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*Old Dominion University*

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**CATALYTIC WET AIR OXIDATION OF MONO AZO DYE ORANGE II:  
CATALYST SELECTION, REACTION KINETICS, AND MODELING**

by

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B. S., June 2000, Istanbul Technical University

M.E., August 2002, Old Dominion University

A Dissertation Submitted to the Faculty of  
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Requirement for the Degree of

DOCTOR OF PHILOSOPHY  
ENVIRONMENTAL ENGINEERING  
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## ABSTRACT

### CATALYTIC WET AIR OXIDATION OF MONO AZO DYE ORANGE II: CATALYST SELECTION, REACTION KINETICS, AND MODELING

Pinar Ozdural  
Old Dominion University, 2008  
Director : Dr. Mujde Erten-Unal

Wastewaters generated as byproducts of dyeing processes are not treatable with conventional methods. It has been estimated that among the 900,000 tons of different dyes produced annually in the world, approximately 10-15 % are lost in wastewater streams during manufacturing and processing operations. Once in rivers and streams, dyes cause major problems, such as reducing light penetration, or displaying toxic effects on aquatic life. Therefore, it is essential that dyes are removed from wastewaters before being discharged into the environment.

This study focuses on the catalytic wet air oxidation (CWAO) of Orange II, a mono azo dye used in large amounts in the United States. Seven metal-based heterogeneous catalysts, CuO/ZnO, CuO/Al<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub>, Pt/SnO<sub>2</sub>/CeO<sub>2</sub>, CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>/CeO<sub>2</sub>, and MnO<sub>2</sub>/CuO were screened for their efficiency in removing Orange-II dye from synthetically prepared wastewaters in a batch autoclave reactor. CuO/Al<sub>2</sub>O<sub>3</sub> was selected as the best alternative catalyst based on TOC and Orange II removal efficiency, catalyst stability, and economic considerations. Kinetics experiments with CuO/Al<sub>2</sub>O<sub>3</sub> revealed that the oxidation reaction proceeds very fast initially, with about 70% reduction in TOC concentrations within the first 10 minutes of reaction time. The overall TOC and Orange II removals increased with increased temperature up to

reaction temperatures of 80°C. The reaction was found to be oxygen concentration limited. A lumped-parameter kinetic model was constructed to describe the reaction kinetics. The reaction rate constants were computed with non-linear regression. There was excellent agreement between experimental values and model computed values. The effects of catalyst concentration and pH on Orange II removal were also investigated. It was observed that lower pH values increased TOC removal.

This dissertation is dedicated to my parents, Necmiye and Husnu Ozdural, and my sister,  
Asli Ozdural, for their never-ending love and support...

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I wish to express my gratitude to my parents and sister, to whom this dissertation is dedicated. Thank you for all you have done for me throughout the years. I would not be the person I am without your constant love, guidance, encouragement, and support. I will consider myself lucky if I can pass even half of what you've taught me on to my own children in the future.

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## CHAPTER I

### INTRODUCTION

Although the art of dyeing textile materials has been practiced for nearly 5,000 years [1, 2]<sup>1</sup>, until 1856 dyes could only be extracted from natural sources like plants and minerals which made them rare and highly valuable. Colored fabrics were only reserved for royalty and noble people who could afford them. Today, there are numerous synthetic organic dyes and pigments used for coloring everything from clothes to plastics and drugs to food. Whereas once it was a sign of wealth and status, today anyone can enjoy wearing colorful t-shirts or eating cake with colorful decorations on it, thanks to the variety of dyes that are available. Unfortunately, most of the time wastewaters generated as byproducts of dyeing processes are not treatable with conventional methods, are toxic to aquatic life [2], and are not as aesthetically pleasing in lakes and rivers as they are on clothing. Cooper [3] states that while the public is more ready to accept blue, green, or brown rivers, “unnatural” colors such as red and purple usually cause more concern. Most synthetic dyes cannot be removed from wastewaters by conventional methods, such as activated sludge systems, and end up in receiving water bodies if not treated. Even one mg/l of dye can lead to visible color in rivers and lakes. As discharge standards become more stringent, the introduction of advanced treatment systems becomes necessary for the treatment of wastewaters containing dye.

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<sup>1</sup> Model journal for reference style is *Catalysis Today*.

Orange II (also known as Acid Orange 7) is one of the dyes that is produced in large amounts in the United States. It is commonly used in pharmaceuticals, food, cosmetics, and the textile industry. It is not amenable to conventional biological treatment. This research focuses on catalytic wet air oxidation (CWAO) as a treatment alternative for the removal of Orange-II dye from wastewaters.

## **BACKGROUND**

Among the 900,000 tons of different dyes produced annually in the world, approximately 10-15 % is lost in wastewater streams during manufacturing and processing operations [4]. Once in rivers and streams, dyes cause major problems, such as reducing light penetration, or displaying toxic effects on aquatic life. Therefore, dyes have to be removed from wastewaters before being discharged into the environment.

Dyes are intensely colored substances used for the coloration of various substrates, including paper, leather, fur, hair, foods, drugs, cosmetics, waxes, greases, petroleum products, plastics, and textile materials. They are applied to these substrates by physical adsorption, salt or metal-complex formation, mechanical retention, or by the formation of chemical covalent bonds. Zollinger [2] stated in 2003 that the global market size of organic colorants was estimated to lie in the order of 0.9 million tons. A little more than half of that production was attributed to textile dyes, and an additional 15% were used for non-textile substrates (such as paper and leather) dyed in a manner similar to textile goods. In terms of value, the global colorant market was estimated at \$12-13

billion, more or less equally distributed among organic dyes, organic pigments, and inorganic pigments. Table 1 depicts different classes of dyes and their market shares.

**Table 1.** Global Market Shares of Different Classes of Dyes [2]

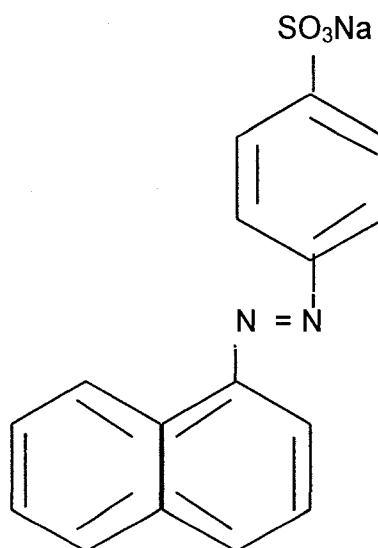
<i>Class of Dye</i>	<i>Substrate</i>	<b>Market Share (%)</b>
Disperse	Polyester, acetate	16.2
Reactive	Cotton, viscose	23.6
Acid	Nylon, wool, silk	18.6
Direct	Cotton, viscose	7.7
Cationic (basic)	Acrylic	7.1
Other *	Various	16.8
*Includes vat, sulfur, mordant, and azoic dyes, as well as indigo		

The demand for dyes and, especially, for organic pigments was forecasted to increase annually by about 3-4 % since 2003 [2].

Among different types of dyes, azo dyes are the largest class of dyes, and consequently account for a great portion of dye pollutants. Azo compounds are characterized by the presence of one or more azo groups ( $-N=N-$ ). Of all classes of dyestuffs, azo dyes have attained the widest range of usage because variations in chemical structure are readily synthesized and methods of application to substrates are generally not complex. There are azo dyes for dyeing all natural substrates such as cotton, silk, leather, paper, and wool as well as the synthetics: polyamides, polyesters, acrylics, polyolefins, viscose rayon, cellulose acetate, etc, for the coloring of paints,

varnishes, plastics, printing inks, rubber, foods, drugs, and cosmetics, for staining polished and absorbed surfaces, and for use in color photography [1].

Orange II is one of the azo dyes that are produced in large amounts in the United States. Figure 1 depicts the chemical structure of Orange II.



**Figure 1.** Chemical Structure of Orange II

Dyes that are manufactured today are mostly “indestructible” under ambient conditions. The main difficulty in removing dyes from wastewaters stems from the fact that it is essential to optimize the application of a dye for a given substrate (paper, fabric, etc.) to obtain the highest possible fastness properties in order to be able to fulfill customer demands. Color removal has become a challenging aspect of industrial wastewater treatment because of the growing concern about residual color that is closely associated with toxicity and aesthetics of the discharged effluent [3].



Dyes enter the environment in wastewater discharges from batch processes in both the dye-manufacturing and dye-consuming industries. Among the dye-consuming industries, textile dyeing mills generate a large portion of the textile industry's total wastewater production. The primary source of wastewater in dyeing operations is spent dye bath and water from washing operations. Such wastewater typically contains by-products, residual dye, and auxiliary chemicals. Additional pollutants include cleaning solvents, such as oxalic acid [5]. Of the 900,000 tons of dye produced annually worldwide, about 10 to 15 percent is disposed of in effluent [6]. The average wastewater generation from a dyeing facility is estimated to be between one to two million gallons per day. Dyeing and rinsing processes for disperse dyeing generate about 12 to 17 gallons of wastewater per pound of product. Similar processes for reactive and direct dyeing generate even more wastewater, about 15 to 20 gallons per pound of product. In typical dyeing and printing processes, 50 to 100 percent of the color is fixed on the fiber. The remainder is discarded in the form of spent dye baths and in wastewater from subsequent textile-washing operations. This corresponds to a daily worldwide release of about 128 tons to the environment [2].

In theory, decoloration of dye-containing water is possible with one or several of the following methods: adsorption, aerobic or anaerobic biological treatment, chemical oxidation, coagulation, electrochemical oxidation, flocculation, or membranes. Complete mineralization to end products, e.g.  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , would be desirable and in principle this is possible, however, a combination of two or more treatment methods is needed and treatment times are usually long. More commonly practiced physico-chemical (i.e. coagulation, activated carbon adsorption, membrane filtration) and

biochemical (aerobic biological treatment) methods have already been proven to be inefficient for decoloration of wastewaters containing dyes [7]. Microorganisms in rivers and lakes do not contain enzymes capable of degrading synthetic dye compounds under aerobic conditions [2]. Under anaerobic conditions, however, dye degradation takes place slowly. Zollinger [2] states that it has yet to be investigated to what extent dyes bioaccumulate in fish and other aquatic organisms.

The choice of treatment for a particular effluent stream is governed by factors such as the organic or inorganic constituent content, their concentration, toxicity, and regulatory discharge standards [8]. Among the available pre-treatment technologies, catalytic wet air oxidation (CWAO) is a suitable technology for treatment of wastewaters containing dyes that are not amenable to biological treatment, either as a complete treatment system by itself, or as a pre-treatment before biological treatment.

Wet oxidation can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of an oxidant (usually oxygen or air, but sometimes ozone and hydrogen peroxide) at elevated temperatures and pressures. It is a well-established technology of major importance for wastewater treatment, especially when the waste is too dilute for incineration and too concentrated for the effective application of advanced oxidation processes [9]. Typical conditions for wet oxidation range from 180°C and 2 MPa (290 psi) to 315°C and 15 MPa (2176 psi). Residence times may vary from 15 to 120 minutes. Organic matter is converted to simpler organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water without emissions of NO<sub>x</sub>, SO<sub>2</sub>, HCl, dioxins, furans, ash, etc. The final residual organic compounds are carboxylic acids, especially acetic acid [10]. Catalytic wet air

oxidation employs catalysts to reduce the severity of the above mentioned reaction conditions since without catalysts, the reaction conditions are severe and result in high operation and maintenance costs. Compared to conventional wet air oxidation, catalytic wet air oxidation offers lower energy requirements and much higher oxidation efficiencies. Current catalytic wet air oxidation processes rely either on supported precious metals and/or base metal oxide catalysts, or on homogeneous catalysts such as Fe or Cu [11]. Matatov-Meytal and Sheintuch [12] state a catalyst for aqueous phase oxidation should provide high oxidation rates, should be nonselective, physically and chemically stable in hot acidic solutions, mechanically strong and resistant to attrition, and should maintain a high activity for a prolonged use at high temperatures. Unlike other treatment processes, such as activated carbon adsorption where the contaminant of interest is adsorbed onto carbon media and then handled as a solid or hazardous waste, catalytic wet air oxidation converts contaminants to either carbon dioxide and water as end products or to less complex organic compounds that are biodegradable and not toxic.

CWAO studies for Orange-II are rare although CWAO is a proven effective abatement method for otherwise refractory dyes. It is evident that elevated concentrations of dyes in waterways are a problem that should be addressed.

## **PROBLEM STATEMENT**

Elevated concentrations of dyes in waterways cause numerous problems. Color removal has become a challenging aspect of industrial wastewater treatment because of the growing concern about residual color that is closely associated with toxicity and

aesthetics of the discharged effluent [3]. There is dearth of research on the kinetics of the catalytic wet air oxidation of Orange II containing wastewaters although catalytic wet air oxidation is an efficient technology for refractory pollutant abatement. This study aims to fill a gap in literature by investigating the catalytic wet air oxidation of Orange II containing wastewaters.

## **RESEARCH OBJECTIVE**

The objective of this study was to investigate the fate of Orange II under various catalyzed wet air oxidation conditions. This objective was achieved in two stages. The first stage was the screening of seven metal-based heterogeneous catalysts for their efficiency in removing Orange-II dye from synthetically prepared wastewaters through catalytic oxidation with the goal of identifying the catalyst with the most favorable effect on Orange II oxidation. The screening process took into account the effects of temperature, pressure, and catalyst concentration on removal efficiency. Cost of catalyst and catalyst stability were also factored into the decision making process. After a catalyst was selected, the second stage study focused on the reaction kinetics, constructing a kinetic model that described the experimental data, and determining reaction rate constants. Effect of pH on removal efficiency was also investigated with the chosen catalyst.

## RESEARCH APPROACH

To achieve the research objectives Orange-II dye was added to water to create synthetically prepared wastewaters of known composition and then treated by CWAO under varying conditions and with different catalysts. From changes in Orange II and total organic carbon (TOC) concentrations, the catalyst that proved to be the most efficient was identified and a chemical kinetic model was fit to the process. The steps taken to achieve this goal were as follows:

1. Preliminary experimental runs were conducted, and the acceptable operating ranges for catalyst screening experiments were identified.
2. A 3-variable half factorial design with replicate experiments was designed for catalyst screening.
3. Catalyst screening experiments were conducted with replicates in a batch reactor, and the TOC and dye reductions were determined.
4. Factors that affect dye removal were identified for each catalyst from the screening experimental results.
5. Temperature Programmed Reduction (TPR) was conducted on catalysts to determine the hydrogen adsorption capacity of the catalysts. TPR analysis was an indicator of the oxidizing capacity of the catalyst and as such helped interpret the experimental results.
6. Catalyst leaching was determined by measuring metal concentrations in treated samples.

7. A decision matrix was constructed to select an effective, stable, and economically feasible catalyst.
8. Kinetics experiments were conducted under different temperatures with the selected catalyst.
9. Different theoretical lumped parameter models were constructed. Collected data was analyzed with non-linear regression to determine reaction rate constants and which model explained the reaction kinetics the best.
10. Temperature dependence of constants was determined.

## **SIGNIFICANCE OF RESEARCH**

CWAO of Orange II under mild reaction conditions such as presented in this study has not been investigated before. The oxidation of Orange II has a very complex reaction mechanism. The rate expression for the removal of Orange II from wastewaters through CWAO is not known. Recent treatment studies with this dye mostly focus on the treatability of Orange II with advanced oxidation processes without attempting to determine the reaction kinetics.

This study identifies a catalyst that effectively works for the CWAO of Orange II and aims to fill a gap in the literature by determining the reaction rate constants that can be used in the design of reactors for the treatment of Orange II-containing wastewaters.

## **DISSERTATION STRUCTURE**

The current and first chapter of this dissertation serves as an overview of the dissertation, where the problem, research objectives and research approach are presented. In the second chapter, literature that is essential to current work is reviewed and discussed in depth. Conventional treatment methods for dye containing wastewaters are discussed, followed by the review of literature on catalytic wet air oxidation of industrial wastewaters. Previous works that address the lumped parameter kinetic model approach are also reviewed in the second chapter. The third chapter describes methods and materials utilized in this study. Results of experimental work are presented and discussed in the fourth chapter. The fifth and final chapter consists of a summary of the study and conclusions. Areas of future research are also discussed in the final chapter.

## **CHAPTER II**

### **LITERATURE REVIEW**

In this chapter, essential literature that addresses treatment of azo dye-containing wastewaters and the catalytic wet air oxidation (CWAO) technology for industrial wastewater treatment are reviewed. The chapter is laid out in four sections. The first section describes the problem of dyes in wastewater. It reviews previous works on treatment technologies related to this problem, elaborating on their advantages and limitations. The second section is dedicated to one of these technologies, CWAO, which is the basis for current work. CWAO utilizes catalysts for the oxidation of refractory organic matter in solution under elevated temperatures and pressures. Background information on heterogeneous catalysis and how it has been applied in CWAO is given in this section. The third section elaborates specifically on the use of CWAO for azo dye wastewaters. The fourth and final section describes previous studies on the lumped-parameter kinetic modeling approach which is utilized to determine reaction kinetics in the current work.

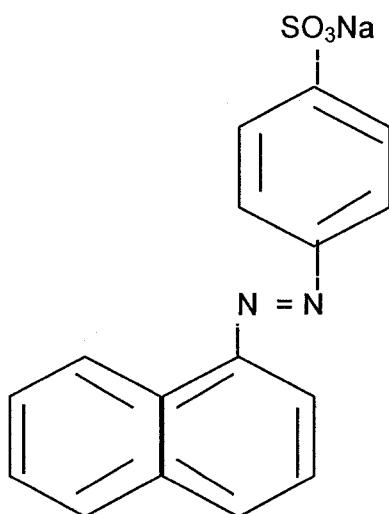


## **AZO DYE WASTEWATER AND CONVENTIONAL TREATMENT TECHNOLOGIES**

This section presents the adverse effects of azo dyes on the environment and discusses conventional methods for azo dye wastewater treatment with their advantages and limitations.

### **Azo Dye Wastewaters**

Azo dyes are compounds that contain azo groups ( $-N=N-$ ) linked to methine or aromatic C-atoms. Colorants composed of single or multiple azo groups are termed mono-, bis-, tris-, and tetrakis azo dyes. The azo groups are mostly bound to benzene or naphthalene rings [2]. The azo dye in question in this study is Orange-II, which is a mono azo dye, categorized as an acid dye with anionic properties. The chemical structure of this dye can be seen in Figure 2.



**Figure 2.** Chemical structure of mono azo dye Orange II

With respect to both number and production volume, azo dyes are by far the largest group of colorants. The widespread use of azo dyes and pigments is due to their easy synthesis, great structural diversity, high molar extinction coefficients (indicative of high light absorption capacity), and medium-to-high fastness properties with respect to both light and wetness [2]. As mentioned in Chapter 1, azo dyes have a wide range of use, especially in the textile, cosmetic, pharmaceutical, printing and food industries. Since they are used heavily, they are the most common type of dyes released into the environment from various industrial operations. Of the 10-15% of dyes lost during the dyeing process in industrial operations, about 20% end up in waterways in effluents from wastewater treatment plants. Once in waterways, dyes can cause problems in a number of ways [13]:

- Depending on exposure time and dye concentration, dyes can have acute and/or chronic toxic effects in exposed organisms.

- Although visibility of dyes in rivers depends on their color and extinction coefficient of dye and on the clarity of the water, they are highly visible. This means that even minor releases of effluents may cause abnormal coloration of surface waters which captures the attention of both the public and authorities.
- Apart from the aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. This hinders the growth of microorganisms and consequently disrupts the food chain.

It has been generally observed that dyes are relatively nontoxic based on acute and oral toxicity tests [14]. However, the case with azo dyes is a little different. During azo dye reduction, cleavage of the azo bond can occur and form amines, which are toxic. Epidemiological studies showed that workers in the dye industry have a greater incidence of bladder cancer than that of the general population [14]. Azo dyes have also been linked to splenic carcinomas, hepatocarcinomas, and nuclear abnormalities in experimental animals, and to chromosomal aberrations in mammalian cells [15]. In particular, benzidine and its derivatives have been detected in the urine of humans and animals exposed to benzidine-based dyes, such as azo dyes, proving that azo reduction of the benzidine-based dyes is facilitated by the microorganisms present in the human intestinal system. Because benzidine is a proven human and animal carcinogen, the use of benzidine-based dyes has been discontinued [15]. However, there is a potential concern that azo dyes can decompose into benzidine in human intestines, and also in rivers and streams. Especially in areas where they are heavily produced and used, azo

dyes are one of the most problematic pollutants in groundwater and surface water. For these reasons, it is essential to treat dye wastewaters with the purpose of not only reducing the concentration of dye but also for a reduction in chemical oxygen demand (COD), total organic carbon (TOC), or biochemical oxygen demand (BOD).

## **Conventional Treatment of Azo Dye Wastewaters**

The choice of treatment for a particular effluent stream is governed by factors such as the organic or inorganic constituent content and concentration, toxicity, and regulatory discharge standards [8]. There are three types of treatment processes that can be applied to azo dye containing wastewaters: physical, chemical and biological processes.

### *Physical Treatment Processes*

The most commonly used methods for physical treatment of dyes are adsorption (i.e. activated carbon) or membrane filtration. Unfortunately, in the case of azo dyes, carbon adsorption is not very effective. One of the main reasons for the observed poor adsorption is the polar nature of these dyes versus the non-polar nature of carbon [16]. Therefore, carbon adsorption is usually preferred as a finishing/polishing step after initial treatment. Studies combining activated carbon adsorption with different forms of pretreatment, namely polymer coagulation and chemical reduction have been successful. The main logic behind combining treatment steps is to reduce the dye into intermediates,

such as amines, which can then be adsorbed onto the carbon surface. Activated carbon adsorption processes are generally not very economical, and the spent activated carbon has to either be handled as additional waste or regenerated. Regeneration of activated carbon is very energy intensive and expensive, and about 15% activated carbon surface is lost during the process. Coupling these factors with the fact that successful adsorption would require extra steps such as the reduction of dye first, activated carbon adsorption is not a very feasible treatment option.

Membrane filtration is another alternative for physical treatment of dye wastewaters. There are four membrane separation processes, namely ultrafiltration, reverse osmosis (hyperfiltration), gas separation, and electrodialysis. Reverse osmosis and ultrafiltration are pressure-driven membrane processes that remove solutes from solution based on particle or molecular size differentials. They are very effective for the removal of color from dyehouse effluents regardless of the type of dyestuff used. Decolorization in these procedures is in the range of 95-100% [17]. The biggest downside of using membrane filtration processes are the high capital costs and associated concentrate wastewater treatment costs.

### *Biological Treatment Processes*

Biological treatment methods for dye containing wastewaters involve aerobic and anaerobic methods. The application of biological treatment to synthetic dyes is an attractive and simple method by operation. However, under aerobic conditions, azo dyes are not readily metabolized [18]. There is only a single example for the presence of an

azo group (N=N) in a natural product (4,4'-dihydroxyazobenzene) and the industrially produced azo dyes are therefore all xenobiotic compounds [19], meaning microorganisms do not have the enzymes to metabolize these compounds. Therefore, azo dyes usually resist biodegradation in conventional aerobic activated sludge systems.

It is generally observed that in conventional aerobic sewage-treatment plants most azo dyes are not degraded by the bacteria, but that a certain percentage (usually about 40–80%) of the dyes physically adsorb to the sewage sludge [19]. Current literature on the biological treatment of azo dyes focuses on specially cultured bacterial strains that can decompose the dye. Some bacterial strains that have been identified to successfully decolorize azo dyes under aerobic conditions are *Xenophilus azovorans*, *Bacillus* strain OY 1-2, *Sphingomonas* sp. Strain 1CX, *Caulobacter subvibrioides* strain C7-D, *Paenibacillus azoreducens*, *Pigmentiphaga kullae* K24, and *Kerstersia* sp. Strain VKY1 [20]. For the aerobic degradation of azo dyes, it's been reported that an external carbon source for the microorganisms other than the dye itself has to be present because the microorganisms cannot use the dye as a carbon source.

Under anaerobic conditions, results are more promising. In contrast to the few reports of aerobic decolorization of azo dyes, a wide range of organisms are able to reduce azo compounds under anaerobic conditions. The main interest in this field has been focused on bacteria from the human intestine that are involved in the metabolism of azo dyes ingested as food additives [19].

Although different bacterial and fungus strains have been reported to decolorize azo dyes under aerobic and anaerobic conditions [21-25], there are some issues that have to be addressed. The first issue is that the strains of microorganisms cultivated are not

naturally found in a typical activated sludge system. They have to be specially cultured and special care has to be taken to establish these microorganisms in a wastewater treatment system. Secondly, there has to be some sort of carbon source added to the wastewater, so the microorganisms can metabolize the dyes. And third, the reported degradation rates in studies are very slow. In typical experiments, about 50-200 mg/l of dyes are decolorized within 1-15 days. Also, in most of these studies, color removal is reported, but other parameters such as TOC or COD reductions are not reported. A reduction in color does not necessarily mean the organics are totally degraded; it is just an indication the dye itself is broken at the chromophore group.

### *Chemical Treatment Processes*

Chemical treatment processes studied for the treatment of azo dyes include chemical oxidation processes such as those that use hydrogen peroxide or ozone as oxidants, photochemical advanced oxidation processes such as Fenton's reagent and  $\text{TiO}_2$  photocatalysis, and wet air oxidation with and without catalysts.

Photocatalysis aims to degrade dye molecules to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  under UV irradiation. It has been determined in the past that the presence of a catalyst, especially  $\text{ZnO}$  or  $\text{TiO}_2$ , considerably improves the efficiency of the oxidation process. Use of  $\text{TiO}_2$  as a catalyst in photocatalytic oxidation is more recent. Tanaka et al. [26] studied the photocatalytic degradation of seven commercial dyes including Orange-II in  $\text{TiO}_2$  suspension. The degradation rates were compared with TOC reduction rates. It took about 150 minutes of reaction time for TOC to be completely oxidized in the case of

Orange-II. Adsorption of dye onto  $\text{TiO}_2$  was found to be one of the most important factors determining the degradation rate. Stylidi et al. [27] also studied the photocatalytic degradation on Orange-II dye in  $\text{TiO}_2$  suspensions. Complete oxidation of COD took around 25 hours. Some reported intermediates formed during reaction include coumarin, 2-naphthol, 2-hydroxy-1,4-naphthoquinone, 1,4-naphthoquinone, phthalide, phthalic acid, 2-acetyl-benzoic acid, phenol, succinic acid, fumaric acid, malonic acid. The pH of the solution during reaction dropped from 5.8 to 2.9 at the end, indicative of the formation of acid products, which the authors also say is evidenced by the change of conductivity during the reaction. The conductivity of the solution increased almost linearly during the first 15 hours of irradiation. Lachheb et al. also studied the photocatalytic degradation of some azo dyes [28]. Complete mineralization of dyes took about 120 minutes. Bauer et al. investigated the interaction between Orange-II and the  $\text{TiO}_2$  surface [29], and concluded the adsorption of Orange-II occurs through a Lewis acid-base reaction which has important implications such as fast electron transfer.

It is probably worth mentioning here again that dyes are designed to resist photodegradation, so the selection of optimal conditions for photocatalytic reactions is not an easy one. Application of photocatalytic oxidation in industry in the past was reported to be problematic due to two factors [30]: The first reason is photocatalytic reaction depends on the chemical properties of the pollutants, so the conversion of large aromatic compounds such as azo dyes is relatively harder and more energy intensive compared to smaller organic compounds. For example, the degradation of di-azo dyes has been shown to be much harder than mono-azo ones. The second is the fact that  $\text{TiO}_2$  catalysts become deactivated easily. During the photocatalytic oxidation of aromatic



compounds, less-reactive intermediates are directly responsible for deactivation of the catalyst. These intermediates are strongly adsorbed on the surface of the  $\text{TiO}_2$  catalyst and deteriorate photoactivity by blocking reaction sites.  $\text{TiO}_2$  catalysts have also been reported to be hard to separate from solution and hard to recover which requires the immobilization of the catalyst on some sort of substrate [31].

Photo-Fenton processes have also been investigated for azo dye treatment. In a homogenous photo-Fenton system, the catalysts, ferrous iron ( $\text{Fe}^{+2}$ ) ions, are dissolved in water. Although these catalysts are generally very efficient, their separation and reuse are very difficult because of their dissolved state. The removal of iron ions needs large amounts of chemicals and manpower which increases the cost of treatment. The production of ferric hydroxide sludge creates disposal problems as well. Furthermore, for the treatment to work, the pH of the solution should be adjusted to between 2 and 4 before the reaction starts. This tight range of pH and difficult separation of catalysts limit application of homogeneous photo-Fenton systems in wastewater treatment [32]. Recent research focuses on finding heterogeneous iron catalysts for the Fenton reaction.

Ozonation is another conventional chemical treatment method investigated for the treatment of dyes. Decoloration of dyes with ozone occurs through the destruction of the chromophore of the dye, in the case of azo dyes, this is the azo bond. Matsui [33] states the reactivity of an azo linkage with ozone is very low, so although ozone would react with the aromatic rings, the azo bond might not be broken, leading to intermediates and color in treated water rather than complete mineralization end products. A disadvantage of ozonation is the short half-life of ozone which is typically around 20 minutes. This time can be further shortened if dyes are present, with stability being affected by the

presence of salts, pH, and temperature [18]. Although the chemistry of ozone has been widely studied, information on the ozonation of dyes is quite sparse, and there are no practical commercial methods for ozone treatment of dye wastewater. This is because of the cost restrictions associated with the ozonation processes. Since ozone has such a short half-life, it has to be continuously generated and supplied during treatment which is very energy intensive and costly.

Other methods that have been investigated for the treatment of azo dyes are sodium-borohydride reduction, which aims to reduce azo dyes into more biologically active species [34] (although the amines formed could potentially be toxic), electrochemical treatment by using electrodes [35], and chemical oxidation using sodium hypochlorite [18]. The use of chlorine for the latter method is becoming less frequent due to negative effects (such as trihalomethane (THM) formation potential) when released into waterways [36].

Another chemical treatment method is catalytic wet air oxidation. This treatment method which is investigated in this study is described in detail in the following section.

## **CWAO FOR INDUSTRIAL WASTEWATER TREATMENT**

In the 1990s CWAO started to gain popularity as a viable method for treating refractory organic containing wastewaters. Among the studies conducted, some studies are more like treatability studies, concentrating on whether the organic compound of interest can be oxidized efficiently while others concentrate on the kinetics and the reaction mechanism. Some studies concentrate on partial oxidation of compounds, trying

to break them down into compounds that can be used beneficially. In all cases, more than one reaction condition (temperature, pressure, catalyst loading, etc.) is examined, and the results are evaluated. A summary of studies discussed in this paper can be found in Appendix A.

The oxidation process for industrial wastewaters is much more complicated than the oxidation of a single species of contaminant. An industrial wastewater does not contain only one type of contaminant but a number of different constituents that can influence reaction with target contaminants. The main goal of treatment is to reduce the overall organic strength and toxicity of the wastewater. Most studies summarized in this paper deal with lumped parameters, such as total organic carbon (TOC) or chemical oxygen demand (COD) as the main pollutant of concern that has to be oxidized and discuss the oxidation kinetics of these parameters instead of individual contaminants.

Unlike other treatment processes, such as activated carbon adsorption where the contaminant of interest is adsorbed onto carbon media and then has to be handled as solid or hazardous waste, CWAO converts contaminants to either carbon dioxide and water as end products or to less complex organic compounds that are biodegradable and non-toxic. In this regard, if economically proven to be feasible, CWAO is a very efficient treatment process for compounds that are otherwise not degradable.

Wet oxidation can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of an oxidant (usually oxygen or air, but sometimes ozone and hydrogen peroxide) at elevated temperatures and pressures. Typical conditions for wet oxidation range from 180°C and 2 MPa to 315°C and 15 MPa. Residence times may vary from 15 to 120 minutes. Insoluble organic matter is converted

to simpler organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water without emissions of  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{HCl}$ , dioxins, furans, ash, etc. The last residual organic compounds are carboxylic acids, especially acetic acid [10].

Catalytic wet oxidation employs catalysts to reduce the severity of the above mentioned reaction conditions. A catalyst is a substance that increases the rate of a reaction toward equilibrium without being appreciably consumed in the process [37]. The fundamental concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on a catalyst forms a complex with reactants, from which products are desorbed, thereby restoring the original site and continuing the cycle. A catalyst cannot change the ultimate equilibrium determined by thermodynamics; its role is restricted to accelerating the rate of approach to equilibrium. It increases the rate of reaction by decreasing the activation energy [37].

Compared to conventional wet air oxidation, CWAO offers lower energy requirements and much higher oxidation efficiencies. Current catalytic wet oxidation processes rely either on supported precious metals and/or base metal oxide catalysts, or organometallic compounds of Fe and Cu [11]. Matatov-Meytal and Sheintuch [12] state that a catalyst for aqueous phase oxidation should have high oxidation rates, should be nonselective, physically and chemically stable in hot acidic solutions, mechanically strong and resistant to attrition, and should maintain a high activity for a prolonged use at high temperatures.

CWAO of different types of industrial wastewaters has been investigated in the past. The Zimpro process by Siemens Water Technologies is an application of CWAO on a commercial level to treat industrial wastewaters.

The next five sections are an overview of different types of wastewaters CWAO has been successfully applied to.

## **CWAO Treatment of Paper and Pulp Industry Wastewaters**

The paper and pulp industry is one of the industries of interest to researchers on CWAO, mostly due to their high-strength nature. Zhang and Chuang [38] studied the CWAO of black liquor from paper and pulp mills. The high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the black liquor comes from the high concentrations of organic matter in the form of suspended solids, colloids, sulfur compounds, pulping chemicals, organic acids, chlorinated lignins, resin acids, phenolics, and unsaturated fatty acids. The authors report based on previous research that without a catalyst, no oxidation of organics occurred, even at temperatures as high as 270°C. For this study, the reactions were carried out in a slurry reactor at a temperature range of 160-190°C and at a pressure range of 1.5-2.2 MPa. The catalysts investigated were Pt-Ce/Al, Pt-Pd/Al, Pd-Ce/al and, Pt-Pd-Ce/Al. All catalysts were prepared by successive impregnation. The reactor had a volume of 300 ml, and for each experiment, one gram of catalyst was fed into the reactor, followed by 120 ml of wastewater sample. The total organic carbon (TOC) of the solution was about 1500 mg/l, and the pH was around 11. Oxygen gas flow rate was held constant at 80 ml/min. The designated reaction time was three hours, at the end of which the liquid sample was taken out, catalyst filtered off, and the filtrate was analyzed for pH and color change. Only carbon dioxide was detected as a gas-phase product. Among the four catalysts tested, the highest efficiency of conversion

was observed for the Pt-Pd-Ce/alumina catalyst, under 190°C and 1.5 MPa pressure. This catalyst was also used for kinetic modeling. The TOC reduction was found to follow first order kinetics. It is not really clear whether the authors used the filtered samples for TOC analysis. There is no information whether the authors determined how much of the organic carbon in the sample was in dissolved form. It should be kept in mind that the filtration process might have removed some of the organic matter that was in suspended form.

An et al. [39] also studied paper and pulp industry wastewaters with the chosen contaminant being combined Kraft pulp mill effluents. Two types of alumina supported-Pd catalysts were used for this study in a trickle bed reactor. The authors monitored TOC reduction and color removal. Over 60 % color removal was achieved with all catalysts at 162-167 °C. TOC conversion was dependent upon temperature and the catalyst type and concentration used. Eggshell catalysts with Pd loading of 0.2 wt% were especially successful for treatment of combined pulp mill effluents with reduction rates of up to 70% at 167 °C.

Another study with Kraft pulp mill effluents was conducted by Pintar et al. [40]. Two different effluents were investigated, one with acidic, and the other with alkaline characteristics. Titania and zirconia supported ruthenium catalysts were used in a batch slurry reactor for oxidation purposes. 0.5 g of catalyst and 100 ml of wastewater were used for each run. The temperature ranges tested were 125-190 °C, and pressures ranges were 4-7 MPa. For both the alkaline and acidic samples, oxides of titanium and zirconium were active in TOC removal. When ruthenium was added on these supports, the TOC removal was better. At eight hours and 190 °C, and 5.5 MPa of air pressure, over

99% TOC reduction was achieved. The reaction was characterized by a fast initial step where large molecules were broken down to short organic acids and a slower second step. Compounds such as acetic acid remained at the end of the reaction, but that is not of much concern, as acetic acid can be biologically treated. If this process is to be viewed as only a pretreatment process where further biological treatment is needed, then long treatment hours and relatively high temperatures may not be necessary.

### **CWAO Treatment of Olive Mill Wastewaters**

Minh et al. [41-43] studied the use of CWAO for the removal of p-hydroxyphenylacetic acid and p-hydroxybenzoic acid, two important compounds present in the olive oil mill wastewaters, in a batch reactor using platinum and ruthenium catalysts supported on titanium and zirconium oxides at 140 °C and 50 bar of total air pressure. Reaction pathways for the oxidation of these two substrates were proposed, with formation of different aromatic compounds and short-chain organic acids through hydroxylation and decarboxylation reactions. The total elimination of p-hydroxyphenylacetic acid with a TOC removal of 65% and nearly total elimination of p-hydroxybenzoic acid with a TOC removal up to 70% were achieved within seven to eight hours of reaction time.

Gomes et al. [44] also studied the use of CWAO for treating olive mill wastewaters. Experiments were performed in a high pressure reactor at 100 and 200 °C under an oxygen partial pressure of 6.9 bars. The catalysts used were carbon supported platinum (1 wt.% Pt) and iridium (5 wt.% Ir). At 100 °C, refractory organic compounds

persisted even after prolonged reaction time (eight hours). At 200 °C, complete total organic carbon and color removal were obtained with the Pt/C catalyst after eight hours of reaction time. The authors successfully developed a kinetic model taking into account catalytic and non-catalytic reactions, formation of refractory compounds and catalyst deactivation. There was very good agreement between the proposed model and CWAO experimental data at 200 °C.

### **CWAO Treatment of Carboxylic Acids**

CWAO also is a suitable pretreatment method for wastewaters containing organic (carboxylic) acids. Gomes et al. [45] studied the oxidation of butyric acid solutions using carbon supported iridium catalysts. The reactor volume used was 160 cm<sup>3</sup>. The reactor was loaded with 70 cm<sup>3</sup> of 5g/l butyric acid solution and 0.8 g of catalyst. 8 hr reaction time, 0.69 MPa of oxygen partial pressure, and 200°C were chosen as the standard reaction conditions for each run. For this study, reaction orders with respect to butyric acid, oxygen, and catalyst load were determined by varying the initial concentration of butyric acid in the range 0.034-0.080 M, the oxygen partial pressure in the range 0.69-1.39 MPa, and the catalyst weight in the range 0.2-0.8g. The activation energy was obtained by varying the reaction temperature between 180-220 °C. The authors observed that carbon supported Pt catalyst was the most active in terms of favoring the oxidation reaction with 70.4% conversion after two hours. The second most active catalyst was the carbon supported Ir catalyst, with a conversion of 42.6% after two hours. The performance of the Ir catalysts was found to be dependent on the method of preparation



and pretreatment used. Two-step incipient wetness impregnated catalysts were observed to be more active than those prepared by a single step incipient wetness impregnation. For the iridium catalyst, after eight hours of reaction time, 72.2% of butyric acid was converted to non-carboxylic acids while the remainder was broken down into refractory intermediates, such as acetic acid and propionic acid. The authors state that these refractory intermediates are then converted to final products of CO<sub>2</sub> and H<sub>2</sub>O; however, it's not really clear whether this conversion occurs during the first eight hours. The degradation of butyric acid followed pseudo-first order kinetics. One variable at a time was changed to examine the effects of different operation conditions on the kinetics. The rate expression for butyric acid CWO was developed as:

$$r_i = 3.2 \times 10^5 e^{-57900/RT} C_{BA} P_{O_2}^{0.61} C_{Ir}^{-0.63}$$

and is valid within the operating ranges mentioned above.

Gomes et al. [46] also conducted another study with butyric acid recently. In this study, carbon supported iridium (~5% Ir) and platinum (~1%Pt) catalysts were used for CWO, at a temperature of 200 °C, and a partial oxygen pressure of 0.69 MPa. No significant leaching of metals was detected during this study. The platinum catalysts were found to be more resistant to deactivation than the iridium catalysts. The authors proposed a Langmuir- Hinshelwood mechanism for the mathematical model of butyric acid oxidation. The introduction of a simple deactivation function into the mathematical model led to a perfect fit of the experimental data. The fact that the proposed model accounts for catalyst deactivation might be useful in designing catalyst systems for the oxidation of butyric acid.

Mantzavinos et al. [47] studied *p*-coumaric acid (PCA), a representative model compound of the biologically recalcitrant polyphenolic fraction present in olive oil production and wine distillery wastewaters, to investigate whether CWO produces end products that can be biologically treated. The authors tested the wet oxidation both with and without the presence of a catalyst. The Co/Bi composite oxide seems to be the most effective catalyst for the oxidation of PCA acid with almost total destruction achieved after 10 min of oxidation. CuO·CoO·ZnO/Al and CuO·ZnO/Al catalysts were of comparable activity to the Co/Bi oxide while Pt/Al and FeO (OH) give significantly lower rates. In all cases, however, the catalyzed reactions removed much higher amounts of *p*-coumaric acid, compared to the uncatalyzed reaction. However, the biological treatability of solutions after CWO was poor which suggests that the end products were inhibitory for biological treatment. In this study, TOC was chosen as the main parameter to be measured, so no record of possible end products exists.

Neri et al. [48] also studied the CWO of *p*-coumaric acid over Fe and Zn promoted ceria catalysts. In this study, the catalysts were prepared by the coprecipitation method. The PCA concentration that was fed to the reactor was 4.5 mM. The temperature range tested in this study was between 80-130 °C, and the air pressure was held constant at 2MPa. Oxidation of PCA into most biodegradable intermediates was achieved at 80°C with the Fe promoted ceria catalyst. The authors investigated the reaction rate for ceria alone as well as ceria promoted with Fe and Zn. The important finding is that with the addition of Zn, the catalytic activity decreased compared to the activity of the ceria catalyst alone. In the case of the Fe addition, the activity was ten times higher than that of ceria alone. The authors suggest this increase is probably due to the structure

modification of ceria rather than just a surface area increase. The PCA was not completely oxidized, and the main intermediates were chain side oxidation products, such as p-hydroxybenzaldehyde, ring cleavage products, such as oxalic and formic acid.

Beziat et al. [49] studied the CWO treatment of carboxylic acids on  $\text{TiO}_2$ -supported ruthenium catalysts. The experiments were carried out in a 250 ml autoclave, and the carboxylic acid solution and the catalyst were loaded into the reactor at the same time. Standard operating conditions were 0.15 liter of 5 g/L carboxylic acid solution, 1 g of 2.8 wt%  $\text{Ru/TiO}_2$ ,  $190^\circ\text{C}$ , and 5 MPa total pressure. This study aimed for complete mineralization of carboxylic acids into  $\text{CO}_2$ . For compounds such as glycolic acid, the reaction took about an hour and the treated water did not contain any organic products (the TOC was zero at the end of the reaction). However, the complete oxidation of acetic acid was harder, and even at a reaction time of 8 hours, only about 80% TOC reduction was achieved, which is in agreement with all the other studies that suggest acetic acid is one of the harder organic acids to oxidize.

Gallezot et al. [50] studied the CWAO treatment of carboxylic acids, namely formic, oxalic, and maleic acids. The reactions were carried out with air at  $20$ - $190^\circ\text{C}$  on carbon supported platinum catalysts. The pressure range tested was  $0.1$ - $1.5$  MPa. Under very moderate conditions (air at atmospheric pressure and at  $53^\circ\text{C}$  or lower temperatures),  $\text{Pt/C}$  catalyst oxidized formic and oxalic acid into carbon dioxide. Maleic acid was also completely oxidized into carbon dioxide, however, at a higher temperature and pressure compared to formic and oxalic acids ( $132^\circ\text{C}$ ,  $1.5$  MPa). The authors verified that the  $\text{Pt/C}$  catalyst does not oxidize acetic acid in the present conditions, which led to the conclusion the oxidation of maleic acid does not produce acetic acid.

Klinghoffer et al. [51] investigated the CWO treatment of acetic acid using platinum on alumina monolith catalyst. The study employed a monolith froth reactor that consisted of three separate systems, namely the feed, the reactor, and the separator. The catalyst was prepared by the incipient wetness method. The only reaction product detected was  $\text{CO}_2$ . No carbon monoxide or partial oxidation products (such as oxalic acid) were detected. The authors state that the higher efficiency of this system compared to previously conducted studies on the CWO of acetic acid comes from the monolithic characteristics of the catalyst as well as the reactor. Duprez et al. [52] studied the CWAO treatment of acetic acid. Ru, Pt, and Rh catalysts supported on titania, ceria, or activated carbon, and Mn/Ce composite oxide catalysts were investigated. Ru/C was found to be a very efficient catalyst for the WAO of acetic acid. The oxidation yielded 97% removal of COD after three hours. Although the system had a high selectivity for carbon dioxide (98%), it was detected that some of the carbon support had been oxidized into carbon dioxide also. This was a major drawback of this study. Mikulova et al. [53] also studied the CWAO of acetic acid with Ru and Pt catalysts supported on  $\text{Zr}_{0.1}\text{Ce}_{0.9}\text{O}_2$  and  $\text{Zr}_{0.1}(\text{Ce}_{0.75}\text{Pr}_{0.25})\text{O}_2$  mixed oxides and commercial pure ceria in an autoclave reactor. The concentration of acetic acid was 78 mmol/L and the catalyst concentration was 4g/l. The reaction temperature was 200°C. Ninety-eight percent mineralization of acetic acid was observed after a three hour reaction time.

Silva et al. [54] studied the CWAO of acrylic acid containing wastewaters in a high pressure reactor at 200 °C and 1.5 MPa oxygen partial pressure. Ag/Ce, Co/Ce, Mn/Ce, CeO, and MnO catalysts were evaluated in terms of activity, selectivity, and stability. The Mn/Ce catalyst showed the highest activity in 2 hours of reaction time.

When a molar ratio of 70/30 was used for this catalyst, 94.1 % TOC reduction was achieved in 30 minutes, and after two hours, 97.7 % TOC reduction was observed. The authors stress the importance of using higher molar percentages of Mn with Ce as smaller ratios give way to the production of refractory end products such as acetic acid.

Bhargava et al. [55] studied the CWAO treatment of ferulic acid with nine different heterogeneous catalysts in a 1.2 L autoclave reactor. The reaction conditions were mild with a reaction temperature of 100°C and 172 kPa of oxygen partial pressure. The most effective catalysts were the Cu-Ni-Ce-Al<sub>2</sub>O<sub>3</sub> and Cu-Mn-Al<sub>2</sub>O<sub>3</sub>, with 81% and 75% TOC removal after 120 minutes of reaction time respectively. It was observed that the presence of manganese in the catalyst greatly reduced the leaching of copper.

Renard et al. [56] studied the CWAO treatment of stearic acid on cerium oxide supported Ru, Pd, Pt, Ir catalysts. They investigated the influence of reaction conditions such as temperature, oxygen pressure and stearic acid concentration on TOC and COD removal. The reactions were carried out in a 0.44 L batch autoclave reactor. The reaction temperatures were in the range of 160-230 °C. Oxygen pressures tested were between 0.1-2 MPa. It was observed the oxidation reaction followed two pathways, one to complete mineralization and the other to smaller carboxylic acids as end products. The 5% Pt/CeO<sub>2</sub> catalyst had the highest initial rate of mineralization and allowed to convert more than 95% of stearic acid into CO<sub>2</sub> in three hours at 200 °C .

## CWAO Treatment of Alcohol and Alcohol Distillery Wastewaters

Belkacemi et al. [57] investigated the CWO of high strength alcohol-distillery liquors. Three heterogeneous catalysts were used to evaluate the CWO reaction efficiency. These were a 1%w/w Pt over  $\gamma$ -alumina catalyst, manganese/cerium composite oxide, and a Cu (II)/NaY zeolite. The experiments were run in a batch reactor with a volume of 300 ml. For each run, 100 ml of distillery waste was fed into the reactor. The zero time for the reactor was taken as the time the catalyst was introduced to the system after the oxygen. Five grams of catalyst was used per liter of liquor. Temperatures of 180-250 °C and pressures of 0.5-2.5 MPa were studied. Only one sample was drawn from each reaction, generating only one data point at given reaction conditions. All samples were analyzed for protein, sugar, total Kjeldahl nitrogen, total organic carbon, and chemical oxygen demand. The Cu (II)/NaY catalyst was the most efficient catalyst under all temperatures; however, some leaching of Cu was detected. The lowest reaction rate was observed with the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Coleman et al. [58] also studied the catalytic oxidation of alcohols although with a different purpose. They aimed at catalyzing alcohols into aldehydes and ketones, using bifunctional osmium-copper system as the catalyst. The catalytic oxidation of various alcohols was carried out at 100 °C using OsO<sub>4</sub> (1 mol %), CuCl (1.5 mol %), and pyridine (5 mol %), in the presence of 1 atm oxygen pressure, with the addition of toluene, or 1,2-dichlorobenzene as the solvent. The catalyst system was found to be selective for only benzylic and allylic alcohols.

Batygina et al. [59] studied the oxidation of wastewater from an alcohol plant called the Luther water. The temperature and pressure ranges investigated were 130-200 °C and 1.5-3.6 MPa, respectively. Ruthenium catalysts supported on graphite-like carbon was found to be highly effective in the oxidation of Luther water. The TOC reduction was 97.5 % at 150 °C after one hour reaction time. Complete oxidation was achieved after 40 minutes when the reaction temperature was increased to 200 °C.

### **CWAO of Miscellaneous Compounds**

Phenol is probably the most investigated compound with CWAO. Numerous authors have been successful in removing this toxic compound from wastewaters by CWAO treatment [47, 60-76].

Silva et al. [77] studied the CWAO treatment of effluents from the formaldehyde industry. The temperature and pressure ranges tested were 190-220 °C and 1.5-3.5 MPa of oxygen partial pressure, respectively. Among the four types of catalysts tried (Mn/Ce, Co/Ce, Ag/Ce, and CuO-ZnO/ Al<sub>2</sub>O<sub>3</sub>), Mn/Ce proved to be the most active catalyst for the oxidation of formaldehyde. The formaldehyde concentration of an industrial formaldehyde containing effluent decreased from 800 ppm to 0.1 ppm in three hours under 200 °C and 1.5 MPa oxygen partial pressure. Kacar et al. [78] studied the CWAO of an alkaloid factory wastewater. The performance of four different catalysts, Ni(NO<sub>3</sub>)<sub>2</sub>, FeCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub> and two catalyst mixtures, Cu(NO<sub>3</sub>)<sub>2</sub>+MnCl<sub>2</sub>, and FeCl<sub>2</sub>+Ni(NO<sub>3</sub>)<sub>2</sub> were evaluated. Except for the, Ni(NO<sub>3</sub>)<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> catalysts, all the other catalysts increased the BOD/COD levels above 0.5 which would mean the

wastewater would be considered biodegradable. However, the COD removal values were really low (~35%) under the reaction conditions of 150°C, and 0.65 MPa.

## CWAO OF DYE WASTEWATERS

Donlagic and Levec [79, 80] studied the wet oxidation of diluted aqueous azo dye solutions with and without a catalyst. The main aim of these studies was to investigate whether the oxidation of the dye solution produced biodegradable effluents that could then be directed to a biological treatment process. The dye chosen as the pollutant was mono azo dye Orange II. Orange II was chosen as the model dye because it produces a wide variety of intermediates as a result of its bulky structure. In the non-catalytic study, the temperature range was 180-240 °C, and oxygen partial pressures were between 1.0-3.0 MPa. The dye concentration was in a range of 100-1000 mg/l to mimic the concentrations present in industrial wastewater streams. The oxidation rate of Orange II was found to be first order with respect to the mother compound. Maximum biodegradability for this dye under non-catalytic conditions was reached at 200°C. As the temperature increased above 200°C, the intermediates formed were found to be less biodegradable. For the CWO study, the catalyst used was a compounded catalyst containing 42% by weight copper oxide, 47% zinc oxide, and 10% aluminum oxide. The experiments were carried out in a temperature range of 180-240 °C, and partial oxygen pressure of 1.0 MPa, and Orange II mass concentration was 0.5 g/l. The concentration of the catalyst was 5 g/l. Acetic acid was the dominant intermediate species in the whole range of temperature investigated in the catalytic oxidation, whereas in the non-catalytic



oxidation, formic acid was more prevalent. After the oxidation processes, the biodegradability of Orange II oxidation by-products was still low. The authors suggest that the intermediates formed may be acting as inhibitors to the microorganisms or their metabolic values may be too small to be utilized.

Lee et al. [81] studied the CWO of reactive dyes with Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in the presence of H<sub>2</sub>/O<sub>2</sub>. The model reactive dyes used were reactive black 5, reactive blue 19 and reactive red 198. The operating pressure was kept as 2.3 MPa, and the temperature was kept at 200 °C. The initial concentration of the reactive dyes was 1000 mg/l. The addition of H<sub>2</sub> with oxygen increased the wet oxidation activity of the bimetallic catalyst significantly. The authors also studied a real effluent from the dyeing industry and concluded that with 0.2 wt.% Pd-1.0 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with H<sub>2</sub>/O<sub>2</sub> mixture, in a continuous flow reactor, the dye could successfully be treated.

Neamtu et al. [82] studied the catalytic wet oxidation of a reactive azo dye, *Procion Marine H-EXL*, in the presence of hydrogen peroxide with Fe-exchanged Y zeolite as the catalyst. After only 10 minutes of reaction time at 50 °C, in the presence of 20 mmol/l H<sub>2</sub>O<sub>2</sub> and 1 g/l catalyst, the color removal was 97% at a pH of 3 and 53% at a pH of 5. After 30 minutes of reaction time under the same conditions, more than 96% of the dye was removed which corresponded to a COD removal of 76%. The pH was found to affect the removal efficiencies during the first 20 minutes of the experiment, but at longer reaction times, the effect of pH was not significant. The other two factors affecting removal were found to be the catalyst concentration and the hydrogen peroxide concentration.

## LUMPED PARAMETER KINETIC MODELING

The mechanism of wet oxidation of organic compounds in industrial wastewaters is very complex because they usually contain more than one type of pollutant. Even with a pure compound such as phenol, the exact mechanism or reaction pathway for degradation has not yet been established. In many cases, the oxidation goes through a very complicated pathway, a series of successive and parallel reactions, and leads to the formation of many different intermediates, such as lower molecular weight carboxylic acids. This makes it very difficult to determine the kinetics of compounds in question. The lumped kinetics approach (LKA) offers a suitable trade-off between tedious mechanistic/kinetic formalisms and oversimplified power-law representations. For reactor design and scale-up considerations, LKA is a useful strategy when dealing with the kinetics of reactions with complex mixtures such as industrial wastewaters [83].

The three-lump generalized lumped kinetic model simplified scheme, which is used in this study, postulates that as the reaction proceeds, all the species can be categorized within three characteristic lumped parameters, namely [83]:

- ☐ Lumped parameter 1 for parent compounds and unstable organic intermediates, except acetic acid
- ☐ Lumped parameter 2 for partial oxidation products and refractory intermediates, acetic acid being a typical representative
- ☐ Lumped parameter 3 for oxidation end-products, such as carbon dioxide and water.

The “lumps” are represented in concentrations of lumped parameters, such as TOC, COD, TN, etc., rather than concentrations of individual compounds. The scheme does not have to be three steps, but can be made as complex as required to describe the reaction mechanism.

Belkacemi et al. [83], Zhang and Chuang [84], Pintar et al. [85], Gomes et al. [44], Shende and Levec [86] have all successfully applied the LKA to determine reaction kinetics in the past . However, generally speaking, reaction kinetics and modeling studies are rare for CWAO, and catalytic wet air oxidation studies with LKA do not exist for the oxidation of dyes. The derivation of the lumped kinetic model for CWAO conversion of Orange II in this study is discussed in detail in Chapter 4.

## CHAPTER III

### METHODOLOGY

In this chapter, materials and methods used in this study are explained in detail. Batch experiments in an autoclave reactor were conducted for the screening of seven different catalysts. For the screening experiments, a three-variable half-factorial design was constructed for each catalyst and experiments were run in replicates. The catalysts were rated based on overall treatment efficiency, effects on the environment, catalyst stability and economic considerations. The activity of catalysts was characterized by temperature programmed reduction (TPR), and catalyst surface areas were measured with the Brunauer-Emmett-Teller (BET) method. For the selected catalyst, reaction kinetics was examined under different reaction temperatures. Effect of pH on reaction kinetics was also investigated. Catalyst leaching was determined by analyzing the metal concentration in the samples collected at the end of treatment. A theoretical triangular lumped kinetic model was constructed to describe reaction kinetics for the oxidation of Orange II in terms of total organic carbon (TOC). Agreement between constructed model and experimental values was evaluated.

## **MATERIALS**

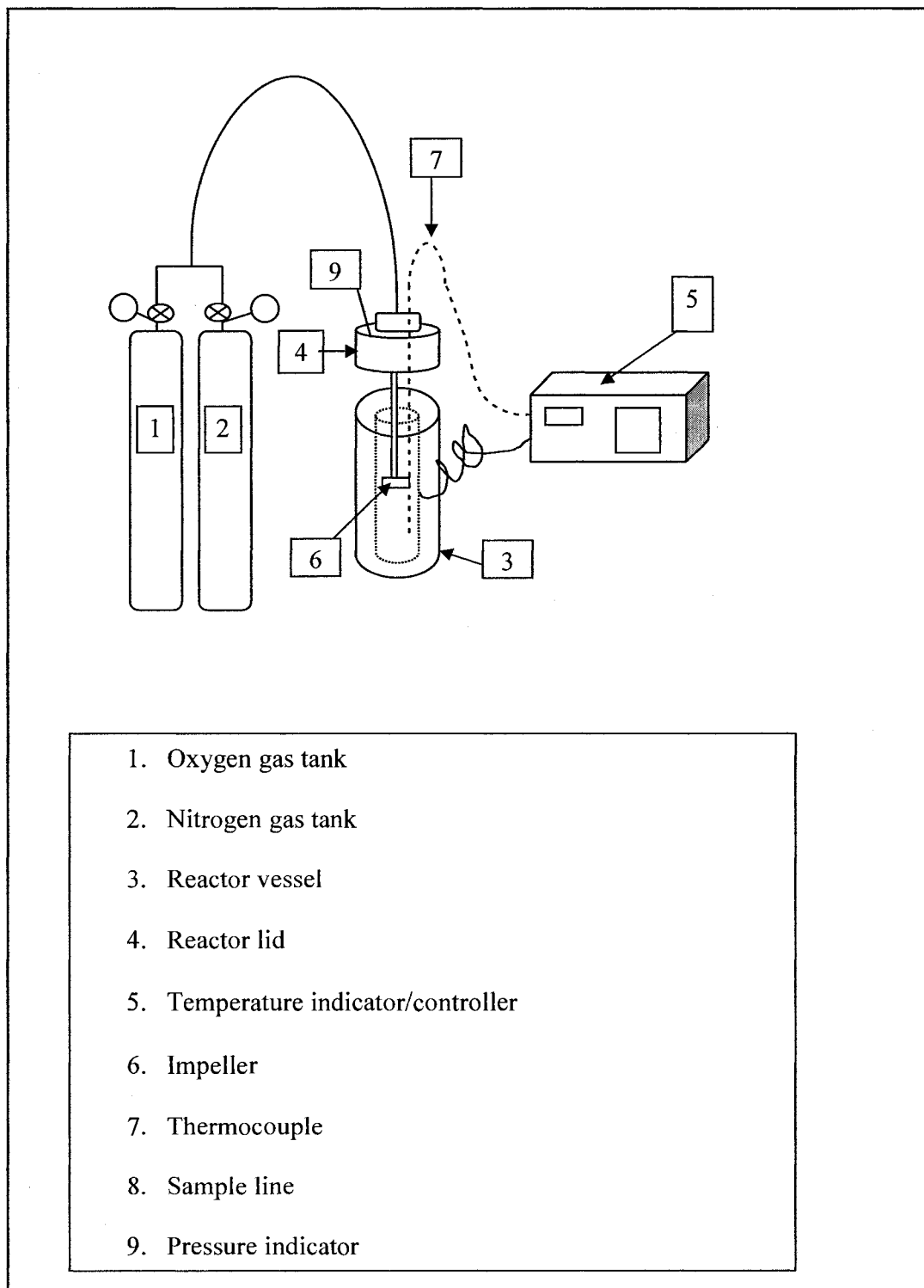
All chemicals in this study were used as received from the manufacturer without further purification. Orange II dye was received from Aldrich, Co. in powder form. The origins of catalysts used in this work are described in Table 3.

## **BATCH REACTOR SET-UP AND OPERATING PROCEDURE**

All catalyst screening and kinetics experiments were carried out in a one-liter stainless steel autoclave reactor custom built by Autoclave Engineers of Erie, Pennsylvania. The reactor consists of two parts: an externally heated reactor vessel where the solution is held during reaction and a cap with eight bolts that sits on the vessel. On the cap, the reactor has a sampling valve for liquid samples, a vent line to relieve pressure when needed and to purge the reactor, a pressure gauge to monitor reaction pressure throughout the experiment, and an impeller for complete mixing during reaction. Two gas tanks, one for nitrogen and one for oxygen, are connected to the reactor at the top with stainless steel tubing. The oven temperature can be adjusted to achieve the desired reaction temperature with a controller. The reaction temperature is monitored with a K-type thermocouple inserted into the reactor from a small hole on the cap of the reactor which is connected to a digital display. A schematic of the reactor is presented in Figure 3.

In a typical run for the catalyst screening experiments, the reactor was filled with 600 ml of 100 mg/l Orange II aqueous solution. A desired amount of catalyst was placed in the reactor; the reactor was closed, and the bolts were tightened using a torque wrench set at 90 ft/lbs. This closing procedure ensured a tight metal-to-metal seal to ensure there were no gas leaks during the experiment. Once the reactor was closed, it was purged with nitrogen gas for five minutes to eliminate any oxygen in the reactor. Then the reactor was heated to the desired reaction temperature under nitrogen atmosphere. Once the desired temperature was reached, this was marked as Time-0 ( $T_0$ ) for the reaction, and oxygen gas was turned on along with the stirrer. For the screening reactions, samples were only taken before reactor heat-up started, then at time 0 and then at 120 minutes, which was the end time for the reactions. The pH values of the samples were measured. The sample collection and preservation method is detailed in the following section.

After a catalyst was chosen for modeling, 800 ml of desired concentration of Orange II was placed in the reactor with 2.4 grams of chosen catalyst, which yields a catalyst concentration of 3 g/l in the reactor. The oxygen pressure was kept constant at 400 psig for reasons explained in the results section. At the beginning, samples were taken at different time intervals, every 10-20 minutes for 120 minutes of reaction time, for a total of seven samples. However, analysis of these samples suggested the majority of the reaction happens within the first 20 minutes, so the sampling times were adjusted to get a better snapshot of the reaction kinetics. Samples were taken at time intervals 0 minute, 1 minute, 2 minutes, 5 minutes, 10 minutes, 20 minutes, and 60 minutes. The samples were collected and preserved and analyzed as described in the following sections.



**Figure 3.** Reactor schematic

## SAMPLE COLLECTION AND PRESERVATION

Samples were collected from the reactor through the sampling valve. From the length and the cross-sectional diameter of the sampling tube, the volume inside the sampling line was calculated to be around 2.4 ml. Before each sample, the sample line was purged by taking 2.5 ml of liquid out and discarding. This was done to ensure the sample taken was representative of the solution inside the reactor and did not come from what was left over in the tube from the previous sample. After the purge, 7.5 ml of sample were collected in a syringe and filtered with a syringe membrane filter with 0.4  $\mu\text{m}$  pore size.

The filter selection process proved to need consideration. Initially, the reactor itself was equipped with a filter that was connected to the sampling line. This filter had 5  $\mu\text{m}$  pore size and was made of stainless steel mesh. During sampling with this filter, a number of occurrences were observed that were contributing to erroneous results. First, the sampling line got clogged when testing the  $\text{C/Cr}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{CuO}$  catalyst. This catalyst was eliminated from the screening list when clogging was observed. The clogging was caused by a gummy substance formed at a reaction temperature of  $180^\circ\text{C}$ , possibly due to polymerization of the dye or intermediates in solution. The clogged filter was changed after attempts to clean it out with different solvents failed. The filter was replaced with a new one of the same kind. After the filter change, it was observed the measured TOC and Orange II concentrations were fluctuating during the experiment. The final sample taken at 120 minutes was colored, but upon opening the reactor it was observed the solution in the reactor had minimal color. Closer investigation revealed that



the dye was adsorbing onto the filter, and then leaching back into the samples. The filter was then taken out permanently, and samples were filtered after collection with 0.4  $\mu\text{m}$  filters into glass sample bottles. The pH of the sample was measured and then the sample was acidified with a drop of sulfuric acid to achieve a pH below 2 to preserve the sample as defined in Standard Methods for the Examination of Water and Wastewater. The samples were stored in a refrigerator at 4°C and were analyzed within 28 days to comply with standard procedures for refractory organics containing water analysis.

## **CHARACTERIZATION OF CATALYSTS**

All catalysts used in this study were solid state heterogeneous catalysts. A list of catalysts used in this study is presented in Table 2. The catalysts were used in powder form, with particle sizes less than 250  $\mu\text{m}$ . Catalysts 1, 3, 4 were already in powder form when received. Catalysts 2 and 5 were in cylindrical bead form. Catalysts 6 and 7 were in precipitate form with no distinct shape. The catalysts that were not in powder form were ground with a mortar and pestle and sieved in a shaker. Catalyst powder collected in the lowest tray (particle size < 250  $\mu\text{m}$ ) was collected and used for the experiments.

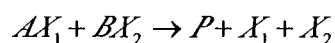
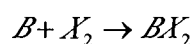
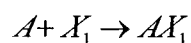
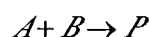
**Table 2.** Catalysts screened in the batch reactor

<i>Catalyst</i> #	<i>Composition</i>	<i>Surface Area</i> ( $m^2/g$ )	<i>Manufacturer</i>
1	CuO/ZnO	32.47	United Catalysts
2	CuO/Al <sub>2</sub> O <sub>3</sub>	158	HU Chem. Eng. Lab
3	Cu <sub>2</sub> Cr <sub>2</sub> O <sub>5</sub>	31	Engelhard
4	Pt/SnO <sub>2</sub> /CeO <sub>2</sub>	58.46	HU Chem. Eng. Lab
5	CuO/CeO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	128	HU Chem. Eng. Lab
6	MnO <sub>2</sub> /CeO <sub>2</sub>	N/A	HU Chem. Eng. Lab
7	MnO <sub>2</sub> /CuO	N/A	HU Chem. Eng. Lab

### Surface Area Measurements

In heterogeneous catalysis, the surface area of a catalyst is an important factor that determines catalyst activity. Reactions catalyzed by solid catalysts occur on the exterior and interior surfaces of the porous catalyst [87]. Highly porous structures have larger surface areas leading to more active catalysts. It is customary to disperse metal catalysts throughout the entire internal surface area of some suitable porous support, such as  $\gamma$ -alumina in order to create a large specific surface area which is entirely accessible because of its open pore structure [87]. In this study, catalysts 2, 4, and 5 were supported on  $\gamma$ -alumina.

In heterogeneous catalysis at least one reactant must be chemisorbed on to the catalyst surface. If two catalytically active sites on a catalyst surface are called  $X_1$  and  $X_2$ , the reaction of two chemical species A and B over the catalyst giving product P can be formulated as follows [88]:



This cycle can be repeated many times, but in practice eventually the site deteriorates. The reaction rate depends on the active catalyst surface area exposed to reactants. Catalysts can only speed up a reaction if they are thermodynamically possible. They cannot change the thermodynamic equilibrium; they can only alter the path. The reaction rate of a catalyzed reaction is determined by the rate of the following events [88]:

- ☐ Transport of reactants: On the outer surface of catalyst and in the pores of the catalyst (this is the diffusion step)
- ☐ Adsorption on catalyst surface: Rate =  $k_a C_A (1 - \Theta)$
- ☐ Surface reaction step: Rate = chemical reaction rate =  $k \Theta_A \Theta_B$
- ☐ Desorption: Rate =  $k_d \Theta_{\text{prod}}$ ,

and;

- ☐ Transport of products from the catalyst surface back into solution where;

$k_a$  = absorption rate constant

$k$  = reaction rate constant

$k_d$  = desorption rate constant

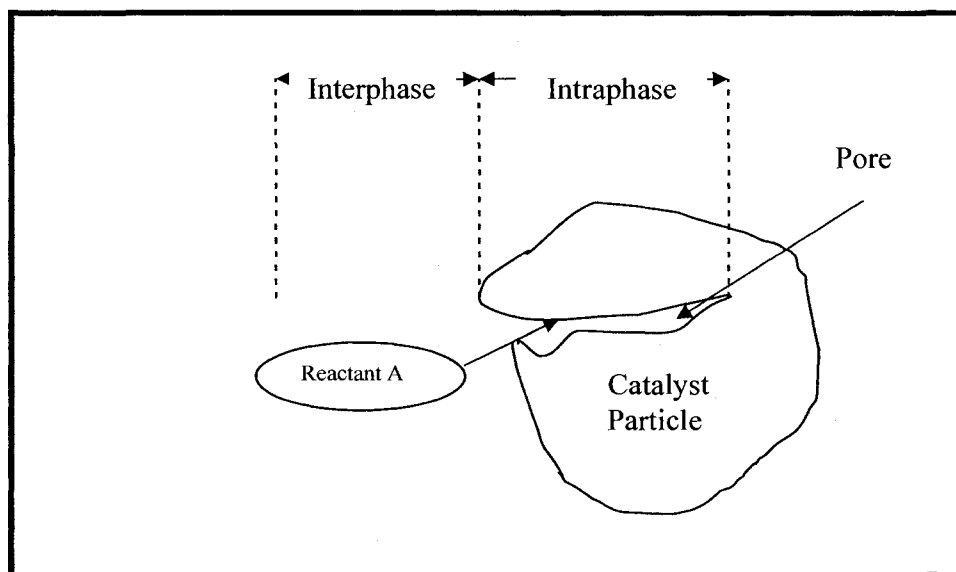
$C$  = molar concentration

$\Theta$  = surface coverage or fraction of catalyst surface covered by adsorbed species

A,B = reactants A and B

The adsorption step is the most important step in catalyzed reactions. There can be two types of adsorption on a catalyst surface, physical and chemical adsorption (chemisorption). Physical adsorption isotherms are used to determine the surface area of catalysts by the Brunauer-Emmett-Teller (BET) method.

Figure 4 displays a depiction of the catalyst particle.



**Figure 4.** Schematic of catalyst particle

There are several models of the relationships among surface coverage  $\Theta$ , concentration  $C_A$ , and adsorption rates. The Langmuir model states that surface coverage for gas adsorption can be calculated by:

$$\Theta = \frac{K \cdot p}{1 + K \cdot p} \quad (3.1)$$

where  $K$  is the adsorption equilibrium constant, and  $p$  is partial pressure. The BET method is an extension of the Langmuir equation. The Langmuir equation is for monolayer gas adsorption. The BET equation is for multilayer adsorption and can be expressed as:

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c} \frac{p}{p_0} \quad (3.2)$$

where  $V$  is volume of gas adsorbed,  $V_m$  is the monolayer volume of gas adsorbed,  $p$  and  $p_0$  are equilibrium and saturation pressure of adsorbates, and  $c$  is the BET constant, which is defined as:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right) \quad (3.3)$$

where  $E_1$  and  $E_L$  are the heat of adsorption of the first and higher layers respectively.

The surface areas of the catalysts for this study were measured by the single point BET gas adsorption method with a Micromeritics 2075 Surface Area Analyzer. The

gases used were nitrogen and helium. About 0.25 grams of catalyst was placed in the sample tube, and the surface areas of catalysts were determined by continuously passing the  $N_2/He$  over the sample at atmospheric pressure. The surface areas were calculated by dividing the adsorption peak by the sample weight.

### **Temperature Programmed Reduction (TPR)**

The Temperature Programmed Reduction (TPR) technique was used to determine the hydrogen consumption capacity (reduction) of the catalysts. The hydrogen consumption capacity (or, in other words, the reducibility of the metal in catalyst) is indicative of its activity. For the TPR analysis, measured amounts of catalysts were placed in the sample tube and placed in the sample tube holder. The catalyst was first pretreated at 150 °C for an hour under nitrogen gas to desorb physically adsorbed species. Then the catalyst was subjected to a programmed temperature rise, while a reducing gas mixture was passed over it ( $H_2/Ar$  mixture), and the hydrogen gas consumption was plotted against time and temperature.

### **HALF-FACTORIAL SCREENING EXPERIMENTS**

Factorial designs are used in experiments involving several factors where it is desired to investigate the joint effects of factors on a response variable. Joint factor effects for factorial design are typically comprised of main effects and interactions. In a case of the factorial design where each of the  $k$  factors of interest has only two levels,

each replicate has exactly  $2^k$  experimental trials or runs that have to be conducted, thus these designs are called  $2^k$  factorial designs. As the number of factors in a  $2^k$  factorial design increases, the number of runs required for a complete replicate of the design may outgrow the resources required for experiments. In such cases, if the experimenter can assume that certain interactions are negligible, information on the main effects and low-order interactions may be obtained by running only a fraction of the complete factorial experiment. These fractional factorial designs are among the most widely used types of experimental design in industry [89]. A major use of fractional factorials is in screening experiments.

In the current study, a one-half fractional factorial design of the  $2^k$  design was utilized for the catalyst screening experiments. Three factors were of interest, namely the catalyst loading, reaction temperature, and pressure, each at two levels. This means that a one-half fraction of a  $2^3$  design is needed, thus the design contains  $2^{3-1} = 4$  treatment combinations for each catalyst. All experiments were run in duplicate to verify the reproducibility of the data; thus 8 experiments were conducted for each catalyst resulting in 56 total screening experiments. The experiment order was randomized to avoid systematic errors. Table 3 lists the design parameter levels for this study.

A commercially available software package, Design Expert, developed by Statease Incorporated, was used to analyze the experimental results.

**Table 3.** Half-factorial design parameter levels

<i>Parameter</i>	<i>Low value</i>	<i>High value</i>
Reaction Temperature, °C	80	120
Total Pressure, psi	300	400
Catalyst Loading, g/600 ml	2	4

## ANALYTICAL PROCEDURES

### pH measurement

The pH values of the samples were measured before acidification using a probe connected to a digital pH meter. The meter was calibrated using standard buffer solutions of pH 4, 7, and 10 before measurements. In between readings, the probe was rinsed with deionized distilled water to prevent cross-contamination of samples.

### Total Organic Carbon (TOC) measurement

Total organic carbon (TOC) concentrations in samples were determined with a Shimadzu TOC-VCSN analyzer using the combustion-infrared method. The instrument was calibrated using dilutions from a 1000 mg/l standard stock solution covering up to 20 mg/l of organic carbon concentrations in standards. The samples had to be diluted 1:4 before measurement with deionized distilled water since the TOC concentration of



untreated samples were expected to be about 3 times higher than the upper limit for the standard curve. Percent TOC removal for each reaction was calculated as follows:

$$\% \text{ [TOC] removal} = \frac{[\text{TOC}]_0 - [\text{TOC}]_t}{[\text{TOC}]_0} \cdot 100 \quad (3.4)$$

where,

$[\text{TOC}]_0$ =Initial TOC concentration

$[\text{TOC}]_t$ =TOC concentration at time t

### **Orange II concentration measurement**

Orange II concentration of samples was measured by a UV-VIS spectrophotometer, Varian Cary Model 50. Initially, a 50 mg/l Orange II solution was scanned for absorbance to determine the maximum absorbance wavelength through a 1 cm path length. The maximum absorbance wavelength ( $\lambda_{\text{max}}$ ) was determined as 486 nm. A standard curve was constructed by plotting known concentrations of dye versus the absorbance at 486 nm. For this curve, the upper dye concentration was 50 mg/l. It was observed that after this concentration the standard curve was not linear. The standard curve was used to determine the Orange II concentrations of samples after reaction, by measuring the absorbance at 486 nm and calculating the corresponding dye concentration from the curve. This curve is displayed in Chapter 4. Samples were diluted 1:2 for measurement, since the initial concentration was more than 50 mg/l. The dilution factor was taken into consideration when calculating actual concentrations.

Percent Orange II dye removal was calculated as follows:

$$\% \text{ dye removal} = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (3.5)$$

where,

$C_0$ =Initial dye concentration

$C_t$ =Dye concentration at time, t

### **Atomic Absorption Spectrometry (AAS) for metals leaching analysis**

Catalyst leaching is a measure of catalyst stability. Catalyst leaching (dissolution of active metal in catalyst, in solution) is an indication the catalyst is not stable under the reaction conditions. Therefore, leaching is not desired. In the current study, catalyst leaching was determined by measuring metal concentrations by Perkin-Elmer 2100 atomic absorption spectrophotometer (AAS). Flame method was used because the concentrations of metal in catalysts were in the g/l range. Standard solutions prepared from commercial stock solutions were used to construct the calibration curve, and this curve was the basis for the analysis of metal concentration in all samples. The samples were diluted 1:5 prior to analysis and acidified to achieve 4%  $\text{HNO}_3$  by volume in the samples. The auto zero solution (blank sample) also contained 4%  $\text{HNO}_3$  by volume.

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

In this chapter, the results of catalyst screening and kinetics experiments are presented and discussed. The first section starts off with a discussion of the screening process and experimental design in general, followed by the catalyst characterization and screening experiment results for each catalyst in sub-sections. The first section concludes with a decision matrix constructed to decide on the best catalyst.

The second section of this chapter discusses the kinetics experiments conducted with the chosen catalyst. Reaction kinetics analysis is presented, and the effect of temperature and pH on reaction kinetics are evaluated. The theoretical kinetic model is presented and agreement between experimental data and the model is discussed.

### **CATALYST CHARACTERIZATION AND SCREENING**

For this study, the catalyst surface areas were measured by the single-point BET method as described in Section III.III. Temperature Programmed Reduction for each catalyst was carried out to determine the catalyst hydrogen consumption profile. Catalyst leaching for each catalyst was determined by measuring the dissolved metal concentration in collected samples. The dependence of Orange II and TOC removal on catalyst mass in reactor, temperature and pressure were evaluated with a  $2^{(3-1)}$  half-fractional factorial design. TOC and Orange II removal efficiencies were one of the

decision criteria for the best catalyst alternative. Finally, catalyst costs and potential environmental effects from release of catalysts into the environment were determined. Based on these criteria, the catalyst selection process was carried out using a decision matrix which is discussed in detail at the end of this section.

Seven catalysts were screened for their efficiency for removing TOC and Orange II from synthetically prepared wastewaters. The compositions of these catalysts are:

- CuO/ZnO (65%/35%)
- CuO/Al<sub>2</sub>O<sub>3</sub> (10% Cu)
- CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (2.5% Cu /7.5% Ce)
- Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> (41% Cu / 32% Cr)
- MnO<sub>2</sub>/CeO<sub>2</sub> (70/30 Mn/Ce molar ratio)
- MnO<sub>2</sub>/CuO (70/30 Mn/Cu molar ratio)
- Pt/SnO<sub>2</sub>/CeO<sub>2</sub> (0.5 % Pt)

Figure 5 shows the TPR profiles for all screened catalysts. Individual TPR profiles are presented under each catalyst section. Hydrogen consumption peak temperatures are displayed in Table 4.

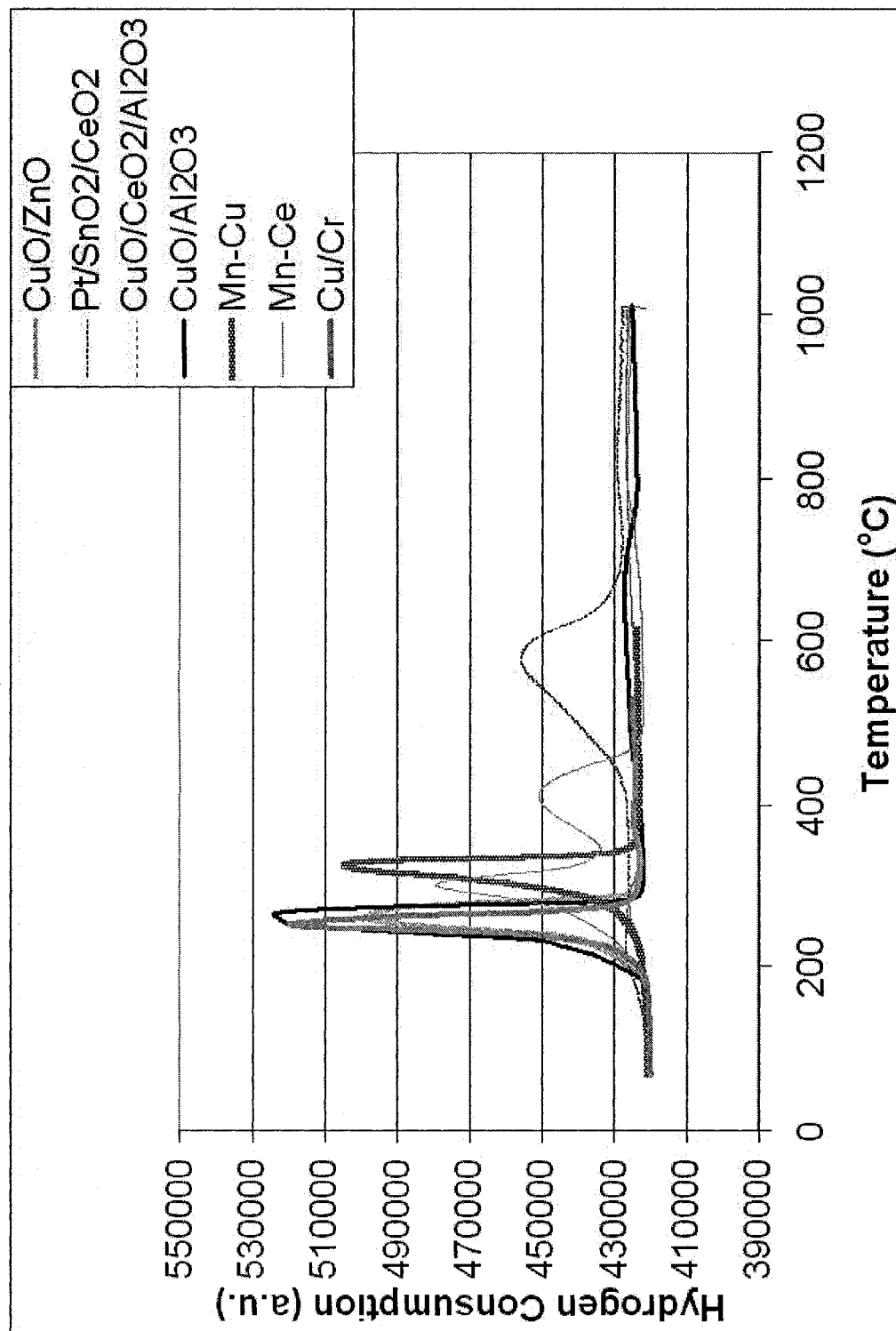


Figure 5. TPR profiles for all screened catalysts

**Table 4.** Hydrogen consumption peak temperatures for screened catalysts

<i>Catalyst</i>	<i>Hydrogen Consumption Peak Temperature (°C)</i>
CuO/ZnO	270
CuO/Al <sub>2</sub> O <sub>3</sub>	260
CuO/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	300, 900
Cu <sub>2</sub> Cr <sub>2</sub> O <sub>5</sub>	250
MnO <sub>2</sub> /CeO <sub>2</sub>	300, 400, 890
MnO <sub>2</sub> /CuO	327
Pt/SnO <sub>2</sub> /CeO <sub>2</sub>	230, 580, 830

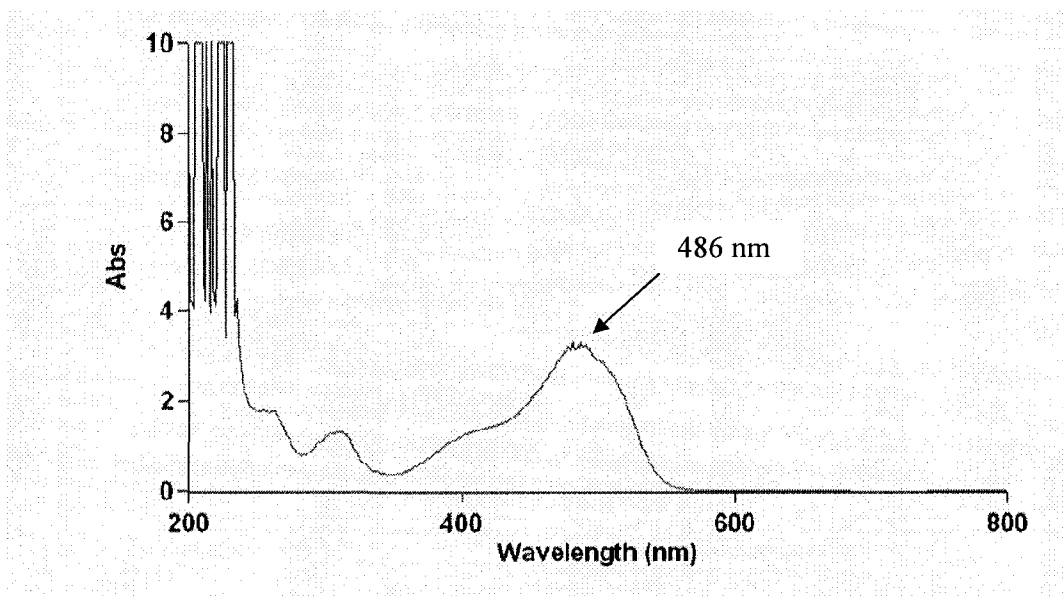
Each peak in the TPR profile for a catalyst represents a reduction process involving a particular component of the catalyst. Hydrogen consumption peaks that occur at lower temperatures indicate the catalyst is active at lower temperatures which is a desired property for the purpose of this study. A catalyst that is active at lower temperatures means CWAQ temperatures can be kept lower, leading to lower operating costs.

In the current work, CuO/ZnO, CuO/Al<sub>2</sub>O<sub>3</sub>, CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub>/CuO catalysts all contain copper. Figure 5 suggests three of these catalysts, CuO/ZnO, CuO/Al<sub>2</sub>O<sub>3</sub>, and Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub>, all display single peaks around 250 °C, and are active at lower temperatures than those that contain manganese and ceria, which display peaks at about 300°C. The interaction of chromium with copper is such that it lowers the peak temperature about 10°C compared to CuO/Al<sub>2</sub>O<sub>3</sub>, and the addition of ZnO leads to a higher peak temperature of 270°C. When comparing the CuO/Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>/CuO

catalysts, the effect of manganese on copper activity comes out such that the consumption peak occurs at a higher temperature. The  $\text{CuO/CeO}_2/\text{Al}_2\text{O}_3$  catalyst has a second peak at  $900^\circ\text{C}$  due to the presence of ceria. This high temperature activity for ceria is also observed in the  $\text{Pt/SnO}_2/\text{CeO}_2$  and  $\text{MnO}_2/\text{CeO}_2$  catalysts, although at slightly lower temperatures of  $830$  and  $890^\circ\text{C}$  respectively, due to interaction with other metals present in the catalysts. The  $\text{Pt/SnO}_2/\text{CeO}_2$  catalyst has the lowest peak temperature at  $230^\circ\text{C}$ , indicating it is more active compared to other catalysts at lower temperatures.

For the screening of catalysts, a three-variable half-factorial experimental design with duplicates was used. The three variables were reaction temperature ( $T$ ,  $^\circ\text{C}$ ), total pressure in reactor, supplied from compressed oxygen tank ( $P$ , psig), and catalyst mass introduced into the reactor (Catalyst, g, depicted as  $C$ ). The high and low values for the half-factorial screening experiments are given in Table 5. The experimental procedure is described in Section III.I. Reduction of TOC and Orange II dye concentrations were chosen as the responses.

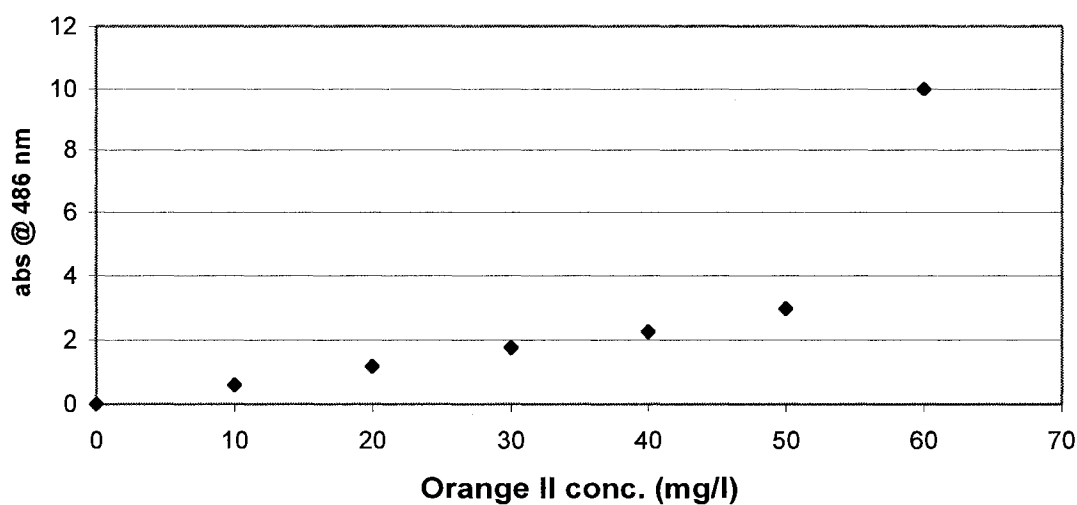
Figure 6 shows the UV-VIS scan graph for  $50\text{ mg/l}$  Orange II. Orange II has a characteristic absorbance peak at  $486\text{ nm}$  due to the chromophore,  $\text{N}=\text{N}$  bond. Orange II also displays absorbance peaks at  $227$  and  $310\text{ nm}$ . These peaks are due to the aromatic rings in the chemical structure of dye.



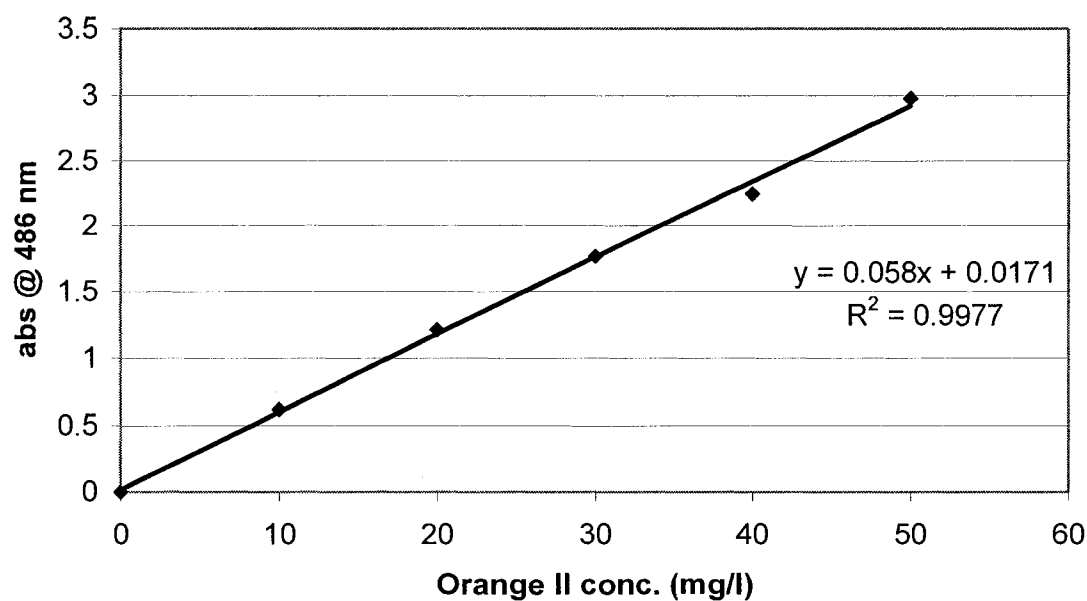
**Figure 6.** UV-VIS scan graph for 50 mg/l Orange II dye

A calibration curve was prepared with known standard concentrations ranging from 0-60 mg/l. Figure 7 displays the absorbance of standards up to 60 mg/l at 486 nm. After 50 mg/l, the calibration curve follows a non-linear trend as displayed in this figure. Therefore, the calibration curve used in this study includes standards up to 50 mg/l, and all samples had to be diluted accordingly before measurement. The maximum absorbance peak and the non-linear nature of the curve at higher concentrations is in agreement with previous studies reported in literature [21, 90-92]. The calibration curve used for this study is displayed in Figure 8.





**Figure 7.** Orange II calibration curve showing absorbance at 486 nm

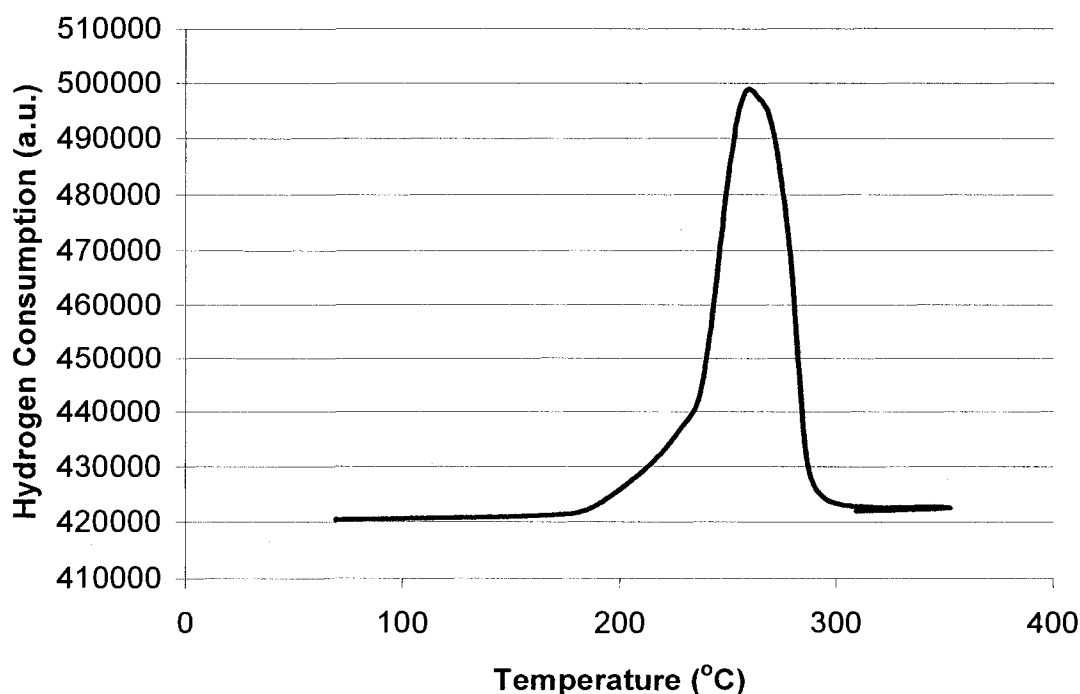


**Figure 8.** Orange II calibration curve at 486 nm for standards up to 50 mg/l

In the following sections, screening results and other factors considered in catalyst selection are presented for each individual catalyst.

### Catalyst 1: The CuO/ZnO Catalyst

The CuO/ZnO catalyst contains 65% CuO and 35% ZnO by mass. It was obtained from United Catalysts Inc. in fine powder form and used as received from the manufacturer. The TPR profile for this catalyst is presented in Figure 5. The catalyst can be reduced at temperatures as low as 200 °C, where hydrogen consumption begins to rise, and has a single peak at 270°C. The single point BET surface area for this catalyst was 32.47 m<sup>2</sup>/g.



**Figure 9.** Temperature programmed reduction (TPR) profile for CuO/ZnO

The results of the screening experiments are presented in Table 5. Figure 10 shows the experimental results in graphical form.

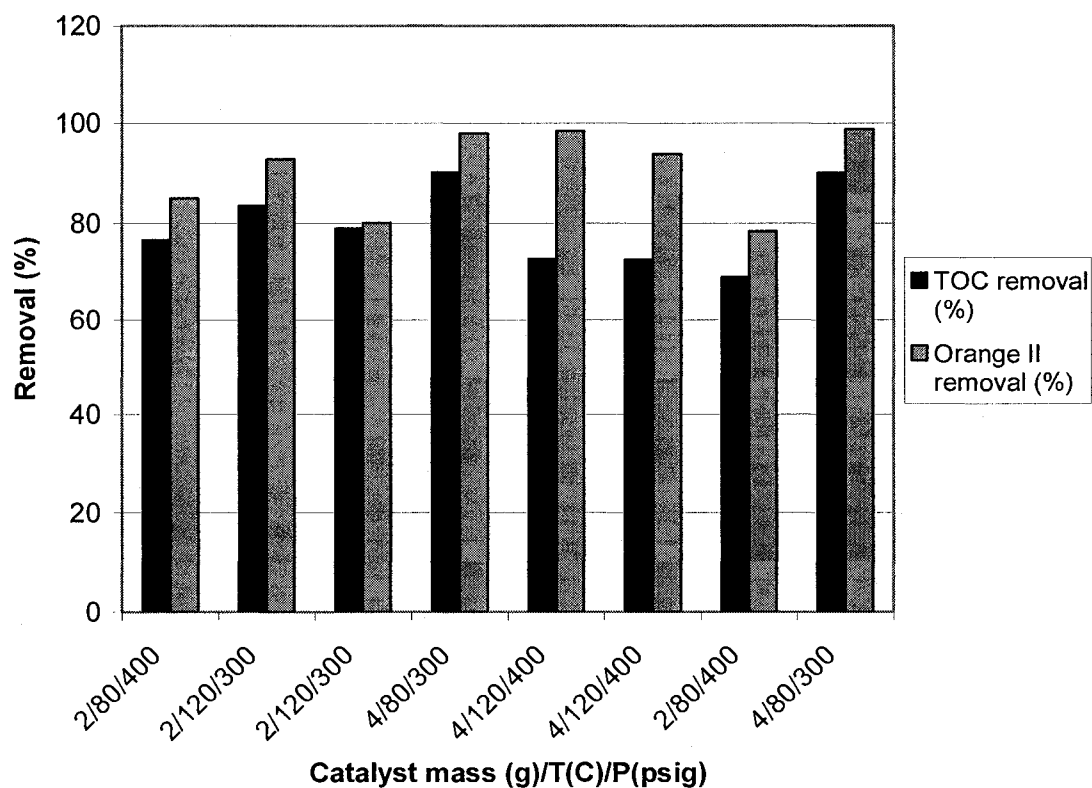
One observation from the screening experiments is that dye removal and TOC removal are not correlated, and Orange II removal percentages are always higher. This is due to the complex nature of the reaction and the intermediates formed. The destruction of the N=N bond is enough to reduce the dye concentration through decolorization, but complete mineralization does not take place.

The ANOVA tables for the experimental results are presented in Appendix B. The Model F-value of 14.23 implies the model is significant, and there is only a 1.34% chance that a "Model F-Value" as large as this could occur due to noise. The model from experimental results is significant. None of the variables are significant for the model, except for the pressure, and as pressure increases overall removal decreases. Such an outcome suggests that the mechanism for dye removal with CuO/ZnO may not be oxidation, since high pressure means higher dissolved oxygen available in solution available for reaction. The mechanism would have to be investigated if CuO/ZnO were chosen as the best alternative.

For this catalyst, highest TOC and dye removals were achieved with four grams of catalyst at 80° C and 300 psig. Leaching of copper (0.016%) was detected in collected samples.

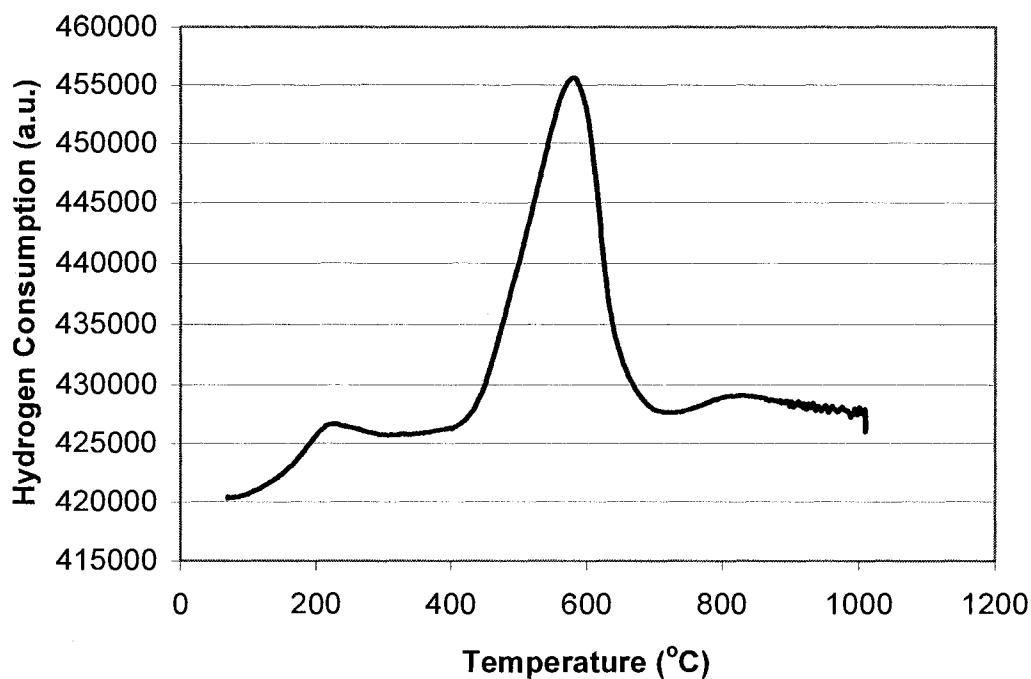
**Table 5.** Screening experiment matrix and results for CuO/ZnO

	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC removal %	Response 2 Orange II removal %
	2	1	Block 1	2.00	80.00	400.00	76.61	85.04
	5	2	Block 1	2.00	120.00	300.00	83.52	92.8
	6	3	Block 1	2.00	120.00	300.00	78.97	80.02
	3	4	Block 1	4.00	80.00	300.00	90.13	98
	7	5	Block 1	4.00	120.00	400.00	72.7	98.43
	8	6	Block 1	4.00	120.00	400.00	72.58	93.79
	1	7	Block 1	2.00	80.00	400.00	69.09	78.37
	4	8	Block 1	4.00	80.00	300.00	90.05	98.81

**Figure 10.** CuO/ZnO catalyst TOC and Orange II removal experimental results

## Catalyst 2: The Pt/SnO<sub>2</sub>/CeO<sub>2</sub> Catalyst

The Pt/SnO<sub>2</sub>/CeO<sub>2</sub> catalyst contains 0.5% platinum by mass. It was prepared at Hampton University Chemical Engineering laboratory. It was in fine powder form and used as received. The TPR profile for this catalyst is presented in Figure 11. This catalyst displayed a three peak profile, a smaller peak around 230°C, a bigger peak at 580°C, and a second smaller peak around 830°C. Such a profile suggests that this catalyst can be reduced over a large range of temperatures, starting at 100°C. As with all noble metal catalysts, this platinum catalyst is a very active catalyst even under mild reaction temperature conditions, and the TPR profile supports this claim.



**Figure 11.** Temperature Programmed Reduction (TPR) profile for Pt/Sn/CeO<sub>2</sub>

The single point BET surface area for this catalyst was 58.46 m<sup>2</sup>/g. The results of the experimental design are summarized in Figure 12. Both the removal of color and removal of TOC with this catalyst were remarkably high at all variable combinations. The results of the screening experiments are displayed in Table 6.

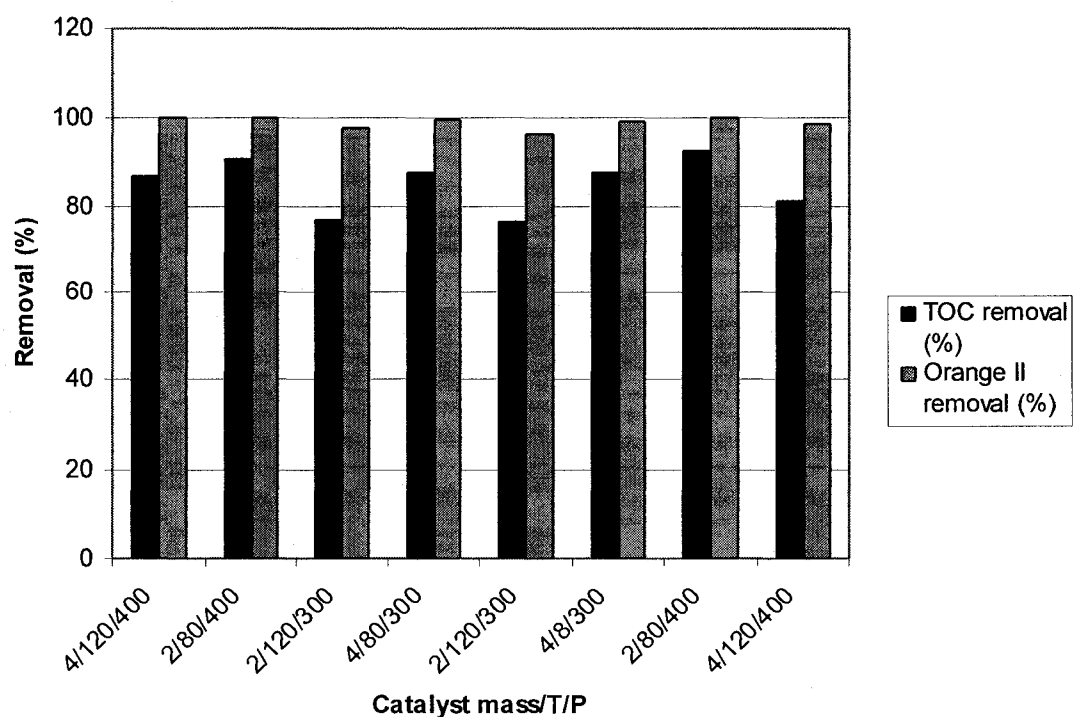
**Table 6.** Screening experiment matrix and results for Pt/Sn/CeO<sub>2</sub>

	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC removal %	Response 2 Orange II removal %
	8	1	Block 1	4.00	120.00	400.00	86.79	100
	1	2	Block 1	2.00	80.00	400.00	90.91	100
	5	3	Block 1	2.00	120.00	300.00	76.92	97.9
	4	4	Block 1	4.00	80.00	300.00	87.84	99.52
	6	5	Block 1	2.00	120.00	300.00	76.47	96.58
	3	6	Block 1	4.00	80.00	300.00	87.84	99.33
	2	7	Block 1	2.00	80.00	400.00	92.59	100
	7	8	Block 1	4.00	120.00	400.00	81.23	98.81

For commercial scale applications, one setback with this catalyst may be the associated costs since platinum is a very expensive metal.

At all treatment variable combinations, Orange II was completely removed, but for TOC reduction, the best combination was two grams catalyst, 80°C, and 400 psig pressure. The ANOVA tables for the experimental results are presented in Appendix B. The ANOVA table suggests reaction temperature and pressure are the important model variables. Catalyst mass in reactor is not a significant variable since the experimental results indicate that catalyst mass is not the limiting factor. Since platinum based catalysts are very efficient oxidation catalysts under mild reaction conditions, even

smaller amounts of this catalyst could be tested. The fact that the lower temperature and higher pressure combination resulted in more TOC removal suggests the reaction is dependent on dissolved oxygen concentration in solution.



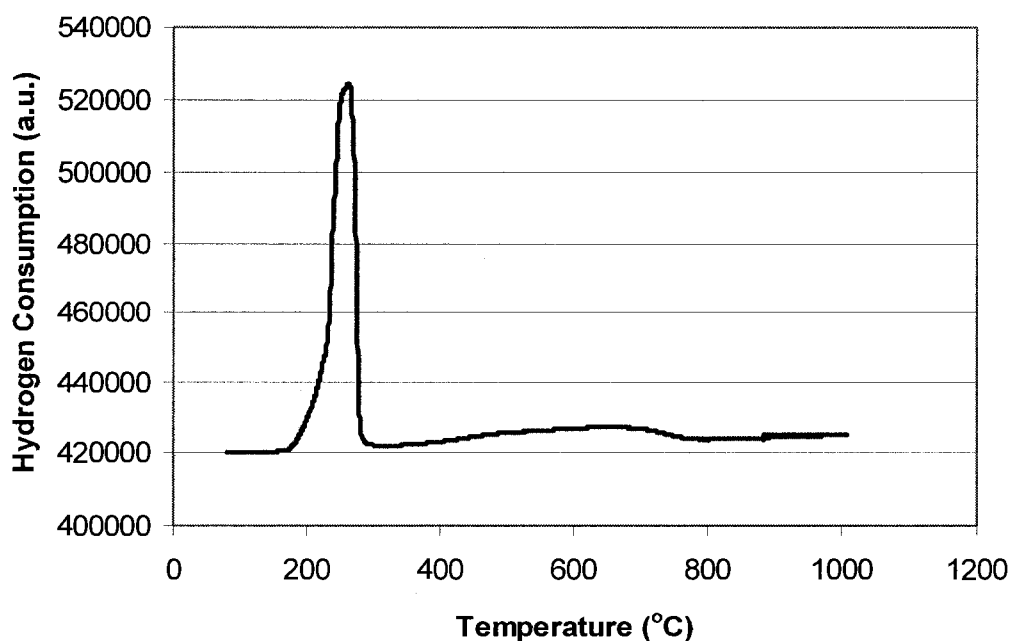
**Figure 12.** Pt/SnO<sub>2</sub>/CeO<sub>2</sub> TOC and Orange II removal experimental results

### Catalyst 3: The CuO/Al<sub>2</sub>O<sub>3</sub> Catalyst

The CuO/Al<sub>2</sub>O<sub>3</sub> catalyst contains 10% copper by mass. It was prepared at Hampton University Chemical Engineering laboratory. It was in spherical pellet form and was ground with a mortar and pestle and sieved through a sieve shaker. It was used

in powder form and particle sizes were smaller than 250  $\mu\text{m}$ . The TPR profile for this catalyst is displayed in Figure 13. The TPR profile displayed a single peak at 260°C, and hydrogen consumption started rising at as low as 170 °C. The measured surface area for this catalyst was 156  $\text{m}^2/\text{g}$ . The results of the screening experiments are presented in Table 7.

Copper leaching was below the detection limit in collected samples, indicating that under the reaction conditions, the catalyst was very stable.



**Figure 13.** Temperature Programmed Reduction (TPR) profile for  $\text{CuO}/\text{Al}_2\text{O}_3$

The ANOVA tables for the experimental results are presented in Appendix B. From the ANOVA table, The Model F-value of 38.47 implies the model is significant.

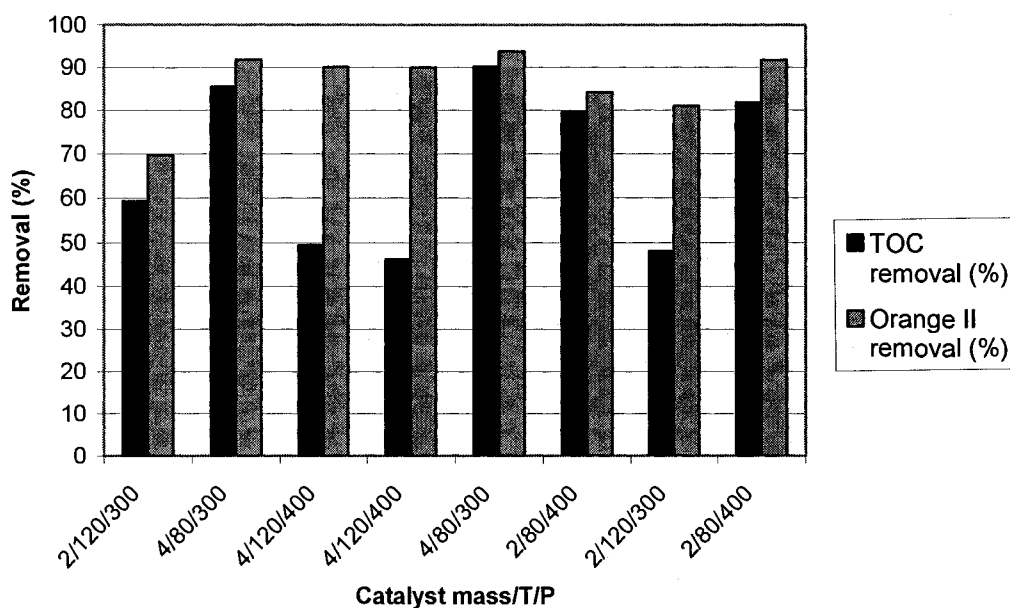


There is only a 0.21% chance that a "Model F-Value" as large as this could occur due to noise.

The important model variable is the reaction temperature. As reaction temperature increases, removal efficiency decreases due to lower concentrations of dissolved oxygen in solution. Figure 14 displays the experimental results in graphical form. Catalyst mass in reactor is not an important variable as even with two grams of catalyst with the combination of lower temperature of 80°C and higher pressure of 400 psig, 90% Orange II and 80% TOC reduction were achieved.

**Table 7.** Screening experiment matrix and results for CuO/Al<sub>2</sub>O<sub>3</sub>

	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC %	Response 2 Orange II removal %
	5	1	Block 1	2.00	120.00	300.00	59.2	69.65
	3	2	Block 1	4.00	80.00	300.00	85.48	91.71
	7	3	Block 1	4.00	120.00	400.00	49.48	90.05
	8	4	Block 1	4.00	120.00	400.00	46.176	89.89
	4	5	Block 1	4.00	80.00	300.00	90.13	93.7
	2	6	Block 1	2.00	80.00	400.00	79.61	84.13
	6	7	Block 1	2.00	120.00	300.00	48.05	80.91
	1	8	Block 1	2.00	80.00	400.00	81.81	91.63

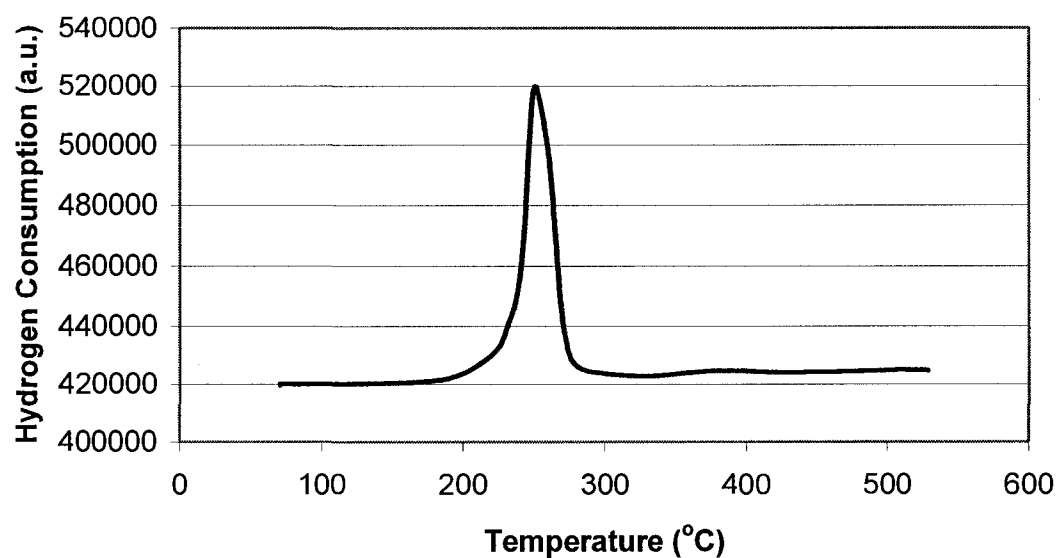


**Figure 14.** CuO/Al<sub>2</sub>O<sub>3</sub> TOC and Orange II removal experimental results

#### Catalyst 4: The Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> Catalyst

The Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> catalyst contains 41 % Cu and 32% Cr by mass. It was manufactured by Engelhard Corporation in fine powder form and was used as received. The TPR profile for this catalyst is presented in Figure 15. The TPR profile displays a single peak at 250°C. The measured surface area for this catalyst was 31 m<sup>2</sup>/g. The results of the screening experiments are displayed in Table 8.

For this catalyst, 0.13% leaching of copper was detected in collected samples indicating the catalyst was not stable for the given reaction conditions.



**Figure 15.** Temperature Programmed Reduction (TPR) profile for  $\text{Cu}_2\text{Cr}_2\text{O}_5$

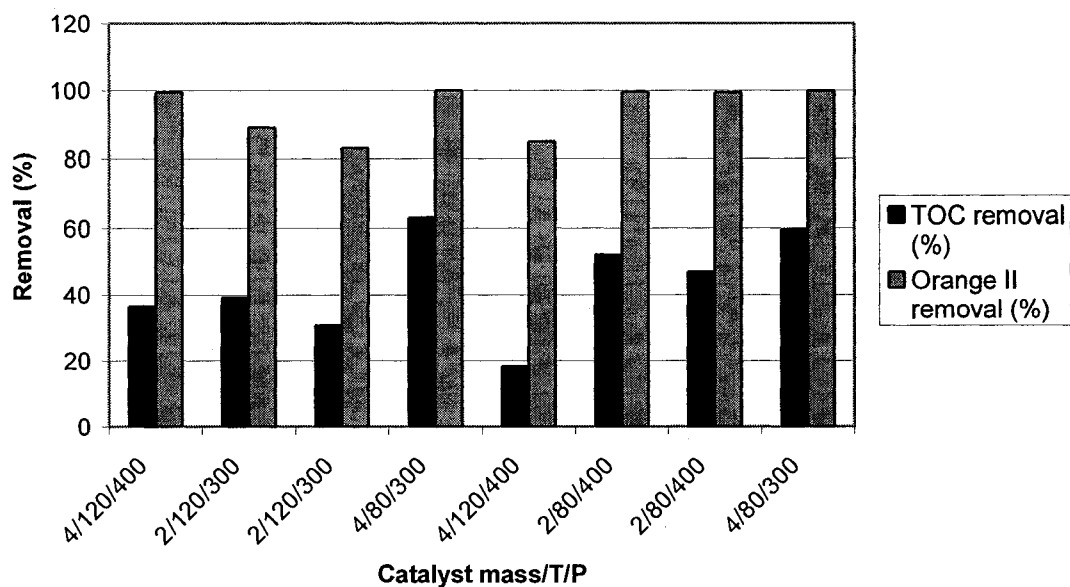
The ANOVA tables for the experimental results are presented in Appendix B.

The Model F-value of 8.27 implies the model is significant. There is only a 3.44% chance that a "Model F-Value" as large as this could occur due to noise. The model is significant with temperature being the significant model variable. As temperature increases, removal efficiency decreases.

**Table 8.** Screening experiment matrix and results for  $\text{Cu}_2\text{Cr}_2\text{O}_5$ 

	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC %	Response 2 Orange II removal %
	8	1	Block 1	4.00	120.00	400.00	36.55	99.5
	6	2	Block 1	2.00	120.00	300.00	39.29	89.14
	5	3	Block 1	2.00	120.00	300.00	30.75	83.07
	4	4	Block 1	4.00	80.00	300.00	63.1	100
	7	5	Block 1	4.00	120.00	400.00	18.35	85
	2	6	Block 1	2.00	80.00	400.00	52.15	99.57
	1	7	Block 1	2.00	80.00	400.00	47	99.34
	3	8	Block 1	4.00	80.00	300.00	59.67	99.87

Although this catalyst displayed almost complete decolorization under all treatment variable combinations, the TOC removals were low. This indicates the dye is broken into intermediates and is not completely mineralized with this catalyst. Figure 16 shows the experimental results in graphical form.



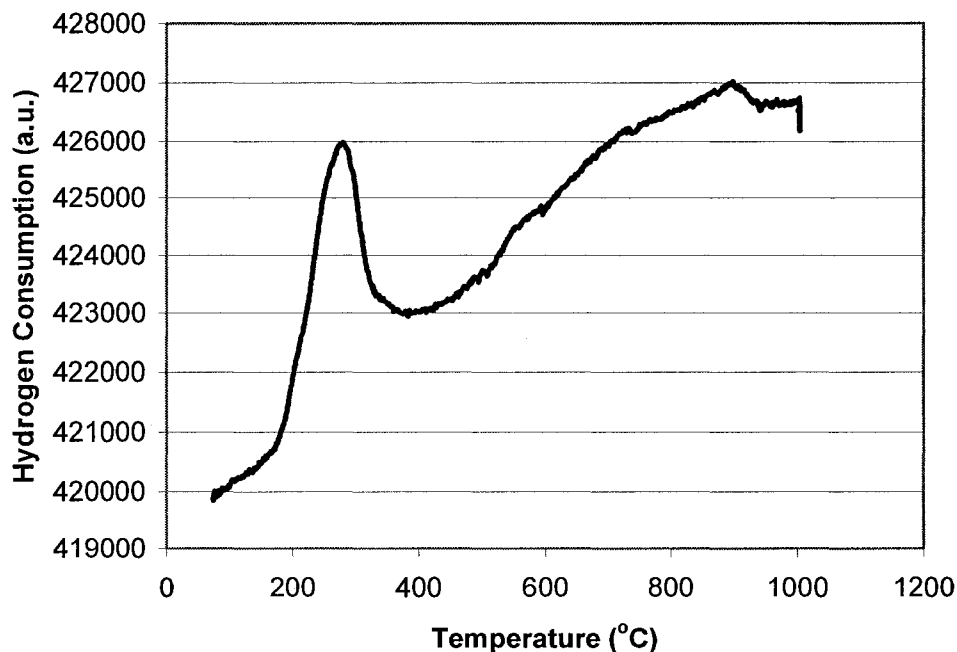
**Figure 16.**  $\text{Cu}_2\text{Cr}_2\text{O}_5$  TOC and Orange II removal experimental results

### Catalyst 5: The $\text{CuO}/\text{CeO}_2/\text{Al}_2\text{O}_3$ Catalyst

The  $\text{CuO}/\text{CeO}_2/\text{Al}_2\text{O}_3$  catalyst contains 2.5 % copper and 7.5 % ceria by mass. It was prepared at the Hampton University Chemical Engineering Laboratory. It was in spherical pellet form and was ground with a mortar and pestle, then sieved with a sieve shaker. Catalyst particles with sizes smaller than 250  $\mu\text{m}$  were used for the experiments. The TPR profile for this catalyst is presented in Figure 17. The TPR profile displays two peaks, one at 300°C, and another one (incomplete) at 900°C. The peak at lower temperature can be attributed to copper whereas the peak at higher temperature comes

from the reduction of ceria. The measured surface area for this catalyst was  $128 \text{ m}^2/\text{g}$ .

The results of the screening experiments are displayed in Table 9.



**Figure 17.** Temperature Programmed Reduction (TPR) profile for  $\text{CuO}/\text{CeO}_2/\text{Al}_2\text{O}_3$

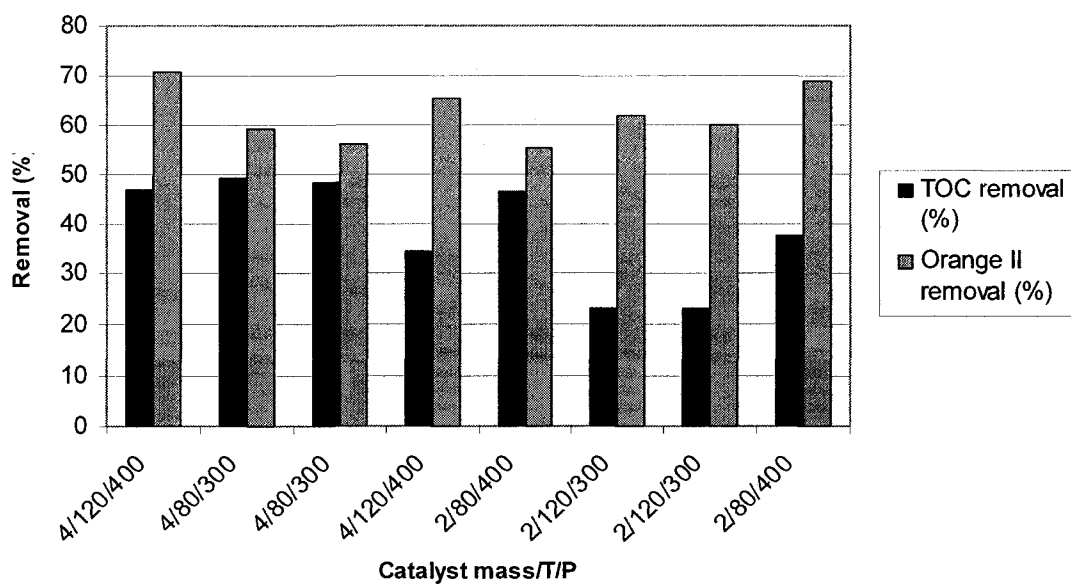
The ANOVA tables for the experimental results are presented in Appendix B. The Model F-value of 8.14 implies the model is significant. There is only a 3.54% chance a "Model F-Value" as large as this could occur due to noise.

The model is significant with catalyst mass and temperature being the significant model variables. Higher catalyst mass resulted in higher removal whereas increased temperature affected removal in a negative way due to lower dissolved oxygen concentration in solution. Figure 18 displays the experimental results in graphical form.

**Table 9.** Screening experiment matrix and results for CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

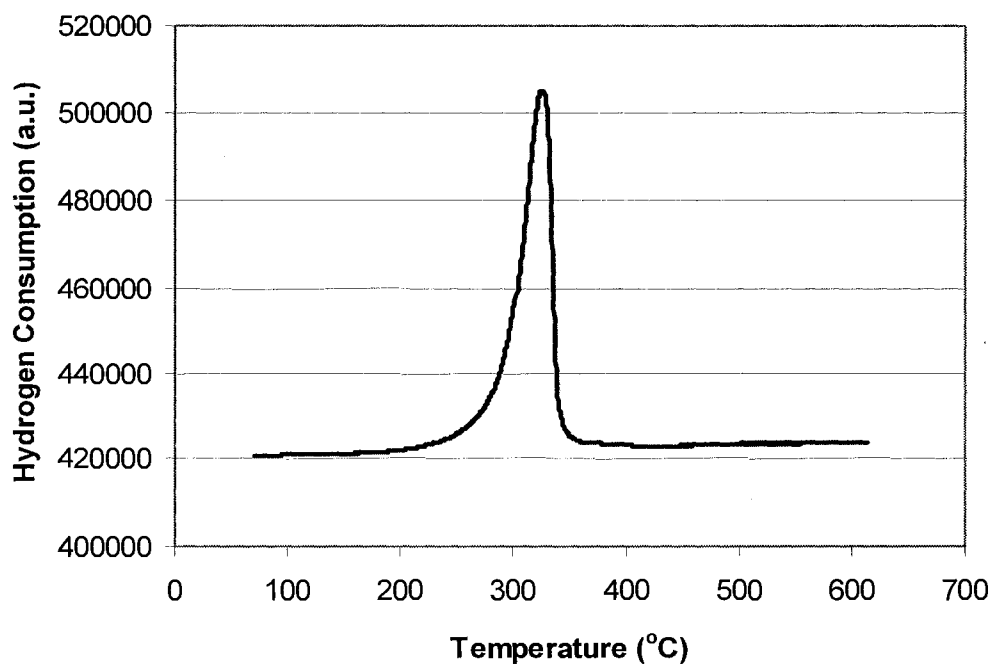
	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC rem. %	Response 2 Untitled
	7	1	Block 1	4.00	120.00	400.00	46.75	70.77
	4	2	Block 1	4.00	80.00	300.00	49.12	59.15
	3	3	Block 1	4.00	80.00	300.00	48.5	56.18
	8	4	Block 1	4.00	120.00	400.00	34.38	65.41
	2	5	Block 1	2.00	80.00	400.00	46.36	55.33
	5	6	Block 1	2.00	120.00	300.00	23.16	61.92
	6	7	Block 1	2.00	120.00	300.00	23.3	60.05
	1	8	Block 1	2.00	80.00	400.00	37.45	68.7

For this catalyst, 0.28% copper leaching was detected in collected samples,  
indicating the catalyst was unstable for given reaction conditions

**Figure 18.** CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> TOC and Orange II removal experimental results

### Catalyst 6: The $\text{MnO}_2/\text{CuO}$ catalyst

The  $\text{MnO}_2/\text{CuO}$  catalyst has a Mn/Cu molar ratio of 70/30. It was prepared at the Hampton University Chemical Engineering Laboratory. It was ground with a mortar and pestle, then sieved with a sieve shaker. Catalyst particles with sizes smaller than  $250\ \mu\text{m}$  were used for the experiments. The TPR profile for this catalyst is presented in Figure 19. The TPR profile displays a single peak at  $327^\circ\text{C}$ .



**Figure 19.** Temperature Programmed Reduction (TPR) profile for  $\text{MnO}/\text{CuO}$



**Table 10.** Screening experiment matrix and results for MnO/CuO

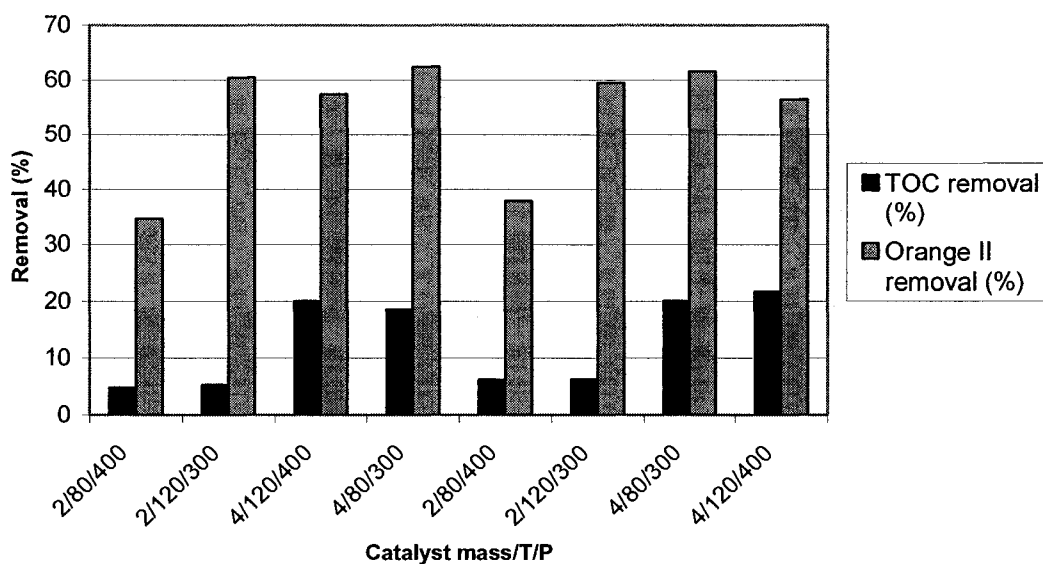
	Std	Run	Block	Factor 1 A:Catalyst	Factor 2 B:T	Factor 3 C:P	Response 1 TOC removal %	Response 2 Orange II removal %
	1	1	Block 1	2.00	80.00	400.00	5.05	34.62
	6	2	Block 1	2.00	120.00	300.00	5.41	60.48
	8	3	Block 1	4.00	120.00	400.00	20.03	57.38
	4	4	Block 1	4.00	80.00	300.00	18.6	62.44
	2	5	Block 1	2.00	80.00	400.00	6.25	37.88
	5	6	Block 1	2.00	120.00	300.00	6.33	59.45
	3	7	Block 1	4.00	80.00	300.00	20.07	61.55
	7	8	Block 1	4.00	120.00	400.00	21.79	56.47

The results of the screening experiments are displayed in Table 10. Figure 20 shows the experimental results in graphical form.

ANOVA tables for the experimental results are presented in Appendix B. The Model F-value of 146.71 implies the model is significant. There is only a 0.02% chance a "Model F-Value" as large as this could occur due to noise.

The model was significant, and the only significant variable was the catalyst mass. Reaction temperature and pressure had no effect on the removal. A possible explanation for this is that reaction TOC removal is controlled by adsorption rather than kinetics. This catalyst had relatively low removal efficiency for Orange II and almost no removal of TOC.

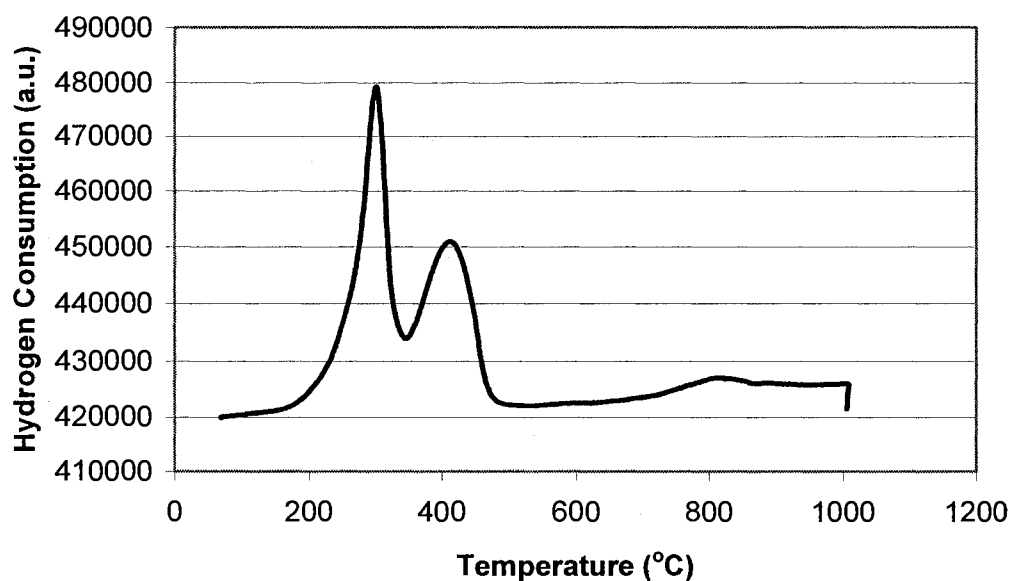
0.026 % manganese and 0.055% copper leaching was detected in samples, indicating the catalyst was not stable under reaction conditions.



**Figure 20.** MnO/CuO TOC and Orange II removal experimental results

### **Catalyst 7: The MnO<sub>2</sub>/CeO<sub>2</sub> Catalyst**

The MnO/CeO<sub>2</sub> catalyst has a Mn/Ce molar ratio of 70/30. It was prepared at the Hampton University Chemical Engineering Laboratory. It was ground with a mortar and pestle then sieved with a sieve shaker. Catalyst particles with sizes smaller than 250  $\mu\text{m}$  were used for the experiments. The TPR profile for this catalyst is presented in Figure 21. The TPR profile displays three peaks, one at 300°C, another at 400°C, and a small one at 890°C. The results of the screening experiments are displayed in Table 11.



**Figure 21.** Temperature Programmed Reduction (TPR) profile for  $\text{MnO}_2/\text{CeO}_2$

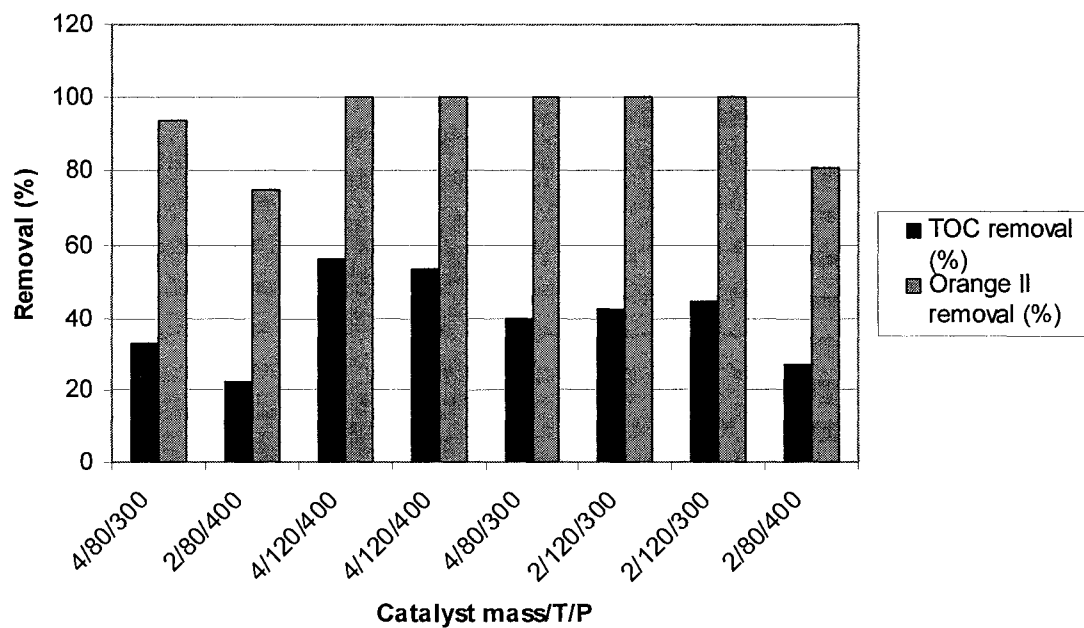
ANOVA tables for the experimental results are presented in Appendix B. The Model F-value of 31.94 implies the model is significant. There is only a 0.30% chance a "Model F-Value" as large as this could occur due to noise.

**Table 11.** Screening experiment matrix and results for  $\text{MnO}/\text{CeO}_2$

	Std	Run	Block	Factor 1 A: Catalyst	Factor 2 B: T	Factor 3 C: P	Response 1 TOC removal %	Response 2 Orange II removal %
	3	1	Block 1	4.00	80.00	300.00	33.07	93.47
	1	2	Block 1	2.00	80.00	400.00	22.39	75.11
	7	3	Block 1	4.00	120.00	400.00	56.14	100
	8	4	Block 1	4.00	120.00	400.00	53.42	100
	4	5	Block 1	4.00	80.00	300.00	40	100
	5	6	Block 1	2.00	120.00	300.00	42.61	100
	6	7	Block 1	2.00	120.00	300.00	44.78	100
	2	8	Block 1	2.00	80.00	400.00	26.87	80.64

Significant model variables are catalyst mass and reaction temperature. This catalyst was very effective for removing color from water; however the TOC removal efficiency was low. The reaction did not go to complete mineralization, but the N=N bond was broken. Increased temperature improved removal efficiency.

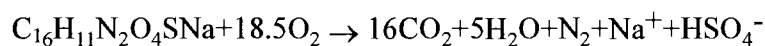
Manganese leaching (0.12%) was detected in collected samples indicating catalyst instability under reaction conditions.



**Figure 22.**  $\text{MnO}_2/\text{CeO}_2$  TOC and Orange II removal summary

## CATALYST SCREENING RESULTS

The results of the catalyst screening experiments are summarized in Figures 23-26. For all cases, Orange II removal was higher than TOC removal. As discussed before, this is due to the fact the reaction does not go through complete mineralization, and the formed intermediates contribute to the TOC, yet the disappearance of the double nitrogen bond is enough to reduce the visible color for Orange II. Also important to note is the fact that generally, increasing temperature had a negative effect on TOC removal. The possible reason for this is that at higher temperature less oxygen can be dissolved in solution. The complete mineralization reaction for Orange II oxidation can be written as:



According to the reaction stoichiometry, one mole of Orange II requires 18.5 moles of  $\text{O}_2$  to go to complete mineralization. At given reaction temperatures and pressures, dissolved oxygen amounts in solution can be calculated with Henry's Law. Table 12 shows oxygen amounts required for complete mineralization calculated through the reaction stoichiometry. The mass of Orange II used for catalyst screening experiments was 60 mg, which corresponds to 0.171 mmole of dye. Therefore, 3.17 mmoles of oxygen would be required for mineralization.

**Table 12.** Oxygen moles required for complete mineralization

mg Orange II	mole	mmole	Needed oxygen mmole
60	0.000171	0.17	3.17
80	0.000228	0.23	4.22
100	0.000285	0.29	5.28

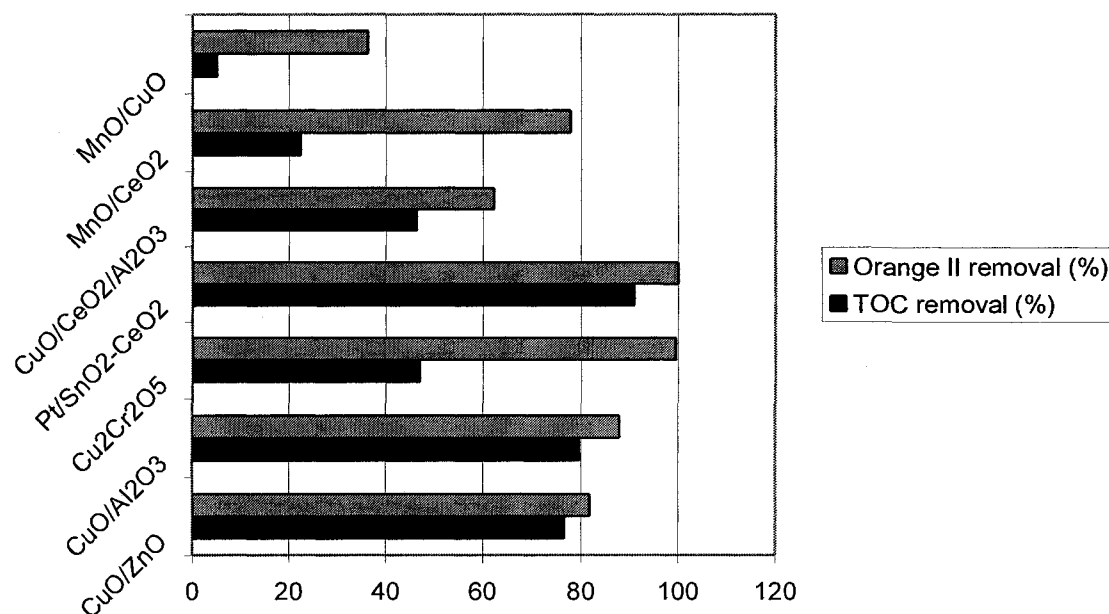
Table 13 displays the available oxygen moles in solution at temperatures ranging from 80-130 °C and pressures of 300 and 400 psig. At a temperature of 120 °C and the lower pressure of 300 psi, there should be 4.20 mmoles of oxygen in solution which is only about 25% in excess compared to the 3.169 mmoles calculated through reaction stoichiometry. Experimental results suggest the reaction might be oxygen concentration limited. Another possible explanation for this occurrence is that different reaction pathways are followed at different temperatures with higher temperatures resulting in more refractory intermediates that are formed.

**Table 13.** Available oxygen amounts for different temperatures and pressures

Temperature (°C)	Temp. (K)	k (L atm/mol)	300 psig	400 psig
			Oxygen (mmol)	Oxygen (mmol)
80	353	1870.919	6.86	9.04
90	363	2136.349	6.01	7.92
100	373	2422.144	5.30	6.98
120	393	3054.433	4.20	5.54
130	403	3400.53	3.78	4.98

In Figures 23 through 26, experimental results for the seven screened catalysts are displayed together, under different reaction variable combinations.

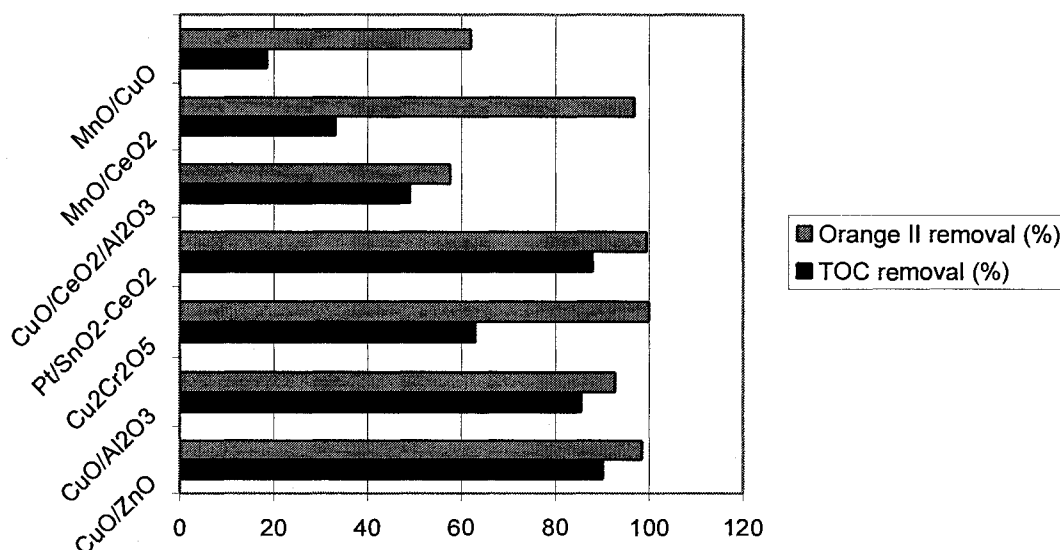
Figure 23 displays results for a reaction temperature of 80°C, reaction pressure of 400 psig, with 2 grams of catalyst in reactor. Under these conditions, highest Orange II removal of 100% is achieved by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub>, and Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> catalysts. Highest TOC removal is achieved by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub> with 90% removal followed by the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst with 80% removal.



**Figure 23.** TOC and Orange II removal for 400 psig, 80°C and 2 g catalyst

Figure 24 displays results for a reaction temperature of 80°C, reaction pressure of 300 psig, with 4 grams of catalyst in reactor. Under these conditions, highest Orange II removal of 100% is achieved by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub>, and Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> catalysts. Highest

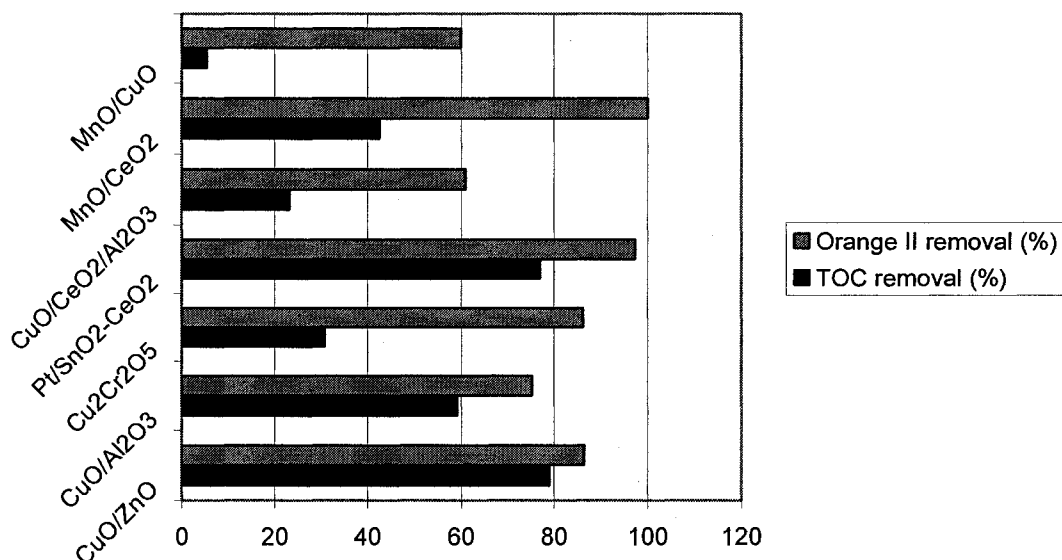
TOC removal is achieved by the CuO/ZnO catalyst with 90% removal followed by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub> and CuO/Al<sub>2</sub>O<sub>3</sub> catalysts with 80% removal.



**Figure 24.** TOC and Orange II removal for 300 psig, 80°C and 4 g catalyst

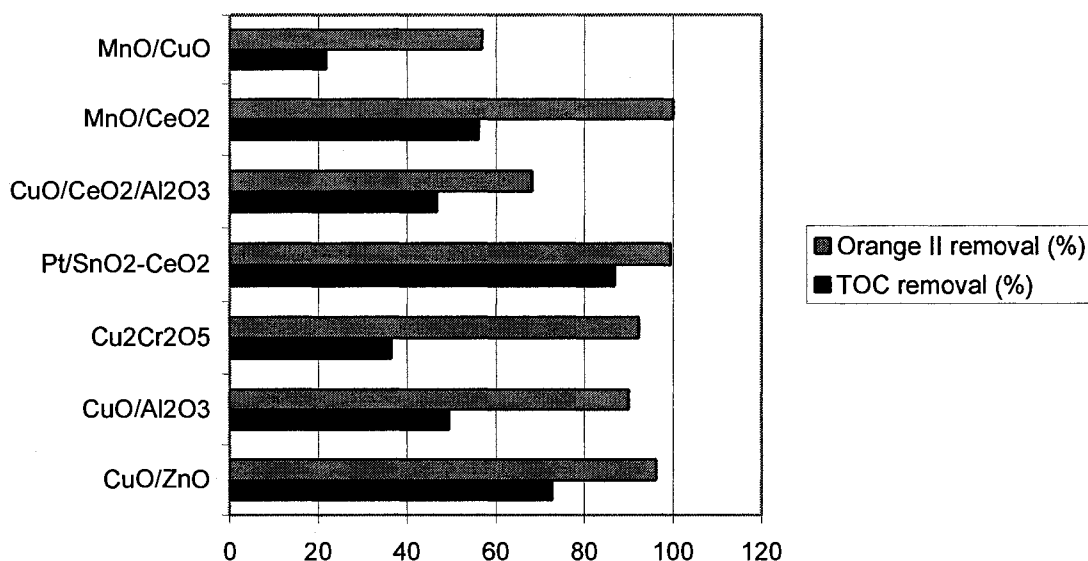
Figure 25 displays results for a reaction temperature of 120°C, reaction pressure of 300 psig, with 2 grams of catalyst in reactor. Under these conditions, highest Orange II removal of 100% is achieved by the MnO<sub>2</sub>/CeO<sub>2</sub> catalyst. Highest TOC removal is achieved by the CuO/ZnO catalyst with 85% removal followed by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub> catalyst.





**Figure 25.** TOC and Orange II removal for 300 psig, 120°C and 2 g catalyst

Figure 26 displays results for a reaction temperature of 120°C, reaction pressure of 400 psig, with 4 grams of catalyst in reactor. Under these conditions, highest Orange II removal of 100% is achieved by the MnO<sub>2</sub>/CeO<sub>2</sub> and Pt/SnO<sub>2</sub>/CeO<sub>2</sub> catalysts. Highest TOC removal is achieved by the Pt/SnO<sub>2</sub>/CeO<sub>2</sub> catalyst.



**Figure 26.** TOC and Orange II removal for 400 psig, 120°C and 4 g catalyst

## DECISION MATRIX FOR CATALYST SELECTION

A decision matrix was constructed to select the best catalyst alternative among the seven screened catalysts. TOC and Orange II removal efficiency as well as leaching, potential environmental impacts (toxicity), and cost were used as the decision making criteria. Orange II and TOC removal efficiencies and environmental impact were given a higher weight of four, whereas leaching and cost were given a lower weight of two. The reasoning behind this is if a catalyst performs exceptionally well, there are no other alternatives, and the pollutants have to be removed, then cost would be a secondary criterion for catalyst selection. Leaching was given a lower weight because the potential environmental impact is incorporated into the toxicity criterion, and if the catalyst is reasonably priced then replacing the catalyst may not be an important issue. However, a

catalyst that does not perform well cannot be used even if it has a cost advantage. Each catalyst was assigned a value of one to five for each criterion, with one indicating poor performance (i.e. high leaching, or low treatment efficiency), and five indicating good performance (i.e. no leaching, high treatment efficiency). The matrix is presented in Table 14.

**Table 14.** Decision matrix for catalyst selection

	<i>Pt/SnO<sub>2</sub></i>	<i>Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub></i>	<i>CuO/ CeO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub></i>	<i>CuO/ Al<sub>2</sub>O<sub>3</sub></i>	<i>CuO/ ZnO</i>	<i>MnO<sub>2</sub>/ CeO<sub>2</sub></i>	<i>MnO<sub>2</sub>/ CuO</i>
Color	5x2	5x2	1x2	4x2	5x2	5x2	1x2
Removal							
TOC	5x2	2x2	3x2	5x2	5x2	1x2	1x2
removal							
Cost	1x1	3x1	4x1	5x1	3x1	2x1	4x1
Leaching	N/A	3x1	1x1	5x1	4x1	3x1	3x1
Toxicity	2x2	2x2	3x2	5x2	5x2	4x2	5x2
<b>Total</b>	26-30	24	21	<b>38</b>	37	25	21

The cost comparison for the catalysts was made by calculating the price of metal in one kilogram of catalyst using metal prices from the metal exchange market. The most expensive catalyst was the Pt/SnO<sub>2</sub>, and the cheapest was CuO/Al<sub>2</sub>O<sub>3</sub>.

Although the leaching values reported for the catalysts seem small when reported in terms of percent metal, the detrimental effects of catalyst leaching cannot be neglected. This is due to the fact the catalyst masses tested were in the grams range whereas

discharge limits on metals are always in the mg/l range. As an example, the CuO/ZnO had only 0.016 % leaching of copper. This corresponds to a concentration of 1.06 mg/l copper in the effluent. For comparison purposes, the Hampton Roads Sanitation District's Industrial Wastewater Discharge Regulations [93] for some metals (monthly average discharge limitations) are presented in Table 15. Depending on the volume of production, even with 0.016% leaching, there is a possibility of being in violation of regulations.

**Table 15.** Monthly average discharge limitations for some metals (from Hampton Roads Sanitation District Industrial Wastewater Discharge Regulations, parameters in mg/l, effluent flow in thousand gallons per day )

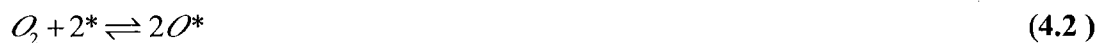
<i>Parameter</i>	<i>0-10K</i>	<i>10-20K</i>	<i>20-30K</i>	<i>30-40K</i>	<i>40-200K</i>	<i>200-400K</i>
Copper	10.0	8.0	6.0	4.0	2.0	1.0
Chromium	10.0	8.0	6.0	4.0	2.0	1.0
Silver	1.25	1.00	0.75	0.50	0.25	0.13
Zinc	10.0	8.0	6.0	4.0	2.0	1.0

The best alternative catalyst in this study was the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst. The kinetics of Orange II and TOC removals were investigated with this catalyst.

## Orange II Lumped Parameter Kinetic Model Derivation

The oxidation of Orange II is a very complex reaction where numerous different intermediates are formed. Appendix C lists intermediates of Orange II reported in literature. A kinetic model that predicts the disappearance rate of this compound would be useful for understanding of reaction mechanisms; however, due to the complex nature of the reaction, a modeling approach that takes into account not only the disappearance of Orange II but also the intermediates formed during reaction is more appropriate. Therefore, in the current work, the rate law is expressed by means of a lumped parameter, total organic carbon (TOC), which accounts for all organic species present in the reactor at a given time.

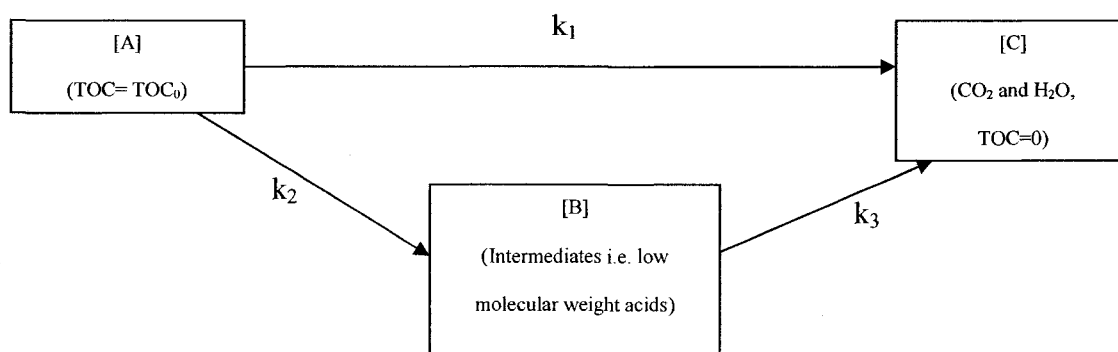
Catalytic oxidation rates are frequently modeled by the classic Langmuir-Hinshelwood kinetics where an irreversible surface reaction between the adsorbed reactants (dye and oxygen in this case) is the rate controlling step. Such a model is derived through the mechanism represented below by equations 4-1 through 4-4.





In the above reactions, OII represents the Orange II dye molecule, \* represents a free catalyst site, and OII\* is the dye adsorbed on the catalyst site. P is a product of the oxidation reaction; in the case of current study, mineralization end products or intermediates that are formed. Since the adsorption and desorption steps happen relatively fast compared to the reaction taking place on the catalyst surface, the surface reaction is the rate controlling step, and the model is written in terms of this reaction.

The reaction mechanism for the disappearance of Orange in terms of TOC is depicted as below for the model proposed in this study:



**Figure 27.** Reaction mechanism for the oxidation of Orange II in terms of TOC

In the model above, [A] is the TOC concentration of Orange II in the solution. At the beginning of the reaction,  $[TOC]_0 = [A]_0$ , meaning all the TOC in the solution comes from the dye itself. As the reaction proceeds, Orange II is oxidized, either into complete mineralization products, [C], or intermediates [B]. The TOC concentration of complete

mineralization products [C] is zero, as there is no organic carbon left when the reaction goes to mineralization. The TOC concentration of intermediates at any time in the reaction is [B], and the model assumes as the reaction proceeds these intermediates also are oxidized into mineralization end products. The  $k_1$ ,  $k_2$  and  $k_3$  are the pseudo reaction rate constants for the complete mineralization of Orange II, oxidation of Orange II into intermediates, and the oxidation of intermediates into mineralization end products, respectively. The kinetic model is derived assuming every step of the reaction is first order with respect to TOC concentration.

The results of the screening experiments revealed the reaction is dependent on temperature and as the temperature increases, TOC removal decreases. Such an occurrence indicates the reaction is oxygen-limited. Thus, the order of oxygen concentration must be accounted for. The  $k_1$ ,  $k_2$ , and  $k_3$  values represented in the model in Figure 27 are pseudo reaction rate constants and stand for:

$$k_1 = k'_1 [O_2]^{\alpha_1} \quad (4.5)$$

$$k_2 = k'_2 [O_2]^{\alpha_2} \quad (4.6)$$

$$k_3 = k'_3 [O_2]^{\alpha_3} \quad (4.7)$$

If there is excess oxygen available in solution for the reaction to take place, then the effect of oxygen concentration on reaction rate can be neglected, assuming the reaction is zero-order with respect to oxygen. In Section IV.II, it was indicated that according to values computed from the reaction stoichiometry, and Henry's Law calculations, under the reaction conditions, there was some excess oxygen dissolved in solution. However, the negative effect of increasing temperature on reaction rate indicates the reaction is oxygen-limited.

The temperature dependence of the  $k'$  values in equations 4.5-4.7 can be defined by the Arrhenius equation as follows:

$$k' = k_0 e^{\frac{-E_a}{RT}} \quad (4.8)$$

where,

$k_0$ =pre-exponential factor, same unit as  $k'$

$E_a$ =activation energy of reaction, J/mol

$R$ =universal gas constant, 8.314472 J/K/mol

$T$ =reaction temperature, K

In Figure 27, for the oxidation of Orange II into mineralization end products and intermediates, the disappearance of Orange II in terms of TOC concentration in time can be written as:

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \quad (4.9)$$

The change in the TOC concentration of intermediates with time can be written as:

$$\frac{d[B]}{dt} = k_2[A] - k_3[B] \quad (4.10)$$

where the intermediates are being formed through A being oxidized and are being consumed by further oxidation into mineralization end products. To compute the concentration of dye at any time during the reaction, we can solve Equation 4-8 as:



$$\ln \frac{[A]_0}{[A]} = (k_1 + k_2)t \quad (4.11)$$

$$[A] = [A]_0 e^{-(k_1 + k_2)t} \quad (4.12)$$

To compute the concentration of intermediates at any time, we can rearrange Equation 4-9 as:

$$\frac{dB}{dt} + k_3[B] = k_2[A]_0 e^{-(k_1 + k_2)t} \quad (4.13)$$

This is a differential equation in the form:

$$\frac{dy}{dx} + yP(x) = Q(x) \quad (4.14)$$

where,

$$y = [B] \quad (4.15)$$

$$Q(x) = k_2[A]_0 e^{-(k_1 + k_2)t} \quad (4.16)$$

$$P(x) = k_3 \quad (4.17)$$

The solution for this differential equation is:

$$\text{Sol}^n: y(x) = \frac{1}{I.F.} \int Q(x) \cdot I.F. dx \quad (4.18)$$

The integrating factor is computed as:

$$\text{Int.Fact.} = e^{\int P(x) dx} = e^{\int k_3 dt} = e^{(k_3 t + C)} \quad (4.19)$$

So the solution for B(t) becomes:

$$B(t) = \frac{[A]_0 k_2 e^{-(k_1 + k_2 - k_3)t - k_3 t}}{-k_1 - k_2 + k_3} + e^{-k_3 t} M \quad (4.20)$$

At t=0, [B]=0, there are no intermediates at the beginning of reaction. The constant M is calculated to be:

$$M = \frac{[A]_0 k_2}{k_1 + k_2 - k_3} \quad (4.21)$$

Substituting M in place, [B] becomes:

$$[B] = \frac{[A]_0 k_2 (e^{-(k_1 + k_2)t} - e^{-k_3 t})}{-k_1 - k_2 + k_3} \quad (4.22)$$

At any given time during the reaction, the ratio of TOC remaining in the reactor to the initial TOC concentration can be written as:

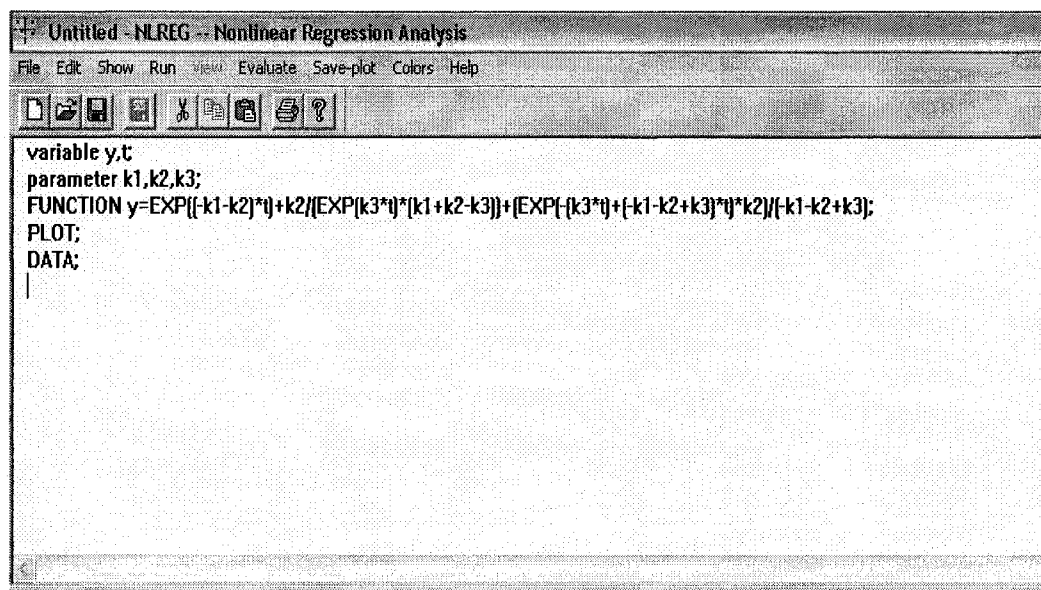
$$\frac{[TOC]}{[TOC]_0} = \frac{[A] + [B]}{[A]_0} \quad (4.23)$$

meaning the total TOC concentration comes from the addition of the TOC of dye still left in solution and the TOC concentrations of the intermediates formed.

Thus the model becomes;

$$\frac{[TOC]}{[TOC]_0} = e^{-(k_1+k_2)t} + \frac{k_2(e^{-(k_1+k_2)t} - e^{-k_3t})}{-k_1 - k_2 + k_3} \quad (4.24)$$

The reaction rate constants  $k_1$ ,  $k_2$ ,  $k_3$  for the reaction can be determined by substituting experimental  $[TOC]/[TOC]_0$  values in the equation with respect to time, and performing a non-linear regression analysis. This was accomplished by using NLREG, a non-linear regression and curve fitting software. A program was written to be entered into the software. A snapshot of the program screen can be seen in Figure 28.



**Figure 28.** Snapshot of nonlinear regression analysis software NLREG

In this program, the defined variables were  $[\text{TOC}]/[\text{TOC}]_0$  which was depicted as  $y$  in the program and the time,  $t$  when the sample was taken. The parameters to be solved for were entered in as  $k_1$ ,  $k_2$ ,  $k_3$ , and the function was entered in appropriate form as derived for the model. Experimental data were entered in the program, and the program was run to compute the  $k_1$ ,  $k_2$ ,  $k_3$  values. The results are discussed in the following section.

## KINETICS EXPERIMENTAL RESULTS

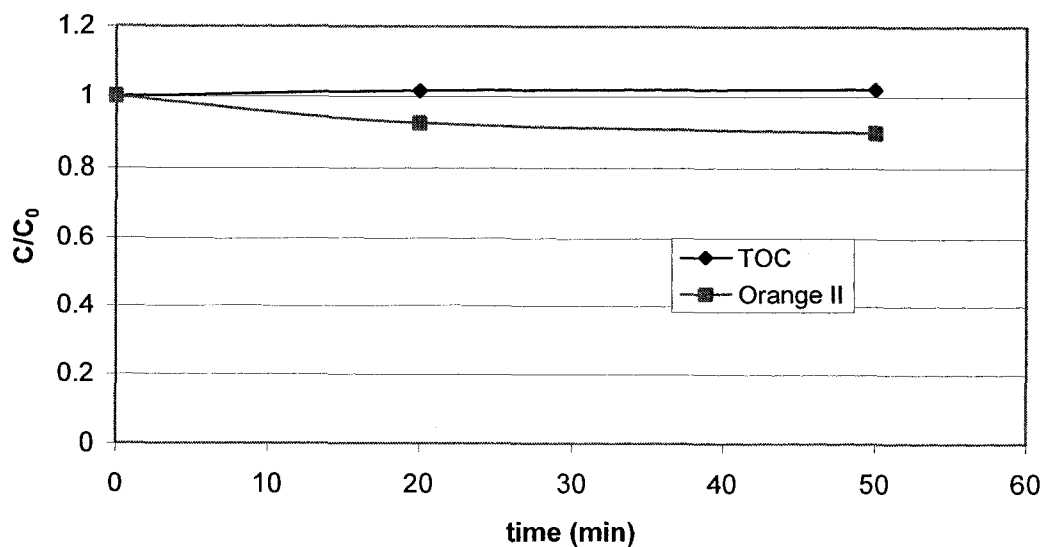
Reaction kinetics for the oxidation of Orange II dye with the chosen  $\text{CuO}/\text{Al}_2\text{O}_3$  catalyst was investigated by taking and analyzing samples at different time intervals under different reaction conditions. A series of control experiments were conducted to confirm the reaction mechanism. The effects of catalyst concentration, temperature, and pH on reaction kinetics were investigated. The pseudo reaction rate constants  $k_1, k_2, k_3$ , the temperature dependence of the actual reaction rate constants  $k_1', k_2', k_3'$ , and the activation energies for the reaction pathways were computed. The order of the reaction with respect to oxygen was determined. Agreement between proposed model and experimental values was evaluated.

### Control experiments

Three types of control experiments were conducted to confirm the reaction mechanism: the WAO of Orange II without catalyst, thermal degradation of Orange II with no oxygen or catalyst, and the investigation of adsorption of dye on catalyst without heat or oxygen.

The first of these experiments was to investigate the WAO of Orange II without a catalyst. The 800 ml of 100 mg/l Orange II dye was placed in the reactor, and the reactor was closed and heated up to 80 °C and 120°C in two different experiments. Oxygen was turned on when the reaction temperature was reached, and the reactor was stirred. No reduction in TOC concentration was observed in either case although the Orange II

concentration decreased about 10% in both cases. A potential reason for the decline in Orange II concentration might be due to a reaction between the reactor wall which is made of stainless steel and Orange II. The fact that the TOC concentration does not decrease is an indication of Orange II breaking down into other organic intermediates rather than mineralization end products. In terms of TOC concentration, the WAO of Orange II does not take place, but in terms of Orange II concentration, the reaction proceeds even if very slowly compared to the catalyzed reaction.



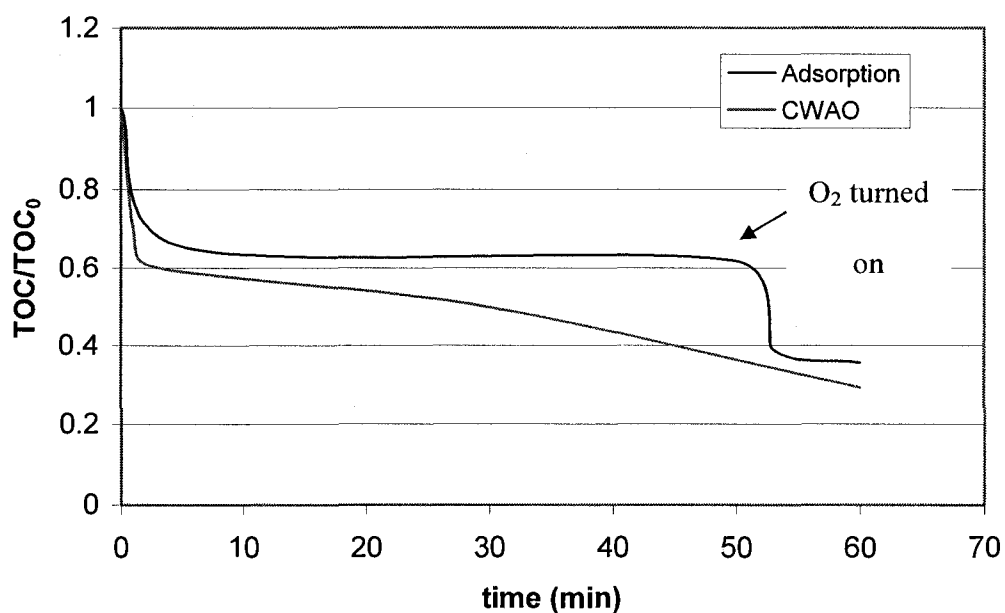
**Figure 29.** Changes in total organic carbon (TOC) and Orange II concentrations during the wet air oxidation (WAO) of Orange II without catalyst at 120°C

Thermal degradation of Orange II has been reported in literature before [80] although at much higher temperatures of 180-240°C than temperatures tested in the current study. Experiments were conducted to test the thermal degradation of Orange II under current reaction conditions, up to 120°C. For these experiments, the reactor was

closed and purged with nitrogen gas then heated up under nitrogen atmosphere. When reaction temperature was reached, reactor was stirred for 120 minutes. No thermal degradation of Orange II was observed indicating the dye was chemically stable under reaction conditions in the absence of oxygen and catalyst.

The adsorption of Orange II onto  $\text{CuO}/\text{Al}_2\text{O}_3$  was investigated to confirm the decreases in Orange II or TOC concentrations were not happening solely through adsorption of dye onto catalyst. For these control experiments, dye solutions were placed in the reactor with catalyst under nitrogen atmosphere at room temperature. The reactor was stirred, and samples were collected at time intervals. It was observed that in the first five minutes, there was about a 35% decrease in initial TOC concentration which declined only slightly during the remaining 45 minutes of reaction. At the fiftieth minute oxygen gas was turned on, and a rapid decline in TOC concentration occurred in three minutes confirming the TOC removal mechanism was not solely adsorption onto the catalyst surface. Some adsorption of dye on catalyst is expected since for a catalyzed reaction to take place, the reactants must be adsorbed onto the catalyst surface. The results for the adsorption experiment are displayed in Figure 30.

It is interesting to note that at the end of 60 minutes of reaction time for both cases, the total TOC removal values were very close. One possible explanation for this occurrence is that when the dye adsorbs onto the catalyst surface, it breaks down into smaller molecules that are easier to oxidize.

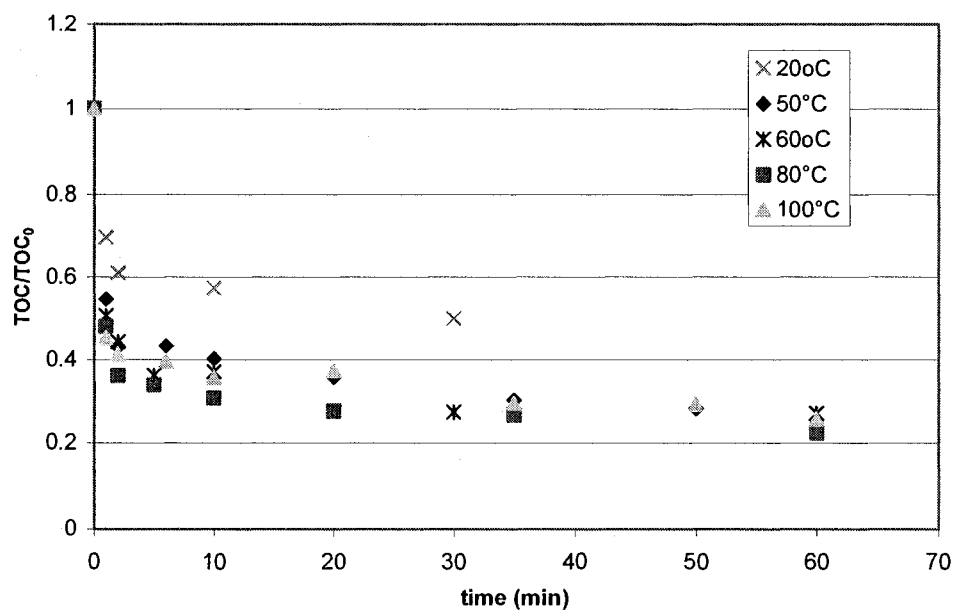


**Figure 30.** Adsorption of Orange II onto catalyst compared with catalytic wet air oxidation (CWAO) at room temperature

### Effect of Temperature on Reaction Kinetics

The effect of temperature on reaction kinetics was investigated by running a series of experiments at different reaction temperatures, ranging from 20°C to 100°C. The pseudo reaction rate constants,  $k_1$ ,  $k_2$ , and  $k_3$  were computed for each reaction temperature as described in Section IV.IV.I with non-linear regression.





**Figure 31.** TOC remaining for the catalytic wet air oxidation (CWAO) of Orange II at different reaction temperatures

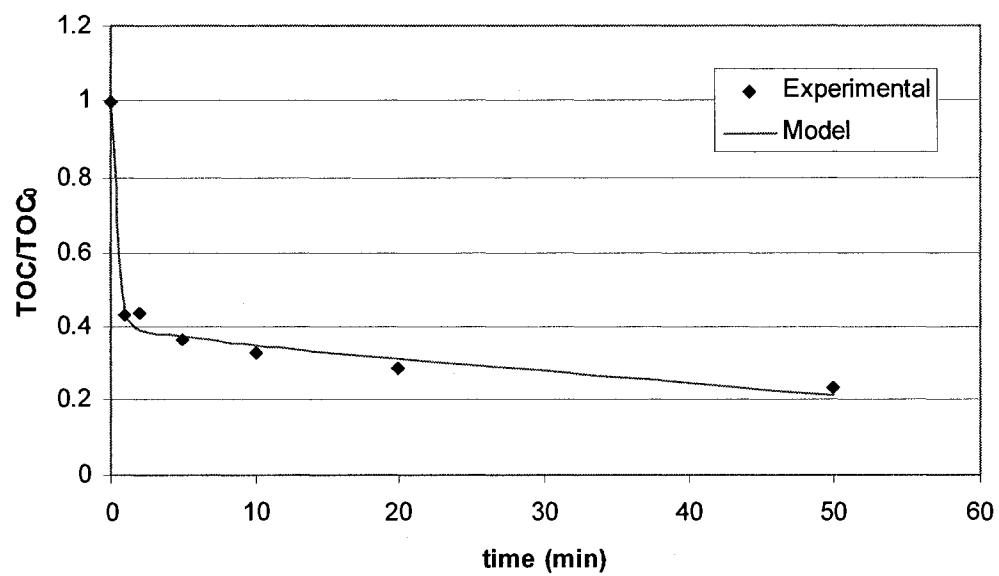
The catalytic oxidation of Orange II had no observed induction period. Even at a temperature of 20°C, the reaction proceeded very fast as soon as oxygen was introduced into the reactor. Table 16 shows the  $k_1$ ,  $k_2$ , and  $k_3$  values computed for each reaction temperature.

**Table 16.** Pseudo reaction rate constant values computed for different temperatures

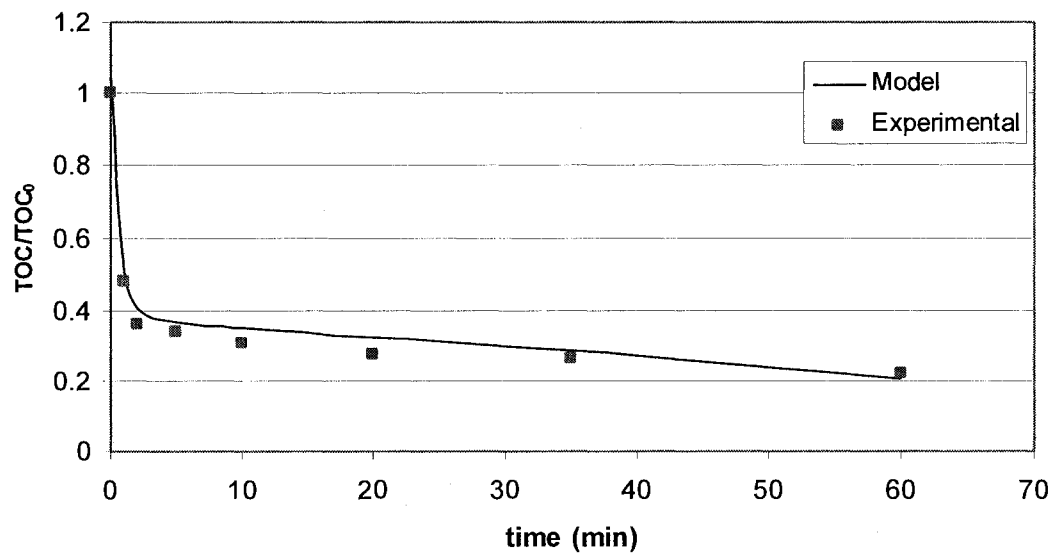
<i>Temperature (°C)</i>	<i>k<sub>1</sub> (min<sup>-1</sup>)</i>	<i>k<sub>2</sub> (min<sup>-1</sup>)</i>	<i>k<sub>3</sub> (min<sup>-1</sup>)</i>
20	0.672	1.177	0.011
50	0.948	0.732	0.010
60	0.932	0.584	0.007
80	1.021	0.519	0.008
100	1.441	0.972	0.007

The pseudo reaction rate constant for the complete mineralization reaction  $k_1$ , shows an increasing trend with increasing temperature. However, for the production of intermediates,  $k_2$  values decrease as temperature increases up to 100°C which indicates reaction rate slows down at higher temperatures. This outcome confirms that the reaction is oxygen-limited. The increase of rate at 100°C might be due to a different reaction pathway occurring at this temperature with different intermediates being formed compared to lower temperatures. The decreasing trend observed with  $k_2$  is also observed with  $k_3$  although the  $k_3$  values are much smaller, indicating a very slow reaction rate compared to  $k_1$  and  $k_2$ . Intermediates that are expected to form in the oxidation of Orange II may be resistant to oxidation at such low reaction temperatures leading to low reaction rate constant values. It has been reported in literature that low molecular acids may be formed during the oxidation of Orange II, and in the case of the oxidation of low molecular weight organic acids, high reaction temperatures of at least 200°C are required for mineralization [45, 46, 48-54, 56, 72-74, 86, 94-96].

(a)



(b)



**Figure 32.** Model predicted versus experimental data for TOC remaining (a) at 80°C and (b) at 60°C for the catalytic wet air oxidation of Orange II.

Figure 32 depicts the results of experimental data versus the model predicted values from computed k values at 60 and 80°C. There was very good agreement between the experimental and model predicted values with 99% of variance explained from the non-linear regression results. Program outputs for k value computation are presented in Appendix D.

The temperature dependence of the reaction rate constants, activation energies, and the order of the reaction with respect to oxygen were also computed with non-linear regression. Combining equations 4.5-4.7 with 4.8, k values can be written as:

$$k_1 = k_0 e^{\frac{-E_a}{RT}} [O_2]^{\alpha_1} \quad (4.25)$$

$$k_2 = k_0 e^{\frac{-E_a}{RT}} [O_2]^{\alpha_2} \quad (4.26)$$

$$k_3 = k_0 e^{\frac{-E_a}{RT}} [O_2]^{\alpha_3} \quad (4.27)$$

where the  $E_a$ ,  $k_0$ , and  $\alpha$  values are different for each reaction pathway. Non-linear regression analysis with three known variables, the pseudo-rate constants, reaction temperatures, and oxygen concentrations in reactor, and three parameters to be solved for,  $E_a$ ,  $k_0$ , and  $\alpha$  yielded the following relationships:

$$k_1 = 44.21 e^{\frac{-8417}{RT}} [O_2]^{0.197} \quad (4.28)$$

$$k_2 = 48341 e^{\frac{-11857}{RT}} [O_2]^{1.79} \quad (4.29)$$

$$k_3 = 19.87 e^{\frac{-9887}{RT}} [O_2]^{1.06} \quad (4.30)$$

These results confirm the reaction is indeed oxygen limited, and the dependence of the rate on oxygen concentration is far greater for intermediates formation and further oxidation of intermediates. The intermediate formation reaction shows close to a second order reaction with respect to oxygen concentration. Activation energies computed are listed in Table 17.

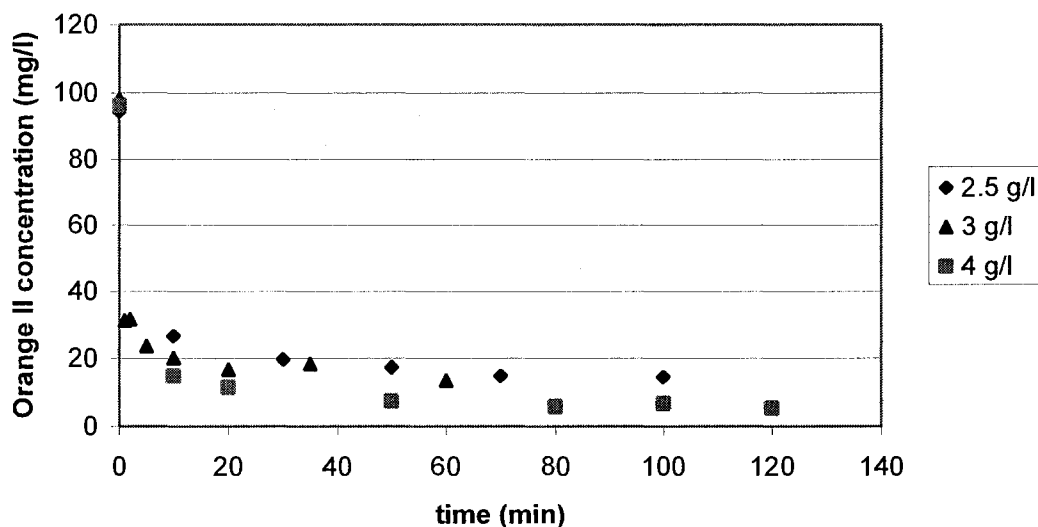
**Table 17.** Activation energy values for the reactions in lumped-parameter kinetic model

<i>Reaction</i>	<b>Activation energy (J/mol)</b>
Orange II to complete mineralization	8417
Orange II to intermediates	11857
Intermediates to complete mineralization	9887

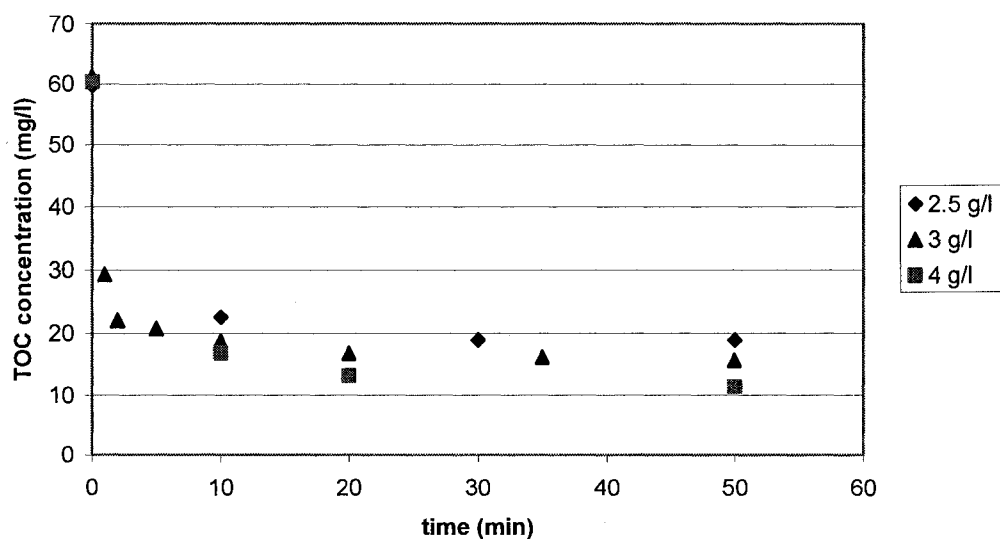
The dependence on oxygen concentration accounts for the slower reaction rates at higher temperatures. This information can be used successfully to drive the reaction to complete mineralization rather than intermediates by optimizing the oxygen concentration in the reactor. Through the screening experiments, it was already determined the pressure had no effect on the model within the variable ranges tested. The pressure in the reactor could be reduced to an optimum value to yield lower dissolved oxygen concentrations enough to oxidize Orange II, thus controlling which way the reaction proceeds as well as reducing operation costs.

## Effect of Catalyst Concentration on Reaction Kinetics

The effect of catalyst loading on reaction kinetics was examined by running experiments with different catalyst concentrations of 2.5, 3, and 4 g/l. Increasing the catalyst concentration in the reactor led to higher Orange II and TOC removal. This is expected as more catalyst means more surface area where the reactants can adsorb and react. Figures 33 and 34 display the change in Orange II and TOC concentrations with respect to time for different catalyst concentrations. Between the 2.5 g/l and 4 g/l catalyst concentrations, there was about 10 % difference in the final TOC concentrations.



**Figure 33.** Change in Orange II concentration for the catalytic wet air oxidation of Orange II with different catalyst concentrations.



**Figure 34.** TOC removal for the catalytic wet air oxidation of Orange II with different catalyst concentrations.

### Effect of pH on Reaction Kinetics

Herrera et al. studied the speciation of Orange II with changing pH. They found that at pH values higher than 8.0 speciation of Orange II gradually changed [97].

Kinetics of Orange II oxidation under pH values of 3.0, 5.0 and 9.0 were investigated for the current study. The acidic pH of 3.0 was achieved by adding 0.1 N HCl to the Orange II solution drop by drop while stirring the solution and monitoring the pH. The basic pH of 9.0 was achieved by adding 1 N NaOH to the dye solution drop by drop and stirring the mixture while monitoring the pH. The pH 5.0 was the pH of Orange II solution without any addition of acid or base. For the basic pH of 9.0, as soon as the

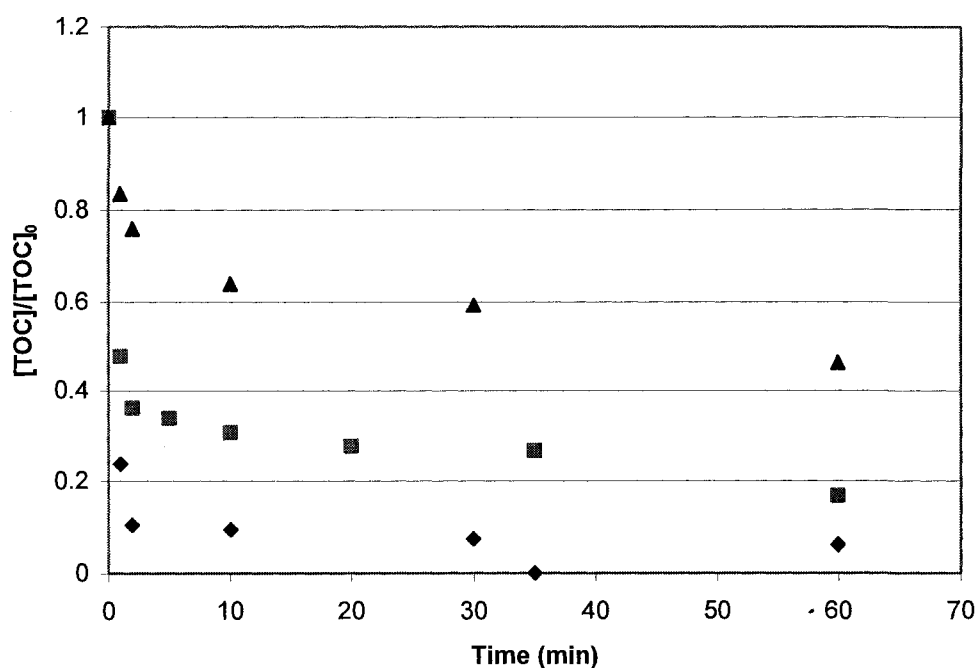
pH value exceeded 8.0, the dye solution started turning into a dark red color rather than orange. This might be due to the speciation change of dye above a pH of 8.

It was observed that the lower pH value of 3.0 yielded a TOC and Orange II removal of 95% after 60 minutes of reaction time whereas with the basic pH of 9 the removal was only 50%.

Addition of strong acids to solution lead to an increase of  $H^+$  ions in solution, possibly leading to the hydrogenation of carbonyl groups.

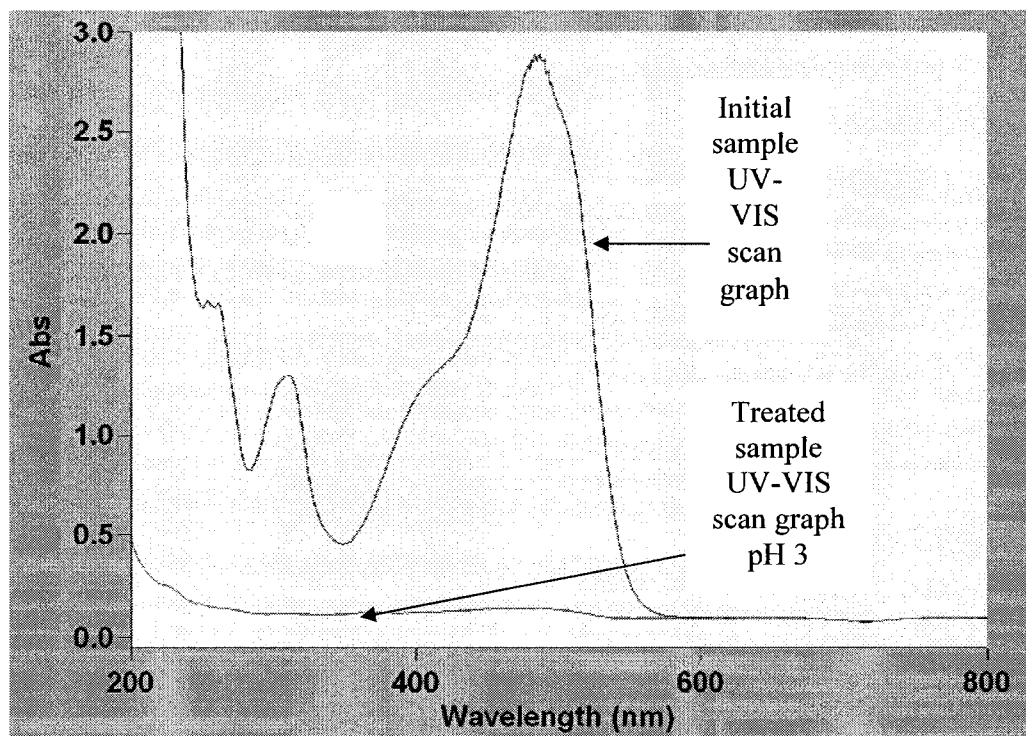
Although at lower pH the removal of Orange II and TOC are high, 1.05 % copper leaching was detected in solution as opposed to 0.00145% detected when no acid was added. This leads to concerns about losing the active metal in the catalyst under more acidic conditions leading to lower removal capacity and also exceeding discharge limits for copper. In addition to leaching concerns, pH adjustment requirement also leads to increased material and operation costs.





**Figure 35.** TOC remaining with time at pH values of 3,5, and 9 for the catalytic wet air oxidation (CWAO) of Orange II.

In Figure 36, the UV-VIS scan of the treated sample is displayed along with the 50 mg/l dye absorbance scan. At pH 3.0, Orange II was completely degraded as proved by the disappearance of the peak at 486nm completely, and the fact that TOC removal was 95%, suggests the reaction went to complete mineralization.



**Figure 36.** UV-VIS absorbance scan graph for initial sample and treated sample at pH 3

## CHAPTER V

### SUMMARY AND CONCLUSIONS

In this chapter, the summary and concluding remarks for the current study are presented. Opportunities for future research are discussed.

### SUMMARY AND CONCLUSIONS

#### Summary

Elevated concentrations of dyes in waterways cause numerous problems. Color removal has become a challenging aspect of industrial wastewater treatment. The objective of this study was to investigate the CWAO of Orange II containing wastewaters in a batch autoclave reactor. Seven metal-based heterogeneous catalysts, CuO/ZnO, CuO/Al<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub>, Pt/SnO<sub>2</sub>/CeO<sub>2</sub>, CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>/CeO<sub>2</sub>, and MnO<sub>2</sub>/CuO were screened for their efficiency in removing Orange-II dye from synthetically prepared wastewaters through catalytic oxidation. A one-half fractional factorial design of the 2<sup>k</sup> design was utilized for the screening experiments. Three factors were of interest, the catalyst mass in reactor, reaction temperature, and pressure, each at two levels. Four treatment combinations for each catalyst were tested. All experiments were run in duplicate to verify the reproducibility of the data, thus eight experiments were run for each catalyst, resulting in 56 total screening experiments. The experiment order was

randomized to avoid systematic errors. TPR profile for each catalyst was utilized to help interpret experimental results.

Dissolved metal concentrations in treated samples were measured as an indicator of catalyst stability.

A decision matrix was constructed to select the best catalyst alternative among the seven screened catalysts. TOC and Orange II removal efficiencies as well as leaching, potential environmental impacts (toxicity), and cost were used as the decision making criteria. Orange II and TOC removal efficiencies and environmental impact were given a higher weight of four, whereas leaching and cost of catalyst were given a lower weight of two. Based on these criteria,  $\text{CuO}/\text{Al}_2\text{O}_3$  was selected for further investigation.

Three types of control experiments were conducted; one for WAO of Orange II with no catalyst present, another one examining the thermal degradation of Orange II at temperatures up to  $120^\circ\text{C}$ , and a third one at room temperature in the absence of oxygen to determine whether the reaction happens only through adsorption.

Reaction kinetics was investigated at temperatures between  $20^\circ\text{C}$  and  $100^\circ\text{C}$ . A triangular lumped-parameter kinetic model was proposed to describe the reaction mechanism. The reaction rate constants and the activation energies of each reaction were determined with non-linear regression. The dependence of reaction rate on catalyst concentration as well as pH was also investigated. The kinetics experiment results are summarized in the following section.

## KINETICS EXPERIMENTAL RESULTS

The screening experiments suggested the removal of Orange II and TOC are not correlated, and that Orange II removals are always higher due to the disappearance of the N=N bond whereas TOC removal values stay higher due to intermediates formation. The kinetic model, therefore, was written in terms of TOC. The proposed model describing reaction kinetics was derived as:

$$\frac{[TOC]}{[TOC]_0} = e^{-(k_1+k_2)t} + \frac{k_2(e^{-(k_1+k_2)t} - e^{-k_3t})}{-k_1 - k_2 + k_3} \quad (5.1)$$

Samples collected at different time intervals during reaction were analyzed for TOC concentrations and by performing a non-linear regression, the k values for each step of the proposed model were computed. The k values in the model are pseudo rate constants, and stand for:

$$k = k_0 e^{\frac{-E_a}{RT}} [O_2]^\alpha \quad (5.2)$$

By using the computed k values at different temperatures and dissolved oxygen concentrations at these temperatures, the dependence of each reaction pathway on oxygen concentration were determined as well as the activation energies. The temperature and oxygen concentration dependence of the rate constant values were determined to be as presented in Equations 5.3-5.5.

$$k_1 = 44.21 e^{\frac{-8417}{RT}} [O_2]^{0.197} \quad (5.3)$$

$$k_2 = 48341 e^{\frac{-11857}{RT}} [O_2]^{1.79} \quad (5.4)$$

$$k_3 = 19.87 e^{\frac{-9887}{RT}} [O_2]^{1.06} \quad (5.5)$$

There was excellent agreement between the proposed model and the experimental results.

Increasing the catalyst concentration increased the overall TOC and Orange II removals. Acidic reaction conditions at pH 3.0 led to 95% TOC removal in 60 minutes of reaction time, although copper leaching of 1.05% was detected in solution indicating loss of catalyst stability at pH 3.0.

## RECOMMENDATIONS FOR FUTURE RESEARCH

For the current work, the concentrations of specific intermediates formed during reaction could not be measured due to lack of access to an HPLC. Determining what intermediates are formed during reaction can help understand the reaction mechanism better.

Assessing the biodegradability of treated effluents is another area where further investigation is needed. If the intermediates formed are non-biodegradable, further research would be required to determine whether the reaction conditions could be optimized to yield biodegradable intermediates.

Development of different more efficient types of catalysts for the CWAQ of Orange II could be investigated. The compositions of the catalysts tested in this work could be altered to investigate whether higher removal of Orange II and TOC could be achieved.

There is a need to investigate whether the reaction is also mass transfer limited for oxygen under the current experimental set-up. In the current study, oxygen was supplied to the reactor directly from the oxygen tank. More efficient oxidation means, such as using diffusers to bubble oxygen in the reactor could improve the overall treatment efficiency since the reaction rate is dependent on the oxygen concentration. It should be tested whether the oxygen concentration dependence of the rate constants could be reduced by improving the oxidation means. If the reaction is mass transfer limited, incorporating this limitation in the proposed model could improve the model.

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## **APPENDICES**

**APPENDIX A**

Summary of literature for catalytic wet air oxidation of industrial wastewaters

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Zhang and Chuang, 1998	Black liquor from paper and pulp industry	Pt-Ce/Al, Pt-Pd/Al, Pd-Ce/Al, Pt-Pd-Ce/Al	T=160-190°C, P=1.5-2.2 MPa	Over 50% TOC reduction was achieved in about an hour at 190 °C and 1.5 MPa.
An et al., 2001	Kraft pulp mill effluents	Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , Pd/ALON	T=80-175°C, P=1.84 MPa	Alumina supported Pd catalysts were very active for TOC and color reduction
Gomes et al., 2002	Butyric acid	Ir/C	T=180, 200, 220°C, P=0.69-1.39 MPa	The degradation of butyric acid follows pseudo-first order kinetics.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Pintar et al., 2001	Kraft bleaching plant effluents	Ru/TiO <sub>2</sub> , Ru/ZrO <sub>2</sub>	T=190°C , P=5.5 MPa	Oxides of titanium and zirconium are considerably active in the TOC removal of both acidic and alkaline effluents. Over 99% TOC reduction could be achieved within 8 hours.
Gomes et al., 2004	Butyric Acid	Pt/C, Ir/C	T=200°C, P=0.69 MPa	Both catalysts were very efficient in butyric acid removal. No leaching of metals was detected. Pt catalysts were more resistant to deactivation than the Ir catalysts.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Mantzavinos et al., 1999	<i>p</i> -coumaric acid	Co/Bi, CuO·CoO·ZnO/ Al, CuO·ZnO/Al, Pt/Al, FeO(OH)	T=100-155°C, P=3 MPa	End products were not amenable to biological treatment
Neri et al., 2002	<i>p</i> -coumaric acid	CeO <sub>2</sub> /Fe, CeO <sub>2</sub> /Zn	T=80-130°C, P=2MPa	With the addition of Zn, the catalytic activity decreased. The Fe promoted ceria catalyst the activity was ten times higher than that of ceria alone.
Silva et al., 2004	Acrylic acid	Ag/Ce, Co/Ce, Mn/Ce, CeO, MnO	T=200°C, P=1.5 MPa	Mn/Ce was the most effective catalyst, with higher molar ratios yielding better removal.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Beziat et al., 1999	Carboxylic acids	Ru/TiO <sub>2</sub>	T=190°C, P=5 MPa	Study aimed complete mineralization of acetic acid, however even after 8 hours of reaction time, only 80% of acetic acid was converted.
Gallezot et al., 1996	Formic, oxalic, maleic acids	Pt/C	T=20-190°C, P=0.1-1.5 MPa	Total conversion of formic and oxalic acids were achieved under atmospheric pressure and 53 °C. Maleic acid was also successfully oxidized into carbon dioxide.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Silva et al, 2003	Formaldehyde industry effluents	Mn/Ce, Co/Ce, Ag/Ce, CuO-ZnO/ Al <sub>2</sub> O <sub>3</sub>	T= 190-220°C P=1.5-3.5 MPa	Mn/Ce catalyst was the most active and stable catalyst. Studies with different molar ratios of Mn/Ce suggested that increasing Mn composition to 60-80% increases the activity of the catalyst for the initial reaction times, but for longer periods of time has no significant effect on the activity.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Kacar et al, 2003	Alcaloide wastewater	Ni(NO <sub>3</sub> ) <sub>2</sub> , FeCl <sub>2</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> , Co(NO <sub>3</sub> ) <sub>2</sub> , Cu(NO <sub>3</sub> ) <sub>2</sub> +MnCl I <sub>2</sub> , FeCl <sub>2</sub> +Ni(NO <sub>3</sub> ) 2	T=150°C P=0.65 MPa	Although the BOD/COD ratio of the wastewater improved, COD removal efficiency was very low (~35%)
Klinghoffer et al., 1998	Acetic acid	Pt/Al	T=200, 220, 240°C, Effect of pressure not analyzed, Influent flowrates=28.47 , 62.59, 107.44 cm <sup>3</sup> /min	Only end product detected was CO <sub>2</sub> gas. Monolithic characteristics of catalyst may have played an important role in the complete conversion of acetic acid.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Duprez et al., 1996	Acetic acid and phenol	Ru, Pt, Rh supported on titania, ceria, and C, Mn/Ce	T=200°C, P= 4 MPa, t=3 hrs	Although the Ru/C catalyst was very efficient in the oxidation of acetic acid, some oxidation of the C support took place.



Reference	Substrate	Catalyst	Reaction conditions	Remarks
Belkacemi et al., 2000	High-strength alcohol distillery liquors	1% w/w Pt/ $\gamma$ -alumina, Mn/Ce composite oxide, Cu(II)/NaY zeolite	T=180-250°C, P=0.5-2.5 MPa	The Cu(II)/NaY catalyst was the most efficient catalyst under all temperatures, however, some leaching of Cu was detected.
Coleman et al., 1999	Alcohols	Bi-functional OsO <sub>4</sub> -CuCl catalyst	T=25-100°C, P=0.1 MPa	This study aimed at catalyzing alcohols into aldehydes and ketones. The system was found to be selective for only benzylic and allylic alcohols.

Reference	Substrate	Catalyst	Reaction conditions	Remarks
Batygina et al., 2000	Wastewater from an alcohol industry (Luther water)	Ru/graphite- like-C	T= 130-200°C , P=1.5-3.6 MPa	Ru/graphite- like-C was found to be very efficient for TOC reduction at 150 °C. After one hour of reaction time, 97.5% TOC was removed.

## APPENDIX B

### ANOVA TABLES FOR CATALYST SCREENING EXPERIMENTS

#### CuO/ZnO Catalyst Factorial Model ANOVA TABLE

Response: TOC removal (%)

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	412.2601	3	137.42	14.22684	0.0134	significant
A-Catalyst	37.28161	1	37.28161	3.859695	0.1209	
B-T	40.99651	1	40.99651	4.244291	0.1084	
C-P	333.982	1	333.982	34.57653	0.0042	
Pure Error	38.63685	4	9.659212			
Cor. Total	450.897	7				

Std.Dev.	3.107927	R-Squared	0.914311
Mean	79.20625	Adj R-Squared	0.850044
C.V. %	3.923841	Pred R-Squared	0.657245
PRESS	154.5474	Adeq Precision	7.940349

**Pt/SnO<sub>2</sub>/CeO<sub>2</sub> Catalyst Factorial Model ANOVA TABLE****Response: TOC removal (%)**

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	247.1189	3	82.37298	19.417	0.0076	significant
A-Catalyst	5.797012	1	5.797012	1.366475	0.3073	
B-T	178.3216	1	178.3216	42.03406	0.0029	
C-P	63.00031	1	63.00031	14.85046	0.0182	
Pure Error	16.96925	4	4.242313			
Cor. Total	264.0882	7				

Std.	2.059687476	R-Squared	0.935744
Dev.			
Mean	85.07375	Adj R-Squared	0.887552
C.V. %	2.42106111	Pred R-Squared	0.742976
PRESS	67.877	Adeq Precision	10.337

**CuO/Al<sub>2</sub>O<sub>3</sub> Catalyst Factorial Model ANOVA TABLE****Response: TOC removal (%)**

	<i>Sum of</i>		<i>Mean</i>	<i>F value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	2332.6	3	777.5334	38.46761	0.0021	significant
A-Catalyst	0.842402	1	0.842402	0.041677	0.8482	
B-T	2248.656	1	2248.656	111.2498	0.0005	
C-P	83.10183	1	83.10183	4.111372	0.1125	
Pure Error	80.85071	4	20.21268			
Cor Total	2413.451	7				

Std.	4.495851	R-Squared	0.9665
Dev.			
Mean	67.492	Adj R-Squared	0.941375
C.V. %	6.66131	Pred R-Squared	0.866
PRESS	323.4028	Adeq Precision	12.57515

**Cu<sub>2</sub>Cr<sub>2</sub>O<sub>5</sub> Catalyst Factorial Model ANOVA TABLE****Response: TOC removal (%)**

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	1372.421	3	457.4737	8.271477	0.0344	significant
A-Catalyst	8.9888	1	8.9888	0.162524	0.7075	
B-T	1175.64	1	1175.64	21.25648	0.0100	
C-P	187.7922	1	187.7922	3.395428	0.1392	
Pure Error	221.2295	4	55.30738			
Cor. Total	1593.651	7				

Std.	7.436893	R-Squared	0.861181
Dev.			
Mean	43.3575	Adj R-Squared	0.757066
C.V. %	17.15249	Pred R-Squared	0.444723
PRESS	884.918	Adeq Precision	6.453144

**CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Catalyst Factorial Model ANOVA TABLE****Response: TOC removal (%)**

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	710.5245	3	236.8415	8.138568	0.0354	significant
A-Catalyst	293.7888	1	293.7888	10.09544	0.0336	
B-T	362.3432	1	362.3432	12.45117	0.0243	
C-P	54.39245	1	54.39245	1.869084	0.2434	
Pure Error	116.4045	4	29.10113			
Cor. Total	826.929	7				

Std.Dev.	5.394546	R-Squared	0.859233
Mean	38.6275	Adj R-Squared	0.753657
C.V. %	13.96556	Pred R-Squared	0.436931
PRESS	465.618	Adeq Precision	6.705955

# MnO<sub>2</sub>/CeO<sub>2</sub> Catalyst Factorial Model ANOVA TABLE

Response: TOC removal (%)

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	960.6243	3	320.2081	31.93992	0.0030	significant
A-Catalyst	264.27005	1	264.2701	26.36025	0.0068	
B-T	696.01805	1	696.0181	69.42598	0.0011	
C-P	0.3362	1	0.3362	0.033535	0.8636	
Pure Error	40.1013	4	10.02533			
Cor Total	1000.7256	7				

Std.	3.166279362	R-Squared	0.959928
Dev.			
Mean	39.91	Adj R-Squared	0.929874
C.V. %	7.933548891	Pred R-Squared	0.839711
PRESS	160.4052	Adeq Precision	13.46645



**MnO<sub>2</sub>/CuO Catalyst Factorial Model ANOVA TABLE****Response: TOC removal (%)**

	<i>Sum of</i>		<i>Mean</i>	<i>F Value</i>	<i>p-value</i>	
	<i>Squares</i>		<i>Square</i>			
Source		df			Prob > F	
Model	415.0918375	3	138.3639	146.7099	0.0002	significant
A-Catalyst	412.5628125	1	412.5628	437.4481	< 0.0001	
B-T	1.6110125	1	1.611013	1.708187	0.2613	
C-P	0.9180125	1	0.918012	0.973386	0.3797	
Pure Error	3.77245	4	0.943112			
Cor Total	418.8642875	7				

Std.	0.971139794	R-Squared	0.990994
Dev.			
Mean	12.94125	Adj R-Squared	0.984239
C.V. %	7.504219409	Pred R-Squared	0.963974
PRESS	15.0898	Adeq Precision	22.22224

## APPENDIX C

## Intermediates of Orange II oxidation reported in literature

<i>Intermediate</i>	<i>Reference</i>
Benzenesulfonic acid	[98]
B-naphthol	[98]
4-hydroxybenzenesulfonic acid	[98]
1,3-isobenzofurandione	[98]
2-hydroxymethylbenzoic acid	[98]
1,2 Benzenedicarboxylic acid	[98]
Glycolic acid	[98]
Acetic acid	[98]
Formic acid	[98]
1,2-naphthoquinone	[91]
Coumarin	[91] [27]
Phthalic Anhydride	[91]
Phthalimide	[91] [27]
2-formyl-benzoic acid	[91] [27]
2-hydroxy-1,4-naphthoquinone	[27]
Phthalic acid	[27]
2-acetyl-benzoic acid	[27]
Succinic acid	[27]
Fumaric acid	[27]
Maleic acid	[27]
Malonic acid	[27]
2-butenic acid	[27]
2-hydroxy butanoic acid	[27]
Oxalic acid	[98]

## APPENDIX D

## Non-linear regression program output and regression statistics from NLREG

k value computation results for 80°C

```

----- Final Results -----
NLREG version 6.4
Copyright (c) 1992-2008 Phillip H. Sherrod.
Number of observations = 7
Maximum allowed number of iterations = 500
Convergence tolerance factor = 1.000000E-010
Stopped due to: Relative function convergence.
Number of iterations performed = 12
Final sum of squared deviations = 4.6675026E-004
Final sum of deviations = 2.0135447E-004
Standard error of estimate = 0.0108022
Average deviation = 0.00635506
Maximum deviation for any observation = 0.0135719
Proportion of variance explained (R^2) = 0.9989 (99.89%)
Adjusted coefficient of multiple determination (Ra^2) = 0.9983 (99.83%)
Durbin-Watson test for autocorrelation = 2.463
Analysis completed 6-Sep-2008 22:28. Runtime = 0.03 seconds.

```

----- Descriptive Statistics for Variables -----				
Variable	Minimum value	Maximum value	Mean value	Standard dev.
y	0.2663132	1	0.4325332	0.2601128
t	0	35	10.42857	12.86931

----- Calculated Parameter Values -----					
Parameter	Initial guess	Final estimate	Standard error	t	Prob(t)
k1	1	1.02111359	0.05408333	18.88	0.00005
k2	1	0.518497441	0.04320831	12.00	0.00028
k3	1	0.00780067362	0.001580176	4.94	0.00784

----- Analysis of Variance -----					
Source	DF	Sum of Squares	Mean Square	F value	Prob(F)
Regression	2	0.4054852	0.2027426	1737.48	0.00001
Error	4	0.0004667503	0.0001166876		
Total	6	0.4059519			

## k value computation results for 50°C

## ---- Final Results ----

NLREG version 6.4

Copyright (c) 1992-2008 Phillip H. Sherrod.

Number of observations = 8

Maximum allowed number of iterations = 500

Convergence tolerance factor = 1.000000E-010

Stopped due to: Both parameter and relative function convergence.

Number of iterations performed = 15

Final sum of squared deviations = 1.0423200E-003

Final sum of deviations = 8.7132876E-004

Standard error of estimate = 0.0144383

Average deviation = 0.00941367

Maximum deviation for any observation = 0.0192724

Proportion of variance explained ( $R^2$ ) = 0.9972 (99.72%)Adjusted coefficient of multiple determination ( $R_a^2$ ) = 0.9961 (99.61%)

Durbin-Watson test for autocorrelation = 2.874

Analysis completed 6-Sep-2008 22:35. Runtime = 0.05 seconds.

## ---- Descriptive Statistics for Variables ----

Variable	Minimum value	Maximum value	Mean value	Standard dev.
y	0.2821824	1	0.468798	0.2301402
t	0	50	15.5	18.2991

## ---- Calculated Parameter Values ----

Parameter	Initial guess	Final estimate	Standard error	t	Prob(t)
k1	1	0.948285428	0.08382529	11.31	0.00009
k2	1	0.732279335	0.08768032	8.35	0.00040
k3	1	0.00950685349	0.001153044	8.25	0.00043

## ---- Analysis of Variance ----

Source	DF	Sum of Squares	Mean Square	F value	Prob(F)
Regression	2	0.3697093	0.1848546	886.75	0.00001
Error	5	0.00104232	0.000208464		
Total	7	0.3707516			

## k value computation results for 100°C

----- Final Results -----  
 NLREG version 6.4  
 Copyright (c) 1992-2008 Phillip H. Sherrod.  
 Number of observations = 7  
 Maximum allowed number of iterations = 500  
 Convergence tolerance factor = 1.000000E-010  
 Stopped due to: Relative function convergence.  
 Number of iterations performed = 13  
 Final sum of squared deviations = 9.5008801E-004  
 Final sum of deviations = 2.3335594E-004  
 Standard error of estimate = 0.0154117  
 Average deviation = 0.00987528  
 Maximum deviation for any observation = 0.017153  
 Proportion of variance explained ( $R^2$ ) = 0.9974 (99.74%)  
 Adjusted coefficient of multiple determination ( $R_a^2$ ) = 0.9961 (99.61%)  
 Durbin-Watson test for autocorrelation = 1.870  
 Analysis completed 6-Sep-2008 22:40. Runtime = 0.06 seconds.

----- Descriptive Statistics for Variables -----				
Variable	Minimum value	Maximum value	Mean value	Standard dev.
y	0.2922757	1	0.4581039	0.2461898
t	0	50	14.85714	19.66747

----- Calculated Parameter Values -----					
Parameter	Initial guess	Final estimate	Standard error	t	Prob(t)
k1	1	1.44161738	0.1990562	7.24	0.00193
k2	1	0.971955902	0.1644008	5.91	0.00410
k3	1	0.00749346554	0.001206275	6.21	0.00342

----- Analysis of Variance -----					
Source	DF	Sum of Squares	Mean Square	F value	Prob(F)
Regression	2	0.3627064	0.1813532	763.52	0.00001
Error	4	0.000950088	0.000237522		
Total	6	0.3636565			

## k value computation results for 20°C

----- Final Results -----  
 NLREG version 6.4  
 Copyright (c) 1992-2008 Phillip H. Sherrod.  
 Number of observations = 6  
 Maximum allowed number of iterations = 500  
 Convergence tolerance factor = 1.000000E-010  
 Stopped due to: Relative function convergence.  
 Number of iterations performed = 18  
 Final sum of squared deviations = 3.5062374E-003  
 Final sum of deviations = -1.8425589E-003  
 Standard error of estimate = 0.0341869  
 Average deviation = 0.0179556  
 Maximum deviation for any observation = 0.0439276  
 Proportion of variance explained ( $R^2$ ) = 0.9872 (98.72%)  
 Adjusted coefficient of multiple determination ( $R_a^2$ ) = 0.9787 (97.87%)  
 Durbin-Watson test for autocorrelation = 2.592  
 Analysis completed 6-Sep-2008 22:44. Runtime = 0.05 seconds.

----- Descriptive Statistics for Variables -----				
Variable	Minimum value	Maximum value	Mean value	Standard dev.
y	0.292608	1	0.6119463	0.2342422
t	0	60	17.16667	23.81946

----- Calculated Parameter Values -----					
Parameter	Initial guess	Final estimate	Standard error	t	Prob(t)
k1	1	0.671598192	0.2614323	2.57	0.08257
k2	1	1.17678982	0.592899	1.98	0.14140
k3	1	0.0114356477	0.002061288	5.55	0.01155

----- Analysis of Variance -----					
Source	DF	Sum of Squares	Mean Square	F value	Prob(F)
Regression	2	0.2708407	0.1354203	115.87	0.00144
Error	3	0.003506237	0.001168746		
Total	5	0.2743469			

## VITA

### PINAR OZDURAL

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M.E.: August 2002, Old Dominion University, Norfolk, VA, USA  
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#### PUBLICATIONS

Ozdural, P., Akyurtlu, J. F., Erten-Unal, M., Akyurtlu, A., "Catalytic wet air oxidation as a treatment solution for alcohol industry wastewaters," Proceedings of Virginia Water Research Symposium 2004, pp. 247-252, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Ozdural, P., Akyurtlu, J. F., Erten-Unal, M., Akyurtlu, A., "Catalytic wet air oxidation of azo-dye orange-II: In search of an efficient catalyst," Poster presented at North American Catalysis Society 20<sup>th</sup> Meeting, June 2007, Houston, Texas.

Ozdural, P., Akyurtlu, J. F., Erten-Unal, M., Akyurtlu, A., "Catalytic Wet Air Oxidation of Orange II-Finding an Efficient Catalyst," Proceedings of the AIChE annual meeting, November 2007, Salt Lake City, Utah.

#### SCIENTIFIC AND PROFESSIONAL SOCIETY MEMBERSHIPS

American Water Works Association  
Water Environment Federation