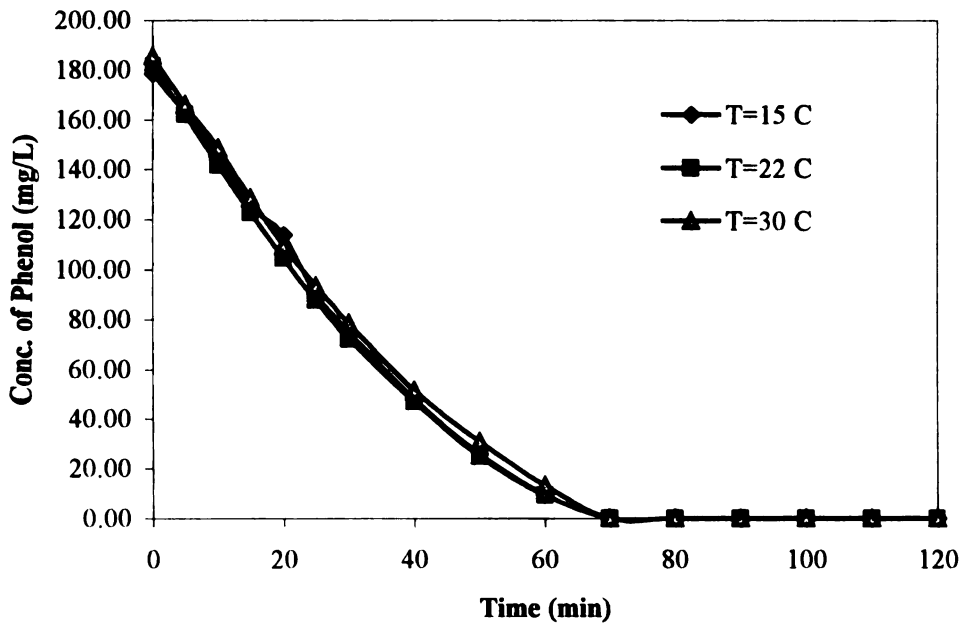

Figure 5.17 Effect of Temperature on the Oxidation of Phenol in the Mixture of Phenolic Compounds at pH 6.7 and Flowrate 300 mL/min

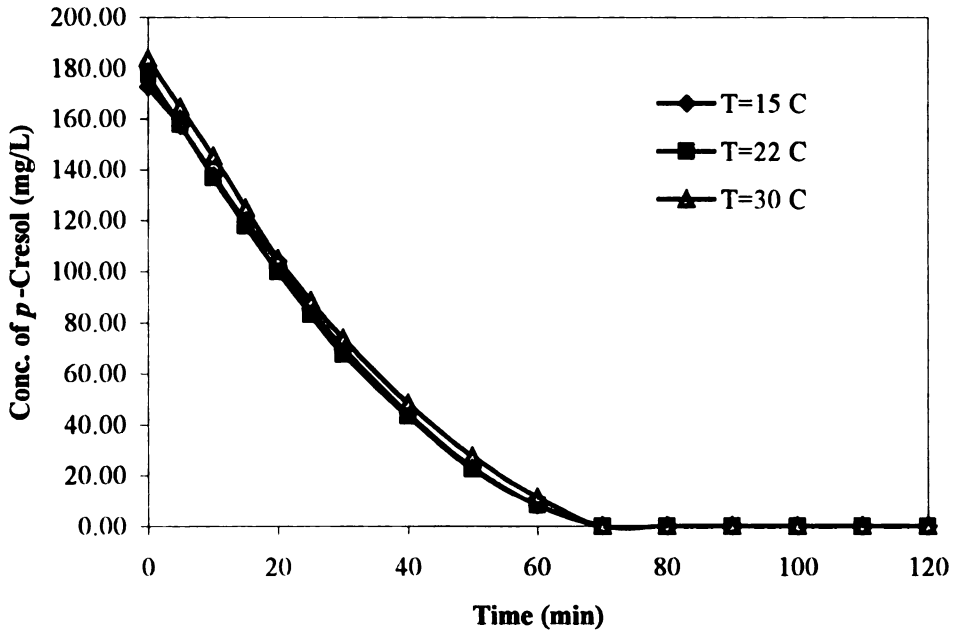

Figure 5.18 Effect of Temperature on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at pH 6.7 and Flowrate 300 mL/min

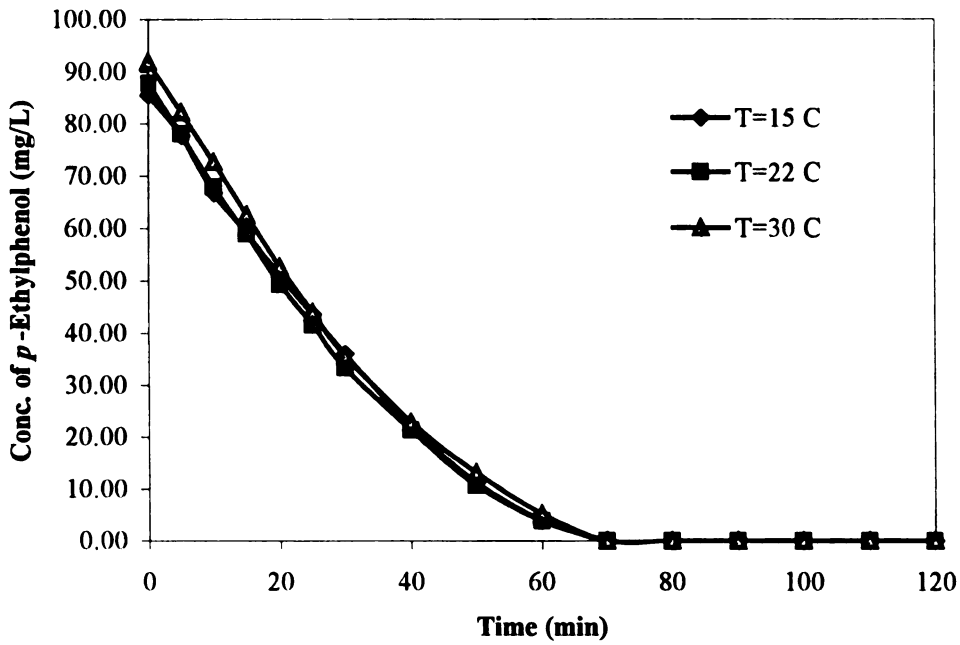

Figure 5.19 Effect of Temperature on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds at pH 6.7 and Flowrate 300 mL/min

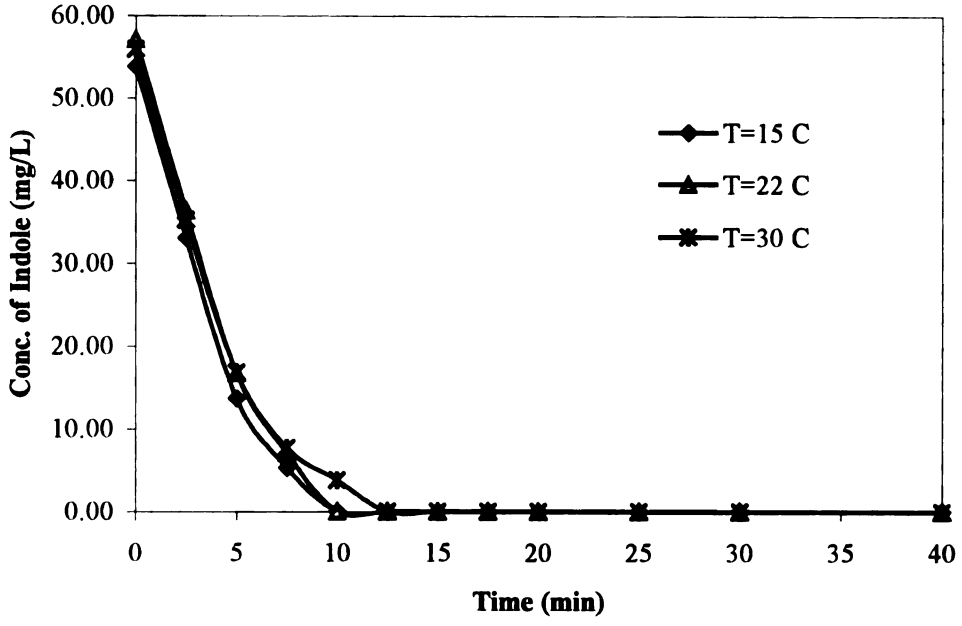

Figure 5.20 Effect of Temperature on the Oxidation of Indole in the Mixture of Indolic Compounds at pH 6.7 and Flowrate 300 mL/min

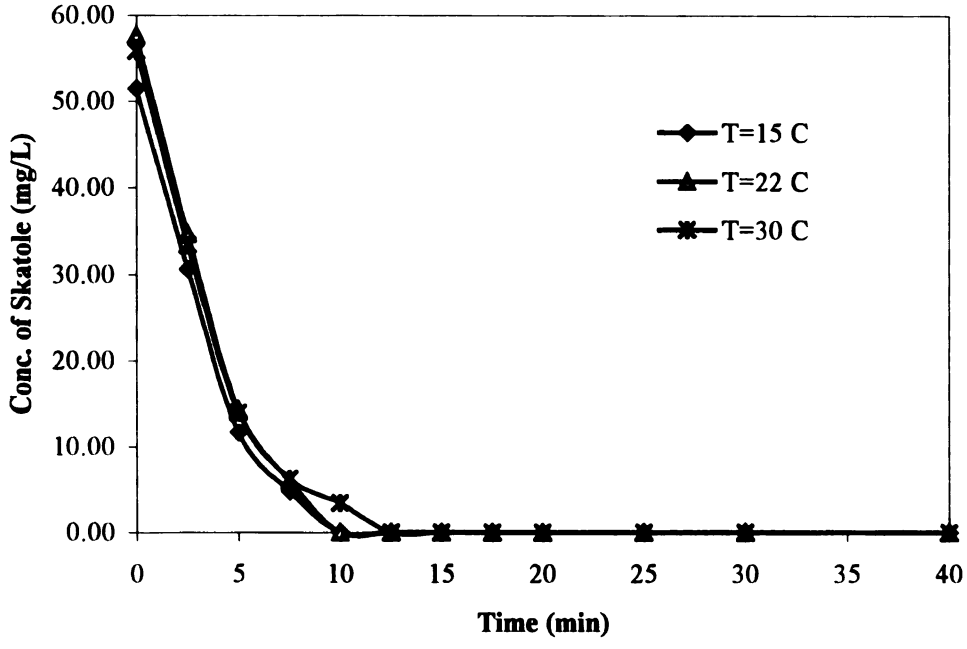

Figure 5.21 Effect of Temperature on the Oxidation of Skatole in the Mixture of Indolic Compounds at pH 6.7 and Flowrate 300 mL/min

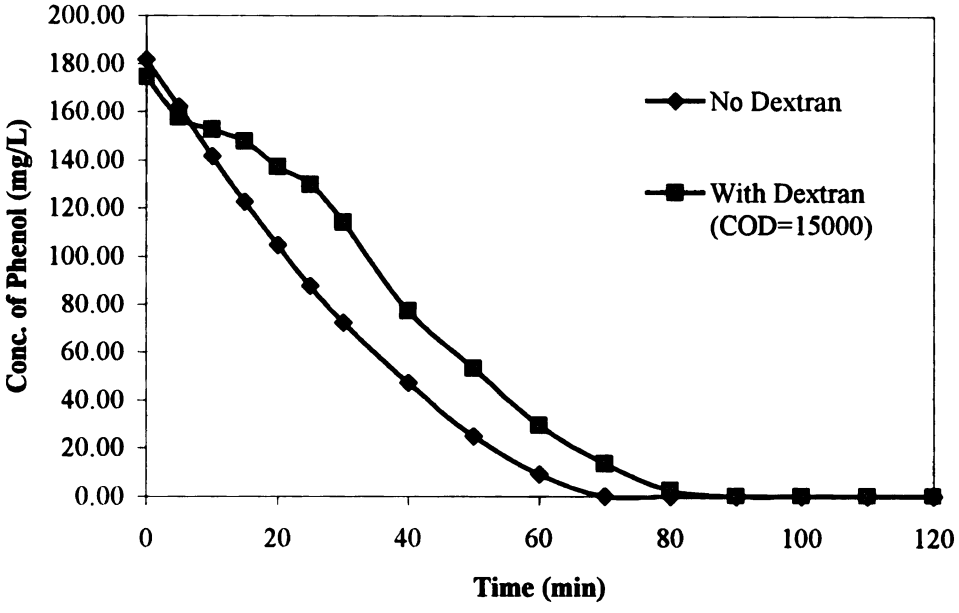

Figure 5.22 Effect of Dextran on the Oxidation of Phenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

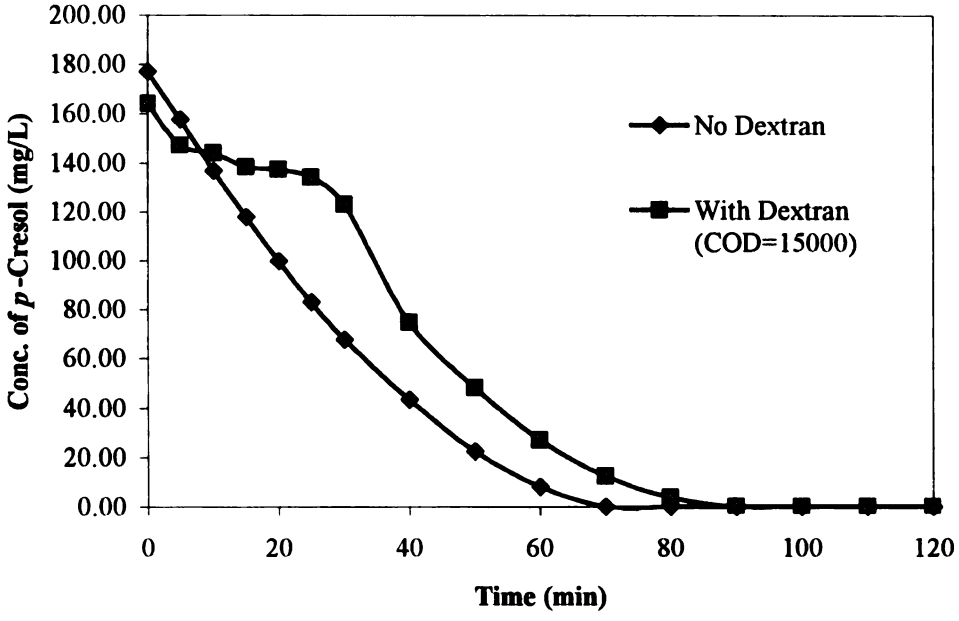

Figure 5.23 Effect of Dextran on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

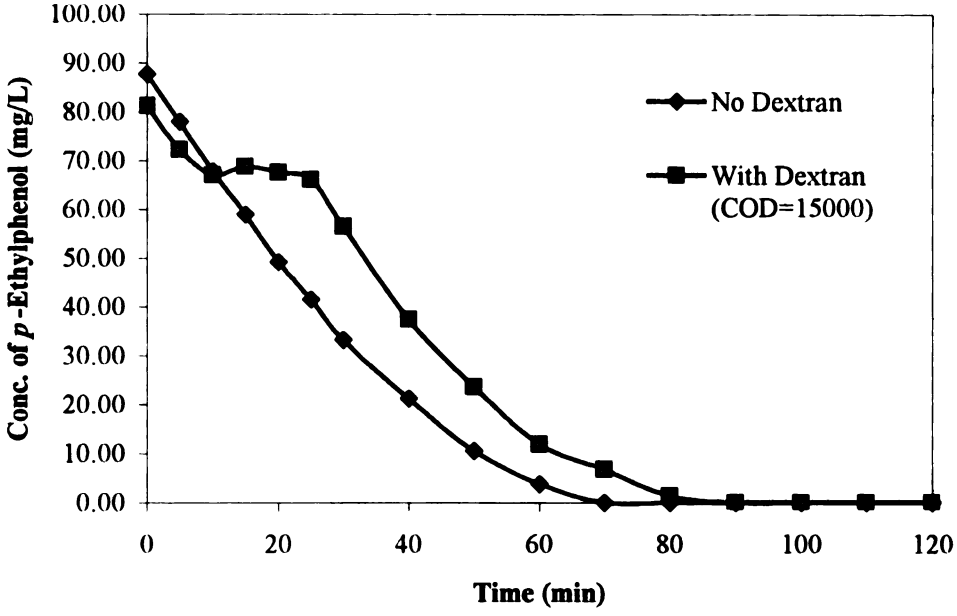

Figure 5.24 Effect of Dextran on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

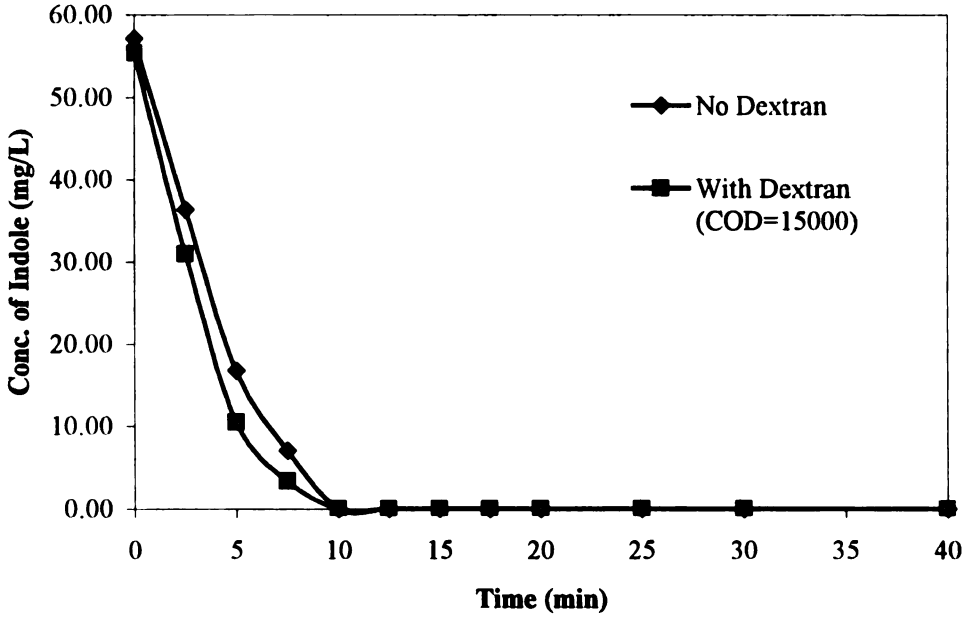

Figure 5.25 Effect of Dextran on the Oxidation of Indole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

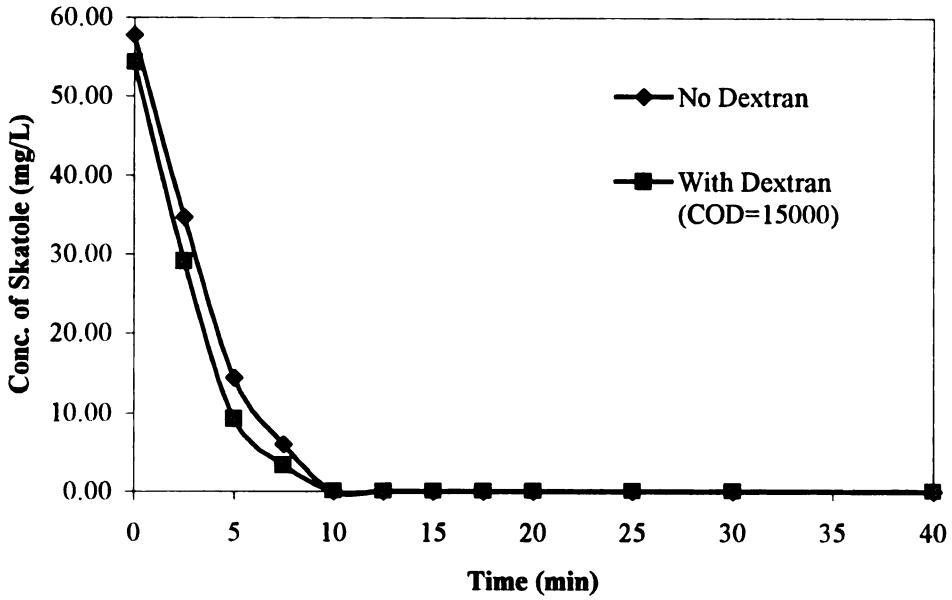

Figure 5.26 Effect of Dextran on the Oxidation of Skatole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

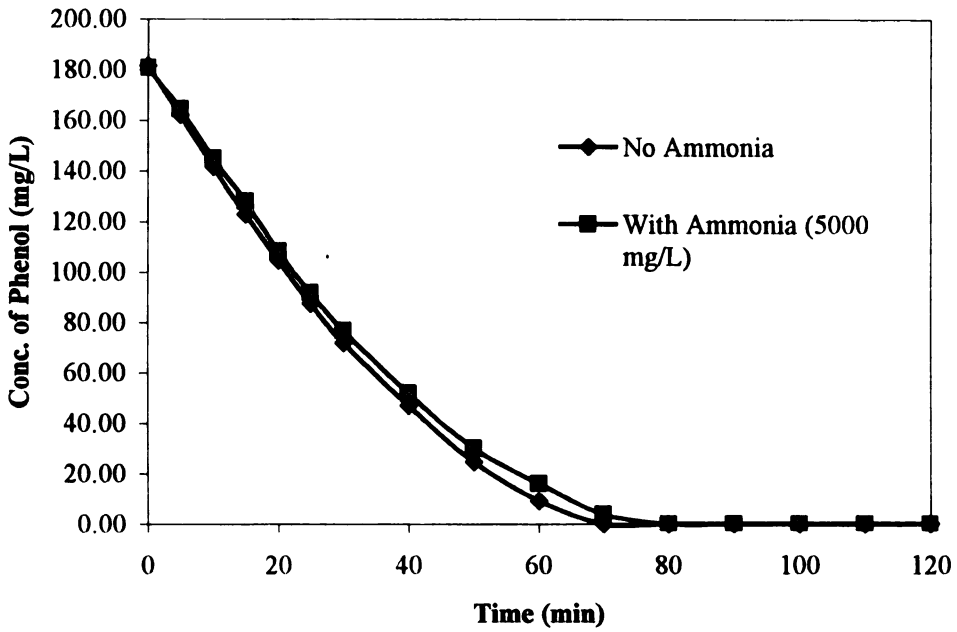

Figure 5.27 Effect of Ammonia on the Oxidation of Phenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

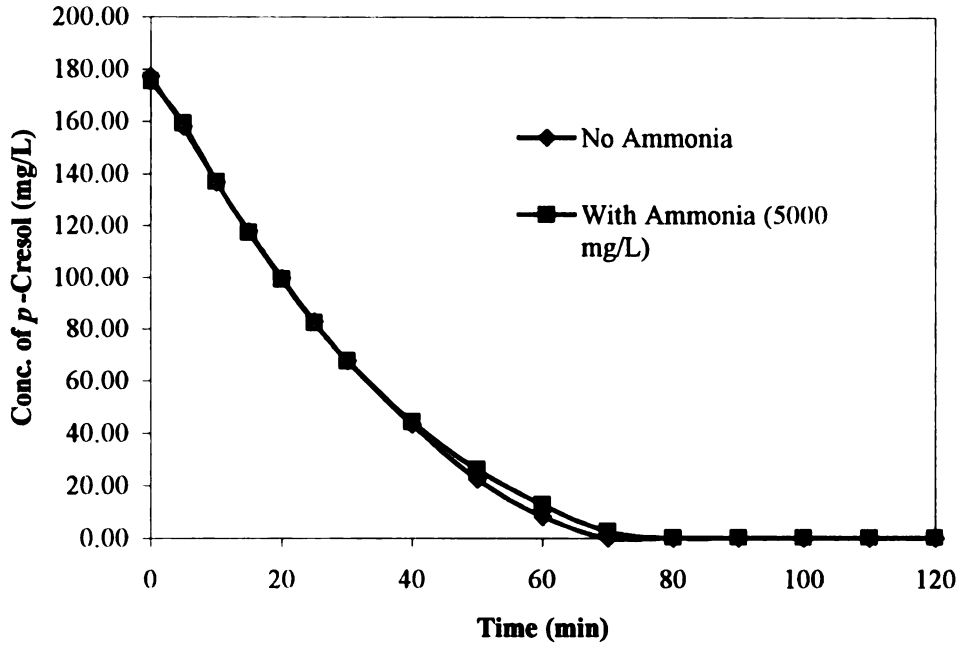

Figure 5.28 Effect of Ammonia on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

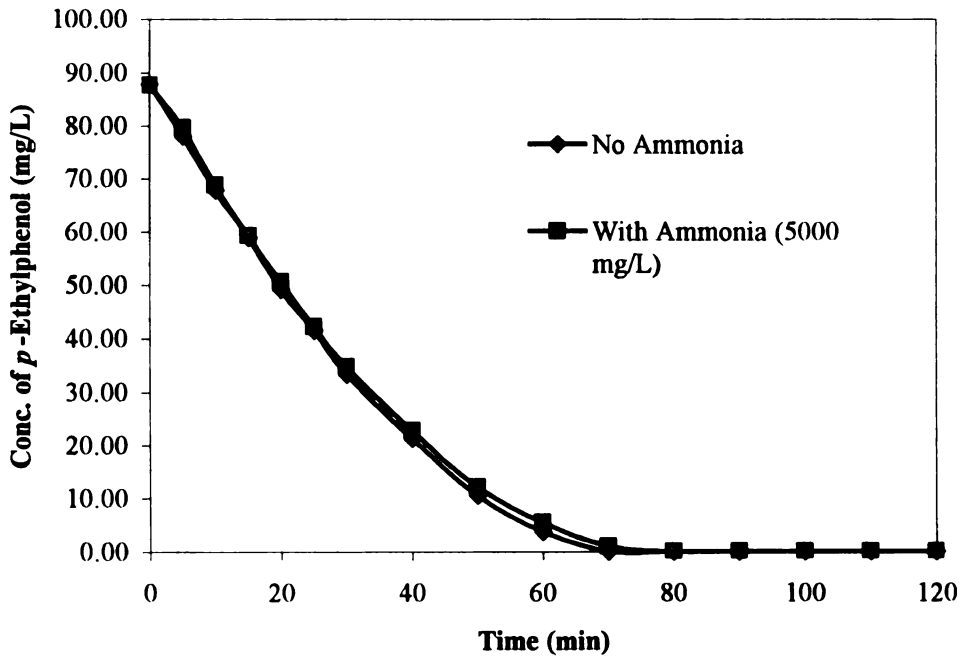

Figure 5.29 Effect of Ammonia on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

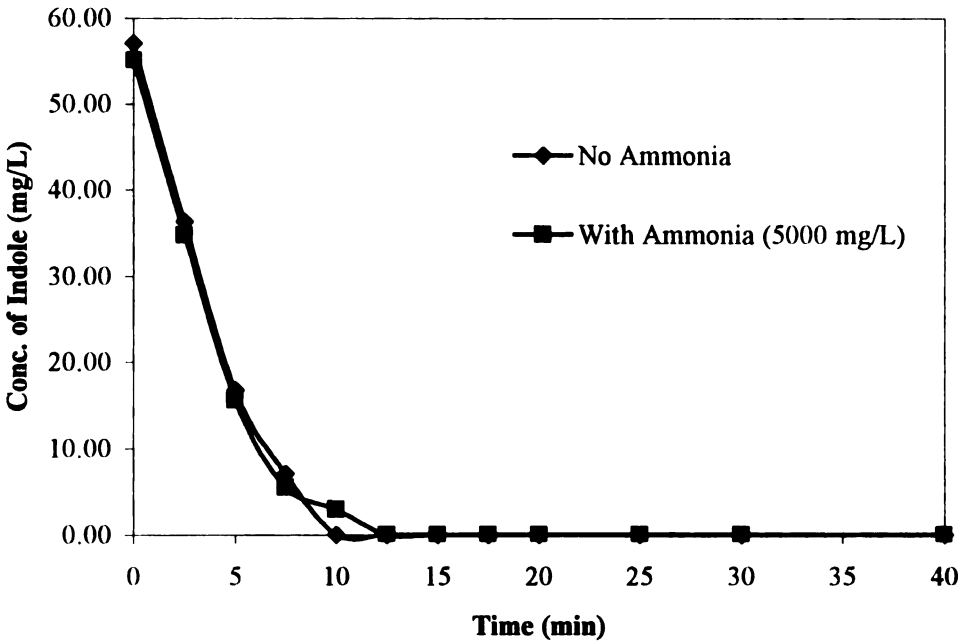

Figure 5.30 Effect of Ammonia on the Oxidation of Indole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

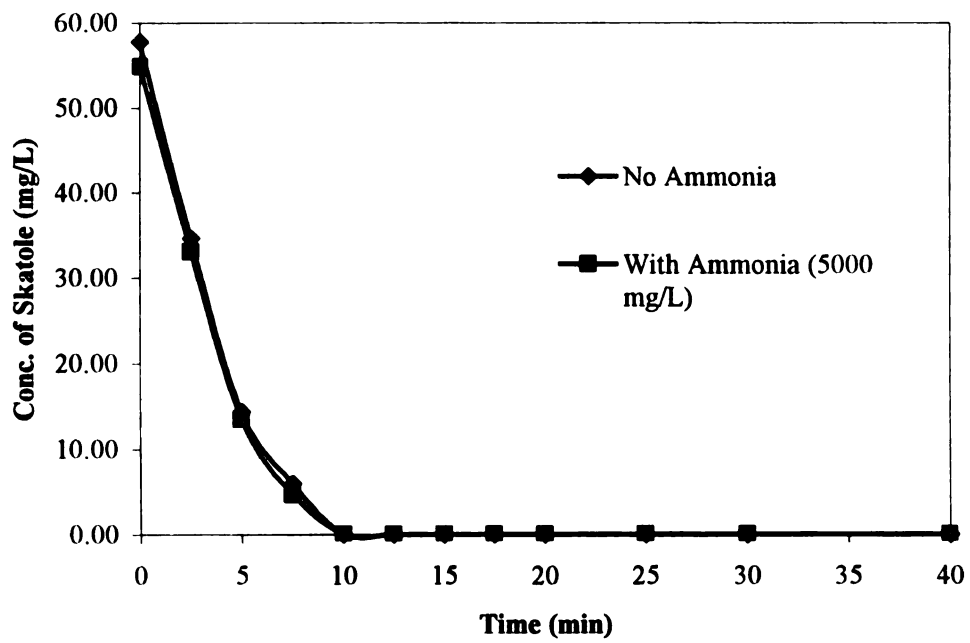

Figure 5.31 Effect of Ammonia on the Oxidation of Skatole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

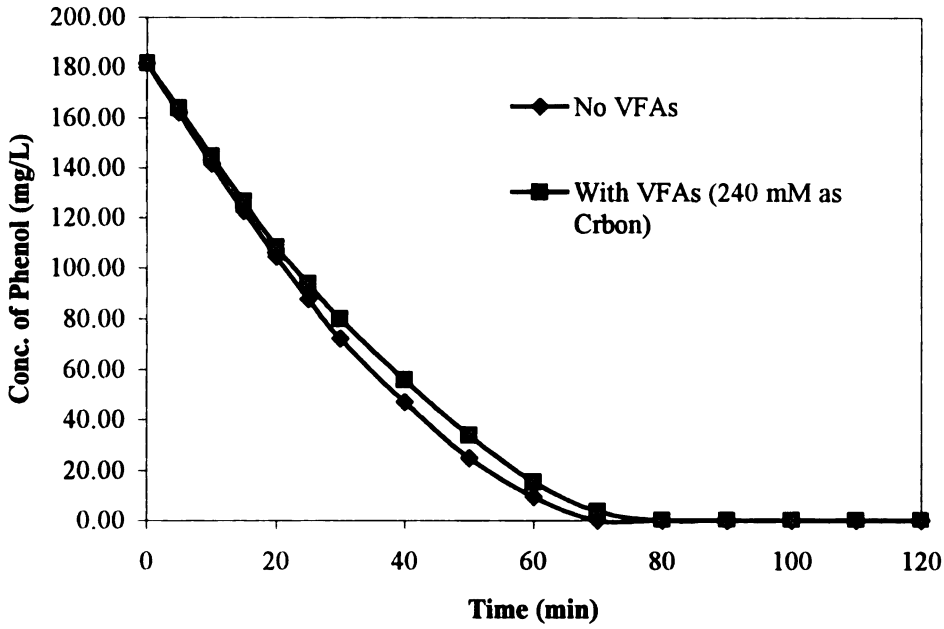

Figure 5.32 Effect of VFAs on the Oxidation of Phenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

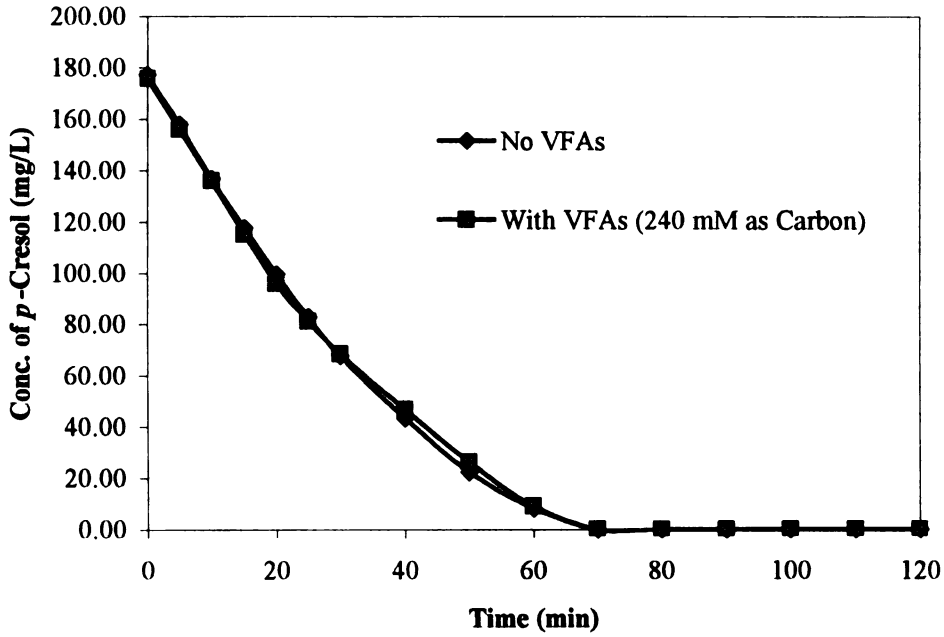

Figure 5.33 Effect of VFAs on the Oxidation of *p*-Cresol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

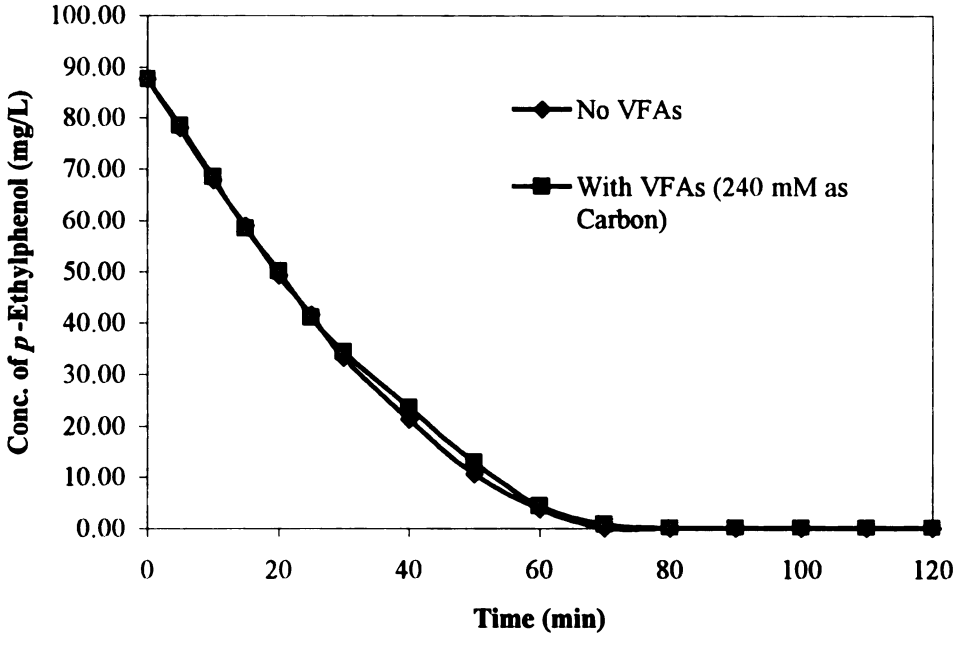

Figure 5.34 Effect of VFAs on the Oxidation of *p*-Ethylphenol in the Mixture of Phenolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

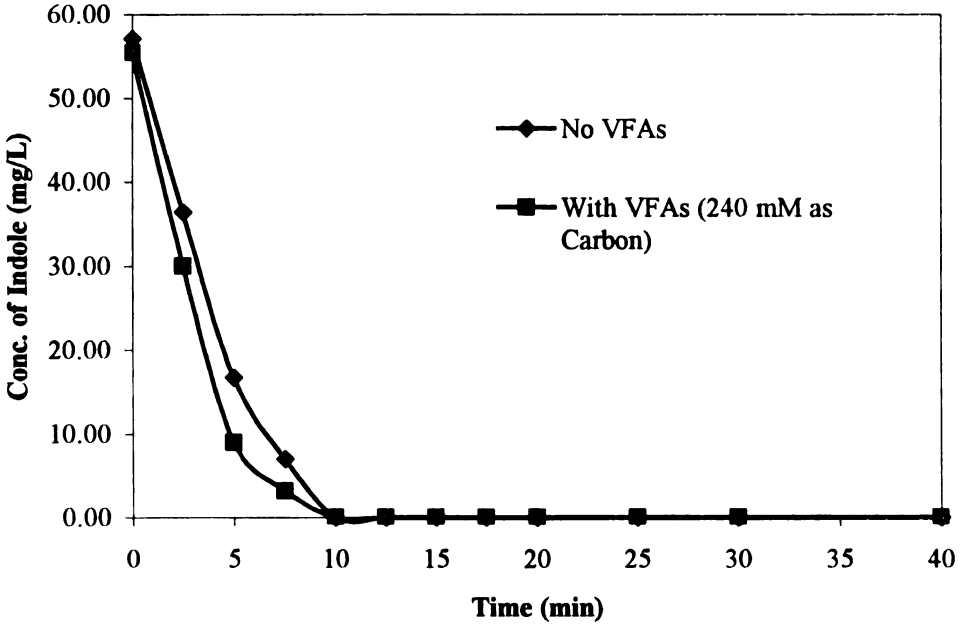

Figure 5.35 Effect of VFAs on the Oxidation of Indole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

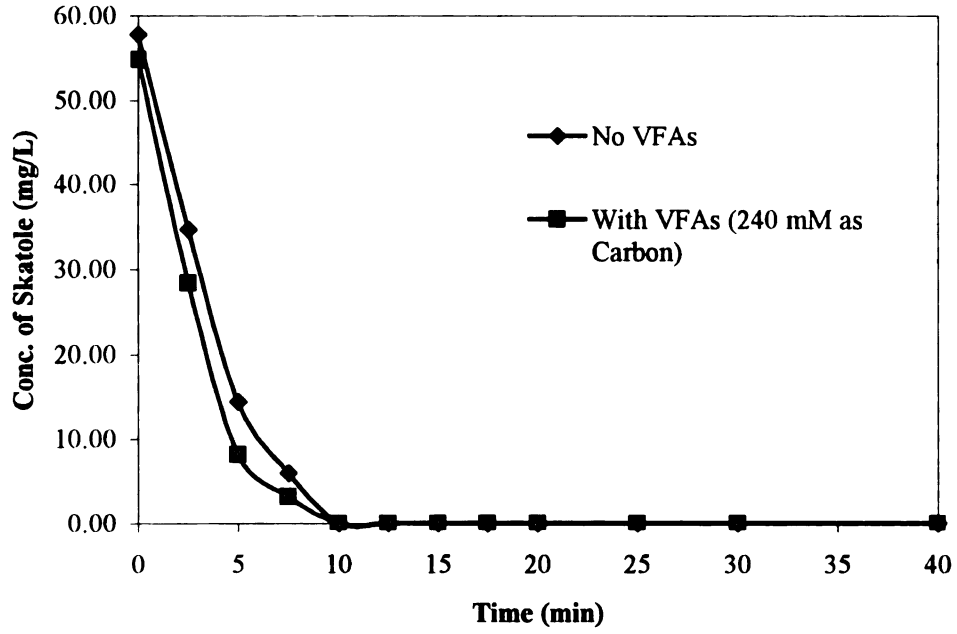

Figure 5.36 Effect of VFAs on the Oxidation of Skatole in the Mixture of Indolic Compounds at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

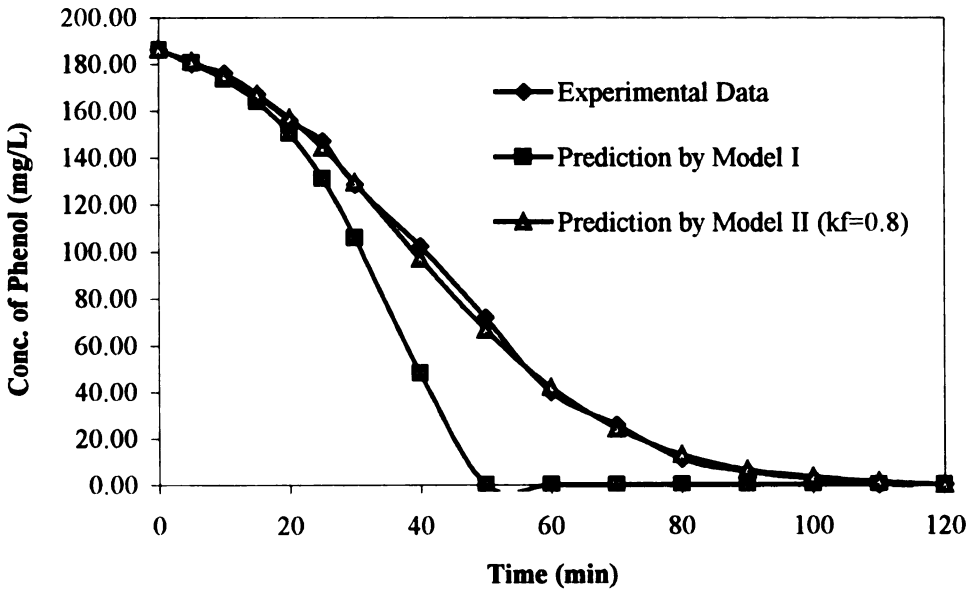

Figure 5.37 Comparison of Phenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 2.1, Flowrate 300 mL/min, and Temperature 22 C

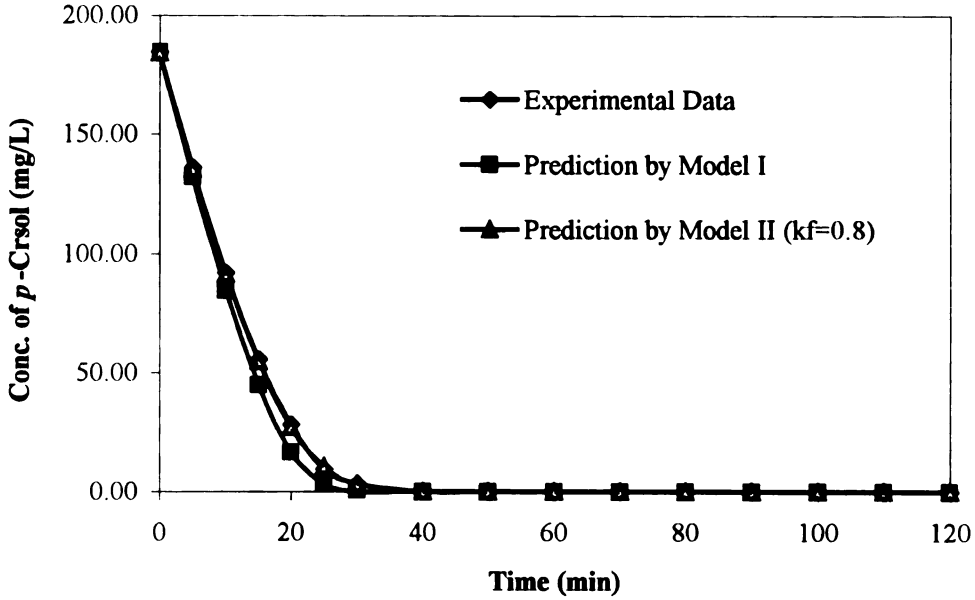

Figure 5.38 Comparison of *p*-Cresol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 2.1, Flowrate 300 mL/min, and Temperature 22 C

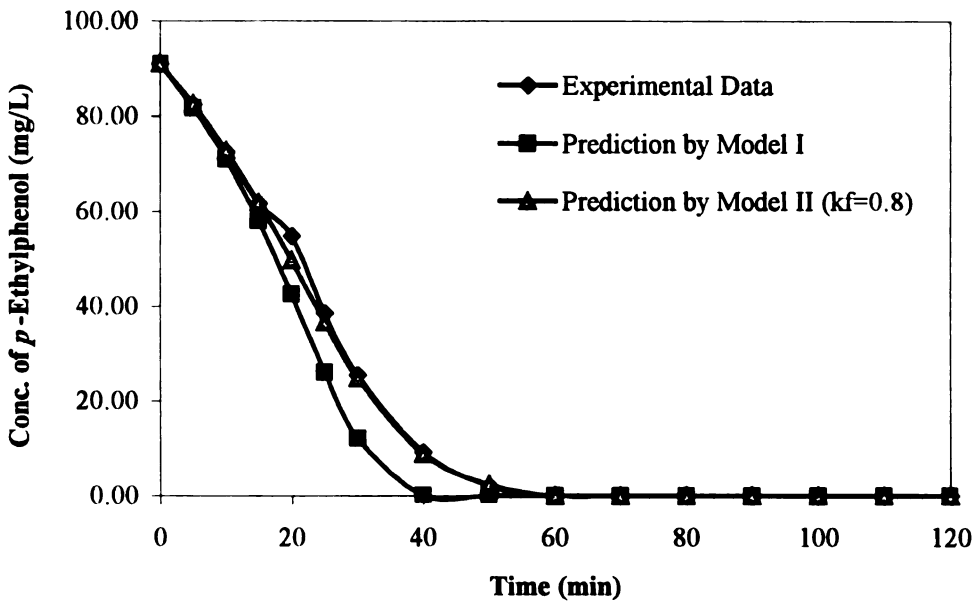

Figure 5.39 Comparison of *p*-Ethylphenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 2.1, Flowrate 300 mL/min, and Temperature 22 C

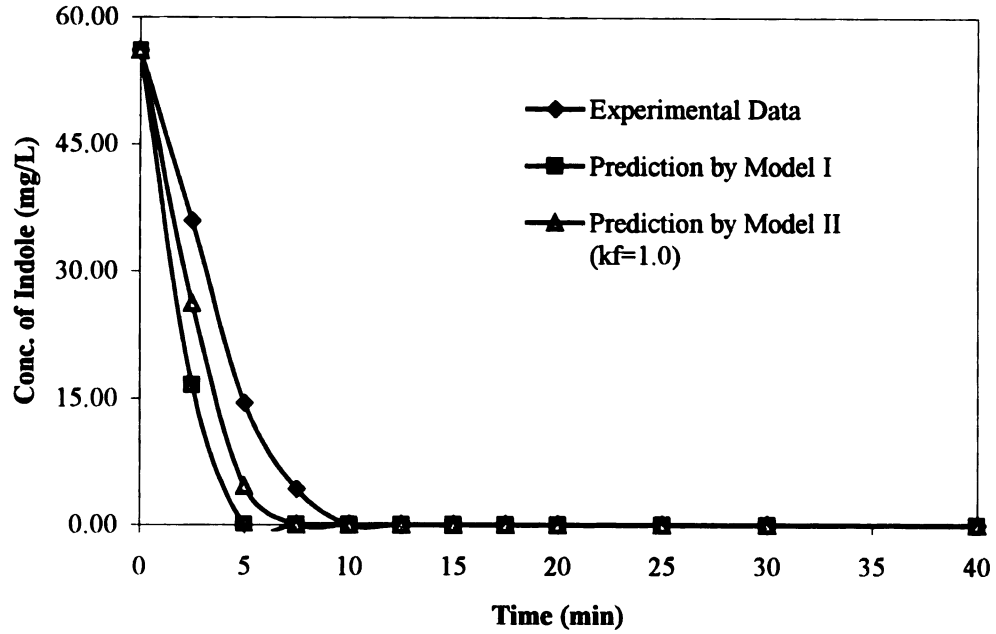

Figure 5.40 Comparison of Indole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 2.1, Flowrate 300 mL/min, and Temperature 22 C

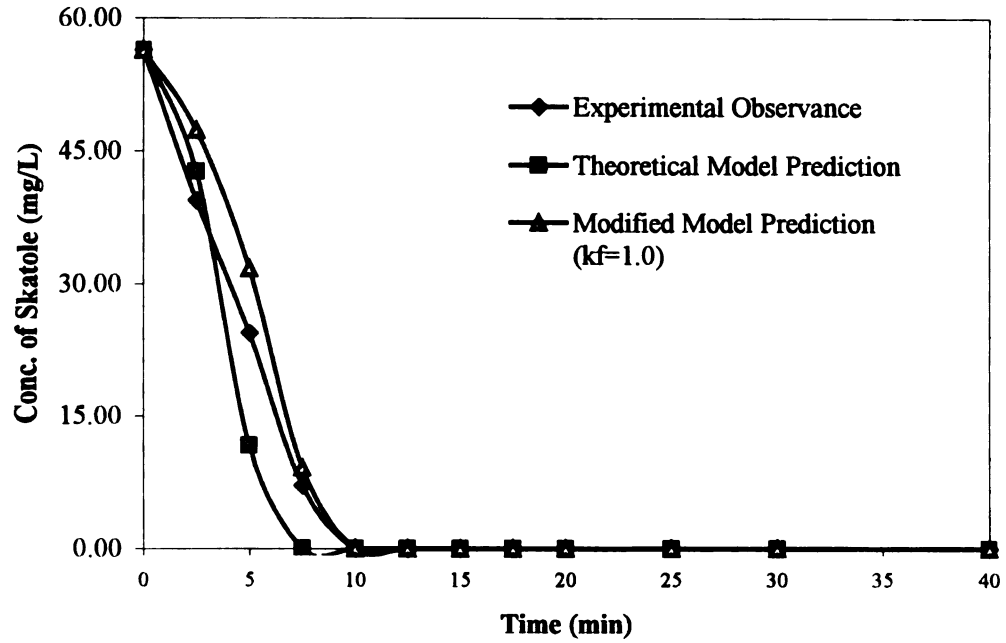

Figure 5.41 Comparison of Skatole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 2.1, Flowrate 300 mL/min, and Temperature 22 C

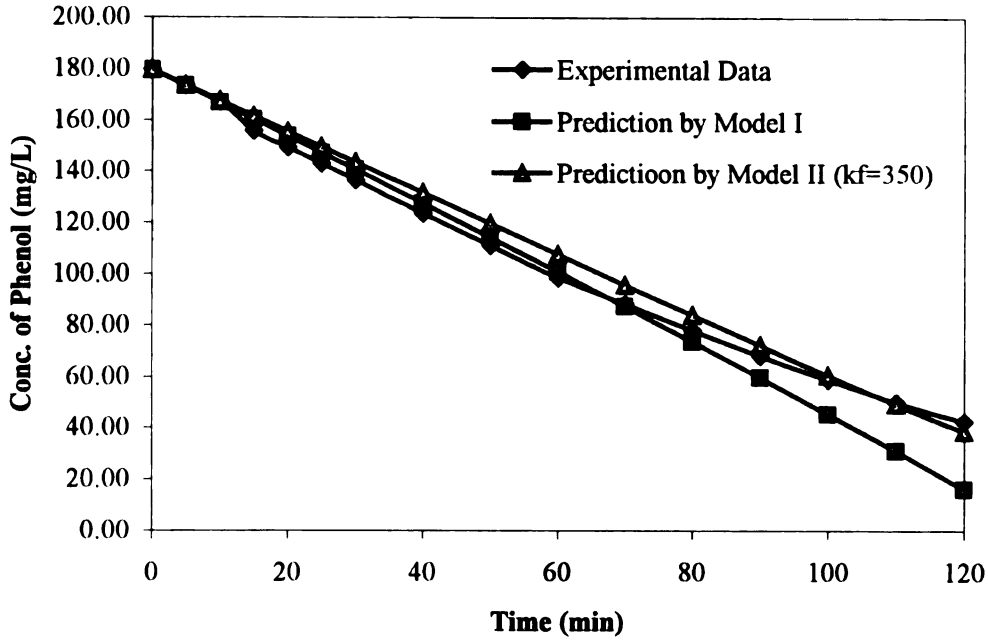

Figure 5.42 Comparison of Phenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

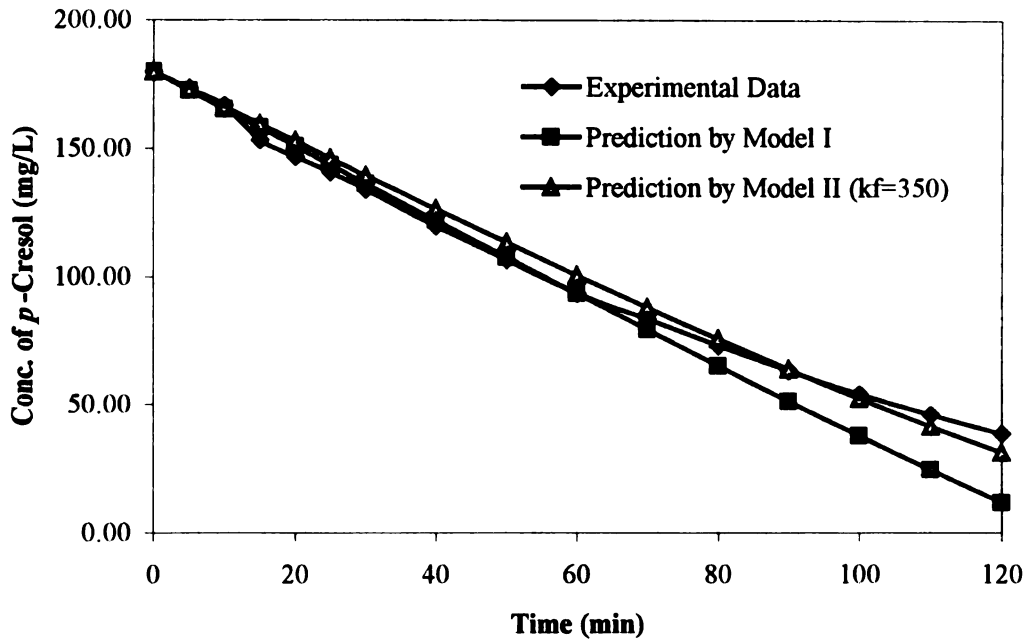

Figure 5.43 Comparison of *p*-Cresol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

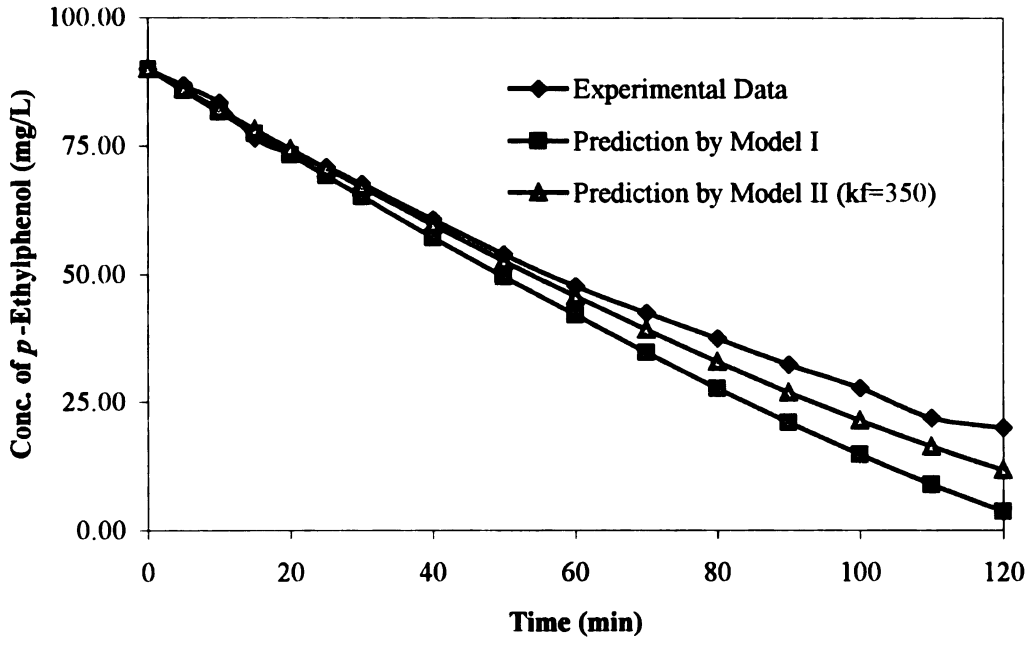

Figure 5.44 Comparison of *p*-Ethylphenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

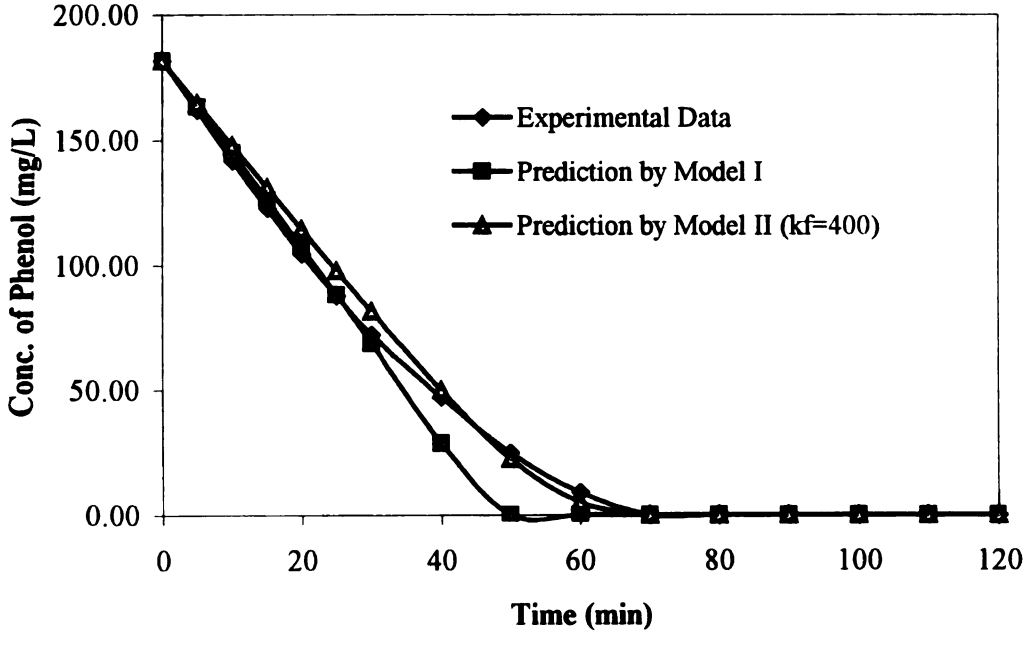

Figure 5.45 Comparison of Phenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

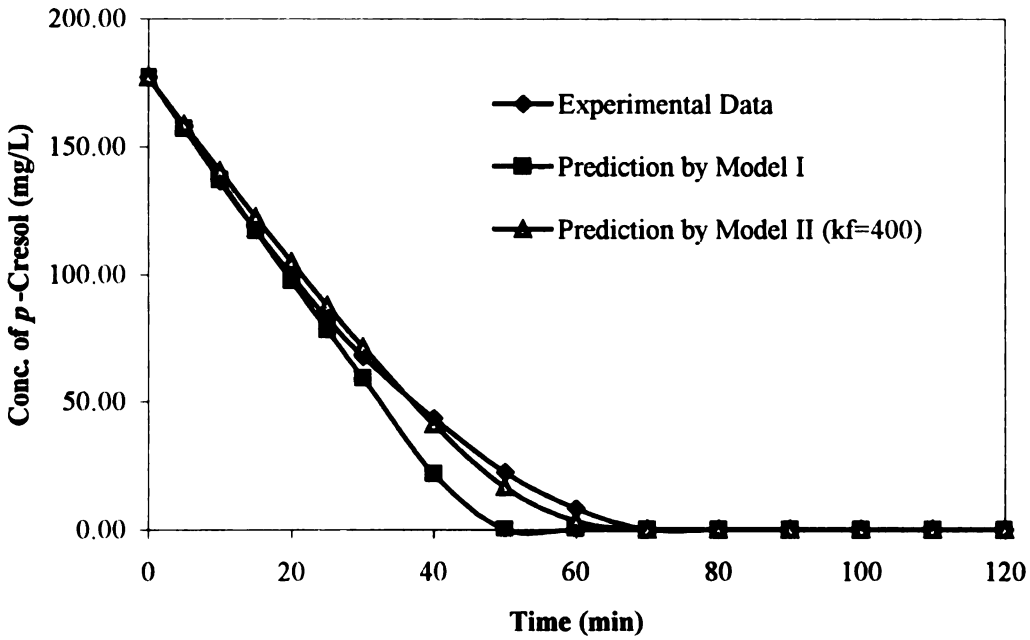

Figure 5.46 Comparison of *p*-Cresol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

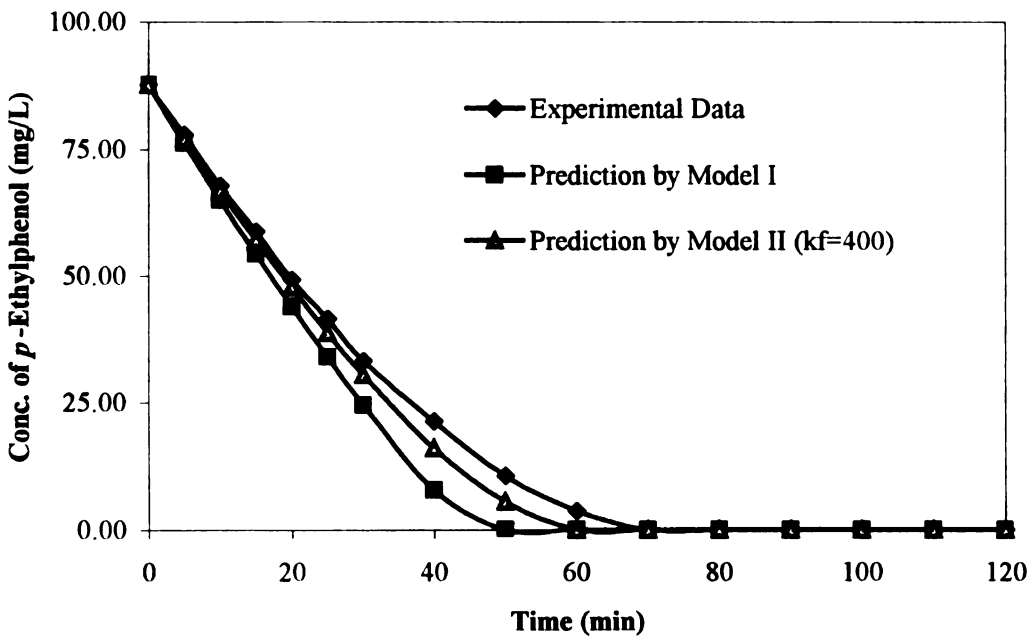

Figure 5.47 Comparison of *p*-Ethylphenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

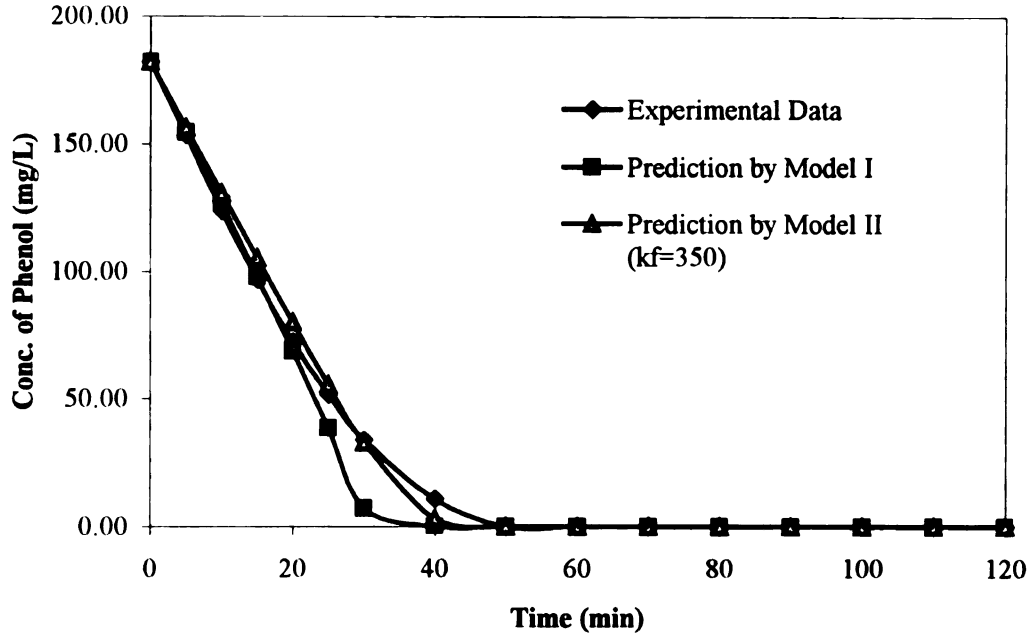

Figure 5.48 Comparison of Phenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

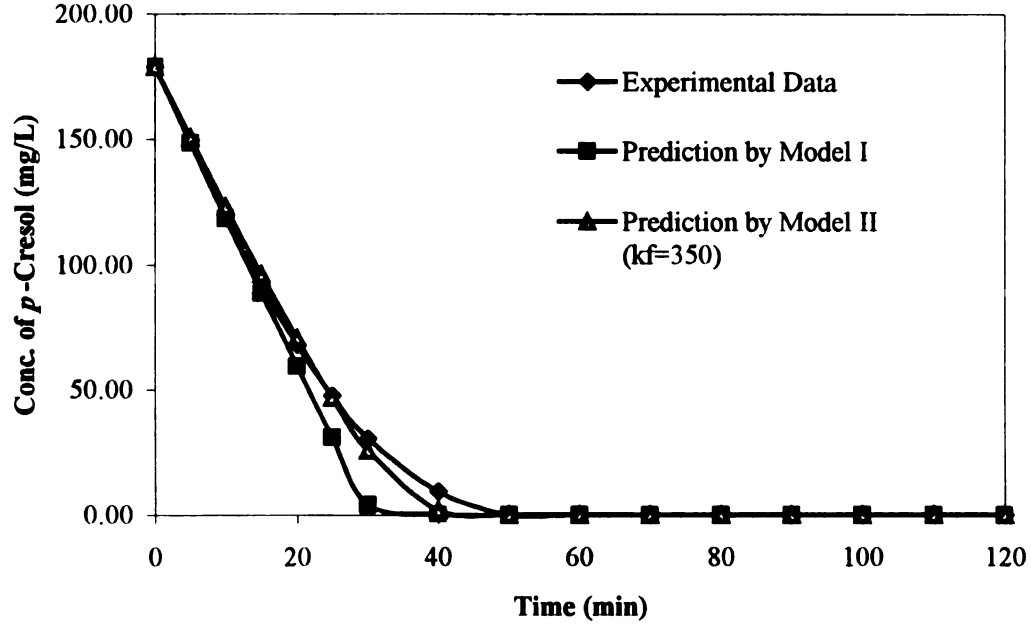

Figure 5.49 Comparison of *p*-Cresol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

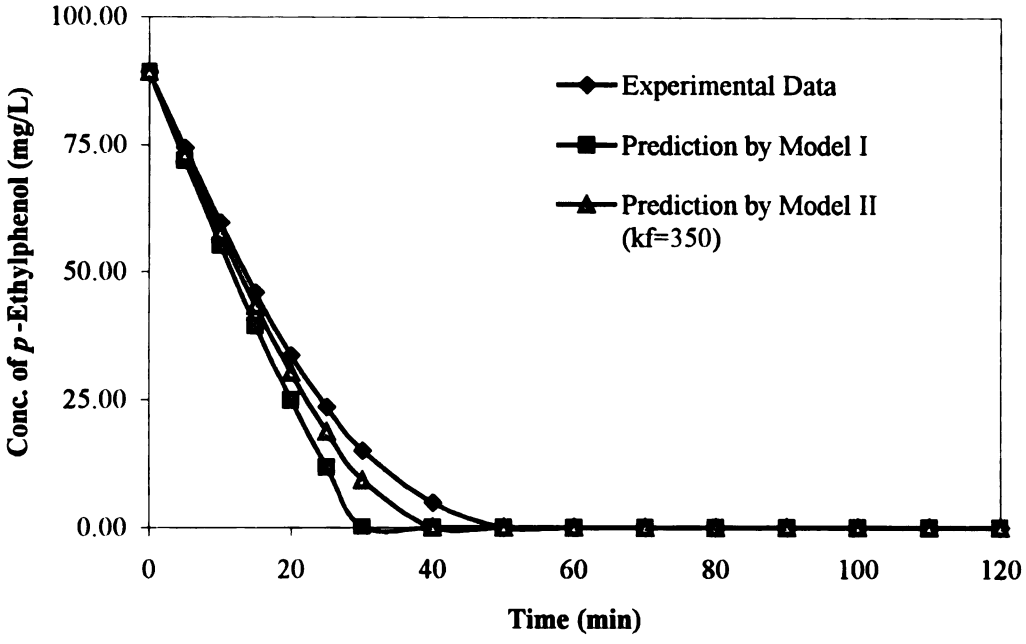

Figure 5.50 Comparison of *p*-Ethylphenol Concentration in the Mixture of Phenolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

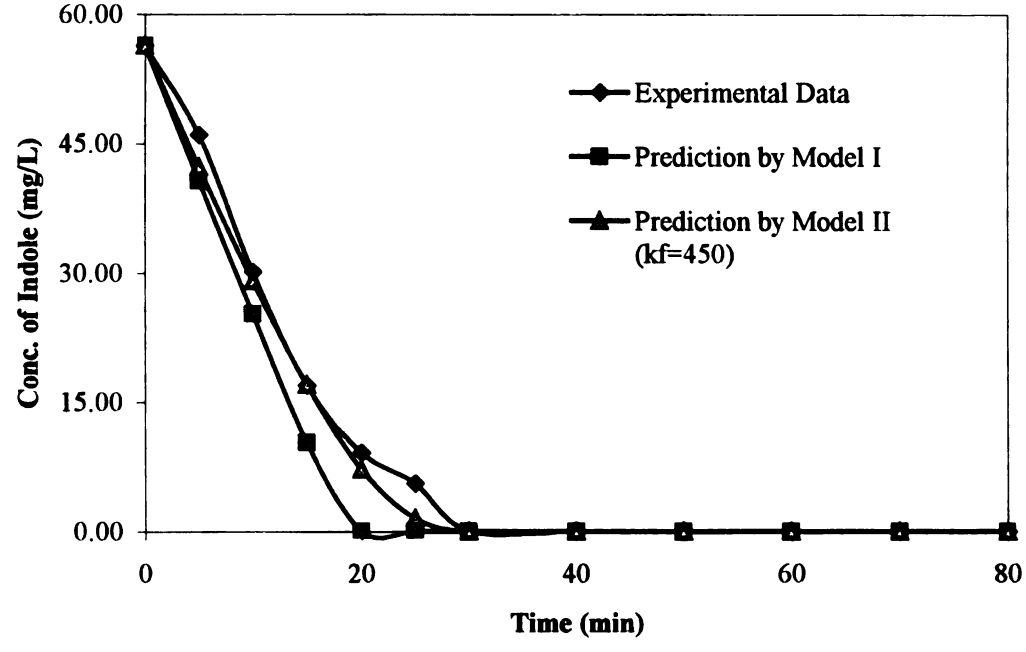

Figure 5.51 Comparison of Indole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

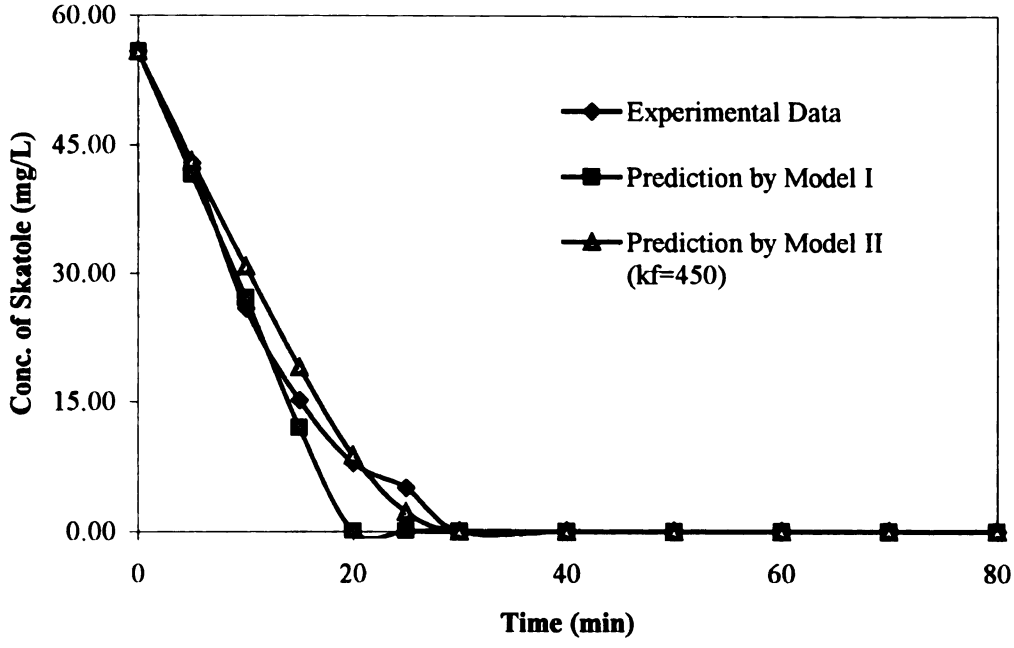

Figure 5.52 Comparison of Skatole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

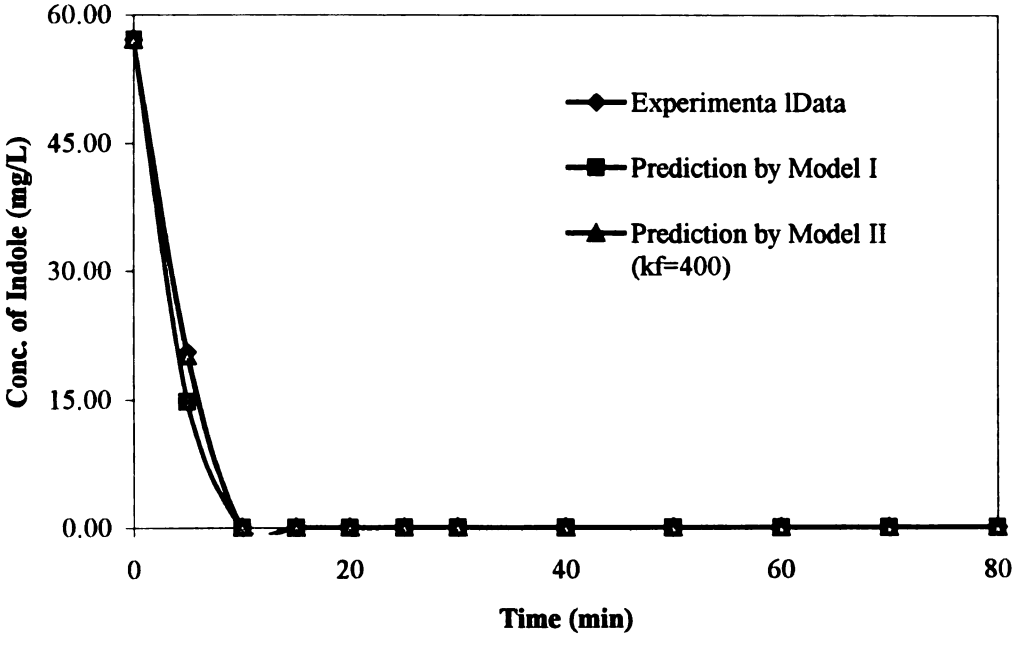

Figure 5.53 Comparison of Indole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

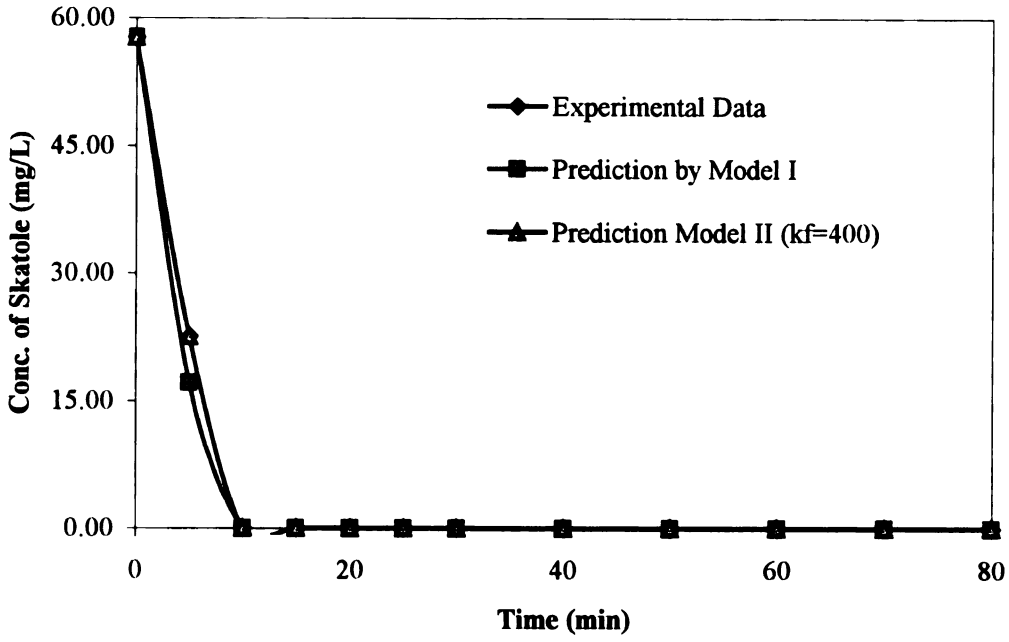

Figure 5.54 Comparison of Skatole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

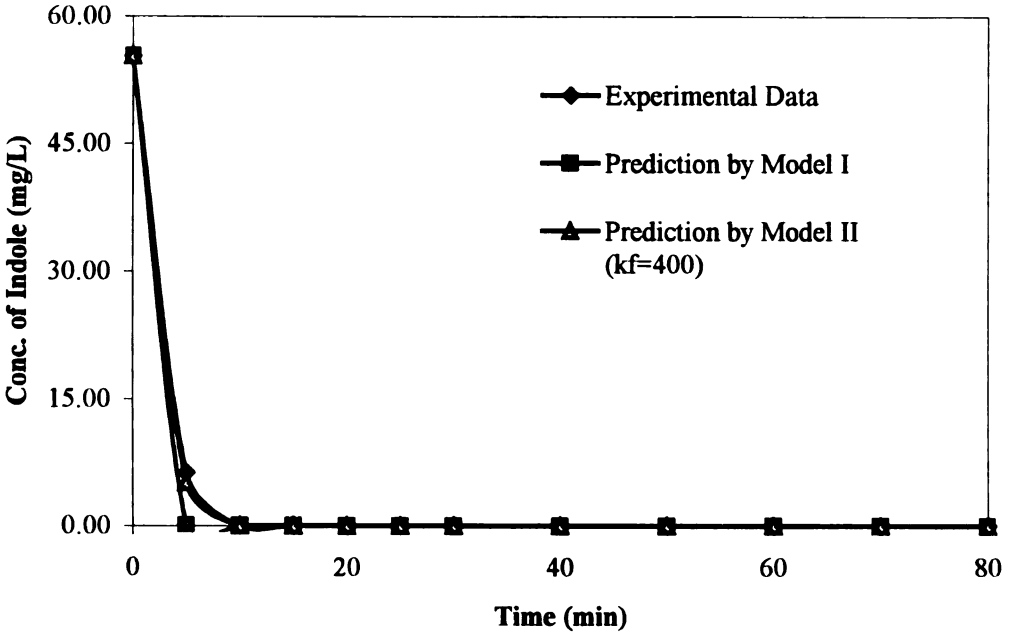

Figure 5.55 Comparison of Indole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

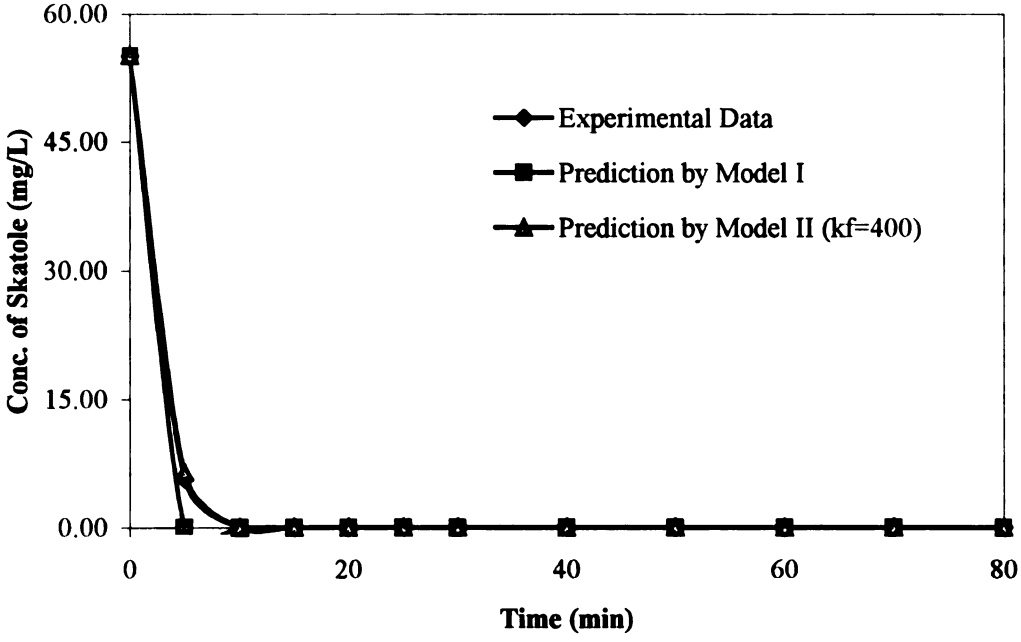

Figure 5.56 Comparison of Skatole Concentration in the Mixture of Indolic Compounds between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

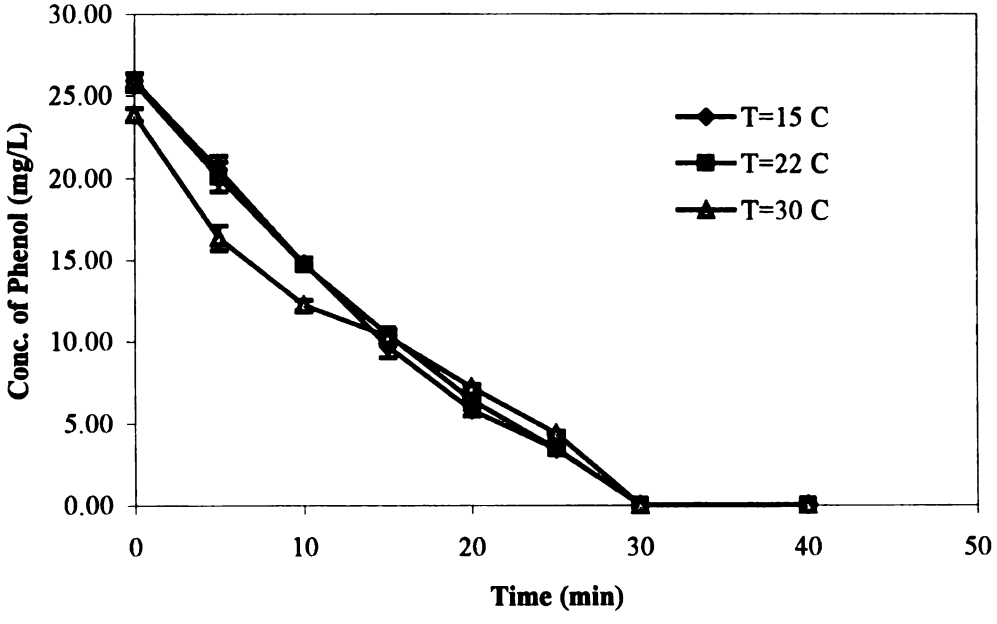

Figure 5.57 Effect of Temperature on the Oxidation of Phenol in Synthetic Manure by Ozone at pH 6.7 and Flowrate 300 mL/min

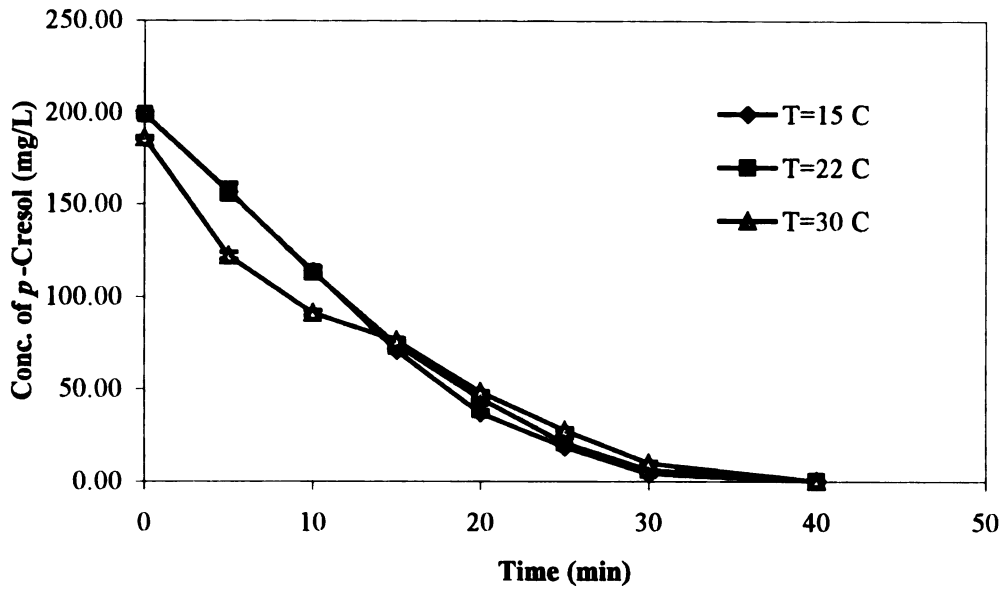

Figure 5.58 Effect of Temperature on the Oxidation of *p*-Cresol in Synthetic Manure by Ozone at pH 6.7 and Flowrate 300 mL/min

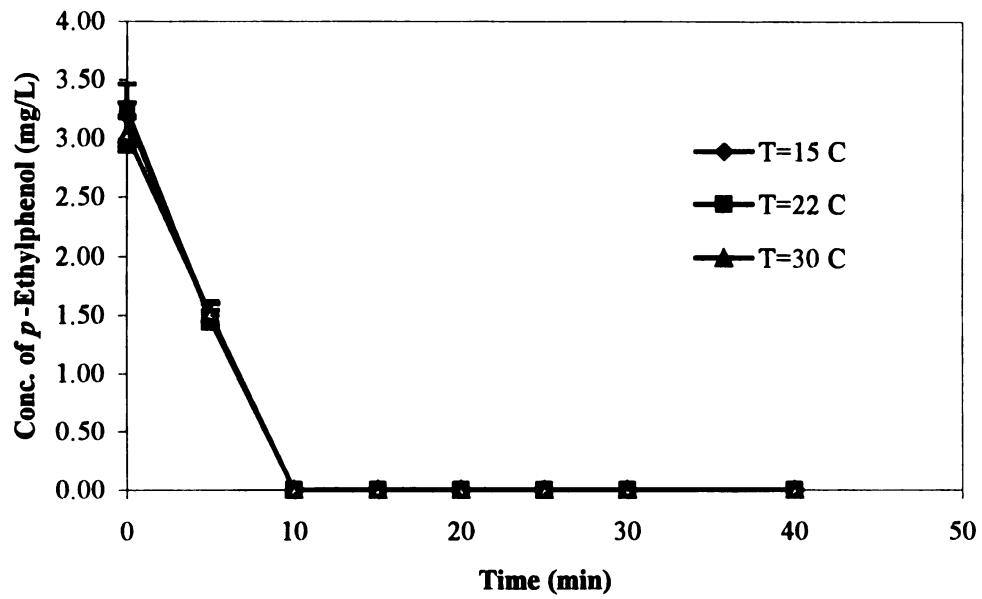

Figure 5.59 Effect of Temperature on the Oxidation of *p*-Ethylphenol in Synthetic Manure by Ozone at pH 6.7 and Flowrate 300 mL/min

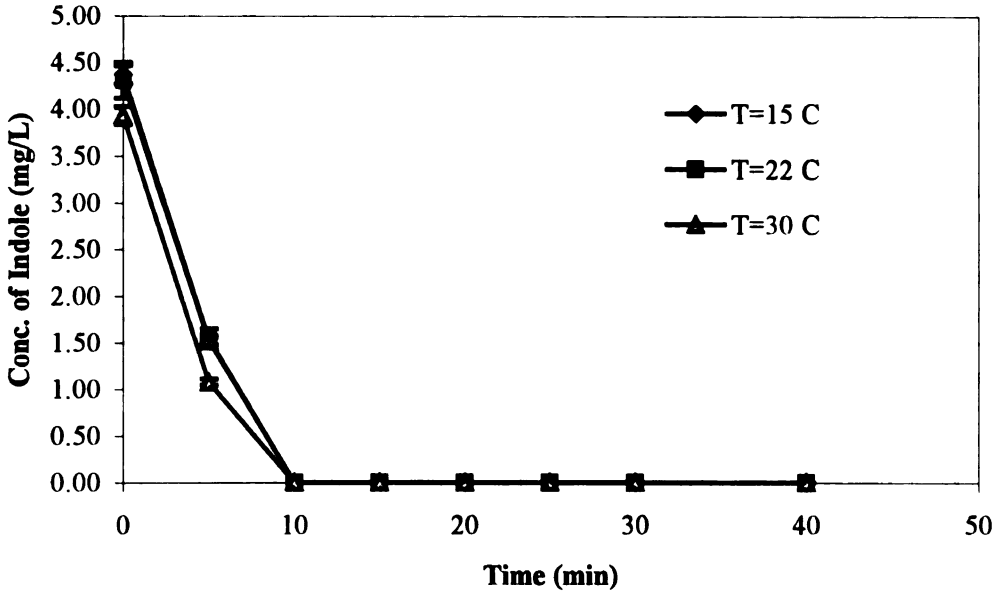

Figure 5.60 Effect of Temperature on the Oxidation of Indole in Synthetic Manure by Ozone at pH 6.7 and Flowrate 300 mL/min

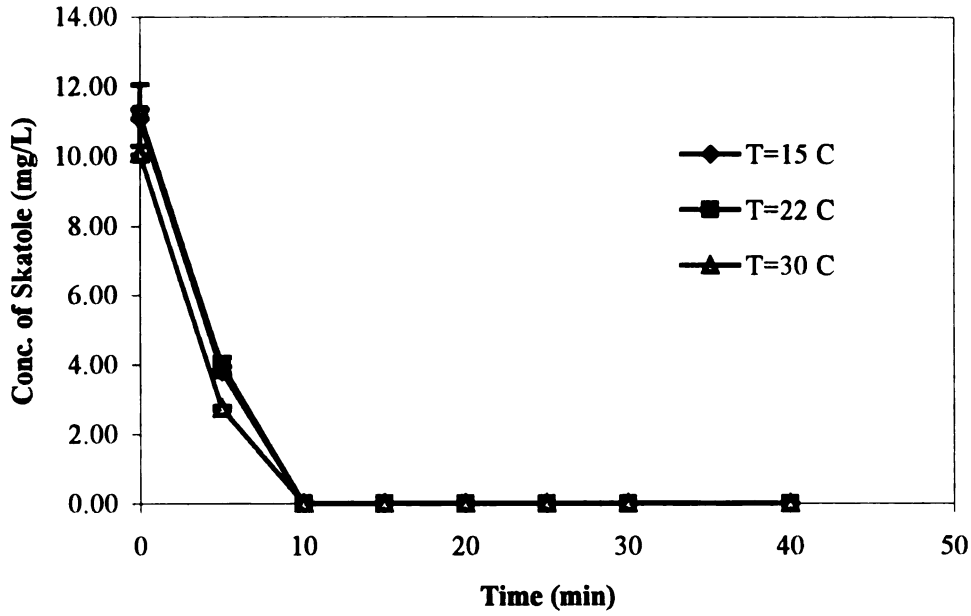

Figure 5.61 Effect of Temperature on the Oxidation of Skatole in Synthetic Manure by Ozone at pH 6.7 and Flowrate 300 mL/min

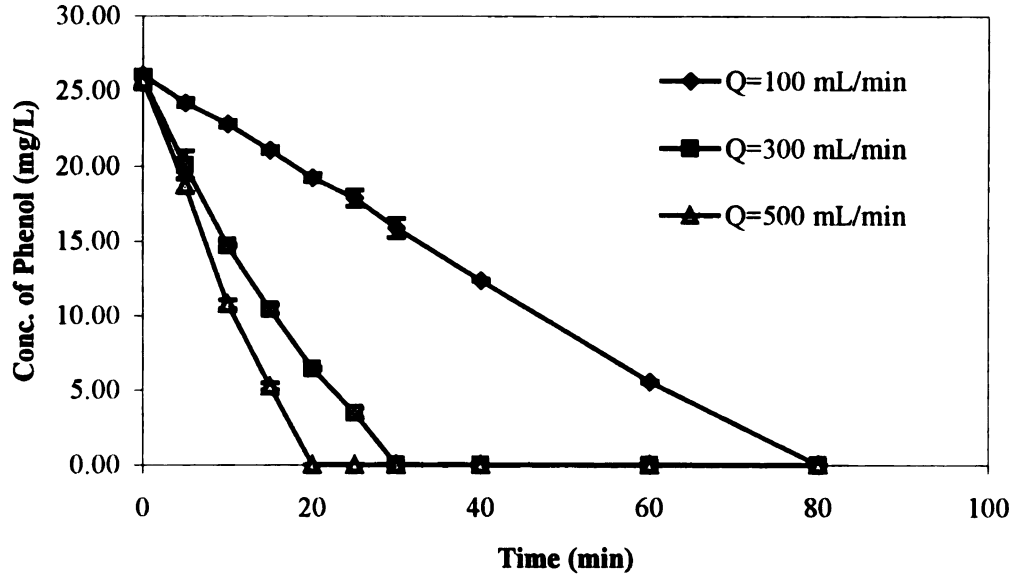

Figure 5.62 Effect of Flowrate on the Oxidation of Phenol in Synthetic Manure at pH 6.7 and Temperature 22 C

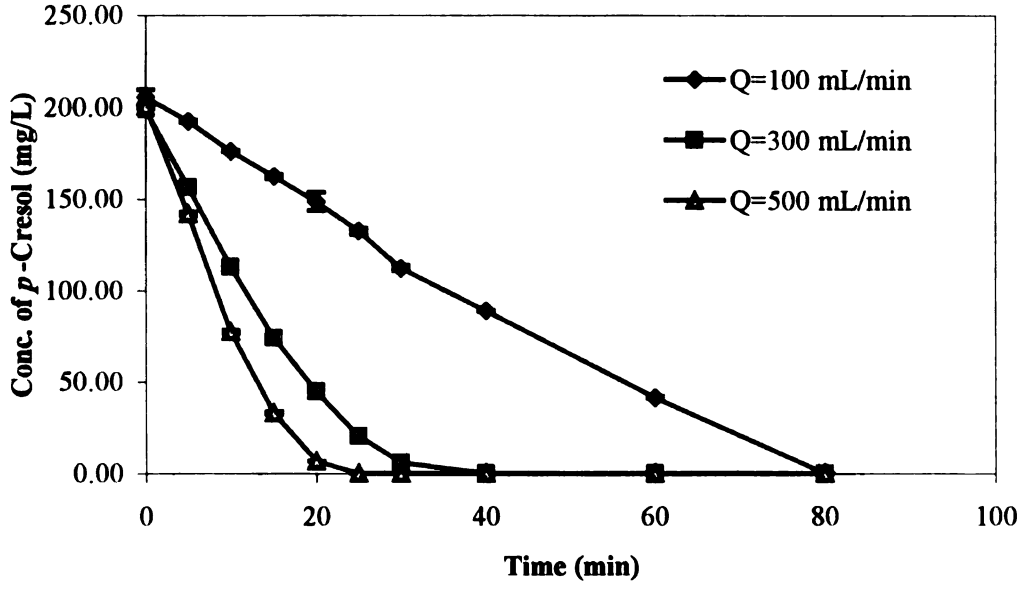

Figure 5.63 Effect of Flowrate on the Oxidation of *p*-Cresol in Synthetic Manure at pH 6.7 and Temperature 22 C

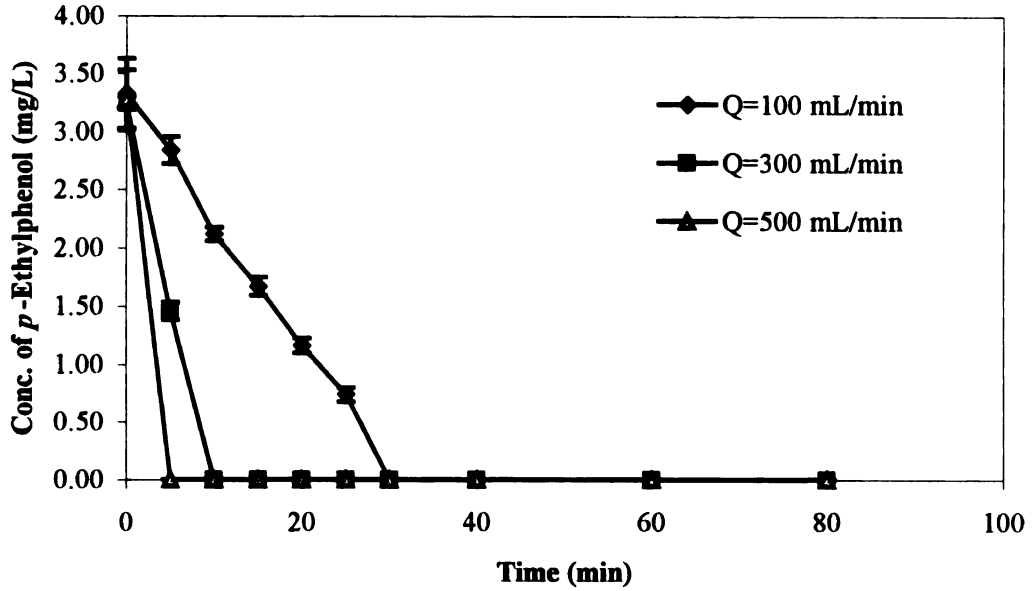

Figure 5.64 Effect of Flowrate on the Oxidation of *p*-Ethylphenol in Synthetic Manure at pH 6.7 and Temperature 22 C

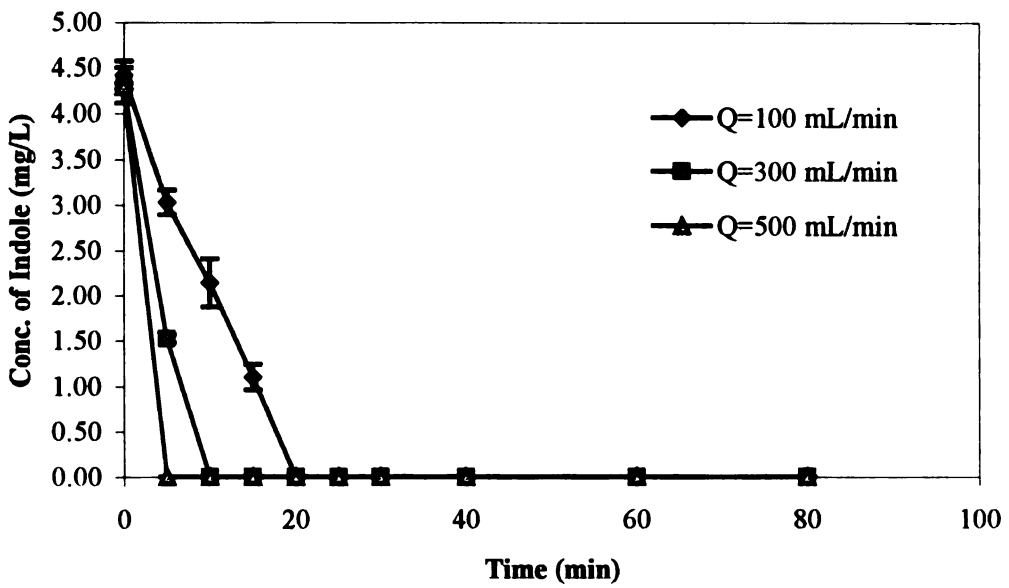

Figure 5.65 Effect of Flowrate on the Oxidation of Indole in Synthetic Manure at pH 6.7 and Temperature 22 C

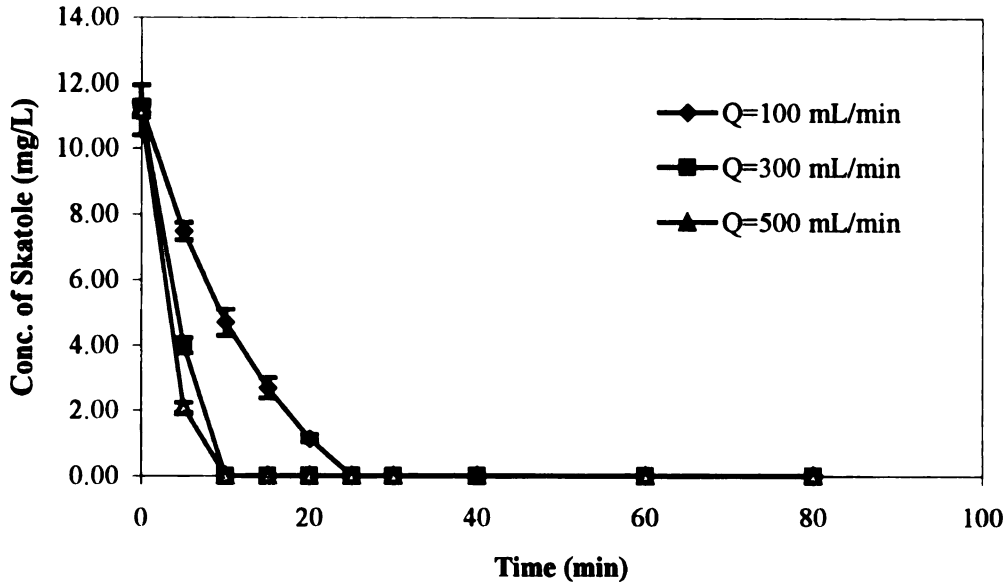

Figure 5.66 Effect of Flowrate on the Oxidation of Skatole in Synthetic Manure at pH 6.7 and Temperature 22 C

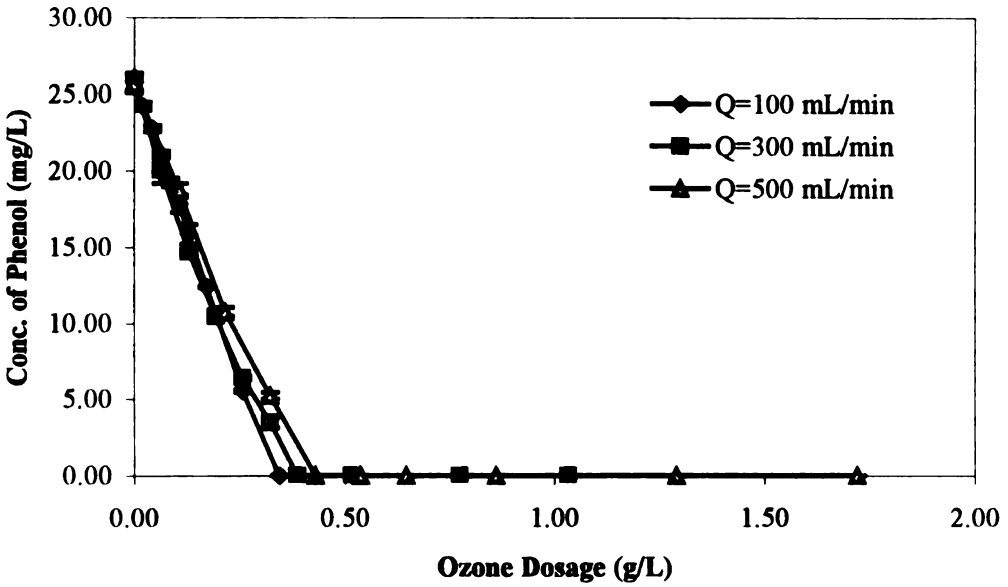

Figure 5.67 Effect of Ozone Dosage on the Oxidation of Phenol in Synthetic Manure by Different Flowrates at pH 6.7 and Temperature 22 C

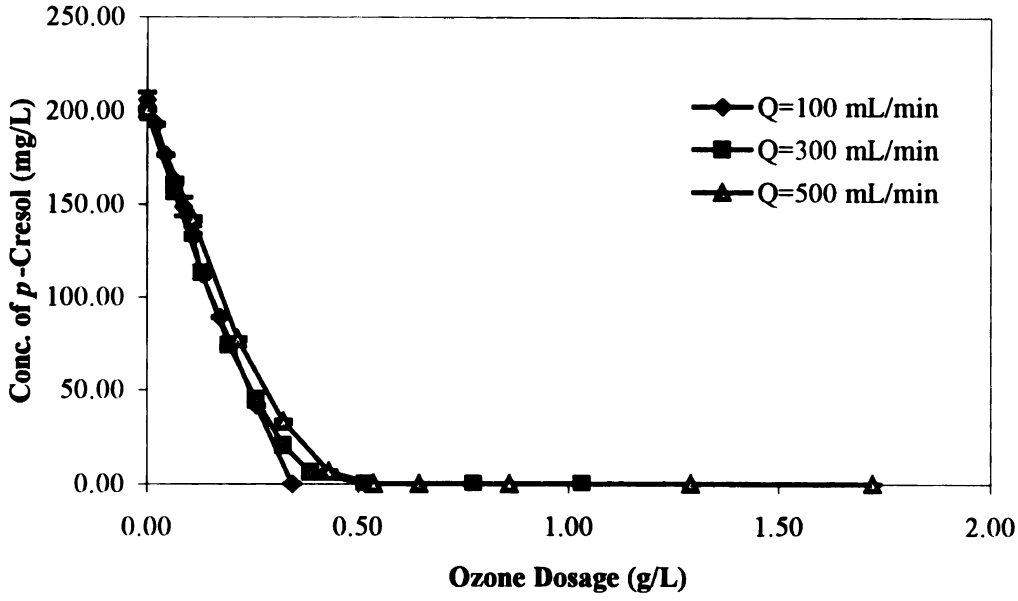

Figure 5.68 Effect of Ozone Dosage on the Oxidation of *p*-Cresol in Synthetic Manure by Different Flowrates at pH 6.7 and Temperature 22 C

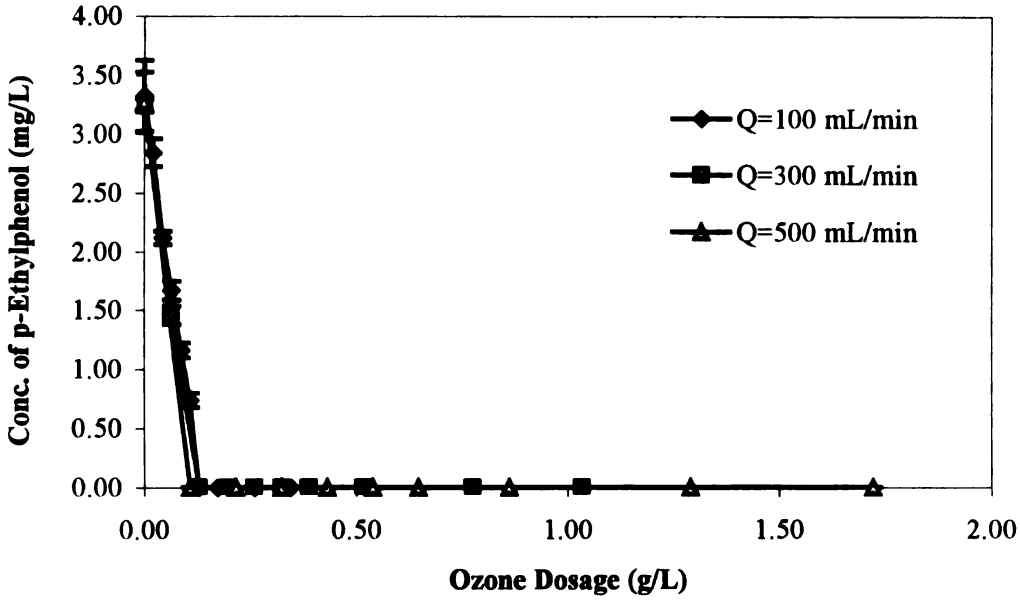

Figure 5.69 Effect of Ozone Dosage on the Oxidation of *p*-Ethylphenol in Synthetic Manure by Different Flowrates at pH 6.7 and Temperature 22 C

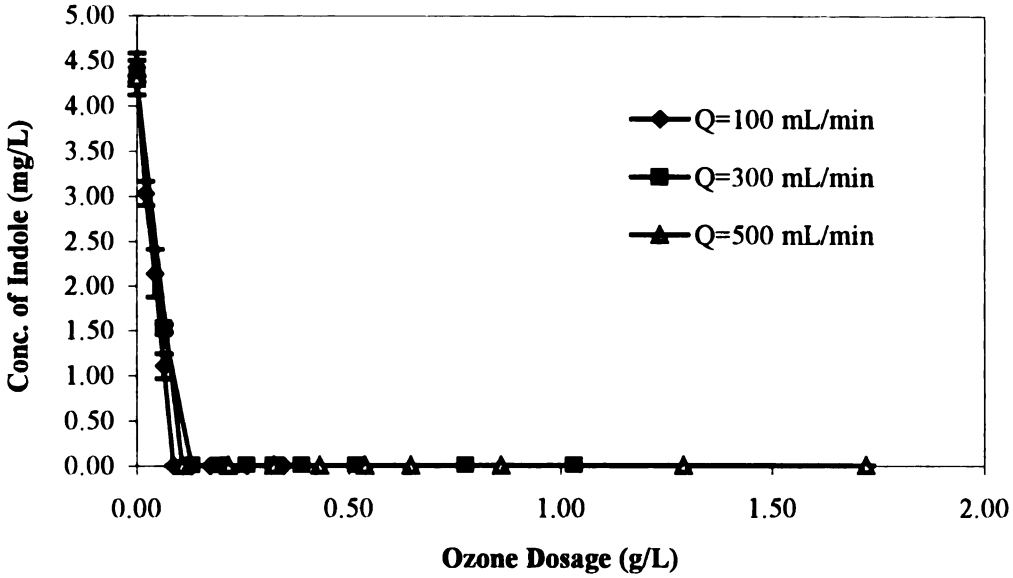

Figure 5.70 Effect of Ozone Dosage on the Oxidation of Indole in Synthetic Manure by Different Flowrates at pH 6.7 and Temperature 22 C

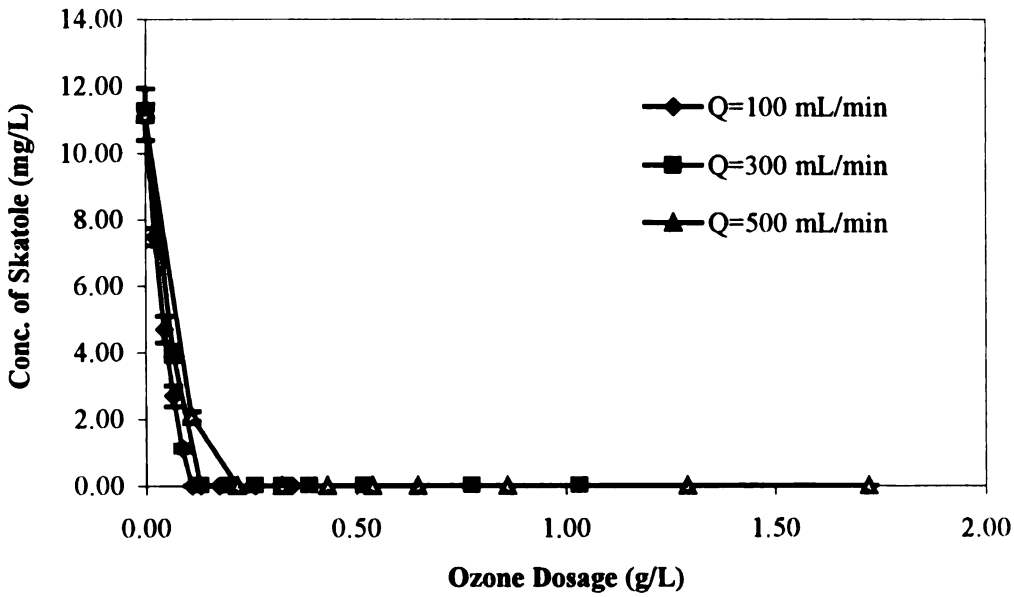

Figure 5.71 Effect of Ozone Dosage on the Oxidation of Skatole in Synthetic Manure by Different Flowrates at pH 6.7 and Temperature 22 C

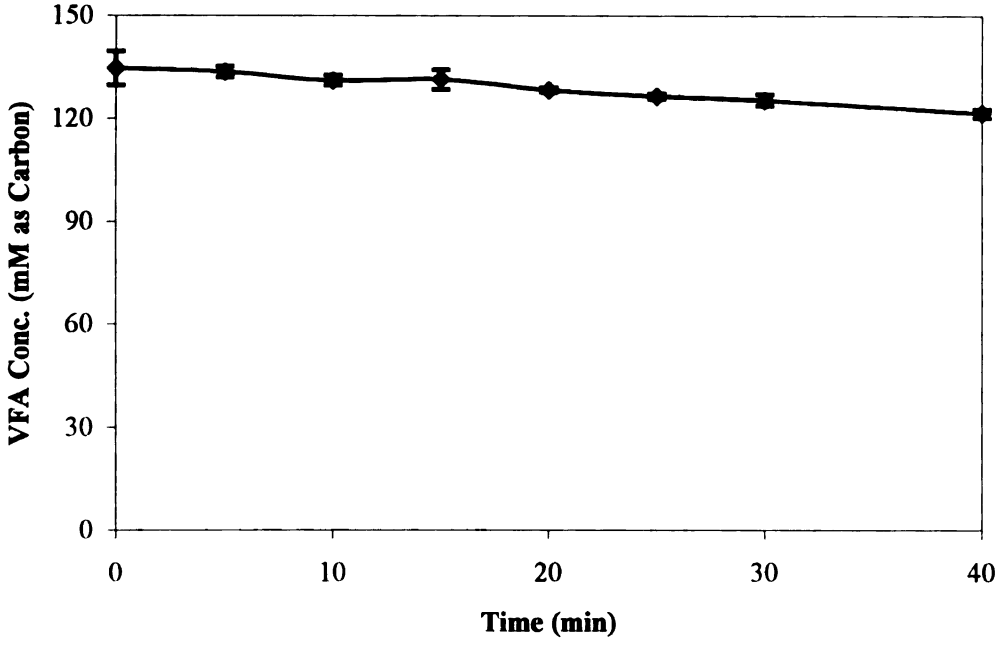

Figure 5.72 Change of VFAs Concentration in Synthetic Manure by Ozonation at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

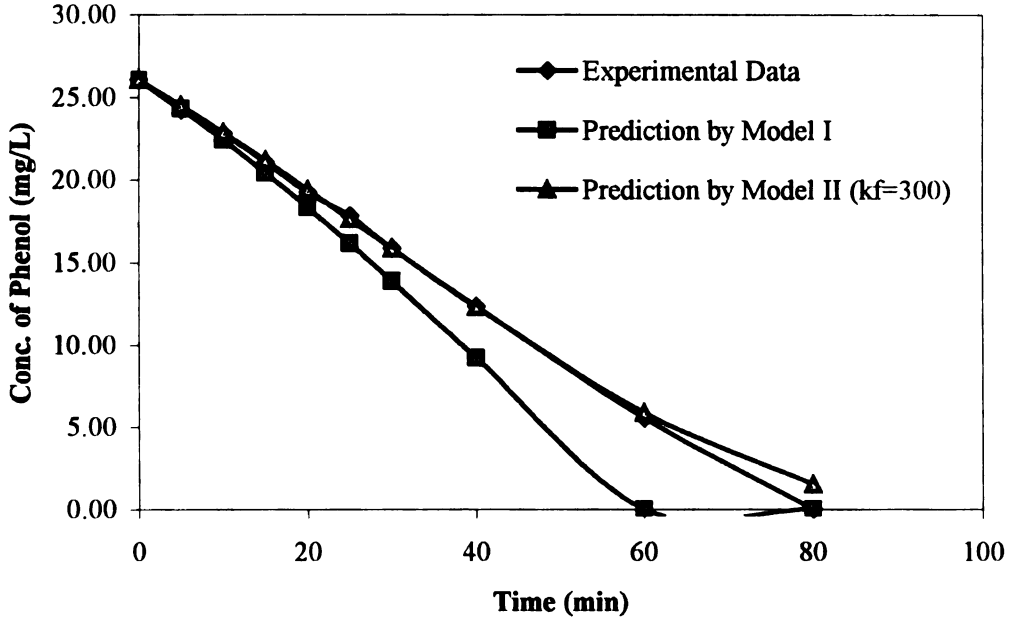

Figure 5.73 Comparison of Phenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

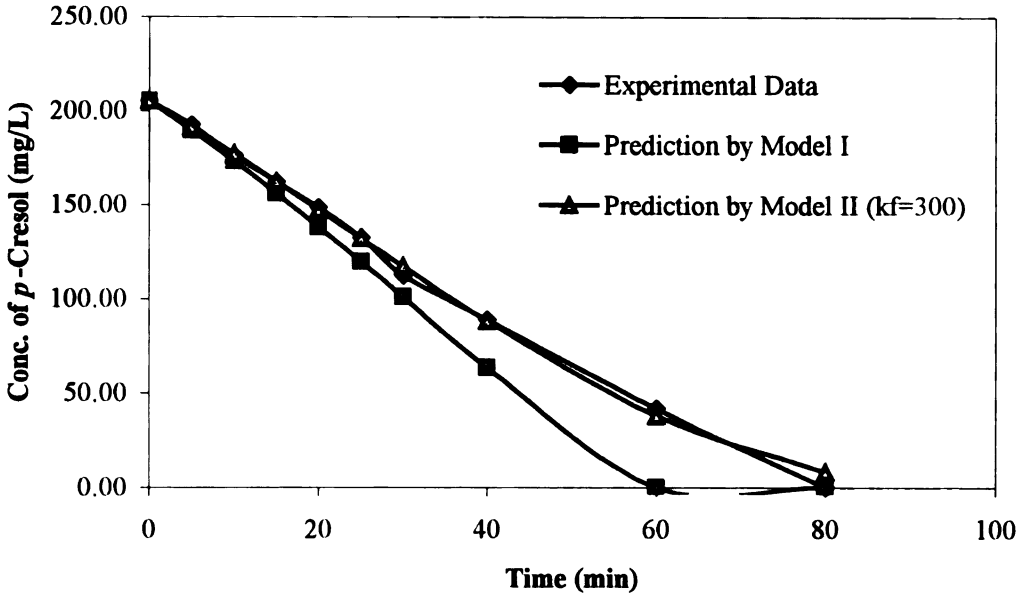

Figure 5.74 Comparison of *p*-Cresol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

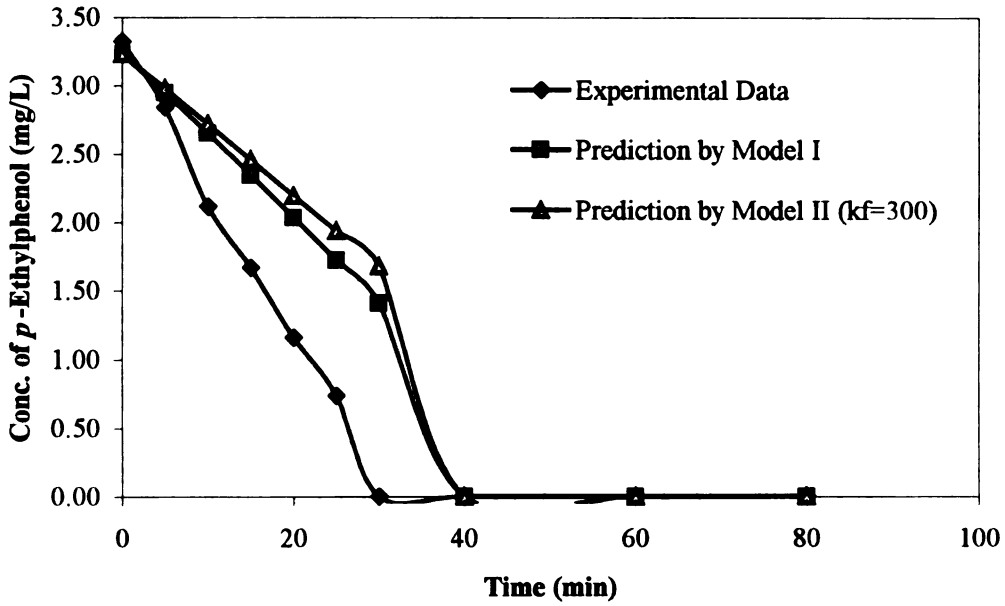

Figure 5.75 Comparison of *p*-Ethylphenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

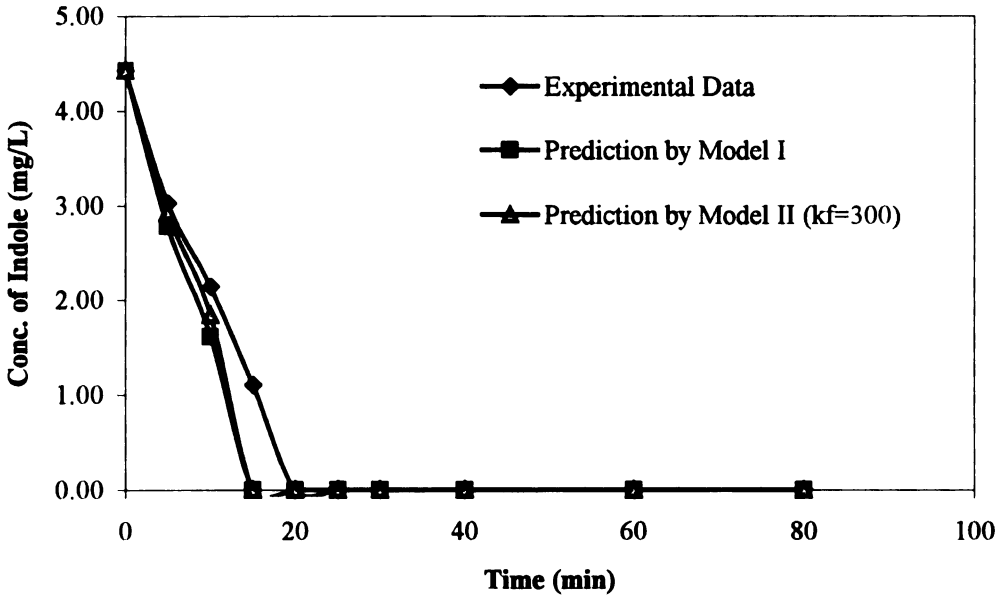

Figure 5.76 Comparison of Indole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

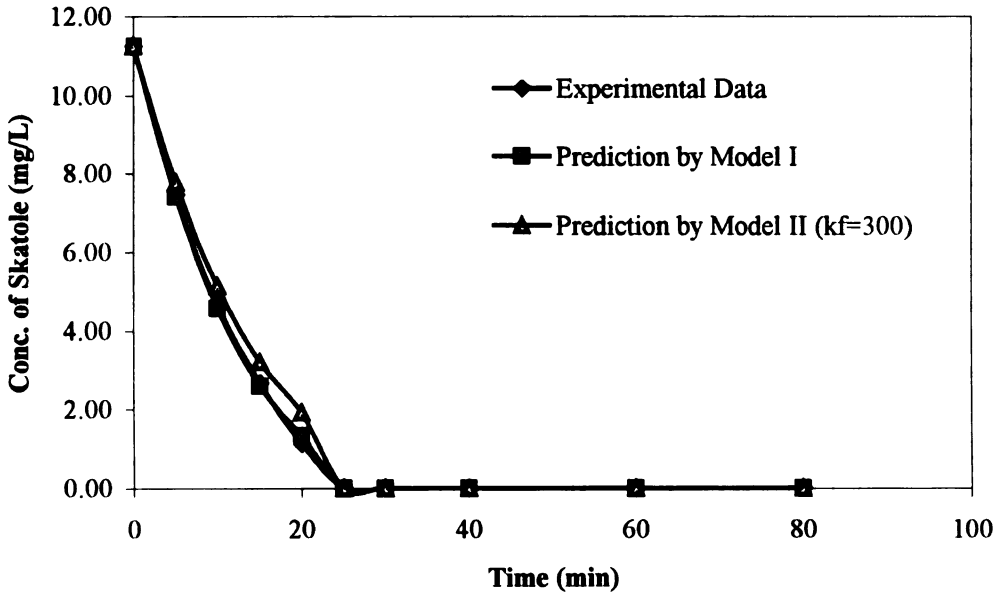

Figure 5.77 Comparison of Skatole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 100 mL/min, and Temperature 22 C

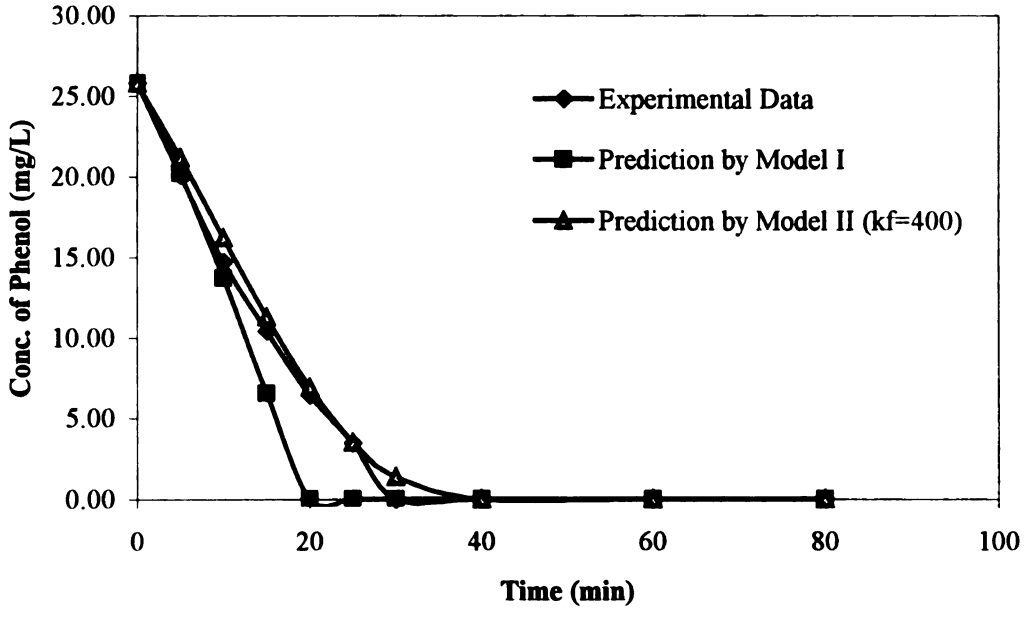

Figure 5.78 Comparison of Phenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

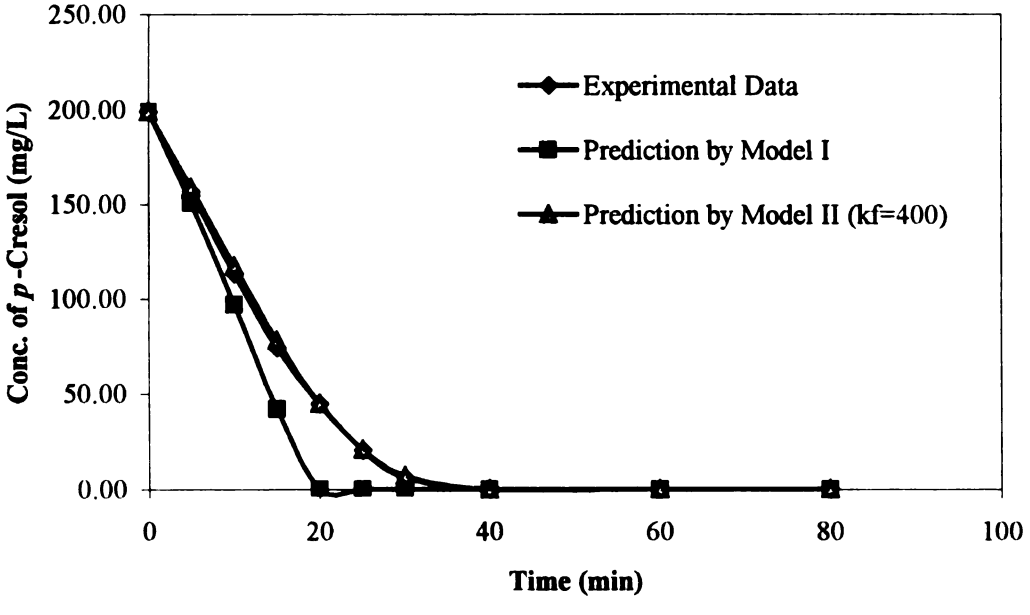

Figure 5.79 Comparison of *p*-Cresol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

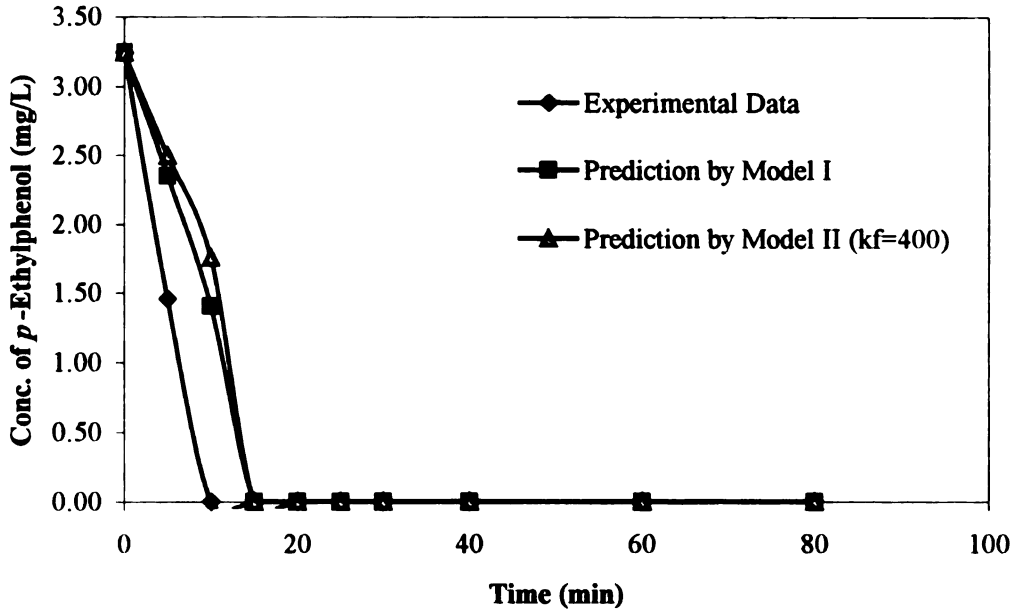

Figure 5.80 Comparison of *p*-Ethylphenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

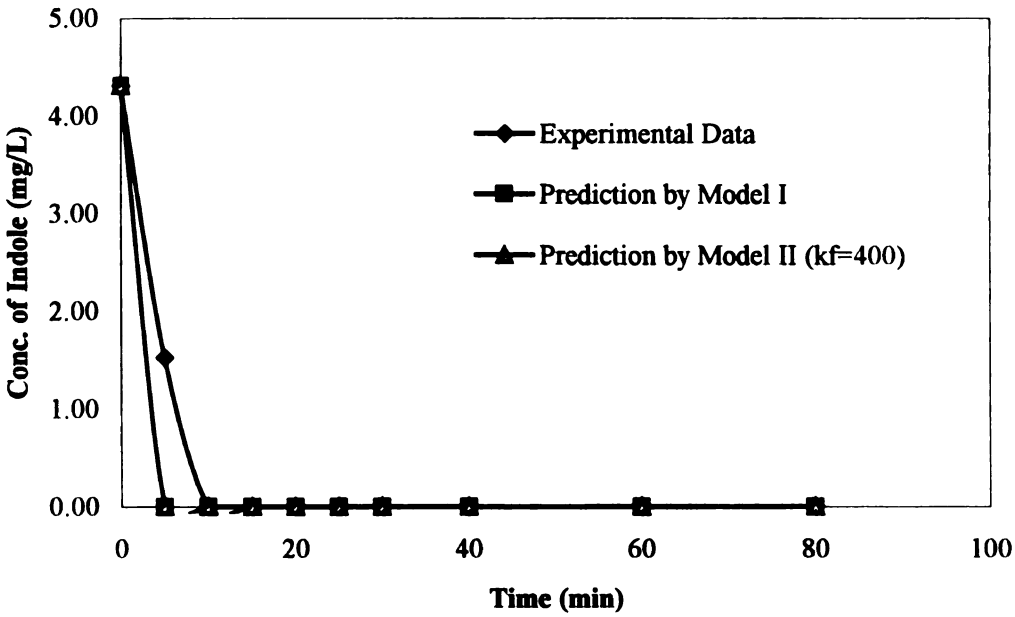

Figure 5.81 Comparison of Indole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

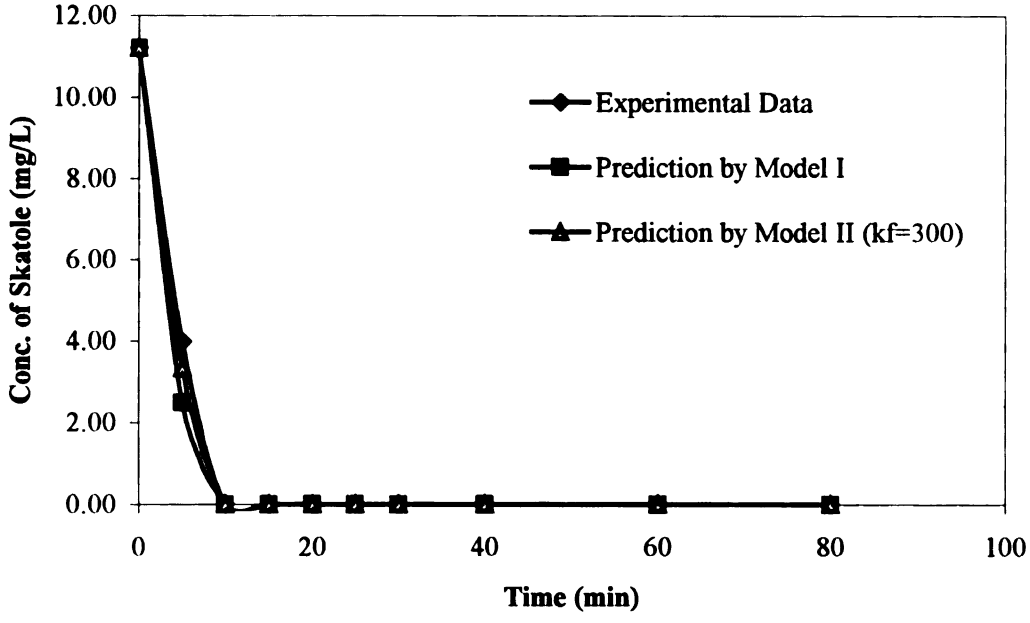

Figure 5.82 Comparison of Skatole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

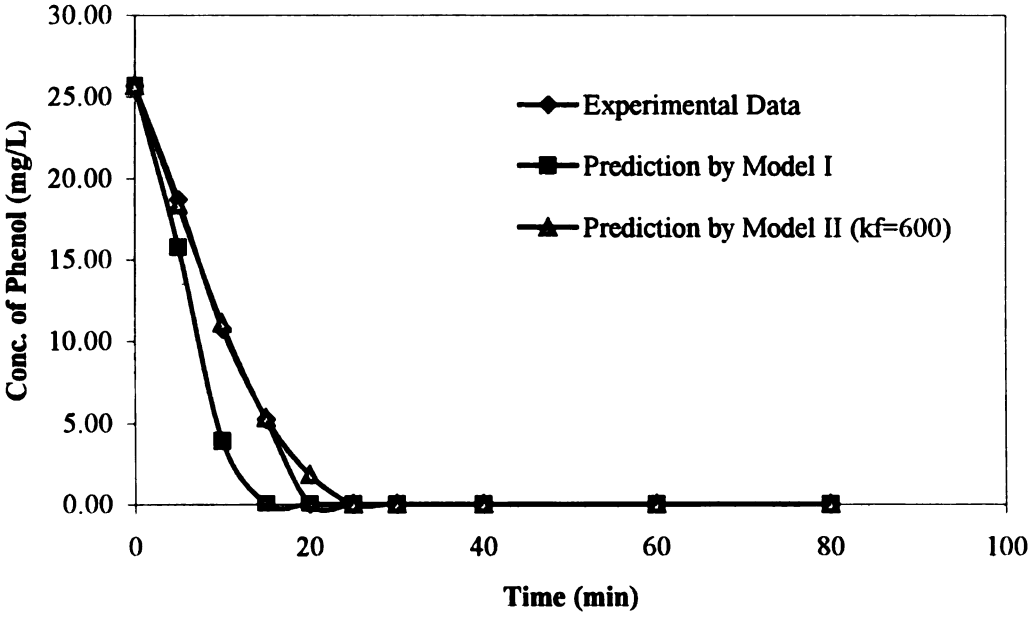

Figure 5.83 Comparison of Phenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

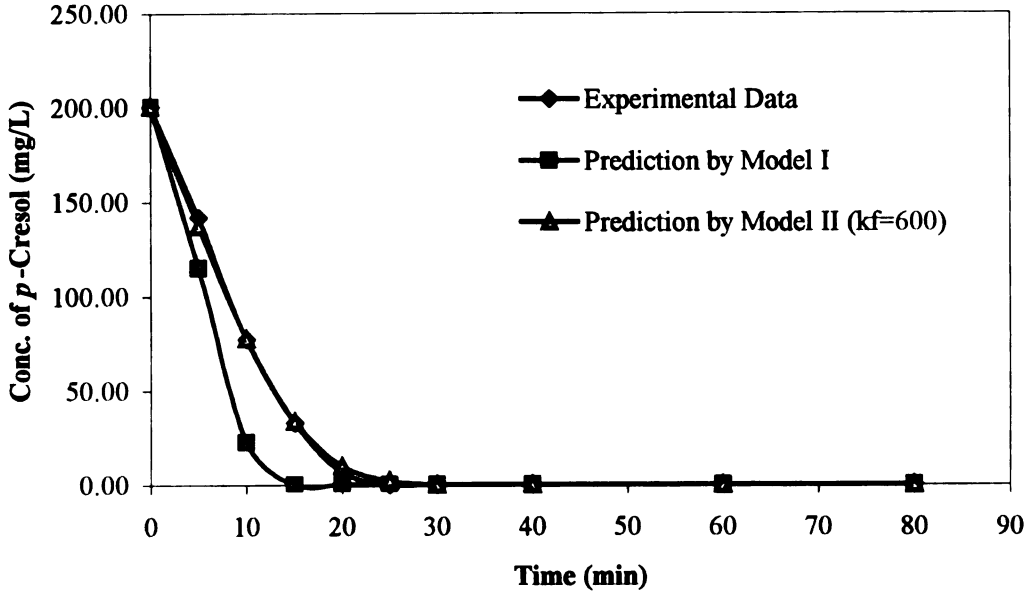

Figure 5.84 Comparison of *p*-Cresol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

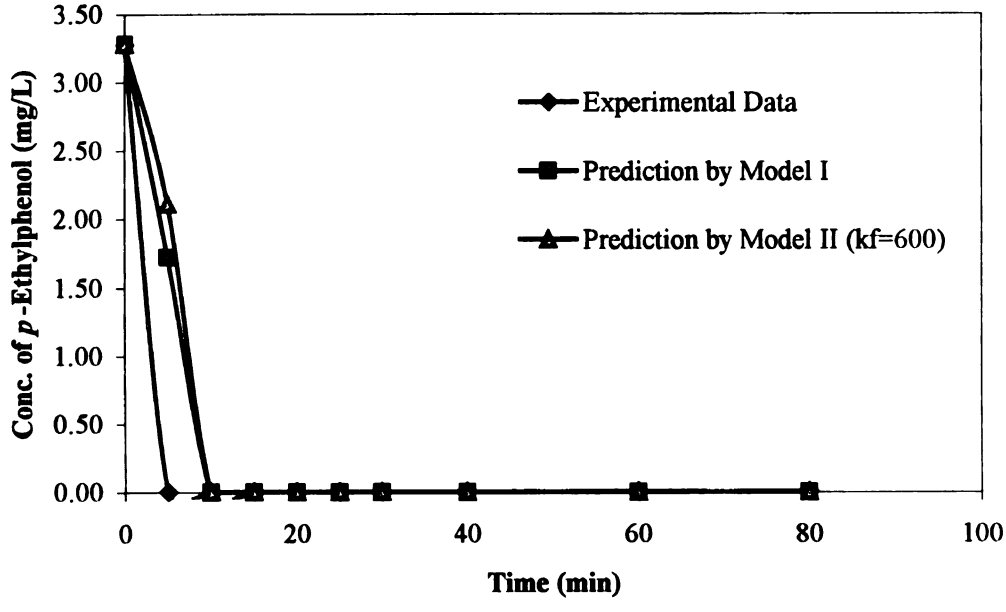

Figure 5.85 Comparison of *p*-Ethylphenol Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

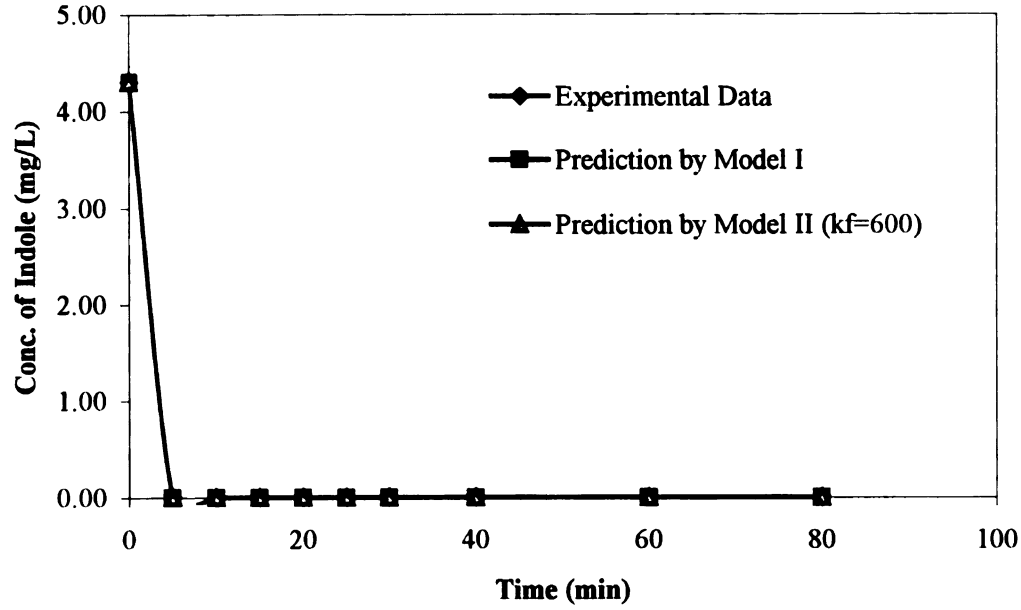

Figure 5.86 Comparison of Indole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

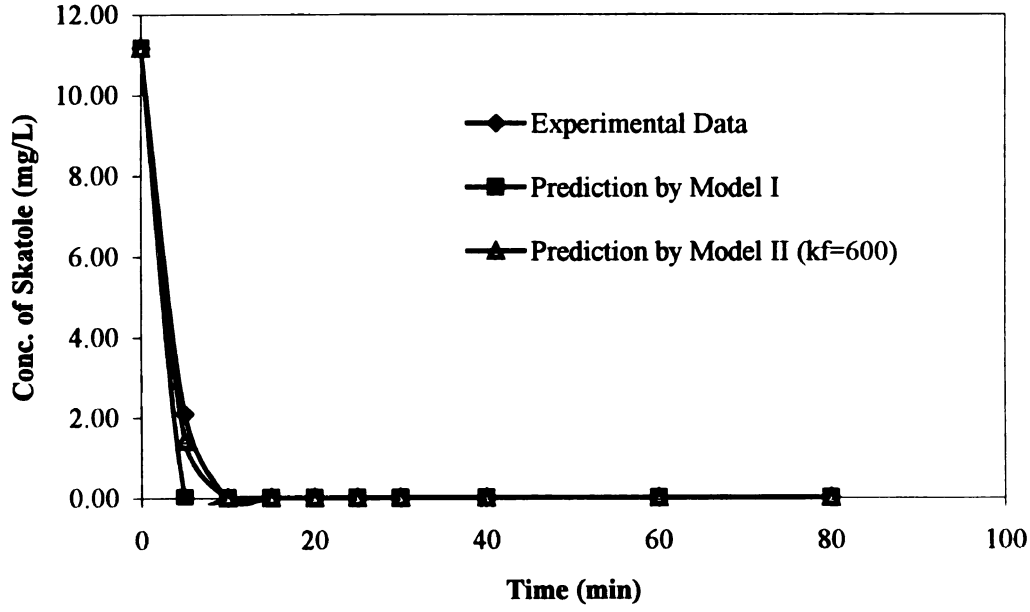

Figure 5.87 Comparison of Skatole Concentration in the Synthetic Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 500 mL/min, and Temperature 22 C

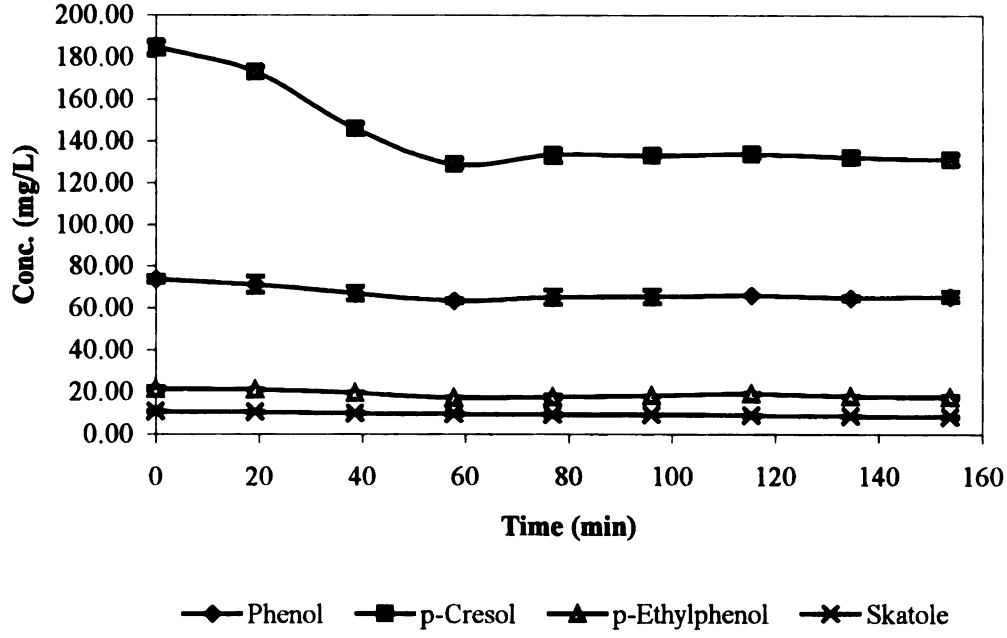

Figure 5.88 Effect of Oxygenation on the Concentration of Phenolic and Indolic Compounds in Real Swine Manure at Flowrate 300 mL/min and Temperature 22 C

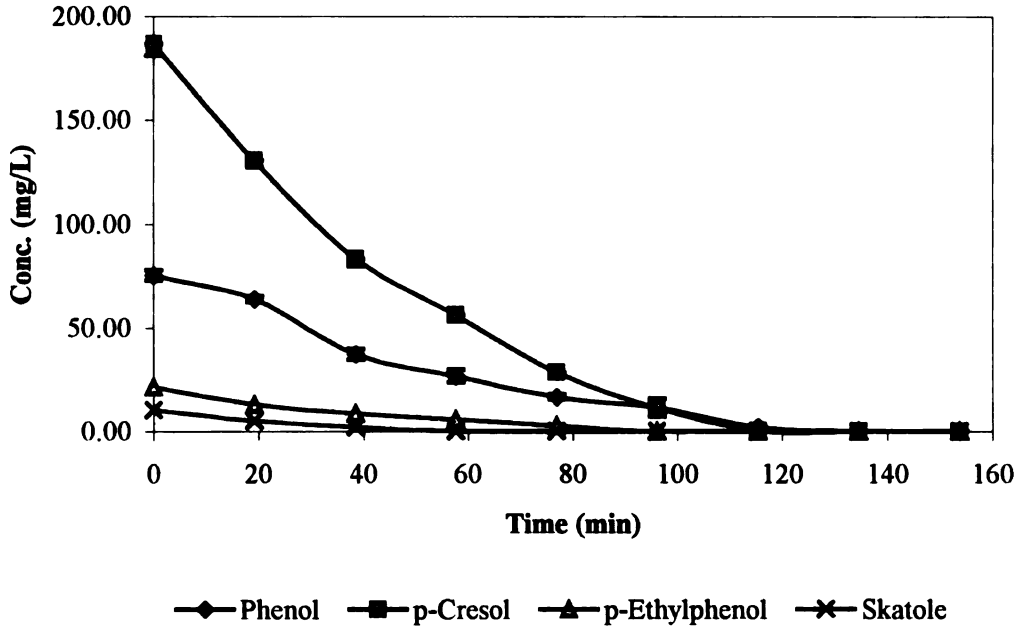

Figure 5.89 Effect of Ozonation on the Concentration of Phenolic and Indolic Compounds in Real Swine Manure at Flowrate 300 mL/min and Temperature 22 C

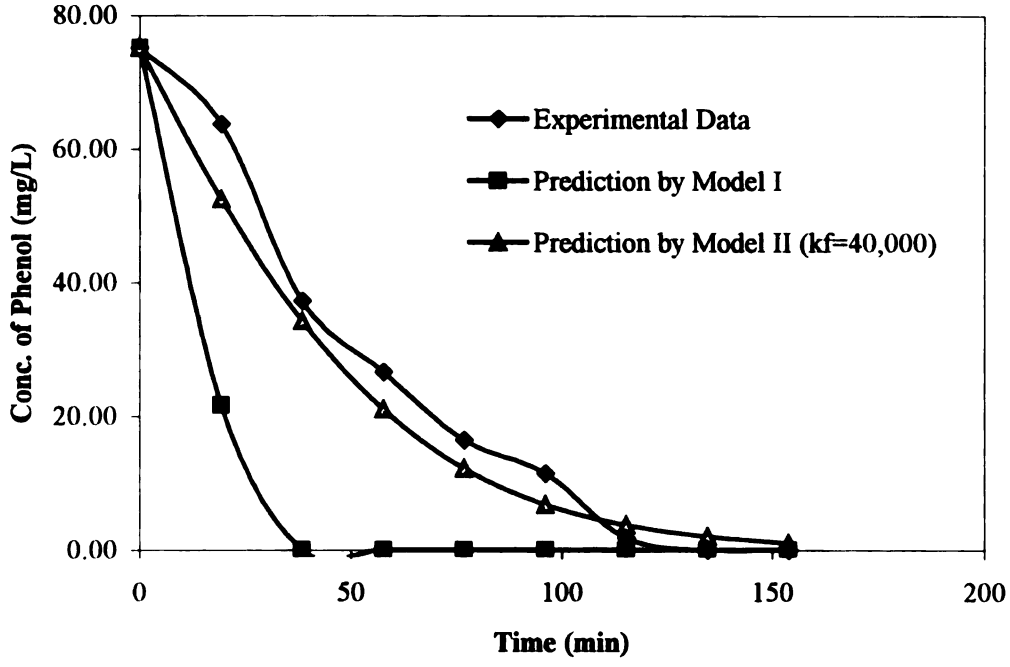

Figure 5.90 Comparison of Phenol Concentration in the Real Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

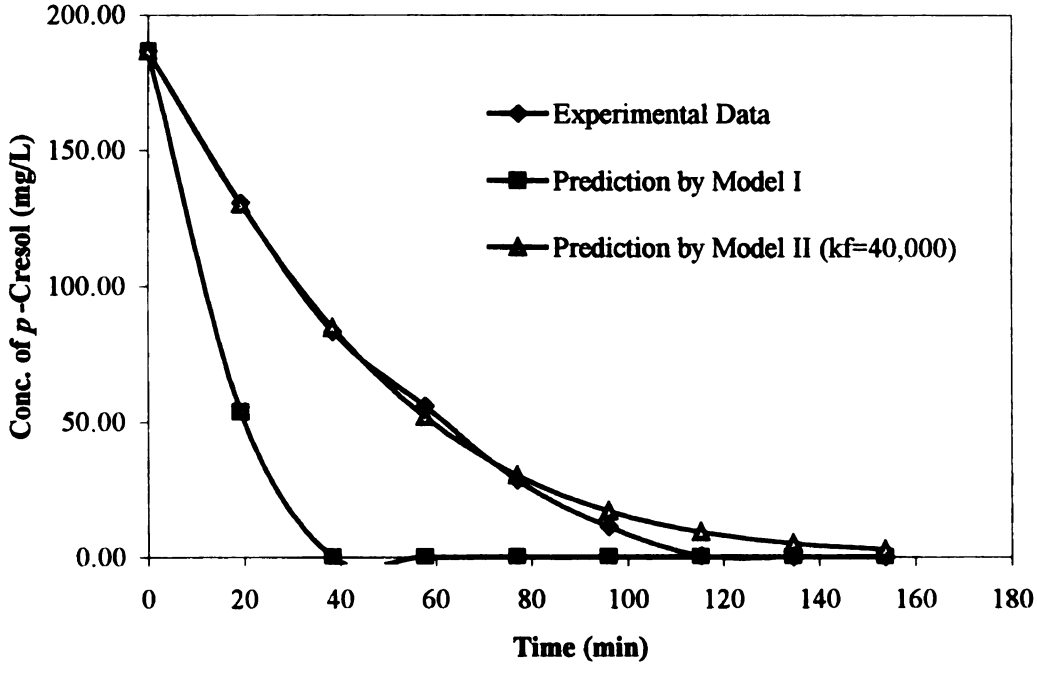

Figure 5.91 Comparison of *p*-Cresol Concentration in the Real Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

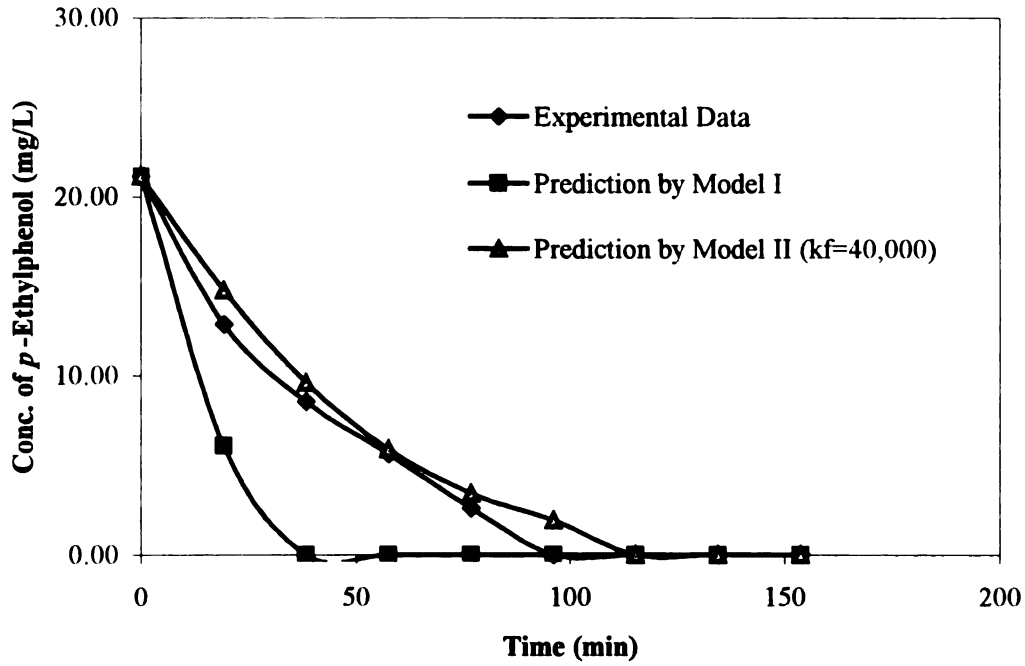

Figure 5.92 Comparison of *p*-Ethylphenol Concentration in the Real Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

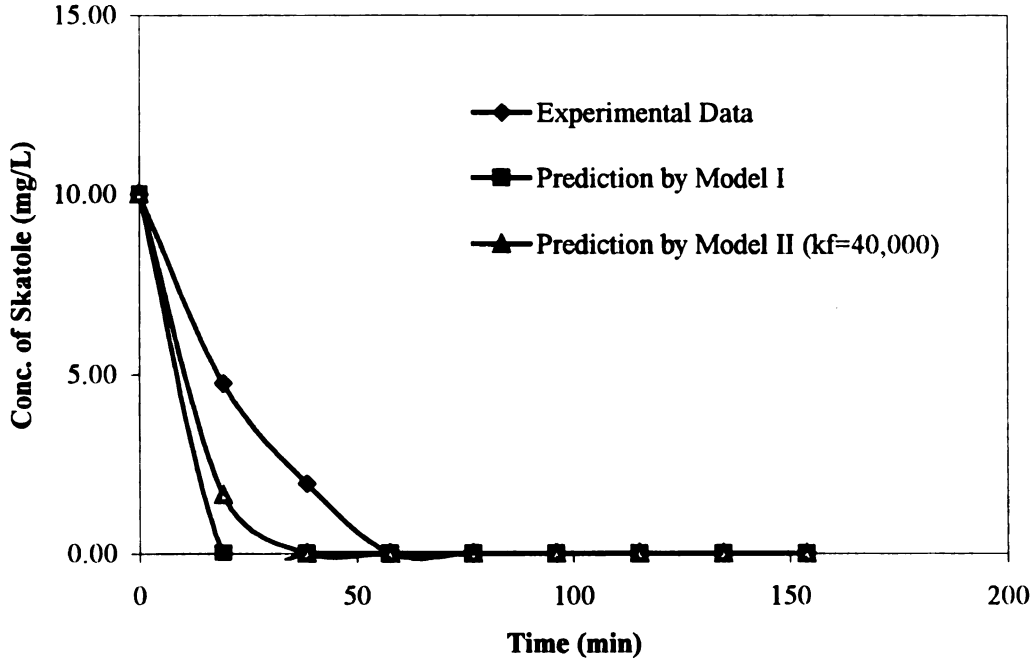

Figure 5.93 Comparison of Skatole Concentration in the Real Manure between Experimental Data and Model Prediction at pH 6.7, Flowrate 300 mL/min, and Temperature 22 C

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The comprehensive objective of this research work was to investigate and understand the formation of malodorous compounds in the swine manure during storage and to explain the process by which ozone controls the malodors of swine manure. The major purposes of this study were to find the minimum ozone dosage that was effective at reducing the concentrations of malodorous metabolites in the swine manure, to determine the major physical and chemical parameters that affected effectiveness of the ozonation process, to establish design guidelines for operation of the pilot-scale system, and to develop the oxidation model that could be used to predict the concentrations of phenolic and indolic compounds from the synthetic and real swine manure.

The malodorous compounds in swine manure are mainly formed by anaerobic decomposition of their precursors, such as proteins and fibers. Malodorants, including phenolic and indolic compounds, sulfides, ammonia, and volatile fatty acids, were accumulated during a storage period of 3 months. Ozone was found to reduce the odor intensity to an acceptable level using the dosage of 1g/L in the lab-scale reactor. Concurrent with the decrease in the odor intensity during ozonation process, is the decrease in the concentrations of phenolic and indolic metabolites and sulfides. The

concentrations of other odorous compounds, however, such as ammonia and volatile fatty acids, remain unchanged. These results suggest that ammonia and VFAs play a minor role in contributing to the odors released from the swine manure.

E. Coli and total coliform were destroyed by ozonation. The aerobic and anaerobic bacteria were also reduced by about 1-2 orders of magnitude at an ozone dosage of 1 g/L. These results indicate that ozone has the potential to kill or inhibit pathogenic microorganisms. Most importantly, the malodors will not reoccur after subsequent storage of ozonated swine manure. This also implies that the land spreading of ozonated swine manure will not result in major odor releases even after several weeks of post-treatment storage. As the nutrient content is unchanged by ozonation, the manure still maintains its nutrient value.

When the ozonation process was enlarged to pilot-scale, the effective ozone dosage of 0.5 g/L was sufficient to bring the odor of the swine manure to an acceptable level. This lower value was made possible by the new reactor design which enhanced ozone mass-transfer in the liquid manure by using a venturi injector and an agitation system. Temperature variations (12-25 °C) did not affect the efficiency of the ozonation process. This implies that the effect of seasonal change will be insignificant. The addition of hydrogen peroxide to ozone did not provide additional oxidation of the malodorous substances. This is because the manure probably contained radical scavengers that consumed the free radicals generated by the reaction of ozone and hydrogen peroxide. Therefore, the advanced oxidation processes may not apply to the treatment of swine manure in reducing the malodors.

An economic analysis was conducted for the pilot-scale system. It appears that $3.80 will be deducted from the profit of selling a 220 lb pig into the market. Therefore, any attempt to reduce the cost of treating the manure will be appreciated by the swine producers. The first alternative is to use the PSA (pressure swing adsorption) for oxygen generation to replace the use of liquid oxygen. Approximately one half of the operational costs are for oxygen cylinder rental. Although the capital cost will increase by using PSA system, the operational cost may be decreased since PSA only requires a small amount of electricity. The second alternative is to install the ozone diffuser directly into the lagoon. By this idea, the capital cost will be reduced significantly since no reactor is required. However, we have to evaluate the efficiency of using in-situ ozonation in the lagoon to control the malodors and the effect of ozone on the ecology of bacteria and microorganisms in the lagoon.

In the mass-transfer study, a model that considered the effect of liquid-gas interaction and headspace on the mass-transfer of ozone was developed to evaluate the mass-tansfer and partition coefficients in both lab-scale and pilot-scale reactors. Temperature is found to be the key factor in influencing the partition coefficient, the most sensitive factor in affecting the concentration profiles of dissolved ozone and gaseous ozone. The factors affecting the mass-transfer coefficient include flowrate, agitation speed, ionic strength, pH, and temperature.

In kinetic studies, the reaction rate constants for phenolic and indolic compounds were pH dependent. At high pH, the reaction rates of these compounds with ozone increased significantly. The stoichiometric factors for phenol is 2 and for *p*-cresol, *p*-ethylphenol, indole, and skatole is 1. In the study of synthetic manure, it was found that

the decrease in the concentrations of phenolic and indolic compounds only depends on the ozone dosage because the concentrations of the dissolved ozone in the solution and gaseous ozone in the outlet stream could not accumulate until those compounds were removed. Finally, a dynamic model incorporating the mass transfer of ozone with the oxidation kinetics was developed to predict the degradation of phenolic and indolic compounds in the synthetic and real swine manure. It was noted that the reactions between ozone and byproducts or impurities should be considered since the concentrations of the target compounds predicted by the model were reduced much faster than those observed in the experiments. Therefore, a reaction coefficient was defined and included in the model to simulate the effect of side reactions on the concentrations of phenolic and indolic compounds. The reaction coefficients found in synthetic and real manure could be related to an easily determined gross parameter (COD). This is especially important if the mathematical relationship can be established, then we can predict the concentrations of malodorous compounds using ozone treatment.

6.2 Recommendations

This study has demonstrated the ability of ozone to reduce the malodors of swine manure using lab-scale and pilot-scale systems. Some recommendations are encouraged to do for the future research.

1. Although ozone has the ability to oxidize the malodorous compounds in the swine manure, high organic loading is still a problem for the protection of groundwater. Therefore, a complete treatment process (for example: preozonation and biological treatment) should be developed to solve the problem.

2. In-situ ozone treatment in a lagoon appears to be a promising technology to control the formation of malodors and to avoid the expense of installing an ozonation reactor. It is worthwhile to evaluate the efficiency of ozonation on lagoon odors and management.
3. Based on the successful use of the oxidation model in predicting the degradation of phenolic and indolic compounds in swine manure, one may modify the reaction coefficient for use with a gross parameter, such as COD, to obtain more precise coefficient for general use.
4. The sulfur-containing compounds contribute to the malodorous characteristics of the swine manure. Therefore, a GC detector (FPD) should be purchased for evaluating the reduction of the sulfur-containing metabolites by ozone.

APPENDIX

Program Used for the Repeated Measures Analysis of Variance in SAS System

```
data ozone;
 input person trtmt smell0 smell1 smell2 smell3;
cards;

1 1 2 2 3 3
1 2 3 3 3 2
1 3 1 2 2 1
1 4 1 2 1 2
1 5 1 1 1 1

2 1 2 2 3 2
2 2 3 2 2 3
2 3 1 1 1 2
2 4 1 1 1 1
2 5 1 1 1 1

3 1 1 3 2 3
3 2 1 2 3 3
3 3 1 1 2 2
3 4 1 1 1 1
3 5 1 1 1 1

4 1 2 3 3 3
4 2 2 3 3 2
4 3 2 2 1 1
4 4 1 1 1 1
4 5 1 1 1 1

5 1 2 2 3 3
5 2 1 2 2 2
5 3 1 1 1 1
5 4 1 1 1 1
5 5 1 1 1 2

;

*Proc glm;
*class person trtmt;
*model smell0 - smell3 = person trtmt;
*repeated time 4 (0 1 2 3) contrast (1)/summary printh printe;
```

```
Proc glm;
class person trtmt;
model smell0 - smell3 = person trtmt;
repeated week 4 (0 1 2 3)/summary printh printe;

contrast '0 vs .25 g/L ' trtmt 1  –1   0   0   0;
contrast '0 vs .5 g/L  ' trtmt 1   0  –1   0   0;
contrast '0 vs .75 g/L ' trtmt 1   0   0  -1   0;
contrast '0 vs  1 g/L  ' trtmt 1   0   0   0  -1;

contrast '0.25 g/L vs  0.5 g/L  ' trtmt 0   1  -1   0   0;
contrast '0.25 g/L vs  0.75 g/L 'trtmt 0   1   0   -1   0;
contrast '0.25 g/L vs  1 g/L    ' trtmt 0   1   0   0  -1;

contrast '0.50 g/L vs  0.75 g/L ' trtmt 0   0  1  -1   0;
contrast '0.50 g/L vs  1 g/L    ' trtmt 0   0  1   0  -1;


run;
```