PHOTOLYTIC AND PHOTOCATALYTIC TREATMENT OF LINEAR

ALKYLBENZENE SULFONATE IN WATER

by

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ABSTRACT

PHOTOLYTIC AND PHOTOCATALYTIC TREATMENT OF LINEAR ALKYLBENZENE SULFONATE IN WATER

Master of Applied Science, 2004
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Treatment of linear alkylbenzene sulfonate using various photolytic and photocatalytic processes is described. Based on first order rates, it is shown that 5,000 mg/L of H_2O_2 for degradation of a 100 mg/L solution of linear alkylbenzene sulfonate is optimum. Two different photocatalysts, Degussa P25 and Hombikat UV 100 TiO_2, are used to degrade LAS in slurry batch reactors. The optimum photocatalyst loading for Degussa P25 is 4.0 g/L while for Hombikat UV 100 2.0 g/L. The photoactivity for Degussa P25 is higher than UV 100 for treatment of LAS since >20% adsorbs to the surface of the UV 100 photocatalyst. Combination of photocatalysts does not improve degradation rates in batch tests. Combination of Degussa P25 and 600 mg/L H_2O_2 and irradiation with either UV light at 254 or 365 nm does not improve degradation rates over the photocatalytic or photolytic processes individually. Photolysis of LAS with UV light at 254 nm and 600 mg/L H_2O_2 added at different time intervals was not successful and no improvement in the first order rate constant was observed. For optimum results, the hydrogen peroxide was added at the beginning of irradiation.

ACKNOWLEDGMENTS

This thesis is dedicated to the memory of my father, Earle Ross Hatfield.

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NOMENCLATURE

AE	Alcohol ethoxylate
AES	Alcohol ethoxylate sulfate
APEO	Alkylphenol ethoxylate
BOD_5	Biological oxygen demand; five day
BS	Sodium benzene sulfonate
Cb	Conduction band
DBS	Dodecyl benzene sulfonate
DOC	Dissolved organic carbon
DS	Sodium dodecylsulfate
DTDMAC	Ditallowdimethyl ammonium chloride
e^-	Electron
E	Energy
E_{bg}	Band gap energy
EO	Ethoxylate group
GC	Gas Chromatography
h^+	Electron hole
HPLC	High performance liquid chromatography
KHP	Potassium hydrogen phtalate
K_{ow}	Octanol water coefficient
LAS	Linear alkylbenzene sulfonate
LOD	Limit of detection
MBAS	Methylene blue active substances
NOEC	No observed effect concentration
NP	Nonylphenol
NPE	Nonylphenol ethoxylate
NPE1	Nonylphenol ethoxylate, one ethoxylate unit
NPE2	Nonylphenol ethoxylate, two ethoxylate units
NPE3	Nonylphenol ethoxylate, three ethoxylate units
NPEO	Nonylphenol ethoxylate

NP_nEO	Nonylphenol ethoxylate, n=number of ethoxylate units
OP	Octylphenol
PCB	Polychlorinated biphenyl
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
SDS	Sodium dodecyl sulfate
STP	Sewage treatment plant
TOC	Total organic carbon
UV	Ultraviolet
V_b	Valence band
VFA	Volatile fatty acid
W	Watt

CHAPTER 1
INTRODUCTION

Surfactants are depended upon worldwide as cleaning agents. Their usage in such large quantities means that the waste and the potential for pollution is high. Many studies have been done over the last three decades encompassing treatment alternatives for both biodegradable and non-biodegradable surfactants and the environmental impact. It is accepted that surfactants pose a threat to the aquatic environment. Surfactants are used on a large-scale basis in everyday household use, industrial cleaning, and textile manufacturing.

It has been well documented that surfactants make up a large percentage of refractory COD in municipal wastewater treatment and in traditional septic-tile bed system effluents. One problem that is a result of surfactant pollution is the ability of surfactants to increase the solubility of other toxic organic compounds when adsorbed to sewage sludge that is applied to land. Increased solubility can have a negative impact on sludge dewatering characteristics at municipal wastewater treatment plants.

Many methods have been employed for the treatment of surfactants including chemical treatment (flocculation and coagulation followed by settling) adsorption, advanced oxidation processes including Fenton's and photo-Fenton's treatment, addition of H_2O_2 and biological treatment. Chemical treatment often produces undesirable by-products such as biological or inorganic sludges and in some cases, toxic intermediate compounds. Advanced oxidation processes such as TiO_2/UV, irradiation with low wavelength UV light (254 nm), hydrogen peroxide combined with UV and ozone do not produce sludges and can be less expensive therefore providing significant advantages. Although ideal, complete

mineralization of organic compounds is not feasible due to the high-energy requirement. However, use of advanced oxidation processes to degrade surfactants to compounds that do not have surfactant properties has potential.

1.1 Objectives

The objectives of this research were to investigate the feasibility of photolysis and photocatalysis as methods for degrading a model surfactant compound. The compound chosen for this study was linear alkylbenzene sulfonate (LAS), a commonly used additive to both household and industrial detergents. Treatment processes tested include TiO_2 combined with UV-A light, UV-C, and UV-C combined with hydrogen peroxide. The following research was completed to study the potential for these processes to degrade LAS:

(1) Photolysis of LAS with UV-A and UV-C

(2) Degradation and mineralization of LAS using UV-C and UV-C combined with hydrogen peroxide.

(3) Degradation and mineralization of LAS with UV-A combined with one of two types of TiO_2.

(4) Investigation of combined processes

      a. UV-C with H_2O_2 added at different times

      b. UV-A with mixtures of P25 and Hombikat UV 100 TiO_2

(5) Degradation of common detergents under optimum conditions.

CHAPTER 2

LITERATURE BACKGROUND

2.1 Outline

A discussion of surfactant properties and treatment in aqueous environments is described in this chapter.

2.2 Introduction

It is well known that surfactants pose a threat to the aquatic environment. Surfactants are used on a large-scale basis worldwide in everyday household use to industrial cleaning and textile manufacturing. Tables 2.1 to 2.3 outline yearly consumption of three surfactants.

Table 2.1: Linear Alkylbenzene Sulfate Consumption

Area	Consumption Metric tonnes/year	Reference
Netherlands	13,550	Feijtel et al., 1999
Western Europe	320,000	Patterson et al., 2001
North America	400,000	Nielsen et al., 2002
United States	415,000	McAvoy et al., 1998
Worldwide	1 500,000-2,000,000	Elsgaard et al., 2001

Table 2.2: Alcohol Ethoxylate Sulfate Consumption

Area	Consumption Metric tonnes/year	Reference
Netherlands	3587	Feijtel et al., 1999
North America	370,000	Nielsen et al., 2002
United States	322,000	McAvoy et al., 1998

Table 2.3:Consumption of Alcohol Ethoxylates

Area	Consumption Metric tonnes/year	Reference
Netherlands	9703	Feijtel et al., 1999
North America	256,000	Neilsen et al., 2002
United States	208,000	McAvoy et al., 1998

It has been documented that surfactants make up a large percentage of refractory chemical oxygen demand (COD) in municipal wastewater treatment and in traditional septic-tile bed system effluents. Other problems that are a result of surfactant pollution include the ability of surfactants to increase the solubility of other toxic organic compounds when adsorbed to sludge, and surfactants can have a negative impact on sludge dewatering characteristics at municipal water treatment plants. Two suggestions for reducing surfactant pollution include dispensing only the quantity required of the major components for a particular wash cycle or to use environmentally friendly detergents (Hack, 1991). The following is a review of the recent literature reporting advances in treatment of surfactants using advanced oxidation processes. Health effects, environmental impact, and the treatment of linear alkylbenzene sulfonate (an anionic surfactant) and alkylphenol ethoxylates (a nonionic surfactant group) including their metabolic products are discussed.

2.3 Fate and Environmental Impact of Surfactants

2.3.1 Fate and Environmental Impact of Linear Alkylbenzene Sulfonate (LAS)

Linear alkylbenzene sulfonate, the primary surfactant in liquid household detergents, has been found both in rivers that receive municipal effluents and in drinking water supplies. In wastewater treatment, more than 99% of LAS is removed while the remaining LAS is released into surface waters. Organisms living near sewage outfalls potentially can

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bioaccumulate LAS (Tolls et al., 2000). In Taiwan, less than 5% of the population's wastewater is treated and concentrations of 135 μg LAS/L have been found downstream from raw sewage outfalls in the Lao-Jie river (Ding et al., 1999). As well, it has been documented that LAS makes up 0-488 mg/kg of the total dry weight of sewage sludge and may influence microbial activity of the soils. Another study reported a mean LAS concentration of 530 mg/kg and a maximum of 16000 mg/kg (dry weight) (Holmstrup and Krogh, 2001). Elsgaard et al. (2001) studied the impact of LAS on agricultural soils that were amended by sewage sludge. They found that the short-term effects varied with LAS concentration and incubation time. As well, a previous study by Elsgaard et al. (2001) showed that LAS has the potential to inhibit biological activity. The data suggested that a terrestrial risk assessment based on short-term effects of LAS completely describes the potential risk when LAS contaminated sewage sludge is applied to agricultural land.

Holmstrup and Krogh (2001) found that LAS in concentrations greater than 40-60 mg/kg had toxic effects on reproduction and growth of soil invertebrates. They found that earthworms and enchytracids were four times more sensitive to LAS than springtails and mites. A study by Gejlsbjerg et al. (2001) showed that LAS is rapidly mineralized (complete degradation to CO_2 and water) in the aerobic part of the sludge-amended soil. Another study by Holmstrup et al. (2001) tested the toxicity of LAS to the Collembolan (*Folsomia fimetaria*) and the earthworm (*Aporrectodia caliginosa*) and concluded that neither the chemical characteristics of the LAS or type of soil have a large impact on toxicity. Kimerle and Swisher (1977) demonstrated that partial degradation of LAS was effective in reducing the toxicity to water fleas (*Daphni magna*) and fathead minnows (*Pimphales promelus*). Alternatively, Jensen et al. (2001) found that LAS does not pose a risk to fauna, plants, and

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essential functions of agricultural soils as a result of regular sewage sludge application.

Mortensen et al. (2001) found that plant growth was stimulated by LAS biodegradation in sludge-amended soils. A study of the migration of LAS in soils based on the effects of freeze-thaw and wet-dry cycles on the formation of macropores showed that LAS was more mobile when these macropores were present (Ou et al., 1999).   Studies have shown that LAS is toxic to anaerobic digestion processes. Mosche and Meyer (2002) studied the inhibition of propionate and acetate in the presence of 14 and 27 mg/L LAS. They found that 14 mg/L LAS caused a 50% inhibition of acetate degradation while 27 mg/L LAS was sufficient to cause a 50% inhibition in propionate degradation. This study concluded that the optimization of anaerobic processes is highly dependent on understanding how surfactants have an effect, especially in industrial wastewaters that have high surfactant loadings.

LAS pollution can also be because of onsite sewage systems that are not functioning properly. Nielsen et al. (2002) showed that LAS degradation exceeded 96% for an onsite system that had been in operation for 25 years (this site was chosen for its potential as a worst case scenario). Although these results show that LAS is fully biodegradable in onsite sewage treatment systems, it is important to note the functional operation varies widely due to installation, climate, and maintenance practices. They concluded that the mechanisms of removal were most likely due to biodegradation and sorption.

2.3.2 Environmental Concentrations of Surfactants

Alkylphenol polyethoxylates (APEO) are non-ionic surfactants used as detergents, emulsifiers, wetting agents, stabilizers, defoaming agents, are intermediates in the synthesis of anionic surfactants, and are used as institutional and industrial surface cleaners

-[(Takasu et al., 2002). APEOs are also used in the preparation of phenolic resins, as heat stabilizers, in polymer production and as antioxidants (Ying et al., 2002). 55% of APEOs manufactured are used in industrial applications other than as cleaning products, 30% are for industrial and institutional cleaning products, and 15% are manufactured for household cleaning products (Ying et al., 2002). APEOs have been found in air (0-81 ng/m^3), surface waters, sediments, and in wastewaters. Tables 2.4 and 2.5 outline the concentrations found in these environments.

Table 2.4: Concentrations of Alkylphenols and Ethoxylates in Various Environmental Compartments in the USA and Canada [1] (Ying et al., 2002).

Location and Environmental Compartment	Number of Samples	NP (µg/L or µg/kg for sediment)	NPE1 (µg/L or µg/kg for sediment)	NPE2 (µg/L or µg/kg for sediment)	NPE3 (µg/L or µg/kg for sediment)	OP (µg/L or µg/kg for sediment)
Canada						
STP Effluent	8	0.8-15.1				0.12-1.7
Surface Waters	38	<LOD-0.92	<LOD-7.8	<LOD-10		<LOD-0.084
Sediments	9	0.1-72	<LOD-38	<LOD-6		<LOD-1.8
USA						
STP Effluent	6	0.18-15.9			8.77-78.8	
	1	16	5.5	0.8		0.15
	6	0.171-37			<LOD-332	<LOD-0.673
Sediments	22	0.077-0.416	0.056-0.326	0.038-0.398	0.026-0.328	0.00156-0.007
	10	6.99-13,700	26.4-13,300	16.1-3580		<LOD-45

Ying et al. (2002) concluded that APEOs and their metabolites are "ubiquitous in the environment" due to their widespread use and lack of adequate treatment. Bennett and Metcalfe (2000) stated that APEO distribution is localized in area close to the point of discharge of sewage treatment plant effluent. A Dutch study of various surfactants in raw sewage, settled sewage, effluent and in primary removal gave the following results

Table 2.5: Average Surfactant Concentrations in raw, settled and treated sewage. [1] (Matthijs et al., 1999).

Surfactant	Concentration in Raw Sewage (mg/L)	Concentration in Settled Sewage (mg/L)	Concentration in Effluent (μg/L)	Primary Removal %	Total Removal %
LAS	5.2 (6)	3.7 (5)	39.1	20.3 (4)	99.1
AE	3.0	2.0 (5)	6.2	26.2	99.7
AES	3.2	1.5 (5)	6.6	29.5	99.7.
Soap	28.1	9.8 (5)	1053	51.4 (5)	96.9

Overall, the concentration in sewage treatment plant effluent is dependent of treatment efficiency and plant design (Ying et al., 2002).

Feijtel et al. (1999) studied the 90th percentile surfactant concentrations 1 kilometre downstream from a sewage outfall by using information obtained on release, removal in sewer, treatment efficiency, in-stream removal and dilution in the Netherlands. Figure 2.0 shows the surfactant or soap concentration versus the in-stream removal rates. For all compounds, the lower the concentration, the higher the removal rate was observed.

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[1] Data from 7 Dutch sewage treatment plants (unless noted otherwise) of LAS-linear alkylbenzene sulfonate; AE-Alcohol ethoxylate; AES-alcohol ethoxylated sulfate. (Numbers in parentheses indicate number of plants were data was obtained).
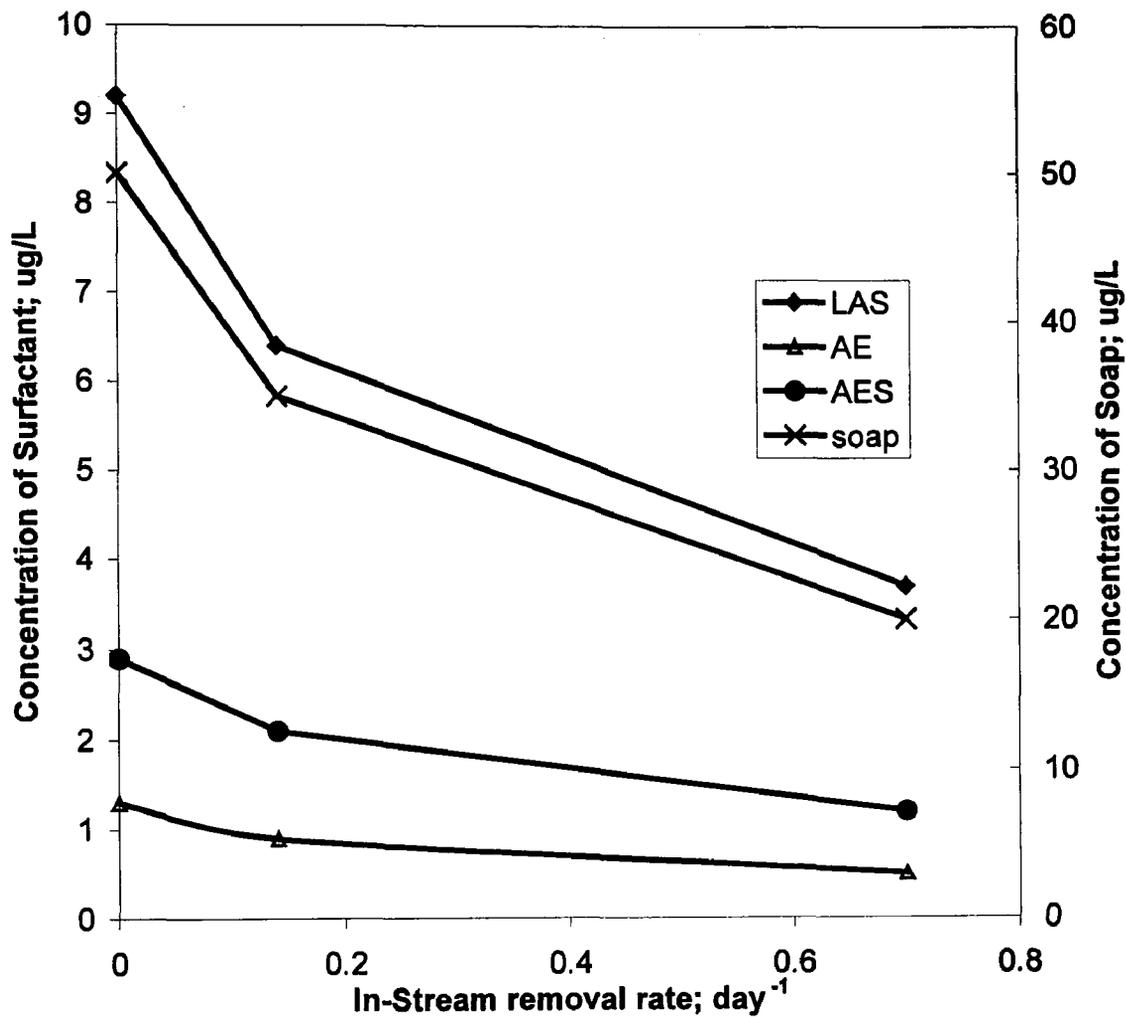
Figure 2.1: Predicted 90th percentile concentrations of soap and surfactants 1 km downstream of a sewage outfall using measured values in raw sewage. (Feijtel et al., 1999).

2.4. Fate and Environmental Impact of Alkylphenol Ethoxylates (APEOs)

APEOs include nonylphenol ethoxylates with varying ethoxylate chain length. Entry into the environment is a result of anthropogenic activity since these compounds are not naturally produced. The majority of APEOs are introduced to the environment through wastewater treatment plant effluent in both the liquid and sludge forms and in pesticide application (Ying et al., 2002). These compounds have also been identified as a result of pollution from onsite systems (Rudel et al., 1998). A study by Nielsen et al. (2002) showed that more than 99% of APEOs were removed in an onsite system that had been in use for 25 years. McAvoy et al. (2002) developed a model to predict the fate of alcohol ethoxylates and alcohol ethoxylate sulfates in onsite sewage treatment systems. La Guardia et al. (2001) concluded that APEO degradation products in biosolids might cause a negative environmental impact in the U.S.A. as a result of widespread biosolids application.

APEOs are of environmental concern because their biodegradation leads to more toxic and persistent compounds that may have estrogenic activity (Giger et al., 1981; LaGuardia et al., 2001; Jobling and Sumpler, 1993; Miles-Richardson et al., 1999). Their toxicological properties are influenced by the number of ethoxylate (EO) units. APEOs with short EO chains (less than four) are lipophilic and may lead to bioaccumulation or bioconcentration and those with greater than ten EO units are hydrophilic. Generally, the toxicity of APEOs increases as the number of EO units decreases (Takasu et al., 2002). Ekelund et al. (1990) studied the bioaccumulation of 4-nonylphenol (a primary metabolite of NPnEOs) in marine animals and found that bioconcentration factors exceeded those previously published for fish and mussels. The bioconcentration factor for fish was determined to be 1300 (5 times greater than published values) and 3400 for mussels (340

times greater than published values). McLeese et al. (1981) determined that the lethal

thresholds for alkylphenols in aquatic fauna decrease with increasing K_{ow} and the

bioconcentration factor increases with increasing K_{ow} in salmon. Nonylphenol ethoxylates

(NPEOs) and their primary degradation products were measured in sediments in the Straight

of Georgia, B.C. near a municipal outfall. It was calculated that 30 tonnes of NPnEO have

been deposited in the Fraser River Delta Sediments while nearly 170 tonnes have been

deposited in the entire Straight of Georgia (Shang et al., 1999).

Ferguson et al. (2001) studied the fate of various alkylphenol ethoxylate metabolites

in Jamaica Bay, Long Island, New York, and found concentrations of 0.05-30 µg/g of

NPnEO (nonylphenol ethoxylate with n ethoxylate groups) and 0.007-0.040 µg/g of

octylphenol ethoxylate metabolites in sediment. Maguire (1999) reported that some of the

degradation products of NPEOs are not readily biodegradable under anaerobic conditions. A

study by Hawrelak et al. (1999) on the fate of alkylphenol ethoxylate primary degradation

products in paper sludge spread onto farmers' fields showed that the concentration decreased

by 84% over a 14-week period. They found an indication of recalcitrant nonylphenol isomers

but concluded that more research needs to be done to assess the risk of APEO degradation

products in these sludges used as soil amendments.

Water treatment processes available to municipal wastewater treatment plants are not

always suitable for the removal of surfactants at low concentrations. The treatment of

surfactants at the pollution source has many advantages including higher concentrations and

the availability of more specialized treatment techniques such as advanced oxidation

processes.

2.5 Influential Factors in Surfactant Toxicity

In the literature, there are many conflicting studies of the toxicity of linear alkylbenzene sulfonates in the aquatic environment. Many ecotoxicological studies have been conducted under laboratory conditions and do not sufficiently represent the varying water conditions in the water column. The main pathways responsible for LAS removal in the natural environment are biodegradation, adsorption, and precipitation. A study of the influence of Ca^{2+} to the toxicity of LAS on algae (*D. Magna*) showed that the toxicity of LAS increased with alkyl chain length and an increase in water hardness. Concentrations of LAS ranged from 33-335 mg/L as water hardness (as $CaCO_3$) was varied from 200-2000 mg/L. Water hardness was found to stress *D. Magna,* thereby increasing LAS toxicity (Verge et al., 2001). This is just one water parameter that varies widely in the environment. The results of this study indicate that controlled laboratory toxicological tests are not a suitable indication of toxicity in the aquatic environment due to these varying parameters.

Rosen et al. (2001) studied the relationship between interfacial properties and toxicity of several surfactants including octyl-, dodecyl-, tetradecyl-, hexadecyl-trimethylammonium chloride, octyl- and decyl-dimethyl-2-hyrdroxy ethyl ammonium chloride, and LAS. This study was completed using an immobilized artificial membrane and Rosen found that surfactant toxicity is primarily a function of the ability of the surfactant to adsorb and penetrate the cell membrane of aquatic organisms. Dyer et al. (2000) studied the structure-activity relationship for both acute and chronic toxicity of a variety of alcohol ether sulfates on *Ceriodaphnia dubia.* Acute toxicity was found to increase with alkyl chain length and decrease with an increasing number of ethoxylate units. Chronic toxicity tests were done using *Brachionus Calyciflorus.* Chronic toxicity was found to be related to the percentage of

the molecular surface associated with atoms possessing partial negative charges and with increasing length of ethoxylate chain.

Tolls et al. (2000) studied the bioconcentration of alcohol ethoxylates in fathead minnows (*Pimphales promelas*) and concluded that it was dependent on alkyl and ethoxylate chain lengths. The bioconcentration factor ranged from less than 5 to 1660 L/kg/day. Metcalfe et al. (2001) studied the estrogenic potency of alkylphenol ethoxylates and their metabolites on the Japanese Medaka. They found that the environmental concentrations of nonylphenol ethoxylates (NPEO1 and NPEO2) were not within the range of estrogenic activity. Spengler et al. (2001) studied the NPEO metabolic compounds in effluents of sewage treatment plants. NPEOs are metabolized to 4-nonylphenol, 4-nonylphenoxyacetic acids and 4-nonylphenoldiethoxylate, and all are known to have estrogenic effects. Korner et al. (2001) tested the estrogenicity of sewage treatment plant effluent and concluded that these effluents are a major source of estrogenic substances in the environment. STP outfalls are a perpetual source of these types of compounds.

Bjerregaard et al. (2001) studied the presence of LAS in the environment close to sewage treatment plant outfalls. The concentration of LAS in sewage treatment plant effluent was in the range of 0.02-1.0 mg/L, which is in the range reported to have a physiological impact on marine life. This study reported that LAS can damage fish gills, cause excess mucus secretion, decrease respiration in the common goby, cause a reduced settling rate, and change swimming patterns in blue mussel larvae. LAS was found to disrupt the ionic homeostasis of epithelial cells (these cells form the outermost barrier between the organism and the environment). Tolls and Sum (1999) found that biotransformation of octaethylene glycol monotridecyl ether in fathead minnows played an important role in reducing the

bioconcentration potential of this surfactant. Jorgensen and Christoffersen (2000) studied

acute effects of LAS on freshwater plankton in field conditions. Different types of freshwater

organisms were examined including bacteria to crustaceans. It was concluded that LAS has a

negative impact on the survival of heterotrophic nanoflagellates and ciliates at very low

concentrations. The no-effect concentration was found to be lower in field tests than for

similar organisms tested under laboratory conditions.

Predicted no-effect concentrations (PNEC) are often used in environmental risk

assessment. PNEC values vary widely for the same surfactant. Table 2.6 shows some PNECs

for common surfactants.

Table 2.6: Predicted no-effect concentrations (μg/L); No Observed Effect Concentrations (NOECs) and Uncertainty Factors for Linear Alkylbenzene Sulfonate (LAS), Alcohol Ethoxylate (AE), Alcohol Ethoxylated Sulfates (AES), and Soap (van de Plassche et al., 1999). C_x and EO_y represent the average carbon and ethoxylate groups respectively.

Surfactant	PNEC based on single species data	Range of field NOECs	Final PNEC	Uncertainty Factor
LAS ($C_{11.6}$)	320	250-500	250	2
AE ($C_{13.3}EO_{18.2}$)	110	42-380	110	5
AES ($C_{12.5}EO_{3.4}$)	400	190-3700	400	5
Soap	27	-----	27	10

Fenner et al. (2002) proposed a method for the application of risk assessment employing

ratios of predicted environmental concentrations (PECs) and predicted no-effect

concentrations (PNECs) to mixtures of surfactants and their metabolites. It was found that the

two main factors influencing the risk assessment of the chemical in question are

consideration of metabolites and/or the number of metabolites considered. Feijtel et al.

(2000) studied predictive exposure modeling and concluded that to understand the fate of chemicals in the environment, it is important to remember that these models do not fully represent the real world although they can provide important statistical distributions of concentrations.

It has been demonstrated in the literature that the widespread usage of surfactants has led to many environmental concerns. Treatment options play an important role in the protection of environmental resources.

2.6 Surfactant Treatment

The following section reviews of the various advanced oxidation processes that have been tested or used to treat surfactants.

2.6.1 Biodegradation of Surfactants

Biodegradability of organic pollutants is a desired property because of the relative ease of removal from waste streams. Toxicity can be reduced or eliminated by biodegradation. Often, biological organisms can completely mineralize pollutants, producing carbon dioxide and water. In the following, the biodegradability of alkylphenol ethoxylates and LAS are discussed.

2.6.2 Biodegradation of Alkylphenol Ethoxylates (APEOs)

Jones and Westmoreland (1998) conducted a study of nonylphenol ethoxylate degradation during sludge composting. The NPEO-contaminated water was a result of the washing of raw wool. This wash water typically is ten times more concentrated than conventional sewage.

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Usually, this wash water is treated using a chemical flocculation process and the sludge ends up with all of the surfactants from the detergent. This sludge was composted and it was shown that 14 weeks was sufficient to reduce the NPEO concentration by more than 96%. Rudling and Solyom (1974) studied the biodegradability of branched NPEOs and showed that there was no significant difference among the biodegradability of NPEOs containing 8 to 30 ethoxylate groups. It was also shown that the removal of NPEO was greater than 90% in activated sludge processes with no prior acclimatization, operating under plant conditions. The biodegradation of NPEOs and LAS (among other organic compounds) in sludge-amended soils was studied (Gejlsbjerg et al., 2001 and Gejlsbjerg et al., 2003). It was concluded that nonylphenol ethoxylates are mineralized in aerobic soil compartments (Gejlsbjerg et al., 2001). It was also determined that as the concentration of NPEO (2 ethoxylate groups) was increased in sludge amended soil, the relative maximum mineralization rate decreased and resulted in an increase in lag times (Gejlsbjerg et al., 2003). Biodegradation of alkylphenol ethoxylates (APEOs), alkyl ethoxylate sulfates (AESs), LAS, and primary metabolites in activated sludge treatment was reviewed by (McAvoy et al., 1998). Alcohol ethoxylates (AE) and alcohol ethoxylate sulfates (AES) were removed with an efficiency of 98% and 97%, respectively. Trickling filter treatment resulted in removal efficiencies for AE, AES and LAS to be 79-99.7%, 69.7-98.2%, and >99%, respectively. Battersby et al. (2001) reported AE removal during activated sludge treatment to be >99% based on measured levels in the influent sewage and the treated effluent. It was estimated that biodegradation was responsible for greater than 98.7% of the removal and the remainder adsorbed to the biomass. During winter operation, biodegradation was responsible for greater than 97.2% of AE removal (Battersby et al., 2001). Marcomini et al. (2000) suggested that

the alkyl chain length of alcohol polyethoxylates controlled the biodegradability rates and

pathways. The half lives of APEOs in acclimated sewage treatment plant sludges for ultimate

biodegradation was one to four weeks (Staples et al., 2001). Anaerobic degradation of

alcohol sulfates was dependent on the surfactant-to-biomass ratios. A low surfactant-to-

biomass ratio was important for efficient biodegradation. In addition, processes that result in

acidification of the wastewater prior to anaerobic treatment improve degradation and allow

for a higher surfactant-to-biomass ratio without causing inhibition (Feitkenhauer and Meyer,

2002).

Biodegradation of alcohol ethoxylates by native soil microbes was studied (Ang and

Abdul, 1992). In-situ surfactant washing is a process for cleaning contaminated soil and

ground water systems. For example, a site with soil contaminated by polychlorinated

biphenyls (PCBs) can be injected with a surfactant solution to enhance the mobility of the

PCBs and, therefore, the biodegradation. This ultimately leaves the surfactant in the soil. The

study was conducted in order to assess the ability of native soil microbes to degrade the

surfactant. It was found that alcohol ethoxylate is readily biodegradable by indigenous

groundwater and soil microbes under laboratory conditions. The rate of surfactant

degradation was enhanced by adding nutrients, such as nitrogen, phosphorus, and oxygen.

2.6.3 Biodegradation of Linear Alkylbenzene Sulfonate (LAS)

Rittmann et al. (2001) studied the biodegradation of LAS in activated sludge treatment, the

importance of sludge adaptation, and mass transfer in the biodegradation process. A model

was developed to analyze the effects of adsorption and biodegradation kinetics on the fate of

LAS in batch experiments with activated sludge adapted to different initial LAS

concentrations. It was shown that in batch experiments the mass transfer kinetics were sufficiently slow so that equilibrium was not reached and, therefore, the long-term biodegradation of LAS was limited by the increasing availability of LAS from the unavailable LAS over time.

McAvoy et al. (1998) reported that LAS removal during activated sludge treatment was greater than 99% while in a trickling filter was 72.2-98.6%. Boeije et al. (2000) built a pilot scale trickling filter to test LAS degradation and to develop a model for chemical fate in trickling filters.

Krueger et al. (1998) studied the biodegradation of LAS in sewage-contaminated groundwater over a range of dissolved oxygen concentrations. This study concluded that the rate of biodegradation increased with increasing alkyl chain length. Removal rates were found to be two to three times higher in laboratory experiments than those in field tests. Doi et al. (2002) investigated the sorption and biodegradability of LAS in three soil types below an onsite sewage system drain field. It was concluded that the rate of ultimate biodegradation of LAS decreased with increasing distance vertically below the surface of the ground. Percent mineralization of LAS was found to be 49.8% and 83.4% during test periods of 45 or 59 days, respectively. McAvoy et al. (2002) studied the applicability of a model developed to predict the fate and transport of surfactants in onsite wastewater treatment systems. The model takes into account adsorption and biodegradation effects on the transport of surfactants through the treatment system. It was found that the model under-predicted the LAS concentrations in groundwater down gradient from the disposal field since the groundwater beneath the disposal bed was sometimes anoxic. In addition, it was determined that the

biodegradation of LAS was faster under fully oxygenated laboratory conditions than that in the field.

Branner et al. (1999) studied the degradation of LAS in soil columns under water-saturated conditions. It was found that primary degradation was close to 100% while mineralization only occurred up to 9%.

2.6.4 Biodegradation of Ditallowdimethyl Ammonium Chloride (DTDMAC)

The biodegradation of ditallowdimethyl ammonium chloride, a cationic surfactant by activated sludge has been studied (Sullivan, 1983). DTDMAC is commonly used as a fabric-softening agent. The biodegradation of DTDMAC was determined in semi-batch activated sludge reactors. It was found that extended periods of aeration resulted in improved degradation rates. Although metabolites of DTDMAC were observed, they did not persist in the sludge. It was concluded that DTDMAC removal is a result of sorption, precipitation, and biodegradation mechanisms.

2.7 Treatment of Surfactants Using Various Advanced Oxidation Technologies and Separation Techniques

In this section, the treatment of various surfactants including alkylphenol ethoxylates (APEOs), alcohol ethoxylates (AEs), and linear alkylbenzene sulfonate (LAS) by advanced oxidation processes including TiO_2/UV, wet air oxidation, sonochemical treatment.

2.7.1 Wet Air Oxidation of Surfactants

In a study of the applicability of wet air oxidation (WAO) of various organic pollutants, Dietrich et al. (1985) outlined the basics of the process. WAO is suitable for the treatment of organic or inorganic pollutants dissolved in water. WAO is dependent on high temperatures and pressures operating in the range of 174-320 °C and 2169-20708 kPa, respectively. At high enough temperatures and pressures, the solubility of oxygen increases and provides the driving force for oxidation. In the Deitrich study, the source of oxygen was either compressed air or pure oxygen under pressure. The high pressures are required to keep the water in a liquid state and also serve as a catalyst.

WAO provides the same oxidative ability as flame combustion but at much lower temperatures. Mantzavinos et al. (2001) studied the WAO of LAS and its effects on the biodegradation of LAS. The experiments were semi-batch with 1000 mg/L LAS at 473 K, O_2 partial pressure of 1.3 MPa and a reaction time of 40 to 390 minutes. It was found that although LAS was easily oxidized by WAO to compounds that do not act as detergents, unoxidized LAS was more readily biodegradable than that of the treated LAS. Biodegradability of LAS decreased with an increasing degree of oxidation. Patterson et al. (2002) studied the WAO of LAS at 1600 mg/L, at temperatures ranging 180-240 °C and pressures ranging from 3.05 to 6.55 MPa. Identified products included low molecular weight VFAs (volatile fatty acids) such as formic and acetic acid, sulfonated aromatics, and sulfate.

Over a reaction time of 120 minutes at 1.5 MPa O_2 partial pressure, increasing the temperature produced an improvement in LAS removal from 79% to 100% and COD removal from 23% to 70%. Increasing the pressure was found to have little impact on TOC and COD removal. In another study, Mantzavinos et al. (2000) studied semi-batch WAO of

LAS at temperatures of 453 and 473 K and total pressures of 2.8 and 3.3 MPa with a reaction time of 40-390 minutes. In agreement with the results obtained by Mantzavinos et al. (2001), LAS was readily degraded to smaller molecules that did not behave as surfactants. TOC removal only reached 50% because of the resistance of small organic acids to further oxidation.

2.7.2 Sonochemical Degradation of Surfactants

Vinodgopal (2001) studied the ultrasound-induced (363 kHz) degradation of nonylphenol ethoxylate. Ultrasonic degradation is a result of ultrasound-induced cavitations. Acoustic cavitation involves the formation, growth, and implosion of very small gas bubbles. The implosion of the bubbles results in near adiabatic heating of the gas and vapour inside the bubble. High local temperatures and pressures are referred to as hot spots. These conditions can result to the homolysis of water molecules to produce $H^{\bullet}$ and $^{\bullet}OH$ radicals. The attack of the surfactant molecules by the radicals and thermal decomposition are the main pathways of degradation. The rates of degradation are dependent on the initial surfactant concentrations. Destaillats et al. (2000) also studied the degradation of alkylphenol ethoxylates by ultrasound. It was shown that the critical micelle concentration effectively shielded surfactant monomers from $H^{\bullet}$ and $^{\bullet}OH$ radicals.

2.7.3 Foam Fractionation of Surfactants

Foam fractionation is accomplished by sparging air to produce tiny bubbles that collect surfactant molecules as they rise to the top of the liquid and produce foam. The thin liquid film between the air bubbles is stabilized by the adsorbed surfactant. The liquid drains form

this thin liquid film due to gravity (Tharapiwattananon et al., 1996). Foam fractionation was used as a method for the treatment of sodium dodecylsulfate contaminated water and provided 90% recovery (Tharapiwattananon et al., 1996). Wungrattanasopon et al. (1996) studied foam fractionation to remove tert-butylphenol by using sodium dodecylsulfate to and confirmed Tharapiwattananon's results of 90% surfactant recovery.

2.7.4 Electrochemically Generated Coagulant Treatment of Surfactants

Electrochemically generated coagulants are formed by passing an electrical current through an iron or aluminum electrode (anode) that in turn releases Al^{3+} or Fe^{2+} as a result of electron consumption. Hydrogen gas forms at the cathode. Depending on the pH, aluminum oxide or iron oxide flocs form and float to the surface carrying the flocs and contaminants.

Ciorba et al. (2002) studied the removal of nonylphenol ethoxylates with electrochemically-generated aluminum and iron coagulants using aluminum and carbon steel electrodes with a current density of 10 A/m^2. It was found that the longer the ethoxylate chain, the more hydrophilic the NPEO, therefore, the less tendency to adsorb the flocs leading to lower removal rates. Removal rates of NP4EO (4 EO groups) were between 40 and 80% and for NP16EO (16 EO groups) 30 to 50%.

2.7.5 Photofenton Treatment of Surfactants

Photofenton treatment involves the irradiation of a solution containing hydrogen peroxide and ferric ions in order to degrade organic pollutants. The ferric ion acts as a catalyst for the generation of hydroxyl radicals.

A simplified photo Fenton reaction is as follows:

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$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad \cdots (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \qquad (2)$$
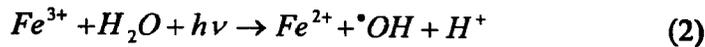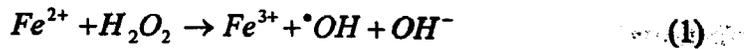
Brand et al. (1998) studied the photofenton degradation of an alkylphenol ethoxylate (trade name Igepal CA 520). A UV source of 365 nm was used. 60% removal was achieved in six hours. Exposure to sunlight for 24 hours resulted in 90% removal.

2.7.6 Fenton's Treatment of Surfactants

The Fenton reaction is as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (3)$$
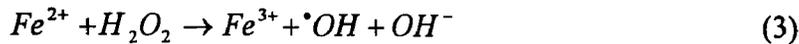
The radicals that are formed react with organic compounds and ultimately degrade them to carbon dioxide and water. Kitis et al. (1999) studied the enhancement of biodegradability of NPEO with Fenton's treatment. 1000 mg/L COD (NPEO) was used with 1000 mg/L hydrogen peroxide with an H_2O_2/Fe^{II} equal to one. Batch aerobic experiments followed to test the biodegradability of the partially oxidized solution. It was concluded that Fenton's pretreatment reduced biodegradability with low hydrogen peroxide dosages and increased the biodegradability at higher H_2O_2 dosages. Lin et al. (1999) found optimum operating conditions for treating 10 mg/L LAS to be 90 mg/L $FeSO_4$, 60 mg/L hydrogen peroxide with a reaction time of 50 minutes at pH 3 to achieve greater than 95% removal. A first order kinetic model was fitted to the experimental results. Final treatment with a chemical coagulant was found to be highly beneficial in removing small iron oxide flocs formed during the reaction.

2.7.7 Ozonation of Surfactants

Narkis et al. (1984) studied the degradation of NPnEOs (n=4-30) in dilute solution. First order reaction rates were observed with respect to NPEO concentration. A linear relationship was observed between first order rate constants and a number of ethoxylate groups. It was concluded that the high O_3 concentrations do not enhance mineralization but low concentrations of O_3 are sufficient to enhance biodegradability. Beltran et al. (2000) studied the effect of pH and organic loading on the treatment of sodium dodecylbenzene sulfonate (SDS) by ozonation. It was determined that alkaline conditions were favoured since hydroxyl radicals were preferentially formed and were the main route of degradation. Ozonation was only able to partially remove SDS and COD but was concluded that combined ozonation and biodegradation might enhance removal of COD.

2.7.8 Treatment of Surfactants with TiO_2 Combined with Ultraviolet Light (UV)

In the last 20 years, the potential for usage of photocatalysts for organic pollutant destruction has been realized (Aye, 2002; Cuzolla et al., 2002; Hidaka et al., 1988; Hidaka et al., 1992; Mehrvar, 1998; Nadarajah et al., 2002; Turchi, 1990; Venkatadri and Peters, 1993). An ideal photocatalyst is chemically and biologically inert, easily recovered, and reusable. Titanium dioxide fits this profile and hence has been tested extensively in the treatment of a wide variety of organic contaminants.

Sherrard et al. (1996) studied the treatment of alcohol ethoxylates and nonylphenol ethoxylates in batch reactors. Experimental conditions were as follows: 0.1% w/v TiO_2 catalyst, 2000 mg/L surfactant and irradiation with a 400W black light lamp. It was found that NPEO more easily degraded than AE. Pelizzetti et al. (1989) studied NP_nEO (where

n=2, 5 or 12) degradation in a batch reactor with P25 TiO_2 and a 1500 W UV lamp in an

NP_nEO solution with a concentration of 0.1 mM. The degradation was monitored by

measuring CO_2 evolution, DOC, and particulate organic carbon. The reaction pathway

involved a hydroxyl radical attack on the ethoxylate chain and on the benzene ring. The rate

of reaction was dependent on adsorption of the surfactant to the titanium dioxide surface.

Horikoshi et al. (2002) studied the degradation of NPEO in a cylindrical reactor where the

titanium dioxide was immobilized on a fiberglass cloth.

Saien et al. (2003) studied the photocatalytic degradation of sodium dodecylbenzene

sulfonate (SDS), a linear alkylbenzene sulfonate with 12 carbon atoms in the alkyl chain.

Degradation using Degussa P25 TiO_2 combined with UV light at 365nm was tested in

batch mode. The batch setup included the UV lamp outside of the reactor placed

symmetrically over top of the 500 mL pyrex reactor. Various optimization parameters were

tested including pH, temperature, SDS and TiO_2 concentration. SDS concentrations tested

were in the range of 4.4-13.8 mg/L and TiO_2 concentrations from 5-32 mg/L. It was found

that the optimum pH was 3, as the temperature increased (up to 45 °C) the rate increased, and

the optimum TiO_2 concentration was 8 mg/L for a 10.8 mg/L SDS solution. Hidaka et al.

(1992) also studied the photocatalytic degradation of SDS under similar conditions. The

concentrations used were 0.1 and 0.01 mM (34.8 and 348 mg/L) and 2.0 g/L Degussa P25

TiO_2. Based on the results obtained from intermediate compounds formed during

degradation, mechanisms for SDS degradation were proposed. The first proposed mechanism

involved radical attack of the aromatic ring (Figure 2.2).
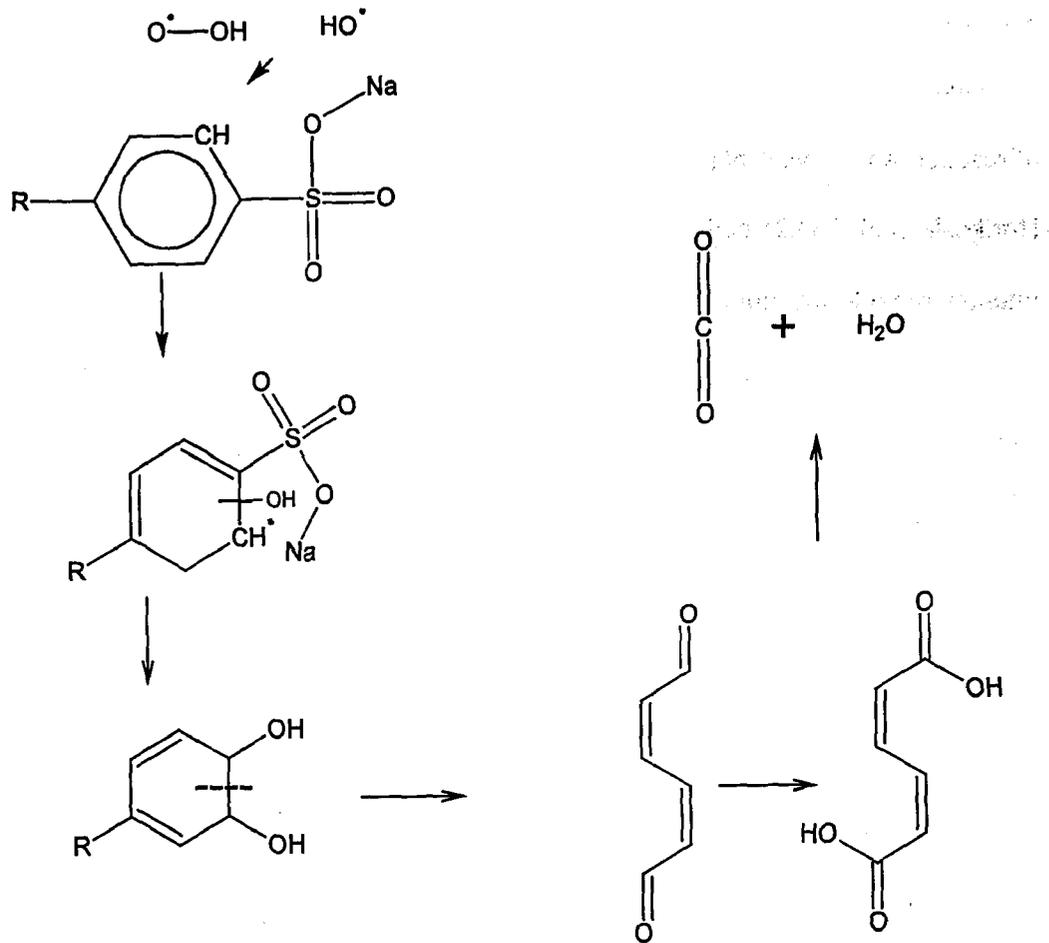
Figure 2.2: Degradation mechanism for radical attack of the aromatic ring in SDS (Hidaka et.al. 1992).
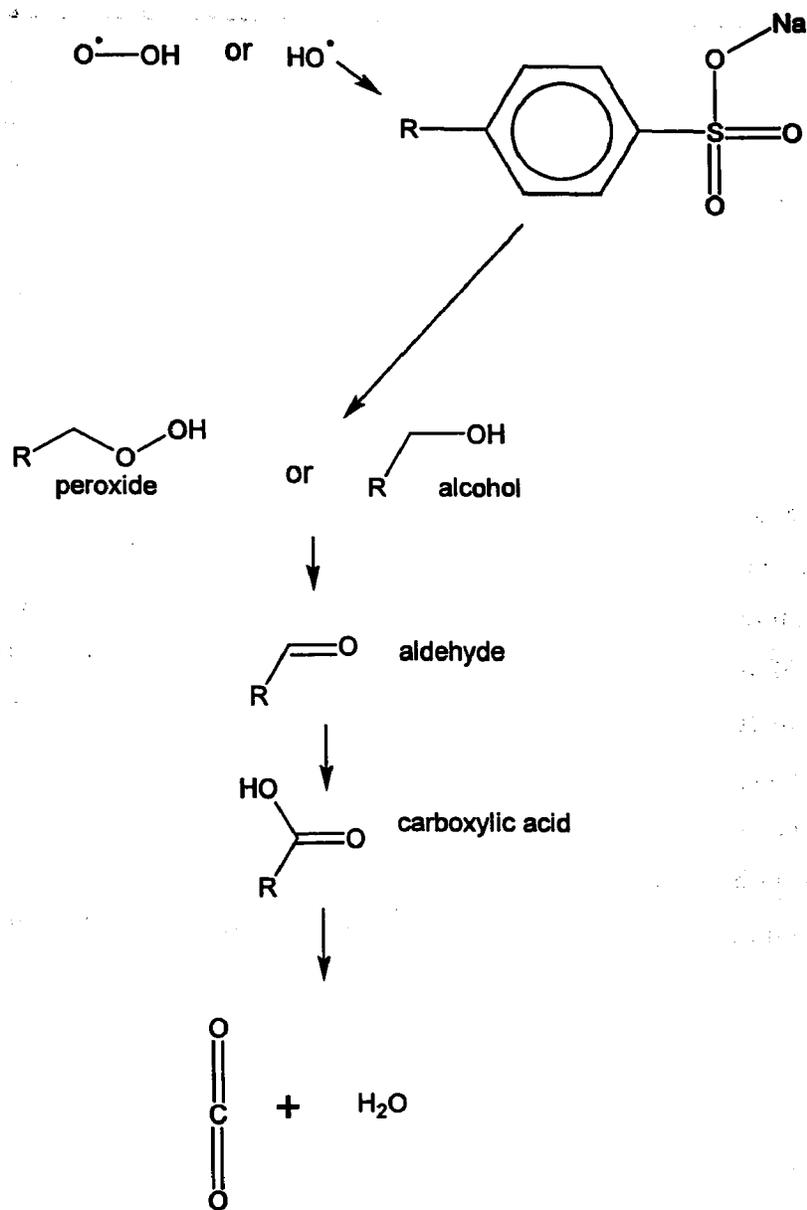
Figure 2.3: Degradation mechanism of SDS by radical attack of alkyl chain (Hidaka et. al, 1992).

The second mechanism proposed involves radical a attack on the alkyl chain. Alkyl groups on aromatic rings behave as activating agents by donating electrons to the aromatic ring. Alkyl groups are ortho and para directors. Electrophilic additions to these locations on an aromatic ring promote stabilization of formed intermediates by inductive and resonance effects. The sulfonate group is a strong electron-withdrawing group and is a meta deactivator. The directing effects of these two substituents oppose each other therefore, in the case of LAS or DBS; the para position to the sulfonate group is the only position open to electrophilic attack (McMurray, 1996). This is in agreement with the mechanism proposed by Hidaka et al. (1992) for SDS. Photocatalytic degradation rates of two compounds, sodium benzene sulfonate (BS) and sodium dodecylsulfate (DS) were compared to the degradation of SDS to determine how the degradation mechanism occurs. Studies of intermediate compounds led to the conclusion that the aromatic and alkyl group competitively adsorb to the titanium dioxide surface and degrade. The rate influencing steps for degradation of SDS were suggested by Hidaka et al. (1992) to be as follows:

(1) Surfactant adsorption on TiO_2 surface

(2) Electron-hole pair formation or radical formation

(3) Rate limiting steps included ring opening, peroxide, carboxylic acid, or aldehyde formation.

(4) Complete mineralization to H_2O and CO_2.

2.7.9 Concluding Remarks

Surfactants play a major role in our society. Ultimately, their usage in such large quantities means that their ultimate fate is highly important (Hatfield Venhuis, S. & M.Mehrvar, 2004). It has been demonstrated that greater than 90% of many surfactants are removed in traditional biological wastewater treatment processes. The remainder can remain adsorbed to the biosolids at end up on agricultural land via reuse programs. Many methods of surfactant

degradation and removal have been discussed in this review and it has been shown that the treatment of surfactant containing wastewaters at the source is a viable option.

2.8 Advanced Oxidation Processes

Advanced oxidation processes refers to processes that utilize highly reactive oxidants such as hydrogen peroxide (H_2O_2), ozone (O_3), Fenton and photo Fenton's reagent (Fe^{3+}/H_2O_2 or $Fe^{3+}/H_2O_2/UV$), ultraviolet (low range UV or near visible) light, and ultraviolet/TiO_2 and any combinations of these processes to degrade organic compounds.

Photocatalysis has many potential applications including degradation of persistent organic pollutants including halogentated organics, metal recovery, air purification, disinfection, and sterilization. There are many advantages and disadvantages to photocatalysis. Some advantages include:

-effective at ambient temperatures,

-complete mineralization for most organic compounds,

-pollutant is not transferred to a secondary medium that requires treatment

-toxicity is generally reduced,

-can enhance biodegradability.

Some disadvantages include:

-difficulty in recovery of the photocatalyst in TiO_2 slurry reactors,

-can be expensive; energy intensive, high chemical cost when combined with H_2O_2 or another molecular oxidant,

-low quantum yield efficiencies,

-occasionally can produce a more toxic end product,

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$\cdot_{\vec{OH}}$ $\cdot_{\text{Ba}}$-may result in recalcitrant intermediates.

2.8.1 Basic Principles of Advanced Oxidation Processes

2.8.1.1. Photocatalysis

Photocatalysis involves the irradiation of a semiconductor metal oxide such as titanium dioxide with ultraviolet light. For a photocatalyst to be useful, several characteristics are desired such as photoactivity, photostability, lifetime, and non-toxic, inexpensive and chemically and biologically inert. Irradiation with ultraviolet light causes different reactions to occur. Semi-conductors are characterized by a filled valence band and an empty conduction band. Semiconductors contain lattice defects that result in electron donating levels (Turchi, 1990).
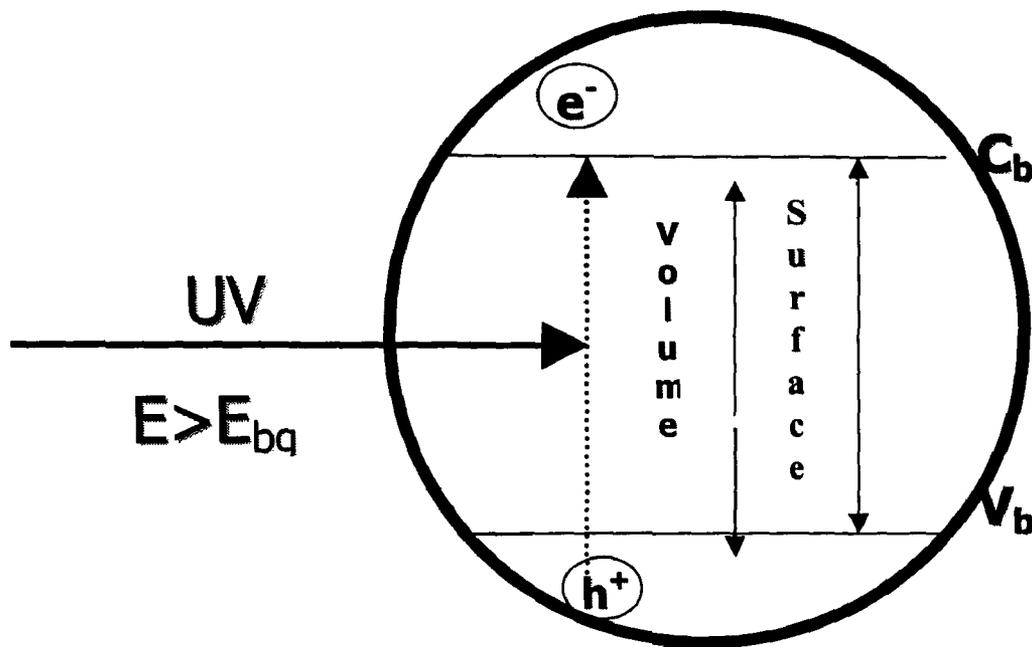
Figure 2.4:Irradiation of a titanium dioxide particle with UV light and Electronic Levels of TiO_2; V_b=valence band; C_b=conduction band, E =energy and E_{bg}= band gap energy, e⁻=electron, h⁺=hole.

There are several possible outcomes of electrons. The predominant outcome is recombination of electrons with holes that results in the low photo efficiency of these reactions. On average, 94% of the electrons recombine. Those that do react can be trapped on the surface forming oxygen or hydroxyl radicals.

Below are the possible mechanisms of photocatalysis (Turchi, 1990).

Excitation

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{4}$$

Adsorption

$$O_L + Ti^{IV} + H_2O \leftrightarrow O_L^{H-} + Ti^{IV} - OH^- \tag{5}$$

$$Ti^{IV} + H_2O \rightarrow Ti^{IV} - H_2O \tag{6}$$

$$R_i + site \leftrightarrow R_{i\,adsorbed} \tag{7}$$

$$Ti^{IV} + {}^{\bullet}OH \leftrightarrow Ti^{IV} - {}^{\bullet}OH \tag{8}$$

Recombination

$$e^- + h^+ \rightarrow heat \tag{9}$$

Trapping

$$Ti^{IV} - OH^- + h^+ \leftrightarrow Ti^{IV} \int {}^{\bullet}OH \tag{10}$$

$$Ti^{IV} - H_2O + h^+ \leftrightarrow Ti^{IV} - {}^{\bullet}OH + H^+ \tag{11}$$

$$Ti^{IV} + e^- \leftrightarrow Ti^{III} \tag{12}$$

$$Ti^{III} + O_2^- \rightarrow Ti^{IV} - O_2^{\bullet-} \tag{13}$$
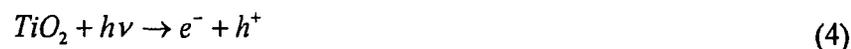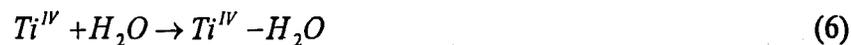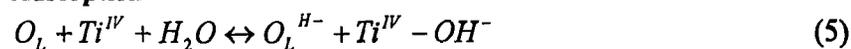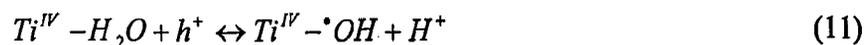
Reactive species such as radicals then attack the organic pollutant at areas of high electron density by addition or abstraction of a hydrogen or halogen atom (Mehrvar, 2001).

Organic compounds that are easily oxidized include aromatic, multiple bond organics such as alkenes and alkynes, amides, amines, thiols, sulphides etc. Compounds that are

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difficult to degrade include those without areas of high electron density such as alkanes and aromatic rings that contain strong electron withdrawing groups.

There are several factors that affect the photocatalytic rate of a reaction including light intensity, metal ions with a band gap similar to titanium dioxide, pH, initial concentration of the contaminant, and competing ions such as carbonate species (Turchi, 1990).

2.8.1.2 Photolysis with Low Wavelength UV Light

Degradation of organic compounds by photolysis occurs by direct bond breakage. Irradiation with UV-A light in the range of 254 nm provides energy higher than that of most organic covalent bonds. Organic molecules with areas of high electron density are particularly susceptible to degradation by photolysis. The following reactions may occur when organic molecules are irradiated with UV light.

$$R + UV \rightarrow R_a^{\bullet} + R_b^{\bullet} + heat \qquad \text{Direct bond breakage} \qquad (14)$$

$$R_a^{\bullet} + R_b^{\bullet} \rightarrow R_{ab} \qquad \text{Recombination of radicals} \qquad (15)$$

$$R_a^{\bullet} + R - H \rightarrow R_a - H + R_c \qquad \text{Degradation of intermediates} \qquad (16)$$

Once radicals have been formed, the degradation process continues to occur via degradation directly with UV light but also includes enhanced degradation with the radicals produced. The radicals generally react by hydrogen or halogen abstraction.

2.8.1.3 Photolysis with Low Wavelength UV Light Combined with H_2O_2

Hydrogen peroxide successfully absorbs UV –A light. The oxygen-oxygen bond breaks forming hydroxyl radicals. Hydroxyl radicals are a powerful oxidant of organic compounds. The following reactions describe this process.

$$H_2O_2 + UV \rightarrow 2\,^{\bullet}OH \tag{17}$$

$$^{\bullet}OH + R \rightarrow inermediates \rightarrow CO_2 + H_2O \tag{18}$$
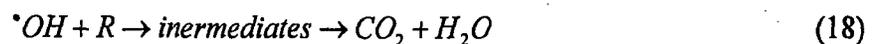
CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The following materials were used in the photolysis and photocatalysis experiments.

3.1.1 Distilled Water

Distilled deionized water was used for all experiments.

3.1.2 Linear Alkyl Benzene Sulfonate (LAS)

Standard LAS with a concentration of 1 mg LAS/mL (average carbon chain length, C=12) was used (Ricca Chemical Company, Arlington, TX). LAS used in experiments was donated by the Stepan Company (Northfield, Illinois, USA) under the trade name Biosoft D 40. Properties of Biosoft D 40 were provided by the manufacturer and are listed in Table 3.1.

Table 3.1: Chemical and Physical Properties of Biosoft D40

Physical or Chemical Property	Value
Boiling Point	100 °C
Specific Gravity	1.0577 g/mL
Viscosity	7.51950 cps @ 25 °C
pH	7.5
Concentration	38.8 %
Freezing Point	-4 °C

The structure of LAS is shown in Figure 3.1.

R_{alkyl} —⟨benzene ring⟩— SO_3Na
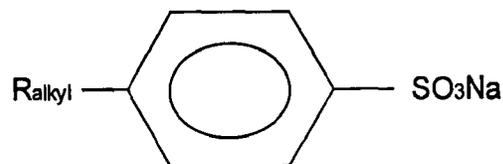
Figure 3.1 Molecular structure of linear alkylbenzene sulfonate (LAS).

R_{alkyl} represents a varying alkyl chain length (12-16 carbon atoms). Para to the alkyl chain is

a sulfonate group with a sodium atom ionically bonded to one of the sulfonate oxygen atoms.

3.1.3 Detergents

Three detergents were selected for comparison of degradation process with LAS. Gain

(Proctor & Gamble, Cincinnati, OH, USA), Tide (Proctor & Gamble, Toronto, ON, Canada)

and Purex (Dial Corporation, USA) were chosen based on cost. Purex is the least expensive

while Tide is the most expensive. Figure 3.2 shows the results of the analysis of the

detergents compared to LAS. Soluble COD, pH and LAS were measured. Detergents contain

many ingredients, some of which are outlined in Table 3.2.

Table 3.2: Typical Detergent Ingredients (Lao, 1997).

Ingredient	Function	% by weight
linear alkylbenzene sulfonate	anionic surfactant	0-15
sodium alkyl ether sulfate	anionic surfactant	0-15
alcohol ethoxylate	nonionic surfactant	0-15
sodium citrate	builder	0-10
monoethanolamine	buffer	0-5
soap	defoamer	0-5
protease	enzyme	0-1.5
fluorescent whitening agents	brightener	0.0-0.5
boric acid	enzyme stabilizer	0-5
ethanol	solvent	0-5
sodium xylenesulfonate	hydrotrope	0-10
preservative		0.05-0.2
fragrance		0.0-0.6
colorant		0.0-0.2
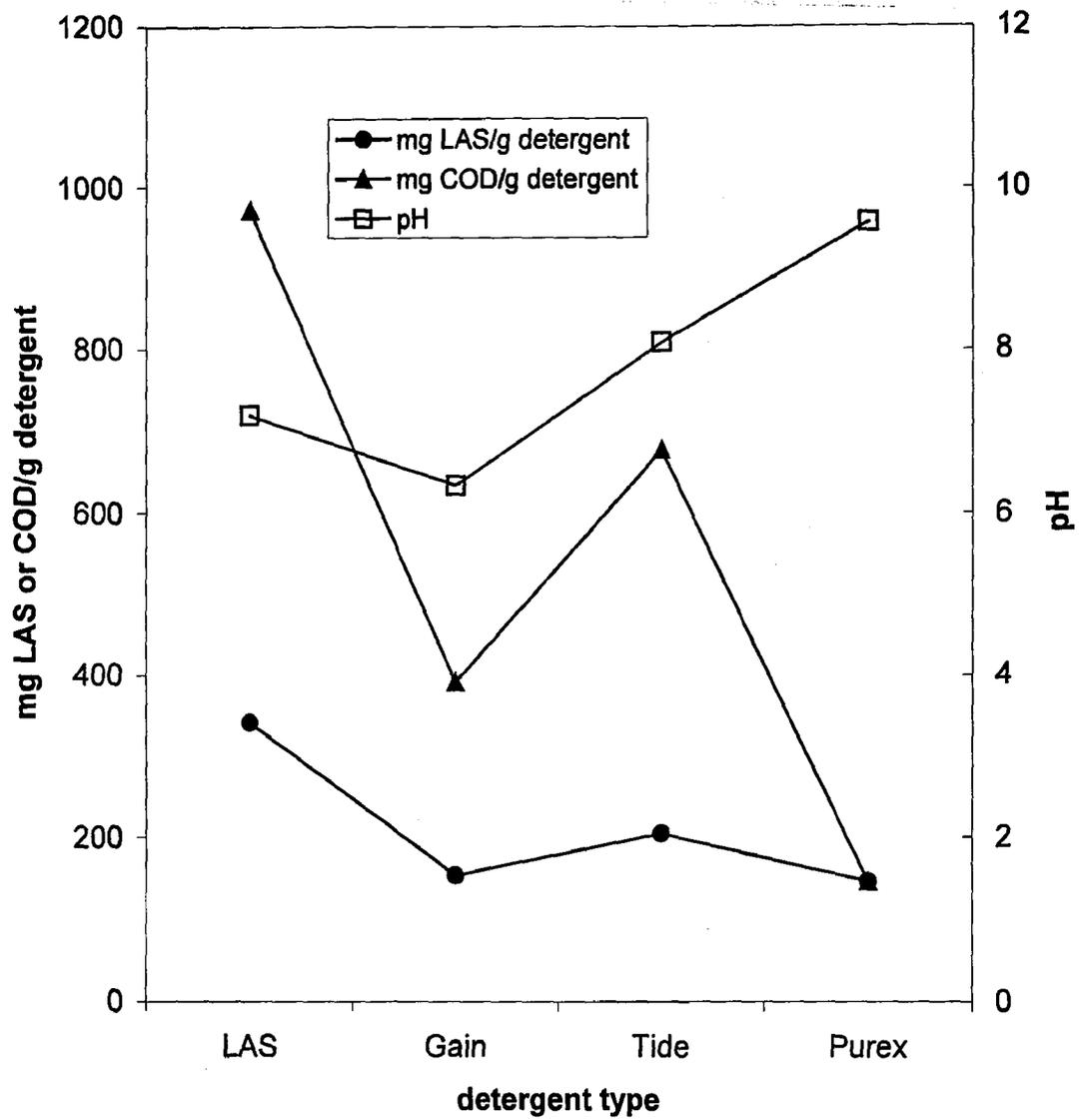
Figure 3.2: Analysis of COD, pH, and LAS concentration per g of detergent for different detergents.

3.1.4 Titanium Dioxide (TiO₂)

Two types of titanium dioxide were used as photocatalysts in this study. Degussa P25 TiO_2 was donated from the Degussa Corporation (Akron, Ohio, USA) and Hombikat UV 100 TiO_2 was donated from Sachtleben Chemie GmbH (Duisburg, Germany). The physical properties of the titanium dioxides are shown in Table 3.2.

Table 3.3: Physical Properties of Two Types of Photocatalysts.

Physical Property	Degussa P25 TiO_2	Hombikat UV 100 TiO_2
% TiO_2	> 99.5%	> 99.9%
Composition	70% anatase, 30% rutile	100% anatase
Average Pore Size (A°)	254.4	31.8
Specific Surface Area (m^2/g)	58.3	345.2
Pore Volume (mL/g)	0.7414	0.5496
Water Solubility	insoluble	0.01 g/L

3.1.5 Hydrogen Peroxide

A 50% w/v solution of hydrogen peroxide was purchased from Hach Co. (Loveland, OH). This solution has a molarity of 17.2. The concentration of hydrogen peroxide was varied to optimize the LAS degradation.

3.1.6 UV Lamps

For the photocatalytic experiments, a Phillips PLS 9W/10/UVA (Microlites Scientific) 365 nm lamp was used as the light source. For the photolysis experiments, a Phillips PLS TUV/PL-59W with a nominal wavelength of 254 nm was used. To ensure constant light intensity during experiments, the intensity of each lamp used was measured and recorded on a monthly basis. To measure the intensity of the lamps, a Spectroline® Digital Radiometer (Spectronics Corporation, NY) was utilized. The radiometer is equipped to measure the intensity of both 365 and 254 nm lamps.

3.1.7 Chloroform

Omni-Solv, GC/HPLC grade chloroform, chemical formula $CHCl_3$ (99.98%, CAS #67-66-3), purchased from EM Science, was used to extract LAS from water samples by transferring an ion pair formed by LAS and methylene blue from the aqueous phase to the organic phase.

3.1.8 Methylene Blue

Methylene blue, chemical formula $C_{16}H_{18}ClN_3S\cdot H_2O$ (CAS# 7220-79-3; EM Science), was used to form an ion pair with LAS in aqueous solution. The ion pair when transferred to the organic chloroform phase absorbs strongly at 652nm and provides a convenient method for determination of LAS.

3.1.9 Phenolphthalein Indicator

For analysis of LAS, phenolphthalein indicator, 1% alcoholic (CAS# 77-09-8; VWR Canlab, Mississauga, ON) was used. For analysis of LAS by methylene blue active substances (MBAS) method, it is important for all samples to be acidic (pH=4.3). The indicator provides a simple visual method for adjusting the sample pH.

3.2 Equipment and Methods

3.2.1 Experimental Setup

The experimental setup for all experiments is shown in Figure 3.3. For all experiments, one litre of a 100 mg LAS/L solution was prepared and the required photocatalyst (Degussa P25 or Hombikat UV 100 TiO_2) or oxidant (H_2O_2) was added to a 1.4 L beaker. The beaker was wrapped with aluminum foil to reflect the light back in to the reaction mixture and to protect eyes and skin. A UV lamp (either 365 for photocatalysis or 254 nm for photolysis) was immersed in the reaction solution. Throughout the reaction, the mixture was stirred using a magnetic stirrer to minimize mass transfer limitations.. All reactions were carried out at room temperature. The pH and temperature were monitored throughout the experiment.
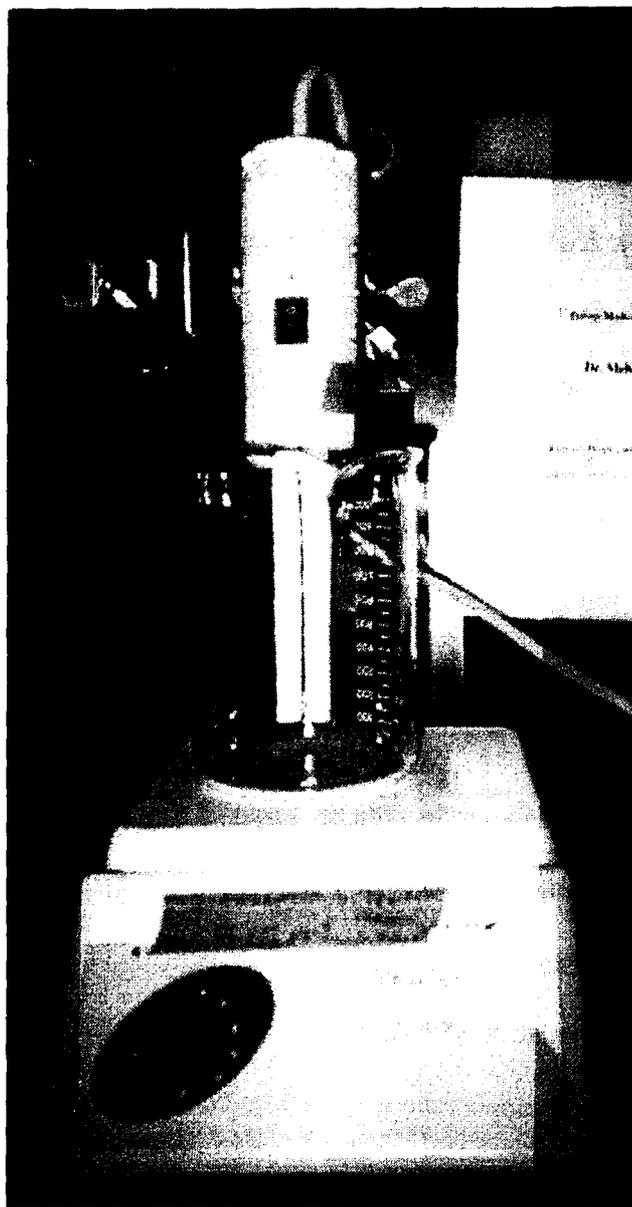
Figure 3.3: Experimental setup for photocatalytic and photolytic experiments.

3.2.2 pH Measurements

The pH of the reaction mixture was monitored using a glass gel filled pH probe (Thermo Orion Model 9107BN) combined with a Thermo Orion Meter model 230A+. Prior to each reaction, the probe was calibrated using buffers with pHs of 4, 7, and 10.

3.2.3 Analytical Techniques for LAS Measurements

The following section describes the analytical method used for determination of LAS including chemical preparation and extraction procedures.

Analysis of LAS was carried out using Standard Methods (1992) determination of anionic surfactants as methylene blue active substances (MBAS). Methylene blue is a cationic dye that forms an ion pair with anionic surfactants in an aqueous phase and can transfer the ion pair to an immiscible organic solvent (chloroform). The blue colour of the ion pair in the chloroform phase is a measure of the methylene blue active substances present in the water sample. This method involves three successive extractions from an acidic aqueous solution (containing an excess of methylene blue) into chloroform followed by backwashing and measurement of the absorbance of the chloroform using a spectrophotometer at 652 nm. The MBAS method is not selective to LAS, however, when LAS is the only anionic surfactant present, the results are quantitative. For experiments using commercial detergents, Gain, Tide and Purex, the MBAS method is not selective to LAS. For these experiments, MBAS method is used to measure the total concentration of anionic surfactants present as LAS. Particulate in samples can cause an interference by adsorption of methylene blue, therefore, all samples containing TiO_2 were centrifuged before analysis using an Adams Physician Compact centrifuge (Clay Adams, Parsippany, NJ).

3.2.3.1 Chemicals for LAS Determination

This section describes the chemicals used and how they were prepared for LAS determination.

3.2.3.1.a. Stock LAS Solution

The stock LAS solution is used for quality control analysis and standards. The stock solution was purchased from Ricca Chemical Company (Arlington, TX) and has a concentration of 1.00 mg LAS/1mL solution (CAS# 7664-93-9).

3.2.3.1.b. Standard LAS

Standard LAS solutions were prepared using the stock LAS solution to make concentrations ranging from 0 to 150 mg LAS/L. Distilled deionized water was used to prepare all standards.

3.2.3.1.c. 1 N NaOH Solution

1 N NaOH solution using ACS grade NaOH (Caledon Chemicals) 97% (CAS#1310-73-2) was prepared by dissolving 1 mole NaOH in distilled deionized water and diluting to 1 L in a volumetric flask.

3.2.3.1.d. 1 and 6 N H_2SO_4 Solutions

Solutions of 1N and 6N H_2SO_4 were prepared by diluting the required amount of concentrated sulfuric acid (98%w/v) with distilled deionized water in a volumetric flask.

3.2.3.1.e. Methylene Blue Reagent

100 mg methylene blue was dissolved in deionized water and diluted to 100 mL in volumetric flask. 30 mL of this solution, 41 mL of 6N H_2SO_4 and 50 g of sodium phosphate, monobasic, monohydrate were diluted to 1 L in a volumetric flask and dissolved.

3.2.3.1.f. Wash Solution

In a 1 L volumetric flask, 41 mL of 6 N H_2SO_4 was added to approximately 500 mL of distilled water. 50 g $Na_2H_2PO_4 \cdot H_2O$ was added and dissolved by inverting the flask. The flask was filled to the 1 L mark and mixed well.

3.2.3.2. Procedure for LAS Determination

This section describes the method followed for analysis of LAS.

3.2.3.2.a. Calibration Curve Preparation

A calibration curve was prepared each time a new batch of analysis chemicals was made. LAS standard solutions were prepared in the range of 0 to 150 mg LAS/L. The extraction procedure was followed (3.2.3.2.b) and the mg LAS/L was plotted against absorption at 652 nm. A typical calibration curve in shown in Appendix A.

3.2.3.2.b. Extraction Procedure

The extraction procedure was modified slightly in order to reduce the required sample size and to use less chloroform since it is toxic and a suspected carcinogen.

The detection limit with the modified method was experimentally found to be 2.0 mg LAS/L or 20 μg LAS. The detection limit reported by Standard Methods is 10 μg LAS.

1. A 10 mL sample is required for each extraction and was added to a clean 14 mL centrifuge tube. If required, the sample was pre-centrifuged or filtered to remove particulate.

2. One drop of phenolphthalein indicator was added to the sample and mixed.

3. 1 N NaOH was added drop-wise to make the solution basic (solution will turn pink).

4. 1 N H_2SO_4 was then added drop-wise until the pink colour just disappeared (solution was slightly acidic).

5. 1 mL $CHCl_3$ and 2.5 mL of methylene blue reagent was added to the tube. The tube was shaken vigorously for 30 seconds and then allowed time to separate.

6. The aqueous layer was withdrawn from the tube with a clean pipet and transferred to another clean tube. The tube with the chloroform fraction was capped to prevent losses. Extraction with 1 mL chloroform was repeated two more times.

7. 5 mL of wash solution was added to the chloroform extracts, shaken vigorously for 30 seconds and then allowed to separate.

8. The wash solution was extracted two times with 1 mL chloroform.

9. The chloroform extracts were diluted to 10 mL and the absorbance was measured at 652 nm against chloroform blank.

3.2.3.2.c. UV Spectrophotometry

For all LAS determinations, a Perkin-Elmer (Norwalk, CT, USA) Lambda 20 UV/VIS

Spectrometer was used. Quartz Hellma cells were used. These cells had a 10 mm path length

and were optically matched.

3.2.4 Chemical Oxygen Demand

COD of samples was measured using prepared vials (Bioscience Inc Analytical, Bethlehem,

PA, USA). Standard range vials were used for all tests (20-900 mg /L). 2 mL of filtered or

centrifuged sample was added to the digestion vial and digested at 150 °C for two hours. The

samples were measured using the same spectrophotometer and quartz cell as in Section

3.2.3.2.c. The absorbance was measured after the samples had cooled to room temperature at

600 nm. The results were compared to a standard curve prepared by using potassium

hydrogen phtalate (KHP) standard solutions.

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, the results from various photocatalytic and photolysis treatments are explained and discussed. Two TiO_2 photocatalysts were tested (Degussa P25 and Hombikat UV 100) to determine the effectiveness of each in destruction of the LAS compound. Batch experiments include treatment of 100 mg LAS/L with UV light with wavelengths of 365 and 254 nm, H_2O_2 combined with UV_{254nm}, titanium dioxide combined with H_2O_2 using either UV_{254nm} or UV_{365nm} and combined TiO_2 with UV_{365nm}.

PHOTOCATALYTIC TREATMENT OF LAS

4.1 Control Experiments

Dark experiments were carried out to ensure that reactions were primarily due to irradiation with UV light and titanium dioxide. The first set of dark adsorption experiments were conducted using the same experimental setup but without the UV lamp turned on. Figure 4.1 shows that there was no significant adsorption of LAS on the experimental setup. The initial concentration of LAS was varied from 100 to 840 mg LAS/L. As demonstrated in Figure 4.1, the LAS concentration did not have any impact on adsorption characteristics. For all experiments without titanium dioxide, adsorption of LAS was of no consequence. In the next set of experiments, adsorption of LAS on Degussa P25 titanium dioxide was completed.
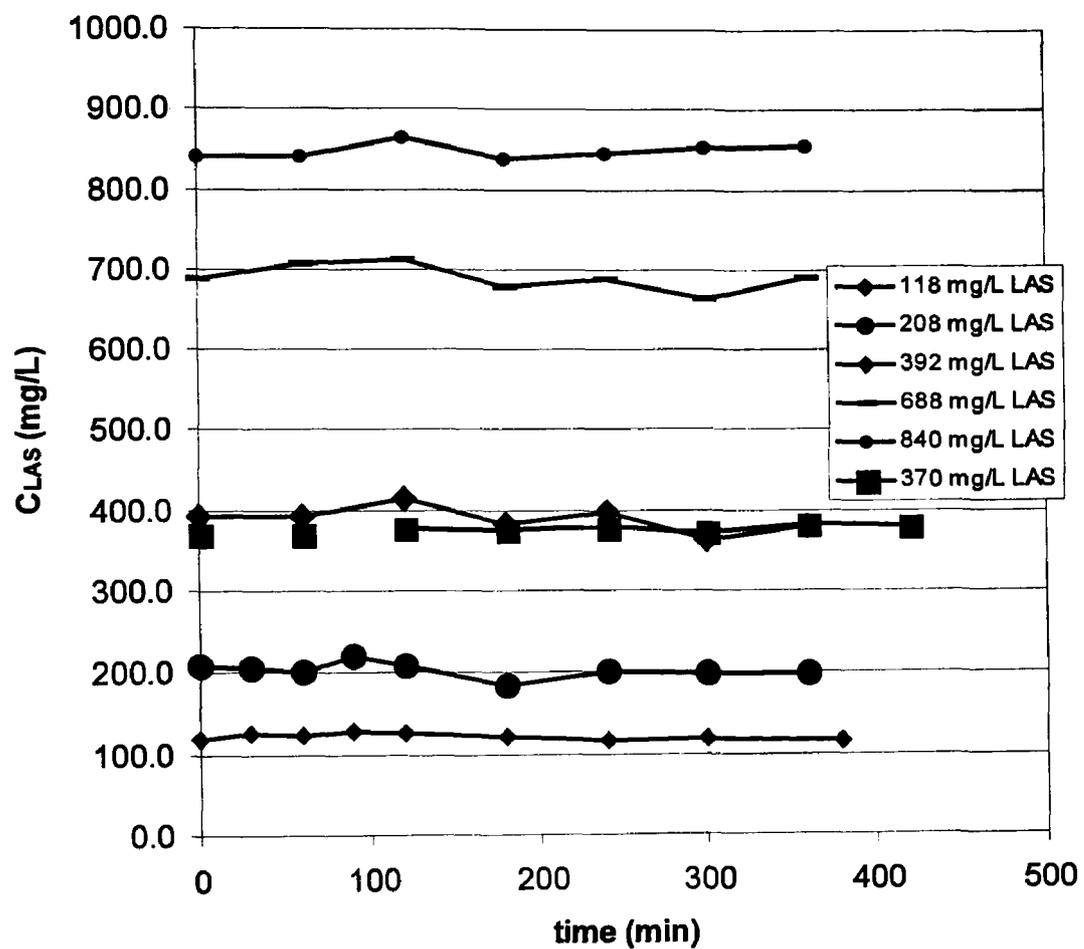
Figure 4.1: Dark Reaction; test for adsorption of LAS on experimental setup; no TiO₂.

All masses of titanium dioxide that were used for degradation were tested for adsorption. The TiO$_2$ slurry was mixed during this test. Figure 4.2 shows that there was limited adsorption on P25 TiO$_2$ over a four-hour period.

The next set of dark reactions involved testing of LAS adsorption on Hombikat UV 100 titanium dioxide. Figure 4.3 shows the results for 2.0g of titanium dioxide. Adsorption of LAS increased as concentration of titanium dioxide in suspension increased. This was a result of increased surface area, therefore, there were more sites for LAS to become adsorbed. Figure 4.4 shows the relationship between the concentration of LAS adsorbed and the mass of titanium dioxide used.
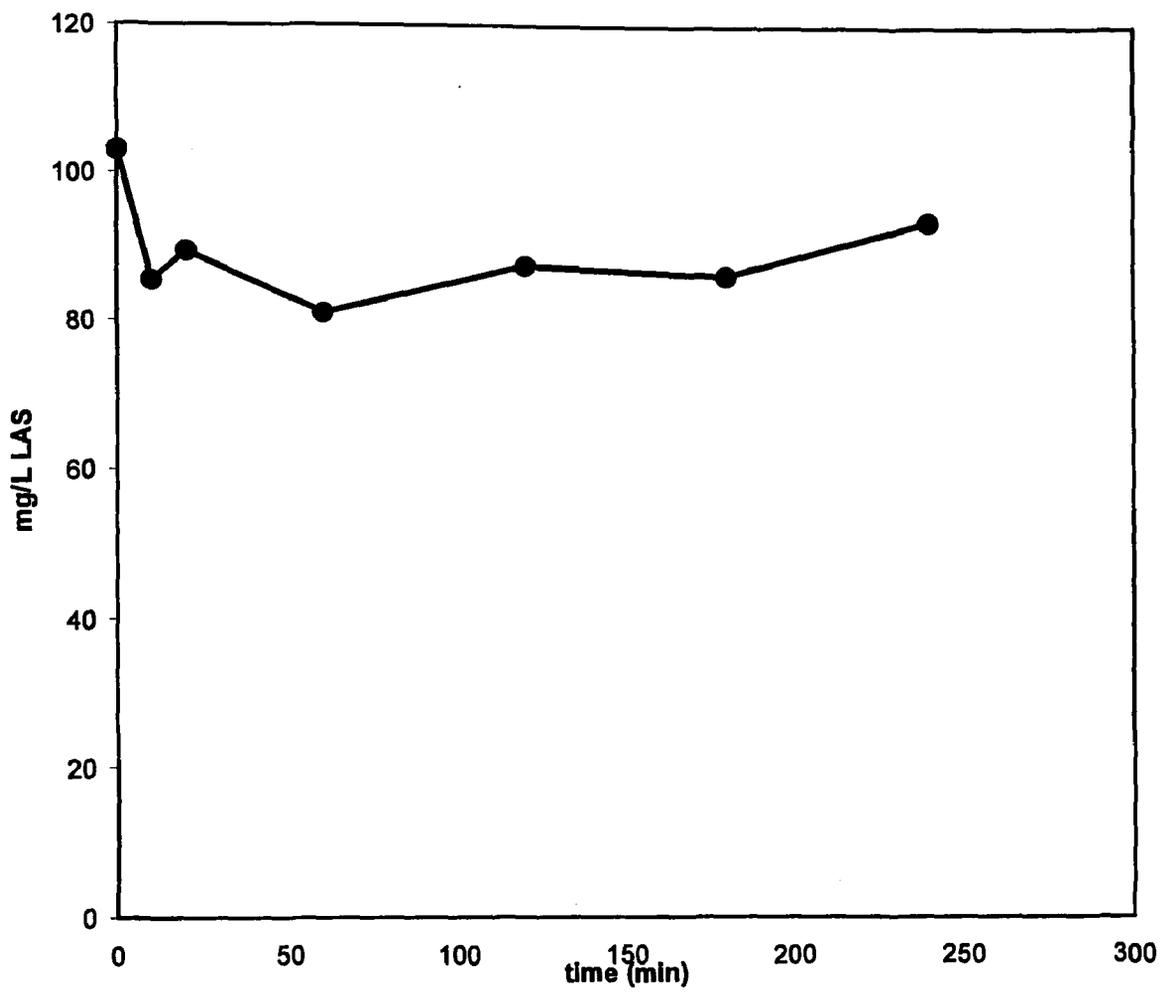
Figure 4.2: Dark reaction of LAS with 3.0g Degussa P25 Titanium Dioxide in the mixture. C_o=100 mg/L.
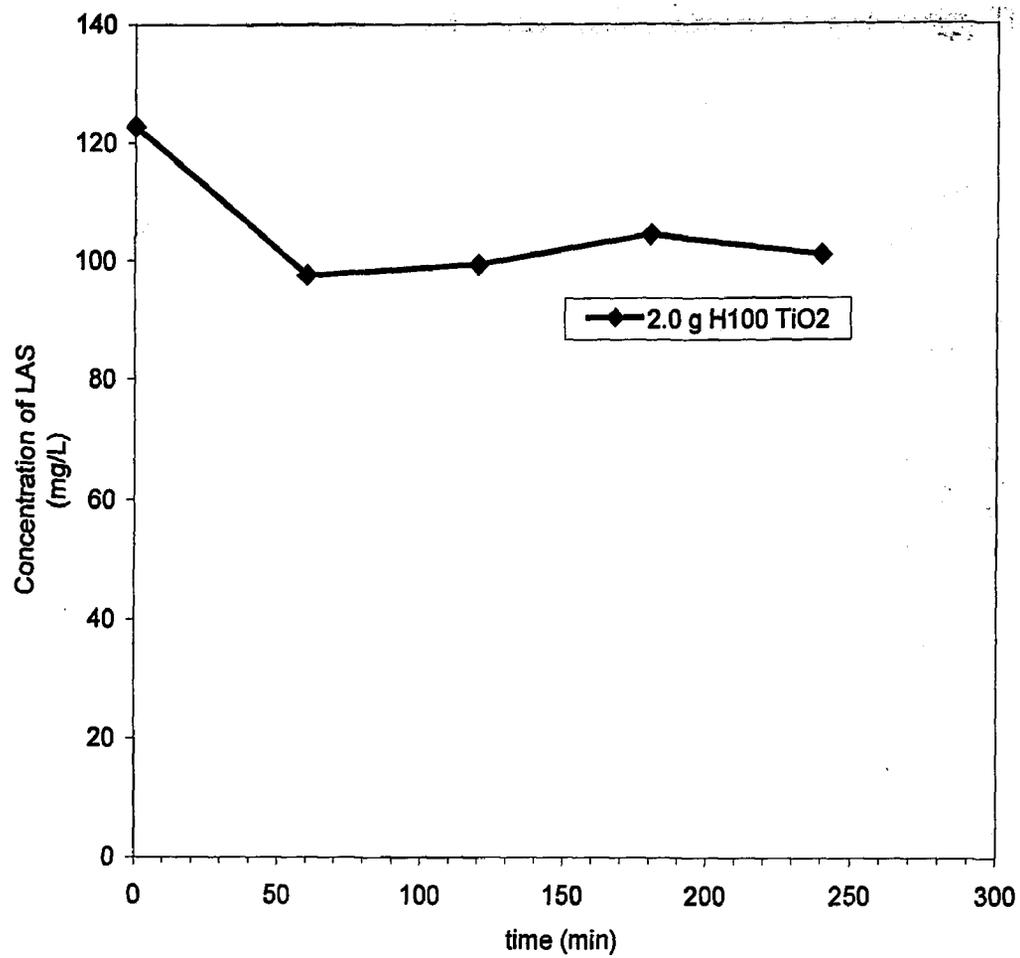
Figure 4.3: Dark Reaction for Adsorption of LAS on 2.0g Hombikat UV 100 TiO₂.
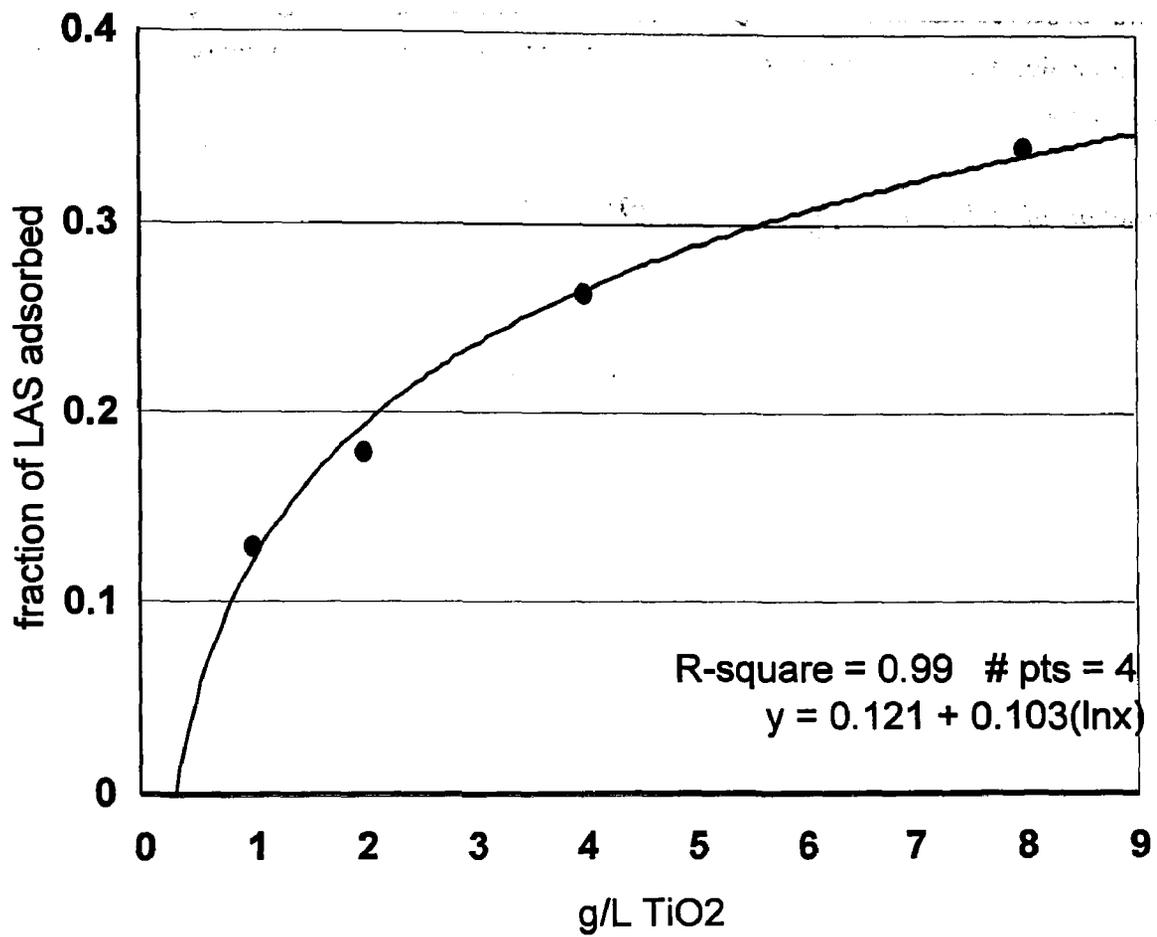
Figure 4.4: LAS adsorption on Hombikat UV 100 TiO_2 as a function of TiO_2 concentration. C_o=100 mg/L LAS.

It was observed that the increasing adsorption with increasing TiO₂ followed a logarithmic relationship. An adsorption factor was determined by using the logarithmic relationship in Figure 4.4.

$$\textit{fraction of LAS adsorbed} = 0.103 * \ln(gTiO_2) + 0.121 \qquad (19)$$

For each experiment, the concentration of LAS adsorbed on the surface of the titanium dioxide was calculated and used to correct the measured concentration.

For reactions where both Degussa P25 and Hombikat UV 100 TiO₂ were used, the dark reactions were completed to confirm that the adsorption equation held true. Figure 4.5 shows exampled of adsorption for combined experiments. The adsorption of LAS on the titanium dioxide occurs within the first thirty minutes of the dark experiment.

4.2 Photolysis

In this section, results from photolysis experiments are presented and discussed.

4.2.1 Photolysis with UV 365 nm Light

Various concentrations of LAS were tested for degradation with UV light at 365 nm. Although theoretically UV light with this energy is not capable of direct bond breakage resulting in degradation, it was important to confirm that degradation of LAS in photocatalysis experiments was a result of titanium dioxide and not photolysis. As seen in the Figure 4.6, no degradation occurs when LAS was irradiated with UV 365nm and this process was not concentration dependent.

4.2.2 Photolysis with UV 254 nm Light

This section summarizes the photolytic experiments that were completed. These experiments were used to compare effectiveness of hydrogen peroxide degradation of LAS with combined processes at low wavelength UV light. Figure 4.7 shows the results of LAS degradation using low wavelength UV light at 254 nm.

Figure 4.8 shows the results of LAS degradation using low wavelength UV light as compared to the three model detergents. The first order rate constant for LAS is significantly greater

than that of any detergent tested. Purex had the highest k followed by Gain and Tide respectively. Table 4.1 shows the numerical results of these experiments.

Table 4.1: 1ˢᵗ order rate comparison of LAS with detergents.

Detergent	k (min⁻¹)
LAS (Biosoft D40)	0.0041
Gain	0.0014
Tide	0.0012
Purex	0.0019

Table 4.1 shows that the best results for the degradation of a detergent is Purex. The variation in rates as compared to LAS from Biosoft D40 suggests that other compounds in the detergent composition exert a significant oxidant demand. It is worth noting that an increase in detergent cost is proportional to LAS concentration, soluble COD, and oxidant demand. Degradation of LAS with UV light does not significantly change the soluble COD over a five-hour period. This shows a lack of mineralization of the compounds in the detergent formulation (Figure 4.9). Figure 4.10 shows the change in pH associated with the degradation using low wavelength UV light. In all cases, the pH decreased throughout the experiment but was more pronounced with the Biosoft D40 (LAS). Biosoft D40 does not have any added buffers as do the detergents.

No temperature control was employed during the experiments. Figure 4.11 shows how the temperature increased as a result of UV irradiation and mixing. In all experiments, the temperature increased from around 22 °C to 33-37 °C as result of mixing and UV lamp intensity. There was no attempt made in these experiments to control the temperature.
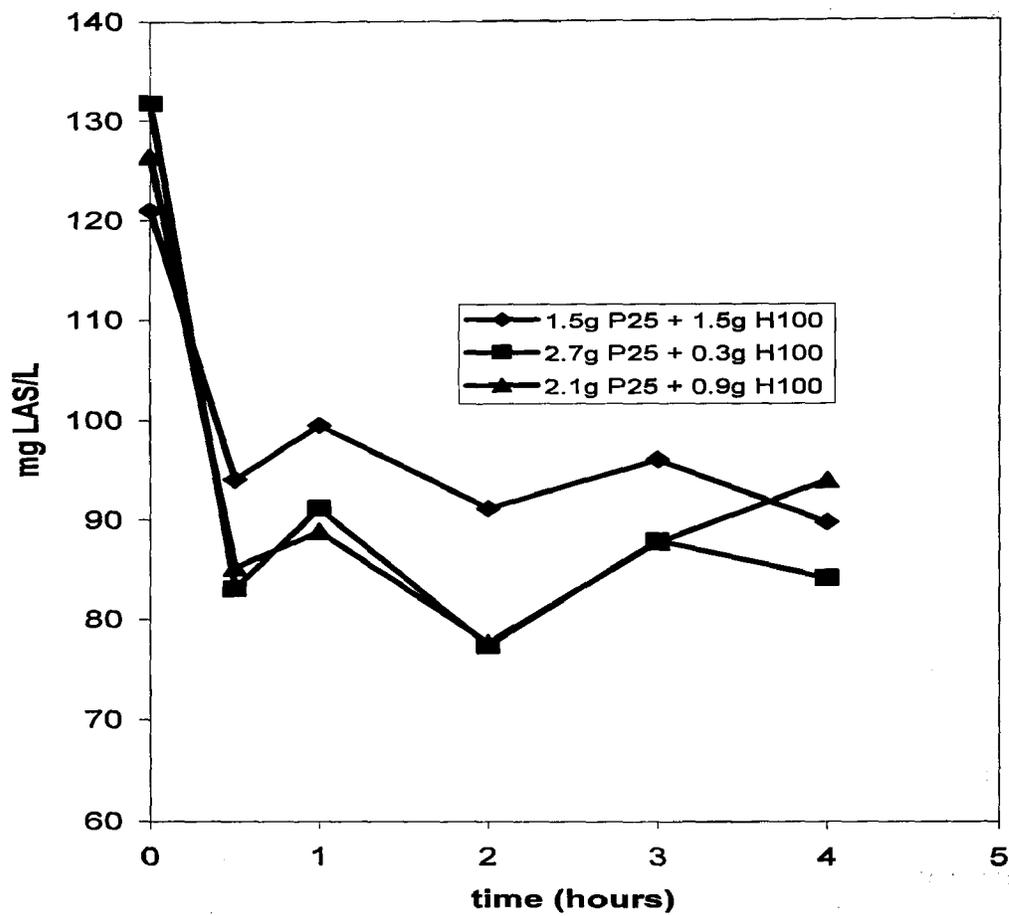
Figure 4.5: Dark reaction of combined Degussa P25 and Hombikat UV 100 TiO₂.
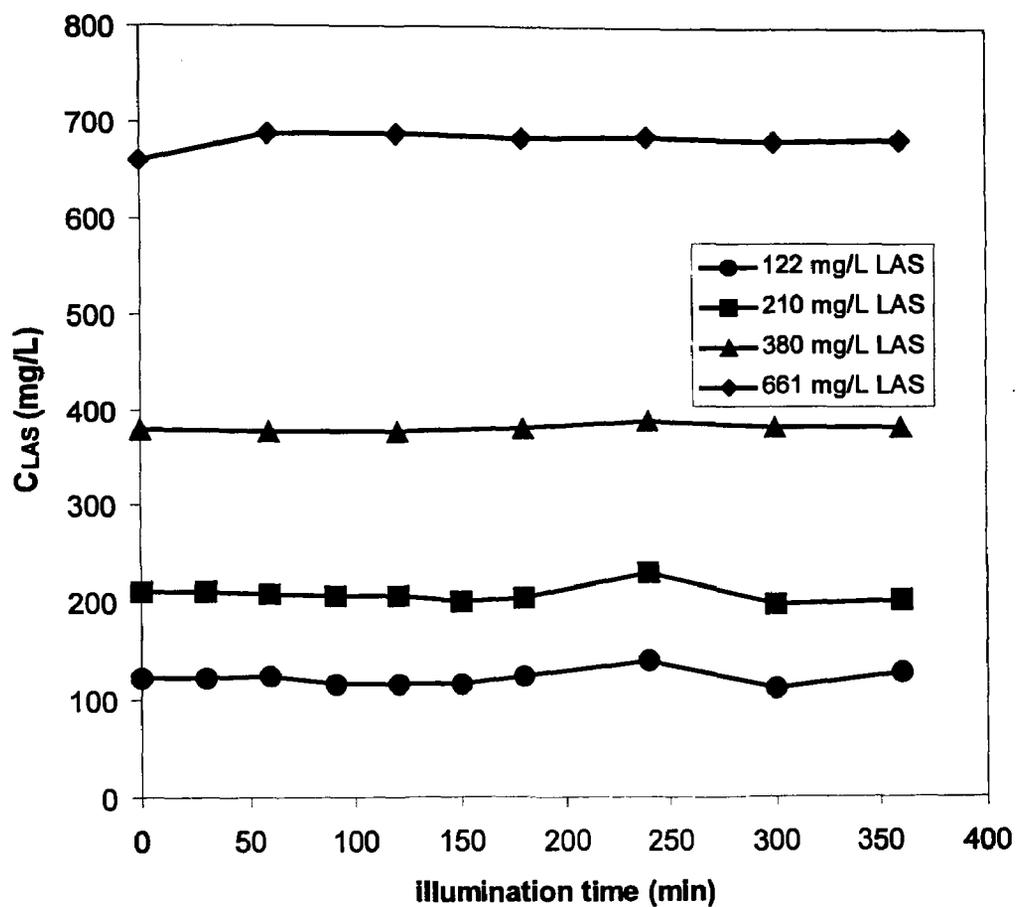
Figure 4.6: Treatment of varied concentrations of LAS with UV 365 nm (no TiO₂).
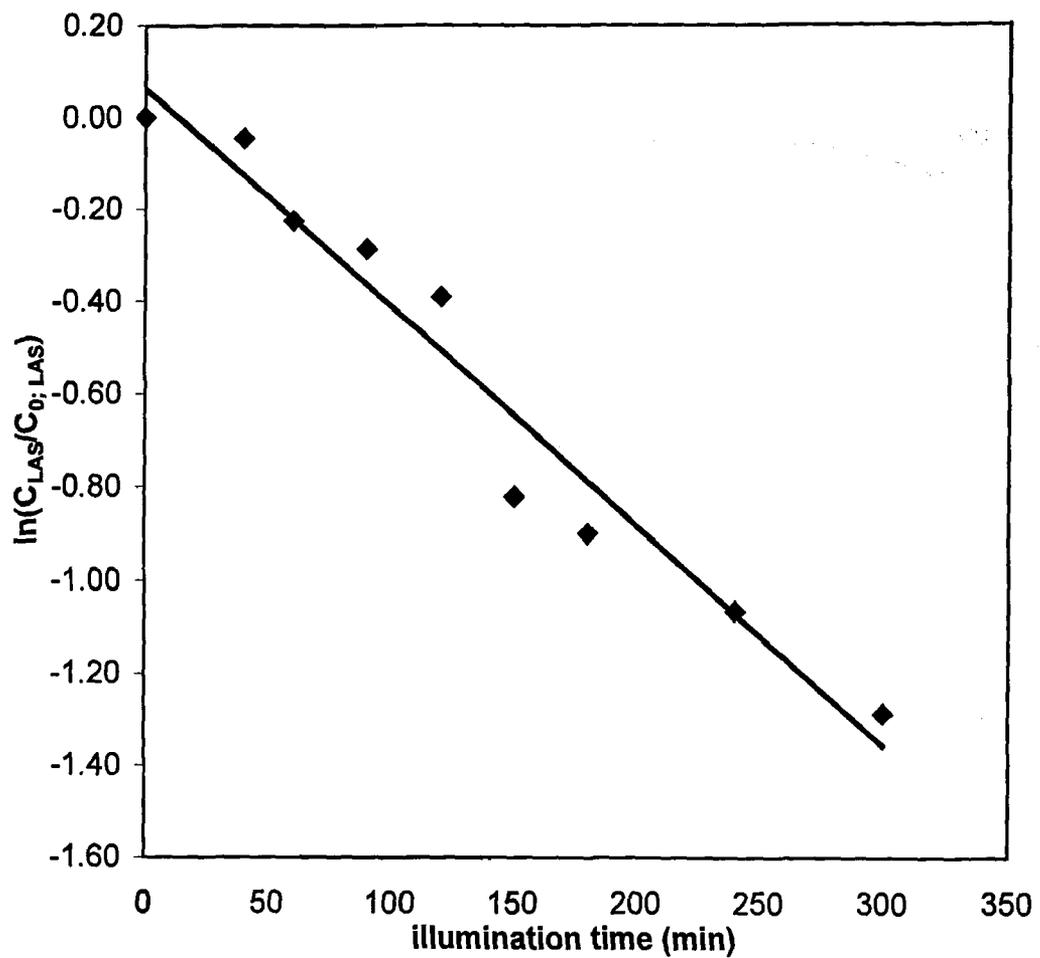
Figure 4.7: Degradation of LAS (C_0=100 mg/L) with low wavelength UV light (254 nm).
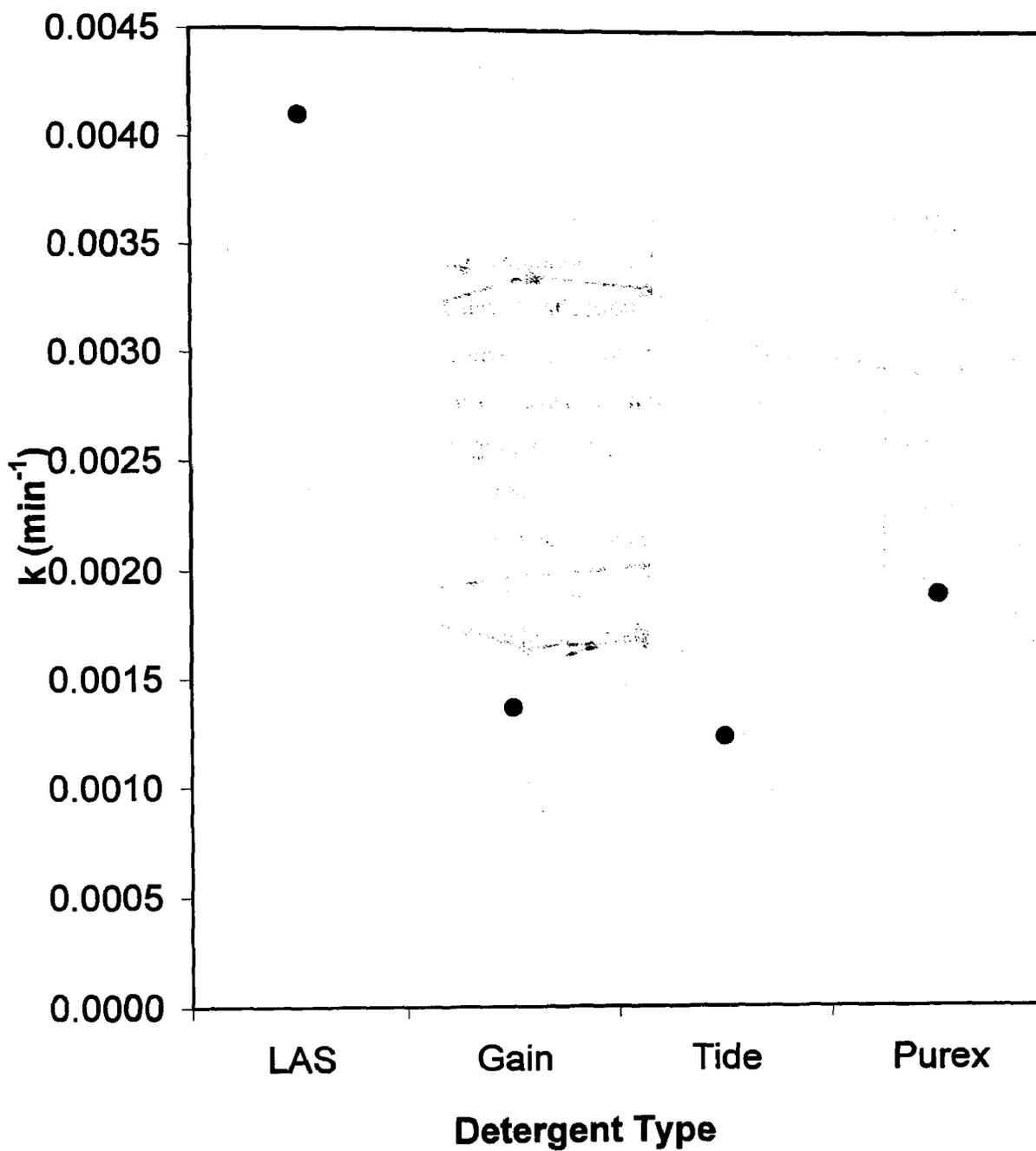
Figure 4.8: First order rate constant comparison of different detergents degradation with UV 254 nm.
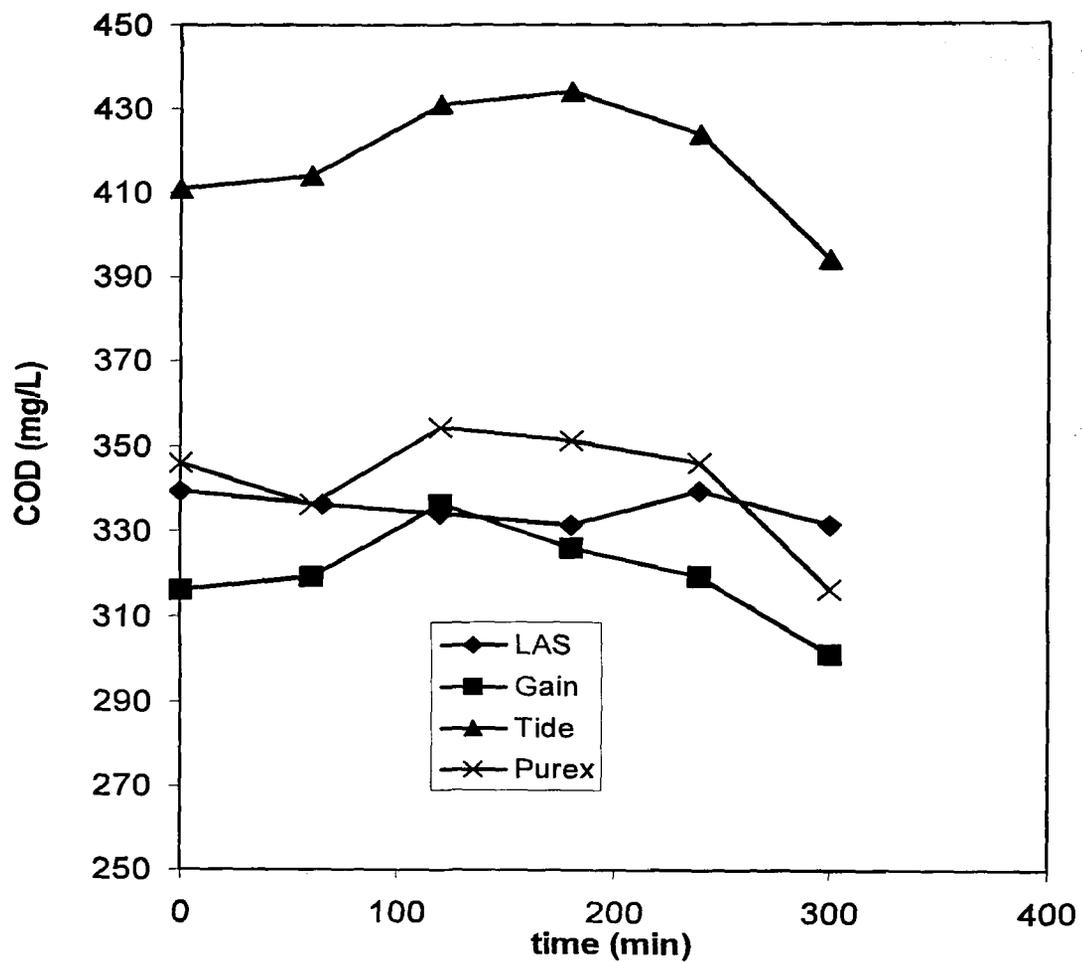
Figure 4.9: Degradation of LAS and detergents with UV 254 nm light. COD comparison.

4.2.3 Photolysis with H_2O_2 combined with UV 254 nm

This section outlines the optimization of UV combined with H_2O_2 as well as a rate comparison of LAS with the selected detergents.

Figure 4.12 shows the optimization of hydrogen peroxide for LAS Biosoft D40.

The optimum rate for degradation of LAS with combined hydrogen peroxide and UV light at 254 nm was at 5,000 mg/L for a 100mg/L solution of LAS. This amount of hydrogen peroxide would not be realistic in a scaled-up situation, therefore, the degradation of detergents was carried out at a lower concentration of hydrogen peroxide (1,560 mg/L). At this concentration, the first order rate was close to 10 times that for the optimum concentration of Degussa P25 TiO_2. Figure 4.13 depicts a comparison of the first order rates for the three detergents compared with LAS. As it is shown in Figure 4.14, LAS had the highest rate constant while Gain and Purex rate constants were almost the same at 0.043 and 0.042 min^{-1}, respectively. Figure 4.14 is an example of how the pH changes during the reaction for pure LAS as compared to the detergents. The pH drop is a result of the formation of organic acids such as different types of carboxylic acids or alcohols, which are commonly found as degradation products for these types of degradation mechanisms (Hatfield Venhuis, S. and M.Mehrvar, 2002). Although it was not confirmed in these experiments, it was accepted that organic acids were a product of organics degradation when using photolytic and photocatalytic treatment.

4.2.4 UV 254 nm degradation of LAS with H_2O_2 added at different time intervals

Hydrogen peroxide was added at different time intervals to solutions of 100 mg/L LAS under constant irradiation of UV light at 254 nm. 600 mg/L H_2O_2 was used in each experiment. Figure 4.15 depicts the results of LAS degradation. It was concluded that there is no improvement in LAS degradation rate when hydrogen peroxide is added at any time after illumination has started. For degradation of LAS, it is most advantageous to add the hydrogen peroxide at the start of irradiation.
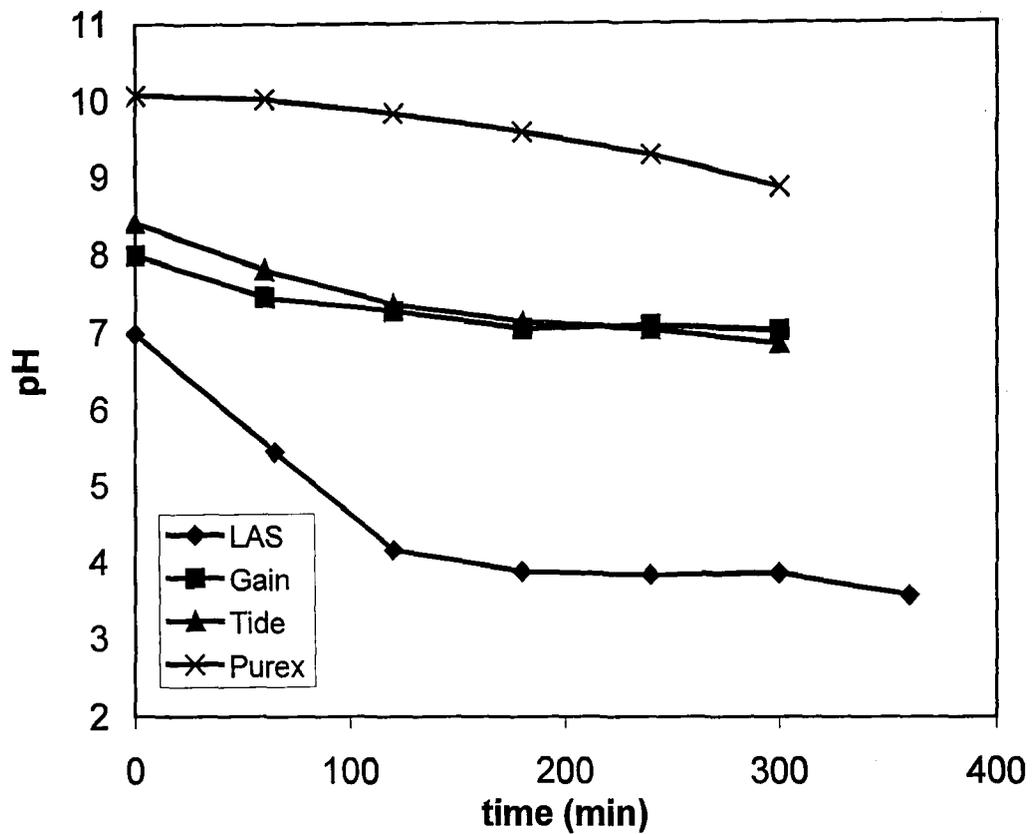
Figure 4.10: pH comparison of LAS and detergents during degradation with UV light at 254 nm.
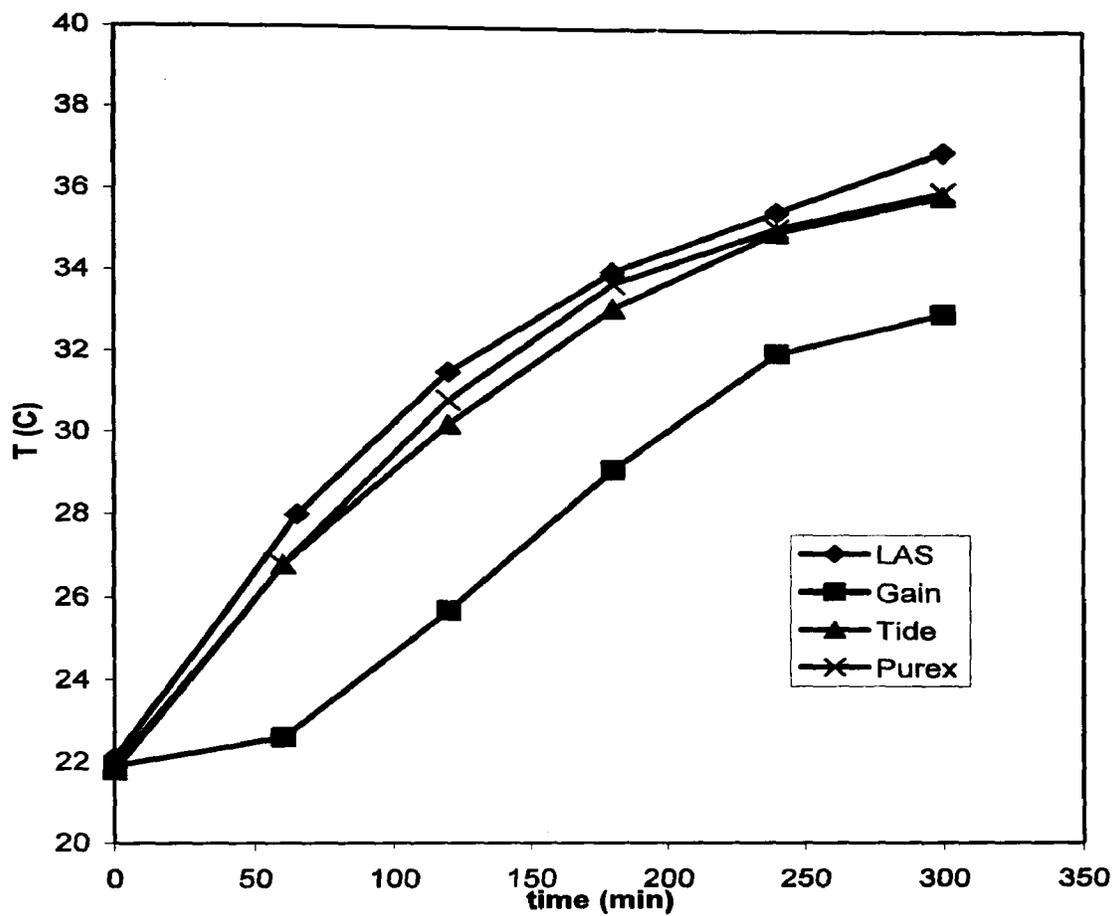
Figure 4.11: Temperature comparison during degradation of LAS and detergents with UV 254 nm.
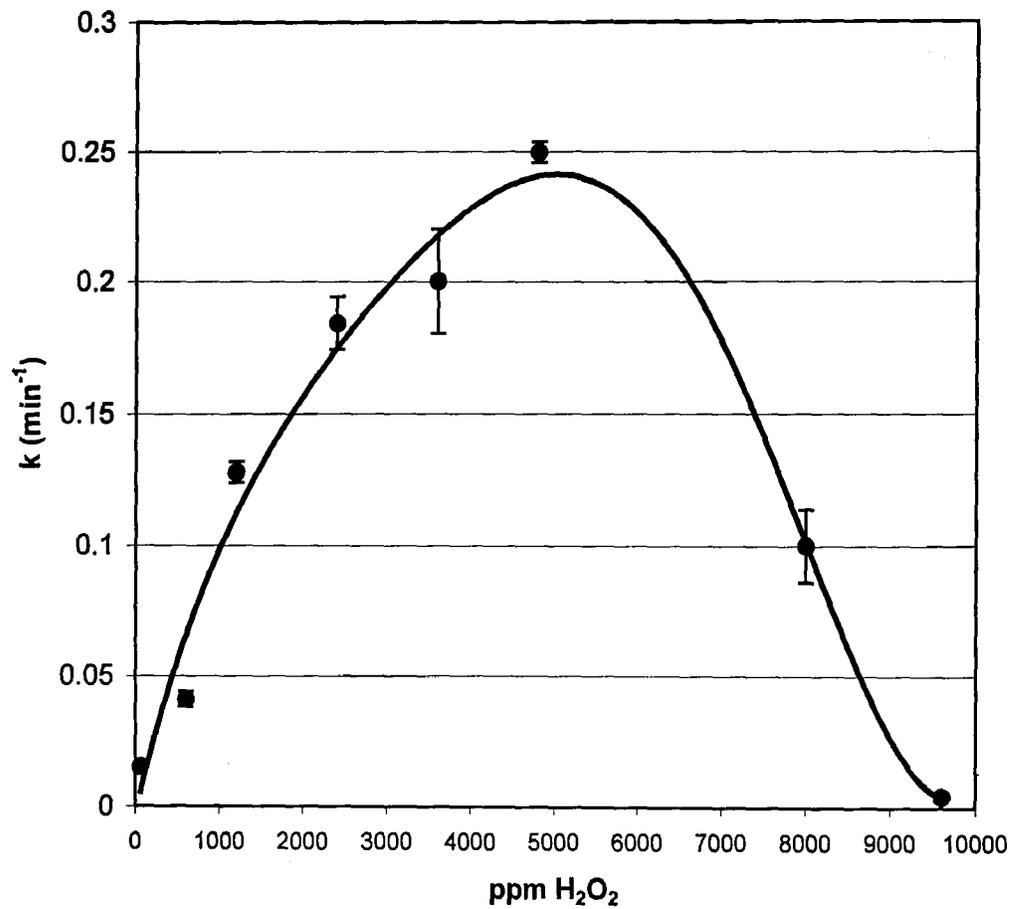
Figure 4.12: LAS degradation with various concentrations of H_2O_2 combined with UV 254 nm. C_o=100 mg/L. First order rate constant comparison for photolytic treatment. Error bars represent ± 1 standard deviation.
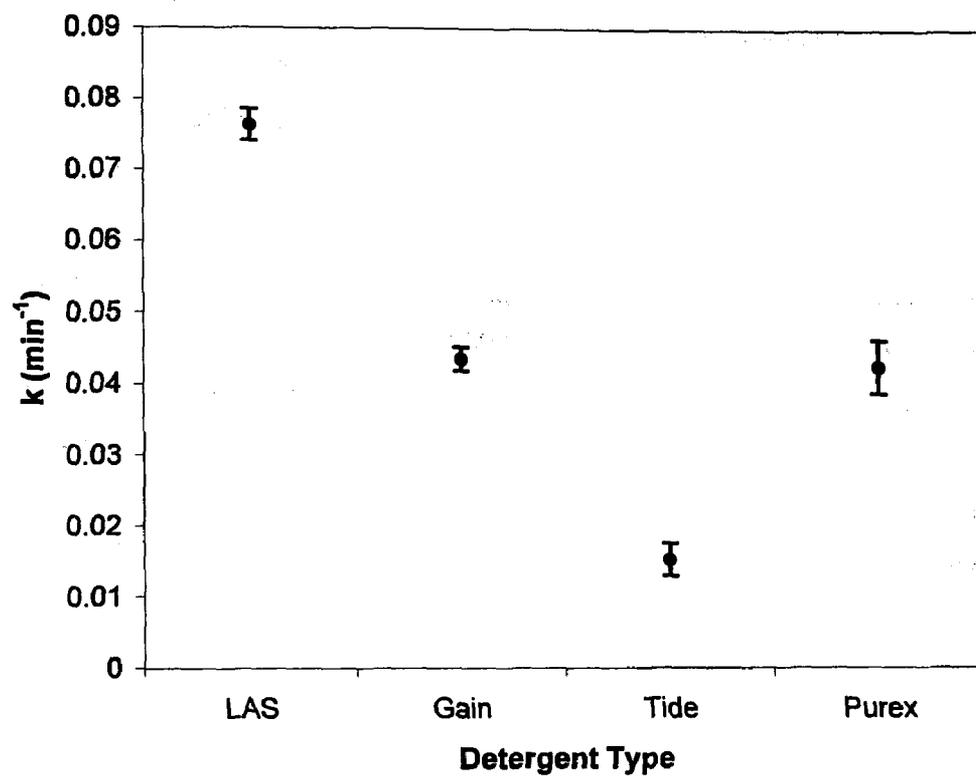
Figure 4.13: Photolytic degradation of LAS and different detergents. 1,560 mg/L H_2O_2 combined with UV 254 nm light.

4.3 Photocatalytic Treatment

This section outlines the optimization experiments as well as degradation of detergents at the optimum titanium dioxide concentration.

4.3.1 Optimization of Degussa P25 TiO₂

Optimization experiments were completed by varying the titanium dioxide concentration by comparing the first order rate constants. Figure 4.16 depicts the results of LAS degradation with different TiO_2 concentrations. At 4.0 g/L TiO_2, the optimum degradation rate occurred for LAS. Above 4.0 g/L, TiO_2, the rate decreased sharply. This was a result of the light blocking effect of the titanium dioxide. Since the UV light was unable to penetrate deep into the solution, the TiO_2 surface area was not effectively used for oxidant production. Figure 4.17 depicts the results of the first order rate constant comparison of LAS with different detergents. For Degussa P25 TiO_2, the best degradation rate occurred with the pure LAS at 0.035 min^{-1} while for the three detergents, the rate varied between 0.01 –0.014 min^{-1}. The first order rate constant experimentally determined for 100 mg/L LAS and 2.0 g/L Degussa P25 TiO_2, 0.012 min^{-1}, was similar to 0.018 min^{-1} found by Hidaka et al. (1992) for 34.8 mg/L sodium dodecylbenzene sulfonate (SDS) and 2.0 g/L TiO_2. The similarity in rate constants was expected since the difference in compounds was limited only to the alkyl chain length. The observed difference may be a result of the difference in LAS or SDS initial concentration. It is important to note the SDS degradation was monitored by the disappearance of the aromatic ring (Hidaka et. al, 1992). The results from this study cannot be directly related to the study by Saien et al. (2003) since the concentrations of both the initial SDS and TiO_2 were much lower. Due to the similarities between SDS and the LAS used in this study (SDS has an alkyl chain with 12 carbon atoms while LAS is a mixture of compounds with 10-14 carbon atoms in the alkyl chain), it is expected that Biosoft D40 will follow a similar degradation path to that proposed by Hidaka et al. (1992).
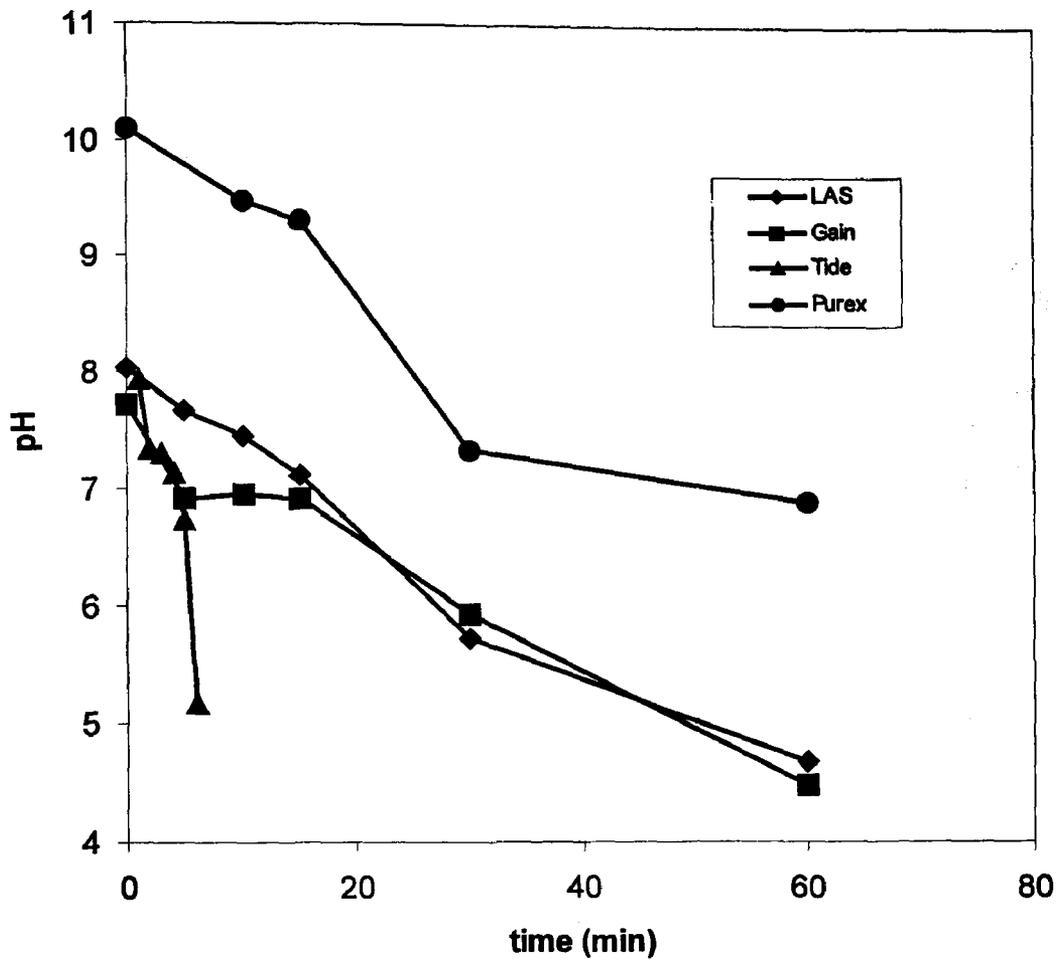
Figure 4.14: Comparison of pH change during degradation of LAS and detergents using 1,560 mg/LH₂O₂ combined with UV light at 254 nm.
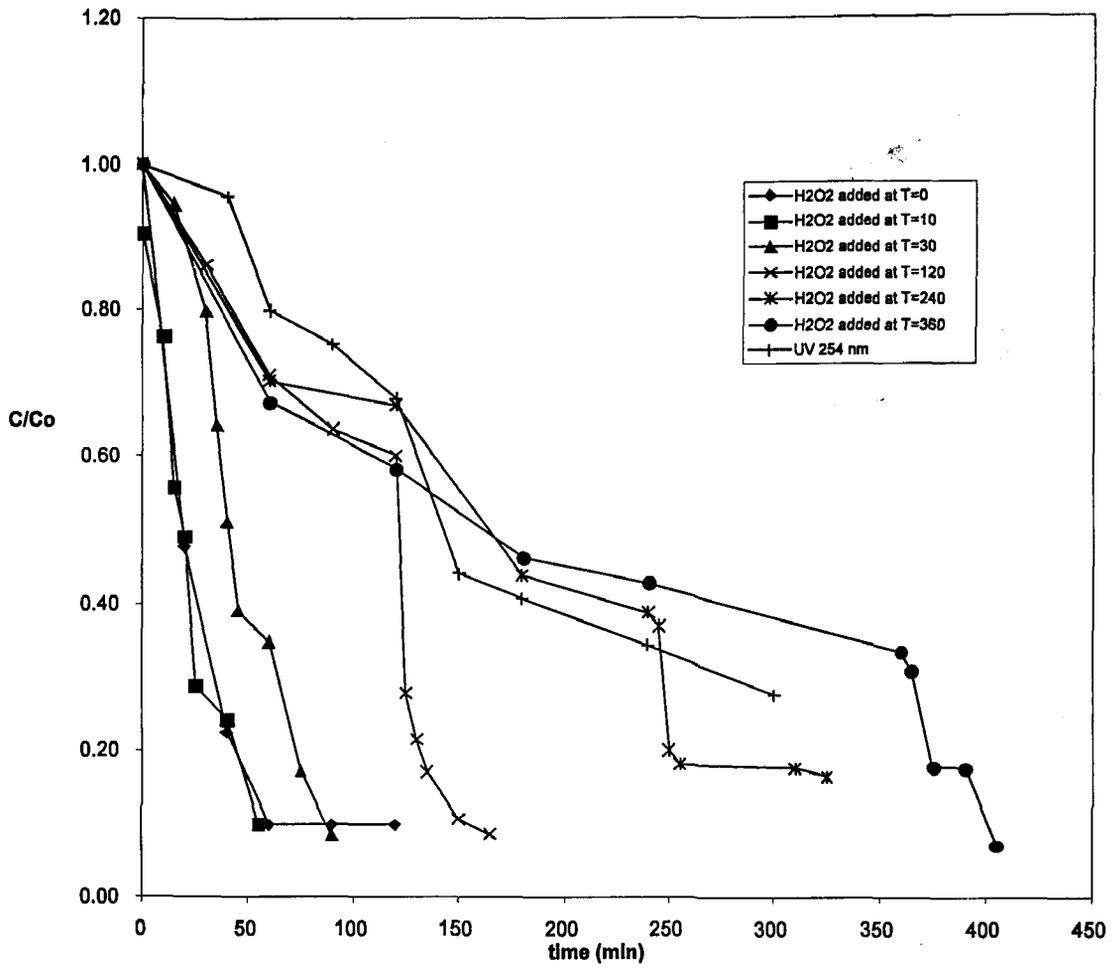
Figure 4.15: Degradation of LAS; 600 mg/L H_2O_2 added at different times. C_o=100 mg/L LAS.
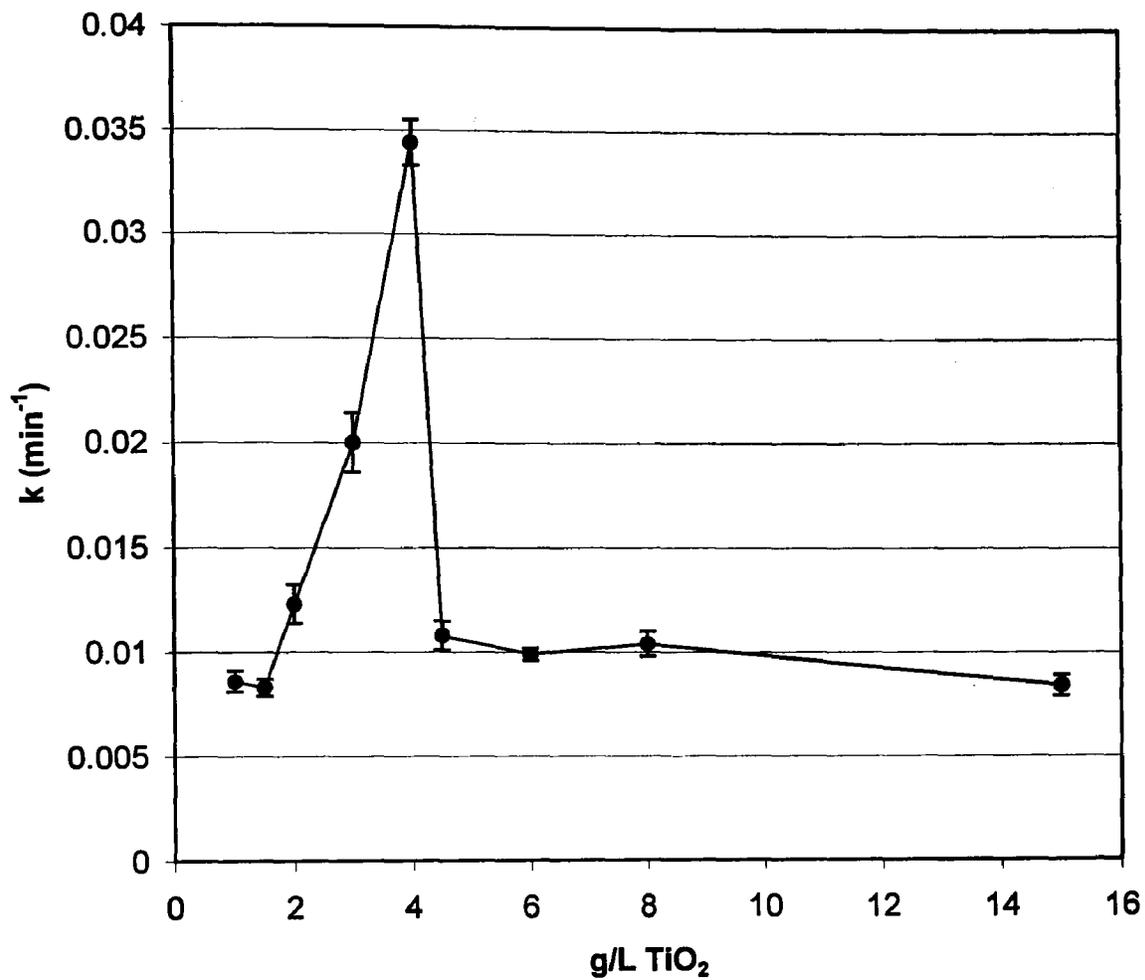
Figure 4.16: Optimization of Degussa P25 TiO$_2$ concentration for treating LAS. Co=100 mg/L LAS. Irradiated with UV 365 nm. Error bars=± 1 standard deviation.

The soluble COD varied significantly between the Biosoft D40 and the detergents tested (Figure 3.1). For Tide and Purex, the soluble COD decreased sharply over the first three hours of the experiment. LAS and Gain showed sharp decreases in soluble COD (Figure 4.18) during the first 20 minutes of the experiment. The difference can be attributed to the differences in detergent ingredients. The pH decreased throughout the degradation experiment as a result of organic acid formation. The pH of Purex decreased from 10 to 7.1, while for Tide, Gain and LAS the pH started at around 8.5 and decreased to just above 7.0. The ultimate pH is dependent upon the initial pH (Figure 4.19).

4.3.2 Optimization of Hombikat UV 100 /UV 365nm

This set of experiments was designed to optimize the Hombikat UV 100 titanium dioxide concentration. The concentration of Hombikat UV 100 TiO_2 was varied and the first order rate constants were compared. Figure 4.20 illustrates the experimental results for the first order rate constants in LAS degradation using Hombikat UV 100 TiO_2 photocatalytic processes. The optimum concentration of Hombikat UV 100 was found to be 2.0 g/L.
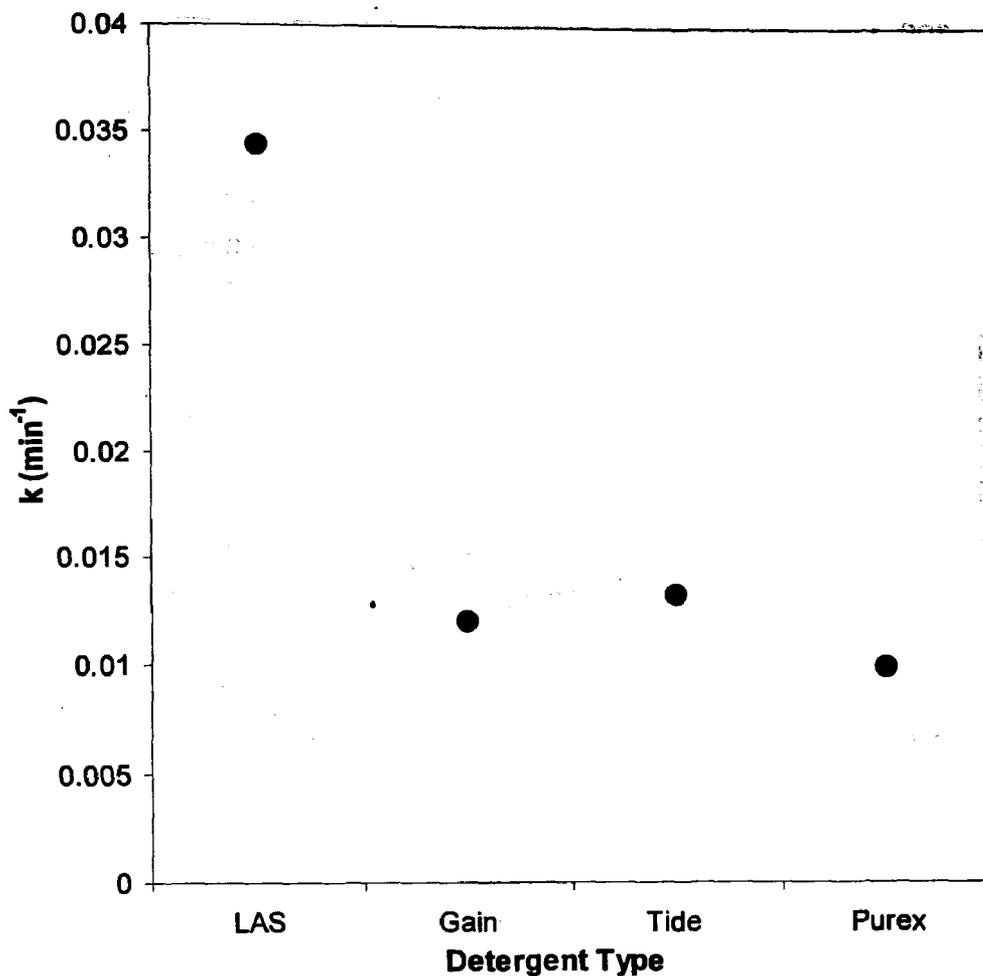
Figure 4.17: Comparison of LAS and detergent degradation with 4.0g/L Degussa P25 TiO_2/UV 365 nm. Co=100 mg/L LAS.
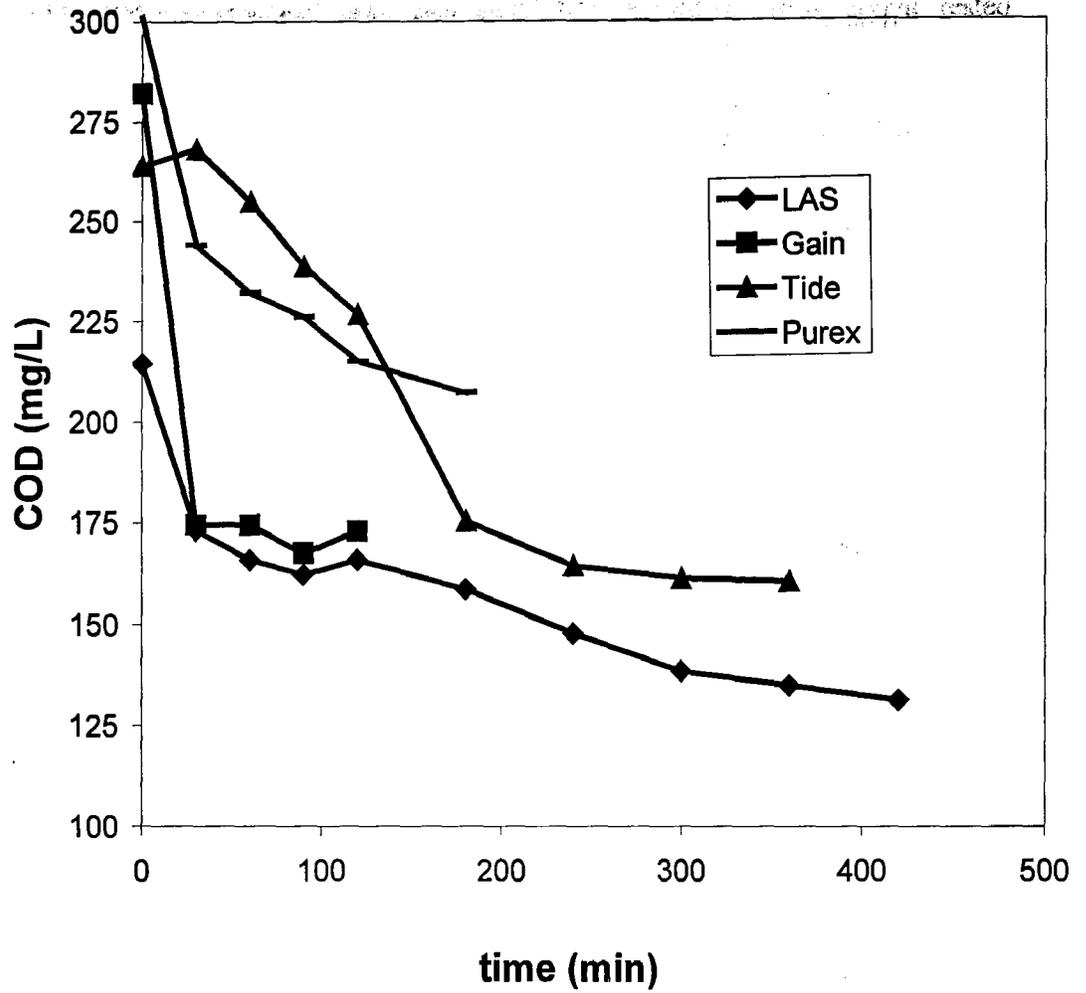
**Figure 4.18: Comparison of soluble COD changes during degradation of detergents with 3.0g Degussa P25 TiO$_2$/UV 365 nm. Co=100 mg/L LAS.**
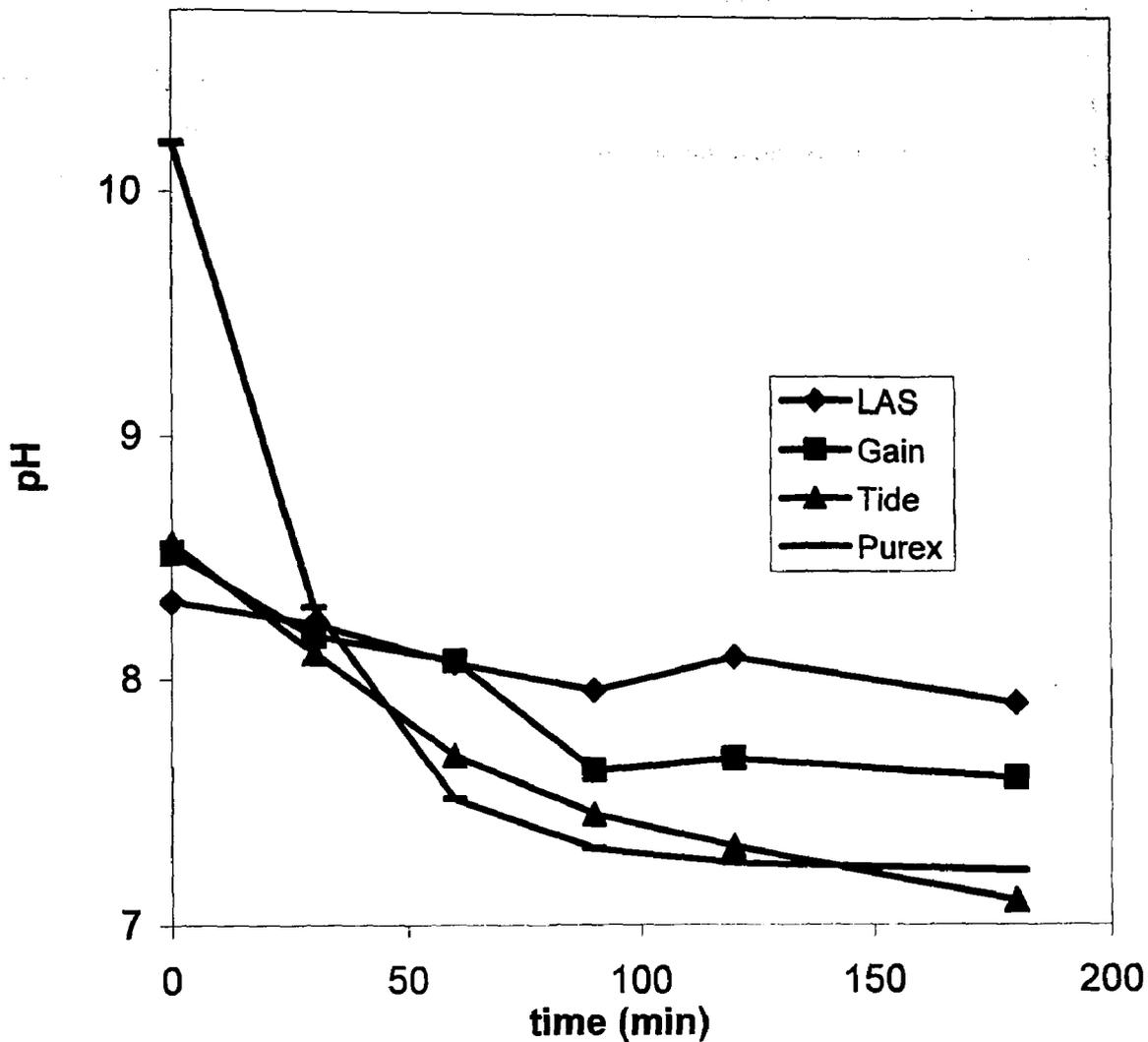
Figure 4.19: Comparison of pH changes during degradation of LAS and detergents with 4.0g Degussa P25 TiO_2/UV 365nm. C_o=100 mg/L LAS.

4.3.3 Comparison of Degussa P25 and Hombikat UV 100 TiO_2 for the degradation of LAS

Degussa P25 TiO_2 had a maximum first order rate constant of 0.035 min^{-1} at 4.0 g/L while Hombikat UV 100 TiO_2 had a maximum first order rate constant of 0.0098 min^{-1} at 2.0 g/L. Figure 4.21 shows the first order rate constants for both types of TiO_2. Since the Hombikat UV 100 titanium dioxide has a higher surface area, therefore, more active sites, the maximum first order rate constant by Hombikat UV 100 TiO_2 should be higher than that for Degussa P25 TiO_2. Based on surface area, UV 100 TiO_2 should have 7 times the photoactivity of Degussa P25. It has been observed that for treatment of some organic compounds, the photoactivity of Hombikat UV 100 TiO_2 is only 2 times that of Degussa P25 TiO_2 (Aye et al., 2003). It has been reported that Hombikat UV 100 TiO_2 exhibits a higher photoactivity than that of Degussa P25 TiO_2 at high loadings (Mehrvar et al., 2002). The reverse was observed in this study. For degradation of LAS, Hombikat UV 100 was found to have a lower photoactivity than Degussa P25 TiO_2. LAS adsorption on the surface of the Hombikat UV 100 TiO_2 (>25% adsorbed) reduces the sites available for oxidant production. Since LAS was not degraded by UV 365 nm alone (Figure 4.5), this severely limits the rate at which the LAS can degrade under these conditions. In studies where Hombikat UV 100 TiO_2 is reported to have a higher photoactivity, the adsorption of the model compounds tested was less than 10% and therefore, could be neglected. Another important observation was that first order rate constants were used in this study to compare photoactivity whereas the method of initial rates was used in other studies in which UV 100 had higher photoactivity. It has been shown that the method of initial rates has sensitivity issues (Mehrvar, 2000).
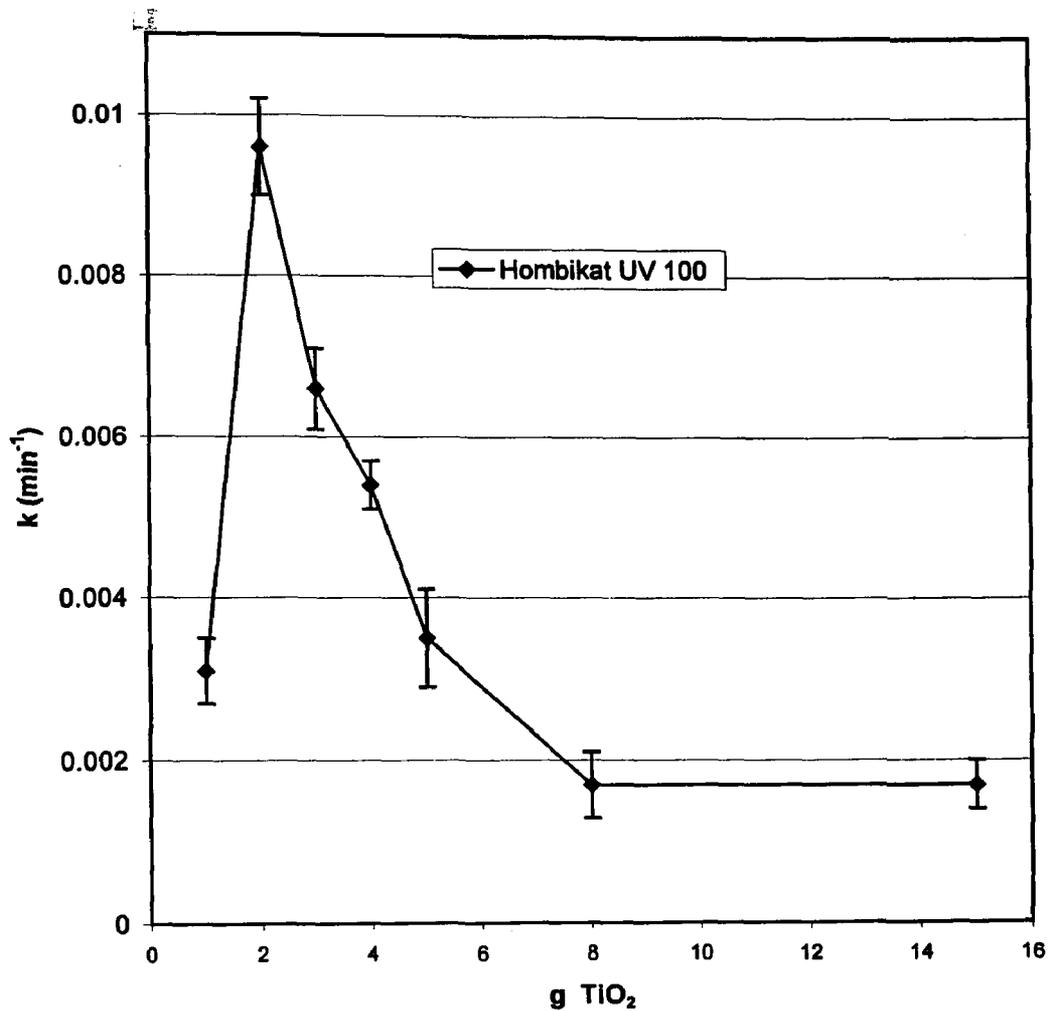
Figure 4.20: Optimization of Hombikat UV 100 TiO₂ concentration for LAS degradation based on the initial rate comparison. C_0=100 mg/L LAS. Error bars=± 1 standard deviation.
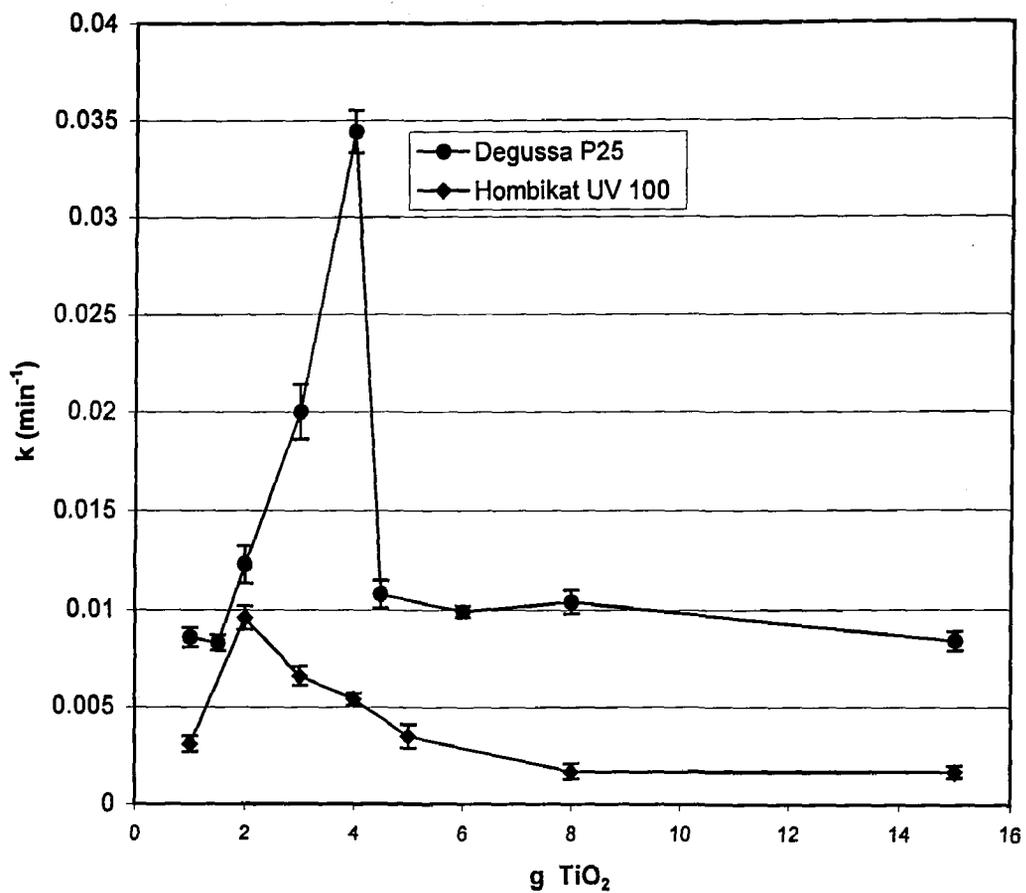
Figure 4.21: Optimization of Degussa P25 and Hombikat UV 100 TiO_2. Error bars=±1 standard
deviation.

4.3.4 Combined Degussa P25 and Hombikat UV 100 TiO_2 at UV 365 nm

The objective of these experiments was to determine if by combining the two types of titanium dioxide the degradation rate could be improved upon. It was thought that by combining the two types of TiO_2, the agglomeration effect discussed in section 4.5 could be effectively reduced, therefore, increasing the number of active sites available for oxidant production on the UV 100 titanium dioxide (Hatfield Venhuis, S. and M. Mehrvar, 2003). Figure 4.22 shows the results of the combined TiO_2 experiments. Based on the above results, there was no added advantage in combining the two types of titanium dioxide. The optimum rate occurs with Degussa P25 TiO_2. Since there was no observed improvement in rates, as a result, the detergents were not tested.

4.3.5 Combined Degussa P25 and H_2O_2

The following set of experiments was completed to test for improved degradation of LAS by combining titanium dioxide and hydrogen peroxide. Since the optimum wavelength for oxidant production on the surface of titanium dioxide was at 365 nm and for photolysis of the oxygen-oxygen bond in hydrogen peroxide for formation of hydroxyl radicals was 254 nm, both wavelengths of light were tested for the combined experiments. The results were compared with H_2O_2 – UV 254 nm and Degussa P25 TiO_2 – UV 365 nm alone. Figure 4.23 shows the results for the photocatalytic and photolytic degradation of LAS. The optimum concentrations for the individual processes were not used because in a real life situation, the cost of 5,000 mg/L H_2O_2 and 4.0 g/L TiO_2 would be inhibitory to any viable treatment process. Degussa P25 TiO_2 was used since it produced the best rate results even though more on a mass basis was required. The hydrogen peroxide concentration used was 600 mg/L. The first experiment was 3.0 g/L TiO_2 and 600 mg/L with H_2O_2 in the presence of light at 365 nm. The first order rate constant was lower than that of the TiO_2/UV 365 nm alone. This was a result of adsorbed hydrogen peroxide using available sites on the surface of the titanium dioxide, therefore, lowering the production of active species. Similar results were seen when TiO_2 was combined with 600 mg/L H_2O_2 and irradiated with UV 254 nm. The adsorbed hydrogen peroxide was not available for reaction with the UV light to produce hydroxyl radicals for reaction with LAS. The best rate was achieved with Degussa P25 TiO_2 combined with UV light 365 nm. Due to the poor results, Gain, Tide, and Purex were not tested.
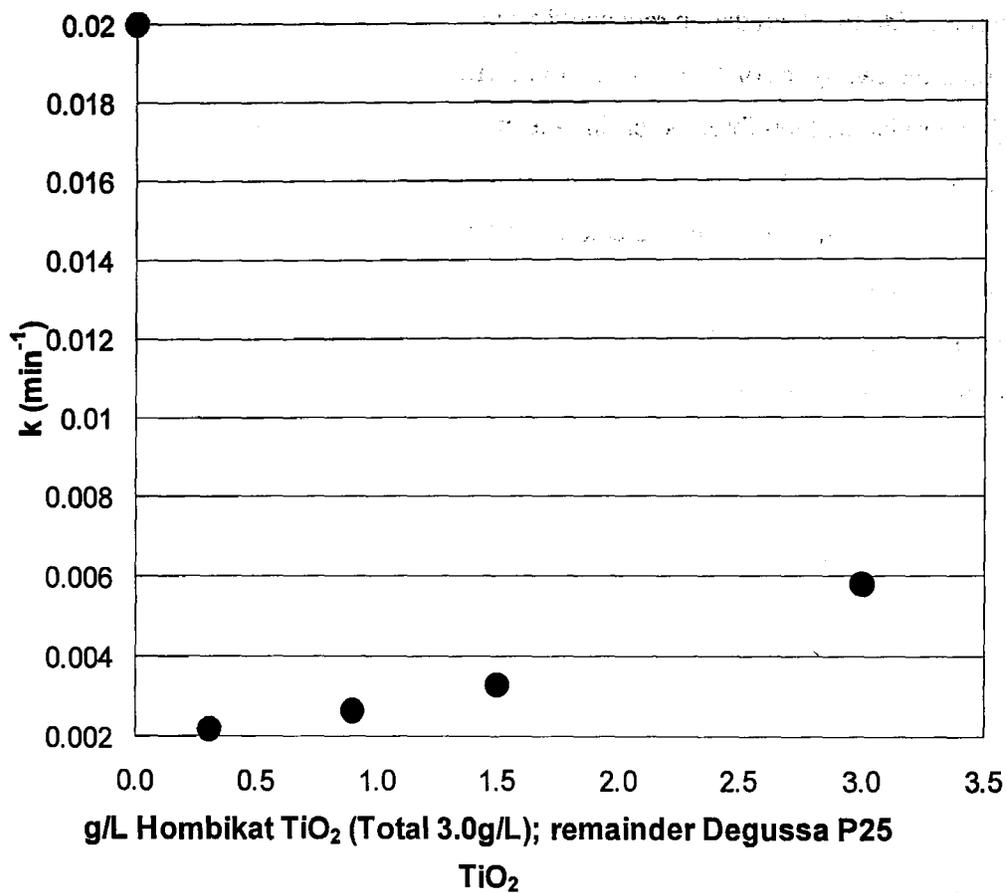
Figure 4.22: Comparison of combined Degussa P25 TiO_2 and Hombikat UV 100 TiO_2. C_o=100 mg/L LAS. Total concentration of TiO_2 used = 3.0g/L.
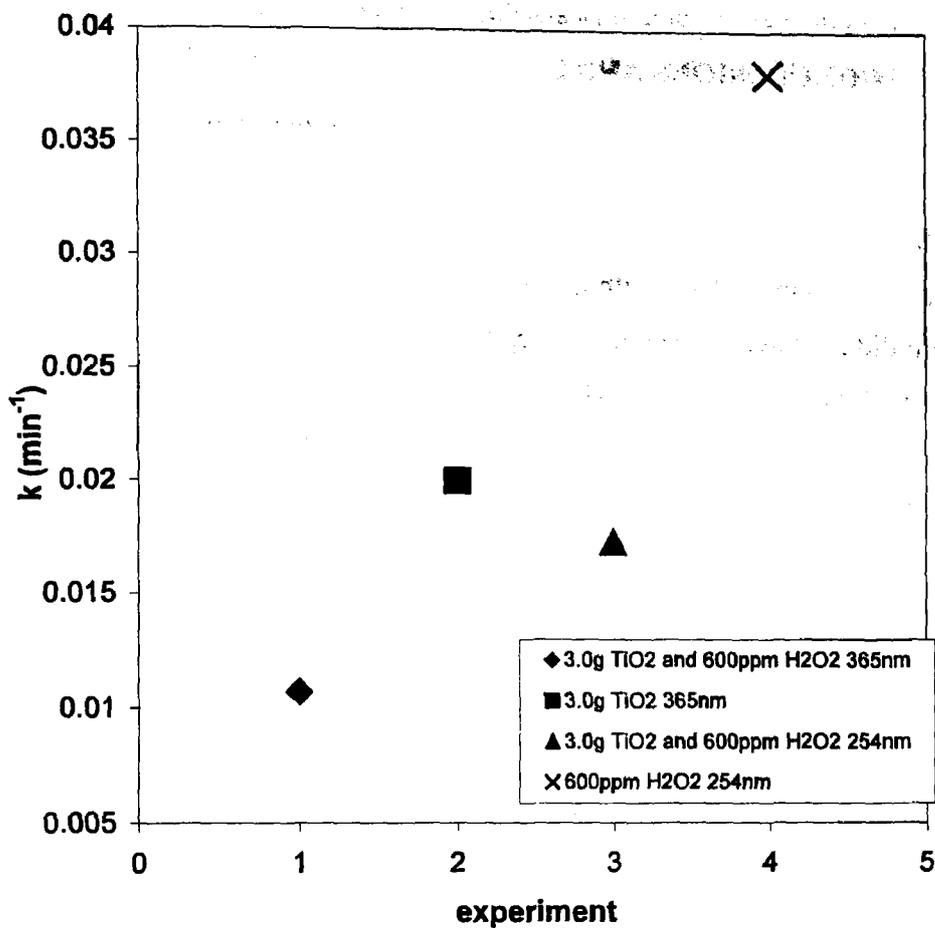
Figure 4.23: Comparison of first order rate constants for LAS treated with combined Degussa P25 TiO$_2$ and H$_2$O$_2$.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions listed below can be drawn from this study.

(1) Irradiation of a 100 mg/L LAS with UV 365 nm was not successful. This wavelength of UV light did not have the required energy for direct bond breakage.

(2) Photolysis with UV 254 nm successfully degraded LAS, however, the long reaction time (5 hours to achieve 80% degradation) was not energetically favourable. The first order rate constant for LAS was highest for BioSoft D40 (LAS) at 0.0041 min^{-1} followed by Purex (0.0019 min^{-1}), Gain (0.0014 min^{-1}) and Tide (0.0012 min^{-1}). The soluble COD did not decrease over a five-hour period.

(3) Optimum photolysis conditions for degradation of LAS were found with 5,000 mg/L H_2O_2 combined with UV light at 254 nm. The first order rate constant for degradation of LAS under these conditions was 0.25 min^{-1}. For comparison of LAS and detergent degradation, 1,560 mg/L H_2O_2 was used. LAS had the highest first order rate constant (0.077 min^{-1}) followed by Gain (0.043 min^{-1}), Purex (0042 min^{-1}) and Tide (0.016 min^{-1}).

(4) Photolysis of LAS with UV light at 254 nm and 600 mg/L H_2O_2 added at different time intervals was not successful. No improvement in reaction rate was observed. For optimum results, the hydrogen peroxide is added at the beginning of irradiation.

(5) The optimum concentration of Degussa P25 TiO_2 was found to be 4.0 g/L for degradation of LAS. At this titanium dioxide loading, the first order rate constant was 0.035 min^{-1} for LAS while for the detergents, the rates ranged from 0.01 to 0.014 min^{-1}.

(6) The optimum concentration of Hombikat UV 100 TiO_2 was 2.0 g/L. The first order rate constant for LAS degradation was 0.0098 min^{-1}.

(7) For degradation of LAS, Hombikat UV 100 TiO_2 had a lower photoactivity than that of Degussa P25 TiO_2. LAS adsorption on the surface of the UV 100 TiO_2 (>25% adsorbed) reduced the number of sites available for oxidant production.

(8) Combination of Degussa P25 and Hombikat UV 100 TiO_2 in different proportions did not provide a superior rate of reaction.

(9) Combination of hydrogen peroxide with Degussa P25 titanium dioxide did not provide a superior rate of reaction.

5.2 Recommendations

All photolysis and photocatalysis experiments gave satisfactory results for the removal of LAS with the exception of irradiation with UV 365nm. Complete mineralization was not achieved with the methods tested. Based on these experiments performed in this study, the following recommendations are proposed for future research on the removal of LAS from water;

(1) Investigation of $TOC/COD/BOD_5$ relationships for various photolytic and photocatalytic LAS degradation processes.

(2) Scaling-up of photocatalytic or photolytic LAS treatment using a pilot scale reactor.

(3) Optimization of photolytic of photocatalytic treatment combined with biological treatment for improved process cost and energy efficiency.

APPENDIX

A1. Standard Curves

Methylene blue active substances (MBAS) for LAS determination
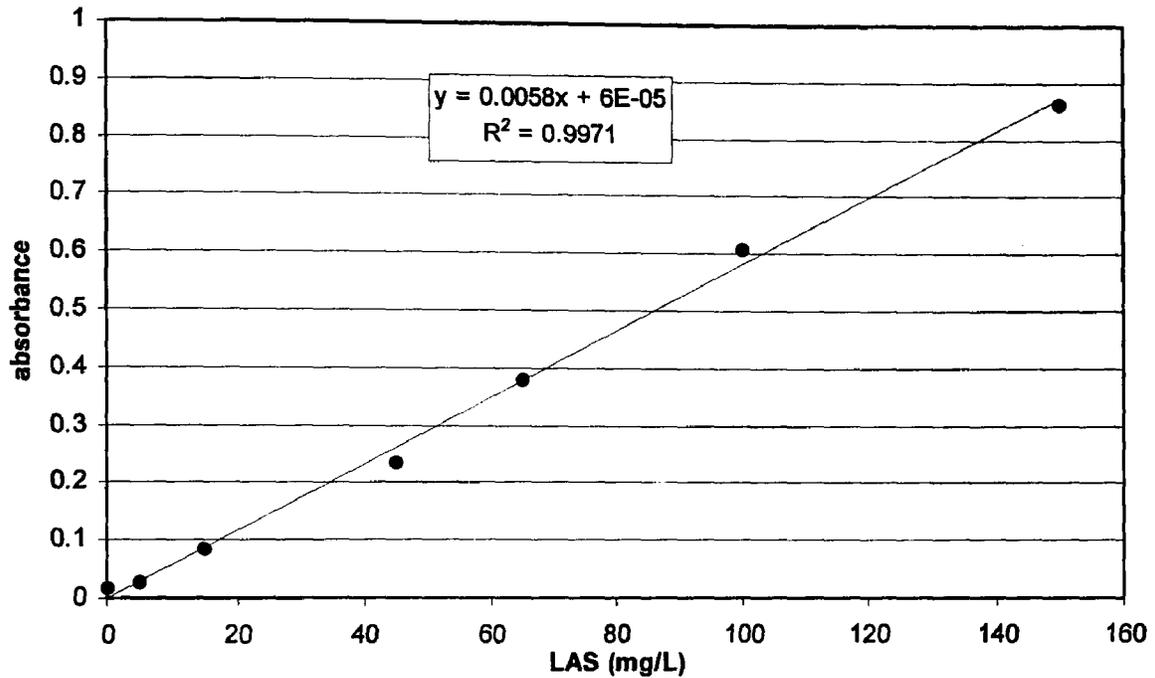
Figure A1:Example of a Standard Curve or LAS determination as MBAS. Absorbance measured at 652 nm according to Standard methods.

Figure A1 depicts an example of a calibration curve for determination of methylene blue active substances as LAS. A calibration curve was prepared each time a new batch of chemicals was prepared. The equation of the line was determined by linear regression analysis and used to convert measured absorbance values to mg/L LAS.

A2. COD Analysis
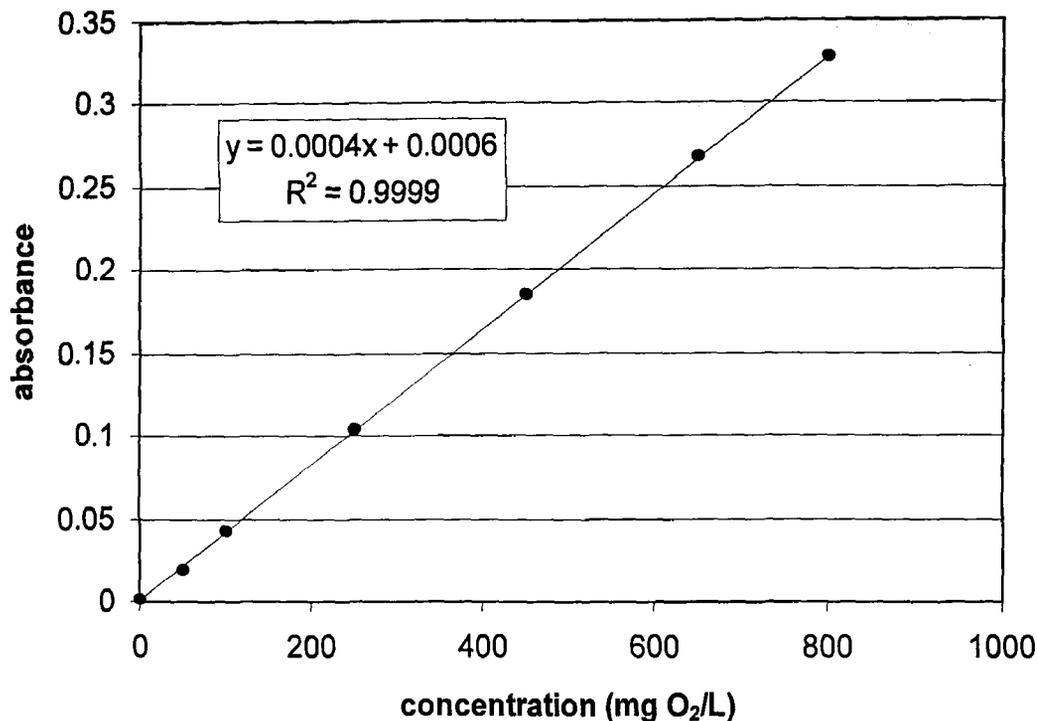
Figure A2: COD calibration curve; KHP (potassium hydrogen phthalate) used as reference compound according to Standard Methods for the Examination of Water and Wastewater (Greenberg et.al, 1992). COD reagent vials (range=20-900 mg/L) were purchased from Bioscience.

COD of samples was measured using pre prepared vials purchased from Bioscience Inc Analytical (Bethlehem, PA, USA). Standard range vials were used for all tests (20-900 mg /L). 2 mL of filtered or centrifuged sample was added to the digestion vial and digested at 150 °C for two hours. The samples were measured using the same spectrophotometer and quartz cell as described in Section 3.2.3.2.c. The absorbance was measured after the samples had cooled to room temperature at 600 nm. The results were compared to a standard curve prepared by using potassium hydrogen phtalate (KHP) standard solutions.

References

Ang, C.C. and A.S. Abdul (1992) "A Laboratory Study of the Biodegradation of an Alcohol Ethoxylate Surfactant by Native Soil Microbes" Journal of Hydrology, 138, 191-209.

Aye, Thandar (2002) "Combined Photocatalytic and Biological Treatment of A Textile Dye (Cibracon Brilliant Yellow 3G-P)" MASc. Thesis; University of Waterloo.

Battersby, N.S.; Sherren, A.J.; Bumpus, R.N.; Eagle, R. and I.K. Molade (2001) "The Fate of Linear Alcohol Ethoxylates During Activated Sludge Sewage Treatment" Chemosphere, 45, 109-121.

Beltran, F.J.; Garcia-Araya, J.F. and P.M. Alvarez (2000) "Sodium Dodecylbenzenesulfonate Removal from Water and Wastewater. 1. Kinetics of Decomposition by Ozonation" Industrial and Engineering Chemistry Research, 39, 2214-2220.

Bennett, E.R. and C.D. Metcalfe (2000) "Distribution of Degradation Products of Alkylphenol Ethoxylates Near Sewage Treatment Plants in the Lower Great Lakes, North America" Environmental Toxicology and Chemistry, 19 (4), 784-792.

Bjerregaard, H.F.; Staermose, S.; and S.S.J. Vang (2001) "Effect of Linear Alkylbenzene Sulfonate (LAS) on Ion Transport and Intracellular Calcium in Kidney Distal Epithelial Cells (A6)" Toxicology in Vitro, 15, 531-537.

Boeije, G.; Vanhooren, H.; Verbrugge, T. and P.A. Vanrolleghem (2000) "Development of a Chemical Fate Model for Trickling Filters Based on the Activated Sludge Model *SimpleTreat*: A Case Study for LAS" Environmental Science and Technology, 34, 4413-4417.

Brand, N.; Mailhot, G. and M. Bolte (1998) "Degradation Photoinduced by Fe(III): Method of Alkylphenol Ethoxylates Removal in Water" Environmental Science and Technology, 32, 2715-2720.

Branner, U.; Mygind, M. and C. Jorgensen (1999) "Degradation of Linear Alkylbenzene Sulfonate In Soil Columns" Environmental Toxicology and Chemistry, **18 (8)**, 1772-1778.

Ciorba, G.A.; Radovan, C.; Vlaicu, I. and S. Masu (2002) "Removal of Nonylphenol Ethoxylates by Electrochemically-Generated Coagulants" Journal of Applied Electrochemistry, **32**, 561-567.

Cuzzola, A.; Bernini, M. and P. Salvadori (2002) "A Preliminary Study on Iron Species as Heterogeneous Catalysts for the Degradation of Linear Alkylbenzene Sulphonic Acids by H_2O_2" Applied Catalysis B: Environmental, **36**, 231-237.

Dietrich, M.J.; Randall, T.L. and P.J. Canney (1985) "Wet Air Oxidation of Hazardous Organics in Wastewater" Environmental Progress, **4 (3)**, 171-177.

Destaillats, H.; Hung, H. and M.R. Hoffmann (2000) "Degradation of Alkylphenol Ethoxylate Surfactants in Water with Ultrasonic Irradiation" Environmental Science and Technology, **34**, 311-317.

Ding, W.; Tzing, S. and J. Lo (1999) "Occurrence and Concentration of Aromatic Surfactants and Their Degradation Products in River Waters of Taiwan" Chemosphere, **38 (11)**, 2597-2606.

Doi, J.; Marks, K.H.; DeCarvalho, A.J.; McAvoy, D.C.; Nielsen, A.M.; Kravetz, L. and M.L. Cano (2002) "Investigation of an Onsite Wastewater Treatment System in Sandy Soil: Sorption and Biodegradation of Linear Alkylbenzene Sulfonate" Environmental Toxicology and Chemistry, **21 (12)**, 2617-2622.

Dyer, S.D.; Stanton, D.T.; Lauth, J.R. and D.S. Cherry (2000) "Structure-Activity Relationships For Acute and Chronic Toxicity of Alcohol Ether Sulfates" Environmental Toxicology and Chemistry, **19 (3)**, 608-616.

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Ekelund, R.; Bergman, A.; Granmo, A. and M. Berggren (1990) "Bioaccumulation of 4-Nonylphenol in Marine Animals – A Re-Evaluation" Environmental Pollution, **64**, 107-120.

Elsgaard, L.; Petersen, S.O. and K. Debosz (2001) "Effects and Risk Assessment of Linear Alkylbenzene Sulfonates in Agricultural Soil. 1. Effects On Soil Microbiology" Environmental Toxicology and Chemistry, **20 (8)**, 1656-1663.

Elsgaard, L.; Petersen, S.O. and K. Debosz (2001) "Effects and Risk Assessment of Linear Alkylbenzene Sulfonates in Agricultural Soil. 2. Effects On Soil Microbiology As Influenced By Sewage Sludge and Incubation Time" Environmental Toxicology and Chemistry, **20 (8)**, 1664-1672.

Feitjtel, T.C.J.; Struijs, J. and E. Matthijs (1999) "Exposure Modeling of Detergent Surfactants – Prediction of 90th –Percentile Concentrations in the Netherlands" Environmental Toxicology and Chemistry, **18 (11)**, 2645-2652.

Feijtel, T.C.J.; Webb, S.F. and E. Matthius (2000) "Predictive Exposure Modeling – A Case Study With a Detergent Surfactant" Food and Chemical Toxicology, **38**, S43-S50.

Feitkenhauer, H. and U. Meyer (2002) "Intermediate Accumulation and efficiency of Anaerobic Digestion Treatment of Surfactant (alcohol Sulfate)-Rich Wastewater at Increasing Surfactant/Biomass Ratios" Journal of Chemical Technology and Biotechnology, **77**, 979-988.

Fenner, K.; Kooijman, C.; Scheringer, M. and K. Hungerbuhler (2002) "Including Transformation Products into the Risk Assessment for Chemicals: The Case of Nonylphenol ethoxylate Usage in Switzerland" Environmental Science and Technology, **36**, 1147-1154.

Ferguson, P.L.; Iden, C.R. and B.J. Brownawell (2001) "Distribution and Fate of Neutral Alkylphenol Ethoxylate Metabolites in a Sewage-Impacted Urban Estuary" Environmental Science and Technology, 35, 2428-2435.

Giger, W.; Stephanou, E. and C. Schaffner (1981) "Persistent Organic Chemicals in Sewage Effluents: I. Identifications of Nonyphenols and Nonylphenolethoxylates By Glass Capillary Gas Chromatography/Mass Spectrometry" Chemosphere, 10, 1253-1261.

Gejlsbjerg, B.; Klinge, C. and T. Madsen (2001) "Mineralization of Organic Contaminants in Sludge-Soil Mixtures" Environmental Toxicology and Chemistry, 20 (4), 698-705.

Gejlsbjerg, B.; Madsen, T. and T.T. Andersen (2003) "Comparison of Biodegradation of Surfactants in Soils and Sludge-Soil Mixtures by Use of ^{14}C-Labelled Compounds and Automated Respirometry" Chemosphere, 50, 321-331.

Greenberg, A.E., Clesceri, L.S. and A.D. Eaton, (1992) "Standard Methods for the Examination of Water and Wastewater" 18th Edition, American Public Health Association.

Hack, J. (1991) "Decreasing Effluent Pollution by the Use of Soap-based Building Kit Detergents" Journal of Chemical Technology and Biotechnology, 50, 379-385.

Hatfield Venhuis, S. and M. Mehrvar, "Health Effects, Environmental Impact, and Photochemical Degradation of Selected Surfactants in Water" International Journal of Photoenergy, 2004, in press.

Hatfield Venhuis, S. and M. Mehrvar, "Photolytic and Photocatalytic Degradation of Linear Alkylbenzene Sulfonate (LAS) in Water", 53rd Canadian Chemical Engineering Conference, Hamilton, Ontario, Canada, October 26-29, 2003.

Hatfield Venhuis, S. and M. Mehrvar, "Photolytic and Photocatalytic Degradation of Linear Alkylbenzene Sulfonate (LAS) in Water", 52nd Canadian Chemical Engineering Conference, Vancouver, British Colombia, Canada, October 20-23, 2002.

Hawrelak, M.: Bennett, E. and C. Metcalfe (1999) "The Environmental Fate of the Primary Degradation Products of Alkylphenol Ethoxylate Surfactants in Recycled Paper Sludge" Chemosphere, 39 (5), 745-752.

Hidaka, H.; Ihara, K.; Fujita, Y.; Yamada, S.; Pelizzetti, E. and N. Serpone (1988) "Photodegradation of Surfactants IV: Photodegradation of Non-Ionic Surfactants in Aqueous Titanium Dioxide Suspensions" Journal of Photochemistry and Photobiology A: Chemistry, 42, 375-381.

Hidaka, H.; Zhao, J.; Pelizzetti, E. and N. Serpone (1992) "Photodegradation of Surfactants, 8. Comparison of Photocatalytic Processes between Anionic Dodecylbenzenesulfonate and Cationic Benzyldocecyldimethylammonium Chloride on the TiO_2 Surface" Journal of Physical Chemistry, 96, 2226-2230.

Holmstrup, M. and P.H. Krogh (2001) "Effects and Risk Assessment of Linear Alkylbenzene Sulfonates in Agricultural Soil. 3. Sub lethal Effects On Soil Invertebrates" Environmental Toxicology and Chemistry, 20 (8), 1673-1679.

Holmstrup, M.; Krogh, P.H.; Lokke, H.; De Wolf, W.; Marshall, S. and K. Fox (2001) "Effects and Risk Assessment of Linear Alkylbenzene Sulfonates In Agricultural Soil. 4. The Influence of Salt Speciation, Soil Type, And Sewage Sludge On Toxicity Using the Collembolan *Folsomia Fimetaria* and the Earthworm *Aporrectodea Caliginosa* As Test Organisms" Environmental Toxicology and Chemistry, 20 (8), 1680-1689.

Horikoshi, S.; Watanabe, N.; Onishi, H.; Hidaka, H. and N. Serpone (2002) "Photodecomposition of a Nonylphenol Polyethoxylate Surfactant in a Cylindrical

Photoreactor With TiO$_2$ Immobilized Fiberglass Cloth" Applied Catalysis B: Environmental, **37**, 117-129.

Jensen, J.; Lokke, H.; Holmstrup, M.; Krogh, P.H. and L. Elsgaard (2001) "Effects and Risk Assessment of Linear Alkylbenzene Sulfonates in Agricultural Soil. 5. Probabilistic Risk Assessment of Linear Alkylbenzene Sulfonates In Sludge-Amended Soils" Environmental Toxicology and Chemistry, **20 (8)**, 1690-1697.

Jobling, S. and J. Sumpter (1993) "Detergent Components in Sewage Effluent Are Weakly Oestrogenic to Fish: An In Vitro Study Using Rainbow Trout (*Oncorhynchus mykiss*) Hepatocytes" Aquatic Toxicology, **27**, 361-372.

Jones, F.W. and D.J. Westmoreland (1998) "Degradation of Nonylphenol Ethoxylates During the Composting of Sludges From Wool Scour Effluents" Environmental Science and Technology, **32**, 2623-2627.

Jorgensen, E. and K. Christoffersen (2000) "Short-Term Effects of Linear Alkylbenzene Sulfonate on Freshwater Plankton Studied Under Field Conditions" Environmental Toxicology and Chemistry, **19 (4)**, 904-911.

Kimerle, R.A. and R.D.Swisher (1977) "Reduction of Aquatic Toxicity of Linear Alkylbenzene Sulfonate (LAS) By Biodegradation" Water Research, **11**, 31-37.

Kitis, M.; Adams, C.D. and G.T. Daigger (1999) "The Effects of Fenton's Reagent Pretreatment on the Biodegradability of Nonionic Surfactants" Water Research, **33 (11)**, 2561-2568.

Korner, W.; Spengler, P.; Bolz, U.; Schuller, W.; Hanf, V. and J.W. Metzger (2001) "Substances With Esterogenic Activity In Effluents Of Sewage Treatment Plants In Southwestern Germany. 2. Biological Analysis" Environmental Toxicology and Chemistry, **20 (10)**, 2142-2151.

Krueger, C.J.; Radakovich, K.M.; Sawyer, T.E.; Barber, L.B.; Smith, R.L.; and J.A.Field (1998) "Biodegradation of the Surfactant Linear Alkylbenzenesulfonate in Sewage-Contaminated Groundwater: A Comparison of Column Experiments and Field Tracer Tests" Environmental Science and technology, 32, 3954-3961.

La Guardia, M.J.; Hale, R.C.; Harvey, E. and T.M. Mainor (2001) "Alkylphenol Ethoxylate Degradation Products in Land-Applied Sewage Sludge (Biosolids)" Environmental Science and Technology, 35, 4798-4804.

Lao, K.Y. Editor (1997). "Liquid Detergents" Science Surfactant Series, Volume 67, Marcel Dekker Inc, NY, NY.

Lin, S.H.; Lin, C.M. and H.G. Leu (1999) "Operating Characteristics and Kinetic Studies of Surfactant Wastewater Treatment By Fenton Oxidation" Water Research, 33 (7), 1735-1741.

Maguire, R.J. (1999) "Review of the Persistence of Nonylphenol and Nonylphenol Ethoxylates in Aquatic Environments" Environmental Toxicology and Chemistry, 34 (1), 37-78.

Mantzavinos, D.; Burrows, D.M.P.; Willey, R.; Lo Biundo, G.; Zhang, S.F.; Livingston, A.G. and I.S. Metcalfe (2001) " Chemical Treatment of Anionic Surfactant Wastewater: Electrospray-MS Studies of Intermediates and Effect on Aerobic Biodegradability" Water Research, 35 (14), 3337-3344.

Mantzavinos, D.; Burrows, D.M.P.; Willey, R.; Lo Biundo, G.; Zhang, S.F.; Livingston, A.G. and I.S. Metcalfe (2000) "Wet Air Oxidation of Aqueous Solutions of Linear Alkylbenzene Sulfonates" Industrial and Engineering Chemistry Research, 39, 3659-3665.

Marcomini, A.; Pojana, G.; Carrer, C.; Cavalli, L.; Cassani, G. and M. Lazzarin (2000) "Aerobic Biodegradation of Monobranched Aliphatic Alcohol Polyethoxylates" Environmental Toxicology and Chemistry, **19 (3)**, 535-560.

Matthijs, E.; Holt, M.S.; Keiwiet, A. and G.B.J. Rus (1999) "Environmental Monitoring For Linear Alkylbenzene Sulfonate, Alcohol Ethoxylate, Alcohol Ethoxy Sulfate, Alcohol Sulfate and Soap" Environmental Toxicology and Chemistry, **18 (11)**, 2634-2644.

McAvoy, D.C.; DeCarvalho, A.J.; Nielsen, A.M. and M.L. Cano (2002) "Investigation of an Onsite Wastewater Treatment System In Sandy Soil: Modeling the Fate of Surfactants" Environmental Toxicology and Chemistry, **21 (12)**, 2623-2630.

McAvoy, D.C.; Dyer, S.D.; Fendinger, N.J.; Eckhoff, W.S.; Lawrence, D.L. and W.M. Begley (1998) "Removal of Alcohol Ethoxylates, Alkyl Ethoxylate Sulfates, And Linear Alkylbenzene Sulfonates in Wastewater Treatment" Environmental Toxicology and Chemistry, **17 (9)**, 1705-1711.

McLeese, D.W.; Zitko, V.; Sergeant, D.B.; Burridge, L.; and C.D. Metcalfe (1981) "Lethality and Accumulation of Alkylphenols In Aquatic Fauna" Chemosphere, **10(7)**, 723-730.

McMurry, J. (1996) "Organic Chemistry" 4th Edition, Brooks/Cole Publishing Company.

Mehrvar, M.; Anderson, W.A. and M. Moo-Young (2002) "Comparison of the Photoactivities of Two Commercial Titanium Dioxide Powders in the Degradation if 1,4-Dioxane" International Journal of Photoenergy, **4**, 141-146.

Mehrvar, M (1998) "Kinetic Modeling and A Novel Packed Bed Photoreactor" PhD Thesis, University of Waterloo, Waterloo, Ontario, Canada.

Metcalfe, C.D.; Metcalfe, T.L.; Kiparissis, Y.; Koenig, B.G.; Khan, C.; Hughes, R.J.; Croley, T.R.; March, R.E. and T. Potter (2001) "Estrogenic Potency of Chemicals Detected in

Sewage Treatment Plant Effluents as Determined By In Vivo Assays With Japanese Medaka (*Oryzias Latipes*)" Environmental Toxicology and Chemistry, **20 (2)**, 297-308.

Miles-Richardson, S.R.; Pierens, S.L.; Nichols, K.M.; Kramer, V.J.; Snyder, E.M.; Snyder, S.A.; Render, J.A.; Fitzgerald, S.D. and J.P. Giesy (1999) "Effects of Waterborne Exposure to 4-Nonylphenol and Nonylphenol Ehtoxylate on Secondary Sex Characteristics and Gonads of Fathead Minnows (Pimephales Promelas)" Environmental Research Section A, **80**, S122-S137.

Mortensen, G.K.; Elsgaard, H.; Ambus, P.; Jensen, E.S. and C. Gron (2001) " Influence of Plant Growth on Degradation of Linear Alkylbenzene Sulfonate In Sludge-Amended Soil" Journal of Environmental Quality, **30(4)**, 1266-1272.

Mosche, M. and U. Meyer (2002) " Toxicity of Linear Alkylbenzene Sulfonate in Anaerobic Digestion: Influence of Exposure Time" Water Research, **36**, 3253-3260.

Nadarajah, N.; Van Hamme, J.; Pannu, J.; Singh, A. and O. Ward (2002) "Enhanced Transformation of Polycyclic Aromatic Hydrocarbons Using A Combined Fenton's Reagent, Microbial Treatment and Surfactants" Applied Microbiology and Biotechnology, **59**, 540-544.

Narkis, N.; Ben-David, B. and M.S. Rotel (1984) "Ozonation of Non-Ionic Surfactants in Aqueous Solutions" Water Science and Technology, **17**, 1069-1080.

Neilsen, A.M.; DeCarvalho, A.J.; McAvoy, D.C.; Kravetz, L.; Cano, M.L. and D.L. Anderson (2002) "Investigation of an Onsite Wastewater Treatment System in Sandy Soil: Site Characterizaion and Fate of Anionic and Nonionic Surfactants" Environmental Toxicology and Chemistry, **21 (12)**, 2606-2616.

Ott, Z.; Jia, L.; Jin, H.; Yediler, A.; Jiang, X.; Kettrup, A. and T. Sun (1999) "Formation of Soil Macropores and Preferential Migration of Linear Alkylbenzene Sulfonate (LAS) in Soils" Chemosphere, **38 (9)**, 1985-1996.

Patterson, D.A.; Metcalfe, I.S.; Xiong, F. and A.G. Livingston (2002) "Biodegradability of Linear Alkylbenzene Sulfonates Subjected to Wet Air Oxidation" Journal of Chemical Technology and Biotechnology, **77**, 1039-1049.

Patterson, D.A.; Metcalfe, I.S.; Xiong, F. and A.G. Livingston (2001) "Wet Air Oxidation of Linear Alkylbenzene Sulfonate 1. Effect of Temperature and Pressure" Industrial Engineering and Chemistry Research, **40**, 5507-5516.

Pelizzetti, E.; Minero, C.; Maurino, V.; Sciafani, A.; Hidaka, H. and N. Serpone (1989) "Photocatalytic Degradation of Nonylphenol Ethoxylated Surfactants" Environmental Science and Technology, **23**, 1380-1385.

Rittmann, B.E.; Tularak, P.; Lee, K.; Federle, T.W.; Itrich, N.R.; Kaiser, S.K.; Shi, J. and D.C. McAvoy (2001) "How Adaptation and Mass Transfer Control the Biodegradation of Linear Alkylbenzene Sulfonate by Activated Sludge" Biodegradation, **12**, 31-37.

Rosen, M.J.; Li, F.; Morrall, S.W. and D.J. Versteeg (2001) "The Relationship Between the Interfacial Properties of Surfactants and Their Toxicity to Aquatic Organisms" Environmental Science and Technology, **35**, 954-959.

Rudel, R.A.; Melly, S.J.; Geno, P.W.; Sun, G. and J.G. Brody (1998) "Identification of Alkylphenols and Other Estrogenic Phenolic Compounds in Wastewater, Septage, and Groundwater on Cape Cod, Massachusetts" Environmental Science and Technology, **32**, 861-869.

Rudling, L. and P. Solyom (1974) "The Investigation of Biodegradability of Branched Nonyl Phenol Ethoxylates" Water Research, **8**, 115-119.

Saien, J., Ardjmand, R.R. and H Iloukhani (2003) "Photocatalytic Decomposition of Sodium Dodecyl Benzene Sulfonate Under Aqueous Media In The Presence of TiO_2" Physics and Chemistry of Liquids, **41**, 519-531.

Shang, D.Y.; Macdonald, R.W. and M.G. Ikonomou (1999) "Persistence of Nonylphenol Ethoxylate Surfactants and Their Primary Degradation Products in Sediments From Near a Municipal Outfall in the Strait of Georgia, British Columbia, Canada" Environmental Science and Technology, **33**, 1366-1372.

Sherrard, K.B; Marriott, P.J.; Amiet, R.G. and M.J. McCormick (1996) "Spectroscopic Analysis of Heterogeneous Photocatalysis Products of Nonylphenol- and Primary Alcohol Ethoxylates Nonionic Surfactants" Chemosphere, **33 (10)**, 1921-1940.

Spengler, P.; Korner, W. and J.W. Metzger (2001) "Substances With Estrogenic Activity In Effluents Of Sewage Treatment Plants in Southwestern Germany. 1. Chemical Analysis" Environmental Toxicology and Chemistry, **20 (10)**, 2133-2141.

Staples, C.A.; Naylor, C.G.; Williams, J.B. and W.E. Gledhill (2001) "Ultimate Biodegradation of Alkylphenol Ethoxylates Surfactants and Their Biodegradation Intermediates" Environmental Toxicology and Chemistry, **20 (11)**, 2450-2455.

Sullivan, D.E. (1983) "Biodegradation of a Cationic Surfactant in Activated Sludge" Water Research, **17 (9)**, 1145-1151.

Takasu, T.; Iles, A. and K. Hasebe (2002) " Determination of Alkylphenols and Alkylphenol Polyethoxylates by Reversed-Phase High-Performance Liquid Chromatography and Solid-Phase Extraction" Analytical and Bioanalytical Chemistry, **372**, 554-561.

Tharapiwattananon, N.; Scamehorn, J.; Osuwan, S.; Harwell, J. and K. Haller (1996) "Surfactant Recovery From Water Using Foam Fractionation" Separation Science and Technology, **31**, 1233-1258.

Tolls, J.; Lehmann, M.P. and D.T.H.M. Sum (2000) "Quantification of In Vivo Biotransformation of the Anionic Surfactant C_{12}-2-Linear Alkylbenzene Sulfonate in Fathead Minnows" Environmental Toxicology and Chemistry, **19 (10)**, 2394-2400.

Tolls, J. and D.T.H.M Sum (1999) "Bioconcentration and Biotransformation of the Nonionic Surfactant Octaethylene Glycol Monotridecyl Ether ^{14}C-$C_{13}EO_8$" Environmental Toxicology and Chemistry, **18 (12)**, 2689-2695.

Turchi, C.S. (1990) "Heterogeneous Photocatalytic Degradation of Organic Water Contaminants: Kinetic and Hydroxyl Radical Mechanisms" PhD Thesis, North Carolina State University.

Van De Plassche, E.; De Bruijn, J.H.M.; Stephenson, R.R.; Marshall, S.J.; Feijtel, T.C.J. and S.E. Belanger (1999) "Predicted No-Effect Concentrations and Risk Characterization of Four Surfactants: Linear Alkyl Benzene Sulfonate, Alcohol Ethoxylates, Alcohol Ethoxylated Sulfates, and Soap" Environmental Toxicology and Chemistry, **18 (11)**, 2653-2663.

Venkatadri, R. and R.W. Peters (1993) "Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide-Assisted Photocatalysis" Hazardous Waste and Hazardous Materials, **10(2)**, 107-149.

Verge, C.; Moreno, A.; Bravo. J. and J.L. Berna (2001) "Influence of Water Hardness on the Bioavailability and Toxicity of Linear Alkylbenzene Sulphonate (LAS)" Chemosphere, **44**, 1749-1757.

Vindogopal, K.; Ashokkumar, M. and F. Grieser (2001) "Sonochemical Degradation of a Polydisperse Nonylphenol Ethoxylate in Aqueous Solution" Journal of Physical Chemistry B, **105**, 3338-3342.

Wungrattanasopon, P.; Scamehorn, J.F.; Chavedej, S.; Saiwan, C. and J. Harwell (1996) "Use of Foam Flotation to Remove tert-Butylphenol from Water" Separation Science and Technology, **31**, 1523-1540.

Ying, G.; Williams, B. and R. Kookana (2002) " Environmental Fate of Alkylphenols and Alkylphenol Ethoxylates-A Review" Environment International, **28**, 215-226.