PILOT PLANT STUDY OF AQUEOUS LINEAR ALKYLBENZENE SULFONATE DEGRADATION BY COMBINED ADVANCE OXIDATION AND BIOLOGICAL PROCESSES

by

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ABSTRACT

Pilot plant study of Aqueous Linear Alkylbenzene Sulfonate degradation by combined Advance Oxidation and Biological Processes

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Photochemical degradation of linear alkylbeneze sulfonate (LAS) using a pilot plant photoreactor is studied. LAS at 100 mg/L is degraded by UV-254 and UV/H_2O_2. Degradation of LAS is effectively enhanced by 720 mg/L H_2O_2. Moreover, the effectiveness of photo-treatment on the biodegradability of LAS is examined. Both pre-treated and untreated LAS are used in biological experiments. Combination of UV-254 with optimum concentration of H_2O_2 effectively enhanced the biodegradability of LAS. However, LAS at 100 mg/L can inhibit the growth of microorganisms. It is observed that the adaptation of activated sludge increases the biodegradation of LAS. However, due to the presence of intermediates in the effluent of the photoreactor, the biodegradability of this effluent is less than the biodegradability of the same as the concentration of untreated LAS. It is also observed that using the integration of UV/H_2O_2 and biological processes instead of single step of UV/H_2O_2, reduces the total residence time in chemical reactor while obtains the desired total efficiency.

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NOMENCLATURE

AOP	Advance Oxidation Process
LAS	Linear Alkylbeneze Sulfonate
WHO	World Health Organization
UV	Ultra Violet
EPA	Environmental Protection Agency
RBC	Rotary Biological Contactor
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
DOC	Dissolved Organic Carbon
TOC	Total Organic Carbon
OUR	Oxygen Uptake Rate
SOUR	Specific Oxygen Uptake Rate
MLSS	Mixed Liquor Suspended Solid
SS	Suspended Solid
TKN	Total Kjeldahl Nitrogen
AOS	Average Oxidation State
MLVSS	Mixed Liquor Volatile Suspended Solid
SVI	Sludge Volume Index
HRT	Hydraulic Retention Time
GPM	Gallons Per Minute
LPM	Liters Per Minute
MBAS	Mathylene Blue Active Substances
ThOD	Theoretical Oxygen Demand
KHP	Potassium Hydrogen Phthalate
SBR	Sequential Batch Reactor
DO	Dissolved Oxygen
UBOD	Ultimate Biological Oxygen Demand
DMP	2,9-dimethyl-1,10-phenanthroline
DPD	N,N-diethyl-p-phenylenediamine

CHAPTER 1

INTRODUCTION

Each year the ecosystem receives large quantities of surfactants, which are the main component of widely used laundry detergents, cleaners, and shampoos. Moreover, surfactants are widely used in industries. Among them, linear alkylbenzene sulfonate (LAS), the most common synthetic anionic surfactant used in domestic and industrial detergents, has a global production of 2.4×10^6 tonnes per year (De Almeida et. al., 1994). LAS was first introduced in 1965 as a biodegradable compound to substitute non-biodegradable compounds in detergents (Huang et al., 2000). It is produced by sulfonation of linear alkylbenzene with sulfur trioxide. Detergents contain 5-25% LAS and the length of its chain ranges from C_{10} to C_{14} (WHO, 1996). As it was reported that higher concentration of LAS does not respond to biological treatments (Zhang et al., 1998), many investigators have tried degrading LAS using chemical processes. Among the several chemical treatments, advanced oxidation processes (AOPs) such as UV and UV/H_2O_2 have been used as an attractive alternative for the treatment of wastewaters containing bioresistant compounds successfully. AOPs are technologies for the production of highly reactive intermediates, mainly hydroxyl radicals ($^{\bullet}OH$), which are able to oxidize almost all organic pollutants. During photolysis, UV light with the wavelength energy of more than bond energy can break the bond directly. While in the case that UV is combined with hydrogen peroxide, H_2O_2 absorbs light at 254 nm to produce hydroxyl radicals. These hydroxyl radicals react with the organic pollutants producing aldehydes, alcohols, and carboxylic acids. In the case of complete mineralization, the products would be CO_2 and H_2O. AOPs have shown their worthiness for toxic compounds elimination in water and wastewater treatment, however, the total mineralization through these processes is very expensive. On the other hand, biological treatment is relatively cheap and reliable process, but there are many non-biodegradable and bioresistant compounds. Therefore, a combination of both processes would mean a cheaper option for total organic degradation from a toxic wastewater or a wastewater containing refractory organics. It has been observed by many investigators that the

coupling of a bioreactor and advanced oxidation processes (AOPs) could reduce the final concentrations of the effluent to the desired values. However, optimizing the total cost of the treatment is a challenge, as AOPs are much more expensive than biological processes alone. Therefore, an appropriate design should not only consider the ability of this coupling to reduce the concentration of organic pollutants, but also try to obtain the desired results in a cost effective process.

The objectives of this research were to investigate the possibility of degrading an anionic surfactant, linear alkylbenzene sulfonate, by combining photolytic with biological treatment. The following experiments were conducted to study that possibility.

- Photolytic treatment of LAS with UV-254 and combination of UV and H_2O_2 to find the rate of degradation of each process
- Effects of photolytic pretreatment of LAS by UV/H_2O_2 on its biodegradability
- Combination of photolytic pretreatment of LAS by UV/H_2O_2 and subsequent aerobic biological treatment using unadapted and adapted activated sludge for an effective treatment of LAS

CHAPTER 2

LITERATURE BACKGROUND

This chapter is divided into two parts. The first part deals with different advanced oxidation processes for the treatment of aqueous organics. Moreover, a comprehensive review on the combination of chemical and biological treatment is presented based on the previous work (Bankian and Mehrvar, 2004). The effects of different parameters during this combination, depending on the type of treatment, are described. A brief discussion of the compounds used in this research is described in the second part of this chapter.

2.1 Introduction

Increased knowledge about the consequences from water pollution, public desire for better quality of water, having a better environment, diminishing water resources, the rapid growth, and the industrial development have created the need to have regulations such as United States Environmental Protection Agency (USEPA). Also the reuse of the municipal and industrial wastewater and the recovery of potential pollutants used in industrial processes become more critical. Hence, the role of the wastewater treatment is becoming more and more important as both the effluent quality and quantity are subjected to more strict regulations. Technological advancement to minimize the use of wastewater may help reduce the effluent quantity, whereas cost-effective wastewater treatment can be adopted to reduce pollutant concentrations to acceptable levels.

Wastewaters from chemical, pharmaceutical, and dye industries most often contain significant amount of non-biodegradable organic compounds. The elimination of these non-biodegradable toxic contaminants is required before biological treatment. Although the biological treatment of wastewater is often the most economical alternative process when compared to other treatment options such as AOPs, the ability of a compound to undergo biological degradation depends on a variety of factors. Such

factors include the concentrations, chemical structures, and the biodegradability of the target molecules. Characteristics of the wastewater, such as pH, alkalinity, or the presence of an inhibitory compound could also play an important role in the biological degradation of pollutants. Although many organic molecules are readily biodegradable, many other synthetic and naturally existing organic molecules are biorecalcitrant, i.e., resistant to biodegradation. Depending on the nature of the pollutants and the level of contaminants, detoxification might be difficult and/or expensive to achieve by conventional biological methods. In such cases, biological processes alone are not able to reach effluent standards for the discharge into municipal sewer or into surface water; therefore, a pre-treatment or post-treatment is required. The choice of the correct combination system must be carried out considering several factors, both technical (treatment efficiency, plant simplicity, flexibility, etc.) and economical (capital and operating costs including reagent and energy consumption, sludge and gas disposal, maintenance, etc.) aspects. In several cases, specific experimental tests are required in order to assess actual efficiency and proper treatment conditions. Moreover, advanced oxidation processes (AOPs) such as UV, UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3, and UV/TiO_2 have been used as an attractive alternative for the treatment of these types of wastewaters. AOPs are technologies for the production of highly reactive intermediates, mainly hydroxyl radicals ($^{\bullet}OH$), which are able to oxidize almost all organic pollutants. Advanced oxidation processes can reduce pollutant concentrations, and some processes produce more oxidized compounds, which are in most cases more easily biodegradable than the former ones. Although AOPs are expensive to install and operate, they may be unavoidable for the tertiary treatment of refractory organics present in industrial effluents to allow safe discharge of industrial contaminants. Despite the effectiveness of AOPs, there are several scenarios that make them economically disadvantageous. Effective treatment of a particular industrial wastewater may require a combination of AOPs and biological processes in order to exploit their individual quantities and, thus, reach the desired quality within reasonable economical limits.

On one hand, AOPs have shown their worthiness for toxic compounds elimination in water and wastewater treatment, however, the total mineralization through these

processes is very expensive. On the other hand, biological treatment is relatively cheap and reliable process but there are substances, which are unable to deal with. A combination of both processes would mean a cheaper option for total organic degradation from a toxic wastewater or a wastewater containing refractory organics.

It has been shown that the combination of biological and advanced oxidation processes has the following advantages (Lee et al., 2001):

1. Synergistic effect as chemical and biological processes are accompanimentf of each other.
2. Protection of the biological culture from inhibitory or toxic compounds by chemical pre-treatment.
3. Reduction in chemical dosage cost by the use of cost-effective biological pre or post-treatment.
4. Flexibility in total residence time as a result of different choices that is possible for chemical and biological reactor residence times in a constant efficiency.
5. Achieving complete pollutant mineralization while minimizing the total cost.

2.2 Advanced Oxidation Processes (AOPs)

AOPs are fairly new technologies which have been developed since 1975 (Zhou and Smith, 2001) and are of considerable interest in water and wastewater treatment. They are promising technologies for the removal of contaminated ground and surface water as well as wastewaters containing non-biodegradable or inhibitory organics to microbial growth. The main advantage of AOPs is their ability to destroy the organic compounds in water without transferring them to another medium or generating secondary waste disposal problems. A broad range of compounds may be treated by AOPs. AOPs work by destroying the organic compounds in water and wastewater by oxidation. The most commonly used AOPs use H_2O_2, O_3, or O_2 as an oxidant. These involve producing free radicals such as $^{\cdot}OH$, from the molecular oxidant by means of energy or catalyst. For example, hydrogen peroxide may generate hydroxyl radicals in the presence of UV light with the wavelength of less than 254 nm based on the following reaction:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (2.1)$$

These hydroxyl radicals are able to attack pollutants by addition to double bond, abstraction a hydrogen atom, or transferring an electron to a halogenated compound according to the following reactions (Braun and Oliveros, 1997):

-Addition $$^{\bullet}OH + X_2C{=}CX_2 \rightarrow X_2C(OH){-}C^{\bullet}X_2 \quad (2.2)$$

-Hydrogen abstraction $$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad (2.3)$$

- Electron transfer $$^{\bullet}OH + RX \rightarrow OH^{-} + XR^{+\bullet} \quad (2.4)$$

where R represents a typical hydrocarbon and X represent a halogenated group.

The products of the organic molecule could be intermediates, or at the final stage either HCO_3^-, Cl^-, NO_3^-, CO_2, or H_2O.

The oxidation of organics is defined by the extent of their degradation to the final oxidation products as follows:

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

An important disadvantage of AOPs is their high capital and operating costs in comparison to the conventional biological treatment. However, by considering their advantages, AOPs could be used as a pre- or post-treatment step to enhance the biodegradability of the wastewater containing recalcitrant or inhibitory organics, and even rendering the wastewater ambient for reuse.

2.2.1 Processes for generating oxidant radicals

The versatility of AOPs is also enhanced by the fact that they offer different ways of producing hydroxyl radicals, which allow gaining specific treatment requirements. The following is a list of different AOPs, which are able to produce the highly reactive hydroxyl radicals:

- UV
- H_2O_2/UV
- O_3/UV
- O_3/UV/H_2O_2
- O_3
- O_3/H_2O_2
- H_2O_2/ Fe^{2+}(Fenton)
- H_2O_2/ Fe^{2+}/ UV(Photo-Fenton)
- TiO_2/UV(Photocatalysis)
- TiO_2/UV/H_2O_2

Types of radicals generated by different methods of AOPs are as listed Table 2.1 (Gulyas, 1997).

2.3 Biological Treatment of Wastewater

Biological oxidation has been the main technology capable of reducing the contaminant level of wastewater for many years. The overall objectives of the biological wastewater treatment are to transform biodegradable compounds into acceptable end products, transform or remove nutrients, capture suspended solids, and incorporate non-settleable colloidal solids into biological flocs. The objective of the industrial wastewater treatment is to remove and reduce the concentration of organic and inorganic compounds. Although some of the organics are toxic or inhibitory to microbial growth, a preliminary chemical oxidation step may eliminate refractory or toxic substances. The main benefit of

Table 2.1: Generator Processes that produces free radicals

Free Radicals	Generator Processes
$^{\bullet}OH$	H_2O_2/ Fe^{2+}
	$H_2O_2/ Fe^{2+}/ UV$
	H_2O_2/UV
	O_3
	O_3/H_2O_2
	O_3/UV
	$O_3/UV/H_2O_2$
	TiO_2/UV
	$TiO_2/UV/H_2O_2$
$HO_2^{\bullet}$	H_2O_2/UV
	O_3
	O_3/H_2O_2
	$O_3/UV/H_2O_2$
$HO^{\bullet}_3$	O_3
	O_3/H_2O_2
	$O_3/UV/H_2O_2$
$^{\bullet}O_2^-$	O_3
	O_3/H_2O_2
	$O_3/UV/H_2O_2$
$HO^{\bullet}_3$	O_3
	O_3/H_2O_2
	$O_3/UV/H_2O_2$

the biological wastewater treatment is its relatively low operating cost and handling huge masses of compounds.

The principal biological processes used for wastewater treatment can be divided into the following main categories (Metcalf and Eddy, 2003, Eckenfelder, 2000):

- Suspended growth processes, in which microorganisms responsible for the conversion of the organic matter in the wastewater are suspended within the liquid (for example: activated sludge and aerated lagoons). The degree of organics removal for the activated sludge process is approximately 90% and for the aerated lagoons it is high in summer but not good in winter.
- Attached growth (biofilm) processes, in which microorganisms responsible for the conversion of the organic matter in the wastewater, are attached to some inert medium, such as rocks, slag, ceramic, or plastic materials (for example: trickling filters, rotary biological contactors (RBCs), and packed-bed reactors). The degree of the removal for these processes is intermediate to high depending on the loading of wastewater.
- Anaerobic processes: such as sludge blanket and upflow anaerobic sludge blanket. Their degree of removal is intermediate.

The successful design and operation require an understanding of the type of microorganisms and organic compounds, the environmental factors that affect the performance, and the types of reactors involved. The successful operation and removal of dissolved compounds in wastewater are done by a variety of microorganisms, principally bacteria. Microorganisms oxidize the dissolved and particulate carbonaceous organics into simple products and extra biomass. Among the environmental factors affecting the treatment process, temperature and pH have important effects on the selection, survival, and the growth of microorganisms. The optimal growth of a specific microorganism occurs in a fairy narrow range of temperature that differs from one group of bacteria to the other. Most bacteria cannot tolerate pH levels above 9.5 or below 4.0. Generally, the optimum pH for the growth and survival of the bacteria lies between 6.5 and 7.5.

2.3 Combined chemical and biological processes for the treatment of organic pollutants in water and wastewater

Previously, a wild range of studies on the integration of biological and advanced oxidation processes prior to 1995 have been reviewed (Scott and Ollis, 1995). In this study, recent developments (1996-2003) on the integration of chemical and biological processes for the degradation and treatment of problematic pollutants in wastewater are classified in Table 2.2 (Bankian and Mehrvar, 2004). The studies were conducted on the integration of chemical and biological processes with different objectives, such as modeling the degradation in chemical and biological reactors, observing the effects of combination on total removal and comparing with individual processes, comparing the effects of different AOPs on the biodegradation of a certain compound, and investigating the effects of different parameters on the combination of processes. The compounds used were mostly difficult to degrade by biological processes alone and needed post- or pre-treatment by AOPs. In most cases there was just one chemical reactor followed by biological reactor or vice versa in series. However, there is one case in which the chemical and biological reactors are parallel (Lee et al., 2001), three cases in which there are more than two stages for the treatment (Helble et al., 1999; Karer et al., 1997; and Fahmi et al, 2003), and four cases in which there is a biological pre-treatment followed by a chemical oxidation treatment step, which is followed by further biological treatment (Bertanza et al. 2001; Ito et al., 1998; Jochimsen and Jekel, 1997; and Mobius and Tolle, 1997). In such processes, the first biological step removes the biodegradable organics and the chemical reactor increases the biodegradability of residual organics for the second biological step.

As Table 2.2 illustrates, the treatment of some chemicals cannot be usually completed by either biological treatment or AOPs alone. In spite of the fact that AOPs are capable to produce high quality effluent in most cases, the important drawback of these processes is their high capital and operating costs such as chemicals, electricity, and sludge disposal. However, in order to avoid the high operation costs for complete oxidation, only partial oxidation is desired. It has been shown that a photochemical pre-treatment step may enhance the biodegradability of wastewater containing recalcitrant or

inhibitory compounds, if and only if, the intermediates produced are biodegradable and are more soluble and less toxic than the parent compounds. It has been frequently shown that the pre-oxidation by AOPs improves the biodegradability of non or poorly biodegradable organic compounds and this effect could be due to the change in their molecular structure. However, little is known about the exact mechanisms during the oxidation. The possible changes after oxidation and their effects on biodegradability could be due to the decrease of aromacity and destruction of high molecular structure, which leads to the formation of functional groups such as hydroxyl, carboxyl, and aldehyde (Jochimsen and Jekel, 1997). The effect on biodegradability of these chemical changes is significant on the enzyme activity. It can also be concluded that the destruction of toxic substances has positive effect on enzyme activity, whereas the formation of toxic metabolites had a negative effect on the inhibition of biochemical processes. Moreover, destruction of organic nitrification inhibitors causes an improvement in nitrification processes (Jochimsen and Jekel, 1997).

As a general treatment strategy, four types of treatment for a chemical compound are possible (Bertanza et al., 2001):

1. In some cases only biological treatment alone is sufficient to enhance the effluent quality.
2. In the presence of some refractory or toxic compounds in wastewater, chemical pretreatment is required.
3. In case biological treatment is not sufficient for biodegradable compounds, chemical post-treatment is also necessary.
4. In some rare cases, combination of chemical and biological treatment in multi-stages is necessary.

A general strategy that can be used to develop a combined advanced oxidation and biological processes for the treatment of a certain wastewater, which might contain non-biodegradable or toxic organics, is as follows:

As a first step to avoid utilization of high cost due to AOPs, it must be confirmed that whether the wastewater contains recalcitrant or toxic organics. If the wastewater is biodegradable, conventional biological reactors are used to treat the waste. If it is

confirmed that wastewater contains recalcitrant or toxic organics, it would be pretreated by AOPs to modify the structure of pollutants by transforming them into less toxic and easily biodegradable intermediates, which are degraded in the subsequent biological reactor in a shorter time. This method can also prove to be less expensive in comparison to the AOPs alone and less time consuming compared to the biological process. Moreover, if the effluent from the final biological reactor has met the requirements, it will leave the treatment plant; otherwise it has to go through the previous cycle.

There are four types of wastewater, which have potential for increasing treatment efficiencies by combined processes as follows (Scott and Ollis, 1995):

1. Recalcitrant compounds
2. Biodegradable wastes with small amounts of recalcitrant compounds
3. Inhibitory compound
4. Intermediate dead-end products.

Table 2.2. Summary of the recent studies on the combined chemical and biological treatment of organic pollutants in water and wastewater between 1995 and 2003

Order of Scheme	Chemicals	Biodegradability	Initial Conc.	Chemical Oxidation Scheme	Biological Degradation Scheme	Measurement of Biodegradability	Grade	References
B-C-B [i]	Landfill leachate	difficult to remove by biodegradation	COD= 640 mg/L	O_3	1.aerobic biological treatment 2.Biological activated carbon	BOD[ii] COD[iii] DOC[iv]	Further work has to be done	Fettig et al., 1996
B-C [v]	Municipal wastewater	contains E.coli and total Coliforms	Number of Bacteria 35000/ 100 mL	TiO_2/UV	activated sludge	BOD COD # of E.Coli Total Coliform	Effective Number of Bacteria 59/100 ml	Li et al., 1996
C-B [vi]	Biologically treated pulp and paper wastewater	Non-biodegradable	COD= 500 mg/L	O_3	low loaded biofilm reactor (Submerged granular biofilter)	COD BOD_5 AOX[vii]	Effective	Mobius and Cordes-Tolle, 1997
C-B	Tannery wastewater	toxic refractory	COD BH[viii]=10 8 mg/l COD TY[ix]=450 mg/L	O_3	aerobic biological reactor	COD BOD UV[x]	Effective	Jochimsen and Jekel, 1997
B-C-B	Tannery wastewater	inhabitant, toxic little biodegradable	COD up to 15000 mg/L	O_3	Pre:anaerobic/aerobic Post: aerobic with mixed culture	COD DOC	Good	Jachimesen and Jekel, 1997
B-C	Landfill leachate	biorefractory	450-1500 mg/L	O_3	adapted fluidized bed biofilm reactor	COD DOC BOD	Good	Karrer et al., 1997

Bio1/Oxi1 Bio2/Oxi2 Bio3/Oxi3	Synthetic wastewater m-chloronitrobenzene Na2HPO4/NaH2PO4 Fe Co Mn Cu Zn NI Al Distilled water	refractory	 2mM 288uM 1.44uM 1.32uM 0.36um 0.02 0.055 0.047 0.034	O_3	biological reactor(BOD_5)	DOC COD BOD	Efficient	Karrer et al., 1997
C-B	2,4-dichlorophenol	non-biodegradable	COD= 300mg/L	O_3	activated sludge(non-adapted)	BOD COD TOC	Effective	Marco et al., 1997
C-B	Subsistent phenols Amino- Nitro- Chloro-	 - degradable -biorecalcitrant -biorecalcitrant	COD= 200 mg/L	O_3	activated sludge	COD	Decrease in Biodegrad-ability Very good Very good	Adams et al., 1997
C-B	m-dinitrobenzene diphenylamine resorcinol	Inhibitory recalcitrant	30 mg/L	TiO_2/UV	BOD5	BOD_1/TOC COD	Good	Bolduc and Anderson, 1997
C-B	Olive mil effluent	inhibitory	COD= 121.8 g/L	O_3	anaerobic biological reactor	COD	Bad effect	Andreozzi et al., 1997
C-B	Urban wastewater	some refractory compounds	COD= 286 mg/L	O_3 VU/O_3 O_3/H_2O_2 UV/H_2O_2	activated sludge	COD BOD_5 BOD_T[xi]	O_3 was The best	Beltran et al., 1997
B-C-B	trihalomethane (THM)	Difficult to remove by biodegradation	THMFP[xii]= 110-20 ug/L	O_3/H_2O_2/UV O_3/H_2O_2 O_3/UV H_2O_2/UV O_3 UV	activated sludge	DOC UV 260	Efficiency decreased from top to bottom	Ito et al., 1998

C-B	Wastewater sludge	excess sludge production	TOC[xiii]= 200 mg/L	O_3	activated sludge	TOC DOC MLSS[xiv] SVI[xv]	Effective	Kamiya and Hirotusuji, 1998
B-C	Photo-processing waste (PW)	refractory toxic	COD_{Mn}= 38000 mg/L COD_{Cr} =70700 mg/L	Fenton oxidation	sulfur-oxidizing bacteria/granular activated carbon	COD BOD_5 TOC T-N[xvi]	94.8% DOC removal Efficient	Lin et al.,1998
C-B	THMFP (trihalomethanes)	toxic	COD= 2.8-4.2 mg/L	O_3	BAC[xvii]	DOC UV_{260}	Bad	Nishijim et al., 1998
C-B	4,4- diaminoslibene-2,2-disulfonic acid (DSD-acid)	non-biodegradable bioresistant	COD= 21900 mg/L	Fenton's reagent/ O_3		BOD/COD Color removal	Improved	Yu et al., 1998
B-C	Kraft bleaching process Textile industry wastewater	toxic refractory	COD textile= 103 mg/L COD Pulp= 1029 mg/L	Photocatalytic+ H_2O_2+ Fenton's	BOD_5	COD TOC BOD_5 Color removal	Potential for reuse, as 97% of organics were removed	Balcioglu and Arsalan, 1998
B-C	Olive mill wastewater	Toxic High inhibitory	COD= 41.95 g/dm^3	O_3	activated sludge	COD Total Aromatic Total Phenolic content	81.1% removed	Benitez et al., 1999
C-B	Olive mill wastewater	toxic high inhibitory	COD= 34.05 g/dm^3	O_3	activated sludge	COD Total Aromatic Total Phenolic content	84.6% removed	Benitez et al., 1999
B-C	Wine distillery wastewater	toxicity inhibitory	COD= 27-29 g/L	$O_3/H_2O_2/UV$	aerobic biological reactor	COD	Effective	Benitez et al., 1999

C-B	Domestic wastewater	some refractory compounds	BOD/ COD= 0.57	O_3	activated sludge	BOD/COD =0.69	Good	Beltran et al., 1999
B-C	Domestic wastewater	some refractory compounds	BOD= 162 COD= 286	O_3	activated sludge (mixed culture)	BOD/COD UV	Good	Beltran et al., 1999
C-B	Azo dyes and wool textile wastewater	non-biodegradable	100 ppm/L	TiO_2/UV	BOD_5	BOD_5/COC	Good	Chun and Yizhong, 1999
C-B two stages	Pulp and paper wastewater	toxic inhibitory	COD= 400mg/L	O_3	fixed bed biofilm reactor	COD BOD	Efficient	Helble et al., 1999
C-B	Polycyclic aromatic hydrocarbons in oil/water emulsion	biodegradability of concentrated PAH has not been approved	_	O_3 (continuous)	aerobic biological reactor	HPLC	Efficient	Kornmuller and Wiesman, 1999
B-C	Dye textile	non-biodegradable toxic	COD= 2000 mg/L	TiO_2/UV	intermittently decanted extended aeration	COD BOD	Good	Li and Zhao, 1999
C-B	Textile wastewater -Anthraquinone dyestuff -Surfactant (softening agent, anionic detergent)	-inhibitory -partially biodegradable	COD= 2154 mg/dm^3	O_3/UV/H_2O_2	activated sludge	EC_{50}[xviii]	Good	Ledakowicz and Gonera, 1999
C-B	EDTA	Non-biodegradable	100 mg/L	-Fenton's reagent -O_3	biological activated carbon	BOD/COD TOC	-Fair -Good	Mochidizuki and Takeuchi, 1999
C-B	Polyester manufacturing plant	biorecalcitrant	COD= 200000 mg/L	H_2O_2/ Fenton's reagent	activated sludge	COD BOD	80% removed	Meric et al., 1999

C-B	P-nitrotoluene- ortho-sulfonic	biorecalcitrant	330 mg C/L	Fenton's reagent	fixed bed reactor	COD BOC	Effective	Pulgarin et al., 1999
C-B	Pulp mill bleaching effluent	toxic inhibitory	COD= 2000 mg/L	TiO_2	activated sludge	TOC COD BOD AOX Color	Efficient	Yeber et al., 1999
C-B	Nonylphenol ethoxylate (NPE)	biorecalcitrant	_	Fenton's reagent	activated sludge	COD	Depend on oxidant dose	Kitis et al., 1999
C-B	Ethylene oxide/ propylene oxide block copolymers	biorecalcitrant	_	Fenton's reagent	activated sludge	COD	Very good	Kitis et al.,1999
C-B	Non-surfactant compound polypropylene glycon (PPG)	biorecalcitrant	_	Fenton's reagent	activated sludge	COD	Very good	Kitis et al., 1999
C-B	EO/PO Block copolymers	biorecalcitrant	_	O_3/H_2O_2	activated sludge	DOC COD	Good	Kitis et al., 2000
C-B	Polypropyleneglycols	biorecalcitrant	_	O_3/H_2O_2	activated sludge	DOC COD	Good	Kitis et al., 2000
C-B	Linear secondary alcoholethyoxylates (LSAE)	partially to biorecalcitrant	_	O_3/H_2O_2	activated sludge	DOC COD	Good	Kitis et al., 2000
C-B	Alkylphenolethoxylates (APE)	Partially Biorecalcitrant	_	O_3/H_2O_2	activated sludge	DOC COD	Good	Kitis et al., 2000
C-B	Quaternary amine surfactant -alkyldimethylbenzyl ammonium chloride (Barquates) -Dictyl-dimethyl ammonium chloride (Bardoc LF)	Biorecalcitrant (enzymatic deficiencies or toxicological properties)	COD= 1000 mg/L	UV/H_2O_2	activated sludge	COD DOC	-Very Good 90% removal -Little effect 15%	Adams and Huzhikanni l 2000

C-B	Agroindustrial & Domestic wastewater	contains some biorecalcitrant	COD= 2443 mg/L	O_3	activated sludge	COD TOC BOD UV 254 TKN[xix]	Effective	Beltran et al., 2000
B-C	Black olive mill wastewater	toxic inhabitant	COD= 67 g/L	O_3	activated sludge	COD TP[xx]	Good	Heredia et al., 2000
C-B	2,3,7,8-tetrachloroibenzo – p-dioxin	toxic	46 ug/Kg soil	Fenton's	activated sludge	TCDD[xxi] conc.	Effective	Kao and Wu, 2000
C-B	Metobromuron/ isoproturon	biorecalcitrant	–	1-Fe^{3+}/H_2O_2 2-UV/FE^{3+}/ H_2O_2 3-UV 4-UV/TiO_2 5-UV/TiO_2/ H_2O_2	fixed bed reactor	TOC	1-Bad 2-Very good 3-Very bad 4-Fair 5-Good	Parra et al., 2000
C-B	Metobromuron isoproturon	non-biodegradable	50 mg/L	Fenton's/ TiO_2	fixed bed reactor	TOC COD/BOD EC_{50}	Effective 95% removed	Parra et al., 2000
C-B	Pyrene	toxic	Conc.=1 mg/L	O_3	BOD	COD BOD GC/FID GC/MS	Effective	Zeng et al., 2000
B-C	Textile industry wastewater	toxic recalcitrant	COD= 325 mg/dm^3	-O_3 -H_2O_2/UV-C -sequential O_3/H_2O_2/UV	BOD	TOC COD UV f_B[xxii]	Overall removal for O_3 was 60% and it was less for the rest of the methods	Arsalan and Balcioglu, 2001
C-B	Olive mill wastewater	toxic high inhibitory	COD= 95 g/L	Fenton's reagent Ozonation	activated sludge	COD BOD_5	Effective	Heredia et al., 2001

Filtration-C-B	Polystyrene wastewater	toxic	COD= 7000-95000	Fenton	activated sludge	COD BOD5 BOD20 SS[xxiii]	COD= 150	Bertanza et al., 2001
C-B	Textile wastewater	toxic	COD=1750mg/L	1-Fenton 2-O_3/H_2O_2 3-UV	activated sludge	COD BOD_5 TOC	1-good 2-bad 3-good	Bertanza et al., 2001
B-C-B	Polyester resin	toxic	COD= 60000-118000 mg/L	Fenton	activated sludge	COD BOD_5 BOD_{20} Aldehydes	COD=100 mg/l	Bertanza et al., 2001
B-C	Distillery wastewater (Cherry Stillage)	some organics are non-biodegradable	COD= 1-7 g/L	O_3	activated sludge with acclimated culture	COD TOC BOD	Good	Beltran et al., 2001
C-B	Textile wastewater consisted of: -Anionic detergent awiwaz KG conc -Softening agent Tetrapol CLB -Anthraquinone dyestuff-acid blue 40, CI2125	little or non-biodegradable inhibitory, toxic	COD= 2159 mg/L	1.UV/H_2O_2 2.UV 3.H_2O_2 4.O_3	activated sludge	COD BOD_5 DOC	1.Good 2.Medium 3.Fair 4.Medium	Ledakowicz et al., 2001
B & C parallel	Textile	toxic	COD= 860-$8000_{mg/L}$	UV/H_2O_2 UV/O_3 $UV/H_2O_2/O_3$	intensive biological treatment	COD BOD_5 Color	COD_f=0	Lee et al., 2001
C-B	Dimethyl Sulphoxide (DMSO)	low treatability	800 mg/L	Fenton's reagent	activated sludge	BOD/COD TOC	Not to effective in compare to cost	Park et al., 2001
C-B	5- amino-6-methyl-2-benzimidazolone	Biorecalcitrant	COD= 18105 mg/L	1.Fe^{3+}/H_2O_2 2.$Fe^{3+}/ H_2O_2/$ UV	fixed bed reactor	DOC AMBI [xxiv]conc. COD BOD_5	Only (2) was effective by80%	Sarria et al., 2001

B-C	Alkaline fruit cannery effluent	non-biodegradable	COD= 45000 mg/L	O_3/H_2O_2 + Granular activated carbon	upflow aerobic sludge blanket	COD Color removal	COD= 75	Sigger et al., 2001
C-B	5- amino-6-methyl-2-benzimidazolone	biorecalcitrant	COD= 18105 mg/L	1.H_2O_2/UV 2.TiO_2/H_2O_2/ UV 3.Fe^{3+}/UV	fixed bed reactor	DOC AMBI con. COD BOD5	Only (3) was Effective by 40%	Sarria et al., 2001
C-B	Contaminant ground water (high conc. Of ammonia)	inhibitory	COD= 19.3 mg/dm^3 NH_4= 100 mg/dm^3	TiO_2/UV	biological nitrification system	COD TOC	Very Good 60% was nitrified	Zhang et al., 2002
C-B	Pentachlorophenol	toxic biorecalcitrant	43 mg/L	O_3	trickling filter	BOD_5 COD GC	Good	Hong and Zeng , 2002
B-C	Pharmaceutical wastewater	partially refractory	COD=13 490 mg/L	O_3	activated sludge	SOUR[xxv] BOD_5/COD	Good	Alaton and Balcioglu, 2002
C-B	Polychlorinated biphenyls(PCBs)	bioaccumulate	1000 mg/L	O_3	aAerobic bioreactor	COD	Good	Cassidy et al., 2002
1.C-B 2.B-C	Log Yard run-off	partially (needs polishing)	COD= 4890 mg/L	O_3	batch aerobic bioreactor	BOD COD EC_{50}	1.3% 2.68% COD removal	Zenaitis et al., 2002
C-B	Polycyclic aromatic hydrocarbons (anthracene, benzopyrene)	bioaccumulate	–	Fenton's reagent in presence of surfactant	mixed and pure culture	% B[a]P [xxvi]remaining	4 times higher than each alone (85%)	Nadarajah et al., 2002
C-B	Isoproturon (IP)	biorecalcitrant	–	TiO_2/UV	fixed bed reactor	COD DOC	Very Good	Parra et al., 2002

C-B	P-nitrotoluene- ortho-sulfonic	biorecalcitrant	_	TiO_2 (coaxial reactor) Fe^{3+}(coil reactor)	fixed bed reactor	COD BOC	Effective	Sarria et al., 2002
C-B	Metobromuron Isoproturun	biorecalcitrant	_	TiO_2 (coaxial reactor) Fe^{3+}(coil reactor)	fixed bed reactor	COD BOC	Effective	Sarria et al., 2002
C-B multistage	Drinking water containing DOM	some refractory compounds	DOC= 9.3 mg/L	O_3 O_3/H_2O_2	biological activated carbon	DOC	Bad Effective	Fahmi et al., 2003
C-B Multi-stage	1-Secondary effluent containing (DOM) 2-Humic substrate	some biorefractory organics	DOC= 10 mg/L for both	O_3	common biological process	DOC	1-Bad 2-Good	Nishijima et al., 2003
C-B	Cibacron brilliant yellow 3G-P	biorecalcitrant	100 mg/L	Photocatalytic reactor	-Conventional BOD -respiromertric -aerobic treatment	BOD COD OUR[xxvii]	no improvement was observed in biodegradability	Aye et al., 2003

[i] The order of the reactors is biological-chemical-biological
[ii] Biological Oxygen Demand
[iii] Chemical Oxygen Demand
[iv] Dissolved Organic Carbon
[v] The order of the reactors is biological-chemical
[vi] The order of the reactors is chemical-biological
[vii] Adsorbable organic halogen
[viii] Tannery substream Beam House wastewater
[ix] Tan-yard wastewater
[x] UV absorbance at specific wavelength
[xi] BOD after T days
[xii] trihalomethane formation potential
[xiii] Total Organic Carbon
[xiv] Mixed Liquor Suspended Solid

[xv] Sludge Volume Index
[xvi] Total Nitrogen
[xvii] Biological Activated Carbon
[xviii] acute toxicity
[xix] Total Kjeldhal Nitrogen
[xx] Total Phosphorous
[xxi] 2,3,7,8-tetrachloroibenzo –p-dioxin
[xxii] biodegradability factor
[xxiii] Suspended Solids
[xxiv] 5- amino-6-methyl-2- benzimidazolone
[xxv] Specific Oxygen Uptake Rate
[xxvi] benzo[a]pyrene
[xxvii] Oxygen Uptake Rate

2.5 Concentration of Oxidants in AOPs

Most of the studies show that there is an optimum oxidant dose rate to remove the maximum amount of pollutants with the lesser oxidant consumption. It has been shown that increasing the oxidant dose in Fenton reaction increases both the extent and the rate of the biodegradation (Parra et al., 2000). The increase in H_2O_2 concentration as a strong electron acceptor also had inhibitory effect on the degradability of herbicides (Parra et al., 2000). The concentration of an optimal H_2O_2/pollutant molar ratio between 10 and 100 (mole H_2O_2)/(mole pollutant) had been proposed by other researchers (Parra et al., 2002). It was also reported that the addition of 32 cm^3 H_2O_2 to 1 dm^3 textile wastewater was equal to 80% decrease in the inhibition effect (Ledakowicz and Gonera, 1999). This was probably due to the auto-oxidation of H_2O_2 into O_2 and H_2O, and recombination of $^{\bullet}OH$ by means of H_2O_2 according to the following reactions:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (2.5)$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \qquad (2.6)$$

$$k = 3.3\times10^{7}\,(mol\cdot s)^{-1}$$

The excess of H_2O_2 reacts with $^{\bullet}OH$, competing with pollutants and, hence, decreasing the efficiency of the treatment (Ledakowicz and Gonera, 1999).

2.6 Treatment Time

The information about the toxicity and the biodegradability of a compound treated by AOPs allows us to determine an optimal treatment time in the AOPs reactor of the coupled system. It has been observed that the toxicity was increased at the beginning of the treatment of isoproturon by AOP followed by a sharp decrease in the toxicity (Parra et al., 2002). It has been indicated that the intermediates formed during the beginning of the treatment are more toxic than the initial compounds. Therefore, the time should be the best compromise between the efficiency of the chemical reactor and its cost. The shorter reaction time avoids the high electrical cost of the reaction. At longer photo-treatment time, the photochemical efficiency is improved by the unnecessary

photo-degradation of pollutants which are biologically degraded. However, the overall efficiency remains almost constant. This implies higher energy consumption without beneficial effect, as about 60% of the total operational cost is electricity (Parra et al., 2002). However, if the reaction time is too short, the intermediates remaining in the system could still have toxicological or biorecalcitrant effects.

Partial oxidation parameters, which correlated with subsequent biodegradation, have been developed (Jochimsen and Jekel, 1997). These parameters set the optimal point for the oxidative treatment. A combination of dissolved organic carbon (DOC) and chemical oxygen demand (COD) concentrations at different times allows differentiating between the oxidation effects of mineralization (total oxidation) and partial oxidation. COD-reduction through partial oxidation is estimated by the following equations (Jochimsen and Jekel, 1997):

$$COD_{partoxi} = \left(\frac{COD_0}{DOC_0} - \frac{COD_t}{DOC_t} \right) \times DOC_t \qquad (2.7)$$

where $COD_{partoxi}$ is partial COD reduction, COD_o and DOC_o represent the initial concentration of the wastewater, and COD_t and DOC_t represent the final concentrations. The degree of COD-removal through partial oxidation is given by Equation (2.8), where $\alpha_{COD_{partoxi}}$ represents the degree of COD removal (Jochimsen and Jekel, 1997):

$$\alpha_{COD_{partoxi}} = 1 - \frac{COD_{partoxi}}{COD_0} \qquad (2.8)$$

The degree of effective partial oxidation ($\mu_{COD_{partoxi}}$) represents the relationship between partial and total oxidation as follows:

$$\mu_{COD_{partoxi}} = \frac{COD_{partoxi}}{COD_0 - COD_t} \qquad (2.9)$$

To compare the electivity of oxidative and biological DOC-removal, the difference between the biodegradable DOC and the DOC after chemical oxidation related to initial DOC is estimated by the following equation (Jochimsen and Jekel, 1997):

$$\alpha_{DOC_{bio}} = \frac{DOC_{oxi} - DOC_{bio}}{DOC_o} \qquad (2.10)$$

where $\alpha_{DOC_{bio}}$, DOC_{oxi}, DOC_{bio}, and DOC_o are the electivity of oxidative and biological DOC-removal, oxidative DOC-removal, biological DOC-removal, and initial DOC, respectively.

2.7 Influence of pH on Degradability

Primary parameters such as temperature and pH have significant effects on the oxidation pathway and the products. It has been found that the best pH for the Fenton reaction is in the range of 3-5. It is also observed that in Fenton treatment, the optimum pH is based on TOC and COD removal efficiency (Park et al., 2001). It has also been shown that the best pH for the degradation of nonionic surfactants is 3 (Adams et al., 1997). However, in the next step, precipitation of oxidized iron $Fe(OH)_3$ has to be performed by adjusting pH to 7-8. It was also observed that the best pH for degrading polycyclic aromatic hydrocarbons by Fenton reaction was 4 (Nadarajah et al., 2002). The same pH range was approved in other studies (Kao and Wu, 2000; Mochidzuki and Takeuchi, 1999; Parra et al., 2000; and Bertanza et al., 2001). It was observed that the pH value was an important parameter for the type of ozone reaction and oxidation products formed during ozonation (Kornmuller and Wiesmann, 1999). At pH≤8, the direct reaction mechanism took place (addition of the $^{\cdot}OH$ to double bond). At alkaline condition, no elimination could be achieved as ozone decayed to hydroxyl radicals. Chain reaction might lead to other radicals and consequently dissolved ozone was diminished. Also at alkaline condition, it was assumed that a great influence of fluid-fluid ozone mass transfer existed. Therefore, it was expected that molecular ozone was the major oxidant at acidic pH. Whereas, a faster and less selective $^{\cdot}OH$ oxidation became dominant at pH >7

as $^{\bullet}OH$ accelerated ozone decomposition, but it resulted to a slow and insufficient removal (Alaton and Balciglu, 2002). It was also observed that at pH 3, COD removal was rather slow but 3 times higher in the presence of UV at acidic pH. This might be due to the selectivity of ozonation for UV absorbance at acidic pH as well as the increased scavenging effect of the high bicarbonate alkalinity present in pharmaceutical wastewater at pH 8. Aromatic compounds and unsaturated double bonds were selectively attacked at alkaline pH. Therefore, UV-sensitive wastewater components were removed at alkaline pH faster than those at acidic pH. Moreover, at high pH the less selectivity of $^{\bullet}OH$ radicals were formed as a result of rapid ozone decomposition. It is known that inorganic and organic compounds in pharmaceutical effluent readily scavenge ozone. Hence, more UV-sensitive parent compounds are removed at alkaline pH than those at acidic pH (Alaton and Balciglu, 2002). The final conversion of organic matter in the wine distillery wastewater, post-treated by ozonation, was defined as follows (Benitez et al., 1999):

$$X_S = \frac{S_0 - S_f}{S_0} \qquad (2.11)$$

where X_s, S_0, and S_f are total substrate removal, substrate initial concentration (gCOD/L), and substrate final concentration (g COD/L) measured after 6 hours of reaction, respectively. It was observed that the conversion was increased when the pH was increased to 9 by combination of UV radiation and H_2O_2 with the ozonation. It can be concluded that the higher pH and ozonatoion rate lead to an improvement of the oxidation process by UV and H_2O_2. It was also observed that pH was an important factor for improving ozonation rate. It was found that when pH of pre-ozonation changes from 2 to 7 and 9, the percentage of convergence of COD (defined by Equation (2.12)) was increased by 23% according to the following equation:

$$\text{Percentage of convergence of COD} = [(COD_o - COD)/COD_o] \times 100 \qquad (2.12)$$

where subscript o indicates the value for non-ozonated wastewater.

However, an increase in biological fraction of wastewater is higher at lower pH. By changing pH from 9 to 2, the biological fraction of wastewater is increased from 25% to 36% (Beltran et al., 1997). These results can be explained by the way ozone attack the compounds present in water. As the hydroxyl radical concentration is increased by increasing pH (decomposition of ozone into free radicals), more reduction in COD was achieved. During the initial periods of ozonation, there was no accumulation of dissolved ozone in water, which indicated that fast and direct ozone reactions was developed (Beltran et al., 1997). It was also observed that the pH 9 had the best effect on COD/COD_o during ozonation. But pH 2 had the least effect on the ratio of COD at any time per initial COD (COD/COD_o). Therefore, it is realized that ozonation at pH 2 cannot decrease the concentration of COD in the wastewater as much as the oznation at pH 9 (Beltran et al., 1997). It was also observed that by removing the carbonates present in municipal wastewater (radical scavengers) and increasing pH from 2 to 9, the percentage convergence of COD varied from 25.5% to 36% during ozonation. The absence of radical scavengers led to an increase in total degradation of wastewater (Beltran et al., 1997). Moreover, it was reported that when tetrahydrofuran and 1,4-dioxane were degraded by photocatalytic process in the presence of carbonate and bicarbonate, the degradation rate of 1,4-dioxane was decreased, but a small increase in the degradation rate of tetrahydrofuran was observed. This increase was believed to be due to the increase in the pH during the reaction (Mehrvar et al., 2001).

2.8 Influence of Temperature on the Degradability of Pollutants

For oil emulsion wastewater oxidized in batch experiment by ozonation, no significant temperature changes have been reported (Beltran et al., 2001). Increasing temperature increases the reduction of COD in a process utilizing Fenton's reagent according to Equation (2.13), in which k′ is the rate constant [$Lmol^{-1}min^{-1}$] (Beltran et al., 2001).

$$k' = 1.43 \times 10^8 \exp(-5334/T)[Fe^{2+}] \quad Lmol^{-1}min^{-1} \qquad (2.13)$$

In the ozonation of the black olive mill, changing the temperature from 10-20°C decreased the concentration of the pollutants by 43%. However, the change in the temperature from 20-30°C caused an increase in the concentration of pollutants by 55%. This could be because when the temperature increases, the kinetic rate constants increase, whereas, the ozone solubility in water decreases. By increasing pH, ozone auto-decomposition in water increases, therefore, the ozone concentration in the liquid decreases (Beltran et al., 2000). No significant effect was observed between 20-30°C for the ozonation of urban wastewater. As a result, it is not convenient to reach temperatures for ozonation above ambient conditions (Beltran et al., 1997).

2.9 Measurement Parameters in Biodegradability

Total organic carbon (TOC) measures the amount of organics, which are depleted to CO_2 during chemical oxidation. In the case of combined AOPs and biological processes, little TOC reduction in the chemical step is desired because mineralization is not intended to achieve in chemical process.

COD is a parameter that measures the oxygen demand necessary for the chemical oxidation of the organics. It can also show the continuous evolution of pollutants during the treatment processes (Beltran et al., 2000).

X_{COD} evaluates the removal of organic matter during the AOP as is shown in Equation (2.14) (Benitez et al., 1999a):

$$X_{COD}=\frac{COD_0-COD_f}{COD_0}\times 100 \qquad (2.14)$$

where X_{COD}, COD_0, and COD_f are total COD removal, initial COD, and final COD [mg/L], respectively.

COD/TOC ratio shows how chemical substrates in the effluent become more oxidized. Lower ratio shows higher degree of oxidation. Samples with smallest

COD/DOC ratio after application of AOP have the largest biodegradable fraction (Parra et al., 2000).

BOD_5 test is an index for the potential extent of a biological oxidation step. Increase in the values of BOD/TOC can indicate either reduction in toxicity or improvement on the biodegradability of the solution. Fast but not reliable biodegradability tests are short line BOD or OUR (oxygen uptake rate) in a respirometer.

To predict the activated sludge response to prompt changes in pollution composition, it is shown that parameters such as COD and BOD_5 used to evaluate the operating performance of the biological processes are often insufficient (Alaton and Balciglu, 2002). Meanwhile, the toxicity tests are very time consuming and expensive. The aerobic bacteria toxicity test measures the oxygen uptake rate (OUR) of the toxicant, but it may also identify the inhibition rate of the aerobic microorganism exposed to the toxicant.

Average oxidation state (AOS) is another parameter that can be considered as another degradability measurement parameter during the treatment of the organics in a chemical reactor. It is defined as (Parra et al., 1999):

$$AOS = \frac{4(TOC - COD)}{TOC} \qquad (2.15)$$

where COD is chemical oxygen demand, and TOC is total organic carbon. AOS takes values between +4 for CO_2 (the most oxidized state of C) and –4 for CH_4 (the most reduced state of C) when the stabilization of this parameter is reached. The photo-treated solution may be considered as biocompatible if only the chemical nature of intermediates is considered.

F/M (ratio of food to microorganisms) is also another important parameter that helps finding the most cost effective treatment. Low F/M implies higher retention time or higher mixed liquor volatile suspended solids (MLVSS) concentration, which negatively affects the cost of the process. Specific oxygen uptake rate (SOUR) also

becomes slower as F/M decreases, but sludge volume index (SVI), which is the ratio of settled sludge volume (mL/L) to suspended solids (mg/L), increases remarkably. Increasing F/M ratio causes a decrease in MLVSS or hydraulic retention time (HRT), which leads to a decrease in COD and BOD reduction. High F/M ratio promotes a log growth of biomass that leads to low BOD removal efficiency, poor settling sludge, and high effluent solids concentration (Beltran et al., 1999). F/M ratio must be adjusted to achieve high organic conversion and cost minimization.

Relative changes in the biodegradability of wastewater samples during advanced oxidation time are expressed in terms of biodegradability factor, f_B, being calculated as follows (Arsalan and Balciglu, 2001):

$$f_B = \frac{BOD_{5,t}(COD_t)^{-1}}{BOD_{5,0}(COD_0)^{-1}} \qquad (2.16)$$

where f_B, COD_o, COD_t, $BOD_{5,t}$, and $BOD_{5,o}$ are biodegradability factor, initial COD, COD at time t, 5-day BOD at time t, and 5-day BOD at time t = 0, respectively.

2.10 Microorganism's Adaptation

The concentration of substrates plays a significant role in the biodegradability of the wastewater (Adams et al., 1997). Sometimes acclimation is necessary to adapt microorganisms to different conditions such as pH and temperature (Beltran et al., 1999). Adaptation can improve the sludge settling characteristic and OUR. The lag time gives an indication of the time required for the unacclimated biomass to acclimate to the organic substrate. The rate of degradation provides a relative measure for the ease of biodegradation after the biomass is acclimated. Some of the pollutants are biodegradable under controlled laboratory conditions following acclimation of a suitable microbial group. However, it is not possible to apply specific acclimated microorganism to wastewater during conventional treatment plants. It was observed that COD removal rate for the distillery wastewater by biological oxidation at pH 7 was much higher than that at pH 4 with nonacclimated microorganisms (Bertlan et al., 2001). The microorganisms

had low activity at acidic pH, however, after a period of acclimation, the biological activity started to improve. Regarding the sludge settleability, sludge volume index (SVI) of the acidic wastewater with acclimated microorganisms was much lower than 100 mg/l (SVI should be between 50-150 mg/L for a good performance of the activated sludge treatment plant).

2.11 Removal of Residual Oxidant

As H_2O_2 is known to be bactericides and inhibitor in the bacteria activity, it should be removed from the pre-treated solution not only to make it suitable for following biological step, but also to stop the oxidation. By choosing an optimal time, H_2O_2 can be removed from the solution completely. Also H_2O_2 less than 200 mg/L may be removed effectively by addition of catalase and keeping the solution for 2 hours without stirring it (Ito et al., 1998). It has been shown that $FeCl_2$ is able to eliminate the residual H_2O_2 (Andreozzi et al., 1998).

2.12 Optimum Situation for Biological Post-Treatment

Theoretical favorable conditions for the bioreactors are in the presence of co-substrates and adapted bacteria, strict pH control, temperature, and aeration for aerobic reactors. Neutralization of the pre-treated solution is necessary as usually the acidity of effluent from the chemical reactor is very high. During the biological post-treatment, the pH should be maintained between 6.5-7.5. After a photo-chemical stage, the effluent may enter into a biological reactor for further treatment if the initial bio-recalcitrant compounds, the inhibitory intermediates, and the residual oxidant, or H_2O_2 have been eliminated and the toxicity test has been carried out.

2.13 Mathematical Models of Chemical and Biological Reactions

A combined process usually consists of a chemical reactor followed by a bioreactor. In the chemical reactor depending on the type of AOPs and the order of the reactions, the compounds could be degraded to a certain point and then it will enter into the bioreactor. In order to be able to gain the maximum benefit from this integration, the residence time of the wastewater in each reactor should be optimized. Moreover, the

initial design of the reactors can be improved by optimization; therefore, the least energy usage and maximum efficiency can be achieved while minimizing the cost. The objective function is the total cost (defined as cost function) and has a close relation with the sum of the liquid phase residence time in chemical and biological reactors which was proposed to be held constant to give a design constraint as follows (Ollis and Scott, 1996):

$$\Theta_C + \Theta_B = \Theta_G = \text{constant} \qquad (2.17)$$

where Θ_C, Θ_B, and Θ_G are chemical, biological, and overall residence time, respectively.

In addition to the objective function, the equality constraints (equations) and the inequality constraints (inequalities) have to be modeled. However, determining the mentioned expressions needs an accurate analysis of the process and well-known physical principles (mass balances, energy balances, empirical relations and implicit concepts). If all of the above expressions are available, a suitable optimization technique could be applied for the whole process. By minimizing the total residence time in both reactors, the optimal residence time in chemical reactor (the most cost consuming treatment) can identify the best residence time in the bioreactor. Moreover, the total efficiency can be defined as (Ollis and Scott, 1996):

$$\eta_C = (C_{Ao}-C_{AC}-C_{SC}) / C_{Ao} \qquad (2.18)$$

$$\eta_B = (C_{SC}-C_{SB}) / C_{Ao} \qquad (2.19)$$

$$\eta_G = (C_{Ao}-C_{SB}-C_{AC}) / C_{Ao} = \eta_C + \eta_B \qquad (2.20)$$

where η is performance efficiency for chemical (η_C), biological (η_B), and overall system or global efficiency (η_G). C_{Ao}, C_{AC}, and C_{SC} are the inlet concentration of compound A, outlet concentration of compound A, and outlet concentration of intermediate S in the chemical reactor, respectively. C_{SB} is the outlet concentration of intermediate S in the bioreactor. The total efficiency can be considered as an equality constraint. Defining a desired efficiency for the whole system can restrict the objective function to give an

answer within its constraints. The effort of most of the researchers working in this area is to develop mathematical models to identify the changes in the concentration of the substrate with respect to time for both chemical and biological reactions, which give the retention time for a compound in each reactor in order to reach to the desired concentration.

2.14 Background (Linear Alkylbenzene Sulfonate)

LAS was first introduced in 1960 as a biodegradable compound to substitute non-biodegradable compounds in detergents. It is produced by sulfonation of linear alkylbenzene with sulfur trioxide. Detergents contain 5-25% LAS, and the length of its chain ranges from C_{10} to C_{14} (WHO, 1996). The concentration of LAS in the influent of domestic wastewater treatment plants was reported in the range of 1 mg/L to 5 mg/L (Kaiser et al., 1997). It has also been reported that the influent and effluent concentrations of LAS in the activated sludge process from ten U.S. domestic wastewater treatment plants range from 3.0-7.7 mg/L and 0.003-0.086 mg/L, respectively (Trehy et al., 1995). The alkyl chain lengths usually range from C_{10} to C_{14} in the United States, and C_{10} to C_{13} in Europe (Huang et al., 2000). As it was reported that higher concentration of LAS does not respond to biological treatments, many investigators have tried degrading LAS using chemical processes. Table 2.3 shows some of the works carried on chemical treatment of LAS.

The intermediates produced by wet air oxidation of LAS were known as volatile fatty acids (VFA), sulfophenyl(di) aldehyde (SP(d)A), and sulfophenyl(di) carboxylate (SP(d)C). It has also been reported that SP(d)Cs are refractory to biodegradation (Patterson et al., 2002). Photocatalytic degradation of LAS with TiO_2 was documented to produce sodiumbenzene sulfonate (BS) and sodium dodecylsulfate (DS) (Venhuis and Mehrvar, 2004).

2.15 Environmental Concerns and Biodegradability of LAS

LAS is the major anthropogenic source of organic compounds in primary sludge in municipal wastewater treatment plants, as it can be adsorbed onto suspended solids

ranging from 30 to 70% (Berna et al., 1989) and, hence, escaping aerobic treatment. It has also been identified in surface water supplies in the concentration of lower than µg/L (Tabor and Barber, 1996) and in drinking water in the range of 0.001-0.008 mg/L in different countries (WHO, 1996). It is also able to enhance the solubility of compounds in water, which are otherwise insoluble in other matrices; hence, it can reduce the resistance to mass transfer (Vazquez et al., 2000).

High mobility of LAS due to its high water solubility and its polarity makes it to be a hazardous contaminant in ground and surface water supplies (Reemtsma, 1996). LAS can be degraded in activated sludge system by consortia of aerobic microorganisms (Van Ginkel, 1996) up to 99.5% and its intermediates up to 99.1% (Trehy et al., 1996). On the other hand, it has been reported that the intermediates produced by biological treatments are 10-100 times less toxic than the parent compounds (WHO, 1996).

The solid residence time (SRT) of mixed culture is very important to preserve adequate surfactants, degrading microorganism in the wastewater treatment plant (Van Ginkel, 1996). Moreover, it was found that in the activated sludge procedure the effluent concentration of LAS was a function of influent concentration when the hydraulic residence time (HRT) was less that 10 h (Kaiser et al., 1997). Some residue of LAS and its intermediates can enter the receiving water by the effluent if the HRT is not chosen properly. Furthermore, some of the countries discharge their effluents either directly or indirectly due to the malfunctioning of the treatment facilities into rivers. Another way that LAS can enter the environment is by using the sludge resulted from wastewater treatment plants on the agricultural lands. As a result, the aquatic and terrestrial organisms are exposed to surfactants.

LAS has shown toxic effects on the Nitrosomonas and Nitrosopria strains (Brandt et al., 2001). The inhibitory effect was observed to be more on growth rate and viability than that on metabolic activity. LAS has shown inhibitory effect on anaerobic biological treatment (Morales et al., 2001, and Gavala and Ahring, 2002). It is also reported that methanogenic and acidogenic microbiotes are sensitive to LAS although after a period of adaptation, there could be a decrease of the inhibitory effect of LAS on

Table 2.3: Chemical degradation of LAS by different advanced oxidation processes

Initial Concentration	*Oxidation scheme*	*Grade*	**Reference**
0.25 to 2 mg/L	Fenton's reaction	90mg $FeSO_4$/L, 60mg H_2O_2/L 95% degraded.	Lin et al., 1999
1000 mg/L	wet air oxidation	LAS was readily oxidized under mild condition	Mantzavinos et al., 2000
1g /L	Fenton's reaction	30 mg$FeSO_4$/L 60 mgH_2O_2/L 38% degraded	Cuzzola et al., 2001
1600 mg/dm^3	wet air oxidation	Increased the biodegradability under higher temperature	Patterson et al., 2002
2.8×10^{-5} mol/dm^3	TiO_2+ UV-C	Conversion rate can be up to 93% in 120 min	Saien et al., 2003
125 mg/L	TiO_2+UV_{365}	Optimum concentration of TiO_2=3 g/L gave r_o=1.7 mg LAS/L.min	Venhuis and Mehrvar, 2004
138 mg/L	UV-254 nm	70% removal in 300 min	Venhuis and Mehrvar, 2004

them (Morales et al., 2001). As the primary sludge stabilizes anaerobically and LAS is not biodegradable by anaerobic treatment, this sludge has environmental effect due to LAS potential for acute toxicity (Hofer et al., 1995, and Lewis, 1991).

It has been reported that LAS in the concentrations of 1-3-10 mg/L is biodegradable under aerobic activated sludge treatment (Rittmann et al., 2001), and its degradation follows Monod's equation over the ranges of 0.1-20 mg/L (Rittmann et al., 2001). Moreover, it has been reported that the fate of LAS can follow first order kinetics for the similar ranges of concentrations (Huang et al., 2000, and Zhang et al., 1999). Also, the effect of biodegradation kinetics should be separated from the sorption kinetics (Rittmann et al., 2001). However, the growth rate of mixed culture of microorganisms can be inhibited at the concentration of 95 mg/L (WHO, 1996). The minimum concentration of LAS which makes it toxic is not known (Patterson et al., 2002). Acute toxicity LC_{50} for different species differs from one to another, as saline water species are more sensitive to LAS than freshwater (WHO, 1996).

LAS biodegradation follows two regimes: 1) primary degradation, which oxidizes alkyl chain resulting sulfophenyl(di)carboxylates, and 2) ultimate biodegradation, which cleavage the phenyl ring and removing sulfonate group. Finally it is converted into CO_2, H_2O, inorganic salts, and biomass. The bacteria that are capable of breaking the ring are not common (Patterson et al., 2002).

It was also investigated that ultimate biodegradation of LAS cannot be achieved at any concentration. Although the inhibitory effect of LAS increases as the concentration of LAS increases and inhibits primary degradation. It suggests that LAS is recalcitrant at very high concentration (3000 mg/dm^3) (Patterson et al., 2002). This can be due to the chemical toxicity and the destruction of cell membrane caused by high concentration of LAS (Patterson et al., 2002). It has been reported that ultimate biodegradation is possible under suitable condition and limiting the concentration of LAS to that found in environment (WHO, 1996).

Hydrophobic and hydrophilic parts of LAS can react with polar and apolar structures such as proteins and peptides. This binding can modify the structure and charge of proteins and peptides; furthermore, it can modify their biological function (Cserhati et al., 2002). Therefore, LAS can accumulate in living organisms, as it can inhibit in the hepatic liposomes of rat and inhibit the activity of some of the enzymes (Cserhati et al., 2002).

LAS can also damage human skin and irritate eyes (WHO, 1996). It has been established that the longer the alkylbenzene chain is, the more severe the skin irritancy potential can be (Cserhati et al., 2002). LAS and its intermediates resulting from biological treatments are not estrogenic (Navas et al., 1999).

2.16 Concluding Remarks

For the removal of recalcitrant organics, biological processes (which are economically beneficial) cannot be chosen, but a variety of non-biological processes exist which can be divided into oxidative and reductive technologies. Among all of them, photochemical degradation processes, or advanced oxidation processes (AOPs), have become increasingly popular in recent years as alternative or complementary treatment. The primary use of AOPs is to destroy organic pollutants in water by oxidation. However, depending on the targeted effluent quality, extended treatment duration may impose unaffordable high operating costs due to high energy and chemical oxidation requirements of AOPs. A recently proposed technique to cope with the environmental regulations and also environmentally safer and economically more attractive strategy is biodegradability enhancement of raw and biological pretreated industrial effluents by applying chemical oxidative pretreatment, in which two or three consecutive chemical and biochemical processes steps are involved. Moreover, as the complete destruction of wastewater pollutants can be hardly achieved by a single treatment method, combination of biological and chemical treatment is often the way to optimize the overall process. Depending on water quality, final requirement and economical aspects, some processes are better suited than others for each case. The strategy of coupling chemical and

biological reactors is not necessarily a unique solution. The practical applications of these integrated processes require a detailed study on kinetic modeling and economic aspects. Chemical, biological, and kinetic studies should be made to ensure that the pre-treatment or the post-treatment increase the biocompatibility of wastewater. A balance between added cost of AOPs and desired quality of treated wastewater is highly recommended to make sure that the AOP pre-treatment induces a beneficial effect on the bio-compatibility of the treated wastewater (or the biological pre-treatment has beneficial effect on the following chemical step).

It has been documented that complete mineralization of LAS is not achievable under biological degradation, especially when the concentration of LAS is high (Zhang et al, 1998). Moreover, LAS can be toxic to microorganisms. Therefore, advanced oxidation processes can be a good choice to chemically degrade LAS. However, as AOP is a relatively expensive method, combination of AOP and biological technique could be a better option. Furthermore, as ultimate biodegradation of LAS involves breakage of phenyl ring, the bacteria that are capable of breaking the ring are not common. Therefore, adaptation of bacteria to LAS can increase the rate of biodegradation.

CHAPTER 3

EXPERIMENTAL WORK

MATERIALS, METHODS, AND EQUIPMENT

3.1 Materials

The following materials were used in chemical and biological experiments.

3.1.1 Linear Alkylbenzene Sulfonate (LAS)

LAS is the sodium salt of dodecylbenzenesulfonic acid, a mixture of phenyl-substituted alkyl chain (Figure 3.1). Sodium salt of dodecylbenzenesulfonic acid was purchased from Aldrich Company to study the degradation characteristics of LAS. The alkyl chain contains 12 carbons with the molecular weight of 348.48. The scanning of UV-spectrophotometer showed that the maximum absorbance for this compound is at 268 nm (Figure 3.2).

3.1.2 Activated Sludge

Activated sludge was collected from North Toronto sewage treatment plant, located in the Don Valley. The concentration of sludge (dry weight) was 4.8 g/L and the amount of LAS initially present in the sludge of treatment plant was 4 mg/L.

3.1.3 Hydrogen Peroxide

Hydrogen peroxide used in all of the experiments was purchased from Aldrich. It was 50 wt% (remaining was water) with molecular weight of 34.04, and density of 1.11 g/cm^3. It should be stored at 2 - 8°C to retain its quality.

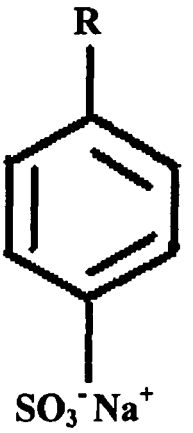

Figure 3.1: Molecular structure of LAS, R represents the alkyl chain

$R= (CH_2)_{11}CH_3$.

Molecular weight = 348.48.

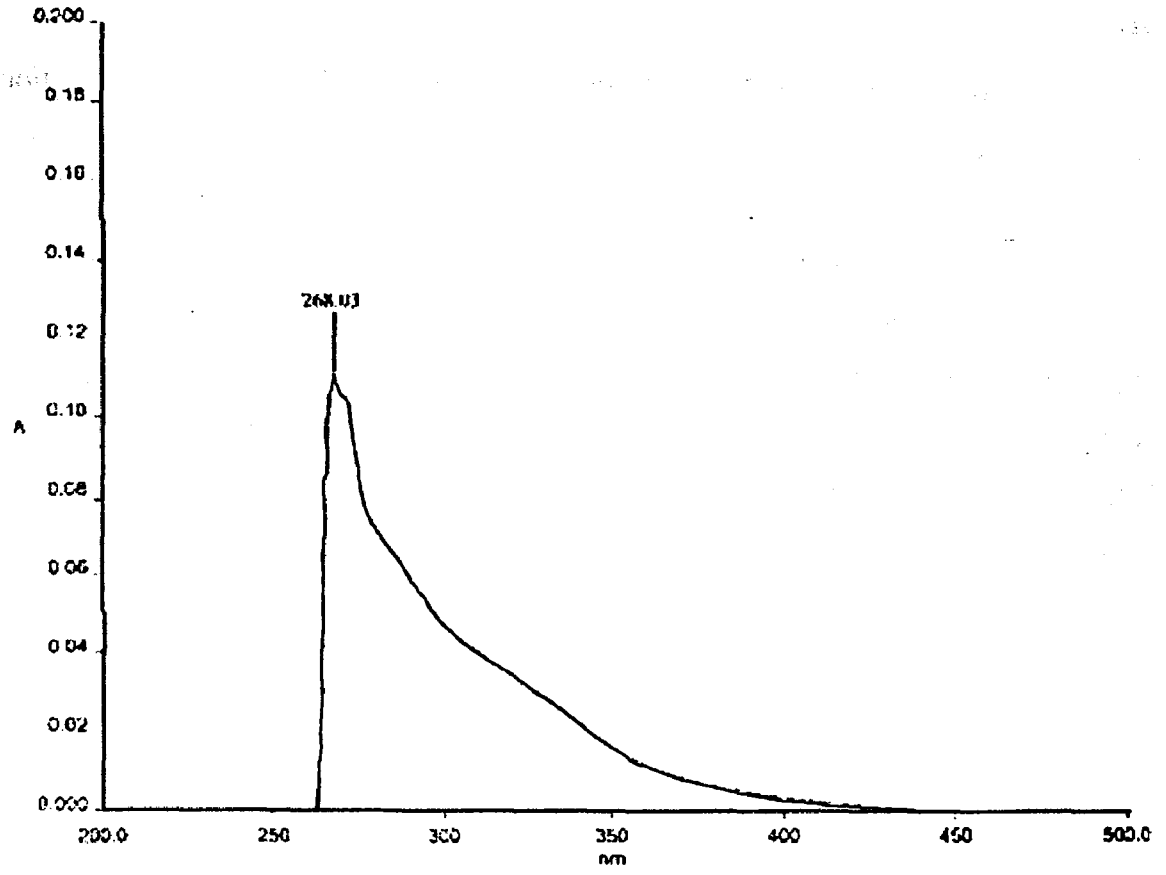

Figure 3.2. The scanning of LAS with UV-spectrophotometer, the concentration of LAS was 100 mg/L.

3.1.4 Catalase

H_2O_2 concentration less than 200 mg/L may be removed effectively by addition of a catalase (2.5 units/mL) by keeping the solution for 2 hours without stirring (Ito et al., 1998). Each molecule of catalase is a tetramer of four polypeptide chains. Each chain is composed of more than 500 amino acids. Located within this tetramer are four porphyrin heme groups that are very much like the familiar hemoglobins, cytochromes, chlorophylls and nitrogen-fixing enzymes in legumes. The heme group is responsible for catalase's enzymatic activity. The mechanism of removal is catalytic decomposition of H_2O_2 into oxygen and water. The chemistry of catalase catalysis has not been precisely solved yet. But the following has been proposed. The catalytic process is thought to occur in two stages (http://biology.kenyon.edu/BMB/Chime/catalase, 2004)

$$H_2O_2 + Fe(III)\text{-}E \rightarrow H_2O + O{=}Fe(IV)\text{-}E\ (1) \qquad (3.1)$$

$$H_2O_2 + O{=}Fe(IV)\text{-}E \rightarrow H_2O + Fe(III)\text{-}E\ (2) + O_2 \qquad (3.2)$$

where Fe-E represents the iron center of the heme attached to the rest of the enzyme (E) (Figure 3.3). Heme consists of a protoporphyrin ring and a central iron (Fe) atom. A protoporphyrin ring is made up of four pyrrole rings linked by methane bridges. Four methyl, two vinyls, and two propionate side chains are attached (http://crystal.uah.edu, 2000).

This enzyme is available in two forms: 1) bovine liver 2) *Aspergillis niger*. The amount of enzyme added depends on its activity and can be found on its label. However, the impact of the enzyme on the sample should be known. The catalase which was used in this experiment was bovine liver type, purchased from SIGMA Company. Molecular weight of catalase is 250,000, and it is stable for 6-12 months when stored at 5°C. It was mentioned on the package that one unit of this catalase has the ability of decomposing 1 μmol of H_2O_2 per minute at pH equal to 7.0 at 25 °C. Each 2380 unit of this catalase is equivalent to 1 mg of catalase.

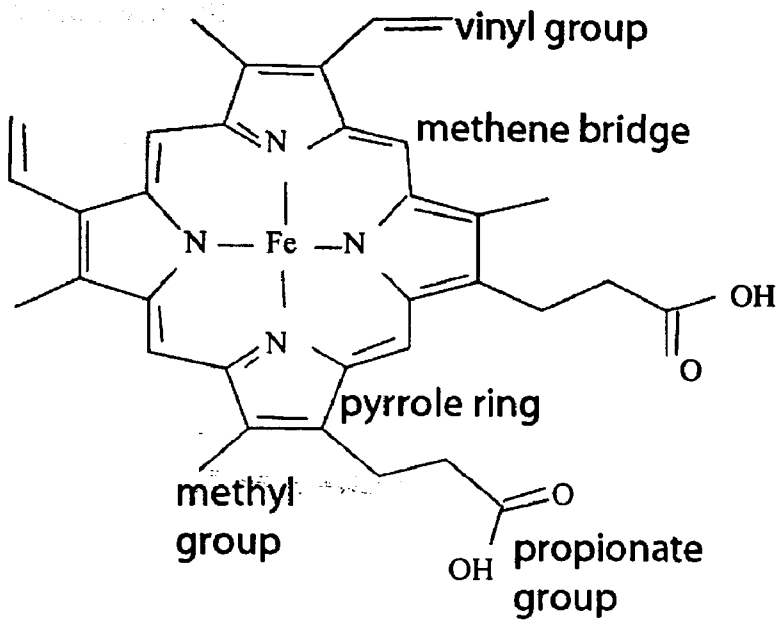

Figure 3.3. Molecular structure of Heme group attaching to the rest of the enzyme, representing the catalase enzyme.

3.1.5 Chemicals for Analysis of LAS

Chloroform ($CHCl_3$, 99.98%) was purchased from EM Science (affiliated with Merck, Germany) and used as received. Methylene blue reagent was purchased from Aldrich. To make 100 mg of methylene blue, it was dissolved in 100 mL of distilled water (stock solution). Thirty mL of the stock solution was transferred to 1000 mL flask and 500 mL of water, 41 mL of 6N H_2SO_4, and 50g Na $H_2PO_4.H_2O$ were added. The solution was diluted to 1000 mL by distilled water after dissolving thoroughly.

Wash solution was prepared by adding 41 mL of 6N H_2SO_4 to 500 mL of distilled water, and 50 g of $NaH_2PO_4.H_2O$ was added to that solution. The solution was diluted to 1000 mL by distilled water after dissolving thoroughly.

Standard LAS solution was prepared by diluting the appropriate weight of LAS, with distilled water.

Sodium hydroxide (NaOH) was 1N, and sulfuric acid (H_2SO_4) was 1N and 6 N. Phenolphthalein indicator solution was purchased from Aldrich Company and used as received.

3.1.6 Nutrients for Biological Measurements

Reagents used for biological measurements are as follows (Standard Methods, 1998):

Nutrients: consist of phosphate buffer solution, magnesium sulfate solution, ferric chloride solution, and calcium chloride solution. These nutrients are essential for the growth of microorganisms.

Phosphate buffer solution: 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $NaHPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl was dissolved in distilled water and diluted to 1000 mL. The pH was 7.2 without adjustment. To keep the pH constant, buffer solution should be added to the diluted water.

Magnesium sulfate solution: 22.5 g $MgSO_4 \cdot 7H_2O$ were dissolved in distilled water and diluted to 1000 mL.

Ferric chloride solution: 0.25 g $FeCl_3 \cdot 6H_2O$ were dissolved in distilled water and diluted to 1000 mL.

Calcium chloride solution: 27.5 g $CaCl_2$ were dissolved in distilled water and diluted to 1000 mL.

3.1.7 Standard Check Solution for Biological Measurements

Standard check solution: was made of glucose-glutamic acid solution. Glucose and glutamic acid were first dried at 103°C in the oven for 1 h. 150 mg of glucose and 150 mg of glutamic acid were dissolved in distilled water and diluted to 1000 mL. This solution was prepared before each use.

3.1.8 Seed Source

Seed source: Seed might also be added to provide enough microbial population. Polyseed (interlab) was used as the seed source. It was a blend of wide range of bacteria (mixed culture) prepared to use in the BOD_5 test.

3.1.9 Reagents for Hydrogen Peroxide Analysis

DMP (2,9-dimethyl-1,10-phenanthroline) reagent (99%) was purchased from Sigma Co. One gram of it was dissolved in 100 mL of ethanol and stored in dark bottle at 4°C. 0.01 M of copper(II) sulphate solution was made by dissolving copper(II) sulphate into distilled water. Moreover, a phosphate buffer solution (0.1M) was prepared from 13.5 g K_2HPO_4 and 12 g NaH_2PO_4. The pH of this solution should be adjusted to 7 by H_2SO_4 (1N) and NaOH (1N) (Kosaka et al., 1998).

3.1.10 Check Kit for Free Chlorine

Chlorine check kit consisted of N,N-diethyl-p –phenylenediamine (DPD) tablets (VWR) and a colorimetric kit. The detection range was between 0.2-2 and 2-10 mg/L free chlorine. To perform the experiment the vial should be filled with water up to the marked point, which would be 2 mL, and one tablet should be added to the water. After crushing the tablet and mixing it thoroughly, the color produced in the vial should be compared to the colors on the kit. Each color on the kit was corresponding to a certain concentration.

By matching to the produced color in the vial to the appropriate color, the concentration of the free chlorine in the water was found in terms of mg/L of free chlorine.

3.2 Equipment and Experimental Methods

This section has been divided into two parts, photolytic and biological processes. Experimental set-up, analytical techniques, and equipment required for each photolytic and biological treatment are described separately.

PHOTOLYTIC PROCESSES

3.2.1 Experimental Set-Up (Photoreactor)

The experiments were performed in a 76.6 L cylindrical batch photoreactor, with the outside diameter of 32 cm and nominal length of 102 cm (Figure 3.4). Six immersed low pressure mercury UV lamps, with the maximum wavelength of 253.7 nm and 40 W each, were symmetrically placed inside the photoreactor. The photoreactor was equipped with 3 mixers, placed on the main axis of the cylindrical photoreactor. The speed of these mixers could be adjusted as desired. The total volume of the feed tank was 210 L, and the minimum volume of water in the tank for operation should be 94 L. A centrifugal pump recirculated the solution into the reactor. The flow rate of the feed was adjustable in gallons per minute (GPM) or liters per minute (LPM). The whole system was equipped with a water bath (Neslab, RTE series) to keep the temperature constant at 20 ± 0.01°C during the experiment. The volume of water in the water bath was kept between 10-12 L. Prior to start the each experiment, 10 g of LAS was added to the 100 L water inside the feed tank. The whole system was turned on, including the water bath and the pump for the period of maximum 1 h, the UV lamps were all off with the feed tank lid closed. After that period which was called stabilization period, the 6 UV lamps were turned on simultaneously. Furthermore, the temperature of the reactor was kept constant at 20°C using the water bath during all the experiment, therefore, the effect of increasing the temperature due to the UV lamps have been eliminated.

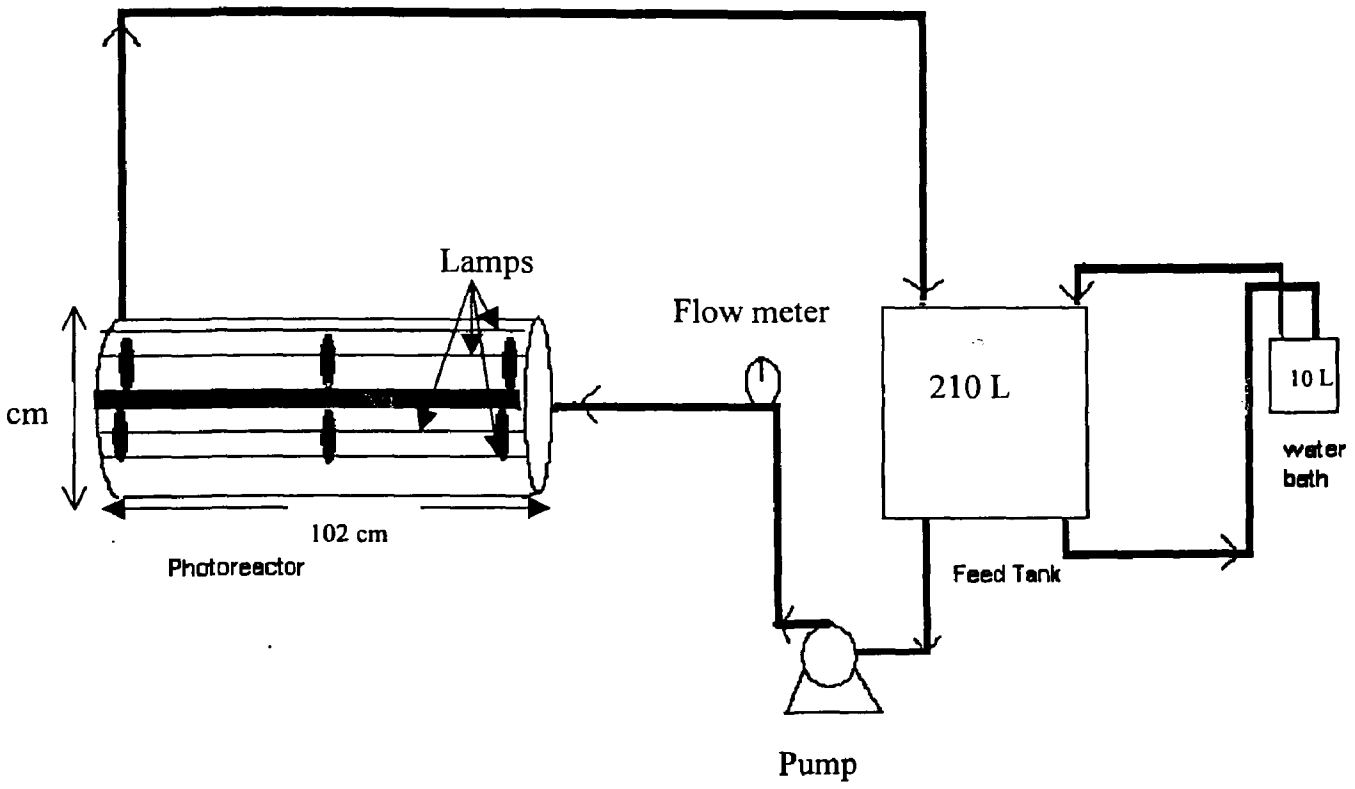

Figure 3.4. Schematic diagram of the cylindrical photolytic reactor.

Three samples were taken every hour from the effluent of the reactor (inlet to the feed tank). and analyzed immediately. The initial concentration of LAS was 100 mg/L. After taking the last sample, the pump was shut down and the lamps were turned off. The water bath was also turned off. The reactor was drained into the feed tank by opening its side valve. After collecting all of the solution inside the feed tank, the tank was drained by pumping the water out. The whole system was cleaned and made ready for the next run.

3.2.2 pH Measurement

pH measurements and its control are important in water treatment systems. As in biological treatment, the life of microorganisms highly depends on a certain range of pH, in chemical treatment, the control of pH is also crucial as changing pH can have a significant effect on the reaction. Moreover, in advance oxidation processes measurements of pH can show that the reaction is moving toward production of acid, which is the expected path.

pH measurements are mainly done by potentiometric measurement using a glass indicator electrode and a reference electrode. The pH meter used in these experiments was model 230 A^+ from Thermo Orion, in which the indicator and reference electrodes were combined into one. The buffers of pH = 4 and pH = 7 were used to calibrate the meter before pH was measured. Those two buffers were chosen in the expected sample range. The calibration was done each day by determining the slope of the electrode. Also calibration can determine if the electrode was working properly.

3.2.3 UV Spectrophotometer

A UV spectrophotometer was used for quantification of color in terms of absorbance. The spectrophotometer used was Ultrospec 1100 *pro* UV/Vis Spectrophotometer (Biochrom Ltd.), with the ability to measure the absorbance, percent Transmission, and concentration values. It can measure absorbance of samples, based on the amount of light that has passed through a sample relative to a blank. While percent transmission mode measures the amount of light that has passed through a sample relative to a blank, it displays the result as a percentage. Concentration mode is used

when a conversion factor is known, and is required to convert the absorbance measurement for a sample at a specific wavelength into a concentration. The wavelength range was within 200-900 nm with the accuracy of ±2 nm.

The light sources are tungsten halogen and deuterium arc (Ultrospec 1100 *pro*). The instrument has a one cell compartment. The detector was from single solid state silicon photodiode. The cell used for the experiments was a standard rectangular quartz cell (optical glass). The cell's volume was 3 mL, and has a polytetrafluoroethylene (PTFE) cover.

3.2.4 Preparation of the Initial Solution for Photolytic Experiments

Ten g of the dodecylbenzenesulfonic acid (flaked sodium salt solid), was added to 100 L of tap water inside the feed tank. Therefore, the concentration of LAS inside the system would be 100 mg/L. The solution was circulated for one hour with lights off in order to make the solution homogeneous throughout the system.

3.2.5 Measurements of Linear Alkylbenzene Sulfonate

The detection method of LAS was based on the transfer of methylene blue active substance (MBAS), which is a cationic dye, from an aqueous solution into an immiscible phase containing anionic surfactant. This transfer is possible by ion pair formation of anionic surfactant and methylene blue. Excess methylene blue was extracted into chloroform and the blue color in the chloroform would be read at 652 nm by UV Spectrophotometer (Standard Methods, 1998). The interference result from all other methylene blue active substances present in the solution. Moreover, cationic surfactants can have a negative effect on the determination as they can compete with methylene blue in the formation of the pairs. Organic sulfonates, sulfates, carboxylates, and phenols can also have positive interference, although their recovery is almost complete by aqueous backwash of the extracted color in chloroform, therefore, the concentration of LAS has been reported here as mg/L MBAS due to the positive error that was explained before. The reagents used in this experiment were those explained in Section 3.1.5.

The samples taken periodically from the effluent of the reactor (inlet to the feed tank) were diluted, so that the measured concentration would be below 2 mg/L. Two mL of samples were diluted to 100 mL. Two mL of the diluted samples were taken; phenolphthalein indicator solution was added drop wise to each sample. The samples were make alkaline by drop-wise addition of NaOH 1N, and the pink color was removed by adding drop wise of H_2SO_4 1N. One mL of chloroform and 2.5 mL of methylene blue were added to each sample and shaken vigorously for 30 s. The aqueous phase was taken to another tube and the extraction procedure was repeated for 3 times. All of the $CHCl_3$ extracts were combined and 5 mL of wash solution were added to them and shaken vigorously for 30 S. The wash solution was extracted twice by $CHCl_3$, 1 mL each time, and the extracts were diluted with $CHCl_3$ to 10 mL. The absorbance at 652 nm were determined against a blank of $CHCl_3$ using the spectrophotometer (Section 3.2.3). Standard curve was prepared by determining the absorbance of known concentrations of standard solutions and the absorbance of each sample was converted into concentration using this curve and dilution factor. Figure 3.5 illustrates the calibration curve for LAS by the mentioned method.

3.2.6 Measurement of Chemical Oxygen Demand (COD)

COD was used to measure the amount of oxygen require to oxidize the organics in a solution by a powerful chemical oxidant. This oxidation is usually done by potassium dichromate in acidic solution.

The drawbacks of this method are as follows (Eckenfelder, 2000):

1. COD cannot oxidize aromatics such as benzene and volatile straight-chain aliphatic compounds; therefore, it is not measured in the COD tests. Therefore, it is lower than theoretical oxygen demand (ThOD).
2. Some reduced substances, such as sulfides, sulfites, and ferrous iron, would also be oxidized and measured as COD.

COD can be determined by different methods, however, as the predicted COD for the samples was above 50 mg/L and there was not any suspended solid present in the sample, the closed refluxed method was chosen as it is more economical over this range of concentration (Standard Method, 1998). This method is based on the oxidation of organics by a mixture of $K_2Cr_2O_7$ and sulfuric acid. Potassium dichromate is a strong oxidizing agent under acidic conditions. (Acidity is usually achieved by the addition of sulfuric acid.) The reaction of potassium dichromate with organic compounds is given by:

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \rightarrow nCO_2 + (a+8d-3c)/2\ H_2O + cNH_4^+ + 2dCr^{3+} \qquad (3.3)$$

where $d = 2n/3 + a/6 - b/3 - c/2$. Most commonly, a 0.25 N solution of potassium dichromate is used for COD determination, although for samples with COD below 50 mg/L, a lower concentration of potassium dichromate is preferred. In the process of oxidizing the organic substances found in the water sample, potassium dichromate is reduced, forming Cr^{3+}. The amount of Cr^{3+} is determined after oxidization is complete, and is used as an indirect measure of the organic contents of the water sample.

In the colorimetric method (closed reflux), oxygen consumption is measured against standards at 600 nm with spectrophotometer. The reagents were prepared in a vials purchased from Bioscience, Inc., in the range of 20-900 mg/L. Each vial contained sulfuric acid, potassium dichromate, silver sulfate (catalyst), mercuric sulfate (reduce the effect of halides), and sulfamic acid. Standard potassium hydrogen phthalate (KHP) was crushed and then dried to constant weight at 120°C. 425 mg of KHP was dissolved in distilled water and diluted to 1000 mg/L. This solution had a theoretical COD of 500 mg/L O_2. Different concentrations of this solution were prepared as reference to prepare calibration curve.

The COD reactor (Bioscience, Inc.) should be preheated to 150 ± 2°C prior to preparing the vials. The vials with the volume of approximately 10 mL were uncapped carefully and 2.5 ml of sample solution was added to the vial from the side of the vial

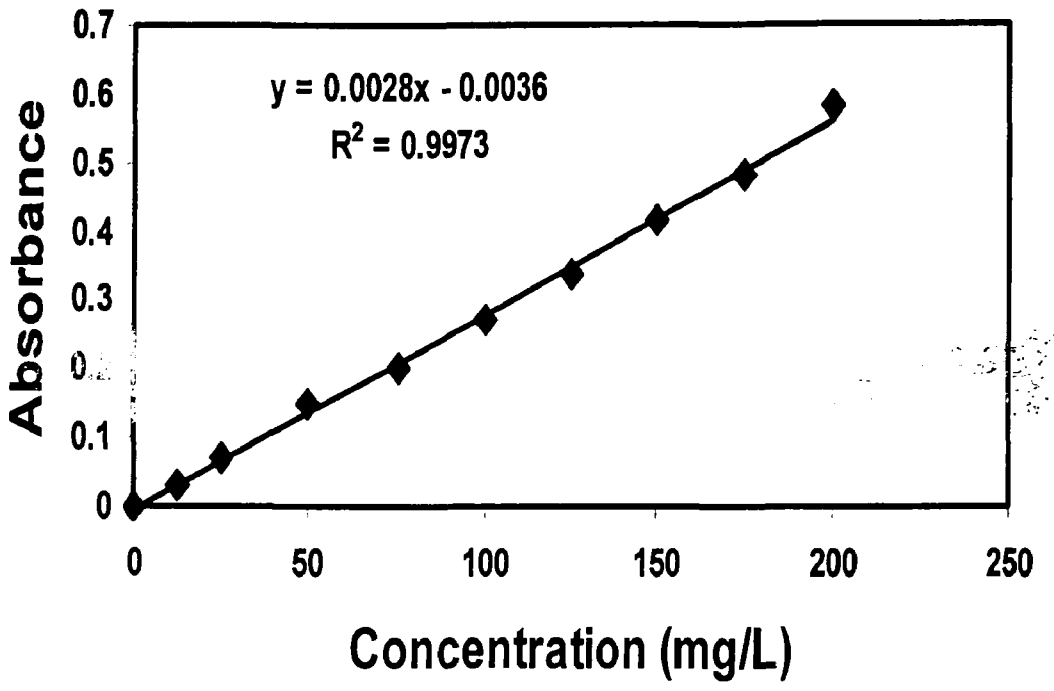

Figure 3.5. The calibration curve for LAS using MBAS method.

Absorbance, or optical density, is a measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light.

with extreme caution. The sample produced a layer on top of the reagents, therefore, the vials were recapped and inverted several times to mix thoroughly.The vial was then ready to be placed in the reactor at 150°C for 2 hours for complete reaction. After 2 hours, the vials were placed in a rack in room temperature to cool off to the room temperature. The absorbance at 600 nm was measured against a blank (distilled water) by spectrophotometer. The standard carve was prepared by adding an appropriate concentration of potassium hydrogen phthalate (KHP) to each vial. The same procedures were followed to prepare the standards and the blank. Figure 3.6 provides a calibration cure for the determination of COD using the above mentioned procedures.

3.2.7 Theoretical Oxygen Demand (ThOD)

Theoretical oxygen demand is the amount of oxygen required for full oxidation of organics. It can be calculated by the stoichiometry of oxidation.

3.2.8. Initial Rate

The initial rate was defined as slope of the concentration versus time at time equal to 0.

3.2.9 Free Chlorine Experiment

It has been reported that free chlorine could react as an oxidant under UV light, and hence, increase the rate of reaction (Zhou and Smith, 2001). Furthermore, the presence of free chlorine could interfere with the determination of a specific compound. For the BOD test, elimination of free chlorine is necessary. Also for determination of H_2O_2, in some methods, free chlorine works as interference. To eliminate the free chlorine present in tap water, chlorine checkit consisted of DPD (N,N-diethyl-p-phenylenediamine) tablets, were used for the following reasons:

1. To determine the initial concentration of free chlorine in the tap water, that was used to prepare the solution.
2. To determine the effect of elimination of free chlorine.

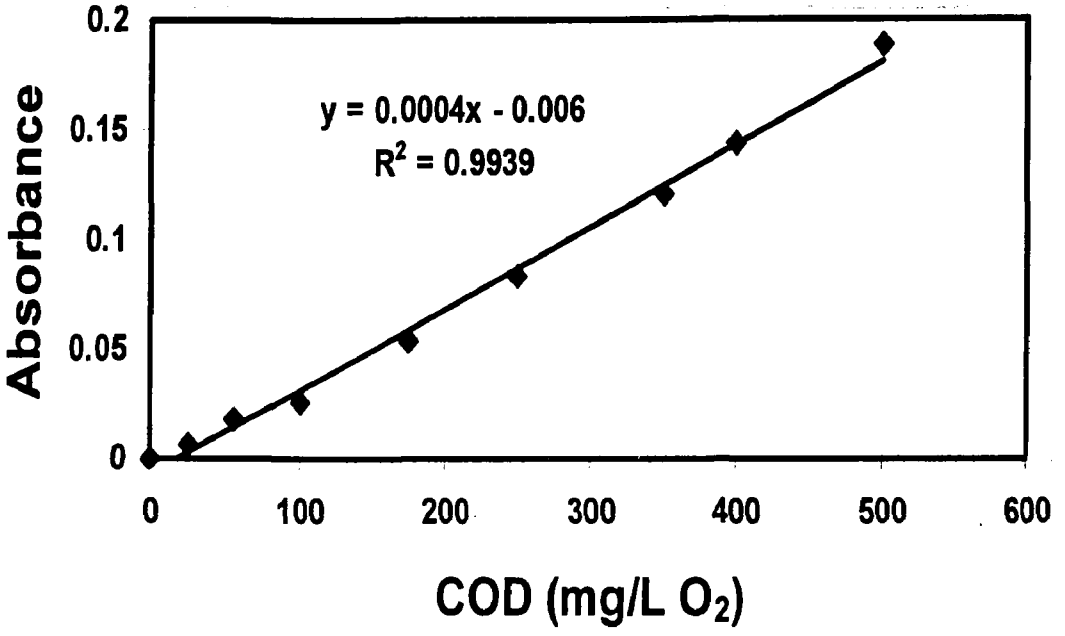

Figure 3.6. Calibration curve for determination of COD, based on the closed refluxed method. Absorbance, or optical density, is a measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light.

The DPD method is based on the reaction of the free chlorine with DPD indicator, which produces a red color instantly. Therefore, it was necessary to remove the free chlorine presence in the tap water before adding LAS to eliminate any increase in the degradation of LAS due to free chlorine. The concentration of free chlorine in the tap water during different runs was examined and it was observed that it varies between 0-1.5 mg/L. Therefore, prior the each run, the feed tank was filled with water and let the free chlorine evaporate during the night by keeping the feed tank lid open. It was observed that this range of concentration of free chlorine could be eliminated by this method successfully. The experiments were conducted at least three times and the error bars which are the standard divisions of the results at each time were calculated.

3.2.10 Dark Reaction Experiment

To quantify the loss of LAS through adsorption, dark reaction experiments were conducted. The changes in the initial concentration of LAS were monitored after 1 h. of stabilization period. For the period of 6 h, the UV lamps were all off with the feed tank lid closed. Three samples were taken every hour from the effluent of the reactor (inlet to the feed tank). In order to minimize the environmental effects on the degradation of LAS, the samples were analyzed immediately.

3.2.11 Photoreaction of LAS by UV-254

In this experiment, all conditions were kept the same as to those of the dark reaction except that the 6 UV lamps were turned on simultaneously after the stabilization period. Furthermore, the temperature of the reactor was kept constant at 20°C using the water bath during all the experiment, therefore, the effect of increasing the temperature due to the UV lamps have been eliminated. Three samples were taken every hour and analyzed immediately. The initial concentration of LAS was 100 mg/L.

3.2.12 Mixing Speed Experiment

In order to determine the effect of mixing speed on the photolytic degradation rate of LAS, different experiments were conducted at different mixing speeds, with constant flow rates. There are different numbers on the mixer ranging from 0-10, and each number

is associated with different speed. Table 4.1 shows the mixing speed associated with each number. The rotational speed of each number was measured by Tachometer (DT-105 A, Electromatic Equipment Co., Inc.).

BIOLOGICAL PROCESSES

3.2.13 Experimental Set-Up (Sequential Batch Reactor)

Sequential batch reactor (SBR) is a suspended growth, mixed- culture reactor. However, it can be categorized as activated sludge treatment (Figure 3.7). Common activated sludge systems are space oriented, however, SBR is time oriented. It is a periodic process which consist of tanks working on a fill and draw basis. The cycles in each tank are divided into the following periods:

- Fill,
- react,
- settle,
- draw, and idle.

During the fill period, the wastewater is added to the tank which contains biomass. Biomass is expressed in term of volatile mixed liquor suspended solids which exist in the tank from the previous cycles. Fill period could be static fill (no mixing and no aeration), mixed fill (mixing and no aeration), and aerated fill (mixing and aeration). Type of filling period depends on the characteristic of wastewater. However the wastewater should be completely mixed in the system before the react period. In the react period, the reactions which have started in the fill period are completed. Aeration is an essential operation in this period. Also the system should have sufficient mixing to increase mass transfer. The react period usually takes 35% of the whole cycle's time. The next period is settlement. The entire tank works as clarifier and separates sludge from the liquor. After the settlement period, effluent is ready to be withdrawn. During this period there should not be any agitation in the system. After drawing, the tank is ready for the new influent. It can be left idle between draw and fill period. This period is required if wasting sludge is necessary.

The reactor used in the experiments had a 7 L volume and the aeration was done by air diffuser as shown in Figure 3.7.

3.2.14 Incubator

The incubator was used to provide a constant temperature during the period of biological reaction. Temperature is a crucial factor on microorganism. It was set at 20°C as it was the optimum temperature for the BOD tests. Moreover, as it could be set to have horizontal plane rotary motion in a 1" circular orbit simultaneously, it was used in the shake flask experiments.

The incubator used was C-25KC classic refrigerated incubator shaker (New Brunswick Scientific Co., Inc.). The speed of this model could be set between 40-400 rpm (with the accuracy of ±2 rpm) and the accuracy for the temperature was ±0.25°C.

3.2.15 Dissolved Oxygen Meter

The oxygen is also an important factor on the life and growth of aerobic microorganism. Therefore, it has to be controlled to avoid the death of aerobic microorganism. Mainly the saturated concentration of oxygen in the aerated water at 20°C can be between 8-10. As a result, the decrease of oxygen in that water could suggest that it is being used by the microorganisms (provided that there is no other way for the water to loss its dissolved oxygen content).

The dissolved oxygen (DO) was measured by YSI 58 dissolved oxygen meter. It has a probe consists of an electrode (compacting cathode and anode in a one bar) and an electrolyte (KCl). They are separated from the outer liquid by a membrane. The anode and cathode are made of silver and gold, respectively. The reduction of oxygen in cathode is proportional to concentration of dissolved oxygen. If the temperature changes, the dissolved oxygen will vary due to the change in the solubility of oxygen at different temperature. This meter should be calibrated prior to each use.

Table 3.1 The corresponding speed in rpm of the mixer installed on the photo-reactor

Number	Speed (rpm)
0	44
1	82
2	133
3	165
4	183
5	193
6	200
7	203
8	205
9	206
10	208

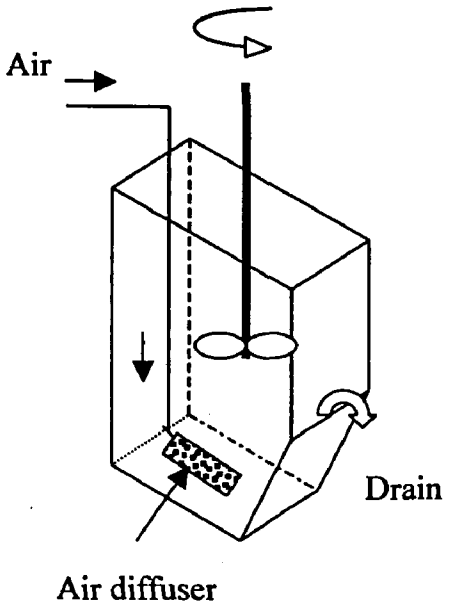

Figure 3.7. Schematic diagram of sequential batch reactor tank (SBR).
Working volume= 7 L .

The probe should be placed in moist air and the meter should be adjusted corresponding to the calibration value for the local altitude. Meter accuracy is about ±0.1 mg/L, and the temperature sensor accuracy is +0.2°C.

To measure the DO when there is no movement in the system; a clean magnetic stirring bar should be placed in each container to mix it. The magnetic should not be removed until the end of the DO reading.

3.2.16 Biological Oxygen Demand (BOD)

BOD depends on the biodegradability of the waste and can identify the amount of oxygen that is necessary to oxidize a waste biologically into CO_2 and water during a specific period of incubation. This parameter can measure the biodegradable organic carbon that is present in the waste along with oxidizable nitrogen. The low value of BOD either shows very clean water or a toxic wastewater which can inhibit microorganisms from growth. The most popular BOD test is 5-day BOD, which measures the amount of oxygen used in 5 days to stabilize the organics in wastewater incubating at 20°C. However, measuring the oxygen required to oxidize the organic matter completely is also possible. This type of BOD is referred to as ultimate BOD (UBOD). It is important to know that BOD is the combination of two parameters, the oxygen used for synthesis of new cells and endogenous respiration. BOD can also be expressed mathematically by assuming a first order reaction rate as follows (Metcalf and Eddy, 2002):

$$\frac{dl}{dt} = -kl \qquad (3.4)$$

where l, k , and t are the amount of oxygen demand at time t, reaction rate constant, and reaction duration, respectively.

Equation (3.4) can be simplified as follows:

$$l = l_o e^{-kt} \qquad (3.5)$$

where l_o is the oxygen required to oxidize the biodegradable organics totally or UBOD. Moreover, to find the amount of BOD at any time, the following equation can be defined:

$$BOD_t = l_o - l \qquad (3.6)$$

where BOD_t is the amount of BOD at time t.
Substituting Equation (3.5) into Equation (3.6), BOD at time t can be calculated directly.

$$BOD_t = l_o(1 - e^{-kt}) \qquad (3.7)$$

The method consists of providing nutrient and oxygen for the microorganisms to oxidize a specific volume of organic wastes in a sealed 300 ml bottles placing in an incubator at 20°C for 5 days. The BOD_5 is calculated by the difference in the initial dissolved oxygen (DO) and the DO after 5 days. However, if the sample has been diluted, the dilution factor should be taken into account.

Dilution water was prepared by adding 1 mL of each nutrient (Section 3.1.6) to one liter of distilled water and aerating the water for at least half an hour. The seed solution (Section 3.1.8) was prepared by adding one capsule of polyseed to 500 mL of dilution water. The solution was aerated for one hour. This solution was then allowed to settle for 5-15 minute prior to use. Five mL of seed solution was added to each 300 mL BOD bottles (VWR Science). The mixture was diluted with dilution water. The bottles were water sealed and placed in dark incubator at 20°C to prevent oxygen transfer. The volume of the waste added to each bottle can be estimated according to Table 3.1. The initial DO (dissolved oxygen) and DO after 5 days were measured using an YSI 58 dissolved oxygen meter (3.2.8). A blank solution was prepared by diluting 5 ml of seed solution in the BOD bottle with dilution water and again its initial DO and DO after 5 days were measured. The BOD_5 was calculated according to the following equation:

$$BOD_5 = \frac{(DO_{s1} - DO_{s2}) - (DO_{B1} - DO_{B2})f}{P} \qquad (3.8)$$

where DO_{s1}, DO_{s2}, DO_{B1}, DO_{B2}, f, and P are initial DO of sample, DO of sample after 5 days, initial DO of blank, DO of blank after 5 days, ratio of seed in diluted sample to seed in seed control, and volumetric fraction of sample used, respectively. P can also be defined as the ratio of volume of sample added to the bottles, to 300 mL (volume of bottles). As BOD test can be influenced by presence of toxicants, improper use of seeding, and error in analytical techniques, it was checked periodically by a standard check solution (3.1.7). Therefore, for a 2% dilution of such a solution, the BOD_5 would be 198 mg/L with a standard deviation of 30.5 mg/L (Standard Methods, 1998).
After each use, the bottles should be cleaned by detergent and dilute HCl (3N) to remove any surface film, and covered with paper to prevent collecting dust.

3.2.17 Ultimate Biological Oxygen Demand (UBOD)

Ultimate Biological Oxygen Demand test is almost the same as BOD_5 test explained before, but with a few different steps. In this method, the bottles should be kept in incubator under the above mentioned conditions for an extended period of time depending on the type of wastewater. The dissolved oxygen should be measured initially and frequently to ensure that the DO is not low and anaerobic condition has not been occurred. If the concentration of dissolved oxygen reaches around 2 mg/L, the sample should be aerated again.

Dissolved oxygen should be measured at intervals of 2 to 5 days over a period of 30 to 60 days. When DO falls around 2 mg/L a small amount of sample should be poured into a beaker and reaerated with air. The new DO should also be recorded. If dilution water blank is used, it should follow the same procedure and the total DO consumed must be subtract from the blank's DO uptake.
Ultimate BOD can be estimated by using Equation (3.7), which can also be expressed in the form of:

$$BOD_t = UBOD(1-e^{-kt}) \qquad (3.9)$$

Table 3.2: The volume of wastewater added to the bottles for BOD measurement (Metcalf and Eddy, 2003).

BOD range	mL of sample adding to BOD bottle
300-1050	2
120-420	5
60-120	10
30-100	20
12-42	50
6-20	100
0-7	300

where BOD_t, k, t, and UBOD are the amount of BOD at time t, reaction rate constant, reaction duration, and UBOD is the ultimate biological oxygen demand, respectively.

3.2.18 Hydrogen Peroxide Measurement

The residual H_2O_2 can interfere with COD measurements due to its reaction with dichromate. Therefore, this reaction could increase the measured COD, as it was observed that 1 mg/L of residual H_2O_2 could generate 0.26 mg/L COD (Lin et al., 1998). Moreover, H_2O_2 is known to be bactericides and inhibitor in the bacteria activity. Therefore residual H_2O_2 can inhibit the bacterial growth in the BOD tests, and hence, underestimate actual BOD. Removal of residual H_2O_2 is specifically important for the biological treatment step that is fed by pre-treated UV/H_2O_2 process.

The concentration of H_2O_2 was measured by two methods:

1. DMP method (2,9-dimethyl-1,10-phenanthroline)
2. DPD method (N,N-diethyl-p-phenylenediamine)

The detection limit for DMP method was 3.4-170 mg/L and for DPD method was 0.1- 40 mg/L.

DPD method has DPD reagent tablets, which are commercially available with a colorimetric kit. It was used when lower concentration of H_2O_2 was expected. On the other hand, DMP method was used when precise determination was desirable and the H_2O_2 concentration was not expected to be very low. The DMP procedure is based on the reduction of copper(II) with H_2O_2 and production of a stable bright yellow complex of $Cu(DMP)_2^+$ with maximal absorbance at 454 nm (Kosaka et al., 1998). The test procedures are as follows:

One mL of each of the reagent solutions describe in Section 3.1.9 were added to a 10 mL volumetric flask and mixed well. Three mL of sample was added to the flask and diluted with distilled water to 10 mL. After mixing, the absorbance of the sample was measured at 454 nm. Blank solution was prepared in the same way but with distilled water instead of sample. To make a calibration curve, different standards with different concentrations of H_2O_2 were prepared and their absorbance was measured at 454 nm. Therefore, the

concentration of the samples could be read directly from the calibration curve (Figure 3.8).

3.2.19 Mixed Liquor Suspended Solids (MLSS)

Mixed liquor suspended solids (MLSS) is a quantitative way to measure the concentration of solids in sludge. It is done by filtering a known volume of sludge using Whatmann glass fiber filter with the pore diameter of 1.58 m. The solids remain on the filter should be dried at 150°C and reported in terms of mg/L of dried solids. If this filter is burned in oven at 550°C, what is obtained, is mixed liquor fixed suspended solids, and what is burned off is mixed liquor volatile suspended solids (MLVSS). Therefore, the mass of organics in the sludge could be calculated. Generally, MLVSS is used as the biomass in the activated sludge.

3.2.20 Shake Flask Tests for Biodegradation of LAS

Shake flask tests were performed to quantify the biodegradation of untreated LAS with the initial concentration of 100 mg/L and pre-treated LAS. Experiments were conducted in 300 mL flasks, and stoppered with a ball of cotton to allow consistent aeration. Flasks were filled with 200 mL of LAS solution and diluted to 300 mL. The aerobic nutrient medium was prepared by KH_2PO_4, K_2HPO_4, $NaHPO_4$. $7H_2O$, NH_4Cl, $MgSO_4$, $FeCl_3$, and $CaCl_2$ (Standard methods, 1998). 0.5 mL of each of the nutrient solution described in Section 3.1.6 was added to each flask. 50 mL activated sludge (from North Toronto Treatment Plant, located in the Don Valley) was fed to the flasks, and the whole solution in the flask was diluted to 300 mL. Each flask was prepared in duplicates. Following addition of all materials, the solution inside the flasks was stirred vigorously for one minute prior to take the first sample. Then, the flasks were incubated in the shaker incubator (150 rpm) and at a controlled temperature of 20°C. During the sampling, the flask was mixed vigorously with a magnetic stirrer.

3.2.21 Biological Treatment of LAS using Sequential Batch Reactors

An aerobic sequential batch reactor (Figure3.7) was used to generate acclimated biomass for biological treatment of LAS.

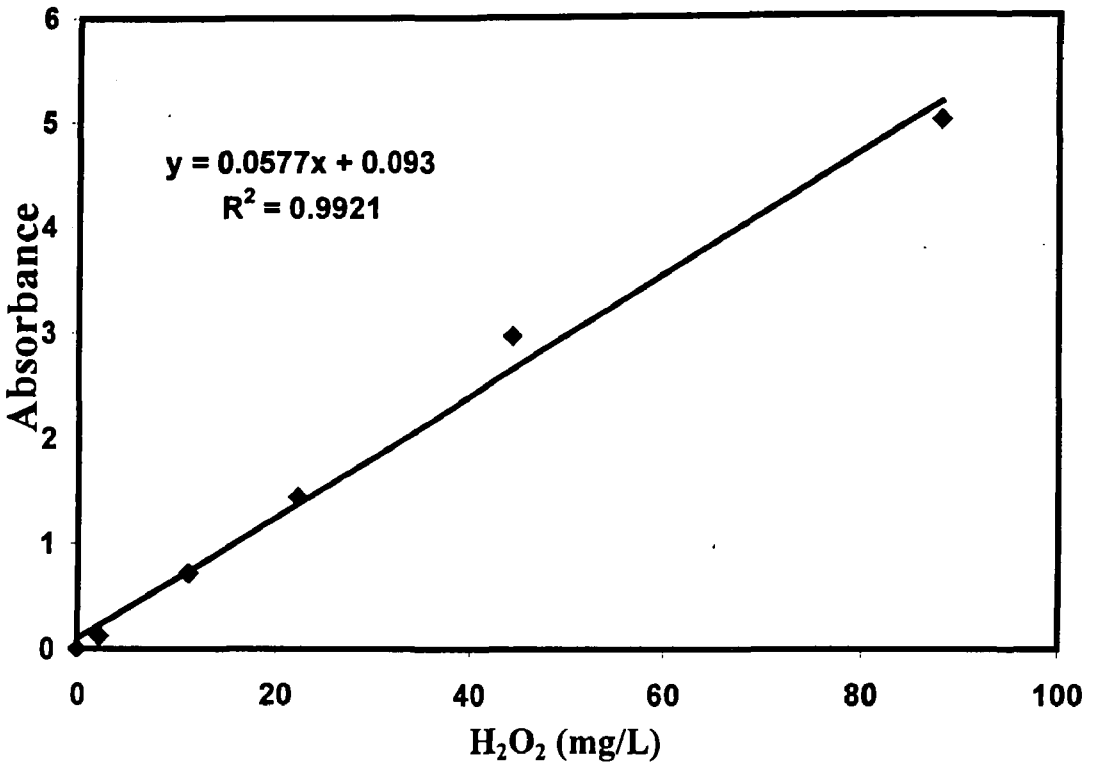

Figure 3.8. Calibration curve for determination of H_2O_2, based on DMP method. Absorbance, or optical density, is a measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light.

The objective of this experiment was to adapt the biomass to a certain concentration of LAS. The effect of acclimation on the biodegradability of LAS was studied. To increase the rate of biomass growth during the acclimation period, LAS was diluted with sodium acetate. This dilution was based on the initial characteristic of LAS. The BOD_5 of LAS at that concentration should be measured. Therefore, the dilution should be in a way to provide the same BOD_5. The experiment was started by addition of sodium acetate with a BOD_5 equal to the BOD_5 of that concentration of LAS to the reactor. Moreover, activated sludge (from North Toronto Treatment Plant) and nutrient with the ratio of BOD:N:P equal to 100:5:1 were fed to the reactor. The nutrient medium was composed of KH_2PO_4, K_2HPO_4, $NaHPO_4$. $7H_2O$, NH_4Cl, $MgSO_4$, $FeCl_3$, and $CaCl_2$ (Standard Methods, 1998). Thirty one mL phosphate buffer and 1.4 mL from each of the $MgSO_4$, $FeCl_3$, and $CaCl_2$ was added to the SBR. The nutrients were added to the system weekly. Air was provided by air diffuser, and the system was mixed at the speed of 300 rpm. The concentration of LAS in the substrate was gradually increased from 0 to 10 mg/L during 23 days; meanwhile, the concentration of sodium acetate was decreased to maintain the pervious BOD_5. The addition of new substrate was provided when the changes in the concentration of LAS in the reactor became steady state, in other words the concentration of LAS became zero. The duration of each phase was as follows:
Fill phase 6 h with aeration, react phase 8.4 h with mixing and aeration, settle phase 4.8 h with no aeration or mixing, draw phase 3.6 h with no aeration or mixing, and idle phase 1.2 h with only aeration. The duration of each cycle was 24 h. the sample was taken at the end of the settled phase and if the concentration of LAS was zero, new feed (according to the explanation mentioned above) was introduced to the system. After the last feed (10 mg/L LAS) was given to the system and was consumed by the microorganisms in the activated sludge, the whole liquor was drained at the end of settled phase but the sludge was kept inside the reactor. The reactor was filled with the fresh sample (could be either untreated LAS or LAS with photolytic pre-treatment). Nutrients as described before were added to the system. The duration of each phase was the same as before and the percentage of removal of LAS at the end of each phase was monitored.

CHAPTER 4

RESULTS AND DISCUSSIONS

In this chapter, the results obtained from photochemical and biological degradation of linear alkylbeneze sulfonate (LAS) using a pilot plant photoreactor and a sequential batch reactor are presented and discussed. LAS at the concentration of 100 mg/L was degraded by UV-254 and combination of UV and H_2O_2 to determine which one has the ability to degrade LAS at a faster rate. Moreover, different experiments were carried out to determine the best working condition for the pilot plant photoreactor. Different experiments on biological treatment of LAS were conducted under aerobic conditions. In conclusion, combination of chemical and biological treatment was examined.

4.1 Photolytic Treatment of LAS

4.1.1 Free Chlorine

The degradation of LAS in the presence and absences of free chlorine was compared in the photolytic reactor (Figure 4.1). Two conditions were examined, with and without mixing in the system. It was observed that:

1. Mixing increased the degradation rate of LAS with free chlorine by 7%, and without free chlorine by 10%, compared to non-mixing system.
2. The degradation of LAS had an increase using tap water containing free chlorine in the system by 5% with mixing, and 8% without mixing.

Therefore, it was concluded that free chlorine could react as an oxidant under UV light, and increase the reaction rate. Figure 4.2 compares the initial rate for those four different cases. The presence of free chlorine (0.8 mg/L) in the system and having mixing in the photoreactor has the highest rate (0.8 mg/L·min) comparing to the rest of the cases. Although, the presence of free chlorine in each case (with mixing or without mixing) had

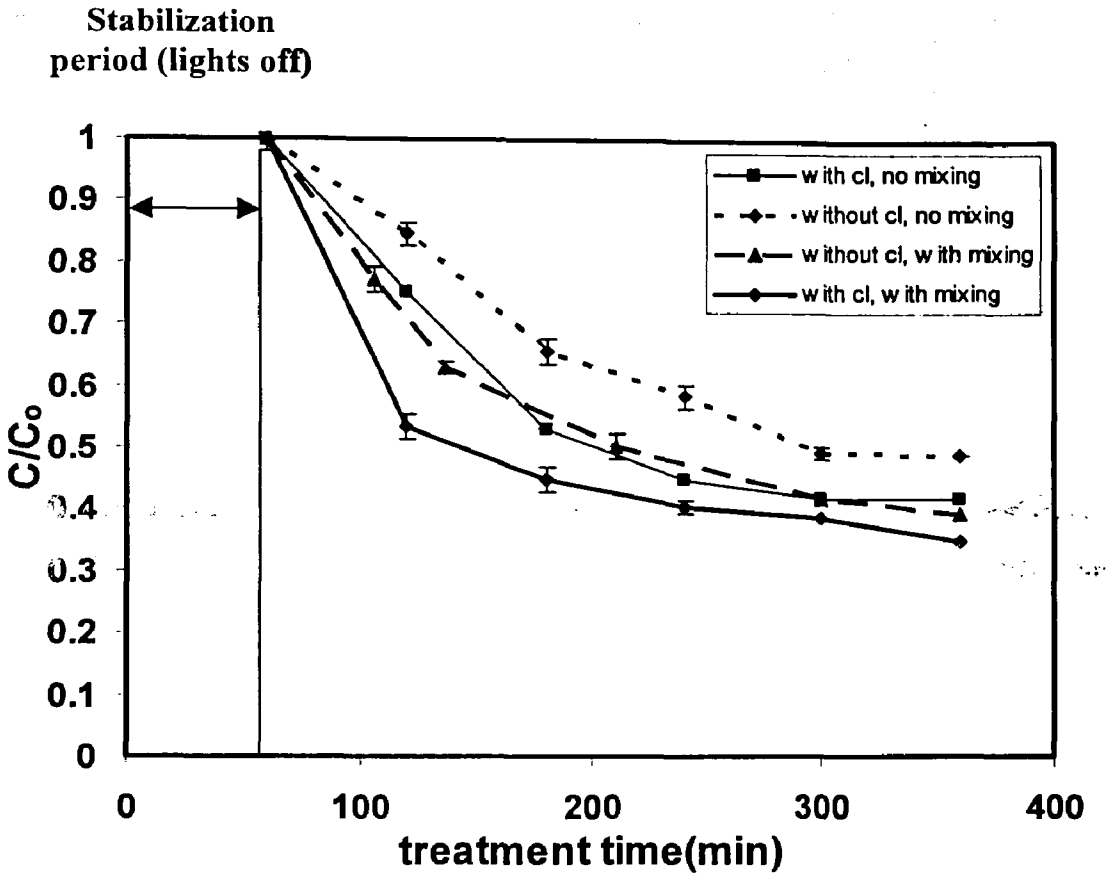

Figure 4.1: Difference between the photolytic degradation of LAS in the presence and absence of free chlorine. Flow rate = 8 L/min, initial concentration of LAS = 100 mg/L. Two different conditions, with and without mixing are compared in the reactor. Total illumination time was 300 min.

Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

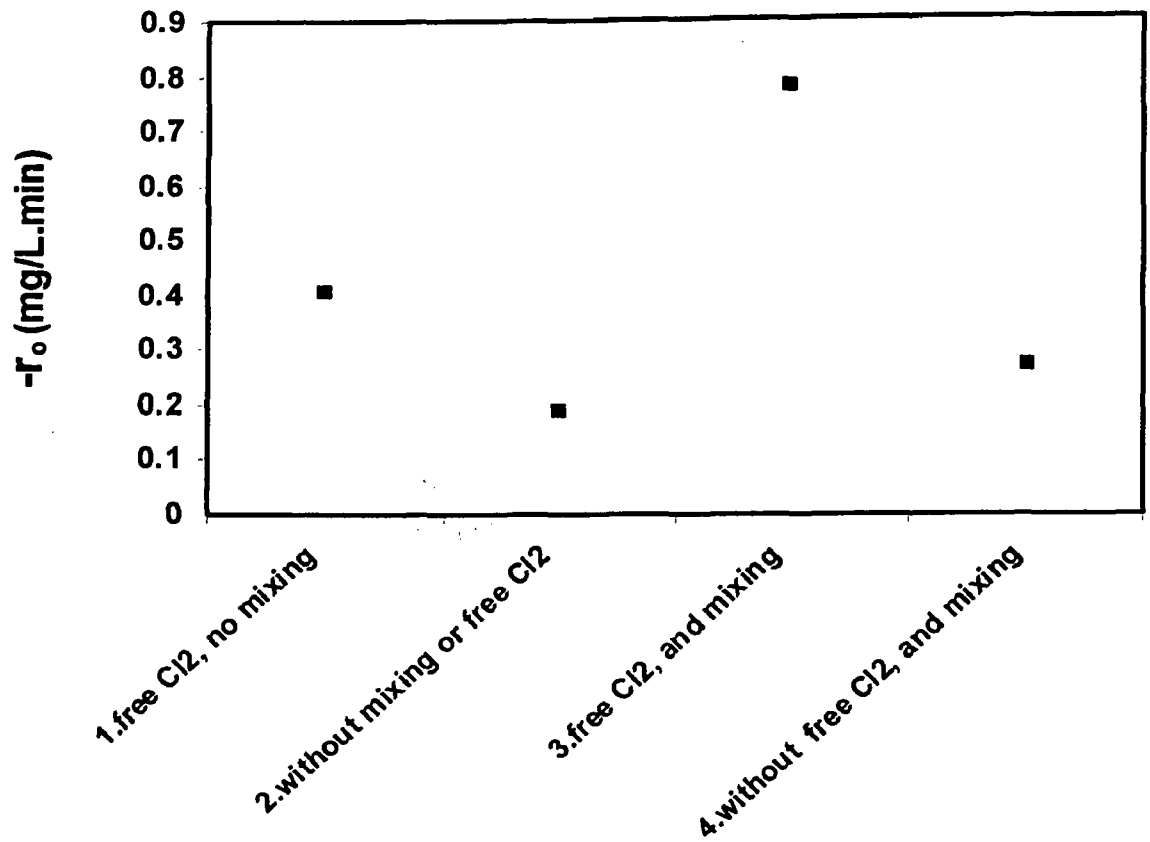

Figure 4.2: Comparing the initial rate for four different cases in photolytic degradation of LAS in the presence and absence of free chlorine. Flow rate = 8 L/min, initial concentration of LAS = 100 mg/L. Four cases are as follows:

1- presence of free chlorine but no mixing
2- presence of free chlorine and mixing
3- absence of free chlorine but no mixing
4- absence of free chlorine and mixing.

shown higher removal of LAS, as the initial rate in the presence of free chlorine in the system without mixing is 0.4 mg/L·min, while this rate is 0.2 mg/L·min for the case of without free chlorine. However, this variation is much more in the presence of mixing in the system, as the initial rate in the presence of free chlorine in the system with mixing is 0.8 mg/L·min, while this rate is 0.27 mg/L·min for the case of mixing but without the presence of free chlorine .

4.1.2 Dark Reaction

It was observed that there were no significant changes in the concentration of LAS during the dark reaction (Figure 4.3). Therefore, LAS is neither degraded nor adsorbed in the absence of UV lights. This experiment was conducted with two different initial concentrations of LAS to compare the effects of initial concentration on the degradation during dark reaction. In Figure 4.3, the changes for the initial concentration of 95 mg/L and 65 mg/L of LAS were monitored and it was observed that there no significant changes in the concentration of LAS.

There was a concern that the concentration of LAS might decrease due to foaming of LAS after 6 h. It was observed that the foaming was increased rapidly from the beginning of the experiment and it was believed that these foams contain an excess of surfactant. However, sampling from the bulk of liquid phase for 6 hours did not show any differences in the concentrations of LAS from beginning until the end of the experiment (Figure 4.3).

After elimination of free chlorine from the tap water inside the feed tank, sufficient LAS was added to the feed tank to make a 100 mg/L of LAS solution. The experiment was not started after addition of flaked LAS to the water, as LAS should be mixed in the tank to produce a uniform concentration throughout the feed tank. Moreover, the temperature of water may not be exactly 20°C, which is the operating temperature. Therefore, the solution was mixed thoroughly in the system for one hour (dark reaction). During this period of time, the temperature of the system was kept at 20°C prior to turning on the UV lamps.

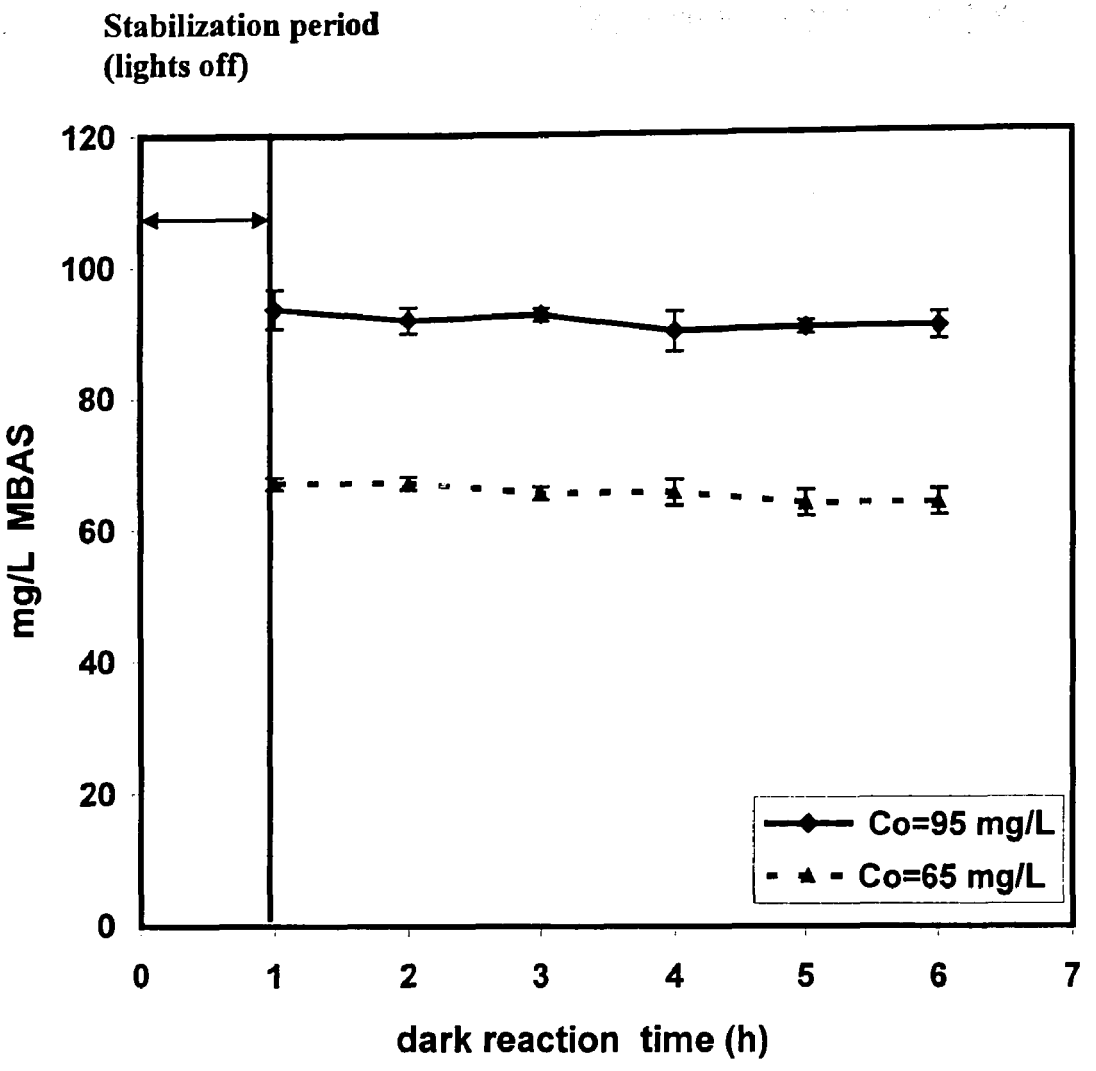

Figure 4.3: Changes in the concentration of LAS during dark reaction. Two different initial concentrations of LAS were examined. Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

During the dark reaction, the concentration of LAS did not change, furthermore, if the duration of stabilization period was known, the experiment could be run with the precise concentration of LAS. Sampling was started exactly after addition of a known amount of LAS to the water. Therefore, the changes in the concentration of LAS from the time of the addition until achieving to the equilibrium concentration of LAS were monitored. As it is shown in Figure 4.4, the concentration of LAS was about 87 mg/L after a few second of addition of 10 g of flaked LAS to the water inside the feed tank and reached to 100 mg/L after 45 min. Therefore, the optimum stabilization time prior to the start of each run was 45 min to one hour. Moreover, it took about 45 min for the system's temperature to reach to 20°C. This period of time could vary depending on the temperature of water being used.

4.1.3. Photoreaction of LAS by UV-254

The flow rate and also the mixing speed were changed during the experiment and the effects of these parameters on the photolytic degradation rate of LAS were studied. In this experiment, all conditions were kept the same as to those of the dark reaction except that the 6 UV lamps were turned on simultaneously after the stabilization period. Furthermore, the temperature of the reactor was kept constant at 20°C using the water bath, during all the experiment, therefore, the effect of increasing the temperature due to the UV lamps have been eliminated. Three Samples were taken every hour and analyzed immediately. The initial concentration of LAS was 100 mg/L. The flow rate and also the mixing speed were changed during the experiment. Therefore, the effects of changing both of those parameters on the photolytic degradation rate of LAS were studied.

4.1.3.1 Effects of Flow Rate

Experiments were carried out to compare the effects of flow rate on the photolytic degradation of LAS with a constant mixing speed for all of the runs. The ranges of flow rates were varied from 4-40 L/min. Lower and higher flow rates were not

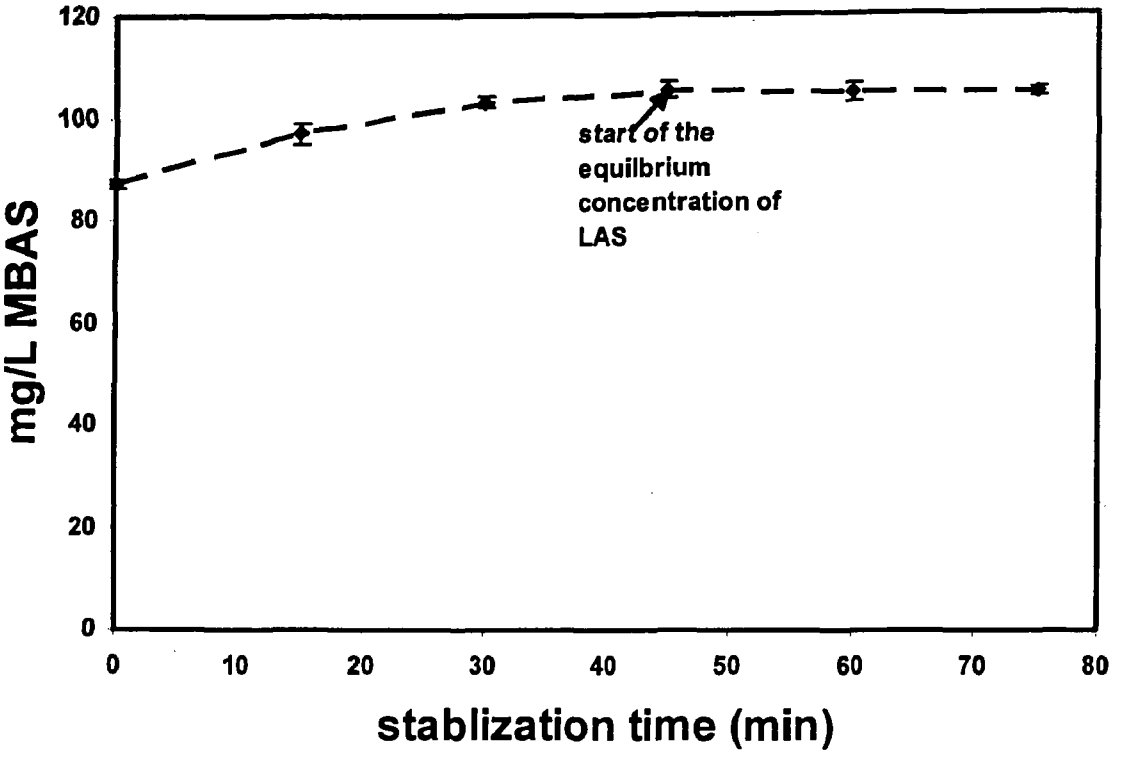

Figure 4.4: LAS concentration in the stabilization period prior to the start of each experiment. During this period the whole system was running, but with no UV light Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

applied due to the system limitations and excessive foaming problem inside the flow meter, which made the flow rate inconsistent.

Figure 4.5 illustrates the flow rate of 8 L/min has the highest initial rate (5×10^{-5} mg/L.h), while the flow rate of 32 L/min has the lowest (3×10^{-5} mg/L.h). It implies that the rate of reaction of the lowest flow rate is faster; hence, it can degrade more than the rest of the flow rates in a given period of time. At flow rate of 8 L/min, LAS can be degraded by 75% during 6 hours. That can be due to the increase in the residence time by decreasing the flow rate, which gives more time to the organics exposed to illumination. Therefore, UV with the wavelength of 254 nm has more time to break the bonds. However, as the whole system is batch and more than 75% of solution inside the feed tank would enter the photoreactor in each cycle, the above mentioned reason might not be reasonable for increasing the initial rate by increasing the flow rate. On the other hand, by increasing the flow rate there is an increase in the amount of foams in the system. The foams might also work as a barrier in higher flow rates to hinder the light from being absorbed by the solution.

First order model was tried for the photolytic degradation of LAS and it was observed that the photolytic degradation of LAS did not follow that model. The reason might be due to the occurrence of two reactions simultaneously. One reacts with slower rate and the other with a faster rate. Therefore, a double exponential model (combination of two first order model) might be a good choice. The other reason for not following first order model might be due to the fact that MBAS method measures all of the anionic compounds that were produced during the photolytic degradation of LAS.

4.1.3.2 Effect of Mixing Speed on the Photolytic Degradation of LAS

It was observed that the degradation of LAS was increased by increasing the mixing speed. This is due to the production of turbulent flow in the system which increases the mass transfer rate inside the reactor. The turbulent flow was initiated after 165 rpm and the sharp increase in the initial rate of reaction after 165 rpm could be due to

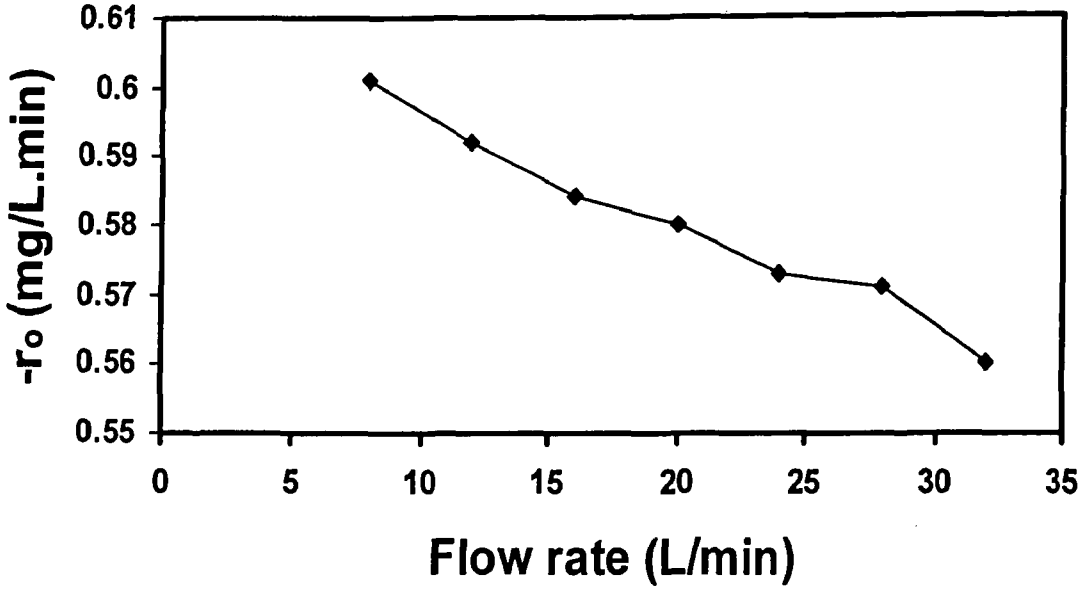

Figure 4.5: The initial rate for photolytic degradation of LAS. Different flow rates at a constant mixing speed were examined. Initial concentration of LAS was 100 mg/L.

the turbulent flow. To predict the type of flow, Reynolds number's calculation was based on the assumption that there is no other movement inside the reactor except for the mixing. Therefore, the lowest flow rate was chosen to produce a laminar flow inside the reactor which gave Reynolds number equal to 132. . It was observed that at 165 rpm the Reynolds number reached to 2750, which is in the range of turbulency. While the Reynolds numbers for the lower mixing speeds have not reached to the turbulence zone. Water flow could also produce small channels within the photoreactor that allows the water to pass rapidly through the reactor without coming into contact with the UV lights. Figure 4.6 shows that the initial rate of degradation was increased by increasing the mixing speed. However, there was almost no difference between the photolytic degradation by changing the speed from 7-10, as the rotational speed for those numbers are almost the same (Table 3.1). The maximum degradation occurred by trying the maximum mixing speed was 80% in 6 hours.

4.1.4 Optimization of H_2O_2 for Degradation of LAS

UV alone could degrade the LAS up to maximum 80% during 6 h. In the next experiments the effects of H_2O_2 on the photolytic degradation of LAS were examined. In order to speed up the degradation rate of LAS, sufficient H_2O_2 is essential so that it can absorb UV light and generates sufficient hydroxyl radicals. Therefore, different concentrations of H_2O_2 were used, while the initial concentration of LAS was kept constant. Figure 4.7 shows that H_2O_2 has the ability to degrade LAS rapidly. Therefore, the reaction time was 4.5 h shorter than that of the previous experiments using UV alone. The addition of 120 mg/L H_2O_2 could degrade LAS up to 80% at two hours, while increasing the concentration of H_2O_2 led to increase in the degradation rate. In order to find the optimum concentration for the hydrogen peroxide, a pseudo-first order model with respect to the concentration of LAS was assumed (Figure 4.8). The degradation constant was increased by increasing the dosage of H_2O_2, but increasing the concentration beyond 720 mg/L showed negative effect on the LAS degradation. Therefore, the optimum concentration of H_2O_2 was about 720 mg/L. Higher concentration of H_2O_2 led to a decrease in degradation rate of LAS.

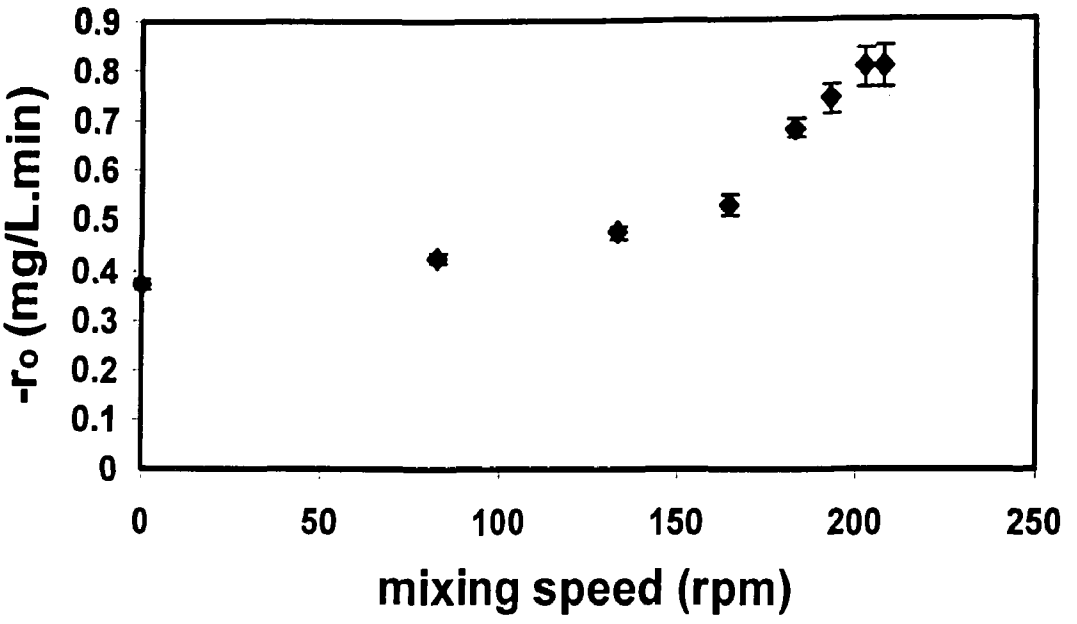

Figure 4.6: Initial rate for of photolytic degradation of LAS versus changing the mixing speed. Initial concentration of LAS = 100 mg/L, flow rate for all cases was 8 L/min. Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

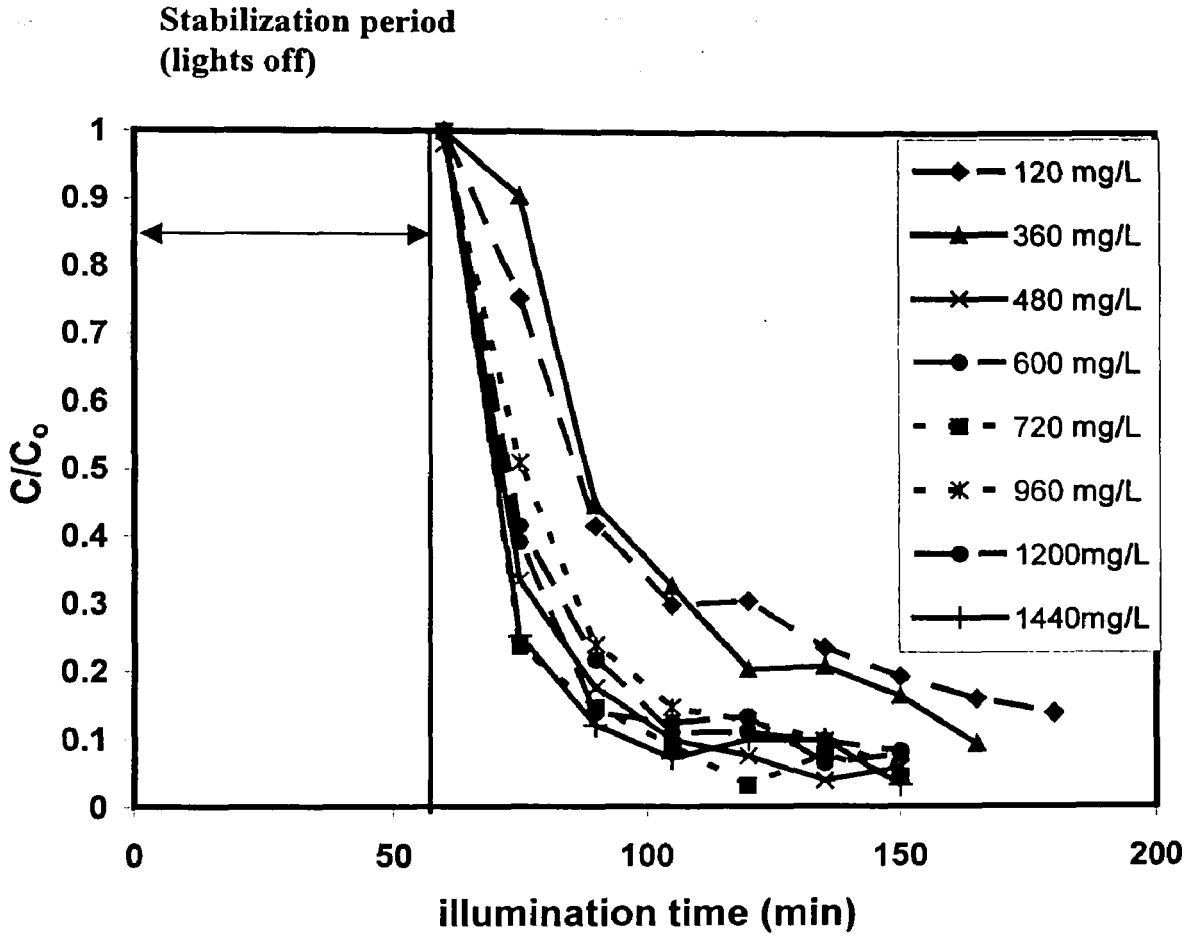

Figure 4.7: Effects of UV-H_2O_2 on LAS removal, flow rate: 12 L/ min, mixing speed=183 rpm, C_o= 100 mg/L. Different concentrations of H_2O_2 had been examined.

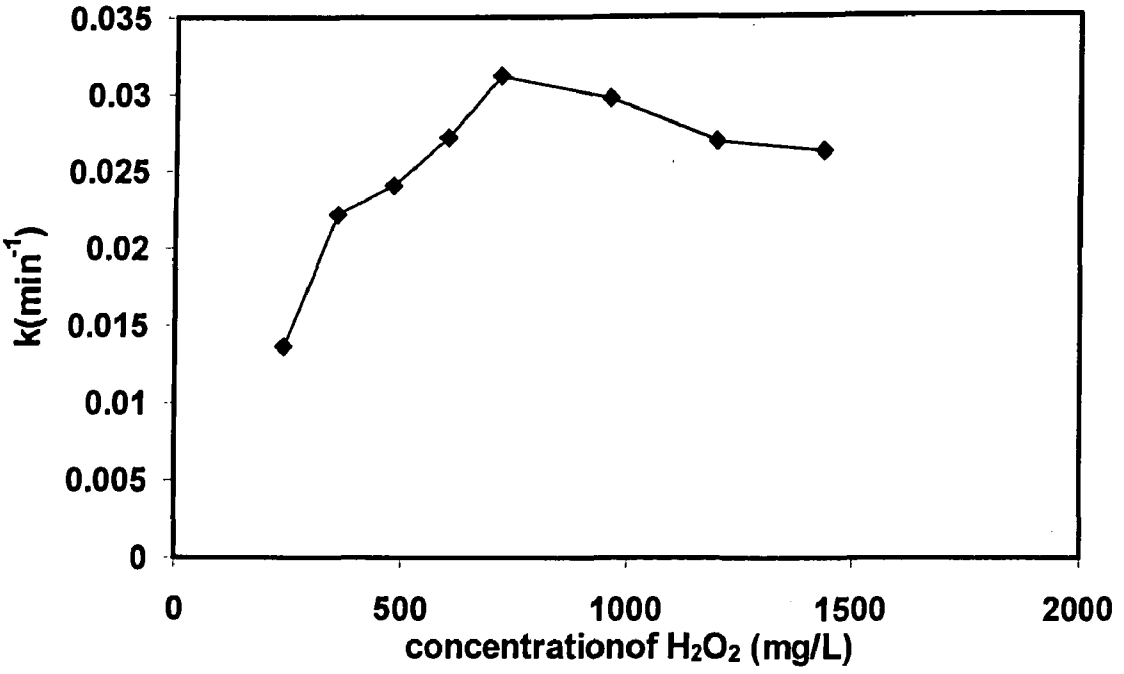

Figure 4.8: Optimum concentration of H_2O_2 assuming a pseudo-first order model for the photolytic degradation of LAS with H_2O_2. First order model constants for different concentrations of H_2O_2.

The initial concentration of LAS was 100 mg/L and flow rate =12 LPM, mixing speed=183 rpm.

This could be due to the following reasons (Ledakowicz and Gonera, 1999):

1. Auto-oxidation of H_2O_2 into O_2 and H_2O, and recombination of $^{\bullet}OH$ by means of H_2O_2 according to the following reactions:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (4.1)$$

2. The excess of H_2O_2 reacts with $^{\bullet}OH$ competing with pollutants and, hence, decreasing the efficiency of the treatment.

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \qquad (4.2)$$
$$k = 3.3 \times 10^7 (mol.s)^{-1}$$

Moreover, the concentration of an optimal H_2O_2/pollutant molar ratio between 10 and 100 has been proposed (Parra et al., 2002). In this experiment this ratio was in that range as it was 72 (mole H_2O_2/mole LAS). The ratio of H_2O_2 to LAS which would result to complete mineralization is 50:1, but what was obtained from experiment was 72:1. This difference might be due to the presences of intermediates which their reaction with $^{\bullet}OH$ could increase this ratio.

4.1.5 Model for the Degradation of LAS with UV+H_2O_2

It was observed that the photolytic degradation of LAS follows first order model (Figure 4.9). Therefore the concentration of LAS at any time during photolytic degradation using H_2O_2 can be expressed by the following model:

$$Ln\left(\frac{C}{C_o}\right) = -0.0326 \quad t \qquad (4.3)$$

where the first order constant (k) and C_o, the initial concentration of LAS, are equal to 0.0326 min^{-1} and 100 mg/L, respectively. Therefore C is the concentration of LAS at time t (min) is as follows:

$$C = 100 \quad e^{-0.0326 \; t} \qquad (4.4)$$

As there was only little decrease in the concentration of H_2O_2 during the degradation of LAS and its concentration was much more than the concentration of LAS during the degradation, the concentration of H_2O_2 was assumed constant, and hence, the degradation model for LAS follows pseudo first order reaction.

However monitoring the COD, showed only 20% decrease during the period of reaction. It was supposed that the degradation of LAS during that period of time had moved toward formation of organics rather than complete oxidation of LAS. However, TOC results are needed to determine the level of total mineralization of the organics.

4.1.6 Photolytic Degradation of LAS by using UV-254, Optimum Concentration of H_2O_2, and their Combination

The degradation of LAS was compared for the following conditions:

1. by the optimum concentration of H_2O_2 along with UV-254
2. by the optimum concentration of 720 mg/L H_2O_2 alone
3. by UV-254 alone

In each of those conditions, the initial concentration of LAS was 100 mg/L. After the illumination period of 120 min, it was observed that H_2O_2+UV could remove LAS up to 95%, while the LAS removal by H_2O_2 alone and UV alone were 13%, and 41%, respectively (Figure 4.10). To investigate the time necessary for the complete photolytic removal of LAS using optimum concentration of H_2O_2, the experiment was run until the concentration of LAS was 0.5 mg/L which is the maximum contamination level set by EPA. Therefore, the illumination time necessary to degrade LAS by this method was 180 min (Figure 4.11).

4.1.7 pH

pH was monitored during all experiments. In all cases the pH was decreased. pH reduction was more significant in the case of treating LAS with UV+H_2O_2.

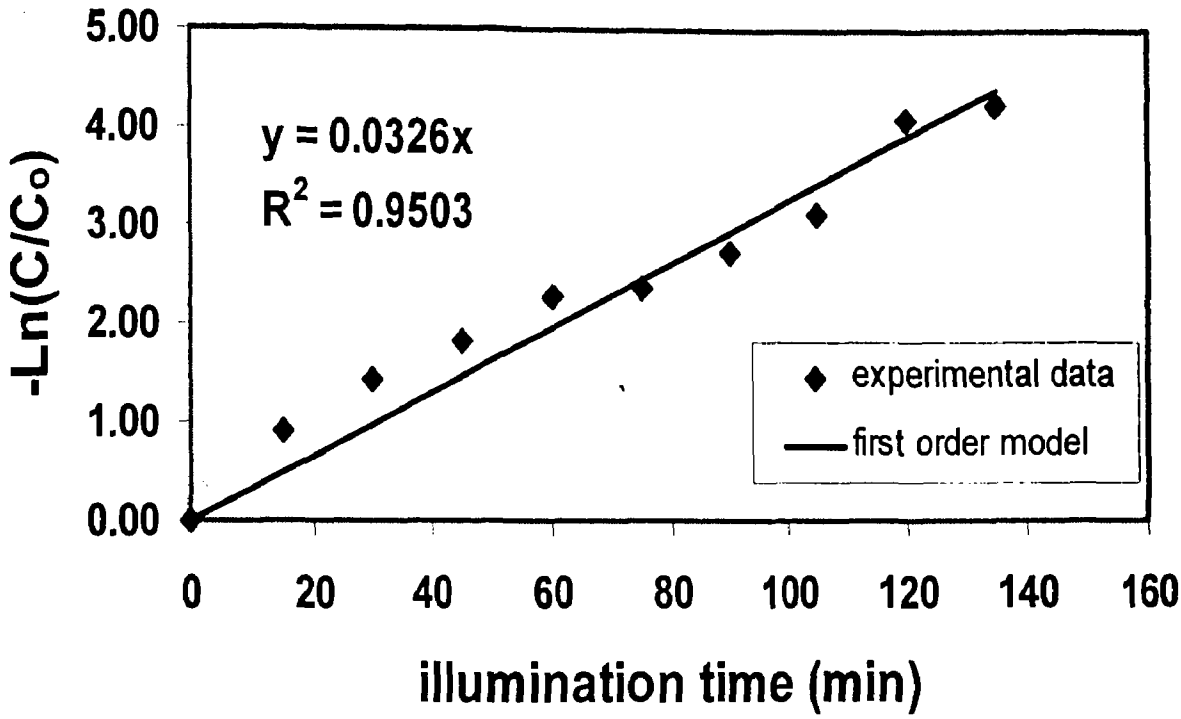

Figure 4.9: Comparison between the experimental data and simulated model for photolytic degradation of LAS with optimum concentration of H_2O_2. Initial concentration of LAS was 100 mg/L and flow rate =12 LPM, mixing speed = 183 rpm.

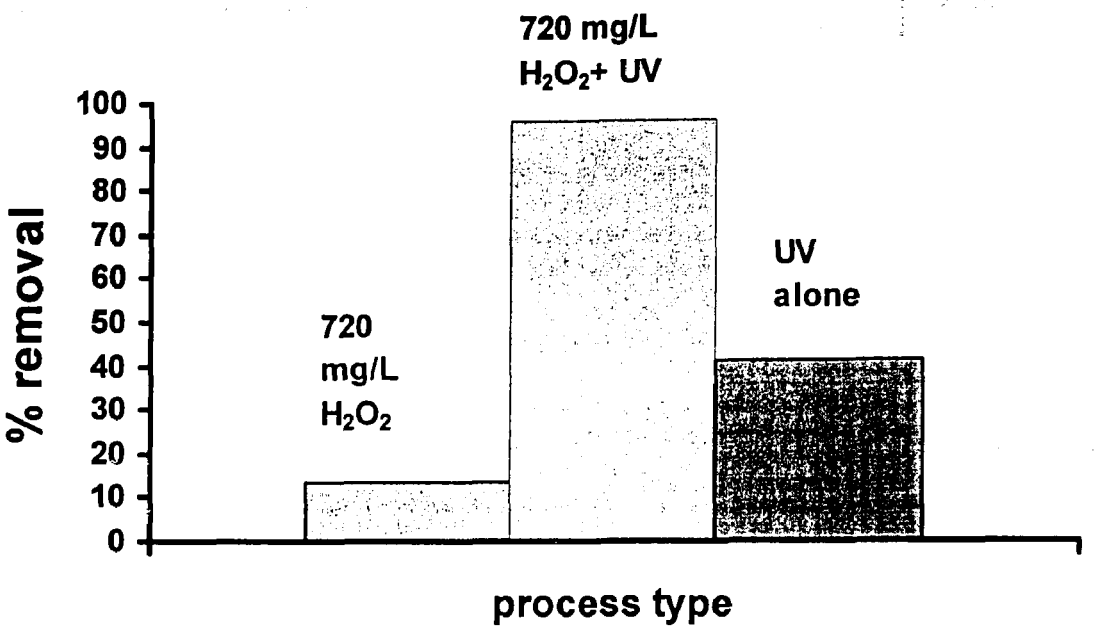

Figure 4.10: Comparison of the degradation for three different situations:

1. The optimum concentration of H_2O_2 with UV-254,
2. The optimum concentration of 720 mg/L H_2O_2,
3. UV-254 alone.

Initial concentration of LAS was 100 mg/L and the illumination time was 120 min. Flow rate and mixing speed are the same in all cases (flow rate =12 LPM, mixing speed=183 rpm).

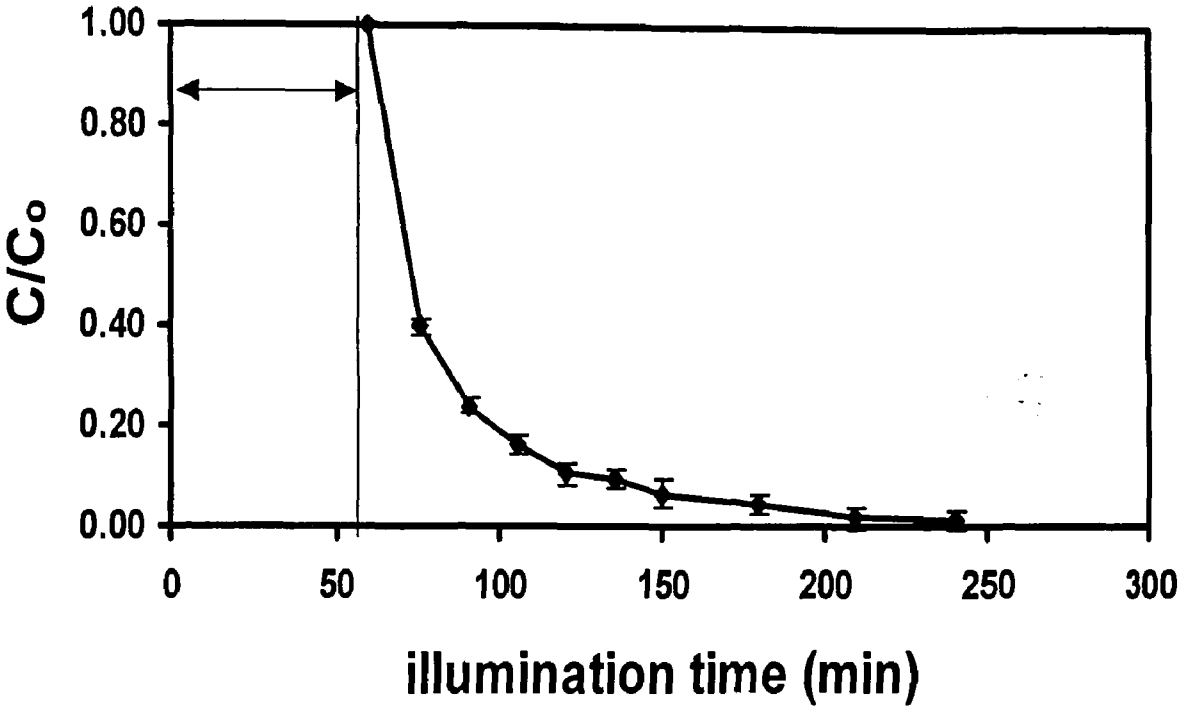

Figure 4.11: The necessary time for the complete photolytic degradation of LAS using optimum concentration of H_2O_2 (720 mg/L). Initial concentration of LAS was 100 mg/L, and flow rate =12 LPM, mixing speed=183 rpm. Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

As it is shown in Figure 4.12, the pH was decreased 2% and 20% in the treatment of LAS by UV and UV/H_2O_2, respectively. This suggests that the photolytic degradation of LAS by UV/H_2O_2 occurs through formation of acids. Decreasing the pH shows that the degradation follows the general degradation pattern for AOPs (production of acids)(Mantazavinos et al, 2000). Nevertheless, as the foaming ability of LAS was decreased by preceding the experiment, it was suggested that there are two mechanisms for degrading LAS (Mantzavinos et al. 2000):

1. Breakage of alkyl chain, which results a shorter chain incapable of behaving as detergent,
2. Attack of free radicals to the aromatic ring and removal of solfoxy group, which destroy the detergency nature.

4.1.8 Impact of the Catalase on Analysis of H_2O_2

To investigate the impact of the addition of insufficient or excessive amount of catalase on the analysis of H_2O_2 and BOD_5 test, different concentrations of catalase were examined. To decompose 60 mg/L of H_2O_2, 0.1 mg of catalase was added to 100 mL of sample and left without stirring for 100 min (Ito et al., 1998). After that time, the concentration of H_2O_2 was measured by DPD method and it was observed that its concentration was zero. Insufficient and excessive amount of catalase were added to 6 samples of H_2O_2 with the volume of 100 mL each. Sodium acetate was chosen as a standard to compare the impact of catalase on the chosen test. Also, the presence of H_2O_2 can interfere with BOD test and inhibit the growth of microorganisms. Therefore, BOD_5 test was chosen as a reference test. Six different samples containing different concentrations of catalase were prepared. Samples 1-5 contained 0, 0.05, 0.1, 0.5, and 1 mg of catalase, respectively. The mentioned masses of catalase were dissolved in 100 mL of H_2O_2 solution with initial concentration of H_2O_2 equal to 60 mg/L.

Sample 6 was 1 mg catalase with no H_2O_2 in it, and sample 7 was just sodium acetate with the concentration of 30 mg/L. Thirty mL of sodium acetate was added to 7 BOD bottles, and 25 mL of samples 1-6 were added to just 6 of those bottles.

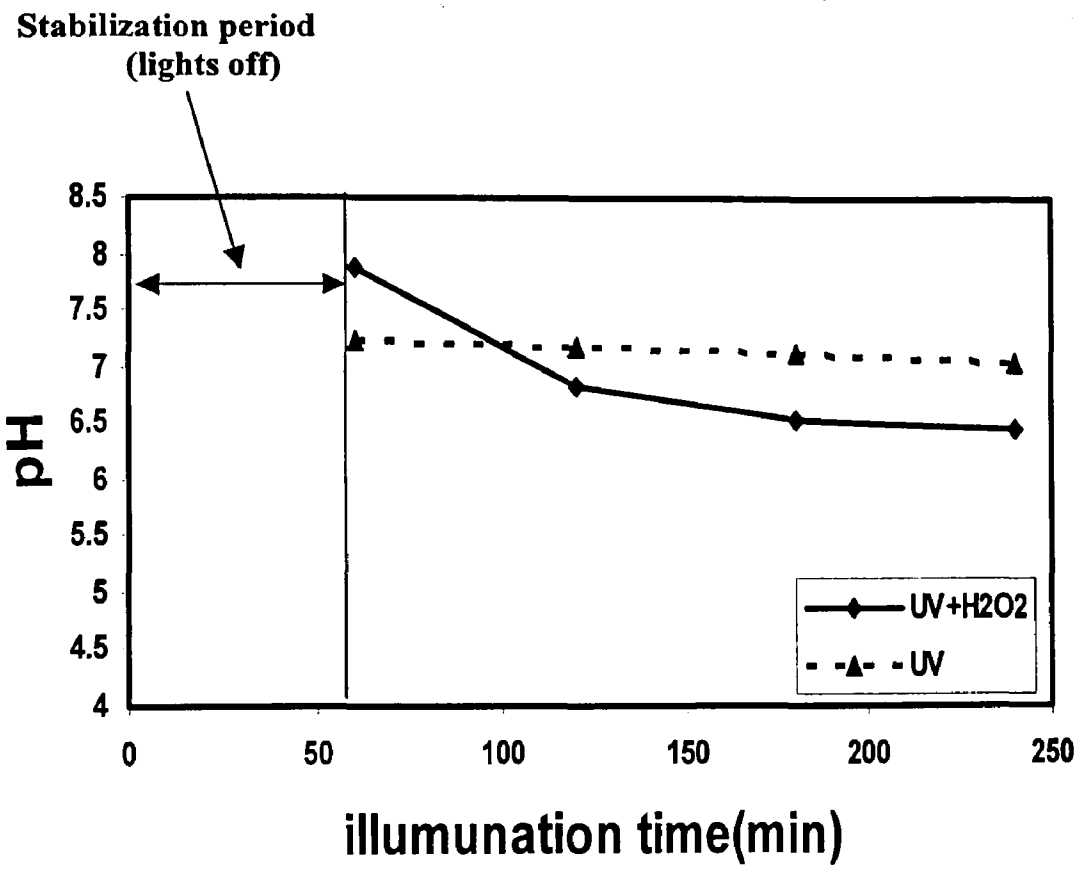

Figure 4.12: Comparison between the changes in pH with UV_{254} and $UV+H_2O_2$, Mixing=183 rpm, flow rare=12 L/min, C_o=100 mg/L.

The rest of the bottles were filled with appropriate amount of seed solution and diluted water (Section 3.2.16). The sealed bottles were kept in incubator at 20°C for 5 days. The results are illustrated in Figure 4.13. It was expected that if the H_2O_2 was reduced by proper amount of catalase, the BOD_5 of the solutions be around the BOD_5 of sodium acetate solution alone. As Figure 4.13 depicts, it can be concluded that when the concentration of catalase is lower than optimum, there are still some H_2O_2 presence in solution. Therefore, residual H_2O_2 produce a toxic effect and reduce the consumption of oxygen, and BOD_5 cannot reach to its true value which is equal to the BOD_5 of sodium acetate alone. Moreover, excessive amount of catalase can increase the consumption of oxygen in the test. Moreover, excess amount of catalase produced the initial dissolved oxygen in the solution above the saturation level (13 mg/L O_2), this dissolved oxygen would decrease dramatically after 5 days of incubation. Therefore, the concentration of catalase should be around its optimum value, which is 0.1 mg of catalase per 100 mL of sample containing H_2O_2 at 60 mg/L, to eliminate 60 mg/L of H_2O_2 effectively.

4.1.9 Impact of H_2O_2 on COD and BOD test

To investigate the impact of H_2O_2 presence on the COD tests, the COD of the samples with H_2O_2 were compared to the same samples where their H_2O_2 had been eliminated. It was observed that the samples with H_2O_2 exert an excessive amount of oxygen for chemical oxidation in comparison to the samples without H_2O_2. Meanwhile, the theoretical oxygen demand of the 100 mg/L of LAS was calculated as 240 mg/L O_2. It is known that COD is usually lower than the theoretical oxygen demand as most of the organic compounds (mainly aromatic) cannot be oxidized chemically under test conditions. Therefore, the COD test was conducted on the LAS samples treated by UV/H_2O_2 for 90 minutes. As these samples contained residual H_2O_2, the COD of these samples were analyzed with residual H_2O_2, and it was compared to the COD of these samples after elimination of H_2O_2.

The COD for the sample with residual H_2O_2, which is higher than ThOD, cannot be the true value for COD (Figure 4.14) as the theoretical value of oxygen consumption is the maximum amount oxygen that a compound can consume during its chemical oxidation.

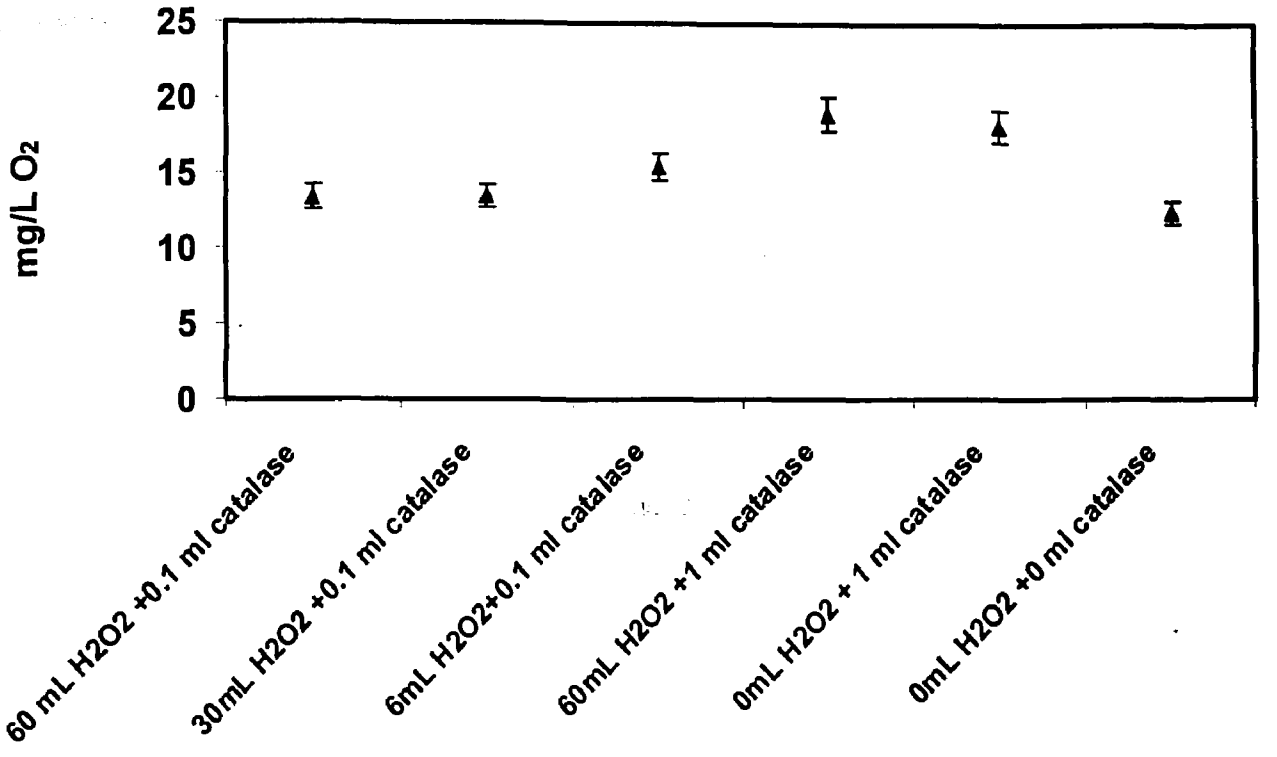

Figure 4.13: The impact of the addition of insufficient or excessive amount of catalase on BOD_5 test for different concentrations of catalase.

The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

Therefore, the residual H_2O_2 can interfere with COD measurements due to its reaction with dichromate, and this reaction could increase the measured COD (Lin et al., 1999). Moreover as it can be observed from Figure 4.13, the sample with residual H_2O_2 consumes less oxygen in BOD_5 test, compared to the sample with no H_2O_2. This is due to the fact that H_2O_2 is bactericide and inhibits the bacteria activity. Therefore, residual H_2O_2 can inhibit the bacterial growth in the BOD tests, and hence, underestimate the actual BOD.

4.1.10 Consumption of H_2O_2 during the Photolytic Reaction of LAS

During the photo-oxidation process, the LAS concentration was decreased. In the photolytic oxidation using UV along with H_2O_2 the degradation rate of LAS was higher than the degradation rate of LAS by UV alone by about 50% in 90 minutes. Consequently, there was a decrease in the concentration of H_2O_2 as it was being used as an oxidant.

The consumption of H_2O_2 was monitored from the beginning of the experiment until the concentration of LAS became about zero. The concentration of H_2O_2 was measured by DMP method, a precise technique. Figure 4.15 shows the consumption of H_2O_2 during three hours of reaction. The decrease in the concentration of H_2O_2 was due to the production of hydroxyl radicals and reaction between hydroxyl radical and organics as follows:

$$H_2O_2 + UV \rightarrow 2^{\bullet}OH \qquad (4.5)$$

$$^{\bullet}OH + \text{organics} \rightarrow \text{intermediate} \rightarrow CO_2 + H_2O \qquad (4.6)$$

Intermediates also react with $^{\bullet}OH$.

The H_2O_2 decrease during this period of time was uniform, and hence, it was observed that its consumption rate followed zero-order model (Figure 4.15).

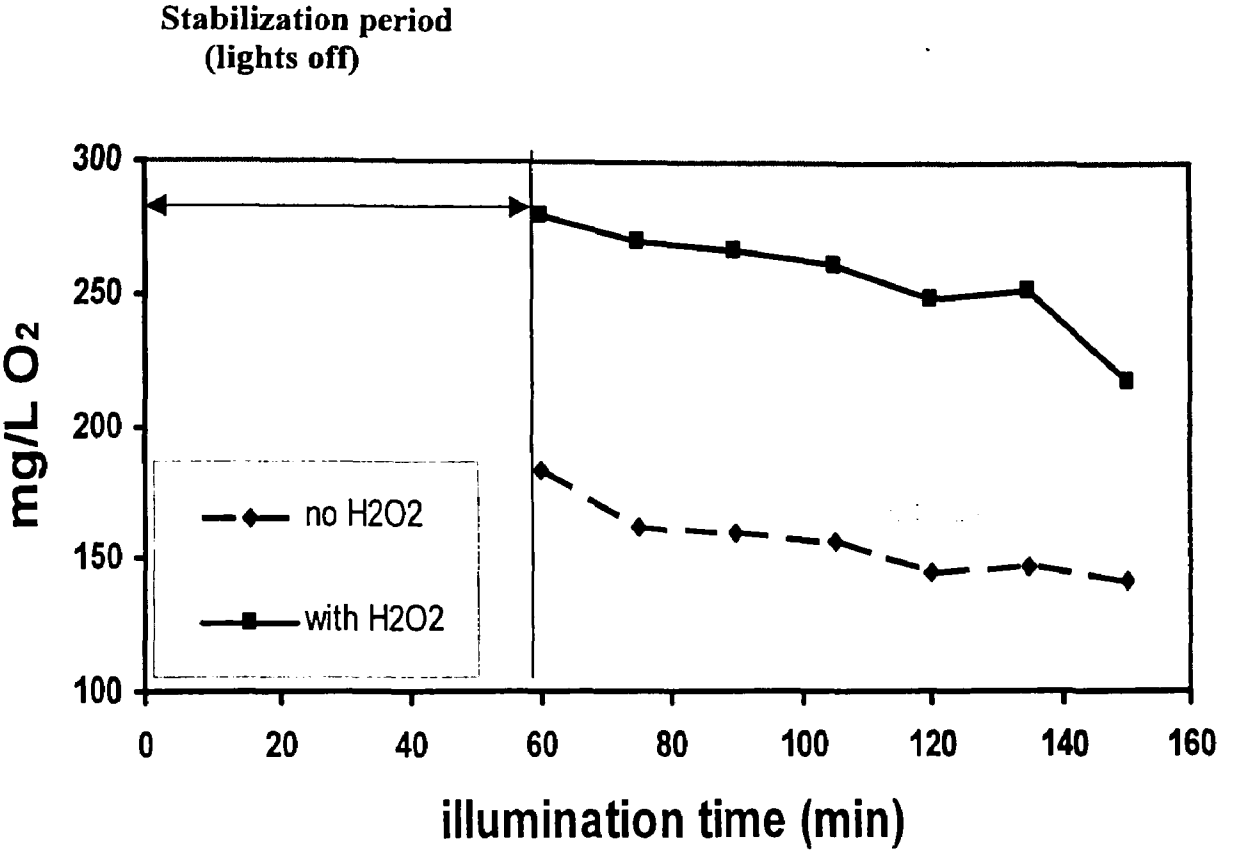

Figure 4.14: Changes in COD during the photolytic degradation of LAS in the presence of H_2O_2, and after removal of H_2O_2 by catalase. Comparison between ThOD and the effect of H_2O_2 on increasing the COD value. Initial ThOD was 240 mg/L O_2.
Illumination time means that the changes in the value of COD were monitored during the photolytic degradation (UV+H_2O_2) of LAS.

The H_2O_2 consumption model is as follows:

$$[H_2O_2] = -3.5786t+691.12 \quad (4.7)$$

where $[H_2O_2]$ is the concentration of H_2O_2 at time t and rate constant is equal to 3.57 min^{-1}. Therefore, the approximate concentration of H_2O_2 can be calculated at each time according to the Equation 4.7, to find the optimum concentration of catalase which is necessary to eliminate the residual H_2O_2 for the subsequent biological treatment (Appendix A).

4.2 Effects of Photolytic Pre-treatment on the Biodegradability of LAS

4.2.1 Biological Oxygen Demand for LAS

It has been shown that the inhibitory effect of LAS in its biodegradability increases by increasing the concentration of LAS (Patterson et al., 2002). The biodegradability of four different concentrations of untreated LAS was examined (100 mg/L, 50 mg/L, 25 mg/L, and 12 mg/L). The BOD_5 tests for all concentrations were performed. As Figure 4.16 shows, by increasing the concentration of LAS the consumption of O_2 was decreased. The consumption of oxygen was decreased by about 50%, by changing the concentration of LAS from 25 mg/L to 100 mg/L. It is obvious that this decrease was not due to the decrease of organics in bottles; however, the microorganisms in the activated sludge could not grow and use oxygen by increasing the LAS concentration. Therefore, LAS has inhibitory effect on microorganisms as its concentration increases. Moreover, the ratio of BOD_5/COD is often used to express the biodegradability of wastewater. Figure 4.17 shows the ratio of BOD_5/COD for the same concentrations of LAS. Values for BOD_5/COD less than 0.4 suggest that the wastewater is difficult to be biodegraded. It can be observed that this ratio for LAS at 100 mg/L is about 0.1, suggesting that LAS is recalcitrant at higher concentrations, and it is resistant to conventional biological treatments (Yu et al., 1998).

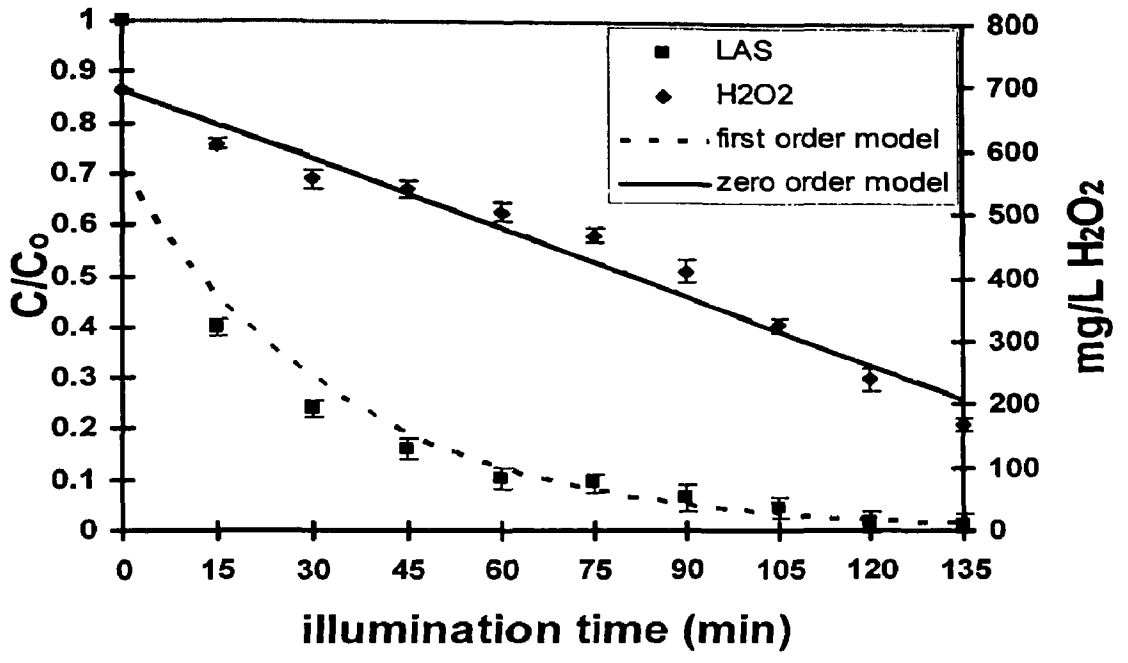

Figure 4.15: Consumption of H_2O_2 during the photolytic reaction of LAS using optimum concentration of H_2O_2 in cylindrical photoreactor, mixing=183 rpm, flow rate=12 L/min, C_{oLAS}=100 mg/L.

Three separate samples were taken and analyzed, in which case the standard deviations (error bars) represent sampling, preparation, and instrument error.

These results were in accordance with another study that the growth rate of mixed culture of microorganisms can be inhibited by LAS at the concentration of 95 mg/L (WHO, 1996).

The effects of photolytic pre-treatment of LAS on its biodegradability during the course of the reaction were studied. As Figure 4.18 depicts, the ratio of C/C_o (concentration of LAS at any time/initial concentration of LAS) was decreased up to 92% during 90 minutes of photolytic reaction using 720 mg/L of H_2O_2 as an oxidant. However, this decrease was sharp during the initial period of the reaction. After 15 minutes, C/C_o decreases gradually. The opposite trend was observed for the ratio of BOD_5/COD. This ratio increases gradually. This suggests that as the concentration of LAS decreases, the intermediates produced are more biodegradable than the parent compounds. After 90 minutes, the BOD_5/COD was 0.4, suggesting that although the untreated LAS was recalcitrant, the intermediates produced at this point were biodegradable under conventional biological treatment.

Relative changes in the biodegradability of wastewater samples during photochemical oxidation time can also be expressed in terms of biodegradability factor, f_B (Equation 2.16). It was observed that the biodegradability factor for the LAS treated in photolytic reactor was increased as the time proceeded (Figure 4.19). Therefore, again it was concluded that pre-treatment of LAS by this method was toward the increasing of its biodegradability. However, this increase was sharp during the first hour and after that increases gradually. It is in accordance with the BOD_5/COD ratio, as this ratio follows the same increasing pattern. On the other hand, comparing this finding with the changes in the concentration of LAS during illumination period, it could also be concluded that LAS decreased very fast during the first hour and after that there was little change in its concentration. To measure the biodegradability of the LAS, residual H_2O_2 was eliminated, as it could inhibit the growth of microorganisms. This elimination was done by catalase using the technique explained before.

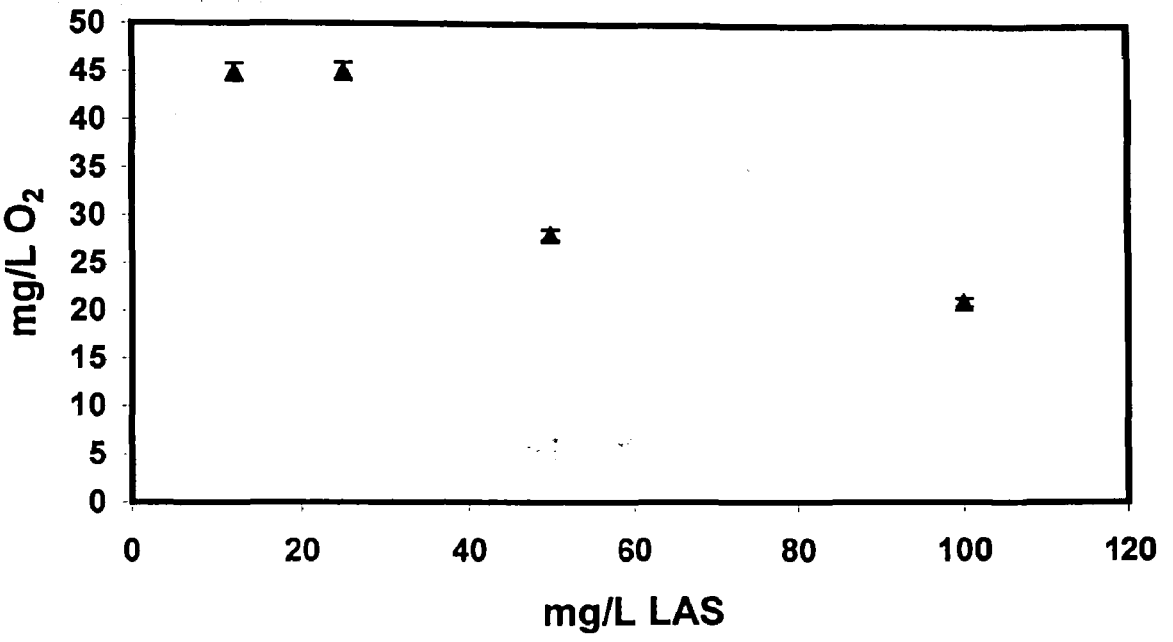

Figure 4.16: BOD_5 test results for 4 different concentrations of untreated LAS. The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

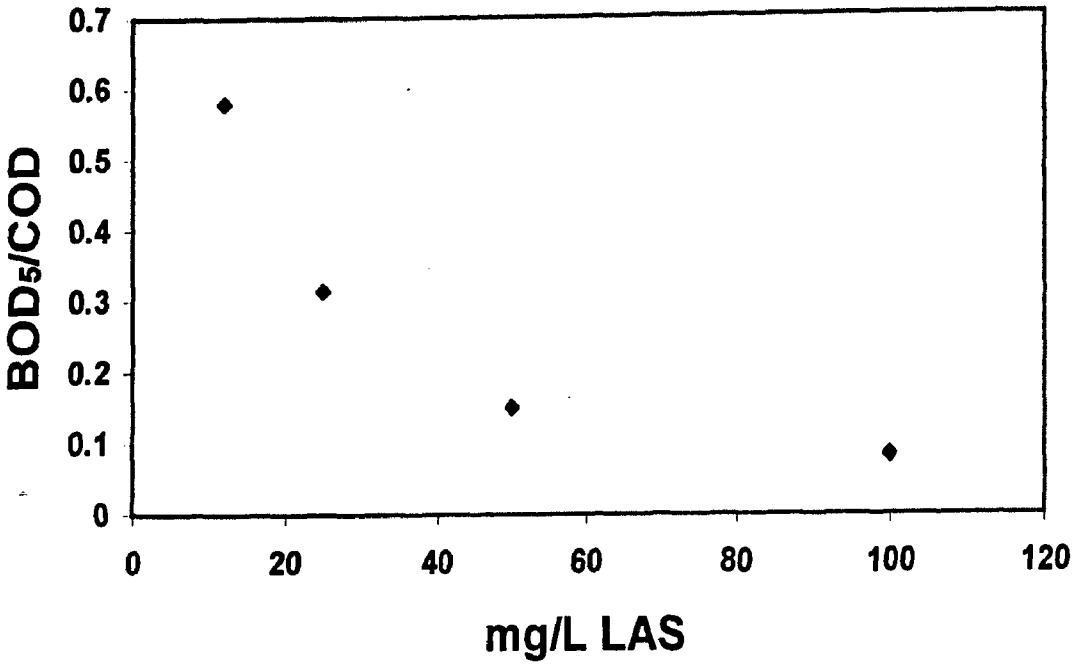

Figure 4.17: Ratio of BOD_5/COD for 4 different concentrations of untreated LAS.

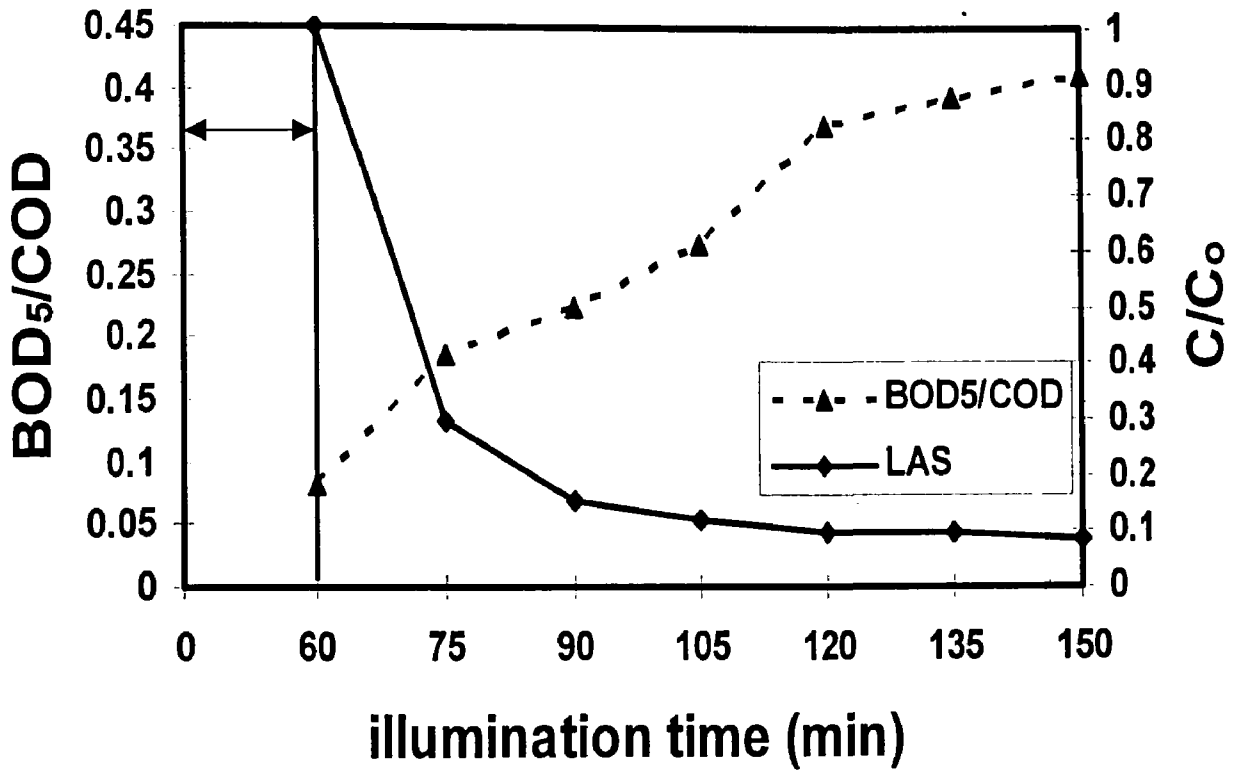

Figure 4.18: Effects of photolytic pre-treatment of LAS using 720 mg/L of H_2O_2 as an oxidant on its biodegradability. Flow rate = 8 LPM, Mixing speed=183 rpm, C_{LAS} =100 mg/L.

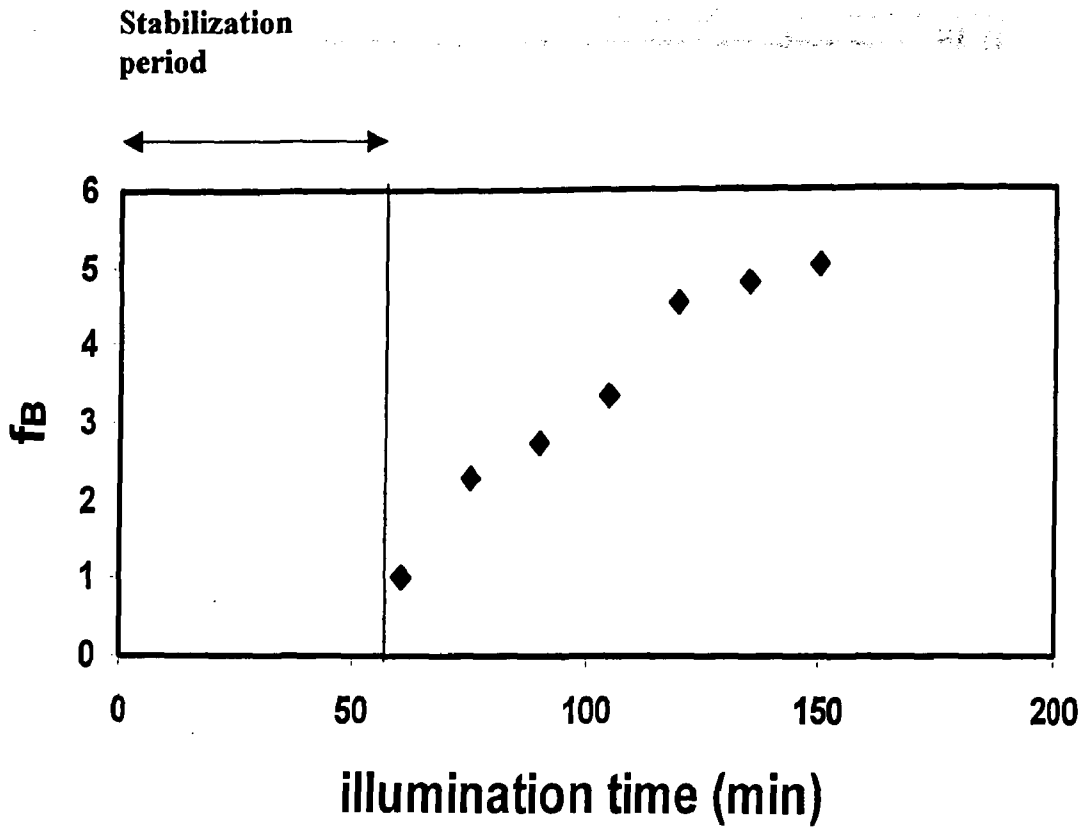

Figure 4.19: Increasing the biodegradability factor of LAS by proceeding the reaction, LAS was treated in photolytic reactor using H_2O_2 (720 mg/L) as an oxidant.

$$f_B = \frac{BOD_{5,t}(COD_t)^{-1}}{BOD_{5,0}(COD_0)^{-1}}$$

4.2.2 Ultimate BOD for the Biodegradation of LAS

The BOD for three different samples of LAS was modeled as follows:

1. Untreated LAS at the concentration of 100 mg/L
2. Pre-treated LAS by UV and optimum concentration of H_2O_2 after 15 minutes of treatment
3. Pre-treated LAS by UV and optimum concentration of H_2O_2 after 1.5 hours of treatment.

The BOD model is as follows (Section 3.2.17):

$$BOD_t = UBOD(1-e^{-kt}) \qquad (4.8)$$

where BOD_t, k, t, and UBOD are the amount of BOD at time t, rate constant, reaction time, and is the ultimate biological oxygen demand, respectively.

Figure 4.20 illustrates the BOD results for those three samples, mentioned above, in a 30-day period. With high concentration of LAS in the untreated sample, oxygen consumption was only 5.2 mg/L O_2 during 30 days, indicating that LAS was toxic to the microorganisms. Therefore, complete mineralization of LAS at the concentration of 100 mg/L was not possible. The consumption of oxygen during 30 days for the second sample was eight times more than first sample (second sample consumed 38 mg/L O_2 during 30 days), but still less than the third sample. The consumption of oxygen during 30 days for the third sample was 57 mg/L O_2. This indicates that the second sample was more biodegradable than the first sample. Therefore, the pre-treatment had the ability to increase the biodegradability of LAS, and as the reaction progress this effect was increased. Plotting the BOD versus time for those samples indicates that the removal of LAS in those samples follow first order model (Equation 4.8). Table 4.1 shows BOD models for each sample. As it can be seen the sample with 1.5 h of photolytic pre-treatment has the fastest reaction rate which is equal to 0.2839 $(day)^{-1}$. Therefore, it would be biodegraded 2 times faster than the untreated sample at 100 mg/L of LAS.

It is documented that the ultimate BOD of a sample is equal to 0.92 times the biodegradable portion of its COD (Eckenfelder, 2000). Therefore, the relation between UBOD and biodegradable COD is as follows:

$$UBOD=0.92 \times (COD)_d \qquad (4.9)$$

where UBOD and $(COD)_d$ are ultimate BOD and biodegradable portion of total COD of the sample, respectively. Moreover, total soluble COD can be calculated as the sum of biodegradable COD and non-biodegradable COD. Therefore, the portion of non-biodegradable COD for the above samples can be calculated easily. It was observed that as the photolytic reaction of LAS proceeded, the portion of non-biodegradable COD was decreased. As the non-biodegradable COD for the sample after 1.5 hours of photolytic treatment with H_2O_2 was 55% of total COD while this value for untreated LAS was 93%. Consequently, half of the total COD in the sample with 1.5 h pre-treatment was biodegradable, whereas almost all of the total COD in the untreated sample was non-biodegradable COD. Therefore, if LAS with photolytic pre-treatment is going to be treated further by biological treatment, all of the organics cannot be removed in the biological treatment. That is due to the presence of some non-biodegradable intermediates in the effluent of photolytic treatment (56% of intermediates were non-biodegradable in the effluent of photolytic treatment after 1.5 h of pre-treatment). This portion of non-biodegradable COD can be corresponded to the primary photolytic degradation of LAS oxidizing alkyl chain, and resulting sulfophenyl(di)carboxylates. It has also been reported that sulfophenyl(di)carboxylates are refractory to biodegradation (Patterson et al., 2002). Consequently, as the photolytic reaction proceeded, the biodegradable portion of COD was produced through cleavage the phenyl ring and removing sulfonate group.

4.2.3 Shake Flask Tests for Biodegradation of LAS

The experiment was done according to the method described in Section 3.2.20. The LAS solutions used were:

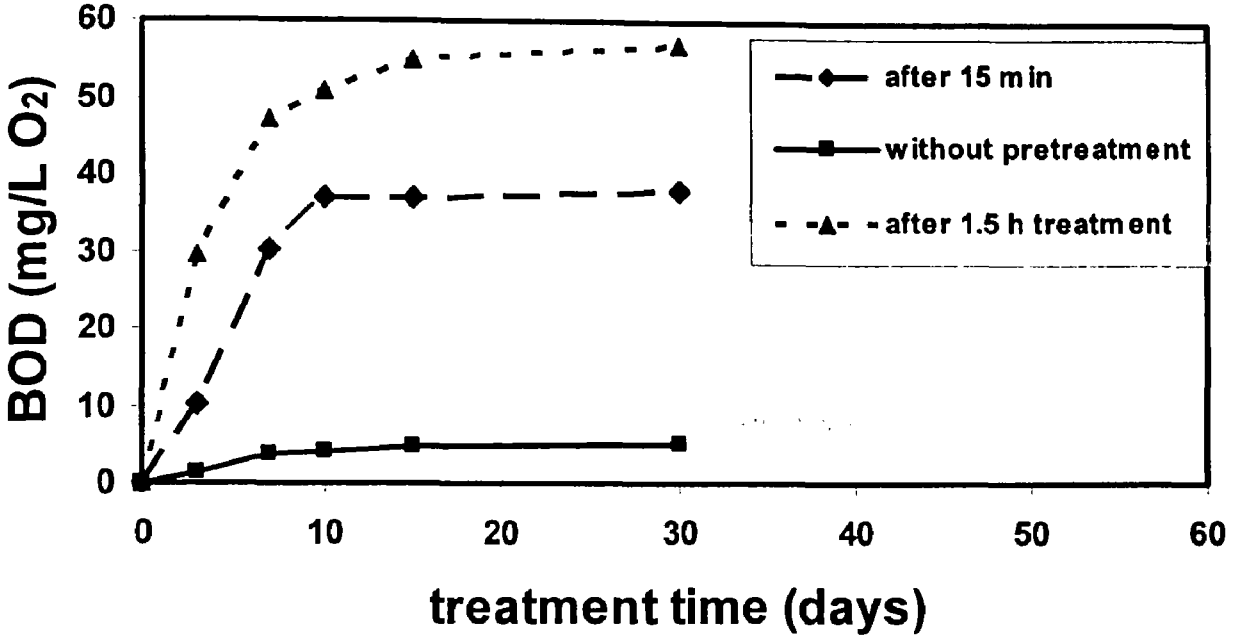

Figure 4.20: BOD tests for three samples in a 30-day treatment period for the following conditions

1. Untreated LAS at the concentration of 100 mg/L,
2. Pre-treated LAS by UV-254 and optimum concentration of H_2O_2 (720 mg/L) after 15 minutes of treatment,
3. Pre-treated LAS by UV-254 and optimum concentration of H_2O_2 (720 mg/L) after 1.5 hours of treatment.

Table 4.1: BOD models for three different samples.

1. Untreated LAS at the concentration of 100 mg/L,
2. Pre-treated LAS by UV-254 and optimum concentration of H_2O_2 (720 mg/L) after 15 min. of treatment,
3. Pre-treated LAS by UV-254 and optimum concentration of H_2O_2 (720 mg/L) after 1.5 hours of treatment.

The BOD model is: $BOD_t = UBOD(1-e^{-kt})$, UBOD, BOD_t , and k are ultimate BOD, BOD at time t, and rate constant, respectively.

Process	UBOD (mg/L O_2)	Rate constant (day^{-1})
Untreated LAS at 100 mg/L	5.2	0.1771
Pre-treated LAS for 15 min	38	0.2538
Pre-treated LAS for 1.5 h	60	0.2839

1. LAS at the concentration of 40 mg/L without any pre-treatment,
2. Pre-treated LAS after 1.5 h by UV-254 and optimum concentration of H_2O_2 (720 mg/L). Therefore, the concentration of LAS used in this experiment was reduced to 10 mg/L,
3. LAS at the concentration of 10 mg/L without pre-treatment,
4. LAS at the concentration of 100 mg/L without pre-treatment.

There were some H_2O_2 residues in the pre-treated sample (the concentration of H_2O_2 was 400 mg/L after 1.5 h of photolytic treatment). The H_2O_2 residue was eliminated with catalase before biological shake flask process according to the calculation described in Appendix A.

During the biological treatment, the concentration of LAS was monitored to compare the degradation of untreated LAS with the one with photolytic pre-treatment. Furthermore, pH and dissolve oxygen (DO) were measured on a daily basis (Figure 4.21). The pH for all types of samples was not adjusted and sample 1,2,3, and 4 had pH equal to 6.76, 6.56, 6.70, and 6.80, respectively. Therefore, the pH was in the acceptable range (the acceptable range for the pH in the biological treatment is between 6 to 8). There was no significant change in pH during the course of the process. DO was also measured during the treatment period, to make sure there was enough oxygen for the microorganism in the system. Each sample from the shake flasks taken was divided into two parts. LAS from the first part was measured directly, but the second part was filtered with Whatmann glass fiber with pore diameter of 1.58 μm (Standard Method, 1998) to separate the sludge from the liquor and then the concentration of LAS in the liquor was measured.

Initially it was observed that the concentration of LAS (40 mg/L) in the liquid phase in the untreated sample had a 16.5% decrease during the first day. However, as it is known that LAS is adsorbed to the sludge in aerobic biological treatment (Berna et al., 1989), the analysis of sludge showed that LAS had been adsorbed to the sludge up to 96%. Figure 4.22 shows the changes in the degradation of LAS in the liquid and sludge

phase. Initially, as the concentration of LAS in the liquid phase decreases, its concentration in the solid phase increased. This increase was up to 8 days and after that LAS in the sludge started to degrade. This suggests that the microorganisms in the sludge were acclimated to LAS and had been capable of degrading the LAS. The same pattern was observed in the literature (Rittmann et al., 2001). As the Figure 4.22 shows, after 31 days the concentration of LAS had not reached zero yet. Moreover, the sludge at day 31 still contained a considerable amount of LAS which was still more than the maximum contamination level. Furthermore, about 30% of the initial LAS remained in sludge, even if the effluent did not contain any LAS. This percentage of remaining LAS in this sludge was also observed in another study (Patterson et al., 2002). However, the total amount of LAS measured in the mixed phased in some days was seemed to be more than the initial concentration of LAS. This could be due to the fact that MBAS method measures the total concentration of anions rather than LAS alone, and hence, produces a positive error which means MBAS method has measured LAS plus other anions present in the solution.

On the other hand, the concentration of the pre-treated LAS reached to zero in 11 days. The concentration of LAS in the sludge had an increase from 4 to 6 mg/L, but it reached to its initial concentration in 15 days (Figure 4.23). Furthermore, the degradation rate of pre-treated and untreated LAS was compared with each other (sample 2 and 3). Figure 4.24 shows the difference between these two. As Figure 4.24 shows, it is obvious that during the first day, the pre-treated LAS was degraded by 30%, while the untreated LAS was degraded by 40%, suggesting that pre-treated LAS was less biodegradable than untreated LAS when dealing with the low concentration of LAS (10 mg/L), due to the presence of some other organics (intermediates). The same results were obtained by comparing the BOD_5/COD for photo treated LAS and untreated LAS with exactly the same concentration. The ratio for BOD_5/COD for pre-treated LAS was 0.4, while this ratio for untreated LAS at the concentration of 10 mg/L was 0.5. This implies that untreated LAS at the concentration of 10 mg/L is more biodegradable than pre-treated LAS at this concentration. This can be due to the presence of sulfophenyl(di)carboxylates produced from photolytic pre-treatment of LAS, which have been reported to be refractory to biodegradation (Patterson et al., 2002). However, reliable conclusion could

only be obtained by having the amount of total organic carbon (TOC) for those two types of wastewater.

The biodegradation rate of LAS in those experiments, as it was reported (Huang et al., 2000, Zhang et al., 1999), follows first order model (Figure 4.25). The pre-treated LAS followed the following model:

$$\ln\left(\frac{C}{C_o}\right) = -0.0104\,t + 0.1128 \qquad (4.10)$$

where C is the concentration of LAS at time t, and C_o is the initial concentration of LAS which is equal to the concentration of the photoreactor effluent.

The biodegradation of untreated LAS at the same concentration also followed the following model:

$$\ln\left(\frac{C}{C_o}\right) = -0.0188\,t + 0.2213 \qquad (4.11)$$

It is obvious that the constant for untreated LAS should be more than pre-treated LAS at the same concentration, as the concentration of LAS decreased in untreated LAS faster than pre-treated one.

However, the untreated LAS at the initial concentration of 40 mg/L followed the following model (Figure 4.26):

$$\ln\left(\frac{C}{C_0}\right) = -0.0039\,t + 0.113 \qquad (4.12)$$

where C is the concentration of LAS at time t, and C_o is the initial concentration of untreated LAS equal to 40 mg/L.

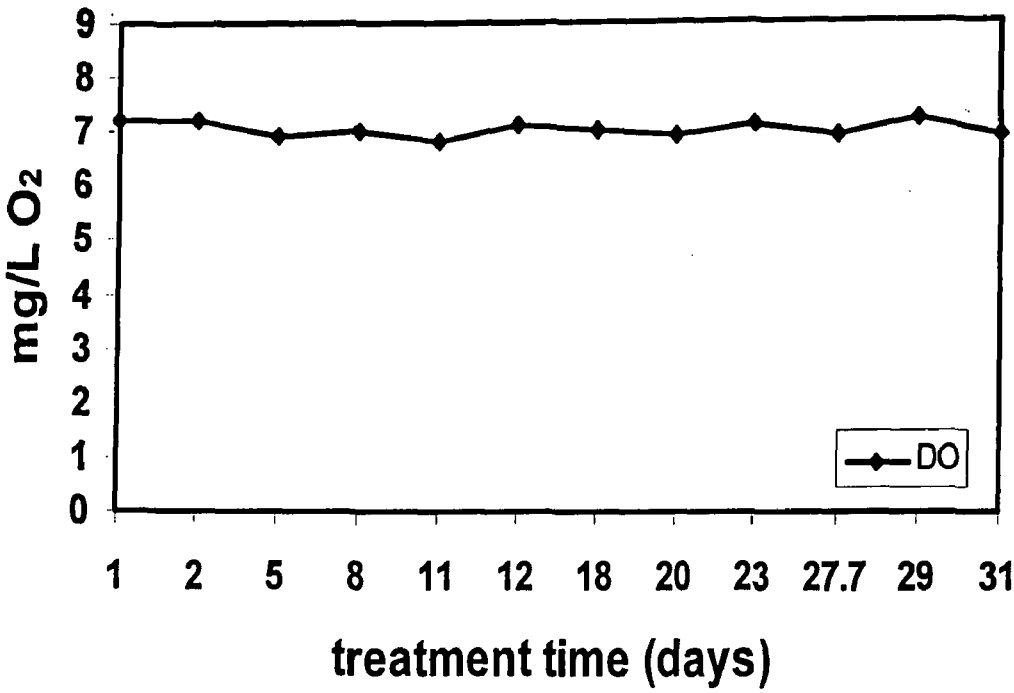

Figure 4.21. Changes in the DO during the shake flask experiment. The initial concentration of LAS was 10 mg/L.

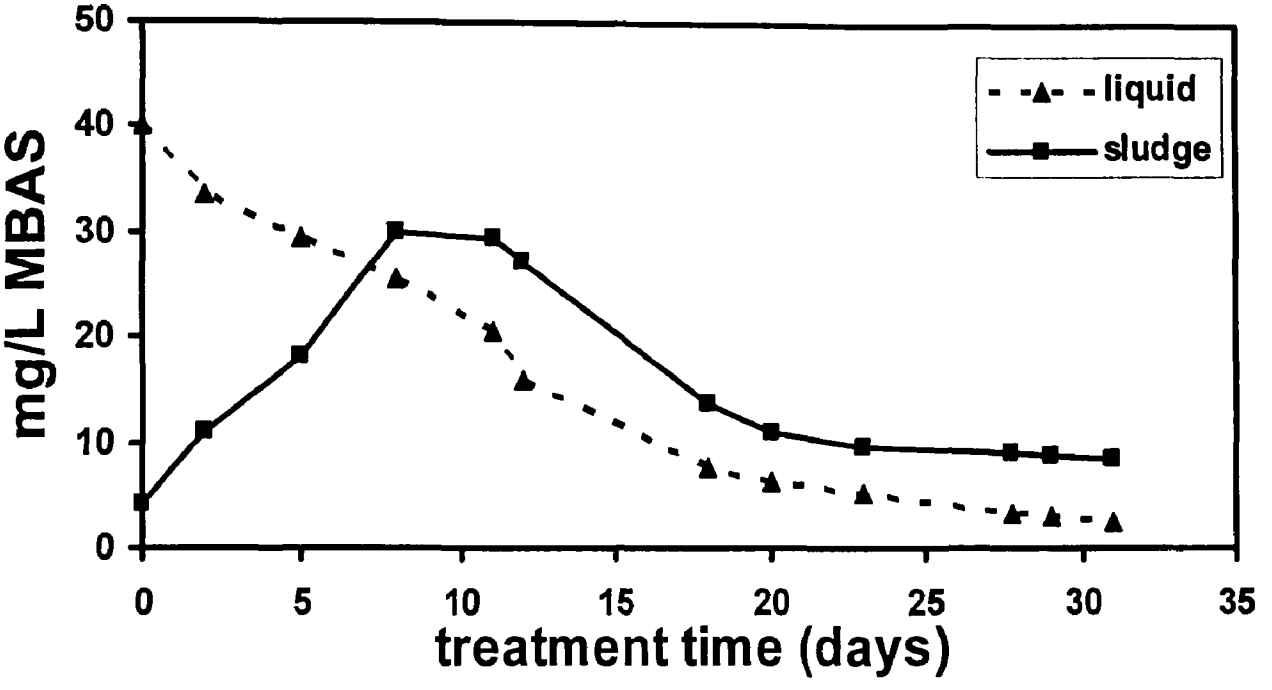

Figure 4.22: The changes in the degradation of untreated LAS at initial concentration of 40 mg/L in the liquid and solid phase in shake flask during 31 days keeping at 20°C.

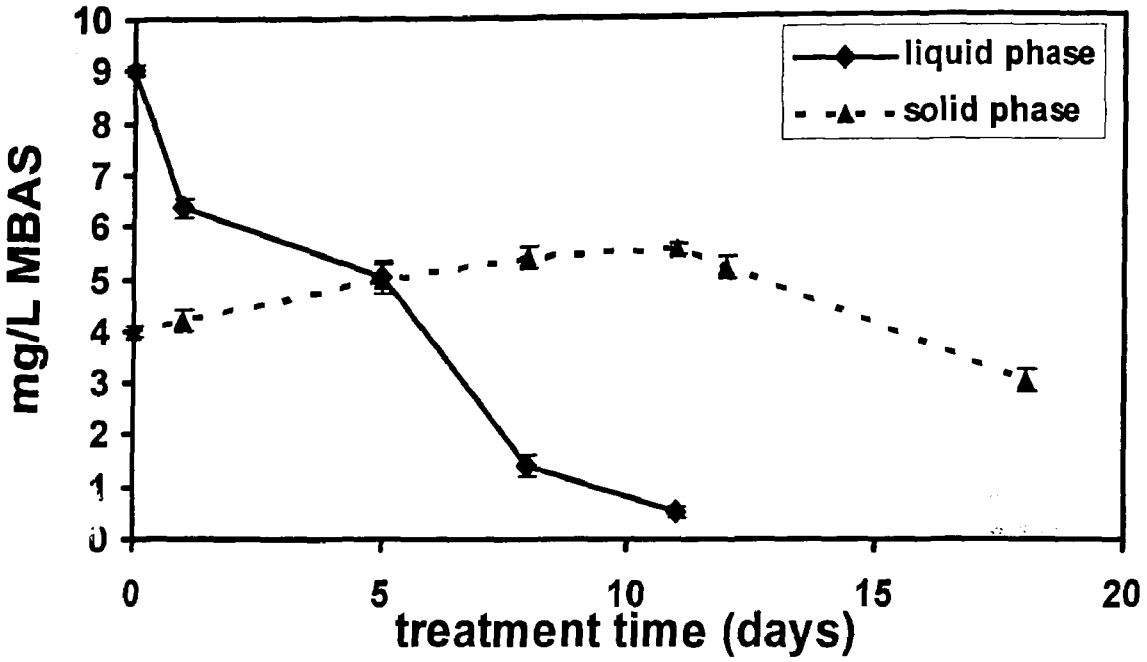

Figure 4.23: The changes in the degradation of pre-treated LAS in the liquid and solid phase in shake flask during 18 days keeping at 20°C, the initial concentration before pre-treatment was 100 mg/L and the sample was pre-treated by UV-254 and 720 mg/L of H_2O_2. The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

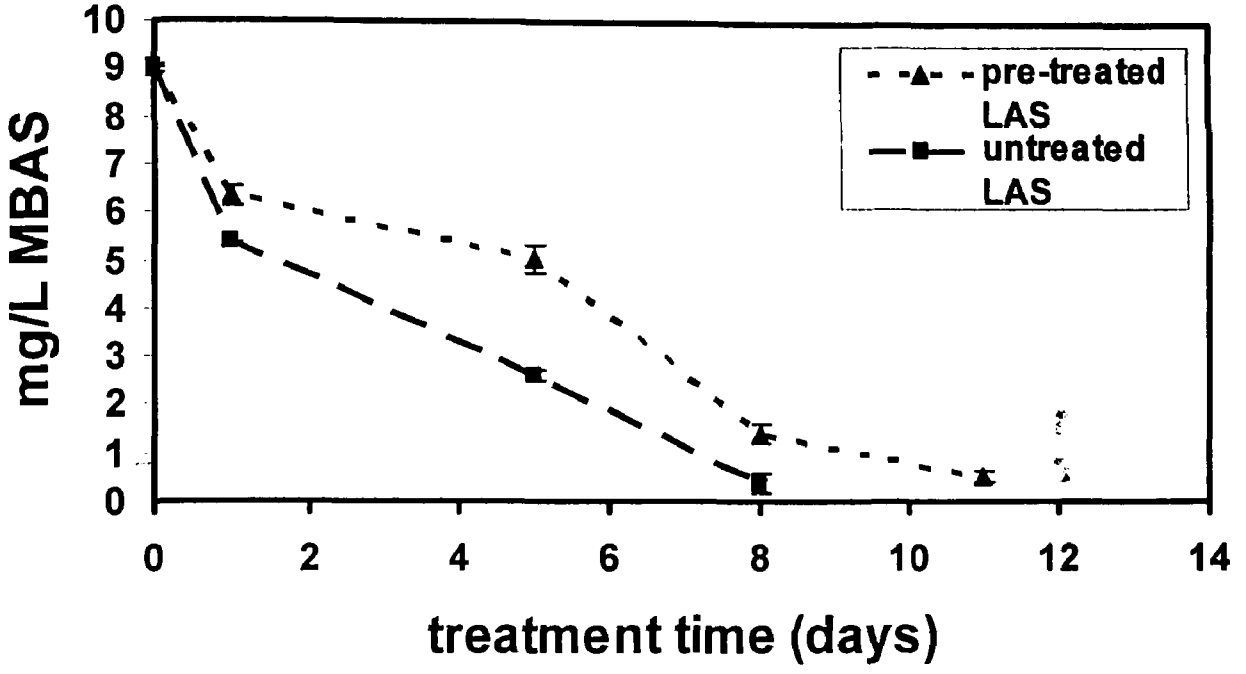

Figure 4.24: The degradation of pre-treated LAS and untreated LAS with no previous pre-treatment but at the same concentration in shake flask during 11 days keeping at 20°C, the initial concentration for biological treatment for both was 10 mg/L.
The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

Therefore, the constant for untreated LAS at the concentration of 10 mg/L is about 5 times faster than that of untreated LAS at 40 mg/L.

The analysis of the LAS at the concentration of 100 mg/L was not successful, as the concentration of LAS did not change in the shake flask after 30 days. Moreover, the analysis of the sludge after 30 days showed a decrease in biomass weight over 30 days. This suggests that the growth rate of mixed culture of microorganisms was inhibited at the concentration of 100 mg/L. This is consistent with the results obtained by Zhang et al. (1999). Furthermore, there was no visible decrease in the foaming of LAS at 100 mg/L during the period of biological treatment. Therefore, it supports the previous test (BOD_5/COD=0.1) which showed that LAS at this concentration had a toxic effect on the microorganisms. As LAS at the concentration of 100 mg/L inhibited the growth of microorganisms, consequently, the microorganisms did not have the ability to degrade LAS at the concentration of 100 mg/L.

4.2.4 Biological Treatment of LAS using Sequential Batch Reactors (SBR)

An aerobic sequential batch reactor was used to generate acclimated biomass for biological treatment of LAS (see Section 3.2.21 for more details). As the concentration of influent to the aerobic treatment (produced from chemical photolytic treatment of LAS with the optimum concentration of H_2O_2) was supposed to be 10 mg/L, the objective of this experiment was to adapt the biomass to that concentration of LAS. The effect of acclimation on the biodegradability of LAS was studied. To increase the rate of biomass growth during the acclimation period, LAS was diluted with sodium acetate. This dilution was based on the initial characteristic of 10 mg/L LAS.

It was observed that LAS at this concentration had a BOD_5 of about 30 mg/L. Therefore, the dilution was in a way to provide the same BOD_5.

It was also observed that sodium acetate at the concentration of 45 mg/L could produce such a BOD_5. Therefore, the experiment was started by addition of 45 mg/L sodium acetate to the SBR reactor.

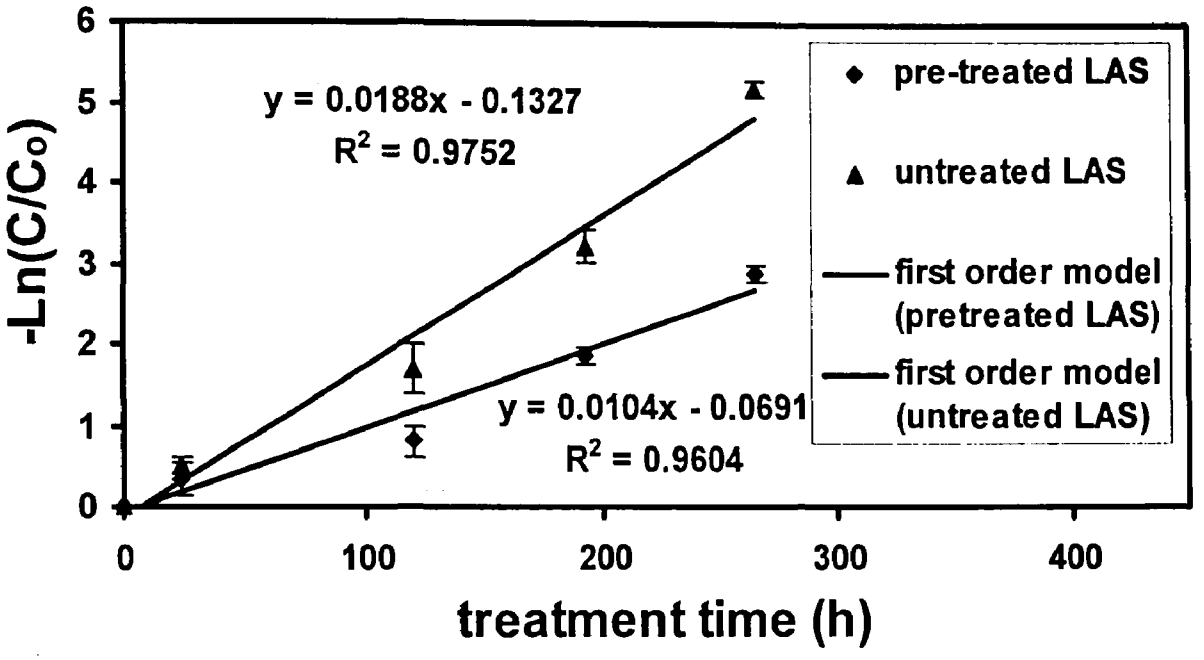

Figure 4.25: First order model for the biological degradation of two kinds of LAS in shake flasks as follows:

1. Pre-treated LAS (photolytic treatment $+H_2O_2$),
2. Untreated LAS.

The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

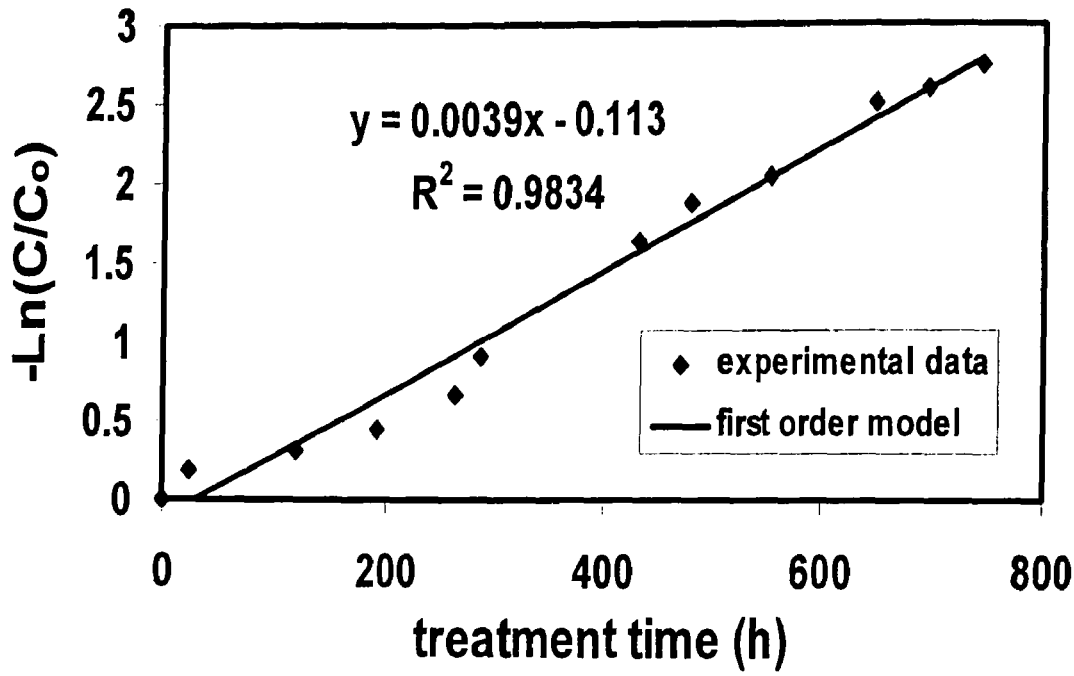

Figure 4.26. First order model for the biological degradation of untreated LAS at the initial concentration of 40 mg/L.

Moreover, activated sludge (from North Toronto Treatment Plant) and nutrient with the ratio of BOD:N:P equal to 100:5:1 were fed to the reactor. The nutrient medium was composed of KH_2PO_4, K_2HPO_4, $NaHPO_4$. $7H_2O$, NH_4Cl, $MgSO_4$, $FeCl_3$, and $CaCl_2$ (Standard Methods, 1998). The nutrients were added to the system weekly.

Air was provided by air diffuser and the system was mixed at the speed of 300 rpm. The concentration of LAS in the substrate was gradually increased according to the Figure 4.27; meanwhile, the concentration of sodium acetate was decreased to maintain BOD_5 equal to 30 mg/L. The addition of new substrate was provided when the changes in the concentration of LAS in the reactor became steady state, in other words the concentration of LAS became zero (Figure 4.27). The concentrations of LAS were measured at the end of settling period. pH, DO, MLVSS, temperature, COD, and the concentration of LAS were monitored daily at the end of settling period. BOD_5 was monitored 3 times per week. DO was almost constant at 7 mg/L O_2 (Figure 4.28), as a result, the system had always enough oxygen during the react period. Figure 4.29 shows the changes in pH during the acclimation period. It shows that pH had a slight variation, but it was always in the proper range of pH. The temperature was around room temperature ($25\pm1^{\circ}C$) and was constant. The BOD_5 results were almost the same during each sampling (Figure 4.28). This suggests in spite of increasing the concentration of LAS in the substrate, the microorganisms needed the same oxygen for metabolism due to acclimation to LAS. Subsequent to completing the acclimation period, the supernatant in the reactor was drawn and the reactor was filled with pre-treated LAS and nutrients. As microorganisms were acclimated to LAS, the associated lag time in the bioassays would decrease. Figure 4.30 shows the changes in the concentration of pre-treated LAS, and its COD and BOD_5 after the adaptation of microorganisms. The concentration of LAS in the biological reactor with the acclimated microorganisms reached zero in two days. COD and BOD_5 also had a decrease during that period, but they did not reach to zero. This might be due to the presence of some other intermediates produced during either biological or chemical treatment of LAS which were less biodegradable than LAS. Although in order to have a precise judgment of whether the concentration of the organics were increasing or decreasing, TOC results are required. Subsequent to the

treatment of each batch, the liquid was drawn during the draw period and filled with a new influent to examine the precision of the previous experiment. The biological treatment of LAS with acclimated sludge was repeated for three times.

Figure 4.31 shows the difference between the biodegradation of pre-treated LAS with the same concentration of LAS without any previous pre-treatment. The biodegradation of pre-treated LAS and untreated LAS at the concentration of 10.5 mg/L with adapted biomass followed the same trend as using unadapted biomass in shake flask experiments. In SBR again, the biodegradation of untreated LAS was faster than pre-treated LAS.

Assuming a first order model for their degradation (Figure 4.32), LAS without pre-treatment had a higher rate constant ($k=0.1312\ h^{-1}$) than LAS with pre-treatment ($k=0.0616\ h^{-1}$). This might be due to the presence of some intermediate produced by chemical treatment of LAS which are less biodegradable than LAS. The same conclusion has reported previously by degradation of LAS by means of wet air oxidation process (Mantzavinos et al., 2001). The degradation rate of pre-treated LAS was best fitted into first order kinetic rate which is in accordance with the previous studies (Huang et al., 2000, Zhang et al., 1999).

The pre-treated LAS in the sequential batch reactor followed the following model:

$$Ln\left(\frac{C}{C_o}\right) = -0.0616\ t \qquad (4.13)$$

where the constant (k) is equal to 0.0616 $(h)^{-1}$ and t (h) is reaction time. Time can also be expressed in minute (Figure 4.33) as follows:

$$Ln\left(\frac{C}{C_o}\right) = -0.001\ t \qquad (4.14)$$

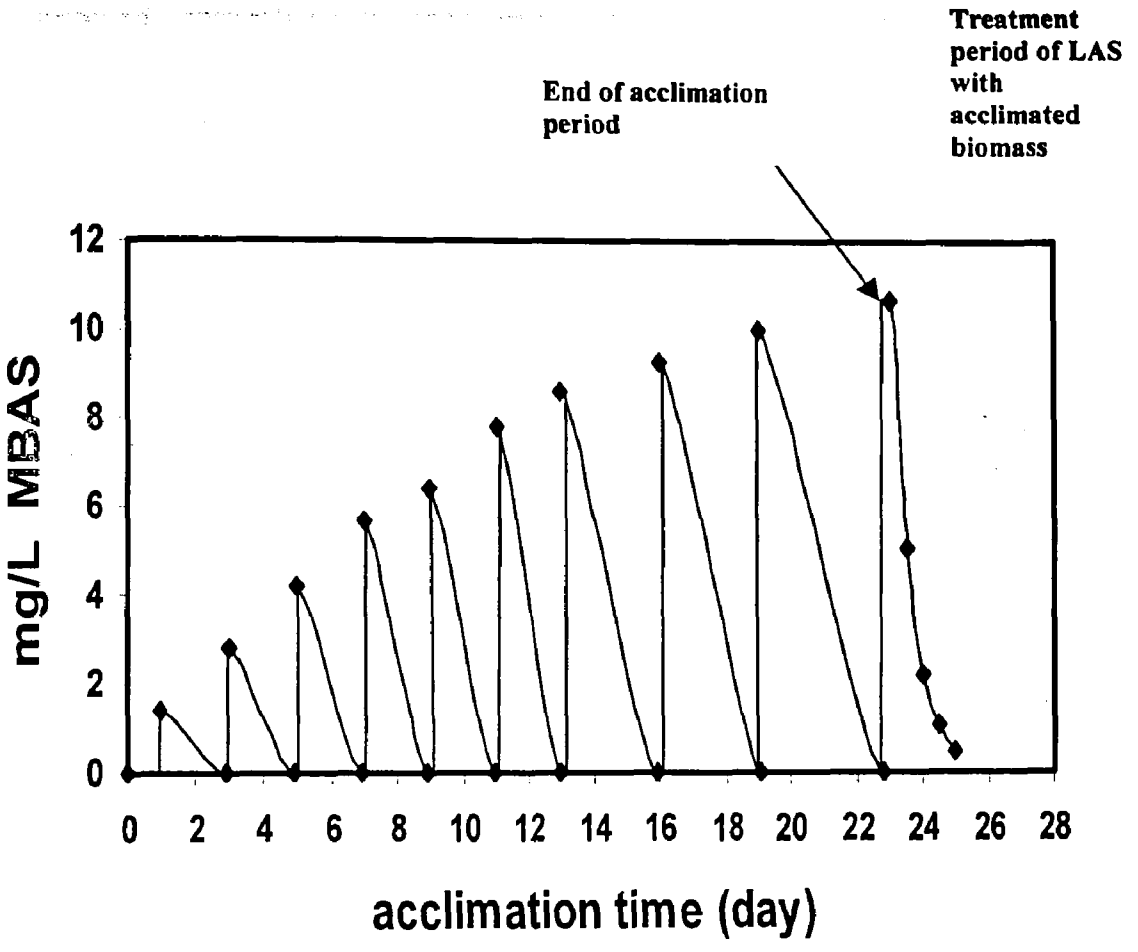

Figure 4.27. Gradual increase in the concentration of LAS which was added to the SBR during the acclimation period. This addition was done when the previous concentration of LAS in the SBR reached zero.

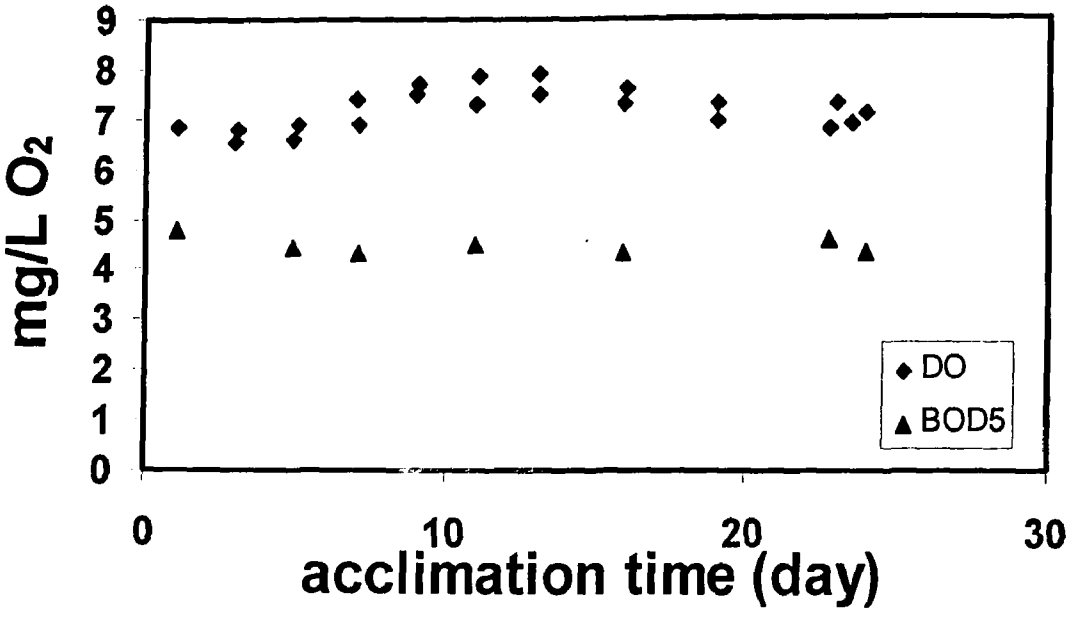

Figure 4.28. Changes in the DO and BOD_5 during the acclimation period of LAS at the initial concentration of 10 mg/L.

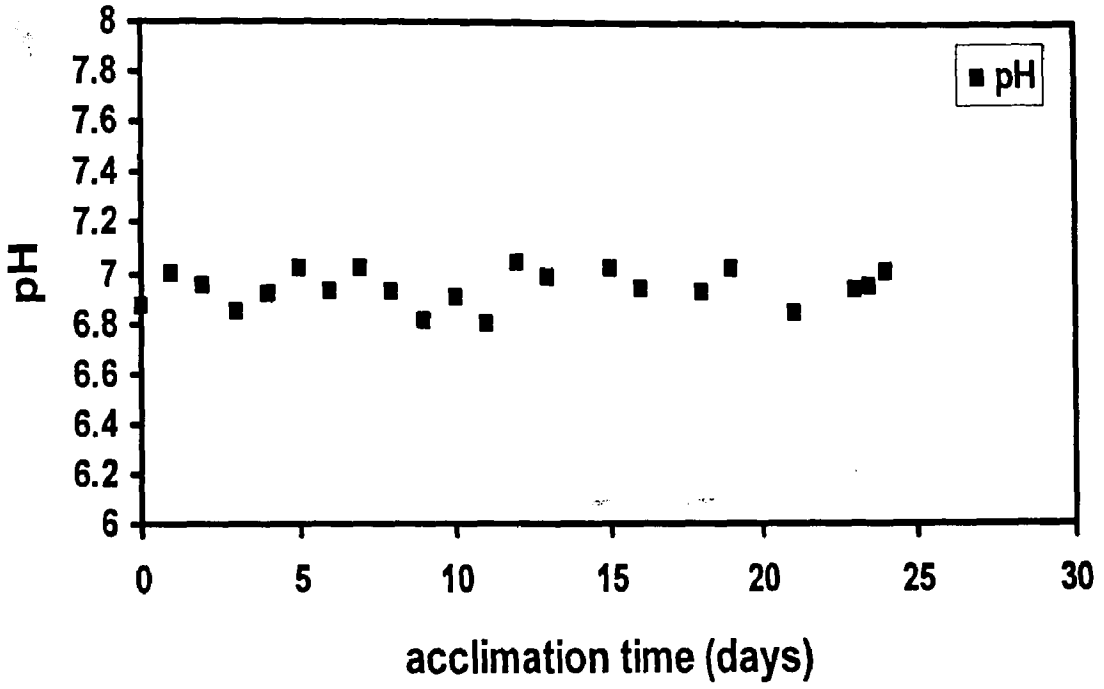

Figure 4.29. Changes in the pH during the acclimation period of LAS at the initial concentration of 10 mg/L.

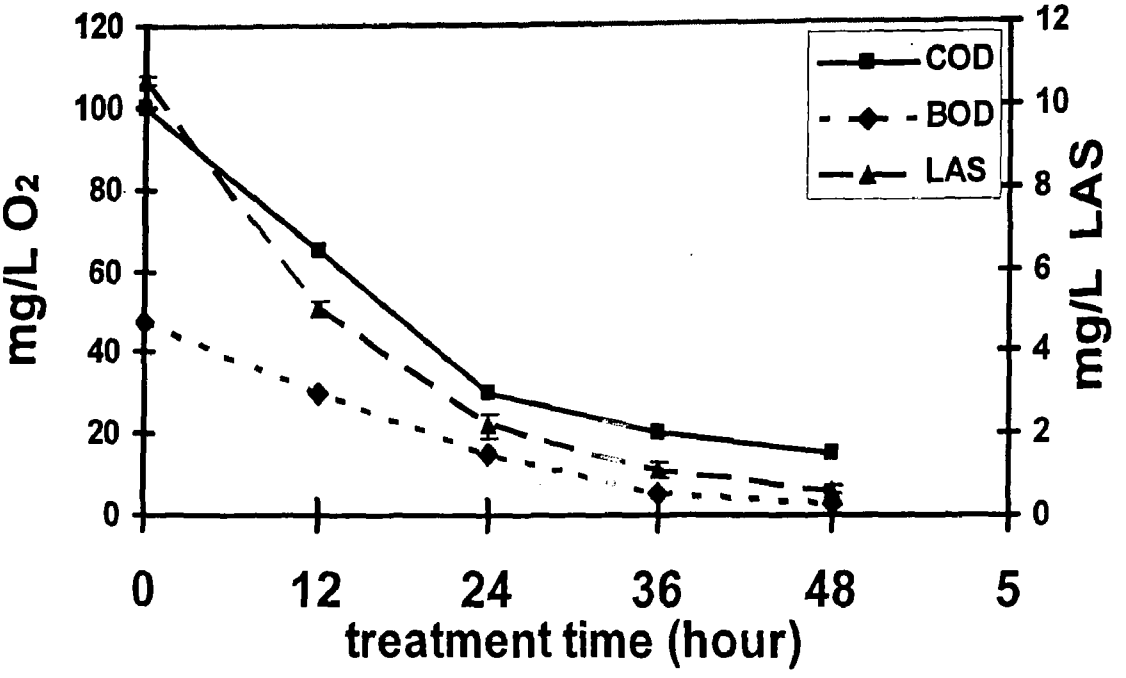

Figure 4.30: Changes in the concentration of pre-treated LAS, and its COD, and BOD_5 after the adaptation of microorganisms during 48 hours. Initial concentration of LAS was 10 mg/L at the beginning of biological treatment. The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

where C_o is the initial concentration of LAS in the influent of biological reactor and k is equal to 0.001 $(min)^{-1}$.

Table 4.2 shows different rate constants for different types of LAS for adapted and non-adapted microorganisms. It can be concluded that biodegradation of LAS with adapted microorganisms had higher constants both for untreated and pre-treated LAS. Moreover, untreated LAS had higher rate constants than pre-treated LAS with the same initial concentration.

4.3 Comparison between Combination of Photochemical and Biological Processes for the Treatment of LAS versus Photochemical Treatment alone

As it was mentioned before, LAS at the concentration of 100 mg/L has inhibitory effect to the microorganisms, therefore, it cannot be treated by biological processes alone. It cannot also be discharged to the environment as its maximum contamination level in ground water is 0.5 mg/L (EPA, 2004). Consequently, there should be a reliable treatment method to decrease its concentration to the desired level. The photolytic treatment of LAS with H_2O_2 is promising for its degradation; however, the operation cost of peroxide treatment is about 10 times more than that of activated sludge treatment (Esplugas and Ollis, 1997). Therefore, an attempt was made to combine these two processes to achieve o a cost efficient method. It was observed that pre-treatment by UV/H_2O_2 could increase the biodegradability of LAS (with the initial concentration of 100 mg/L) by 30% (measured by BOD_5 test). However, different residence times for both chemical and biological reactors may be applied. No specific residence time for either chemical or biological processes could be suggested unless considering a time that optimizes the treatment cost for this combination. In the following sections the relative cost of utilizing combination of photochemical and biological treatment has been compared versus photo-chemical treatment alone. As this is only a comparison, no treatment cost has been calculated and only their relative costs versus each other has been compared.

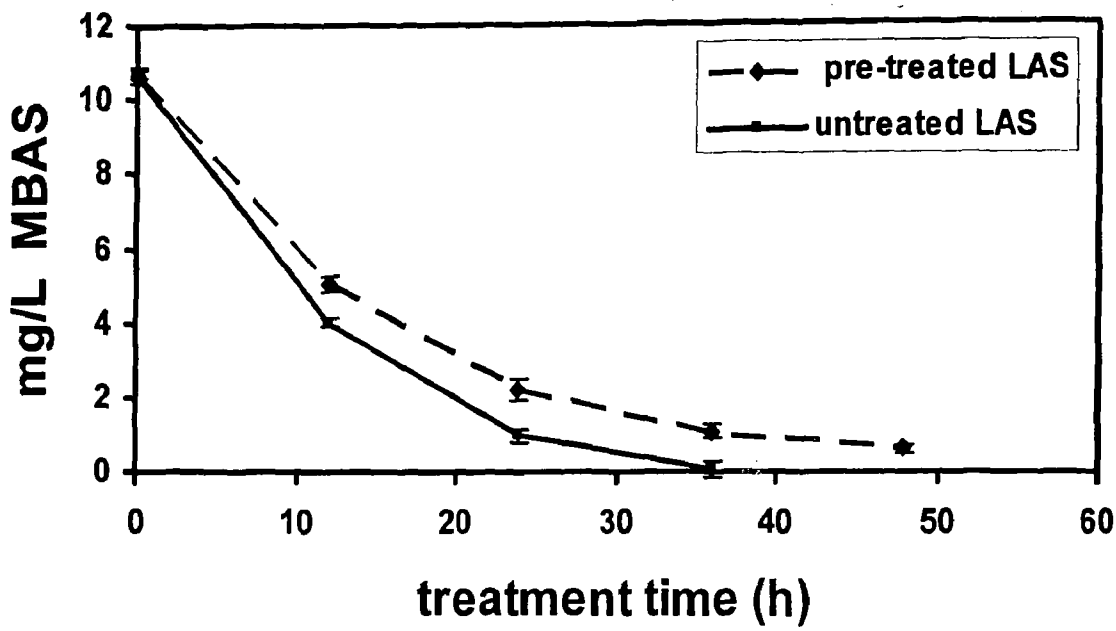

Figure 4.31: The difference between the biodegradation of pre-treated LAS with the same initial concentration of LAS without any pre-treatment in SBR with adapted microorganisms, the initial concentration of LAS was 10.5 mg/L. The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

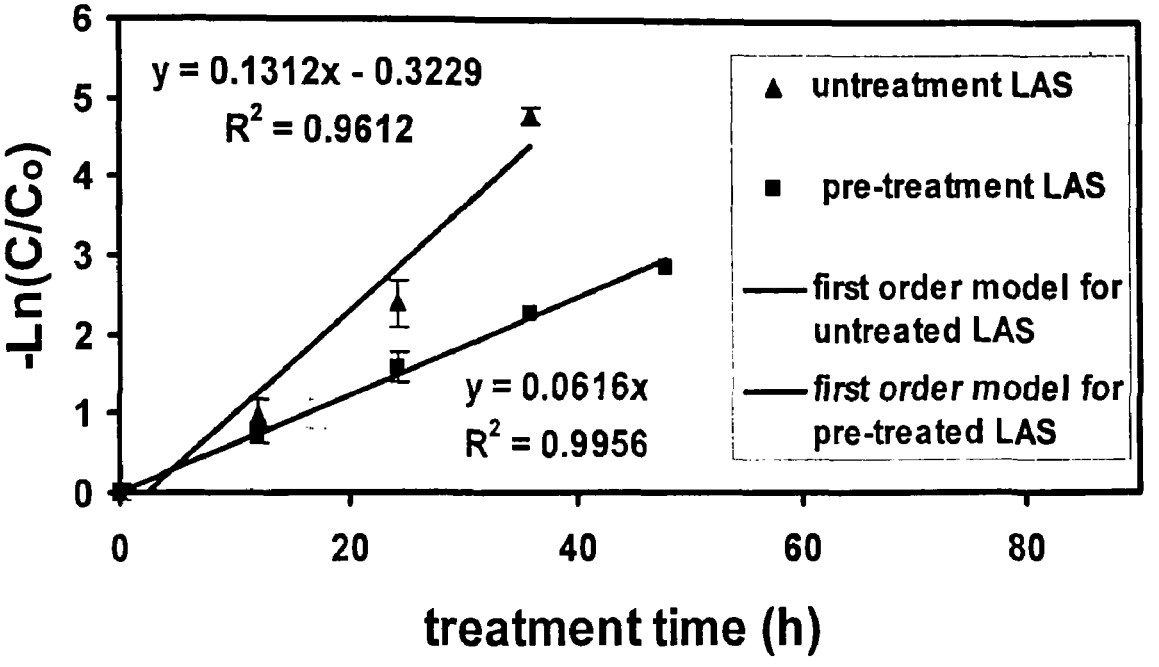

Figure 4.32: First order model for the biological degradation of LAS in SBR with adapted microorganisms. The error bars represent the standard deviation of three replicate aliquots of a single sample, in which case the standard deviation represents preparation and instrument error.

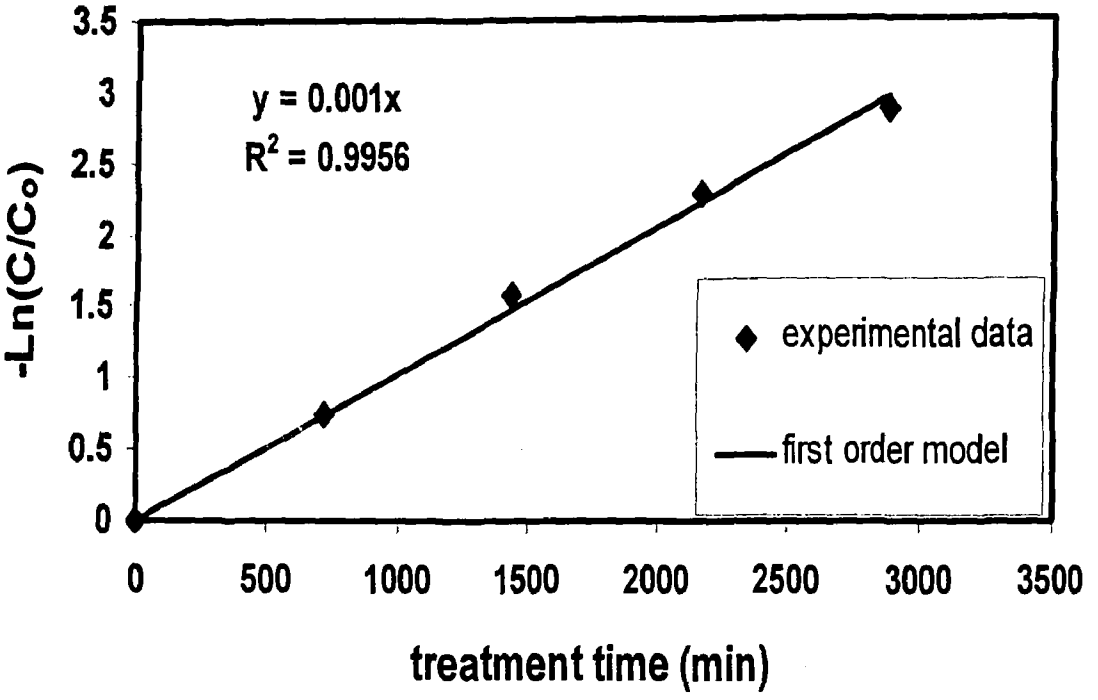

Figure 4.33: Comparison between experimental data for biological treatment pre-treated LAS in SBR with simulated data of first order model. The treatment time is considered in minute.

Table 4.2. Constants for first order model of removal of LAS in shake flasks (non-adapted microorganisms) and SBR (adapted microorganisms).

Process	Adapted microorganisms	Non-adapted microorganisms
Pre-treated LAS at 10 mg/L	0.0616 h^{-1}	0.0104 h^{-1}
Untreated LAS at 10 mg/L	0.1312 h^{-1}	0.0188 h^{-1}

4.15.1 Characteristics of the Integration of Photochemical and Biological processes

The combined system for the treatment of LAS at 100 mg/L is defined as follows: Compound A (LAS) is fed into the combined process. The combination consists of a photolytic reactor followed by a SBR. Therefore, compound A is first fed into the photolytic reactor and degrades into biodegradable compounds. However, only one of the measurable and significant intermediate for LAS is considered for the simplicity purposes. Moreover, the reaction time in the chemical reactor is set to degrade compound A partially. The effluent (consists of A and intermediate S) is then fed into the bioreactor for complete degradation. The objective is to define an optimal residence time in chemical and biological reactors that minimizes the relative cost of the combined processes.

The total residence time is defined by Equation (2.17) and the overall, chemical, and biological efficiencies are defined by Equations (2.18), (2.19), and (2.20), respectively.

The overall system in the chemical process acted as a batch reactor. H_2O_2 was used as an oxidant and the optimum concentration of H_2O_2 is known. It is assumed that the main intermediate produced by degradation of LAS with UV-254/H_2O_2 was known to be sodium benzene sulfonate. Therefore, the intermediate was produced during the degradation of LAS and then undergo photolytic degradation defined by first-order kinetics as follows:

$$A \xrightarrow{k_A} S \xrightarrow{k_S} R \qquad (4.15)$$

where S is the intermediate and R is final product from the degradation of the intermediate S in chemical reactor, preferably it is the complete mineralization of S.

LAS was observed to follow the first order kinetic model with respect to LAS during its photolytic degradation (Equation 4.5):

$$Ln\left(\frac{C_A}{C_{A_o}}\right) = -0.032t \qquad (4.5)$$

where C_A is the concentration of LAS at time t, and C_{A_0} is initial concentration of LAS which was 100 mg/L.

The concentration of S in this study could be written as the following expression:

$$\frac{C_S}{C_{Ao}} = \frac{k_A}{k_S - k_A}(e^{-k_A t_c} - e^{-k_S t_c}) \qquad (4.16)$$

where C_S, C_A, C_{Ao}, k_A, k_S, and t_c are the concentration of S in the chemical reactor effluent at time t, the concentration of A at time t, initial concentration of A, first-order rate constant for A, first-order rate constant for S, and the residence time in chemical reactor, respectively. It is supposed that the intermediate still posses the benzene ring, as the breakage of aromatic ring is unlikely due to its high bond energy. Therefore, the degradation constant for the intermediate was assumed to be smaller than that of LAS, as a result it was supposed to be equal to 0.001 min^{-1}.

The effluent of chemical reactor with t_c minutes of residence time enters into the biological reactor. However, due to the high concentration of H_2O_2 in the effluent of chemical reactor, the residues of H_2O_2 should be eliminated first. That effluent contains both LAS and its intermediate. As the objective was to decrease the concentration of LAS to 0.5 mg/L (maximum contamination level set by EPA), the solution remains in biological reactor until it meets that concentration. In the bioreactor, it was observed that the degradation of LAS follows the first order reaction model as mentioned in Equation (4.14):

$$Ln\left(\frac{C}{C_o}\right) = -0.001\,t \qquad (4.14)$$

where C is the concentration of LAS in the bioreactor at time t and C_o is the initial concentration in the bioreactor which was equal to the concentration of LAS in the

effluent of chemical reactor. The degradation of intermediate was also assumed to follow first order reaction model as follows:

$$Ln\left(\frac{C_{SB}}{C_S}\right) = -kt \qquad (4.17)$$

where C_{SB}, C_S, and k are the concentrations of intermediate at time t in the bioreactor, initial concentration of intermediate in the bioreactor which was equal to the concentration of intermediate in the effluent of the chemical reactor, and the first order reaction constant (min^{-1}) for the biodegradation of the intermediate, respectively.

During the biological experiments, it was observed that the intermediate produced during the photolytic degradation of LAS was less biodegradable than LAS (which might be due to the high concentration of intermediate at that time). k for the degradation of intermediate was assumed to be equal to 0.0009 min^{-1} which is less than the constant for the biodegradation of untreated LAS.

The chemical efficiency was defined as the reduction in concentration in AOP over 100% reductions in concentration of LAS; therefore, it can be expressed as follows (Scott and Ollis, 1996):

$$X = \frac{C_{A_o} - (C_A + C_S)}{C_{A_o}} \qquad (4.18)$$

where C_{Ao}, C_A, and C_S are the initial concentration of LAS equal to 100 mg/L, the concentration of LAS in the effluent of chemical reactor at time t, and the concentration of intermediate at time t equal to t_C in the effluent, respectively.

The biological efficiency was also expressed as reduction in the concentration of compounds in the biological reactor versus 100% concentration reduction (Scott and Ollis, 1996):

$$Y = \frac{(C_A + C_S) - (C_{AB} + C_{SB})}{C_{A_o}} \qquad (4.19)$$

where C_{AB} and C_{SB} are the concentrations of LAS and the concentration of intermediate in the effluent of biological reactor at time t equal to t_B. Therefore the total efficiency is equal to(Scott and Ollis, 1996):

$$Z=X+Y=\frac{C_{A_o}-(C_{AB}+C_{SB})}{C_{Ao}} \qquad (4.20)$$

where Z is the global efficiency. Consequently, as AOPs are more expensive than the biological treatment, ideally most organic removal should occur in biological stage (Patterson et al., 2002). Therefore, Y should be greater than X.

The objective function for the optimization of the integration of biological and chemical processes for this example is as follows (Esplugas and Ollis, 1997):

$$C=t_B{}^b+at_C{}^c \qquad (4.21)$$

where C is the relative cost function and a ($a\geq1$), and b ($b=0.6$) and c ($c=0.6$) are the volumetric cost ratio between AOP and biological reactor, and time constants, respectively. The volumetric cost is the ratio for the operating cost of chemical to biological treatment per each volume of wastewater treated. The relative cost is used as a tool to compare of different combinations of chemical and biological processes from the economic point of view. It is not the actual cost of treatment, and higher values of the relative cost imply that the treatment cost would be higher. On the other hand, the low value of relative cost shows lower treatment cost. In other words, the relative cost expresses the ratio of chemical treatment to biological treatment cost. b was chosen equal to 0.6 as in the absence of the actual cost and when it is necessary to estimate the cost of equipment, good results can be obtained by using six-tenths-factor rule (Peters and Timmerhaus, 1991). Moreover, simply combining the treatment time in bioreactor and chemical reactor was not possible as the residence time in chemical reactor is 50 times less than that of biological reactor. However, the operating cost of chemical treatment is 10 times more than biological treatment.

The constraints for this optimization example are set as follows:

a) equality constraints:

$$\eta_G = Z = \frac{C_{Ao} - C_{AB} - C_{SB}}{C_{Ao}} = 0.95 \quad \text{(the desired efficiency is 95\%)} \tag{4.22}$$

where η_G, C_{Ao}, C_{AB}, and C_{SB} are total (global) efficiency, the initial concentration of pollutant (mg/L), the concentration of the LAS in the bioreactor effluent (mg/L), and the concentration of intermediate in the bioreactor influent (mg/L), respectively.

b) inequality constraints:

$$0 \leq C_A \leq C_{Ao} \tag{4.23}$$

$$C_S \geq 0 \tag{4.24}$$

$$t_C \geq 0 \tag{4.25}$$

$$t_B \geq 0 \tag{4.26}$$

$$C_{AB} \leq 0.5 \text{ mg/L} \tag{4.27}$$

where C_S, C_{AB}, t_B, and t_C are the concentration of intermediate leaving chemical reactor (mg/L), the concentration of the LAS in the bioreactor effluent (mg/L), the residence time in the bioreactor, and residence time in chemical reactor, respectively. The residence times are chosen to be positive as negative residence time is not acceptable in the process and that is the same for the concentrations. Moreover, it is expected that the concentration of A in the effluent should be less than the inlet concentration of A in the chemical reactor.

4.15.2 Solution of the Optimization Procedures

According to the Equation 4.21, the applicable method is nonlinear equation with constraints. Therefore, the problem was solved numerically. The GRG2 (generalized reduced gradient) code is used to solve the model. Constant "a" in Equation (4.24) was chosen to be 10 as it is reported that the cost of peroxide treatment is about 10 times of

activated sludge treatment (Esplugas and Ollis, 1997). Constants "b" and "c" were chosen to be 0.6 for the same reason as suggested in a previous study (Esplugas and Ollis, 1997). Therefore, the objective function which provides an indication of the relative costs of the combined system would be in the form of:

$$C=t_B^{0.6}+10t_C^{0.6} \qquad (4.28)$$

After solving the objective function of Equation (4.28) along with the constraints in Equations (4.22-4.27), the results of the optimization are summarized in Table 4.3. As indicated in Table 4.3, the residence time in the chemical and biological reactors are 61.51 and 3365.58 minutes, respectively. Those residence times lead to decrease the concentration of A from 100 mg/L to 13.88 mg/L in chemical reactor. Meanwhile, in the bioreactor, the concentration of S decreases from 82.72 mg/L to 4 mg/L. This configuration minimizes the total cost of these integrated processes. Many other combinations for this global efficiency is possible that might even further decrease the final concentration of the biological effluent, but these residence times for photolytic and biological reactors are the most cost effective one. Moreover, as it was mentioned before, in this combination, the efficiency of chemical reactor is much less than the efficiency of the biological reactor. If only the goal was to reach the efficiency of the photochemical reactor to 95%, it was estimated that the residence time in the chemical reactor should be 2940 min. This residence time would give a relative cost of equal to 1205, while the concentration of the intermediates reached to 5.4 mg/L. Moreover, the LAS at the initial concentration of 100 mg/L did not have the ability to be degraded biologically. Therefore, LAS at the concentration of 100 mg/L could not be treated by biological treatment alone.

Figure 4.34 illustrates the degradation of compound A and formation of compound S during the course of the reaction in the chemical reactor. It is clear that the rate of degradation of A and formation of S are influenced by their rate constants. Decreasing the rate constant of degradation of S can lead to increase the concentration of S in the

Table 4.3: Optimization results for the combination of photochemical (UV/H_2O_2) and biological (activated sludge, SBR) processes for the treatment of LAS

Parameter	Values
t_c	61.51 min
t_B	3365.58 min
μ_G	0.95
C_A	13.88 mg/L
C_{AB}	0.5 mg/L
C_{SA}	82.72 mg/L
C_{SB}	4.00 mg/L
μ_c	0.04
μ_B	0.91
Relative cost	249.10 $/volume of wastewater treated/min
Residue H_2O_2	471.0 mg/L

photo-reactor's effluent, and hence, the concentration of the intermediate increases in the bioreactor. Therefore, the rate constant of the S in the bioreactor decreases. Consequently, decreasing the degradation rate of S alone did not show significant effect on the relative cost. As decreasing it by 4 orders of magnitudes, only it reduced the relative cost by 2%. Therefore, in the optimization of the relative cost of the combination, the degradation rate constant of LAS has a significant effect. This can be due to the assumption that LAS do not mineralize completely during pre-treatment and only produces intermediates with high bond energy that are supposed to be mineralized in the biological step. If these intermediates had a rate constant higher than the LAS degradation rate constant in the chemical stage, they would degrade faster than LAS and the chemical effluent contains almost no intermediate. This cannot be true due to the following reasons:

1. The biodegradability tests showed that the effluent from the chemical reactor is less biodegradable than LAS at the same concentration, when dealing with LAS at lower concentrations (10 mg/L), and this is due to presence of intermediates which are less biodegradable than LAS at the concentration of 10 mg/L.
2. The COD test after pre-treatment showed little decrease. If it was true and the intermediates had the ability to be degraded rapidly, there should be a sharp decrease in the COD during the pre-treatment, as the concentration of organics were decreasing rapidly
3. As the intermediate contains aromatic ring, the breakage of this ring is more difficult than the breakage of the side chains. Therefore, the degradation of an intermediate with high bond energy is slower than its production, which is due to the breakage of the side chain of LAS.

As a result, the assumption that the degradation of the intermediate was less than the degradation of LAS was a correct assumption.

The optimum operating conditions occur due to the design constraints and the global residence time. Using the integration of chemical and biological processes for LAS treatment instead of single step of AOP appears to reduce the total residence time in both chemical and biological reactors while obtaining the desired total efficiency.

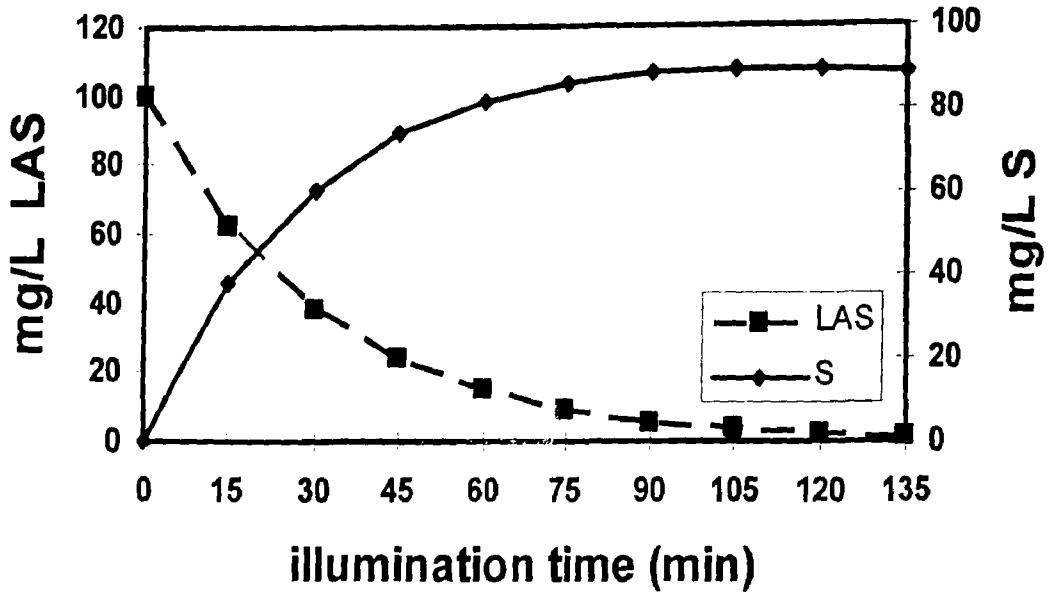

Figure 4.34: The kinetic model for A and S in the photolytic reactor. A is the compound to be degraded and S is its intermediate produced during the reaction.

However, both capital and operating cost are less for biological treatment than those for AOP. Moreover, different chemical and biological residence times can give the same efficiency, but just one of these residence times (t_c=61 min and t_b=3365.58 min) can minimize the relative treatment cost.

CHAPTER 5

CONCLUSIONS AND RECOMANDATIONS

5.1. Conclusions

The following conclusions could be drawn from the thesis:

1. The LAS degradation was increased by decreasing the flow rate, as the residence time of LAS in photoreactor increased. For the best case, using maximum mixing speed and lowest flow rate, the maximum degradation of LAS was 80% during 6 hours of photolytic treatment.
2. Photolytic treatment alone is capable of degrading LAS in 120 min with the degradation rate of only 40%. UV-C alone can degrade the organics by breaking their bonds directly. This breakage is possible only when the bond energy is less than the wavelength energy.
3. The optimum concentration of H_2O_2 which should be used for the photochemical treatment of LAS with UV and H_2O_2 was 720 mg/L. The photolytic treatment with the aid of hydrogen peroxide can degrade LAS up to 95% in 120 min. This can be due to the ability of hydrogen peroxide to produce hydroxyl radicals, which in tern can react with the organics directly.
4. The chemical degradation of LAS led to produce intermediates, which were more biodegradable than LAS at the concentration of 100 mg/L. This increase was much more while UV was combined by hydrogen peroxide.
5. The biodegradability of LAS highly depends on its concentration. LAS at the concentration of 100 mg/L is non-biodegradable and has inhibitory effect on microorganisms, while LAS at the concentration of 10 mg/L is more biodegradable than LAS at 100 mg/L.
6. The biodegradation of pre-treated LAS by combination of UV and H_2O_2 by mixed culture of microorganisms was successful. The concentration of pre-treated LAS decreased to 0.5 mg/L during 11 days in shake flask experiment.

7. Adapting the activated sludge in the SBR to LAS at the concentration of 10 mg/L resulted to an increase in the degradation rate of LAS. As the pre-treated LAS was degraded only in 48 hours.
8. Adsorption of LAS to the sludge plays an important role in the removal of LAS from the liquid phase. This problem becomes more obvious at the higher concentrations. Therefore, chemical pre-treatment for higher concentrations of LAS is highly recommended.
9. The pre-treated LAS at concentration of 10 mg/L is less biodegradable than that of untreated LAS at 10 mg/L. This can be due to the high concentration of the intermediates in the effluent of photo-chemical treatment. This implies that LAS at the lower concentration (10 mg/L) is even more biodegradable than pre-treated LAS, but at higher concentrations (100 mg/L) pre-treated LAS is more biodegradable than untreated LAS.
10. By mathematical calculations it was observed that to obtain the total efficiency of 95% in the chemical reactor alone, the residence time of chemical reactor should be about 50 hours; however, coupling the chemical reactor with the biological reactor led the chemical residence time to about 1 hour (61 min). Moreover, this coupling can decrease the relative cost.

5.2 Recommendations

The following recommendations could be suggested:

1. The main problem in the biological experiments was the presence of unknown intermediates, which were produced during photolytic oxidation of LAS. If those intermediates were known, the acclimation procedures could be done by using them instead of LAS, as they are supposed to present in the chemical effluent in high concentrations. Therefore, the biomass in the activated sludge was adapted to them and could degrade the pre-treated influent in a very short period of time. Moreover, the intermediates should be known and the kinetic parameters for the intermediates could be measured and the optimization procedures could be done more accurately.

However, modeling the removal of LAS considering the mass transfer between liquid and solid phases could be a better model.

2. It is suggested that TOC analysis are done, as it could predict the degrees of removal of organics during both chemical and biological processes. Furthermore, DOC results could be used to calculate the partial oxidation parameters, which set the optimal point for the oxidative treatment. The shorter reaction time avoids the high electrical cost of the reaction. At longer photo-treatment time, the photochemical efficiency is improved by the unnecessary photo-degradation of pollutants which are biologically degraded. This point could then be compared with what was obtained through optimization techniques.
3. It is suggested to model the optimization of photochemical treatment of LAS combined by biological process by knowing the exact kinetic rate constants for the intermediates and considering the effect of adsorption of LAS to the sludge during its biological treatment.

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APPENDIX A

(a) Calculation for BOD_5

Initial DO in the blank: 8.24 mg/L

Initial DO in the sample: 8.30 mg/L

DO after 5 days in the blank: 7.59 mg/L

DO after 5 days in the sample: 6.13 mg/L

Volume of sample added to BOD bottles: 30 mL

f: ratio of seed in diluted sample to seed in seed control =1

P: volumetric fraction of sample = 30/300=0.1

Using Equation (3.8) (Metcalf and Eddy, 2002):

$$BOD_5=\frac{(8.30-6.13)-(8.24-7.59)}{0.1}=15.2 \quad \text{mg/L } O_2$$

(b) Biodegradability factor, f_B

COD_o, COD of untreated LAS= 183 mg/L O_2

COD_t, COD after 1 h. pre-treatment=145 mg/L O_2

$BOD_{5,t}$, BOD_5 after 1 h. pre-treatment=54 mg/L O_2

$BOD_{5,o}$, BOD_5 of untreated LAS=15 mg/L O_2

$$f_B=\frac{BOD_{5,t}(COD_t)^{-1}}{BOD_{5,0}(COD_0)^{-1}}$$ (Eq. 2.16) (Arsalan and Balciglu, 2001):

$$f_B=\frac{54\times(145)^{-1}}{15\times(183)^{-1}}=4.5$$

(c) COD removal

COD_o, COD of untreated LAS= 183 mg/L O_2

COD_t, COD after 1 h. pre-treatment=145 mg/L O_2

$$X_{COD}=\frac{COD_o-COD_f}{COD_o}\times 100$$ (Eq. 2.14) (Benitez et al., 1999a)

$$X_{COD}=\frac{183-145}{183}\times 100=21\%$$

(d) Calculation for the non-biodegradable COD

For pre-treated sample for 1.5 hours:

UBOD=60 mg/L O_2

T(COD)=145 mg/L O_2

UBOD=0.92 × $(COD)_d$ (Eq. 4.9) (Eckenfelder, 2000)

$\because$ $(COD)_d$= 65 mg/L O_2

T(COD)=$(COD)_d$+$(COD)_{nondegradable}$

$\because$ $(COD)_n$=80 mg/L O_2

(e) Theoretical Oxygen Demand (ThOD)

$C_{12}H_{25}C_6H_4SO_3Na$

$$ThOD=\frac{(18C+7.25H_2+2S-3/2O_2+1/2Na)\times 32}{FW}$$

FW=348.48 g/gmol

$ThOD\approx 240$ mg/L O_2

(f) Calculation for MLSS

Initial weight of filter: 109 mg

Weight of filter+ sludge : 157.3 mg

Volume of sludge used: 10 mL

$$MLSS = \frac{\text{Weight of filter and sludge} + \text{Initial weight of filter}}{\text{Volume of sludge used}}$$ (Standard Methods,1998)

$$MLSS = \frac{157.3 - 109}{10} = 4.83 \text{ g/L}$$

(g) Calculation for the nitrogen and phosphorus in nutrient for biological treatment

BOD_5:N:P=100:5:1 (Eckenfelder, 2000)

BOD_5=40 mg/L O_2

Nitrogen = 40×0.05=2 mg/L

Phosphorous=40×0.01=0.4 mg/L

(h) Calculation for Reynolds number

Mixer Reynolds number = $\frac{d^2 Np}{\mu}$ (Treybal, 1980)

d = mixer diameter=0.1 m

N = mixer speed= 165 rpm = 2.75 r/s

p = density of liquid = 100 kg/m^3

μ = viscosity= 0.001 kg/m.s

Re = 2750

(i) Calculation for the optimum concentration of catalase to remove H_2O_2 completely.

One unit of the catalase used in this study has the ability of decomposing 1 μmol of H_2O_2 per minute, and each 2380 unit of this catalase is equivalent to 1 mg of catalase. 1 μmol of H_2O_2 can be removed per minute, and 10^{-4} mol of H_2O_2 would be removed in

100 minutes. Therefore, to decompose H_2O_2 at 60 mg/L which is equal to H_2O_2 at 1.7 mol/L, 0.71 mg of catalase should be added to one liter of 60 mg/L H_2O_2 solution. This amount would be 0.071 mg of catalase in 100 mL solution. However, as the detection limit for the balance used couldn't cover this range, 0.1 mg of catalase was used.

(j) Kinetic model for the intermediate

$$A \xrightarrow{k_A} S \xrightarrow{k_S} R$$ (Levenspiel, 1999)

$$r_A = \frac{dC_A}{dt} = -k_A C_A$$

$$r_S = \frac{dC_S}{dt} = k_A C_A - k_S C_S$$

$$\frac{C_A}{C_{Ao}} = e^{-k_A t}$$

$$\frac{dC_S}{dt} + k_S C_S = k_A C_{Ao} e^{-k_A t}$$

By solving the first order linear differential equation:

$$\frac{C_S}{C_{Ao}} = \frac{k_A}{k_S - k_A}(e^{-k_A t/c} - e^{-k_S t/c})$$

(k) Generalized reduced gradient (GRG 2)

GRG2 uses an implementation of the generalized reduced gradient (GRG) algorithm. It seeks a feasible solution first (if one is not provided) and then retains feasibility as the objective is improved. It uses the quasi-Newton algorithm as its default choice for determining a search direction.

(l) Programming reports

Adjustable Cells

Cell	Name	Original Value	Final Value
J15	ec Sa	13.8838292	13.8838292
K15	ec Sb	0.5	0.5

Constraints

Cell	Name	Cell Value	Formula	Status	Slack
F5	tc	61.50920218	F5>=0	Not Binding	61.50920218
G5	tb	3365.871977	G5>=0	Not Binding	3365.871977
J15	ec Sa	13.8838292	J15>=K15	Not Binding	13.3838292
D15	ec	0.03388381	D15>=0	Not Binding	0.03388381
D10	effiecency	0.950000943	D10=0.95	Not Binding	0
K15	ec Sb	0.5	K15<=0.5	Binding	0

Microsoft Excel 10.0 Sensitivity Report
Worksheet: [optimization.xis]Sheet1
Report Created: 7/20/2004 5:38:21 PM

Adjustable Cells

Cell	Name	Final Value	Reduced Gradient
J15	ec Sa	13.8838292	0
K15	ec Sb	0.5	-74.73466845

Constraints

Cell	Name	Final Value	Lagrange Multiplier
F5	tc	61.50920218	0
G5	tb	3365.871977	0
J15	ec Sa	13.8838292	0
D15	ec	0.03388381	0
D10	effiecency	0.950000943	-305.8680046

Microsoft Excel 10.0 Limits Report
Worksheet: [optimization.xls]Limits Report 1
Report Created: 7/20/2004 5:38:22 PM

Cell	Target Name	Value
J5	cost	249.0982425

Cell	Adjustable Name	Value	Lower Limit	Target Result	Upper Limit	Target Result
J15	ec Sa	13.8838292	13.8838292	249.0982425	13.8838292	249.0982425
K15	ec Sb	0.5	0.5	249.0982425	0.5	249.0982425

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