PHOTOOXIDATION OF A TM PULP AND PAPER MILL EFFLUENT WITH HYDROGEN PEROXIDE

by

Philippe Boissinot

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements of the
degree of Masters in Engineering

Department of Chemical Engineering

McGill University

Montréal, Québec
Canada

July 1996

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ISBN 0-612-19861-8

ABSTRACT

The photooxidation of a Thermo-Mechanical (TM) pulp and paper mill effluent with hydrogen peroxide (H_2O_2) was investigated at different experimental conditions by using a batch photochemical reactor operating at a dominant UV light wavelength of 253.7 nm. Photolysis of H_2O_2 produces hydroxyl radicals (•OH), which are very powerful oxidizing species. The effluent consisted of a "heat condensate" obtained from toxic vapors generated during various stages of the pulping process. Several operational parameters were varied and their effects on the process were observed and analyzed, in order to achieve its optimization. In addition, heterogeneous photocatalysts such as cupric oxide (CuO) were also investigated as a complement to the photooxidation process.

The main parameter used to determine the quality of the wastewater before and after photooxidation was the Chemical Oxygen Demand (COD), using a closed reflux standard procedure. COD values of the treated solution were determined at subsequent time intervals and used to draw curves illustrating the rate of oxidation of the wastewater. Other parameters, such as Dissolved Organic Carbon (DOC) and dissolved lignin concentration, were investigated towards the end of the research in order to obtain a more complete characterization of the quality of the wastewater after treatment.

The experimental data reveal that there is an optimal H_2O_2 concentration that is best suited for the photooxidation of the effluent. Moreover, an increase in temperature accelerates the rate of elimination of COD. An increase in effluent concentration is detrimental to the speed of the process, since it causes an increase in its absorbance which can act as a barrier against UV light. The efficiency of the photooxidation process is not affected by variations in the initial pH of the wastewater. Cupric oxide (CuO), when exposed to UV light, efficiently catalyzes the production of OH radicals and is therefore very beneficial to the photooxidation process.

RÉSUMÉ

La photooxidation d'un effluent provenant d'un moulin à pâtes et papiers de type Thermo-Mécanique (TM) avec du péroxyde d'hydrogène (H_2O_2) a été étudiée à différentes conditions expérimentales à l'aide d'un réacteur photochimique de laboratoire, dont les lampes émettent de la lumière UV à une longueur d'onde dominante de 253.7 nm. La photolyse de l'H_2O_2 génère des radicaux hydroxyles (•OH), qui sont des réactifs oxydants très puissants. L'effluent consistait en un "condensat d'évaporation" obtenu de vapeurs toxiques générées par différents stages du procédé de mise en pâte. Plusieurs paramètres opérationels fûrent variés et leurs effets sur le procédé ont été observés et analysés, de façon à l'optimiser. De plus, certains photocatalystes hétérogènes tels que le monoxyde de cuivre (CuO) ont été étudiés.

Le principal paramètre utilisé pour déterminer la qualité de l'effluent avant et après la photooxidation fût la Demande Chimique en Oxygène (DCO), en se servant d'une méthode titrimétrique standard. Les valeurs de DCO de la solution traitée fûrent déterminées à des intervalles de temps subséquentes et utilisées afin de créer des courbes illustrant la vitesse d'oxidation de l'effluent. D'autres paramètres descriptifs, tels que le Carbone Organique Dissous (COD) et la concentration en lignine dissoute, fûrent aussi analysés vers la fin de la recherche afin d'obtenir une charactérisation plus complète de la qualité de l'effluent après le traitement.

Les résultats démontrent qu'il y a une concentration optimale de H_2O_2 nécessaire pour une photooxidation efficace de l'effluent. De plus, une augmentation de la température fait accélérer la vitesse d'élimination de la DCO. Une augmentation de la concentration de l'effluent affecte négativement la rapidité du procédé, puisque cela cause une augmentation de son absorbance qui peut ainsi agir comme écran contre les rayons UV. L'efficacité d'un procédé de photooxidation n'est pas affecté par des variations de pH initial de l'effluent. Il a été observé expérimentalement que le monoxyde de cuivre, lorsqu'il est exposé à la lumière UV, catalyses efficacement la production de radicaux OH et s'avère donc très utile au procédé.

ACKNOWLEDGMENTS

I would like to thank my supervisor, Dr.G.J. Kubes for his support and guidance during the experimental phase and preparation of this thesis.

I would also like to thank the technicians and research assistants from the Pulp and Paper Research Institute at McGill University for their technical support, in particular Yujing Meng and Nilgun Ulkem for assisting me in various aspects of theoritical and analytical chemistry.

Thanks to the department of Chemical Engineering and all the teachers who offered me their technical and moral support during my years at McGill University. I would especially like to thank Dr. D. Berk for his help on some aspects of my research work.

Thanks to the staff of stores, purchasing, and the machine shops of the departments of Chemical Engineering and Chemistry at McGill University.

A very special word of thanks to Jean Dumont from the Chemical Engineering store for all his help in equipment selection.

I would like to thank Abitibi-Price for gracefully lending us the photochemical reactor.

I would also like to thank McGill University and Paprican for their financial support and for the funds provided for equipment and supplies.

Thanks to Mr Jik Ing from Paprican for his analytical measurements made on some samples of my effluent.

I would like to thank my friends for their friendship, encouragement and help.

Lastly, I would like to thank my parents and family for their continuous love, support and encouragement through the years.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 INTRODUCTION

Thermo-mechanical pulping (TMP) and chemi-thermo-mechanical pulping (CTMP) are two major processes used in Canada by the newsprint industry. Despite their popularity, these processes generate plenty of toxic wastes which are a threat to the environment (1, 2, 3). Moreover, the federal and provincial governmental regulations concerning industrial discharges are also becoming more and more severe. It is therefore necessary to find ways to treat the mill effluents efficiently and economically.

There is a multitude of wastewater treatment technologies available for the treatment of various municipal and industrial effluents. For the past few years most TMP and CTMP mills in Canada have treated their effluent by using only a primary treatment, i.e. removal of solid particles by sedimentation. The solid particles are collected to form a sludge which is disposed of, usually by burning or landfilling. The remaining aqueous effluent is discharged into the environment. A number of pulp and paper mills further decontaminate this primary effluent with a secondary treatment, i.e. aerobic and/or anaerobic biological treatment. Those who still rely solely on primary treatment will have to make necessary additions to their wastewater treatment in the very near future in order to obey new, more severe regulations.

Biological treatment processes generate sludge that requires further treatment and disposal. In addition, biological treatment processes are reported to have low contaminant removal rates (4). It has been observed repeatedly that biological treatment of pulp mill effluents is fairly effective in the elimination of easily biodegradable organic material which resulted in a reduction of BOD, TOC, and suspended solids (5, 6). However, the fragments of lignin present in the effluents are not degradable and remain unaltered in this treatment, which implies that most of the color-producing compounds are not eliminated. The elimination of color is the most costly and difficult aspect of the total treatment of pulp mill effluents.

Other wastewater treatment technologies currently in use, such as air-stripping and carbon adsorption, are not problem-free either. For instance, the removal of volatile contaminants by air stripping transforms a water pollution problem into an air pollution one, and carbon adsorption produces a hazardous solid waste which must be subsequently disposed of. These phase transfer approaches are usually employed as a tertiary treatment for the so-called "polishing" of the effluent coming out of a biological treatment stage. The environmental pressures of the last decade have produced a trend in technology development which is more oriented towards destructive technologies, i.e. technologies which not only remove contaminants from water but also destroy them in the process.

Conventional chemical oxidation has been used in the treatment of waters polluted by organic chemicals for a number of years, with oxidants such as potassium permanganate, chlorine and chlorine dioxide. The disadvantages of these processes are that they can only attack a certain fraction of the organics, and they produce chlorinated organics or other toxic by-products.

Some of the newer approaches to wastewater treatment are advanced oxidation processes (AOP), such as wet air oxidation, homogeneous photooxidation with hydrogen peroxide and/or ozone, heterogeneous photooxidation with reactive metal oxides, etc. AOPs are promising technologies for the treatment of water that has been contaminated with organic chemicals, because 1) these processes are capable of converting the organic contaminant completely to carbon dioxide and water, 2) they are effective against most organic compounds and 3) the chemicals used in the process decompose to harmless or beneficial by-products. In addition to being environmentally clean, these processes are now becoming more cost-effective than it was thought earlier, due to improvements in the technology and the high liability now associated with discharge of contaminants into the environment (7). However, the practicality of the AOPs depends heavily on the efficiency with which the relatively expensive oxidants are used.

Basis for research

An important challenge for the pulp and paper industry nowadays is to minimize as much as possible the volume of wastewater discharged into the environment. In order to do so, industries must achieve a closed-cycle technology. The effluent must be treated in such a way that the resulting water, when recycled back into the mill, will not have an impact on the mill operation, and will not affect the characteristics of the newsprint by wet-end chemistry effects.

In general, a closed-cycle technology is comprised of four separate operations (see figure 1.1). First, the industrial effluent goes through a primary treatment process, usually a clarifier, in which the suspended solids are separated from the wastewater by sedimentation. This process strips most of the toxics away from the effluent, resulting in the creation of two streams. One stream is composed of accumulated solid particles that have settled, and it is usually very dense and highly toxic. It forms a sludge which is disposed of by burning, landfilling, etc. The other stream is a relatively clear wastewater which still contains a high concentration of contaminants, mostly dissolved organic compounds. This clarified effluent is then sent into a secondary treatment process, which destroys most of the organic compounds and decontaminate the water to an appreciable degree. This is usually done through an aerobic biological treatment process. Finally, the treated effluent enters a tertiary treatment process, or polishing stage, in which the water gets cleaned and desinfected. This is usually done by carbon adsorption or air-stripping. In this last stage, the water is purified to such an extent that its quality meets the standards needed for recycling it back into the mill operation.

This study will focus primarly on the secondary treatment process of the closed-cycle technology. The effluents that are to be treated in laboratory have already gone through a primary treatment process and are relatively free of suspended solids.

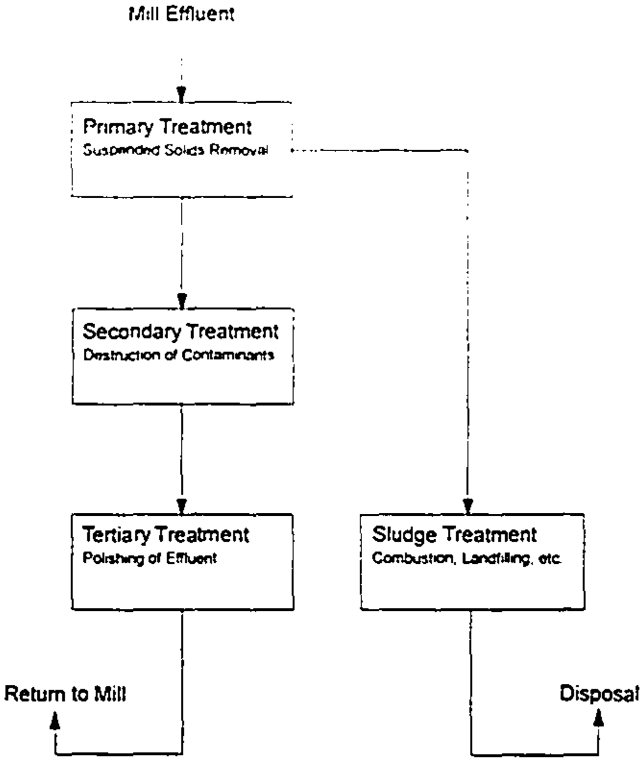

Figure 1.1. Closed-cycle technology

As a secondary treatment alternative, an advanced oxidation process will be investigated. Advanced oxidation processes often incorporate the use of ozone. Due to the high capital cost and maintenance that ozonation requires, it will not be considered in this experiment. The role of ozone in a photooxidation process can be seen as solely complementary, and its usefulness does not necessarily justify its high cost. Ozone is an unstable gas that must be generated on site and transferred into the liquid by diffusion with air. Bubbles of ozone can also strip volatile components into the air. The use of hydrogen peroxide (H_2O_2) as an oxidant has the following advantages over ozone: the water solubility of H_2O_2 greatly simplifies the reactor design, mixing of the reactants, and elimination of concern over fugitive toxic gases (8). Furthermore, advantages of H2O2 also include the possibility of storage to better accomodate process demands, and costs that are less sensitive to scale of operation than ozone (9). The main process investigated in this study consists of photooxidation using UV light and hydrogen peroxide

(UV/peroxidation). In addition, heterogeneous photocatalysis using either titanium dioxide (TiO_2) or copper complexes, and photo-Fenton oxidation, are briefly examined.

Even though UV/peroxidation and other photooxidations are relatively recent innovations, these processes have been used for a number of years and research has been continuing to support photooxidation as a process of choice for its technical and economical aspects.

Research objectives

UV/peroxidation, to our knowledge, has not been tested yet as a process for the treatment of CTMP/TMP mill effluents. The main objectives of this study are:

1) To examine the feasibility of the UV/peroxidation process for the treatment of CTMP/TMP mill effluents.
2) To investigate the effect of changing operational parameters, such as pH, temperature, etc., on the efficiency of the process.
3) To experiment with additional photocatalysts such as TiO_2, Cu^{+2}, etc.
4) To optimize the overall process.

CHAPTER 2 PHOTOOXIDATION LITERATURE REVIEW

Introduction

Advanced Oxidation Processes (AOPs) have been generally defined as those aqueous phase oxidation processes which are primarily involved with the intermediacy of the hydroxyl radical in the mechanisms leading to the destruction of a target pollutant or contaminant compound (10).

AOPs which involve ultraviolet (UV) light include the photolysis of hydrogen peroxide (H_2O_2), and/or ozone (O_3), and the surface photolysis of the semiconductor titanium dioxide (TiO_2). When these photoexcited reactants are combined with a contaminant, reactions involving H_2O_2 and O_3 are homogeneous in nature, while reactions that employ TiO_2 are heterogeneous. The most direct method, and in principle, the method which should give the highest yield of hydroxyl radicals (•OH), is direct photolysis of H_2O_2 (11).

UV irradiation can either be generated by an artificial source such as a typical mercury vapor lamp operating at a dominant wavelength between 200 and 400 nm, or directly by natural sunlight illumination which possess a near-UV component.

Most studies on UV-catalyzed oxidation processes have emphasized on the treatment of pure compounds or complex natural mixtures, such as humic matter (12). In practice, mixtures of chemical compounds are often found in contaminated water. Moreover, toxic industrial effluents are usually very complex in nature and are composed of many interacting components. To study the practical aspect of UV catalyzed oxidation processes, it is important to test them by using a real effluent coming directly out of an industrial process. Such an approach is necessary to follow for the design of oxidative treatment processes.

Very few of the reviewed experiments done on photocatalyzed oxidation deal with industrial or municipal effluents taken at the source. Most of the research work has been performed on aqueous solutions of organic contaminants which are not slurry in nature, such as common herbicides and pesticides. Contaminated groundwater has also been a source of choice for the demonstration of commercial photocatalyzed oxidation processes (4,8,11,13-16). All these wastewaters have in common the absence of suspended solids and therefore an ability to allow UV light to penetrate through them and activate photosensitive oxidants. The main difficulties that might be encountered by using a real effluent in the study of a photooxidation process is the high concentration of suspended solids, and the possible interactions between reacting components. An effluent with a too high concentration of suspended solids, grease and/or oil should be pretreated by dilution or sedimentation for instance, such that it becomes more suitable for an efficient photooxidation treatment.

Researchers use various ways to determine the efficiency of photooxidation processes. Most of them study the elimination of a pure compound, and thus they only need to measure the concentration of the compound at different time intervals during and/or at the end of a reaction. In situations where complex mixtures are being oxidized, and therefore individual components can not be singled out, parameters determining the quality of the water, such as Total Organic Carbon (TOC) (17,18), colour (5,6), COD and BOD (5), etc., must be used. Another way to determine the efficiency of a photooxidation process is by observing the rate of formation of carbon dioxide (CO_2) (19), as the main product of the oxidation of organics. The rate of formation of CO_2 is therefore a good indication of the efficiency of the process, and its concentration can be measured with a gas chromatograph at regular intervals.

Homogeneous Photooxidation with H_2O_2

The treatment of an organic waste with homogeneous photooxidation using H_2O_2 involves an aqueous mixture of the contaminant(s) and pure hydrogen peroxide which is irradiated by UV light. This process is sometimes also called UV- or photo-peroxidation. Various photochemical reactors are available to researchers, and most experiments are performed using a batch reactor in such a way that UV radiation can reach the H_2O_2 and organic molecules in solution. Continuous flow reactors are mostly used in the demonstration of commercial systems. The lamps used most of the time are low pressure mercury vapor lamps operating at a dominant wavelength of ~ 254 nm.

Significant research has been done in the past few years on the photooxidation of contaminants with hydrogen peroxide. Experiments were performed on many different pollutants, such as chlorinated phenols,ethanols, and ethylene; atrazine, benzene, microorganisms, etc. (4,9,12,17,20-22). In all cases the UV/H_2O_2 process was successful in destroying these organic and aromatic compounds. Studies were made on the photooxidation of organics-contaminated groundwater with hydrogen peroxide, yielding similar results (4). The UV/H_2O_2 process was also evaluated for the decolorization of kraft pulp mill effluents (5,6) and as a tertiary process for the treatment of an aqueous effluent from a hazardous waste treatment facility (18). The role of H_2O_2 as a photooxidant was also investigated in the transformation of atmospheric pollutants (23). The UV/H_2O_2 process has attracted a lot of attention from researchers in the past and thus the available literature on the subject is quite extensive.

The sole use of UV light without the addition of an oxidant has been investigated as a wastewater treatment alternative. UV light alone has been proved to be a very effective desinfection process for the destruction of microorganisms in water (24) and wastewater (25), but in most cases its efficiency for the destruction of organics is very poor. Moreover, hydrogen peroxide by itself could also be used for the treatment of wastewaters, since it is a relatively strong oxidant. Some studies have compared the efficiencies of oxidation by UV photolysis alone, by H_2O_2 alone, and by combination of UV light and H_2O_2, on a series of pollutants (6,9,21,26,27). In all cases the performance of the UV/H_2O_2 system was far more superior over UV and H_2O_2 used separately. This comparison was made by Castrantas and Gibilisco (26), who studied the oxidation of phenols under different conditions. Starting with an initial phenol concentration of 10 mg/l, their results indicated that 90% of the initial phenol solution was destroyed with a UV/H_2O_2 system after 15 minutes, compared to only a 5% destruction with UV light alone, and no detectable destruction with H_2O_2 alone. These results clearly show the necessity of combining UV light to H_2O_2 for an optimization of the oxidation process.

Treatment times varied from one experimental system to another. In some instances it was 60 minutes (17) and it went up to 3 hrs in other experiments (6). In general it takes more time to photooxidize a pollutant mixture having a high turbidity such as a real industrial effluent, and less time to photooxide a pure compound with a low absorbance. The time necessary for the treatment of a wastewater is a very important consideration since it is an economical factor that plays a major role in the comparison of different wastewater treatment alternatives.

In a series of experiments, the oxidation of organic pollutants followed a first order rate of reaction (9,12,22) with respect to the concentration of pollutant. In all cases the semi-log plots of the residual fraction of pollutant versus time were nearly linear, suggesting reactions close to first order. It was thus possible to calculate pseudo-first order rate constants for each experimental run.

Influence of operating parameters on homogeneous photooxidation with H_2O_2

The efficiency of a UV/H_2O_2 process is dependent on the following parameters which must be investigated in order to achieve a maximum efficiency.

The concentration of hydrogen peroxide needed for the photooxidation process has to be carefully monitored, since not enough or too much of it can render the system inefficient. In many cases the oxidation rate of a pollutant increases with increasing initial H_2O_2 concentration, until a critical value is attained, after which a supplemental increase in H_2O_2 has a negative effect on the oxidation rate (12,17,20-22). There is therefore a treshold of H_2O_2 concentration over which the process becomes no longer effective. This value is obviously not constant from one system to another, since it is a function of many variables, especially the nature of the compound to be oxidized. For each new mixture of pollutants and/or different experimental conditions, the optimal H_2O_2 concentration has to be determined. It is known that a large number of organic contaminants require "activation" by direct UV light absorption in order to facilitate their oxidation. H_2O_2 in excess concentration can absorb too much photonic energy, thus inhibiting the direct UV activation and resulting in poorer overall performance. Hydrogen peroxide can also act as a scavenger of hydroxyl radicals in solution, thereby reducing their concentration in solution, and since these are considered to be the main oxidizing agents in the process, their decrease will have a negative effect on the UV/H_2O_2 process. For instance, Beltran *et al* (21) found that the rate of photooxidation of atrazine, a hazardous pesticide, with H_2O_2 concentrations higher than 0.01 M in solution is even lower than that obtained from direct UV photolysis without H_2O_2. However, Yue and Legrini (17) observed that changing the concentration of hydrogen peroxide did not have a significant effect on the destruction rate of a series of organics nor the residual TOC concentration at the end of a 4 hours run. It would appear that in their case a very low concentration of hydrogen peroxide was required to achieve optimal efficiency of the photooxidation process.

Another operating parameter of major concern is the initial pH of the mixture that gets photooxidized. The effect of changing initial pH will vary from one experiment to another. According to the kinetic model developed by Nicole *et al* (28), an increase in pH would lead to an increase in the rate of photodecomposition of hydrogen peroxide and consequently to an increase in the production rate of hydroxyl radicals. However, there is a paradoxal effect with this, since a higher light absorption by H_2O_2 causes an overall reduction in available light energy that is required by the contaminants for their photo-activation in solution. This observation was corroborated by results from De Laat *et al* (20), who studied the photooxidation of atrazine. They showed that an increase in pH is detrimental to the process, since an over-absorption of light by H_2O_2 produced an inhibition of the photonic power potential. In their case, the effect of the pH on the rate of generation of hydroxyl radicals was negligible. It was therefore concluded that an increase in pH was not beneficial to the process. On the other hand, in Prat *et al*'s experiments with a kraft mill effluent, the highest pH, i.e. 11.15, turned out to give the fastest rate of oxidation and decolorization (6). Their results indicated clearly that the kinetic constant of the oxidation process increased with the pH and contributed favorably to an increase in the rate of reaction.

According to Froelich, some organic contaminants oxidize faster at a specific pH, while some photooxidation systems with a catalyst would function better below a certain pH (16). Following this strategy, Ku and Ho (22) found a specific optimal pH for each of the compounds they photooxidized with H_2O_2 and O_2. Their experiments indicated that the optimum pH occured at about 6 for the photooxidation of phenol, about 4 for 2-chlorophenol, and at about 10 for 2,4-dichlorophenol. Finally Lewis *et al.* suggested that the applied pH adjustment depends on the incoming pH of the water (4). If the water had an alkalinity greater than 400 mg/l as calcium carbonate, then lowering the pH to a range of 4 to 6 would improve the treatment efficiency. If the carbonate alkalinity was low, then a high pH would improve the treatment efficiency. From this, one can conclude that there is no general trend in the influence of initial pH on the UV/H_2O_2 process from one system to another. The effect of varying initial pH depends on a lot of factors and has to be determined for each new set of experiments.

A possible way to improve a UV/H_2O_2 process would be to increase the UV light intensity in order to deliver more photonic energy to the mixture of pollutants and oxidant. However, more UV power represents additional operating costs and therefore its enhancement should be economically justified. Castrantas and Gibilisco investigated the effect of varying light intensity in their study of the photooxidation of phenols with a UV/H_2O_2 process (26). By using two lamps and comparing these results to ones obtained with eight lamps, they found that a four-fold increase in light power results in only a 25% increase in phenol destruction. Thus, varying the light intensity does not greatly affect the oxidation process, and a corelation between the additional costs and the improvement of the process has to be determined, with respect to minimization of operating costs.

Influence of the composition of the wastewater

The efficiency of wastewater treatment by photooxidation depends on the nature of the compound(s) being oxidized. Pollutants that have a high absorbance and/or intense color in solution will be more difficult to oxidize since they might not allow enough light penetration. However, it is also necessary for the pollutants to have a sufficiently high absorbance at a wavelength of 254 nm, so they can be photoactivated by UV radiation, which thereafter facilitates hydroxyl radical attack.

According to Meardon *et al*, UV H_2O_2 photooxidation is most effective in the destruction of chlorinated, aromatic, and higher molecular weight organics and least effective on low molecular weight alcohols, amines, and carboxylic acids (18).

Sundström *et al* compared the elimination rates of benzene and trichloroethylene by UV-catalyzed oxidation with hydrogen peroxide (12). First they treated both contaminants separately, and then combined them into a single effluent, while varying the concentrations of pollutants and H_2O_2. When each component was treated individually, its rate of disappearance increased with increasing H_2O_2 concentration, and decreased with increasing pollutant concentration. The effects of adding the other component to pure solutions of benzene or trichloroethylene were studied. This proved to be detrimental to the process, since the rate constant for benzene elimination decreased significantly when it was combined with trichloroethylene. Similarly, the rate constant for the disappearance of trichloroethylene decreased extensively when benzene was added to it in solution. Also, in contrast to the single component results, the reaction rate for trichloroethylene increased as its concentration in the mixture was increased. Since an increase in trichloroethylene concentration is associated with a decrease in benzene concentration, these results suggest strong interactions between the reacting components. Additional experiments were done by Sundström *et al* to compare rate constants for solutions of pure components and mixtures of both components having the same initial organic carbon concentration. In all cases, the rate constants for the elimination of pure benzene were similar in magnitude to those for the elimination of benzene in a mixed solution with trichloroethylene. On the other hand, the rate constants for trichloroethylene in mixture were about one-half of their values as pure components. These results show that the aromatic component, benzene, has a strong adverse effect on the rate of destruction of the aliphatic component, trichloroethylene. This effect may be due not only to the benzene itself, but also to the reaction intermediates formed as benzene gets oxidized by hydroxyl radical attack. The presence of benzene and its aromatic oxidation products may inhibit the destruction of trichloroethylene through competition for available UV photons and hydroxyl radicals. In fact a separate study done by the same group showed that benzene competes more effectively for light and reactive species than trichloroethylene, when comparing their corresponding rates of oxidation in a UV/H_2O_2 process (9). This strong interaction between components demonstrates the need to study actual mixtures instead of attempting to predict their behavior from pure component data.

In a complex mixture of pollutants which make up an industrial effluent, there can be substances which are scavengers of hydroxyl radicals. These compounds can react with hydroxyl radicals and as a consequence reduce their concentration in solution, which lowers their availability for organic pollutants. Thus the presence of radical scavengers will negatively affect the oxidation process. Known scavengers of hydroxyl radicals are bicarbonate ions and humic substances (20,21), and other anions such as carbonate, sulfide, nitrite, bromide, and cyanide (4). In all cases an increase in bicarbonate ions or humic substances will slow down the rate of oxidation of organic matter. In a photooxidation experiment, Beltran *et al* observed that the concentration of atrazine is stabilized in the presence of these scavengers (21). While bicarbonate ions act solely as hydroxyl radical scavengers, the stabilization of atrazine in the presence of humic substances can be attributed to both the scavenging of hydroxyl radicals and to the competition of humic substances for the radiation flux. The action of bicarbonate ions demonstrates that the main pathway of atrazine oxidation is through hydroxyl radical attack. De Laat *et al* also studied the effect of the presence of an organic matrix (fulvic acid) in their photooxidation system, and found that it will lower the efficiency of the elimination process of trichloro-1,1,2 ethane (20).

It is well known that some soluble inorganic compounds such as calcium and iron can precipitate out of solution due to small changes in temperature, pH, etc. A possible impact of this occurence on a UV/H_2O_2 system is a coating of its quartz tubes by the precipitated minerals, which negatively affects the performance of the system by blocking UV light transmittance. Scraping, mechanical cleaning, acid washing or other chemical treatment can be effective in removing scaling, but the best way to prevent this problem is by stabilizing the water prior to the photooxidation treatment. Manufacturers of photooxidation equipment propose various alternatives to solve this problem. Solarchem's solution to the deposit formation is a pneumatically-driven circular wiper that shoots up and down the quartz tube every few minutes, while Peroxidation Systems reduces deposition problems by pre-oxidation followed by precipitation and ion filtration, and by reduction of pH to inhibit scaling (29). Ultrasounds could also be used to prevent this problem by keeping the minerals from sticking to the quartz tubes through sonic vibrations. In spite of this, most soluble inorganic chemicals do not have a significant impact on the design and operation of a UV/H_2O_2 system, according to Froelich (16).

Additional experimental considerations and observations

During the course of a photooxidation experiment, characteristics other than the concentration of residual pollutant can be monitored with time. Yue and Legrini measured the pH of a solution of organic contaminants at different time intervals during its oxidation by a UV/H_2O_2 process (17). Their results showed that pH dropped from an initial value of 6 to 3.2 in the first 15 minutes and then stayed at about 3.5 for the remaining time of experiment. This indicates a formation of acids as a result of the oxidation of chlorinated compounds that get partially converted to hydrochloric acid (HCl). Such a drop in pH is therefore a positive indication of the efficiency of the UV/H_2O_2 process. Sundström *et al.* in their study on the photooxidation of benzene, monitored the absorbance of the solution with time (9). The absorbances of reacting aromatic solutions initially increased rapidly with time, reached a maximum, and then decreased to a negligible value. According to them, the increase in absorbance is caused by the formation of reaction intermediates that absorb UV light more strongly than the parent compounds.

In a photooxidation system, gas-phase oxidants such as oxygen (O_2) and ozone (O_3) can be added to a UV/H_2O_2 process in an attempt to improve oxidation rates (4,22). Introducing these gases by bubbling them through the irradiated mixture enhances the production of hydroxyl radicals. However, it also represents additional operating costs and a necessity for gas storage that must be financially taken into account. Ku and Ho found that adding dissolved oxygen (DO) to their UV/H_2O_2 system had little effect on the destruction rate of phenols. They even observed a slight decrease in the removal of these compounds when the concentration of DO was increased in solution (22).

Many studies have been reported on the disinfection of waters by UV radiation or hydrogen peroxide alone, but their combination has received little attention in this field. Sundström *et al* studied the destruction of microorganisms in water using ultraviolet-catalyzed oxidation with hydrogen peroxide as the oxidizing agent (9). Their results showed that the presence of H_2O_2 greatly enhanced the rates of inactivation of microorganisms when added to a UV disinfection system. However, the rates of inactivation of microorganisms were strongly affected by the thickness of the liquid layer because of the high absorption of light by H_2O_2. By using a reactor with a thin liquid layer, the combination of UV light and hydrogen peroxide provided rapid rates of disinfection. Generally, the design of a UV/H_2O_2 reactor has to take into account the thickness of the liquid layer, since there is a certain limit up to which UV light can penetrate an aqueous solution. In some cases it is important to keep a thin liquid layer for the photooxidation process to be efficient.

Heterogeneous photooxidation with TiO_2

The photooxidation of a pollutant can also be achieved by using the semiconductor, titanium dioxide (TiO_2). The principles of operation are essentially the same as in a UV/H_2O_2 process with the difference that TiO_2 is a heterogenous photocatalyst which does not dissolve in water. Kutal defines photocatalysis as "the acceleration of a photoreaction by the presence of a catalyst."(30). Furthermore, still according to Kutal, "the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction.". After introducing a quantity of TiO_2 in the photochemical reactor with the contaminated water solution, its surface gets irradiated with UV light and becomes a source of hydroxyl radicals. These highly reactive species are, as in a UV/H_2O_2 process, the main oxidizing agents responsible for the destruction of the pollutant.

Al-Ekabi and Serpone (31) have investigated the photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over fixed TiO_2. They showed that the degradation of phenol is indeed a light-induced reaction mediated by illuminated TiO_2, as no change was observed under direct irradiation (no TiO_2) or with TiO_2 in the dark.

Most heterogeneous photocatalysis studies to date have used ~ 0.1 wt% slurries of titanium dioxide particles, of specific size ranging from 0.1 to 30 mm depending on the source (32). The standard photocatalyst of choice for a lot of researchers is the Degussa-P25 titanium dioxide, anatase form. This brand of TiO_2 is very popular because of its high surface area to volume ratio and its capacity to adhere tenaciously to glass. Matthews studied another form of TiO_2 and observed that the rate of reaction in a photochemical system is proportional to the surface area of the TiO_2 (19). Thus he found that the rate of degradation of 4-chlorophenol using La Porte TiO_2, a brand with a much smaller surface area, was much lower than the value obtained using Degussa-P25 TiO_2. Other semiconductor oxides that have proved to be nearly as effective as TiO_2 include tungsten oxide (WO_3) and zinc oxide (ZnO) for the decomposition of some contaminants (32).

Photochemical reactors used for TiO_2-assisted oxidation usually have an artificial UV light source operating at a dominant wavelenght lower than 400 nm, similar to the ones used in a UV/H_2O_2 process. However, heterogeneous photocatalysis has also been proved to be effective with natural sunlight, since titanium dioxide can be photoactivated with the near-UV component of sunlight. Matthews used a solar reactor and compared its performance to that of an "artificial" photochemical reactor. Using CO_2 formation as a basis for comparison in the photooxidation of 4-chlorophenol, his results indicated that the rate of formation of CO_2 in the solar reactor was over three times the value found for the photochemical reactor (19).

TiO_2 can either be used in suspension in an aqueous solution of contaminated water, or supported on a matrix. If a photocatalyst is used in suspension in a continuous flow system, there is a need to resuspend it in solution and/or filter it out of solution at a certain stage in the process. This can be avoided by immobilizing the photocatalyst in the reactor. It is then necessary to find a way to fix the TiO_2 on a matrix (10,31,33). A number of papers have examined means of catalyst immobilization on beads, inside tubes of either glass or Teflon, on fiber glass, or on woven mesh. As in all other areas of heterogeneous catalysis, catalyst immobilization on progressively larger particles, although very convenient, leads to an increased average convective-diffusion distance from fluid to catalyst surface, and this consequence can result in reactions that are mass transfer limited (32 and sources cited herein). Still, thin films of TiO_2 have proved to adhere tenaciously to glass and have been used as such in many experiments. For instance, Al-Ekabi and Serpone were able to use TiO_2 in a stationary phase by coating a thin film of it either onto the internal surface of a glass coil or the external surface of glass beads (31), and Matthews constructed photoreactors in which the TiO_2 was attached to a glass surface (33). It is highly probable that there will be more experiments done in the future on the immobilization of TiO_2 in a photochemical reactor in such a way that mass transfer limitations can be minimized.

The types of pollutants used for studies on heterogenous photocatalytic oxidation are similar to the ones found in photooxidation with hydrogen peroxide, i.e. chlorinated compounds, phenols, benzene, etc. Similarly to homogeneous photooxidation, the efficiency of the process often depends on the nature of the compound being oxidized. Matthews treated twenty-one organic compounds known to be possible contaminants of water with UV-illuminated TiO_2 powder in aqueous suspension, and in each case the organic material was converted to carbon dioxide (19). He found that the rate of oxidation was increased when the number of chlorine substitutions on the aromatic ring was increased from one to two. This was observed for both the chlorobenzenes and the chlorophenols. He concluded that overall, there is little variation in the rate of destruction of the different contaminants. It appeared that the reaction was indiscriminate and powerfully oxidizing.

The concentration of TiO_2 and pollutants in the photochemical reactor have to be carefully monitored in order to optimize the process. A too high concentration of pollutants will lower the fluorescence intensity of the mixture (31), and thereby reduce its capacity to absorb UV light. Also, a high catalyst concentration may create an excess in turbidity which will have the same effect. Changes in these concentrations will affect a heterogenous photocatalyst process in the same way that they affect homogeneous processes with hydrogen peroxide.

In their study of the photocatalytic oxidation of phenol using TiO_2 and UV light, Tseng and Huang found that an increase in temperature greatly raised the rate of phenol decomposition (34). The influence of temperature is important to consider in a wastewater treatment process, since in many circumstances an actual industrial effluent will be exiting at very high temperatures, as in the case of condensed contaminated vapors.

In many studies the importance of introducing oxygen to complete a heterogenous photocatalytic system is brought forward. Many experiments have been perfcrmed using aqueous solutions that were aerated (19,31,32). In their study of the photooxidation of phenol in an aqueous solution using a TiO_2 slurry, Tseng and Huang demonstrated that the concentration of dissolved oxygen in a solution played a significant role in the photooxidation process. They found it was much more efficient when the TiO_2 photooxidation was taking place in an oxygen-saturated solution, rather than in a nitrogen-saturated one (34).

The rates of reaction encountered in heterogenous photooxidation usually follow first order kinetics, as in a homogenous UV/H_2O_2 system.

As for UV/H_2O_2 experiments, the influence of pH in a UV/TiO_2 process varies from one experiment to another. Tseng and Huang found the optimum pH for the photocatalytic degradation of phenol to be in the neutral pH region, e.g. 5-9 (34). Matthews found similar results, since for each studied compound he obtained higher rates of oxidations at pH 4.4 rather than at pH 2.9 (19). All three researchers observed an initial drop in pH upon illumination, suggesting the formation of strongly acidic intermediate substances. The pH was then stabilized and remained constant after a certain time of reaction.

Photocatalysis with Fenton's reagent

The combination of a ferrous salt and hydrogen peroxide, known as the "Fenton reagent" has been used as one of the most effective oxidants of organic substances (27 and sources cited herein). The general classic procedure consists of the addition of hydrogen peroxide to a solution in the presence of ferrous (II) ions. In the past few years, some work has been done on catalyzing "Fenton" oxidation with UV radiation. This type of photooxidation is sometimes referred to as "photo-Fenton oxidation".

Lipczynska-Kochany (27) has performed a series of experiments on the degradation of nitrobenzene and nitrophenols in homogeneous aqueous solutions. For the treatment of both aromatic compounds, she compared four different UV/oxidation processes. When using direct photolysis with UV light (without chemical oxidant), there was almost no degradation. However, when H_2O_2 was added to the UV-irradiated solution, a slight oxidation took place. A better oxidation performance was achieved with the use of the Fenton reagent ($FeCl_3/H_2O_2$) in the dark, but the best results by far were obtained by combining the Fenton reagent with UV radiation. Pignatello and Sun (35) achieved similar results in their study on the degradation of the chlorophenoxyalkanoic acid herbicides 2,4-D and 2,4,5-T, by combining UV light with ferric ion (Fe^{3+}) and hydrogen peroxide. With this process they managed to convert both pollutants to chloride and CO_2 in less than two hours. They found that the transformation of 2,4-D was faster in the photo-assisted reaction ($UV/H_2O_2/Fe^{3+}$) than in the thermal reaction (H_2O_2/Fe^{3+}), and much faster than in the photolyzed single-reactant systems (UV/Fe^{3+} and UV/H_2O_2). In fact, they observed that UV/H_2O_2 reactions were insignificant to the degradation process. Other studies confirmed that UV light strongly accelerates the Fenton reaction (36).

Sometimes the treatment of highly toxic effluents is difficult to achieve with the use of traditional wastewater treatment technologies, such as biological treatment. Photo-Fenton oxidation is an interesting alternative that should be considered for the treatment of these wastes, since it can practically oxidize any type of organic compound. Pignatello and Huang studied the degradation of polychlorinated dibenzo-*p*-dioxin and dibenzofuran contaminants in 2,4,5-t by photoassisted iron-catalyzed hydrogen peroxide (37). These extremely toxic compounds are present in various waste products, including commercial polychlorinated biphenyls (PCBs). The photo-Fenton oxidation treatment resulted in complete or nearly complete removal of all PCDD and PCDF contaminants.

As in other photooxidation processes, there is no general recipe for the effect of pH on the efficiency of the photo-Fenton oxidation process. In their study of a $UV/H_2O_2/Fe^{3+}$ process, Pignatello and Sun found an optimum pH for the degradation of herbicide wastes (35). They found that the reaction rate drops steeply on either side of the pH 2.7-2.8. Above the optimum pH, reactivity decreases because Fe^{3+} ions precipitate as ferric oxyhydroxide; while below this optimum, the formation of $Fe\text{-}O_2H^{2+}$, which is the initial step leading to the genration of active oxidants, is inhibited. Zepp *et al* (36) initiated a detailed study on the influence of pH in the generation of hydroxyl radicals by Fe(II) combined with H_2O_2 and UV light. They performed kinetic studies on the photooxidation of trace nitrobenzene and anisole, and they found that hydroxyl radicals can be efficiently produced with pH ranging from 3 to 8 in solution. The photo-Fenton oxidation process can then be used at the neutral pH values that are usually encountered in polluted waters. This would make the process very practical since no pH adjustment would be needed in the treatment of industrial wastewaters.

Heterogeneous photocatalysis with copper complexes

According to Kölle, the majority of studies found in the literature on photocatalytic transformations involving inorganic salts and complexes (e.g. copper) are concerned in the first place with scope and conditions of catalyzed reactions with some organic substrate (38). As a consequence, in most cases very little information on the mechanics of the reactions is available. In a complex reaction scheme, it is sometimes not clear which of the steps are light dependent. Therefore it is generally not possible to classify the reactions according to the role that light plays in the process, i.e. wether these are photoinduced, photoassisted, catalytic in photons or in one chemical component. However, all these reactions share the common condition that they require light in order to proceed, and that in the absence of the catalyst they will run at a much slower rate or even not run at all.

Two main classes of photooxidations in the presence of copper complexes can be distinguished: photosensitized and photoassisted. Sykora *et al* give a list of representative examples in a brief overview (39).

Very few studies have been made on the photocatalytic treatment of organic substances using copper complexes. Sykora *et al* (39) performed a series of experiments on the photooxidation of organic substrates in the presence of copper ions. The emphasis was put on a Cu(I)-Cu(II) photoredox cycle, which they developed experimentally and treated in detail. Using a photocatalytic system, they oxidized organic substrates containing hydroxyl groups, such as aliphatic alcohols and phenols combined with copper complexes, and described possible reaction schemes taking place inside the photoredox cycle.

Sedlak and Holgné have studied the effects of a transition metal (Cu) and of photooxidants (•OH, H_2O_2) on the aqueous-phase oxidation of S(IV), in order to simulate the transformation of certain atmospheric pollutants in clouds. They have developed an understanding of how dissolved Cu in cloud droplets catalyze the conversion of HO_2/O_2 into H_2O_2 (23).

Modelling of photooxidation processes

It is often desirable for a researcher to be able to predict the outcome of an advanced oxidation process before actually applying it to a solution of contaminant(s). A mathematical model describing the processes that simultaneously occur in an AOP is required so that investigators can understand the chemistry of a particular system under study. Models can also be useful for estimating the effect of changing a process parameter, eliminating unproductive areas of parameter variation and suggesting potential fruitful ones. Since the reactions taking place in an AOPs are very complex in nature, and the general idea that "more is better" does not generally apply to AOPs, any researcher or designing engineer would benefit from a model that would help him/her set up an experimental procedure to follow.

Peyton assembled a very useful and extensive set of guidelines for the selection of a chemical model for advanced oxidation processes (7).

Ollis and Turchi developed a useful model and design considerations for a photooxidation reactor by providing 1) current rate equations for photocatalyzed simultaneous destruction of multiple oxidizable organic contaminants and 2) simplified convective transport equations appropriate to photoreactor design under various degrees of fluid mixing and simultaneous reaction contributions by photocatalyzed heterogeneous as well as homogeneous reactions (40).

Nicole *et al* examined the influence of technological characteristics of photochemical reactors on the rate of photodegradation of hydrogen peroxide in aqueous solution (28). Their study resulted in a model which has been subsequently used by other researchers (20). An experimental procedure was also developed for the determination of photonic fluxes at 253.7 nm emitted by low-pressure mercury vapour lamps. This is particularly useful since compared to classical methods of photonic flux determination by potassium ferrioxalate or uranyl oxalate actinometry, the utilization of H_2O_2 as an actinometer is an attractive and simple alternative.

Commercial photooxidation systems

A number of companies have already been marketing photooxidation technologies for many years.

The Ultrox UV/oxidation treatment system uses UV radiation, ozone, and hydrogen peroxide to oxidize organics in water (4,14). It was developed by Ultrox International of Santa Ana, California, and the company was issued a process patent in 1988 for the application of their system to a broad range of organic compounds in water. Since the Ultrox system treats wastewaters by bubbling ozone gas through it, some Volatile Organic Carbon (VOC) removal could be attributed to stripping in addition to oxidation. Still, no harmful emissions are emitted to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit. Stripping can be a significant removal pathway for compounds that are difficult to oxidize. More importantly, by adding ozone there is a synergistic effect that enhances the reaction of transforming hydrogen peroxide into hydroxyl radicals, therefore reducing the required amount in power supply. This treatment has been proved for its efficiency in treating contaminated groundwaters (13). The same study showed removal efficiencies for contaminants such as trichloroethylene and total VOCs that were as high as 99 percent and 90 percent, respectively.

Another commercial application of a UV/peroxidation technology was created by Peroxidation Systems, Inc., based in Tucson, Arizona (8,16). Development of their oxidation system, called the perox-pure™ system, began in the late 1970's, and there are now about seventy full-scale treatment systems in operation. The process uses high intensity UV light, hydrogen peroxide, and a patented reactor design to oxidize toxic organics in water. Recent improvements (1992) have been made that provide operating cost savings of up to 50%.

An interesting innovation to a photooxidation system was brought up by Solarchem Environmental Systems, based in Richmond Hill, Ontario (15). They observed that there are a number of substances (e.g. chloroalkanes, aliphatic ketones and certain nitro-compounds) which degrade very slowly under hydroxyl radical oxidation. Based on the premise that substances that are difficult to oxidize ought to be easy to reduce, they have developed a new photodegradation process called RAYOX®, which features the generation of one of the strongest reducing agents known, the hydrated electron. Its reductive potential is $E^\circ = -2.9$ V. The hydrated electron (e_{aq}^-) is a species that is formed when electrons are thermalized in aqueous solutions, through a photolytic process, for instance. The RAYOX® system has its own patented photochemical reducing agent as a source of hydrated electrons. The process has proved to be more efficient in the treatment of chloroethanes and other contaminants than a process utilizing solely UV light and hydrogen peroxide, by up to a factor of 4. It has also been demonstrated that the RAYOX ® treatment is very effective with polluted waters having a very high salt content.

Another photooxidation process called UVOX was developed during the early 1980s by Jansson Consulting Services Inc. based in Regina, Saskatchewan. It utilizes UV radiaition to produce hydroxyl radicals from the photolysis of H_2O_2 with air-cooled UV units (11).

Previous applications of photooxidation to pulp mill effluents

Some studies have already been made on the possibilities of treating pulp mill effluents using some type of photooxidation process. McKelvey and Dugal (1975) performed the decolorization of kraft mill effluents and effluents generated by the washing of neutral sulfite semichemical pulps, by using ultraviolet light and oxygen (5). Their treatment also resulted in a significant reduction in BOD and COD. Even though a complete decolorization was achieved for all efluents, it was felt that the irradiation times were excessively long (1 to 2 hrs) and therefore an attempt was made to find additives that would improve the photooxidation efficiency. One of these additives was hydrogen peroxide which they used as a source of free hydroxyl radicals, and it appeared to be the most promising additive.

Prat *et al* (6) examined the use of hydrogen peroxide in combination with ultraviolet radiation for the treatment of wastewaters generated by the chlorination and alkaline extraction stages of kraft pulp bleaching operation. Their results were reasonably good as they managed to eliminate 75% of the initial color by using a UV/H_2O_2 process. However, even in the most favorable conditions, it was found that the treatment times were very long (~ 3hrs). With hydrogen peroxide alone, the color removal was 40%, while with the addition of ultraviolet radiation up to 75% of the initial color gets degraded. In spite of this, they concluded that the use of the hydrogen peroxide treatment together with ultraviolet radiation, although it does bring with it in all cases a greater reduction of color in the effluent than when this oxidant is used in darkness, does not turn out to be economically competitive. This is due to the fact that the improvement in the rate of reaction is not high enough to compensate for the complexity of the necessary installation, nor the additional operating costs. On the other hand, the residual hydrogen peroxide would not be detrimental to the posterior biological processes, obtaining an overall reduction of the color in the final effluent. Furthermore, the posterior stage of pulp bleaching with hydrogen peroxide could provide the reactant at a very low cost, if the residual hydrogen peroxide content of the effluent from that stage were used.

Comparative evaluation of UV/H_2O_2 as a tiertary treatment process

In order to determine the feasibility of a UV/H_2O_2 process for the treatment of wastewaters, its performance and total cost must be evaluated and compared to other processes already used in the marketplace.

Meardon *et al* (18) used UV/peroxidation as a tertiary process for the treatment of an aqueous effluent from a hazardous waste treatment facility. The aqueous effluent contained residual amounts of various organics and heavy metals. The treatment followed evaporative crystallization (primary process) and activated sludge bio-treatment and/or reverse osmosis (secondary processes), and was compared to the performance of another tertiary treatment process, carbon adsorption. Their test results indicated a successful reduction in TOC content for all feedstocks given sufficient peroxide dose, UV light power, and reaction time. However, when compared to carbon adsorption, the UV-peroxidation process was not an economically attractive option for tertiary treatment of biological effluents or reverse osmosis permeates derived from the condensate feedstock. The authors attributed the relatively unattractive performance of the UV-peroxidation system to the high percentage of TOC content in the feedstocks tested, which consisted mainly of low molecular weight alcohols, ketones, and carboxylic acid. These compounds were found to be refractive to photooxidation by a UV/H_2O_2 process.

CHAPTER 3 PHOTOOXIDATION THEORY

Introduction

An advanced photooxidation process features the action of a very powerful oxidizing agent, the hydroxyl radical (•OH). There are various ways to generate hydroxyl radicals in solution, either homogeneously or heterogeneously, with the assistance of UV radiation. A homogeneous photooxidation process involves the use of a liquid-phase oxydant, such as hydrogen peroxide (H_2O_2). A combination of this oxydant with a solution of contaminated liquid can form a well-mixed, homogeneous mixture. A heterogeneous photooxidation process involves the use of a solid-phase catalyst, such as titanium dioxide, for the generation of hydroxyl radicals. This catalyst is introduced into the contaminated liquid and does not dissolve in it. Such a mixture is heterogeneous in nature, and the catalyst particles have to either be kept continuously in suspension, or fixed on a matrix.

A hydroxyl radical is a very strong oxidizer which reacts with organic contaminants in an aqueous solution. The oxidative potentials for common oxidants are listed in table 3.1. As shown, the hydroxyl radical is approximately twice as powerful as chlorine and 1.5 times as powerful as hydrogen peroxide. It is second only to fluorine in oxidizing power.

A photooxidation process that combines hydrogen peroxide and UV light is a fast and effective way to oxidize organic pollutants which involves three possible oxidation pathways: direct photolysis, by which organics absorb UV light, oxidation with peroxide (although this contribution is negligible in most cases) and via hydroxyl radical attack. Although light alone or oxidant alone produces contaminant partial destruction, only the simultaneous use of light and an oxidant has often been shown to yield complete conversion of organic carbon to carbon dioxide (32).

Rel. oxidation power (Chlorine = 1.0)	Species	Oxidative potential (Volts)
2.23	Fluorine	3.03
2.06	Hydroxyl Radical	2.80
1.78	Atomic Oxygen (singlet)	2.42
1.52	Ozone	2.07
1.31	Hydrogen Peroxide	1.76
1.25	Perhydroxyl Radical	1.70
1.24	Permanganate	1.68
1.17	Hypochlorous Acid	1.59
1.15	Chlorine Dioxide	1.57
1.10	Hypochlorous Acid	1.49
1.07	Hypoiodous Acid	1.45
1.00	Chlorine	1.36
0.80	Bromine	1.09
0.39	Iodine	0.54

Table 3.1. Oxidative potentials of some typical oxidants. (source: Bernardin, F.E. (8))

A photooxidation process has the potential to carry the original contaminant through a series of higher oxidized intermediates to carbon dioxide. Complete oxidation of an organic compound can also be referred to as mineralization.

Absorption of UV light

According to the literature, the maximum absorbance of UV radiation by hydrogen peroxide occurs at a light wavelength of approximately 220 nanometers (nm)

(4). A spectrophotometric scan of five solutions of H_2O_2 is shown in figure 3.1. These solutions have concentrations of 0.1, 0.2, 0.4, 0.5 and 1.0% w/v H_2O_2 respectively. Figure 3.1 indicates that all five solutions absorb light in the photonic wavelengths range of 190 to 310 nm, with an absorbance peak (y-coordinate) between the wavelengths 210 and 250 nm (x-coordinate). The clearest absorbance peak can be observed with the 0.1% w/v solution, and is at a wavelength of approximately 212 nm, which is close to the value of 220 nm given in the literature.

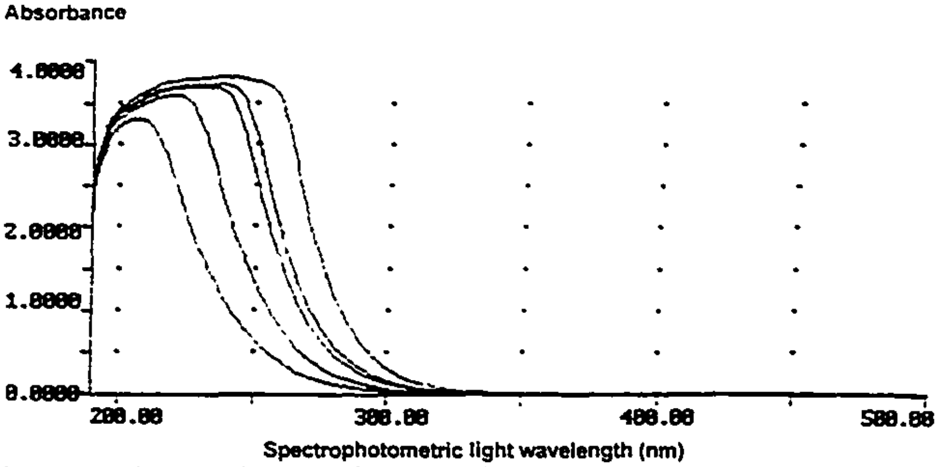

Figure 3.1. Spectrophotometric scans of different H_2O_2 concentrations. Highest curve: 1.0% w/v H2O2, followed respectively by 0.5, 0.4, 0.2 and finally 0.1 % w/v H2O2 represented by the lowest absorbance curve.

In this study, like in most commercial applications, low-pressure mercury vapor UV lamps are used to generate UV radiation. These lamps provide the most efficient generation of light in the 200-300 nm range of wavelengths. They are approximately 30% efficient in converting electrical energy to light energy (41). The range of emission wavelengths emitted by those lamps is illustrated in figure 3.2, taken from a typical low-pressure mercury vapor lamp manufactured by Helma Canada inc. It can be observed that the dominant emission wavelength of these lamps occurs at about 254 nm. Since the wavelength at which H_2O_2 shows maximum absorbance does not match the dominant emission wavelength of the UV lamp, these lamps may not be the best choice for a UV/H_2O_2 photooxidation process. In fact, according to the literature, the absorptivity of hydrogen peroxide at 220 nm is about five times its absorptivity at 254 nm (41).

However, low-pressure mercury vapor UV lamp are relatively cheap and are easily available on the market, since they have been used for a number of years in different applications, including the desinfection of waters. Furthermore, the advantage of an increased absorptivity of H_2O_2 with a 220 nm lamp might be balanced by the decreased efficiency of the lamp producing this wavelength (41). Also, a UV lamp operating at 220 nm is not very common, and therefore the use of such a lamp in a commercial application might end up being very expensive and increase the cost of the UV/H_2O_2 system dramatically.

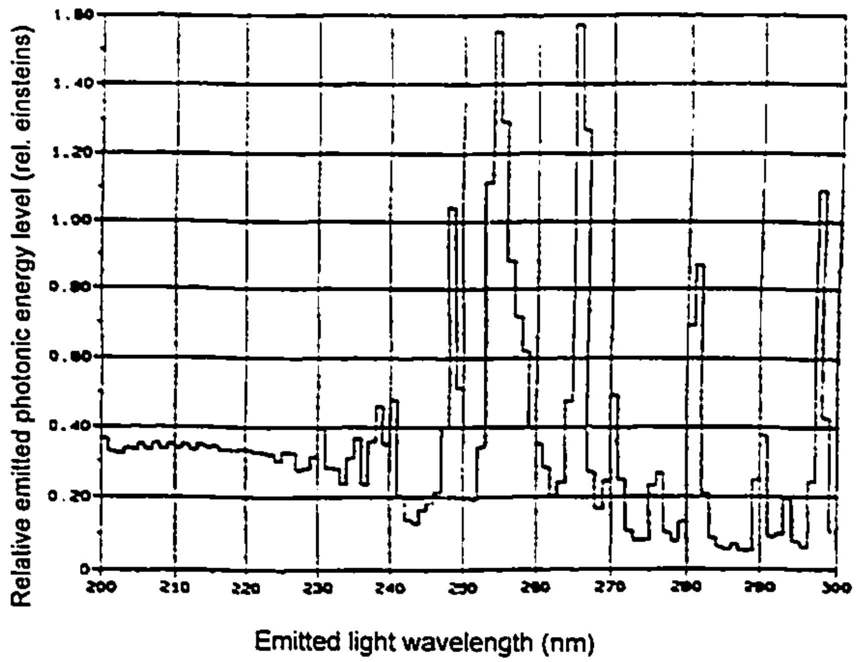

Figure 3.2. Energy levels distribution of a typical low-pressure mercury vapor UV lamp over a range of photonic wavelengths. Dominant emission wavelength close to 254 nm. (Source: Helma Canada Inc.)

Since hydrogen peroxide does not have a relatively high absorbance at 254 nm, organic compounds which strongly absorb light at that wavelength can compete for it and go under direct photolysis (9). A spectrophotometric scan of a typical pulp and paper mill effluent is illustrated in figure 3.3. In this effluent, the constituents, which are mainly organic compounds, are strong light-absorbers in photonic wavelengths ranging from 190 to 320 nm. Therefore, below a certain hydrogen peroxide concentration, most of the light emitted by the source of irradiation can be absorbed by the effluent, not by hydrogen peroxide. In such a case, direct photolysis can contribute significantly to the overall rate of reaction.

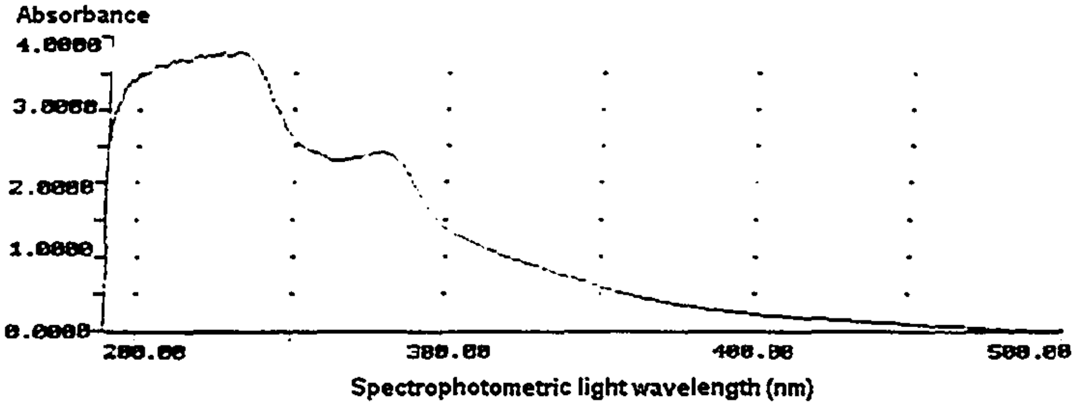

Figure 3.3. Spectrophotometric scan of a typical TM pulp and paper effluent

Photolysis of hydrogen peroxide

The absorption of radiated UV light by hydrogen peroxide (H_2O_2) leads to the production of two moles of hydroxyl radicals (•OH) per mole of hydrogen peroxide decomposed. This reaction is described as follows:

$$H_2O_2 \xrightarrow{h\nu} 2\,{\bullet}OH \qquad [3.1]$$

in which $h\nu$ represents the energy delivered by the light source onto the compound. For each photon of light, the energy produced is equivalent to:

$$E = h\nu = hc/\lambda \qquad [3.2]$$

where E = energy delivered by the photon (in ergs; 1 erg = 10^{-7} J);

h = Planck's constant = 6.6256 x 10^{-27} erg-sec/quanta;

ν = frequency of the photon (in sec^{-1});

c = velocity of light in a vacuum = 2.9979×10^{10} cm/s;

λ = wavelength of the photon (in cm);

A common way of expressing the total amount of energy delivered by the light source is the Einstein, a unit equivalent to the energy in ergs of 1 mole of photons. It may be calculated by multiplying the energy of a single photon by N, Avogadro's number, 6.023 x 10^{23} (42).

After photolysis, the generated hydroxyl radicals are free and likely to recombine immediately to give back H_2O_2. This creates a possible "cage" effect which keeps the hydroxyl radicals from escaping their source. Thus the radical-radical recombination is an important reaction pathway in the absence of other reactants (41):

$$2\,{\bullet}OH \longrightarrow H_2O_2 \qquad [3.3]$$

Therefore, there is typically a fifty percent efficiency which gives about one radical produced per photon absorbed, rather than two which would be arising from an irreversible reaction, and reaction (1) can be expressed as:

$$H_2O_2 \overset{h\nu}{\longleftrightarrow} 2\,{\bullet}OH \qquad [3.4]$$

Even though it is well established that hydroxyl radicals are the main primary photoproducts resulting from the photoirradiation of acidic and neutral solutions of hydrogen peroxide (27 and sources cited herein), small amounts of $HO_2{\bullet}$ radicals are also formed:

$$H_2O_2 \xrightarrow{h\nu} \bullet H + \bullet O_2H \qquad [3.5]$$

$$\bullet OH + H_2O_2 \longrightarrow HO_2\bullet + H_2O \qquad [3.6]$$

$$\bullet H + H_2O_2 \longrightarrow H_2O + \bullet OH \qquad [3.7]$$

$$HO_2 + H_2O_2 \longrightarrow HO\bullet + H_2O + O_2 \qquad [3.8]$$

$$HO_2\bullet + HO_2\bullet \longrightarrow H_2O_2 + O_2 \qquad [3.9]$$

Excitation by light absorption

It is well known that light absorption leads to an electronic excitation of the absorber. Electronically excited species have a different reactivity than those in an unexcited state. It has been experimentally observed that the electron density of an excited molecule is different from that of the ground-state molecule (43). A simple example can illustrate this. The electronic structure of Lithium in its ground state is represented in the familiar form Li $1s^2\,2s^1$: the electrons are positioned in the lowest orbitals available to them. An electronically excited state of Lithium is represented by the configuration Li $1s^2\,3p^1$, and this one lies at a higher energy level than the Li $1s^2\,2s^1$ configuration. Since the chemistry of a species strongly depends on its electronic structure, the reactivity of the excited lithium atom can be expected to differ from that of the ground state atom (44). Light absorption strongly affects the electronic structure of a molecule, thus it will also affect its reactivity. Moreover, a molecule which has absorbed a quantum of radiation becomes "energy-rich" in the absorption process. This absorbed energy also has a great effect on the reactivity of the molecule.

Comparison of thermolysis and photolysis of peroxides

Photochemical and thermal decomposition of peroxides such as H_2O_2 are similar since in both cases the primary reaction is the homolytic fission of peroxide linkage (O-O) producing oxygen radicals. However, there are several aspects over which the two processes differ. The photolysis is initiated by the absorption of light energy, which excites hydrogen peroxide to cleave the O-O bond. Therefore, the produced radicals are in an excited state, or in other words, "hot" radicals are produced by photolysis. These radicals often have a different behavior than those in the ground state, or those produced by thermal decomposition (27).

It was experimentally observed that the oxygen radicals formed by the photolysis of esthers are so electronically unstable that they decompose before being able to take part in further intermolecular reactions (43 and references herein). As an example, consider the photolysis of diisopropyl peroxide, which produces an excited isopropoxy radical, (i-PrO•*) that readily decomposes to give mostly acetaldehyde and methyl radical before it reacts with other molecules:

$$(CH_3)_2CHO{-}OCH(CH_3)_2 \xrightarrow{h\nu} (CH_3)_2CHO\bullet^* + (CH_3)_2CHO\bullet \qquad [3.10]$$

$$(CH_3)_2CHO\bullet^* \longrightarrow CH_3\bullet + CH_3CHO \qquad [3.11]$$

On the other hand, ground-state (ordinary) alkoxy radicals formed by thermolysis can be trapped completely by scavengers such as nitric oxide. Considering our example, the unexcited isopropoxy radical (i-PrO•) reacts with nitric oxide to give isopropyl nitrite and then acetone (equation 3.12 and 3.13):

$$(CH_3)_2CHO\bullet + NO \longrightarrow (CH_3)_2CHONO \qquad [3.12]$$

$$(CH_3)_2CHONO \longrightarrow CH_3COCH_3 + HNO \qquad [3.13]$$

However, excited alkoxy radicals are not trapped by nitric oxide, but decompose according to equation (3.11). Not all radicals produced by photolysis are electronically excited. In this particular case, i.e. photolysis of diisopropyl peroxide, experimental observations have showed that more than half of the alkoxy radicals are excited (43).

Thus, there are two main aspects over which photochemical reactions differ from thermal reactions. First, photochemical reactions involve relatively high concentrations of highly excited species which may react faster than the ground-state species, and may even participate isothermally in processes which are endothermic for the latter, and secondly, if the excitation is electronic, by the changes in chemical reactivity which may accompany the new electronic configuration of the species (44).

Direct photolysis of organics

Direct photolysis is usually beneficial to a photooxidation process. An organic molecule that gets irradiated with UV light can absorb some photonic energy and become "photoexcited". This can lead to an oxidation-reduction of the compound, but it also facilitates its oxidation by hydroxyl radicals. As shown below, the ground state R_0 of a molecule absorbs light to produce an excited singlet state R_1^* (41):

$$R_0 \xrightarrow{h\nu} R_1^* \qquad [3.14]$$

This excited molecule can then undergo oxidation by OH radicals.

Extinction coefficient of H_2O_2

The fraction of light being transmitted through an absorbing system can be represented by the relation

$$\frac{It}{Io} = 10^{-\varepsilon C d} \qquad [3.15]$$

where *I*t and *I*o are transmitted and incident light intensities, *C* is the concentration of the absorber, and *d* is the depth of absorber through which the light beam passes. ε is a constant of proportionality known as the extinction coefficient and its units are liters per moles-centimeters (l mol^{-1} cm^{-1}). It is generally used to express the capacity of a solution to absorb light through it, and is sometimes also referred to as the molar extinction coefficient (M^{-1} cm^{-1}, since M = mol/l). The extinction coefficient is dependent on the wavelength of radiation and may occasionally vary with C (44).

The molar extinction coefficient, or absorptivity of hydrogen peroxyde at 254 nm is 19.6 M^{-1} cm^{-1}, which is exceptionally low for a primary absorber in a photochemical process. In comparison, the value for ozone is 3300 M^{-1} cm^{-1} (11 and references cited herein). Because of the low molar extinction coefficient, a high concentration of hydrogen peroxide is needed in the medium to generate sufficient hydroxyl radicals. Compared to ozone, a much higher concentration of H_2O_2 is required to produce the same amount of OH radicals in solution.

At wavelengths higher than 254 nm, the molar extinction coefficients of solutions of H_2O_2 (at pH = 7.5) are even lower, i.e. 0.40 and 0.00661 M^{-1} cm^{-1} for light wavelengths of 313.5 and 365 nm respectively. Some studies have demonstrated that the contribution of irradiation at a wavelength higher than 254 nm in the degradation of hydrogen peroxide is very negligible and inferior to 2 % (28 and sources cited herein).

Quantum yields

A widely used concept in photochemistry is the quantum yield, ϕ, which is defined as the number of molecules of reactant consumed for each photon of light absorbed. It is a good indication of the efficiency of a primary photochemical process with respect to chemical transformation, and also of the extent of a secondary reaction (44). The primary quantum yield of hydrogen peroxide at 254 nm is very high, i.e. ϕH_2O_2 = 0.5 mol $photon^{-1}$ (21 and sources cited herein). This means on average that one mole of H_2O_2 gets photolyzed for two absorbed photons. This is due to a "cage" effect caused by the possible recombination of OH radicals, as explained previously.

In order to predict organic conversions due to direct photolysis it is necessary to know, among other parameters, the organic quantum yield. Determination of the quantum yield of a wastewater would require the knowledge of the product composition of wastewater photolysis and other parameters. According to the literature, there are several ways to obtain the quantum yield of a wastewater (44).

Since in a photooxidation process we are usually more interested in knowing how much of the original concentration of organic contaminants gets mineralized with respect to the photonic flux delivered by the UV lamps, it is more useful to consider the true quantum yield (TQY), defined as

$$\mathrm{TQY} = \frac{\text{moles of organic compound mineralized}}{\text{moles of incident photons}} \qquad [3.16]$$

To calculate the TQY, the moles of organic compounds mineralized can be determined from the total organic carbon (TOC) mineralized during the process. The number of moles of incident photons, which is equivalent to absorbed light intensity, requires a more complex method of measurement. To determine it, one needs to know the intensity of the light incident on the front surface of the absorbing substance and the fraction of light absorbed. The fraction of light absorbed may be calculated directly from the measured concentration of absorber, along with its known extinction coefficient, by using the Beer-Lambert law (equation 3.15). The intensity of the light incident on the absorber surface can be determined experimentally by using a thermopile or a photocell. Basically, a thermopile consists of an assembly of thermocouples, connected in series, whose front junctions are blackened. A simplified thermopile assembly is illustrated in figure 3.4(a). A difference in temperature between the illuminated front junctions and the unexposed rear junctions produces an electromagnetic field (e.m.f.), which can be measured using a galvanometer. The radiation energy can then be calculated with the e.m.f. value. A photocell consists of a photocathode and a collector enclosed in an evacuated bulb. The diagram of a photocell circuit is shown in figure 3.4(b). When illuminated, the photocathode releases electrons, and since the collector is charged positively and acts like a anode, a current will flow in the external circuit. The light intensity reaching the photocathode can be determined since it is proportional to the flowing current (44).

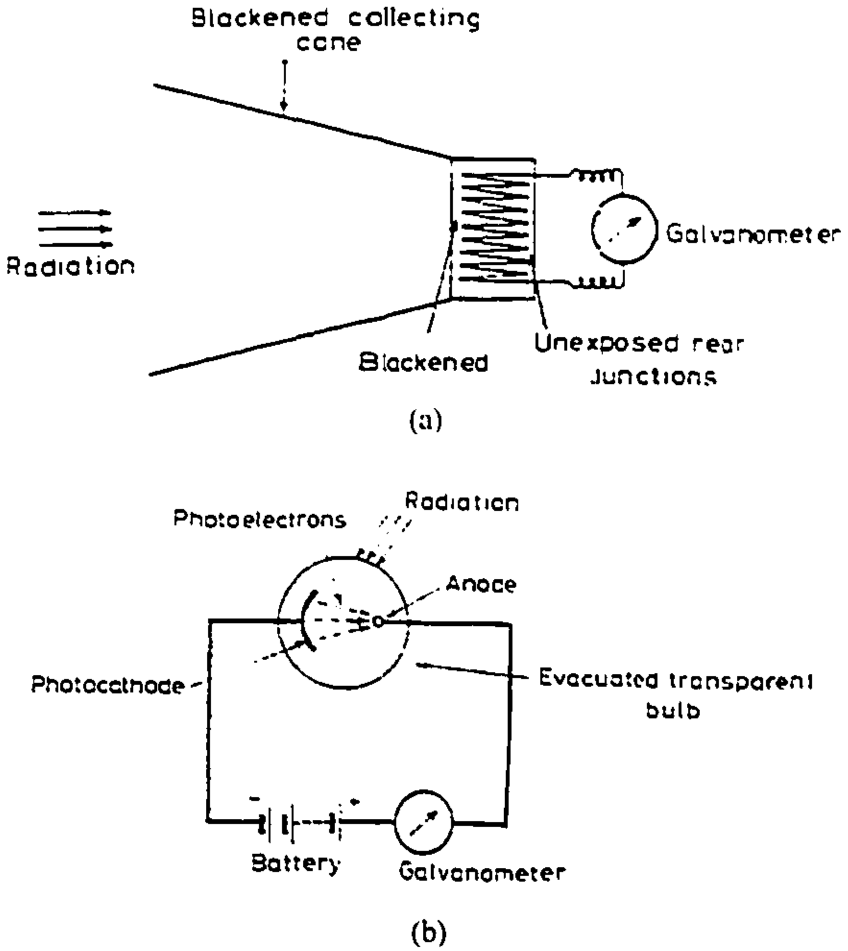

Figure 3.4. Typical arrangements of UV radiation detectors: (a) thermopile; (b) photocell (source: Wayne. R.P.(44)).

Due to the complexity and cost of these arrangements, the actual incident light intensity on the wastewater/oxydant solution was never measured during the course of this research.

Production of hydroxyl radicals with TiO_2

Hydroxyl radicals can be photo-generated heterogeneously in solution by employing an oxide semiconductor. When a semiconductor, such as titanium dioxide

(TiO_2), is illuminated with UV radiation, it gets photoactivated and as a consequence a series of reactions follows. A simplified mechanism for the photoactivation of a semiconductor particle is illustrated in figure 3.5. When this one is illuminated with photons of sufficient energy, i.e. an energy equivalent to the band-gap energy (Eg) or greater, an electron gets excited by a photon and moves from the valence band to the conduction band, leaving behind an electronic vacancy called a hole (h_{vb}^+) in the valence band. The minimum amount of energy required for exciting the electron is called the band-gap energy. For TiO_2, the value of the band-gap energy is of approximately 3.2 eV, which is equivalent to approximately 400 nm wavelength of light. Therefore, TiO_2 can be photoactivated by near-UV radiation (200-400 nm). The hole (h_{vb}^+) and the conduction band electron (e_{cb}^-) can either recombine in the solid, producing luminescence, or react at the external surface (45).

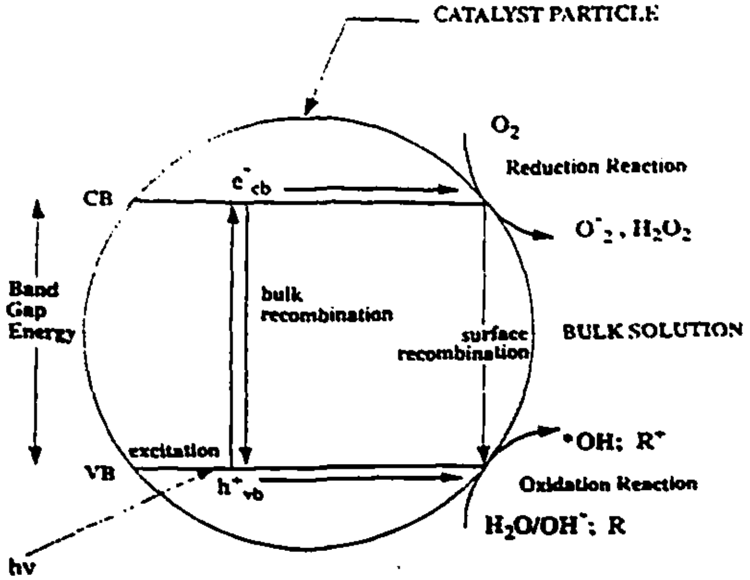

Figure 3.5 Simplified mechanism for the photoactivation of a semiconductor catalyst (source: Suri *et al* (45)). (note: CB : atom Conduction Band; VB : atom Valence Band; e^-_{cb} : electron; h^+_{vb} : hole; hv : light energy).

It has been suggested that formation of OH radicals comes from the reaction of valence-band holes with either adsorbed H_2O or OH- groups on the surface of the TiO_2 particle (19,31-34,45,46):

$$TiO_2 \xrightarrow{h\nu} h_{vb}^{+} + e_{cb}^{-} \qquad [3.17]$$

$$H_2O_{(s)} + h_{vb}^{+} \longrightarrow \bullet OH + H^{+} \qquad [3.18]$$

$$OH^{-}_{(s)} + h_{vb}^{+} \longrightarrow \bullet OH \qquad [3.19]$$

As for UV/peroxidation, the photon activation step indicates a stoichiometric requirement for photons (10). At the interface between the particle and the water, oxidation/reduction can take place with other species adsorbed on the surface. Positive holes, acting as strong oxidizing agents, may react with reducible species and photoelectrons may react with oxygen to give the superoxide radical (19,31,33,34,45,46):

$$h_{vb}^{+} + R^{-} \longrightarrow \bullet R \qquad [3.20]$$

$$e_{cb}^{-} + O_2 \longrightarrow \bullet O_2^{-} \qquad [3.21]$$

H_2O_2 can be formed or regenerated via the following reactions (1):

$$\bullet O_2^{-} + H^{+} \longrightarrow \bullet HO_2 \qquad [3.22]$$

$$\bullet HO_2 + \bullet HO_2 \longrightarrow H_2O_2 + O_2 \qquad [3.23]$$

$$\bullet O_2^{-} + \bullet HO_2 \longrightarrow HO_2^{-} + O_2 \qquad [3.24]$$

$$HO_2^{-} + H^{+} \longrightarrow H_2O_2 \qquad [3.25]$$

Furthermore, OH radicals can also be generated by H_2O_2 reacting with electrons or superoxide radicals (31):

$$H_2O_2 + e_{cb}^{-} \longrightarrow \bullet OH + OH^{-} \qquad [3.26]$$

$$H_2O_2 + \bullet O_2^{-} \longrightarrow \bullet OH + OH^{-} + O_2 \qquad [3.27]$$

Adding a homogeneous oxidant such as O_2 or H_2O_2 to a photocatalytic process does not only promote the creation of more oxidizing agents, but it also helps prevent the recombination of electron-hole pairs at the surface (10,31,34,45):

$$e_{cb}^{-} + h_{vb}^{+} \longrightarrow \text{luminescence / heat} \qquad [3.28]$$

The electron-hole recombination can also take place in the bulk of the solid phase, and it may be catalyzed by impurities (10). Since the reverse reactions of photoactivation provide appreciable penalties for photocatalysis, the presence of a homogeneous oxidant acting as a electron-trapper is essential to improve the efficiency of heterogeneous photocatalysis. Hydrogen peroxyde might be more helpful than oxygen in enhancing a photocatalytic treatment, since it is known to be a better electron acceptor

Since there might be some compounds competing significantly with the oxidant for the electrons, a reducing reaction can take place between the compounds and the electrons, forming products which are thereafter more vulnerable to attack by oxidizing radical species (19). The fact that photocatalysis is a combination of oxidation and reduction processes greatly widens its applicability to various wastes.

Degradation reactions can take place in the adsorbed state (effluent adsorbed to TiO_2 particle) or between photoproduced redox agents (which desorb into solution) and organic compounds (31).

Equation (3.19) suggests that the consumption of hydroxyl radicals ions by positive holes results in a pH drop (34). This suggests that heterogenerous photocatalysis is strongly pH dependent. In order to ensure a sufficient concentration of OH ions in solution, so that enough OH radicals can be generated, it is preferable to keep the pH at a high value. Therefore, to keep the process as efficient as possible, an effluent with a low pH should be preferably adjusted to basic conditions (i.e. pH>10) prior to photocatalytic treatment.

Photooxidation using Fenton's reagent

A method of generating hydroxyl radicals without UV light is by adding a soluble iron salt to an acid solution of hydrogen peroxide. This process is already in commercial use to destroy organics, but is limited to reactions carried under acid conditions. The following mechanism of the reaction in acidic media is proposed by Lipczynska and Kochany (27):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + \bullet OH \qquad [3.29]$$

$$H_2O_2 + HO\bullet \longrightarrow HO_2\bullet + H_2O \qquad [3.30]$$

$$Fe^{2+} + HO_2\bullet \longrightarrow Fe^{3+} + HO_2^- \qquad [3.31]$$

$$Fe^{2+} + HO_2\bullet \longrightarrow Fe^{3+} + HO_2^- \qquad [3.32]$$

$$Fe^{3+} + HO_2^- + H^+ + e^- \longrightarrow H_2O_2 + Fe^{2+} \qquad [3.33]$$

$$Fe^{3+} + HO_2\bullet \longrightarrow Fe^{2+} + H^+ + O_2 \qquad [3.34]$$

$$Fe^{3+} + H_2O_2 \longrightarrow HO_2\bullet + H^+ + Fe^{2+} \qquad [3.35]$$

Similar sequences of reaction pathways can also be found in other studies (35,26,37). It is generally known that this reaction mechanism is strongly pH dependent (26,27). For instance, above a certain pH the Fe^{3+} ion precipitates as ferric oxyhydroxide and thus the Fenton oxidation wheel gets stopped (35). Hydroxyl radicals can also be generated from the oxidation of $FeOH^+$ species (27):

$$Fe^{2+} + HO^- \longrightarrow Fe(OH)^+ \qquad [3.36]$$

$$Fe(OH)^+ + H_2O_2 \longrightarrow Fe(OH)^{2+} + 2\ \bullet OH + e^- \qquad [3.37]$$

It has been known for a long time that photoirradiation of ferric species leads to their reduction (27 and sources cited herein). In acidic solution, this reaction can be illustrated as follows:

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + \bullet OH + H^+ \qquad [3.38]$$

The photoreduction of Fe^{3+} in the presence of organic aromatic compounds results in their hydroxylation. It has also been observed that an addition of ferric ions increases the rate of the photodecomposition of hydrogen peroxide, and so catalyzes the photolytic hydroxylation of organic molecules by hydrogen peroxide (27 and sources cited herein).

In the reaction described above, the primary step involves the photoreduction of ferric species (Fe^{3+}) which becomes Fe^{2+}. This ferric ion is composing Fenton's reagent. That process therefore consists in a regeneration of the Fenton reagent. The role of the UV light in a photo-Fenton reaction is then not to generate but to regenerate the Fenton reagent, and so the step [3.38] plays the role of a feedback reaction (27).

The powerful ability of photo-Fenton oxidation is the result of many processes taking place simultaneously and can be summarized as follows: thermally, it is due partly to Fenton type reactions which generate hydroxyl radicals. The contributing photochemical reactions include: photoreduction of Fe^{3+}, which gives $\bullet OH$ (27); photo-decomposition of Fe^{3+} complexes of starting material and/or intermediate degradation products containing $-OH^{-}$ or $-{}^{-}COOH$ groups; and an unknown Fe^{3+} -sensitized reaction. These last two reaction contributions are proposed by Zepp *et al* (37).

Production of hydroxyl radicals with copper complexes

Relatively very few studies have been made on the photooxidation of organic contaminants in the presence of copper compounds, and therefore not much theory has been developed on the subject. However, Fukatsu and Takahata (47) performed a series of experiments on the formation of hydroxyl radicals from the reaction of Cu(II)/wool keratin complex with hydrogen peroxide. Their results indicate that a Cu(II) complex appears to catalyze hydroxyl radical formation from the hydrogen peroxide superoxide radical being formed as an intermediate. There are two mechanisms through which the formation of hydroxyl radicals can occur. These reaction pathways can occur simultaneously and are therefore competitive with one another. The first one involves the superoxide radical in the metal complex catalyzed decomposition of hydrogen peroxide, that is, a Haber-Weiss reaction:

$$H_2O_2 + \bullet O_2^- \xrightarrow{Cu(II)} O_2 + OH^- + \bullet OH \qquad [3.39]$$

The second one takes place in the presence of a suitable reductant, in which the metal complex catalyzes hydroxyl radical formation from hydrogen peroxide with no superoxide radical formed as an intermediate:

$$H_2O_2 + H^+ + e^- \xrightarrow{Cu(II)} H_2O + \bullet OH \qquad [3.40]$$

In a system where cupric oxide (CuO) is added to a photochemical reaction, the cupric ion (Cu^{+2}) can be possibly obtained by the photolysis of CuO exposed to UV radiation:

$$CuO \xrightarrow{hv} Cu^{+2} + O^{-2} \qquad [3.41]$$

This cupric ion can then act as a catalyst for the decomposition of hydrogen peroxide as described in reactions (above), leading to the formation of hydroxyl radicals. Therefore, when added to a UV/peroxidation system, cupric oxide leads to a possible pathway for the formation of hydroxyl radicals in solution.

Hydroxyl radical oxidation (Hydroxylation)

Hydroxyl radicals are powerful oxidizers of organic contaminants. They have been found to completely mineralize a large number of organic compounds resulting in only carbon dioxide, water, and dilute acids as the products (48). Many intermediate reactions take place in the course of oxidation, but a typical conversion can be summarized in the following reaction, illustrating only the primary reactants and final products:

$$C_xH_yO_zCl_w + H_2O_2 \xrightarrow{h\nu} CO_2 + H_2O + HCl \qquad [3.42]$$

Obviously, this chemical reaction is very simplified, since for one thing the hydroxyl radical is not even represented, yet it is the main oxidizing agent in the process. The above reaction just shows what comes in a photooxidation reactor, and what should ideally come out of it. A more complex illustration of the UV/peroxide mechanism is proposed by Peyton and Smith, and is shown in figure 3.6 (10):

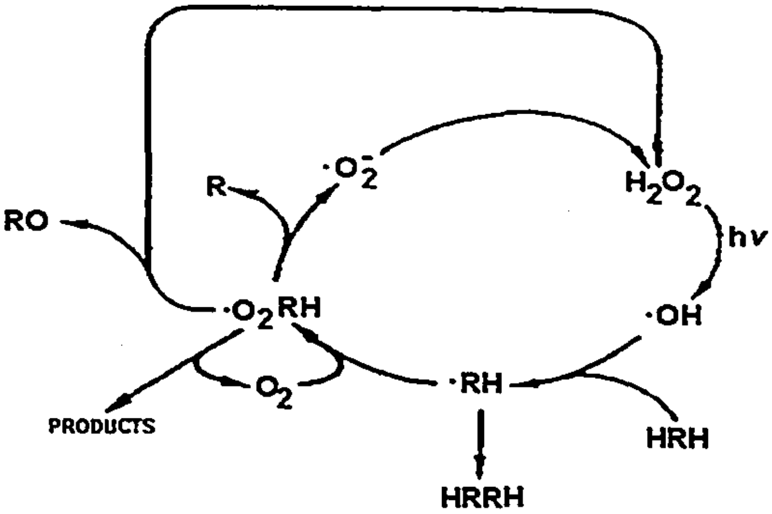

Figure 3.6. Reaction pathways for the UV-hydrogen peroxide advanced oxidation process (source: Peyton and Smith (10)).

As indicated, the mechanism of UV/peroxide is argued to involve a "wheel" of reactive intermediates (10 and sources cited herein). It can be seen that the consumption of photons is fixed stoichiometrically, since every passage around the wheel requires one photon. With the absorption of a photon, OH radicals are produced from the photolysis of

H_2O_2 and go on to attack organic matter, represented as R. Many complex reaction pathways take place, and H_2O_2 gets regenerated in solution by reaction of $\cdot O_2^-$ with H_2O, for instance.

In the course of mineralization of any organic contaminant, oxidation will logically involve a series of intermediates of progressively higher oxygen-to-carbon ratios on the way to CO_2. Such intermediates make the conversion process multicomponent, even if the feed is originally composed of a single contaminant (32). Reaction intermediates in a UV/peroxidation process may be as harmful to the environment as the original wastewater solution, and therefore sufficient hydrogen peroxide and extended treatment times must be ensured to completely eliminate these intermediate compounds. However, these intermediates may be stable and resistant to further degradation, and thereafter may not be acceptable for discharge into the environment. In order to remove these newly formed contaminants, a process can be used to follow and complement UV/peroxidation: for instance carbon adsorption or air stripping. Therefore demonstration of the formation and elimination of intermediates is important for showing complete removal of undesirable compounds

Inhibitors to hydroxyl radical oxidation

In a UV/H_2O_2 process, the objective is to oxidize organic contaminants completely with hydroxyl radicals. Therefore, any other species which react with hydroxyl radicals create a burden to the system. These inhibitors can greatly affect the degradation rate of the target contaminant.

Bicarbonate ions are highly reactive with OH radicals and their combination will lead to the formation of the less reactive carbonate radical anion ($\bullet CO_3^-$) and the hydroxyl ion (OH^-) (10):

$$\bullet OH + CO_3^{2-} \longrightarrow OH^- + \bullet CO_3^- \qquad [3.43]$$

The effect of this reaction will vary from one process to another, depending on the reactants being photooxidized. For instance, an initial reagent such as phenol may be easily attacked by both hydroxyl and carbonate radical anion, whereas later partial oxidation products such as methanol or formaldehyde may only be attacked by hydroxyl radical (10). One fact is certain, the hydroxyl radical always remains the most powerful oxydizing agent in any advanced photooxidation process.

Effect of operating parameters

The efficiency of a UV/H_2O_2 process with respect to the degradation rate of organic contaminants depends on a series of process variables which can have an influence on the production and absorption of hydroxyl radicals and thus on their concentration in solution.

Among these parameters, the nature of the organic contaminant is very important to consider. Ideally, the compound to be treated should have a high reactivity towards OH radicals, and be relatively free of suspended solids. It should absorb enough UV light at 254 nm such that the organic molecules can get directly photolyzed and/or excited by UV radiation, in order to facilitate oxidation. It is well known that UV light changes the electronic structures, and consequently, the reactivity of chemical compounds (27). Still, a too high absorbance of the waste solution at 254 nm would block UV light away from hydrogen peroxide and affect its photolysis and thereby the generation of hydroxyl radicals. Thus the effluent should also not be too concentrated, since absorbance increases linearly with concentration.

The concentration of oxidant needed for a UV/H_2O_2 process has to be investigated carefully. There is an optimum concentration of H_2O_2 that must be determined experimentally using bench-scale tests. Too much H_2O_2 can negatively affect the photooxidation process since H_2O_2 can act as a hydroxyl radical scavenger itself (4), and/or absorb too much UV radiation which is needed to photolyze and/or excite organic molecules.

The addition of a heterogeneous photocatalyst (for instance TiO_2) should have a positive effect on the oxidation treatment, but like H_2O_2, an increase in catalyst concentration will increase the rate of oxidation up to the point where slurry opacity is obtained and UV light gets blocked out of solution.

Each component in the waste solution which absorbs light at 254 nm is a possible competitor for UV radiation: H_2O_2, photocatalyst(s), organic contaminants, organic matrix, humic substances, etc. There is an ideal concentration ratio between organic contaminants and H_2O_2 that must be found, since they both need their share of the UV light in order to get photoactivated. Moreover, the stoichiometric requirements for oxidant and light will increase with organic content, since as pollutant concentration is increased at constant peroxide concentration, the number of hydroxyl radicals available to react with each pollutant molecule is decreased.

The efficiency of a photooxidation process is also dependent of the physico-chemical characteristics of the wastewater. It is generally believed that pH should have a significant effect on the degradation process (17). A high pH is an indication of a high concentration of OH ions in solution, and these play a critical role in the formation of OH radicals. This is especially relevant in a heterogeneous photocatalytic process. As demonstrated in reaction (3.19), a high concentration of OH ions will produce a high concentration of OH radicals in solution. Moreover, the absorbance of a solution is usually more or less a function of its pH. For these reasons it might be necessary to adjust the wastewater pH prior to treatment in order to ensure its optimization. The temperature of the treated water will have an effect on the process. An increase in temperature will always lead to an increase in the reaction rate. Since industrial effluents often exit at a high temperature, this can only be beneficial to the photooxidation process. A wastewater may also contain a high concentration of minerals reactive with OH radicals. This is unwanted, since anything that reacts with OH radicals other than the target pollutant is detrimental to the process. Furthermore, minerals can react with OH radicals and then precipitate in solution, causing an obstruction to UV light. Other compounds such as oil and grease would reduce UV transmission, thereby reducing the treatment efficiency. For all these reasons, pretreatment may be required for proper functioning of a UV/H_2O_2 process depending on the wastewater characteristics.

A photooxidation process can be very efficient if the photochemical reactor is properly designed. The UV lamps should be positioned inside the reactor in such a way that the delivery of UV light is optimized and that the wastewater gets exposed to as much UV radiation as possible. In a homogeneous photooxidation process with H_2O_2, the dominant emission wavelength of the lamps should be 253.7 nm, which is typical of low-pressure mercury vapor lamps. The light intensity given off by the lamps has to be carefully adjusted not only with respect to a desired efficiency, but also in terms of economics. Serpone *et al* (32) observed in many photocatalytic studies that there is an efficiency penalty for sufficiently intense lamps. Thus a more expensive high-intensity UV lamp is not necessarily beneficial to a photochemical system. Along with photonic energy, UV lamps also deliver an extensive amount of heat to the solution being treated, thereby increasing the rate of oxidation. Since the molar extinction coefficient, or absorptivity, of H_2O_2 at 254 nm is relatively low (19.6 $M^{-1}cm^{-1}$), the volume thickness of the wastewater/H_2O_2 mixture should not be too large in order to allow sufficient light penetration and increase the photoreactivity potential. In a continuous photochemical system, the flow of wastewater should be kept at a constant rate. This can be achieved by using an equalization basin, for instance. The flow rate has to be slow enough to allow for sufficient oxidation reaction time, but for economic reasons it should also be maximized. As in any other chemical reactor, mixing of the effluent/oxidant solution should be ensured continuously during the whole process, especially if a batch reactor is used, in which case stirring is highly required.

CHAPTER 4 PHOTOOXIDATION EXPERIMENTAL APPARATUS, MATERIALS AND METHODS

Introduction

An experimental apparatus was designed and assembled in order to perform the experiments required for this study. Different models of photochemical reactors were investigated, and a choice was made while considering budget limitations.

The objectives of this study are to improve the quality of a pulp and paper mill effluent, based on analytical measurements performed on wastewater solutions before and after treatment. Since these tests form a major part of this thesis, they are described in details in this chapter.

Design considerations for apparatus

There exist two main types of commercial photochemical reactors on the market, that are designed for laboratory experimental research. In both cases, experiments are usually carried out in a batch mode. A photochemical reactor includes a reaction vessel in which the aqueous waste solution gets irradiated with UV light. In one common type of reactor, a single UV lamp stands inside the reaction vessel, while in the other type a series of UV lamps are fixed outside the reaction vessel, usually in a circular fashion. In the present experiment, the latter type of reactor is used. Most importantly, for any kind of photochemical reactor, the glassware, which in fact acts as an interface between the source of light and the solution being treated, should always be made of quartz or of any other material which allows a high percentage of UV light to get through (49).

Description of photochemical reactor apparatus

A rough sketch of the photochemical apparatus used for this research is illustrated in figure 4.1. The photochemical reactor was gracefully loaned by the Abitibi-Price Research Centre, which used to be located in Mississauga, Ontario. It consists of a Rayonet® Chamber Reactor, model no. RPR-208, manufactured by the Southern New England Ultraviolet Company, in Branford, Connecticut. Inside the reactor there are eight RUL-2537A° low-pressure mercury vapour UV lamps disposed in a circle. The dominant emission wavelength of these lamps is 253.7 nm. In the centre of the reactor, a Rayonet® Photochemical Reaction Vessel is supported vertically with an aluminum stand. The reaction vessel is made of quartz and has a capacity of 660 ml. At the bottom of the reaction vessel, a magnetic pellet ensures continous stirring, by being activated with a magnetic stirring plate located right below the apparatus. Cold tap water is circulated through a "cold finger", a cooling device inserted in the reaction vessel. A constant temperature is maintained inside the reactor with a PID controller interfaced between the tap water outlet and the cold finger inlet. The controller is connected to a thermocouple which records the temperature of the solution inside the vessel. A small hole pierced at the top of the reaction vessel allows multiple uptakings of samples with a 10 ml volumetric pipette throughout the reaction time period. The chamber reactor has opaque walls which keep all UV light from escaping and possibly causing retinal and/or skin injuries to the user(s). The top of the reactor is sealed off with a retractable wooden box.

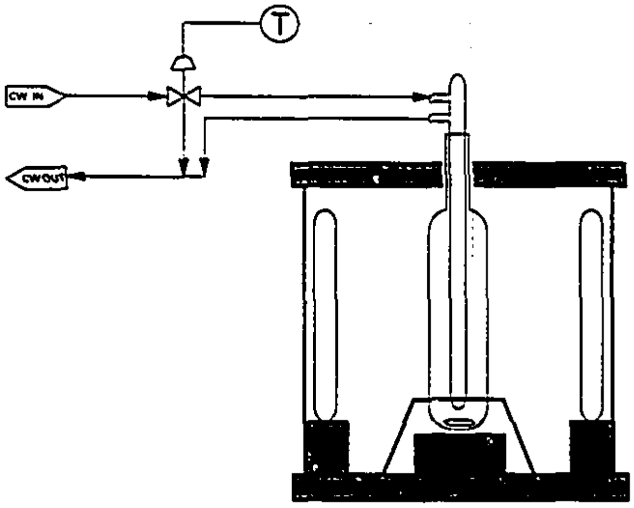

Figure 4.1. Experimental apparatus for photochemical oxidation.

Description of typical photooxidation experiment with H_2O_2

All experimental runs were performed using the same photochemical reactor and equipment. Operational parameters and chemical concentrations were varied from one experiment to another such that their effects could be observed and the process could be optimized. Each run involved the same series of steps and the procedure was generally as follows:

First, approximately 500 ml of effluent is taken out of the refrigerator. This volume of wastewater is then transferred into a beaker and brought to room temperature. Once the effluent sample has reached a temperature of approximately 25°C, exactly 400 ml of it is measured with a graduated cylinder, and then poured into the photochemical reaction vessel. Afterwards, 100 ml of H_2O_2 solution is added to the effluent sample by using a volumetric pipet. A 1" long magnetic pellet is dropped into the reaction vessel to rest at its bottom. The "cold finger" is then inserted inside the reaction vessel, along with the thermocouple. Mixing is activated by turning on the magnetic stirring plate which acts on the pellet at the bottom of the vessel. The faucet valves for cold and hot water are open and their relative outputs are adjusted in such a way that the outcoming water is at the right temperature for efficient cooling. The electronic PID controller/thermometer is then turned on. Finally the top wooden box is closed off and afterwards the UV lamps are turned on. At the same time, a stopwatch is started to measure the time of reaction. One has to ensure that mixing is smooth, the initial temperature reading is accurate, there are no leaks, the temperature remains constant and the whole apparatus in general remains stable during the whole experiment. Due to seasonal variations in tap water temperature and controller limitations, the hot and cold water flowrates might need adjustments during the first hour of the experiment such that the wastewater/oxydant solution remains at a constant temperature the whole time. Using a volumetric pipet, 10 ml samples of the solution are taken out of the reaction vessel at 20, 40, 60, 90 and 120 minutes after the start of the experiment. After a period of 180 minutes, the reactor, the magnetic stirrer, the controller and the water valves are turned off. The solution is then taken out of the reaction vessel and analytical measurements are made.

In the last set of experiments, 500 ml of effluent were used instead of the usual 400, without any dilution. Moreover, no sample was taken for analysis during the treatment process; the effluent was taken out and analyzed only at the end of the reaction time.

Operating parameters were varied to observe their effects on the photooxidation process. The concentration of chemicals, i.e. effluent and/or H_2O_2, heterogeneous catalysts, etc. were varied simply by changing their relative quantities in solution. The pH of the solution was decreased by adding small quantities of 10% sulfuric acid, using a drop counter, and it was increased by adding small dosages of sodium hydroxyde (NaOH) at various concentrations. The temperature of the solution in the photochemical vessel was adjusted by varying the set point on the PID temperature controller while simultaneously adjusting the temperature of the tap water going into the cooling finger.

Description and characteristics of wastewater

The wastewater used for all the experiments is a real industrial effluent generated by a TMP mill located in the province of Quebec. The effluent consists of a combination of accumulated vapors that are generated during the pulp refining process, where wood chips are being pre-steamed and then mechanically refined at high temperature and pressure, to become pulp. The emitted vapors cool off to form a heat condensate, a liquid substance which is very toxic. The heat condensate has a brown-yellowish colour, and lets enough light through it so it appears to be suitable for the process of photooxidation. Its viscosity is similar to that of water, and it contains very few suspended solids.

Since the heat condensate is generated during the process of pulping, its toxic constituents are mainly dissolved components of woodchips. The main components of wood are cellulose and hemicellulose, lignin, and extractives such as resin and fatty acids. These components are leached from wood into the water during the pulping process. The concentration levels of these compounds in the effluent were not measured, however, the high COD of the effluent is enough to demonstrate its high toxicity. Leach and Thakore developed a fairly complete breakdown of toxic constituents usually found in mechanical pulping effluents (50). Wood extractives, especially resin acids, have long been considered to be the major toxicants in a pulp and paper mill effluent (51 and references cited herein). It has been shown that they account for 60-90 percent of the toxicity in a TMP effluent (50). Moreover, lignin, an aromatic polymer, is generally the compound that is most difficult to take care of in a conventional wastewater treatment (52). Experimental studies by Stenberg and Norberg have showed that a typical biological treatment process is not efficient for the degradation of lignin in a mechanical pulping effluent (53).

There are probably also other toxic compounds present in the heat condensate effluent which are not constituents of wood, but are process-derived contaminants. Since in this case the pulping process is officially free of chemicals, a very small concentration of such contaminants should be present in the wastewater. If the process at the mill involved sulphite pulping, for instance, there would be many phenolic compounds, which are produced from the degradation of lignin (52).

Description of chemical reagents used in experimental procedure

Hydrogen peroxide (H_2O_2) solutions were made by diluting measured volumes of 30% w/v commercial H_2O_2 in distilled water.

The titanium dioxide (TiO_2) used for heterogeneous photooxidation was of the type Degussa P25 grade, BET surface area 50 ± 15 m^2 g^{-1}, average particle size 30 nn., anatase form. This brand was used because it is generally accepted as the photocatalyst of choice for photooxidation with TiO_2 (48). Solutions of TiO_2 used in experiments were prepared by adding a measured quantity of TiO_2 into a known volume of distilled water. This milky mixture was then immersed in an ultrasound bath for thirty minutes to ensure a homogeneous solution and keep TiO_2 particles in suspension. After this step, a measured dosage of TiO_2 solution was introduced into the wastewater solution right before its illumination with UV light. The TiO_2 particles were resuspended in solution with the ultrasound bath before each new experiment.

Aluminum oxide (Al_2O_3) and cupric oxide (CuO) samples were in a powder form and taken from commercial sources.

Ferric chloride ($FeCl_3$) samples were in a powderish form and taken from commercial source. Ferric perchlorate ($Fe(ClO_4)_3$), on the other hand, had a granular form and was borrowed from the Department of Chemistry at McGill University. When both of these catalysts were used, the pH of the effluent was initally lowered to a value of approximately 2-3, using small added quantities of hydrochloric acid (HCl) in the case of $FeCl_3$, and perchloric acid ($HClO_4$) in experiments with $Fe(ClO_4)_3$. This acidification has the primary objective of facilitating the release of the Fe^{3+} ion, which is an essential component of Fenton's reagent.

Background information on Chemical Oxygen Demand (COD)

A parameter that is commonly used by environmental researchers to analyze the quality of a wastewater is the Chemical Oxygen Demand (COD). Its determination is easy, accurate, cheap, rapid, and a large number of tests can be performed at once. It is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variability of samples, and ease of manipulation (54). Oxidation of most organic compounds with this method represents 95 to 100% of the theoritical value. For all these reasons, the COD was chosen to be the main parameter used in this experiment to determine the quality of the wastewater solution before and after treatment, and thereby as an indicator of the photooxidation process overall efficiency.

There are three known methods for the determination of COD using potassium dichromate as the oxidizing agent. The open reflux method is suitable for wastes having a high concentration of suspended solids, since a large sample volume is required. The two closed reflux methods are more practical and more economical in terms of reagents, but a homogenization of samples containing suspended solids is required to obtain reproducible results. One closed reflux method involves measurements of absorbance with a spectrophotometer. In the course of this experimental work, the absorbance method was initially preferred over the other one since it required less time to produce results and less chemicals were required. However, it was found to be unsuitable since solid particles remaining in suspension had an effect on the absorbance of the samples, leading to unreproducible results. It was therefore decided to choose the other closed reflux method, which involves titration of the samples. This method was found to produce very accurate results, and was still relatively easy to perform.

Measurement of COD

The closed reflux, titrimetric method used to measure the COD is taken from the book "Standard Methods for the Examination of Water and Wastewater" (54), with a few modifications. It is important to note that this method can only be used with samples having a COD of >50 mg O_2/l. Moreover, if the COD of the sample is expected to be higher than 900 mg O_2/l, it must be diluted appropriately and this dilution must then be taken into account for the final calculation of COD.

The reagents are prepared as follows:

a. Standard potassium dichromate digestion solution, 0.0167 M: Add to about 500 ml distilled water 4.913 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for 2 h, 167 ml concentrated H_2SO_4. Dissolve, cool to room temperature, and dilute to 1000 ml.

b. Sulfuric acid reagent: Add Ag_2SO_4, reagent or technical grade, crystals or powder, to concentrated H_2SO_4 at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4. Let stand 1 to 2 days to dissolve Ag_2SO_4.

c. Ferroin indicator solution: already prepared commercial solution was used.

d. Standard ferrous ammonium sulfate titrant (FAS), approximately 0.010M: Dissolve 3.92 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 2 ml concentrated H_2SO_4, cool, and dilute to 1000 ml.

Borosilicate culture tubes (16 x 100 mm) with TFE-lined screw caps are used for the procedure. First, 2.5 ml of sample is placed inside the tube and 1.5 ml of digestion solution is added, followed by 3.5 ml of sulfuric acid reagent. The tubes are then tightly capped and inverted several times for complete mixing. Afterwards, the tubes are placed in a heating block preheated at 150°C and their content gets refluxed for 2 h. The tubes are then cooled to room temperature and placed in a test tube rack. The content of a tube is carefully transferred to a 100 ml Erlenmeyer flask, and 1-2 drops of ferroin indicator are added to the solution. Each solution gets titrated with 0.005-0.010 M FAS. The end point is a sharp color change from blue-green to reddish brown. In the same manner, a blank containing the reagents and a volume of distilled water equal to that of the sample is refluxed and titrated. The COD can then be measured using the following equation:

$$\text{COD as mg } O_2/L = \frac{(A - B) \times M \times 8000}{\text{mL sample}} \qquad [4.1]$$

where:

A = ml FAS used for blank,

B = ml FAS used for sample, and

M = molarity of FAS.

The molarity of the FAS solution is standardized daily against standard $K_2Cr_2O_7$ digestion solution as follows:

Volumes of reagents from the method described above are added to a tube containing distilled water substituted for sample. The tube is cooled to room temperature and transferred to an Erlenmeyer flask with distilled water in which 1-2 drops of ferroin indicator is added. The solution then gets titrated with FAS titrant and the molarity is determined as follows:

$$\text{Molarity of FAS solution} = \frac{\text{Volume 0.0167 M } K_2Cr_2O_7 \text{ solution titrated, mL}}{\text{Volume FAS used in titration, mL}} \times 0.10 \qquad [4.2]$$

For all samples, blanks and FAS molarity tests, the procedure is repeated three times such that an average titrant volume is used for calculations, to improve accuracy of results.

Interference of H_2O_2 on the COD test

The determination of COD fundamentally involves organic matter reacting with a strong oxidant, potassium dichromate. For most experiments, samples of solution were analyzed through the whole reaction, and there was always a remaining quantity of H_2O_2 which did not fully decompose during irradiation.

H_2O_2 is essentially a strong oxidizing compound. However, when reacting with a strong oxidizing agent, it acts as a reductant. According to Talinli and Anderson (55 and references herein), dichromate ions react with H_2O_2 in an acidified solution and form peroxidichromic acid ($H_2Cr_2O_{12}$) which is blue in colour. The reaction is a molecular addition:

$$H_2Cr_2O_7 + 5H_2O_2 \longrightarrow H_2Cr_2O_{12} + 5H_2O \qquad [4.3]$$

This compound is not stable and is reduced immediately to Cr(III) salts:

$$H_2Cr_2O_{12} + 8H_2O_2 \longrightarrow Cr_2O_3 + 9H_2O + 8O_2 \qquad [4.4]$$

Thus the presence of H_2O_2 leads to an increase in K_2Cr_2O7 consumption, causing an interference on the COD testing of the wastewater.

To account for the presence of H_2O_2 in a sample which needs to be tested for COD, Talinli and Anderson developed a method for calculating the true COD value:

$$\text{COD (mg/l)} = \frac{(a-b)\cdot c\cdot 8000}{\text{ml original sample}} - d\cdot f \qquad [4.5]$$

or

$$\text{COD(mg/l)} = \text{COD}_m - d\cdot f \qquad [4.6]$$

where

COD_m = measured COD (mg/l)
d = H_2O_2 concentration in the sample (mg/l)
f = correction factor = 0.25. It is valid for 20-1000 mg/l H_2O_2.

Measurement of Dissolved COD (DCOD)

In this experiment it was desired to study the kinetics of the process using COD as a reference. A 10 ml sample of wastewater was taken out of the reactor at different time intervals during the reaction. This volume was insufficient for the determination of the concentration of H_2O_2 in each sample, and thus the standard COD method could not be used due to the interference of H_2O_2, as explained previously.

Another way to measure COD using only 10 ml of wastewater is by eliminating the unreacted H_2O_2 without affecting the rest of the solution. This is done by using manganese dioxide (MnO_2), which catalyzes the decomposition of hydrogen peroxide into oxygen and water:

$$2\,H_2O_2 \xrightarrow{MnO_2} O_2 + 2\,H_2O. \qquad [4.7]$$

Thus, approximately 50 mg of MnO_2 is added to each 10 ml sample, and the mixture gets stirred for a few hours in a small beaker covered with parafilm. Afterwards, the MnO_2 is filtered out using a Whatman 934AH glass microfibre filter, pore size 1.5 µm. This way, most of the MnO_2 is removed out of solution. If there is still a small portion of MnO_2 remaining, its effect on the COD measurement is very negligible. The COD of the filtrate can then be measured using the standard procedure. In this experiment, the COD value thus obtained is referred to as Dissolved COD, or DCOD.

To verify the accuracy of this methodic approach, a test was done using a wastewater solution with a known DCOD value to which some H_2O_2 was added and then eliminated with MnO_2. The value of the DCOD afterwards was the same as before, unaffected by the MnO_2 catalysis process.

Measurement of H_2O_2 concentration

The concentration of H_2O_2 in solution was determined by using a method developped by the CPPA and updated by Mrs. Yujing Menjing, formerly of the Pulp and Paper Research Centre of McGill University (PAPRICAN).

The reagents are prepared as follows:

a. Potassium Iodide, 10% solution: Dissolve 25 g reagent grade KI in 250 ml of distilled water.

b. Sulfuric Acid, 2N: Dissolve 53 ml conc. H_2SO_4 in 700 ml distilled water, then dilute it to 1000 mL.

c. Ammonium Molybdate, 3% solution: Dissolve 3g of reagent grade $(NH_4)_6Mo_7O_{24}$ $4H_2O$ in 100 ml distilled water.

d. Starch indicator: Make a paste of 1g of soluble starch in 50 ml of water. Pour the paste into 500 ml boiling water and boil until it is clear. Note: Replace with a fresh solution every two weeks.

e. Standard Sodium Thiosulfate Solution, 0.05 M.: Dissolve 12.4 g $Na_2S_2O_3 \cdot 5H_2O$ (or 7.916 g $Na_2S_2O_3$) in 1000 ml distilled water.

The volume of sample needed for the determination of H_2O_2 concentration has to be investigated at first, since it is difficult in some cases to predict approximately how much titrant will be required for the procedure. The test specimen is an appropriate volume of sample which is chosen such that 20-40 ml of standard sodium thiosulphate is required to perform the titration. First, the test specimen is transferred to a 250 ml Erlenmeyer flask. Then 50 ml distilled water and 50 ml 2N H_2SO_4 are added, the total volume of the solution being 100-120 mL. Afterwards, 5 ml 10% KI and 3 drops of aluminum molybdate are added. The solution is immediately titrated with sodium thiosulphate until the solution has lost almost all its color (pale yellow). Then 2 ml of starch indicator is added and the titration is completed. The end point is a sharp change from dark blue to clear transparency of the solution. The H_2O_2 concentration, in percentage, can then be calculated as follows:

$$H_2O_2\,\% = \frac{17 \times M \times V \times F}{1000 \times A} \times 100\% \qquad [4.8]$$

where

M = Molarity of standard sodium thiosulphate

V = Volume of standard sodium thiosulphate, mL

A = Volume of test specimen, mL

F = Dilution factor.

Sodium thiosulphate has to be standardized frequently. Its molarity can be determined by following exactly the same steps of this method, and by replacing the sample containing H_2O_2 with a small amount of dry, reagent grade potassium iodate (KIO_3), approximately 0.04-0.08 g. The molarity of the standard sodium thiosulphate can then be calculated as follows:

$$\text{Molarity of standard sodium thiosulfate} = \frac{W \times 1000}{35.67 \times V} \qquad [4.9]$$

where

W = Weight of KIO_3, gm

V = Volume of standard sodium thiosulphate, ml.

Each analytical measurement was repeated three times and an average value was taken for better accuracy of results.

Measurement of pH

The pH of the solution was measured with a portable pH meter. The model actually used in this experiment was a single-point pH meter and could not be calibrated by using two separate pH points and a resulting slope. Thus a particular method had to be used by the operator to optimize the accuracy of the results.

Before each new reading, the pH meter is calibrated by using a buffer solution of pH 7. The pH meter electrode is then plunged into a sample of the effluent solution and a rough measurement is recorded, indicating in what range of values the effluent pH is actually located. The pH meter is then re-calibrated with a buffer solution of pH which is closest to the value obtained previously with the rough measurement. This way the calibration point of the pH meter is located as close as possible to the actual pH of the solution. After this re-calibration, the electrode is finally inserted back into the effluent solution and its pH is recorded.

Measurement of temperature

The temperature was measured continuously during the whole process with a thermocouple inserted into the reaction vessel. This thermocouple was connected to a PID controller which gave a digital reading of the recorded temperature.

Measurement of turbidity

Turbidity of the wastewater before and after treatment is determined with a standard portable turbiditimeter. It is initially calibrated with a special solution that is turbidity-free and supplied with the equipment. The glass vial containing the turbidity-free solution is inserted into the turbidimeter, which is then adjusted to a zero digital reading with a knob. After removing the calibration solution, a sample of treated effluent solution (≈ 50 ml) is poured into a glass vial which is inserted into the turbiditimeter. After selecting the appropriate range of measurement and waiting five seconds, the digital turbidity reading indicated on the turbidimeter is recorded.

Measurement of absorbance and lignin concentration

The absorbance, colour, and lignin concentration of the wastewater before and after treatment are determined with a spectrophotometer.

To measure the absorbance of the solution, a 10 ml sample of wastewater is taken. It is usually required to filter a sample in order to get rid of all suspended solids prior to recording its absorbance. However, in this case, the objective is to find the capacity of the effluent to absorb UV light emitted at 253.7 nm before and following the photooxidation treatment. Thus, the complete mixture with all its suspended solids, is considered for absorbance determination. First, the spectrophotometer is adjusted to absorbance = 0 (transmittance = 100%) at a wavelength of 253.7 nm, using distilled water as the reference solution. A portion of the wastewater sample is then transferred into a square cuvet which has a light path of 10 mm. The absorbance is then recorded on the spectrophotometer. This can be done a few times to obtain an average absorbance value.

The concentration of soluble lignin in the effluent is determined using a method supplied by the Pulp and Paper Research Institute of Canada in Pointe-Claire, Que. This method is a slight adaption of the TAPPI Useful Method no. 250 for soluble lignin determination (56). First, the spectrophotometer is adjusted to absorbance = 0 at a wavelength of 205 nm, using distilled water as a reference solution. Then, a cuvet with a 10 mm light path is filled with a sample of wastewater previously filtered with a Millipore membrane filter (nominal pore size 0.8μm), and the absorbance is recorded. The lignin concentration is calculated as follows:

$$\text{Lignin, g/L} = \frac{A \times D}{100} \qquad [4.10]$$

where:

A is the absorbance of the sample at 205 nm.

D is the dilution factor.

Measurement of Dissolved Organic Carbon (DOC)

Samples were initially filtered using a Millipore membrane filter, nominal pore size 0.8 μm. For each experiment a filtered sample was sent to the Pulp and Paper Research Institute of Canada (PAPRICAN) located in Pointe-Claire, Qué. There the Total Organic Carbon (TOC) of each sample was determined by M. Jik Ing. Since all solids were eliminated from the samples prior to their analysis, the TOC values that were determined at PAPRICAN are in fact equivalent to the Dissolved Organic Carbon (DOC) content of each sample.

The method used for the determination of TOC is a modified version of the TOC method developed by the Technicon Instruments Corporation (57). Measurements are made using the Technicon Auto-analyzer System (TAS). The TAS consists of a series of interconnected automated modules which can perform a series of operations which are usually manually performed for chemical analysis. The system at PAPRICAN can withdraw samples from a sample tray, dilute and mix them with reagents, and then heat and analyze them. All operations are performed automatically once samples have been placed in the tray.

The original method was modified by two researchers from PAPRICAN, so that it could be well suited for the measurement of pulp liquor and mill effluents.

The samples are analyzed in two steps, first for Total Carbon (TC), and then for Total Inorganic Carbon (TIC). The difference yields Total Organic Carbon (TOC = TC - TIC). For the analysis of TC, an aliquot of effluent sample is mixed with potassium persulphate and a phosphate buffer solution and exposed to ultraviolet (UV) radiation. Both the organics and inorganics present in the effluent sample are digested and converted to CO_2. The carbon dioxide gas is then dialyzed through a silicone rubber membrane into an indicator solution. The decrease in colour intensity of this indicator solution, due to the formation of carbonic acid, is proportional to the carbon concentration in the original effluent sample. The colour intensity decrease is detected with a spectrophotometer operating at 550 nm, and recorded on a strip chart recorder.

For the determination of TIC, a fresh aliquot from the same effluent sample is run following a similar procedure, except that phosphoric acid alone is added, instead of the potassium persulphate and the phosphate buffer solution, and the irradiation with UV is omitted. Thus, only the inorganic carbon in the sample is converted to CO_2 and detected.

The TOC, in mg/l, can then be calculated by substracting the TIC from the TC.

Measurement of solids

The determination of solids content in the effluent solution before and after the treatment process was performed by using a slightly modified version of the CPPA standard method no. H.1 (58). This procedure defines and prescribes methods for solids determinations (total and volatile fractions of suspended and dissolved solids) in pulp and paper mill effluents.

Throughout this procedure all weighings are recorded to 1 mg, and are made after equilibration to room temperature in a desiccator with silica gel desiccant. Constant weight is considered to have been attained when consecutive weighings differ by no more than 2 mg. The filtration apparatus consists of a buchner funnel resting and sealed on a filtering flask which is connected to a vacuum line. The different types of solids in the effluent were measured as follows:

(a) Total Suspended Solids (TSS).

Total Suspended Solids include all material which can be removed from the effluent by filtration through a Whatman 42, ashless paper filter, nominal pore size 2.5 μ m. All samples are well mixed while taking test specimens for suspended solids determination. First, a Whatman 42 paper filter, diameter 90 mm, is dried to constant weight at 105 ± 5 °C, and its weight is recorded. The dry filter is placed on a buchner funnel and sealed by drawing a small volume through the filter with suction. The flask is then replaced with a dry filtering flask. A measured volume of effluent, usually 200 ml, is filtered (Volume I). The filtrate is retained for the determination of dissolved solids. The paper filter is then transferred into a dry aluminum dish and placed in a drying oven set at 105 ± 5 °C until constant weight. After, the filter is allowed to cool off in a desiccator. Its weight is then recorded, and by substracting it from the initial weight of the filter, the weight of total suspended solids is obtained. The TSS concentration can then be calculated:

$$\text{Total Suspended Solids, mg/L} = \frac{\text{weight total suspended solids, g} \times 10^6}{\text{Volume I, mL}}$$

[4.11]

(b) Total Dissolved Solids (TDS).

Total Dissolved Solids consists of the residue after filtration of the effluent through a 2.5 μm paper filter and evaporation of the filtrate to dryness at 105 ± 5 °C. The weight of a ceramic crucible after drying to constant weight at 105 ± 5 °C, and cooling in a desiccator, is recorded. An aliquot of the filtrate obtained in procedure (a), usually 100 or 200 ml, is taken (Volume II). It is then poured into the ceramic crucible and evaporated in a drying oven. The weight of the crucible after complete evaporation is recorded, and substracting from it the initial weight of the crucible, the weight of total dissolved solids is obtained. Total Dissolved Solids are calculated as follows:

$$\text{Total Dissolved Solids, mg/L} = \frac{\text{weight total dissolved solids, g} \times 10^6}{\text{Volume II, mL}}$$

[4.12]

(c) Volatile Suspended Solids (VSS).

Volatile Suspended Solids is that portion of the Total Suspended Solids which volatilizes upon ignition. The paper filter and precipitate from procedure (a) are placed in a ceramic crucible. The filter and precipitate are ignited carefully using a bunsen burner flame which heats the outer surface of the crucible at a very high temperature. The inside of the crucible is all burned off and the remains of the filter and precipitate are combusted until no more apparent reaction occurs. The crucible is then cooled in a desiccator and its weight is recorded. The inital weight of the crucible combined with the precipitate, less the weight of the crucible after ignition, gives the weight of Volatile Suspended Solids. The VSS concentration is calculated as follows:

$$\text{Volatile Suspended Solids, mg/L} = \frac{\text{weight volatile suspended solids, g} \times 10^6}{\text{Volume I, mL}} \qquad [4.13]$$

(d) Volatile Dissolved Solids (VDS).

Volatile Dissolved Solids is that portion of the Total Dissolved Solids which volatilizes upon ignition. The dry crucible containing the Total Dissolved Solids from procedure (b) is ignited using a bunsen burner flame, until no more combustion reaction is apparent. The crucible is then allowed to cool in a desiccator and its weight is recorded. The difference between the weight of the crucible before and after ignition gives the weight of Volatile Dissolved Solids. The VDS concentration is then determined:

$$\text{Volatile Dissolved Solids, mg/L} = \frac{\text{weight volatile dissolved solids, g} \times 10^6}{\text{Volume II, mL}} \qquad [4.14]$$

(e) Total Solids (TS).

Total Solids is the sum of Total Suspended Solids (procedure (a)) and Total Dissolved Solids (procedure (b)):

$$\text{Total Solids, mg/L} = \text{Total Suspended Solids, mg/L} + \text{Total Dissolved Solids, mg/L} \qquad [4.15]$$

(f) Volatile Solids (VS).

Volatile Solids is the sum of Volatile Suspended Solids (procedure (c)) and Volatile Dissolved Solids (procedure (d)):

$$\text{Volatile Solids, mg/L} = \text{Volatile Suspended Solids, mg/L} + \text{Volatile Dissolved Solids, mg/L.} \quad [4.16]$$

CHAPTER 5 PHOTOOXIDATION EXPERIMENTAL RESULTS AND DISCUSSION

Introduction

Most of the published results from past photooxidation experiments involve solutions of pure chemicals, which were used in laboratory to simulate toxic effluents. There are very few publications which describe the photooxidation of real concentrated industrial effluents, such as those from a pulp and paper mill.

There is no standard "recipe" on how to start up and optimize a photooxidation experimental study with a given solution of contaminants. Moreover, a pulp and paper mill effluent is very complex in nature and has many different components which can contribute to its high degree of toxicity. For these reasons, in any new photooxidation study, and especially in this case, it is necessary to initially perform an extensive series of preliminary experiments which are generally done by trial and error.

An experimental schedule was initially made for this research work. The first thing that had to be done was to find a range of hydrogen peroxide concentrations in which photooxidation of the effluent was applicable in established conditions. Once that was determined through preliminary experiments, the rest of the experimental work was to be performed within this range. Operational parameters could then be varied in order to observe their effect on the process and optimize its efficiency. From published literature and theory, the relevant parameters that should be examined in a photooxidation study are the initial concentration of hydrogen peroxide, the concentration of effluent solution, the initial pH of the solution, the operating temperature, potential photocatalysts such as TiO_2 and their concentrations in solution, etc.

The characterization of the process results was made by measuring the Dissolved COD of the effluent before, during, and after photooxidation treatment. Towards the end of the experimental schedule, a final series of experiments were performed in order to measure other characteristics of the treated effluent such as absorbance, turbidity, pH, total COD, lignin concentration, remaining hydrogen peroxide concentration, solids, Dissolved Organic Carbon (DOC), etc. These parameters make up a more complete characterization of the effluent and help identify more precisely which constituents of the wastewater the photooxidation process is most capable of eliminating.

Preliminary experiments

It is necessary in a photo-peroxidation process to have a sufficient amount of hydrogen peroxide in solution for a .eaction to occur, however, too much of it can have an adverse effect on the process, as explained in the theory section. It is also logical that the efficiency of photooxidation is strongly dependant on the absorbance of the effluent, since the solution must be clear enough to allow light fluxes to go through and activate the photooxidation reactions. No indication of a desirable range of absorbance values for a similar experiment can be found in the literature, so this had to be determined experimentally by trial and error.

A series of preliminary experiments were performed by varying the concentration of hydrogen peroxide in solution, as well as the concentration/absorbance of the effluent solution. The absorbance of the effluent solution was modified either by filtration using a Watman 934-AH filter paper, or simply by diluting volumes of pure effluent in distilled water to obtain solutions with 50% and 25% concentrations. The results obtained with these preliminary experiments are summarized in table 5.1.

As demonstrated in table 5.1, reductions of DCOD were most noticeable when the effluent was filtered or diluted prior to photooxidation experiments. Other pretreatment methods for the removal of particles in suspension and/or color were investigated, such as adding activated carbon, or a coagulant, etc., to the effluent solution. But then, it was decided that there should be no pretreatment whatsoever since the objective of this experiment is to actually prove that the photooxidation process is suitable for the destruction of everything present in the heat condensate effluent, including all particles in suspension and color-producing organic compounds.

H_2O_2 in (% w/v)	Effluent in	H_2O_2 cons. (% w/v)	DCOD in (mg O_2/l)	DCOD out (mg O_2/l)	DCOD diff. (mg O_2/l)	DCOD red. (%)
0.05 %	H.C., pure	0.016	515.0	502.6	12.4	2.4 %
0.05 %	H.C., filtered	0.021	515.0	373.2	141.8	27.5 %
0.05 %	H.C., diluted 1/2	0.025	257.5	204.8	52.7	20.5 %
0.10 %	H.C., pure	0.032	515.0	508.8	6.2	1.2 %
0.10 %	H.C., filtered	0.032	515.0	325.5	189.5	36.8 %
0.10 %	H.C., diluted 1/2	0.048	257.5	145.3	112.2	43.4 %
0.10 %	H.C., diluted 1/4	0.057	128.8	63.2	65.5	50.8 %
0.50 %	H.C., pure	0.065	515.0	490.5	24.5	4.8 %
0.50 %	H.C., filtered	0.125	515.0	334.6	180.4	35.0 %
0.50 %	H.C., diluted 1/2	0.207	257.5	198.0	59.5	23.1 %
0.50 %	H.C., diluted 1/4	0.119	128.8	108.4	20.3	15.6 %
1.00 %	H.C., pure	0.113	515.0	493.7	21.3	4.1 %
1.00 %	H.C., filtered	0.246	515.0	348.4	166.6	32.3 %

Table 5.1: UV/peroxidation preliminary experimental results. Initial conditions: effluent = TMP heat condensate, $pH_{in} = 4.02$. Duration of each experiment = 1 hour (note: H_2O_2 cons. = H_2O_2 consumption; DCOD diff. = DCOD in - DCOD out; DCOD red. = DCOD reduction).

Two conclusions can be drawn from these results. First, the absorbance of the effluent solution has a major effect on the efficiency of the process. For this reason it was decided to dilute the effluent by 50% for most of the remaining portion of experiments, in such a way that the effects of varying other operating parameters could be more easily noticeable for the optimization of the process. Second, the results from table 5.1 indicate that hydrogen peroxide concentrations lying between 0.05 % and 1.00 % w/v represent a suitable operating range for further experimental investigations.

Characterization of heat condensate effluent.

Due to storage technical difficulties (i.e. electrical shutdown in the cold room), it was necessary to get rid of the first batch of heat condensate effluent and replace it with a new one taken at the same TMP mill. Thus, a new series of tests had to be performed on the new effluent. It consisted roughly of a yellowish, non-viscous mixture with few suspended solids and had the following measured characteristics:

- pH = 4.70;
- TCOD = 1161 mg O_2/l;
- DCOD = 637 mg O_2/l;
- Total Suspended Solids = 115 mg/l;
- Total Dissolved Solids = 489 mg/l;
- Total Solids = 637 mg/l.

Moreover, there were many yellow strips of suspended matter in the effluent. These were gummy in nature, and were expected to be precipitated lignin. This new batch of heat condensate effluent was to be used for the remaining experiments.

Determination of optimai H_2O_2 concentration.

An experimental run was performed using a solution of heat condensate effluent without adding any hydrogen peroxide to it. By exposing the effluent to UV radiation alone, it would be possible to see potential oxidation effects by direct photolysis alone. It is likely that UV light would attack bonds of organic molecules, creating a resonance effect leading to the decomposition of toxic constituents. However, as demonstrated in figure 5.1, the DCOD of the effluent solution diminishes very slowly and the rate of degradation is very small. This means that direct photolysis alone is not sufficient for a fast degradation of the effluent. A photochemical oxidant has to be initially added to the effluent in order for the degradation process to be efficiently accelerated.

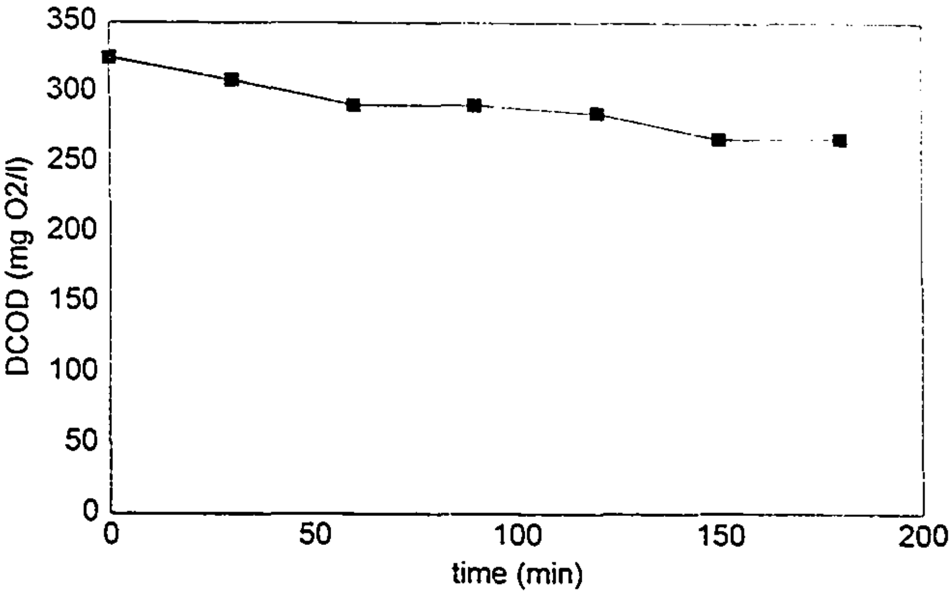

Figure 5.1. Heat condensate diluted 50% exposed to UV light. T = 25°C

The effect of adding hydrogen peroxide to the effluent solution prior to its exposure to UV radiation is showed in figure 5.2, where results obtained with various initial concentrations in % weight per volume of hydrogen peroxide, i.e. 0.05 %, 0.10 % and 0.15 % w/v are illustrated. It can be seen that the rate of oxidation increases with the initial hydrogen peroxide concentration. However, when the initial concentration of hydrogen peroxide is higher than 0.15 %, there is an adverse effect on the process and the rate of oxidation is slowed down. This can be observed in figure 5.3, where results obtained with concentrations of 0.20 % and 0.25 % hydrogen peroxide are demonstrated. The effect of the hydrogen peroxide surplus is especially noticeable towards the ends of the curves, where the difference between residual DCOD values is greater. This trend can be explained: at the beginning of the process, the effluent solution has a high absorbance and an overloading of hydrogen peroxide does not affect the process, but as the effluent gets oxidized, its color-producing organic components are destroyed, and the solution becomes clearer and clearer, thereby absorbing more UV light. A surplus of remaining hydrogen peroxide can then absorb too much of this UV light, keeping it from reaching the effluent molecules, and a surplus of it can also lead to an effect where OH radicals are recombining, causing a reduction in the efficiency of the process.

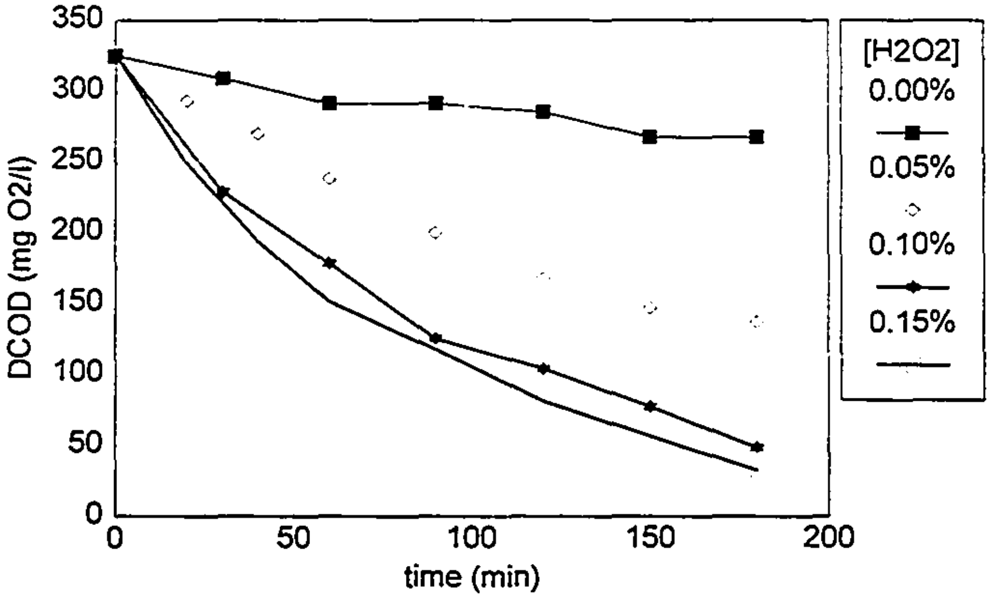

Figure 5.2. Heat condensate (50% dil.) with initial concentrations of H_2O_2 ranging from 0.00% to 0.15%. T = 25°C.

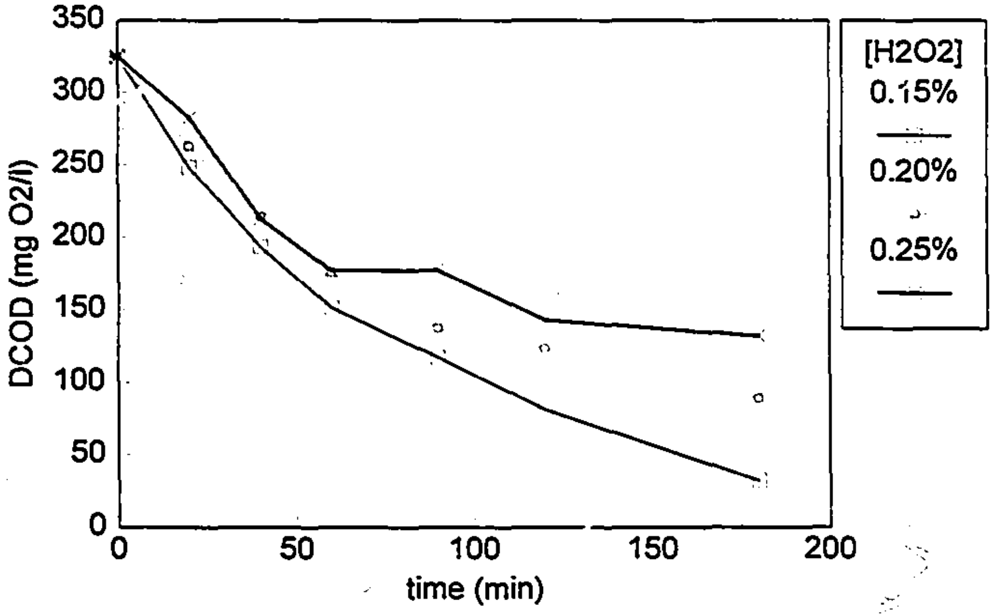

Figure 5.3. Heat condensate (50% dil.) with initial concentrations of H_2O_2 ranging from 0.15% to 0.25%. T = 25°C.

Based on these results it was concluded that the optimal hydrogen peroxide concentration, for these particular conditions, i.e. heat condensate diluted 50%, operating temperature 25° C, nature of effluent, etc., was of 0.15 % weight per volume. However, it must be kept in mind that this optimal concentration applies to these particular conditions, and a change in experimental conditions would probably require a different optimal H_2O_2 concentration.

To clearly see the positive effect of combining hydrogen peroxide with UV radiation, an experiment was done by using a concentration of 0.15 % H_2O_2 in a solution of heat condensate and stirring it for three hours under the same conditions as before but without turning on the UV lamps in the reactor. This way the effluent gets decomposed by the oxidizing action of hydrogen peroxide alone. Experimental curves illustrating oxidation by hydrogen peroxide alone, oxidation by UV light alone, and the combination of both processes, are illustrated in figure 5.4. The two curves in the top portion of the graph represent results obtained with oxidation by H_2O_2 alone and oxidation by UV alone. Both of these processes, when operated individually, achieve a low degree of oxidation. In three hours, only approximately 50 mg/l of Dissolved COD is eliminated, and the rate of oxidation of the wastewater is very slow. However, when these two processes are combined to form UV/peroxidation, the rate of oxidation is much faster, and after three hours of reaction time there is an elimination of 292 mg/l of Dissolved COD. It is evident therefore that UV irradiation greatly accelerates the oxidation process. In fact, one cannot regard UV irradiation simply as a catalysis to peroxidation, since the chemical reactions involved are very different from one process to another. In peroxidation, the main oxidant is considered to be hydrogen peroxide itself, while in UV/peroxidation, the main oxidant is the hydroxil radical (•OH).

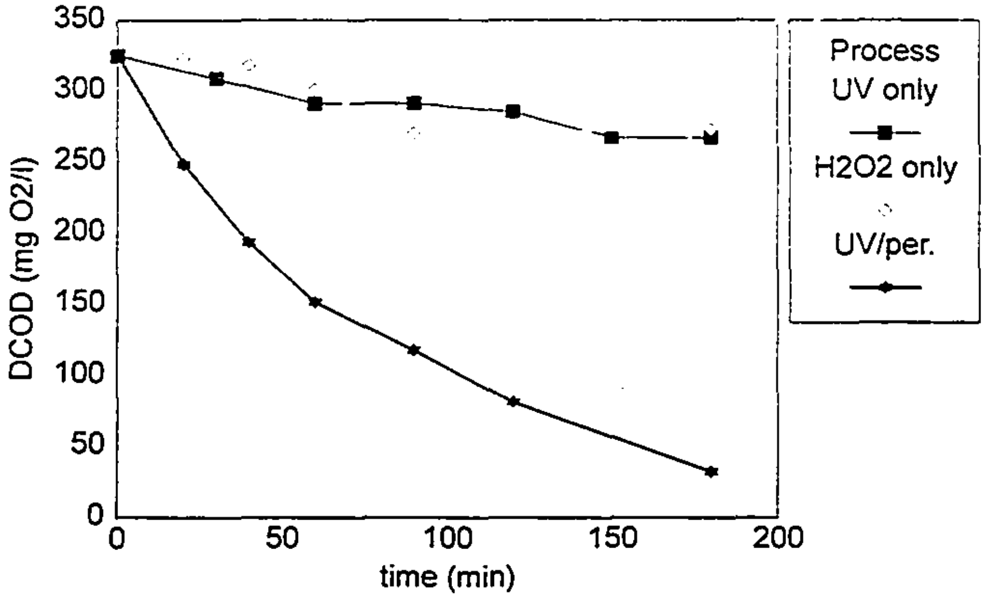

Figure 5.4. Comparative oxidations of heat condensate (dil.50%) by UV alone, 0.15% H_2O_2 alone, and combination of UV with 0.15% H_2O_2 (note: UV/per.= UV/peroxidation)

Brief kinetics of UV/peroxidation

In order to better understand the underlying concepts of H_2O_2 photooxidation, it is essential to study the kinetics of the process.

The curve illustrated in figure 5.5 represents the results of a series of H_2O_2 photooxidation experiments using an initial concentration of 0.1% H_2O_2 in 500 ml of diluted heat condensate. The experiments lasted 30, 60, 90, 120, 150 and 180 minutes. After each experiment the DCOD and remaining H_2O_2 concentration of the effluent solution were determined analytically. For the same experiment the consumption of H_2O_2 with time was analyzed and is illustrated in figure 5.6. The shape of this curve is very similar to the one in figure 5.5. Since the photooxidation process consists in a combination of the DCOD and H_2O_2 reacting together, the rate of disappearance of the DCOD is a function of both of these compounds and can be expressed as follows:

$$r_{DCOD} = -k[\mathrm{DCOD}]^{\alpha}[\mathrm{H_2O_2}]^{\beta} \qquad [5.1]$$

where: r_{DCOD} = rate of disappearance of DCOD

k = kinetic reaction rate constant

α = constant

β = constant

Since these results are obtained from batch reactor experiments, the rate of disappearance of DCOD can be mathematically rewritten as:

$$\frac{d[\mathrm{DCOD}]}{dt} = -k[\mathrm{DCOD}]^{\alpha}[\mathrm{H_2O_2}]^{\beta} \qquad [5.2]$$

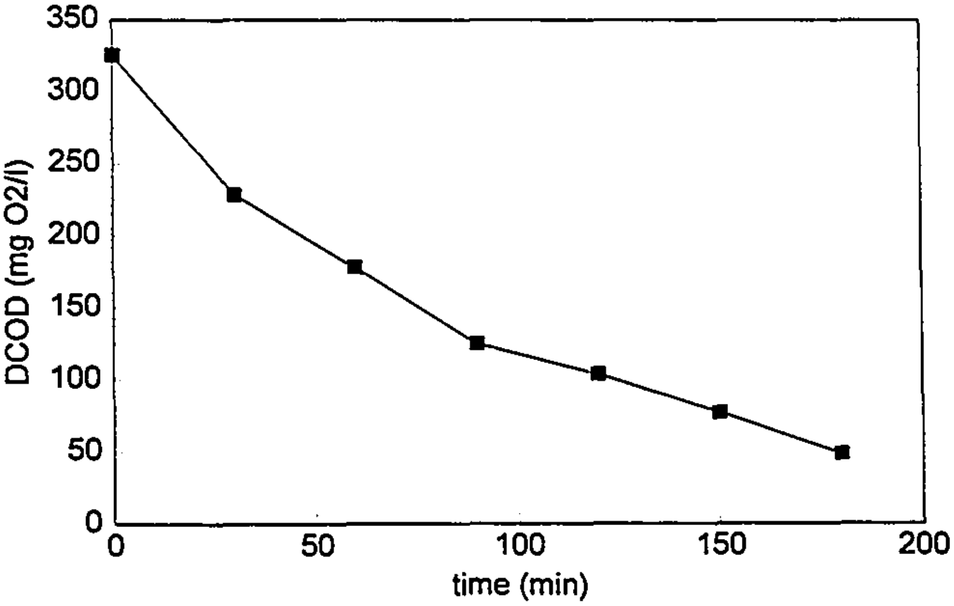

Figure 5.5. Elimination of DCOD with time. Initial conditions: heat condensate (dil.50%), 0.1% H_2O_2. T = 25°C.

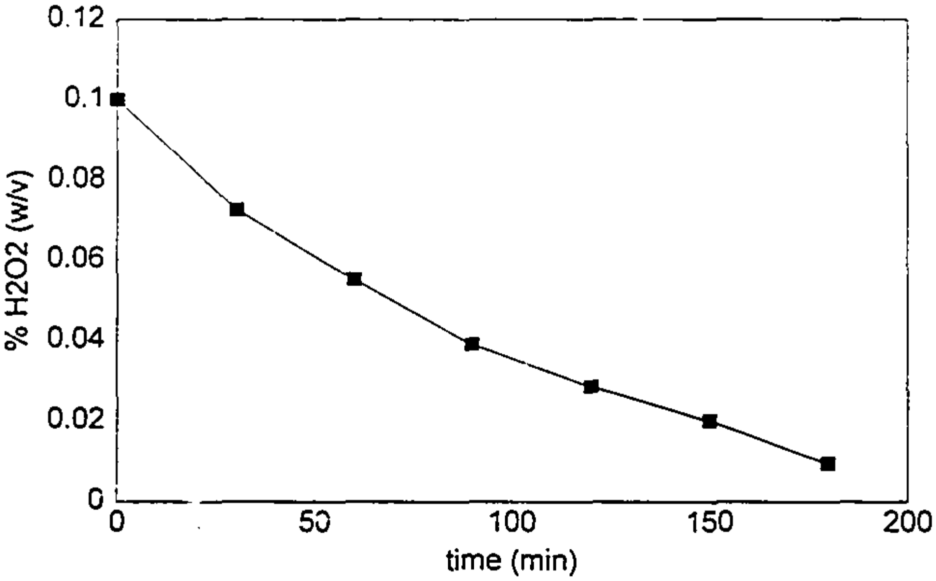

Figure 5.6. Concentration of residual H_2O_2 with time, in % w/v. Initial conditions: heat condensate (dil.50%), 0.1% H_2O_2, T = 25° C.

In most chemical reactions, and especially in an oxidation process, it is generally expected that there would be a limiting reactant for the rate of reaction. In the present experiment the two main chemical reactants are the oxidant, •OH, which is proportional to the concentration of H_2O_2 in solution, and the oxidizable species, the organic content of the effluent, which is proportional to the DCOD. As demonstrated in figures 5.5 and 5.6, both compounds get consumed continuously over a long period of time, and there is no initial sharp drop in their concentrations at the beginning of the oxidation process. An assumption can be made as an attempt to explain the aspects of these two curves. That is, the rate of degradation of the DCOD is not only a function of the concentrations of DCOD and H_2O_2 with time, but also of the transmittance of the solution with time. Here, UV radiation acts as a physical contributor to the oxidation process, and the rate of reaction is influenced by the quantity of transmissible light. Therefore it would be appropriate to say that the rate of decomposition of DCOD is not only a function of DCOD and H_2O_2, but also of the transmittance of the solution at a light wavelength of 253.7 nm. Another way to express this would be by stating that the rate of reaction kinetic constant, i.e. k in equation 5.1, is a function of the solution transmittance which may vary with time. Transmittance is an indication of how much light can pass through a given sample of solution. It is inversely proportional to the absorbance of the solution by the following relationship:

$$\% \text{ transmittance} = \log^{-1}(\text{-absorbance}) \times 100\% \qquad [5.3]$$

The transmittance of the effluent/H_2O_2 mixture with time is illustrated in figure 5.7. These data were obtained under the same previous experimental conditions used for the determination of the data in figure 5.5 and 5.6. At the beginning of the photooxidation experiment, the transmittance of the effluent/H_2O_2 solution is at its lowest, and most of the light gets absorbed by the cloudy effluent which is more likely to absorb light than hydrogen peroxide. This shielding effect slows down the rate of formation of hydroxyl radicals and incidently the rate of oxidation of the effluent. Thus in the initial stages of the process the DCOD of the effluent and the H_2O_2 are slowly being decomposed. The highly-coloured organic molecules of the effluent get oxidized with time under the action of H_2O_2 and UV radiation. As these compounds are destroyed by UV/peroxidation, the effluent solution becomes clearer and its transmittance increases, allowing more and more light to enter. This way the photooxidation process continues slowly and steadily with time. Towards the end of the reaction time, as there is less residual H_2O_2 in solution, the transmittance of the effluent is very high thus allowing the production of additional hydroxyl radicals which can photolyze the remaining organic compounds.

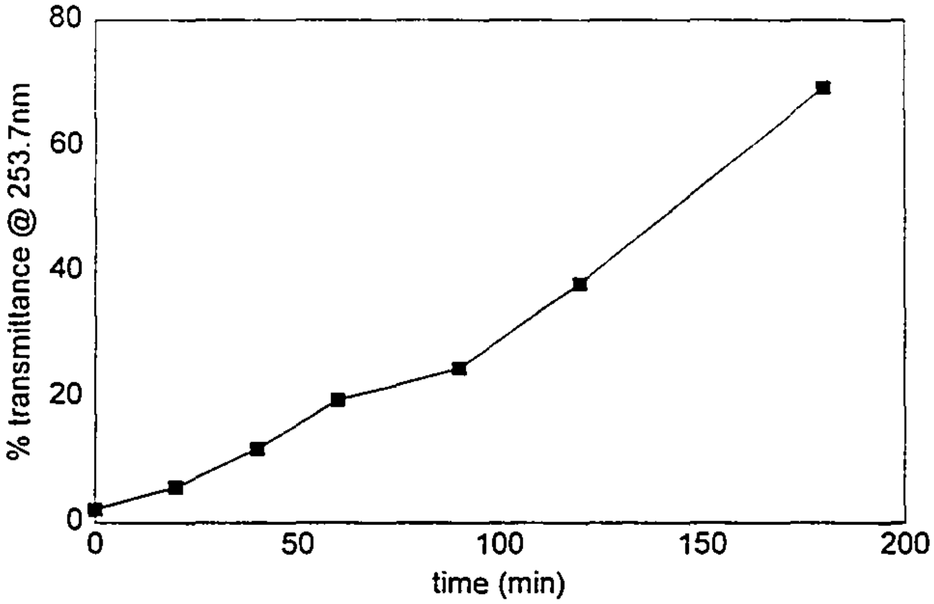

Figure 5.7. Transmittance (%) of heat condensate with time. Initial conditions: heat condensate (dil.50%), 0.1% H_2O_2, T = 25° C.

Effect of pH on the H_2O_2/photooxidation process

As put forward in the literature review, there is a high possibility that the pH of the reacting mixture influences the oxidation rate of the effluent. However, its effect on the process cannot really be predicted since this has to be determined for each new effluent to be treated. The pH of the effluent solution was then adjusted to various values prior to its exposure to UV radiation. The original pH of the effluent being 5.74, its pH was adjusted subsequently to 5, 9, and 11 in order to cover a sensible range of values. The results obtained at these values did not justify the investigation of a wider range of pH values.

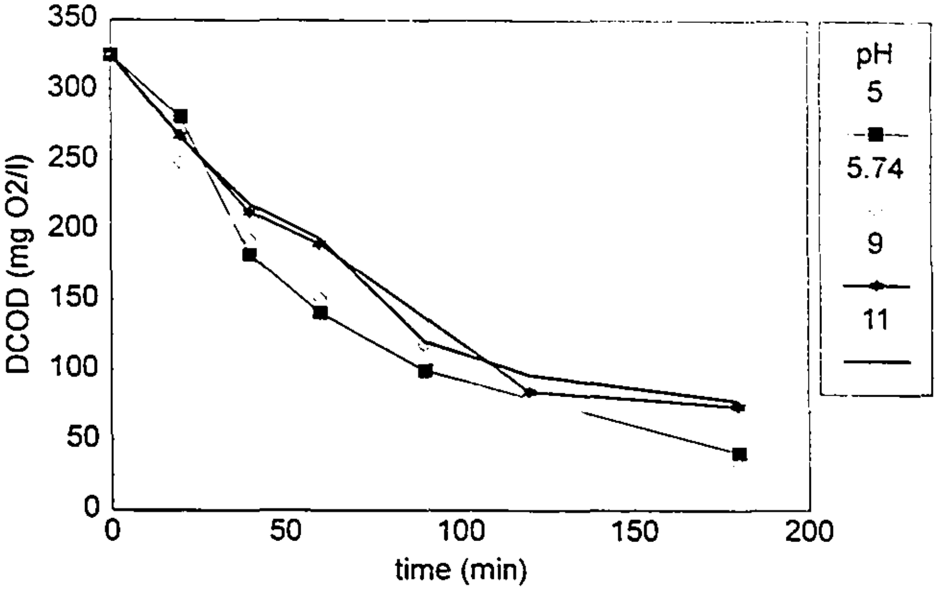

Figure 5.8. Photooxidation of heat condensate (50% dil.) at adjusted pH of 5, 9 and 11, and original pH of 5.74. Initial $[H_2O_2]$ = 0.15%. T = 25°C.

The results of a photooxidation process using a concentration of 0.15 % H_2O_2 in a diluted heat condensate solution are illustrated in figure 5.8. It can readily be observed that for this experiment the pH has practically no effect on the photooxidation process. This shows that in the present case of homogeneous photooxidation the main source of OH radicals is from the fission of the H_2O_2 molecule, since this process consists of one single reaction which is stoichiometrically unaffected by the presence of H^+ and OH^- in solution. The reactivity of H_2O_2 with photonic light energy is therefore unaffected by the pH of the mixture.

It was expected however that a high pH could lead to better photooxidation results, since this increases the concentration of OH^- ions in solution, and these can sometimes become a source of OH• radicals. However, as explained in the theory section, the OH^- ions need to react with positive holes h_V^+ to become OH radicals (reaction 3.19). There is no indication of the formation of positive holes in a homogeneous photooxidation process such as this one. However, a heterogeneous photooxidation process with the presence of TiO_2 particles would be more likely to produce positive holes and therefore be more affected by a pH adjustment.

It is well known that the colour of a solution is more or less affected by a variation of its pH. This might be more relevant however in a mixture with a light colour, where the concentration of color-producing compounds is lower, and therefore can be affected more easily by a chemical change. A solution with a relatively high colour has a strong concentration of colour-producing compounds and therefore a buffering resistance against changes in colour. This is the case for the heat condensate solution, since no extensive change in colour takes place when its pH is varied.

Effect of temperature on the H_2O_2/photooxidation process

An effluent resulting from the condensation of toxic vapors is likely to exit from a pulp and paper mill at a very high temperature. It is therefore important to examine the efficiency of the treatment process under the influence of an elevated temperature.

To study the effect of temperature on the H_2O_2/photooxidation process, the temperature of the solution was raised from 25 to 45°C and this value was kept constant during the complete reaction time. In figure 5.9 is illustrated the effect of raising the temperature. This proves to be highly beneficial to the process, since the oxidation reaction rate is much faster at 45°C. As a comparison, it takes 60 minutes for the 25°C operation to bring the DCOD down to a value of approximately 150 mg O_2/l, while 40 minutes are needed to achieve the same result at a temperature of 45°C. Moreover, it takes 90 minutes for the 25°C experiment to decrease the DCOD to approximately 120 mg O_2/l, while the one at 45°C requires 60 minutes to reach a similar value.

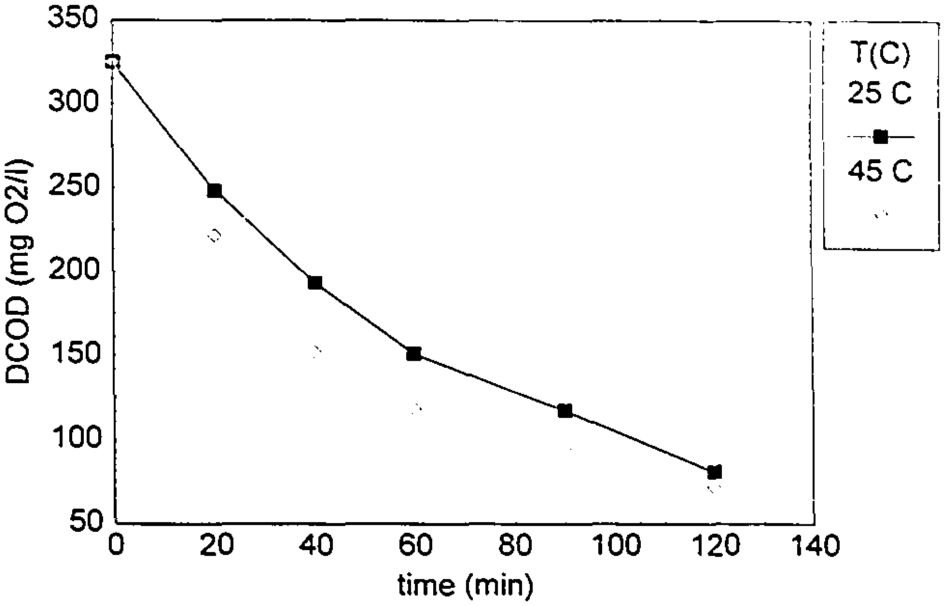

Figure 5.9. Photooxidation of heat condensate (50% dil.) at T = 25°C and T = 45°C. Initial $[H_2O_2]$ = 0.15%.

Both of these oxidation processes can be described by a rate of degradation of the DCOD, as expressed in equation 5.1. The rate of disappearance of DCOD is faster for the experiment at 45°. A faster rate of oxidation necessarily means a higher reaction rate constant. This increase of the reaction rate constant with temperature can be explained by Arrhenius's law, which states that the reaction rate constant of a process is exponentionally proportional to the absolute operating temperature and activation energy of the process, i.e.:

$$k = \mathrm{A}e^{-\frac{\mathrm{E}}{\mathrm{RT}}} \qquad [5.5]$$

where: k = reaction rate constant

A = frequency factor

E = activation energy

R = gas constant

T - temperature

Thus, the generally elevated temperature of an actual heat condensate effluent would be highly beneficial to its treatment with a photooxidation process.

Effect of effluent dilution on the H_2O_2/photooxidation process

The absorbance of an effluent solution varies linearly with its concentration. A series of diluted solutions of heat condensate were made and their absorbance measured with a spectrophotometer at a wavelength of 253.7 nm. These results are plotted in figure 5.10 and a linear relationship was developed, producing an equation describing the regression and relating absorbance to the concentration fraction of heat condensate:

$$\text{Absorbance} = \text{concentration fraction}/.3515 \qquad [5.6]$$

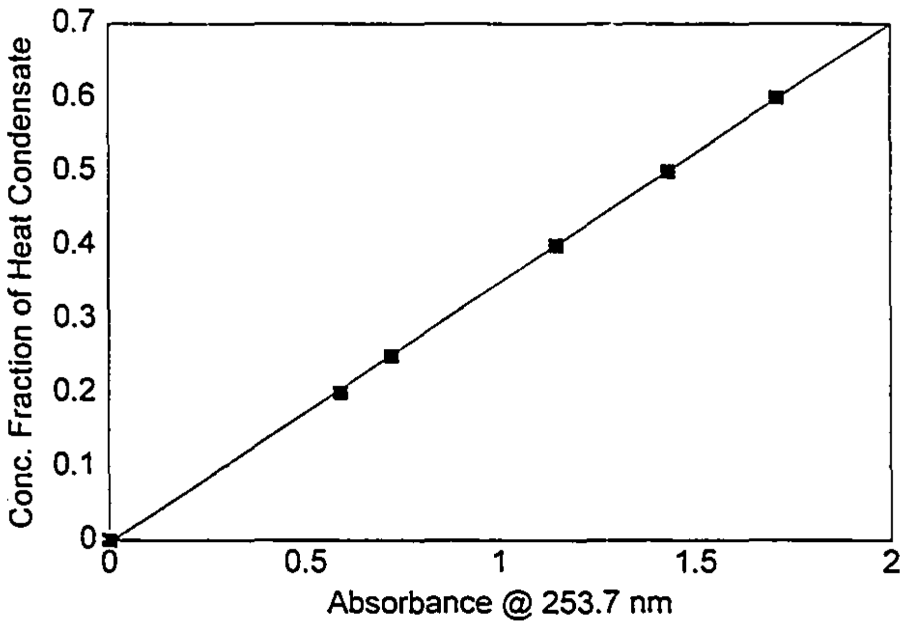

Figure 5.10. Absorbance of heat condensate as a function of its concentration. Absorbance = conc. fraction / 0.3515.

Thus, a solution of 50% heat condensate has an absorbance of 1.4 at 253.7 nm, while solutions of 75% and 100% have absorbances of 2.1 and 2.9 respectively. A diluted solution of effluent would therefore be easier to treat with a photooxidation process. In the first set of photooxidation experiments the heat condensate effluent was diluted by 50% to reduce the organic charge and thereby facilitate the oxidation process, so that the effects of varying operational parameters could be more easily observed. To verify the revelancy of this dilution, an experimental run with undiluted heat condensate was conducted, along with an experimental run where the effluent was diluted to 75%. The results of those two tests are presented and compared to the previous 50% heat condensate experiment in figure 5.11. Each experiment had the same initial concentration of hydrogen peroxide.

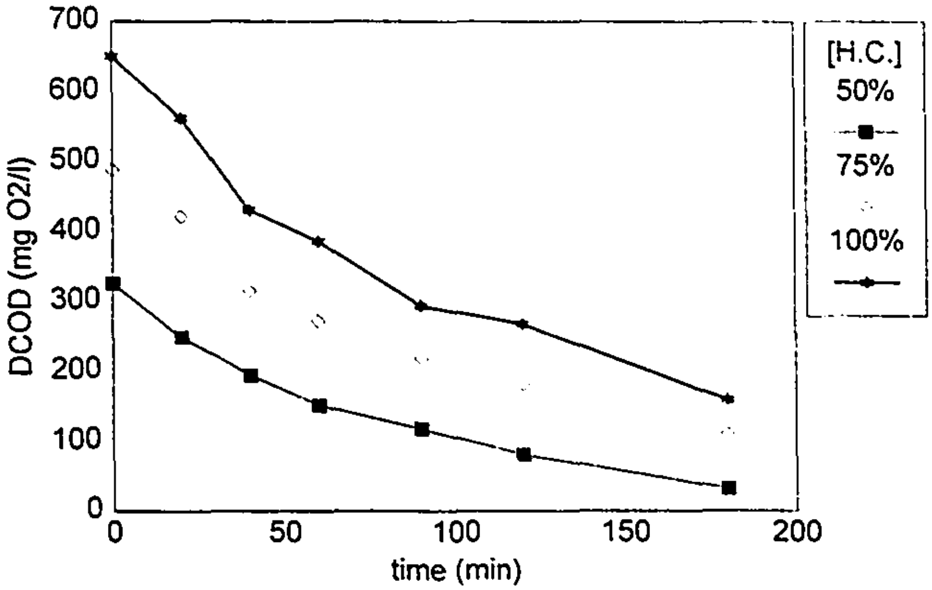

Figure 5.11. Photooxidation of heat condensate at dilution concentrations of 50%, 75% and 100% (undiluted). Initial concentration of H_2O_2 = 0.15%. T = 25°C.

The experiments done with purer solutions of heat condensate produce excellent results. However, in terms of final DCOD value, the best results are obtained with the most diluted effluent solution, which is expected, since this one has the lowest initial organic content and DCOD value. In terms of organic content removal, the experiment with the pure undiluted effluent delivers the best results with a DCOD difference of 390.4 mg O2/l, compared to DCOD removals of 376.7 and 291.7 mg O_2/l for the experiments with 75% and 50% dilutions respectively.

Each experiment shown in figure 5.11 begins with a different initial DCOD value. Results of the same experiments expressed in terms of the fraction of initial DCOD are illustrated in figure 5.12, so that each curve starts at a value of 1 on the y-axis which represents the fraction of initial DCOD.

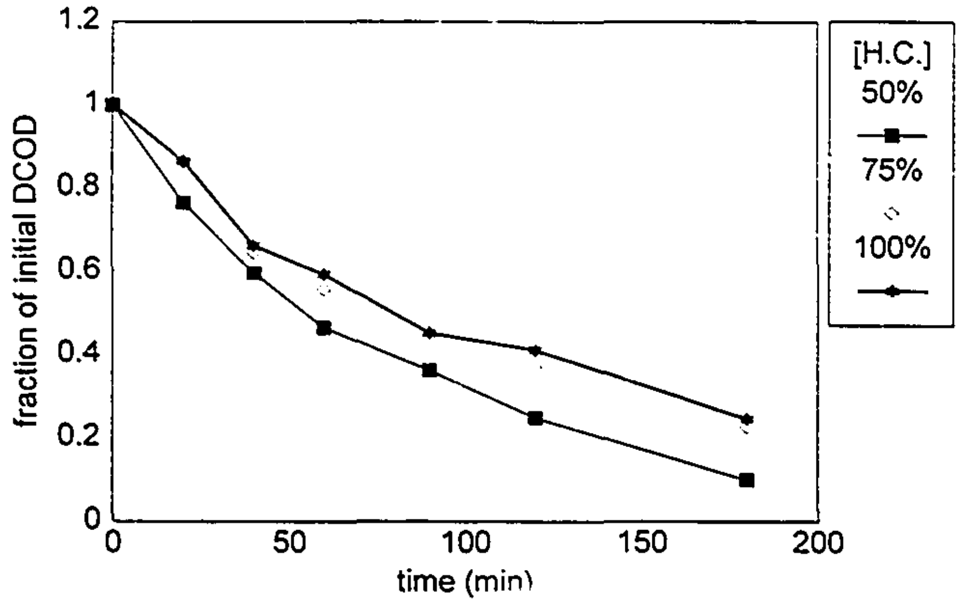

Figure 5.12. Photooxidation of heat condensate solutions of concentrations 50%, 75% and 100% (undiluted) with results expressed as fraction of initial DCOD of effluent solution. Initial concentration of H_2O_2 = 0.15%. T = 25°C.

This figure indicates that the highest percentage of DCOD diminution occurs when the effluent is initially diluted to 50%. However, the small differences in the final DCOD values makes the idea of performing photooxidation experiments with a highly diluted effluent questionable. For this reason, it was decided to keep using 50% diluted solutions of heat condensate in the remaining experiments, and try experiments with pure solutions of effluent as well, since diluting the effluent is not practical nor economical in an actual situation. The need to dilute the effluent in the first stages of this experimental research was primarly to facilitate research work and lead to a more torough observation of the effects caused by the variation of operating parameters.

Evaluation of potential heterogeneous photocatalysts

A preliminary set of experiments was performed to evaluate the performance of various compounds potentially suitable for the heterogeneous catalysis of a photooxidation process. Of the five investigated, four compounds have proved in previous experiments to be effective for the photooxidation of some contaminants. It is not known if aluminum oxide (Al_2O_3) is efficient at all for catalyzing a photooxidation reaction. However, it was tested for the following reasons: it is unsoluble in water under normal conditions, it is a semiconductor oxide (like titanium dioxide), it is white in colour and therefore is likely to reflect light without absorbing it too much. Moreover, Al_2O_3 is already used in papermaking as a filler. It would thus be readily available in a mill and its presence in the wastewater would be advantageous to the treatment process. The other studied compounds were titanium dioxide (TiO_2), cupric oxide (CuO), ferric chloride ($FeCl_3$), and ferric perchlorate ($Fe(ClO_4)_3$).

Initial experiments using dosages of 2 mM of CuO and Al_2O_3 were performed and their results are illustrated in figure 5.13, where their performance can be compared to a photooxidation process with the same initial hydrogen peroxide but without any added heterogeneous species. It can be seen that Al_2O_3 did not improve the process at all, as in the first half of the reaction period it actually imposed a negative effect on the oxidation process, this probably because it absorbed some light away from the effluent and/or hydrogen peroxide. CuO, on the other hand, showed some great promise since it appeared to accelerate the photooxidation process. Results in figure 5.13 indicate that by adding CuO to the UV/H_2O_2 process, the DCOD of the effluent gets reduced to approximately 40 mg O_2/l in 90 minutes, that is, in half the time required by UV/H_2O_2 alone to obtain similar results. However, this consists of only one single experiment and some technical difficulties were encountered in the measurement of the DCOD after 120 minutes of reaction time. The distorted shape of the CuO curve makes it rather difficult to develop an expression for the rate of reaction, determine its order, and calculate a corresponding rate constant. To really find out the relevancy of adding CuO to the process, as well as prove the repeatability of such results, further experiments had to be performed using this compound.

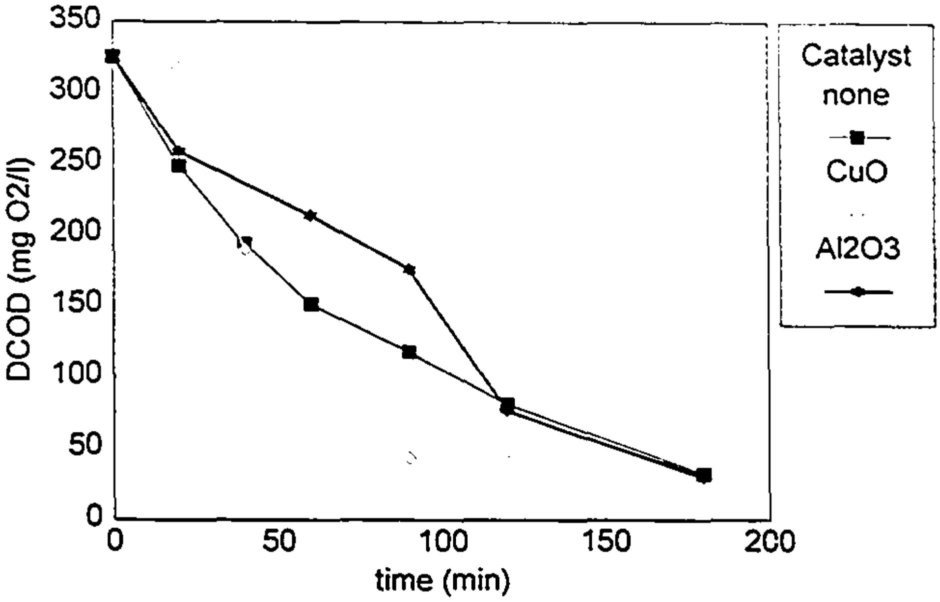

Figure 5.13. Effect of adding Al_2O_3 and CuO on photooxidation of heat condensate (50% dil.). Initial concentration of H_2O_2 = 0.15%, initial concentration of heterogeneous catalysts = 2 mM. T = 25°C.

The next catalysts being tested were TiO_2, $FeCl_3$, and $Fe(ClO_4)_3$. The last two compounds, when combined with H_2O_2, form what is known as a Fenton's reagent, as explained before in chapter 3. Even though most of the experiments done elsewhere with TiO_2 were performed with UV light set at a wavelength of approximately 400 nm, and that the lamps in this research have a dominant wavelength of 253.7 nm, it was decided nevertheless to test TiO_2 with UV/H_2O_2 using the present experimental setup. Since TiO_2 is highly photoreactive, it was thought that it could also react at a wavelength of 253.7

nm, and/or that the range of the UV lamp would be wide enough to deliver a significant amount of photonic energy at 400 nm. The results obtained with these catalysts are illustrated in figure 5.14.

The experiment using TiO_2 did not seem to improve the photooxidation process at all. This was probably due to an incompatibility of TiO_2 with the photonic wavelength 253.7 nm in terms of photoreactivity. TiO_2 is much less photoreactive at a light wavelenght of 253.7 nm than it would be at a wavelength of 400 nm. According to the literature, this latter value is the wavelength of choice for many researchers for photocatalysis using TiO_2. It is therefore reasonable to expect that TiO_2 might not function properly as a photocatalyst at a different light wavelength, as demonstrated in this experiment. This shows that adjustments in UV light wavelenght are very critical in a photooxidation process. The compound which acts as a source of hydroxyl radicals must be photoreactive at the same wavelength as the dominant UV light wavelength emitted by the lamps in the photochemical reactor. For this reason it was decided to abandon the use of TiO_2 in further experiments.

Results of catalyzing the UV/peroxidation process with Fenton's reagent were very successful. $FeCl_3$ and $Fe(ClO_4)_3$ produced identical results when they were combined with hydrogen peroxide. This is expected, since their contribution to the Fenton's reagent is strictly the ferric ion (Fe^{3+}) which is at the same oxidation state for both compounds. Even though the rate of DCOD degradation was very fast, the contribution of UV light to the oxidation process is arguable, since the Fenton's reagent by itself is already a very powerful oxidizer which does not necessarily need UV light catalysis. This is especially true for the present case, since the initial organic content of the effluent solution is relatively weak. However, two major problems are created with the use of Fenton's reagent in such an experiment. First, the chemical species supplying the Fe^{3+} ion contain chlorine compounds, so these are added to the wastewater during the treatment and might remain in solution afterwards. It is well known that chlorine is considered more and more as a source of toxicity by environmental strategists. Adding it to the water can then lead to an environmental problem. Second, the effluent must be acidified to a pH as low as approximately 2.7 prior to the addition of the ferric compound to the water in order for the process to be efficient. Adding an acid to the water can lead to hazardous handling problems and process complications, and represents an additional cost. Moreover, a low pH is considered environmentally inappropriate and therefore would have to be readjusted following the treatment, increasing even more the cost and control of the operation. For these reasons the use of Fenton's reagent was not considered relevant for the present study, and it would not be tested in further experiments. It is too powerful for the purpose of oxidizing a weak effluent such as diluted heat condensate. However, Fenton's reagent combined with UV would probably be more economically appropriate for the destruction of highly toxic contaminants, such as poly-chlorinated biphenyls (PCBs) for instance.

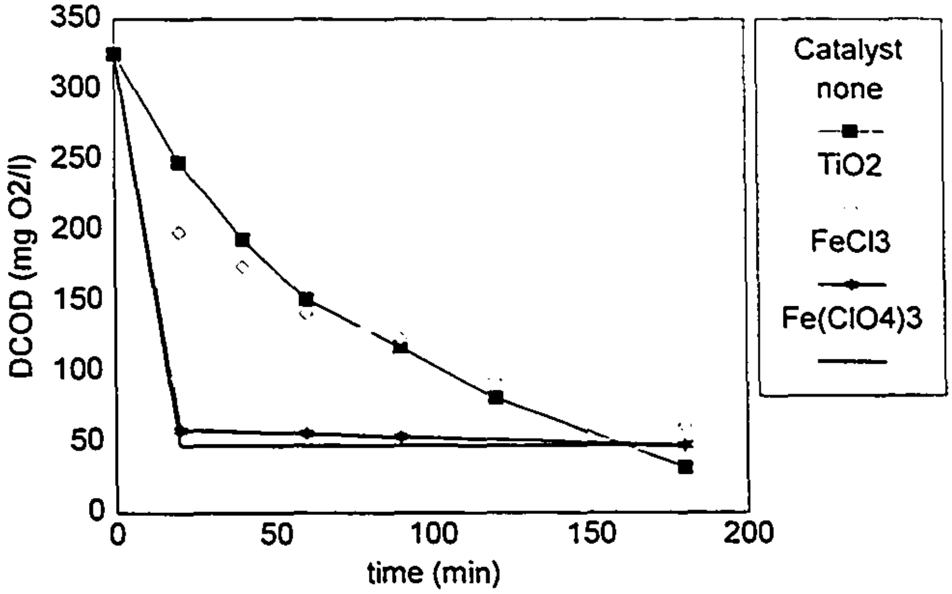

Figure 5.14. Effect of adding TiO_2, $FeCl_3$, and $Fe(ClO_4)_3$ on photooxidation of heat condensate (50% dil.). Initial concentration of H_2O_2 = 0.15%, initial concentration of heterogeneous catalysts = 2 mM. T = 25°C.

Additional experiments with CuO

For the remaining experiments, it was decided to stop using diluted solutions of heat condensate effluent. The main purpose of diluted solutions was to facilitate the investigation and optimization of operating parameters. This way, differences in results caused by varying experimental parameters could be more easily observed. After that all targeted operating parameters had been analyzed, and their effects on the process were known, there was no more need to keep on using diluted solutions of effluent. Moreover, it had already been proved that the photooxidation process is efficient with undiluted solutions of effluent, as demonstrated in figure 5.11.

Using undiluted solutions of heat condensate effluent, the compound CuO was tested again as a potential heterogeneous photocatalyst. Different dosages of this compound were added to the effluent in order to determine its optimal concentration and observe its effect on the process. These experiments were very successful. All of these, as illustrated in figure 5.15, significantly improved the UV/peroxidation process. These results not only supported what was previously obtained with the diluted effluent, but also demonstrated the effect of varying the CuO dosage on the efficiency of the photooxidation process. The most favorable results were obtained at the lowest CuO concentration, i.e. 0.5 mM. When this dosage was added to the effluent/H_2O_2 solution, the rate of reaction was accelerated such that the DCOD of the effluent got reduced to 200 mg O_2/l in only two hours, instead of three when solely hydrogen peroxide was used. An increase in the concentration of CuO had a negative effect on its catalyzing ability. This powdered oxide compound is black in nature, and therefore it probably absorbs a lot of light, so therefore an overdosage of it could lead to undesirable UV light shielding effects. However, its light absorbing nature might also partly explain its high photoreactivity. By absorbing UV light, CuO gets photolyzed and creates cupric ions (Cu^{+2}) which help form hydroxyl radicals from hydrogen peroxide (reactions 3.39, 3.40 and 3.41). Because of time constraints, it was not possible to perform experiments with CuO at concentrations lower than 0.5 mM. This is unfortunate, since the lower limit of the range of potential CuO concentrations could not be determined. Figure 5.15 shows that lowering the CuO dosage from 2 to 0.5 mM improves the process, and this indicates that a dosage lower than 0.5 mM would possibly be even more beneficial to the process and produce better results.

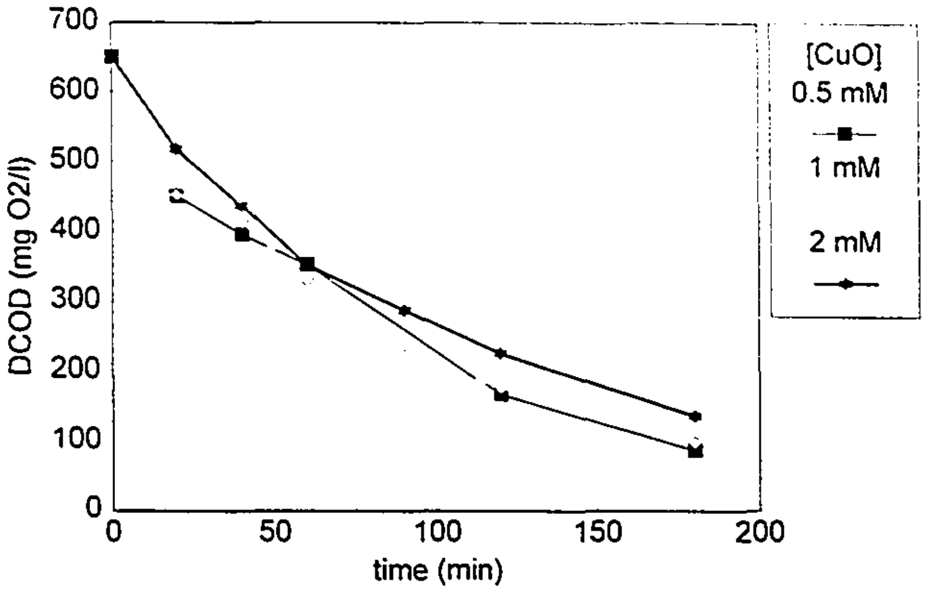

Figure 5.15. Photooxidation of undiluted heat condensate with different added concentrations of CuO. Initial concentration of H_2O_2 = 0.15%. T = 25°C.

Final series of experiments

So far, the efficiency of the UV/peroxidation process has been demonstrated solely by the change in the DCOD of the effluent during and after oxidation. However, there are many additional parameters that are generally used to characterize the quality of an effluent, such as Dissolved Organic Carbon (DOC), suspended solids, etc. To be complete, a study of a wastewater treatment technology must include an extensive description of the effluent before and after treatment, to reveal the true efficiency of the process with respect to changes in various characteristics of the effluent, and examine the possible strengths and weaknesses of the treatment process. In general, the full treatment of an industrial wastewater implies many steps, and each step plays a role in the removal of a specific parameter. For instance, a step of the treatment chain could be in charge of removing suspended solids, while another would be responsible for the removal of colour. It is therefore important to understand which parameters of the effluent can be efficiently removed, and to which extent, using the H_2O_2 photooxidation process. This way the possible role of this technology in the treatment of an industrial wastewater can be determined as well as its position in a sequential order of treatments.

The characteristic parameters that were measured in this set of experiments are:

- pH:
- Total Chemical Oxygen Demand (TCOD):
- Dissolved Chemical Oxygen Demand (DCOD):
- Dissolved Organic Carbon (DOC):
- Total Solids (TS):
- Total Volatile Solids (TVS):
- Total Suspended Solids (TSS):
- Total Volatile Suspended Solids (TVSS):
- Total Dissolved Solids (TDS):
- Total Volatile Dissolved Solids (TVDS):
- hydrogen peroxide concentration (% w/v H_2O_2):
- dissolved lignin concentration:
- absorbance @ 253.7 nm:

It was decided for most experiments to use undiluted solutions of heat condensate effluent, to simulate a process closer to real field operating conditions. As well, instead of the usual 50 ml of H_2O_2 solution used for previous experiments, concentrated solutions of it (30%) were used and injected directly into the system, so that the additional volume of H_2O_2 and its dilution effects could be minimized. The analysis for a characterisation of the wastewater were performed once for the pure, untreated heat condensate, and after each completed experiment.

The experiments that were performed are described as follows, indicating respectively the initial concentration of effluent, initial concentration of hydrogen peroxide, time of reaction, operating temperature of the system, and concentration of heterogeneous catalyst (if any):

1.) 50% diluted heat condensate, 0.15% H_2O_2, t = 3 hrs, T = 25°C;

2.) pure heat condensate, 0.20% H_2O_2, t = 3 hrs, T = 25°C;

3.) pure heat condensate, 0.15% H_2O_2, t = 3 hrs, T = 25°C;

4.) pure heat condensate, 0.20% H_2O_2, t = 3 hrs, T = 45°C;

5.) pure heat condensate, 0.20% H_2O_2, t = 3 hrs, T = 25°C, 0.5 mM CuO;

6.) pure heat condensate, 0.20% H_2O_2, t = 4 hrs, T = 25°C.

Results obtained with these experiments are presented in tables 5.2 (experiment 1) and 5.3 (experiments 2 to 6) and compared to the initial characteristics of the effluent prior to photooxidation.

These results can lead to a series of observations on the effect of varying operational parameters on different quality aspects of the wastewater after oxidation with UV/H_2O_2. This can be done by comparing the effluent characteristics after each experiment. It is rather difficult, however, to compare results obtained in experiment 1 with the other results, since the initial effluent concentration in this case was half the one used in all other experiments.

The changes in Total COD for experiments 2 and 4 are very similar, with eliminations of 27.3 % and 27.5 % respectively of the initial TCOD of the wastewater. The low TCOD removal obtained in experiment 2 (11.4 % of initial TCOD) shows that with a pure heat condensate solution, the initial H_2O_2 concentration should preferably be 0.20% rather than 0.15%. The TCOD removals obtained with experiments 5 and 6 are much better, with 54.3 % and 48.1 % eliminations of the initial TCOD respectively. This shows that, in terms of TCOD reductions, adding 0.5 mM of CuO to the wastewater/H_2O_2 solution prior to photooxidation with a reaction time of 3 hours, is equivalent to a reaction time of 4 hours when H_2O_2 is used by itself. Thus CuO can greatly accelerate the rate of photooxidation of the wastewater and lead to appreciable time savings. The ultimate TCOD removal in terms of percentage of the inital value, however, was obtained with experiment 1 in which a 50 % diluted solution of heat condensate effluent was utilized. A 63.6 % reduction in TCOD was obtained, and this superior performance was expected because of the low initial concentration of organics and absorbance of the wastewater solution. The percentage removals of Dissolved COD are similar to the removals of TCOD and follow the same pattern from one experiment to another.

Characteristic	**50% H.C.**	**Exp.1**
TCOD (mg O_2/l)	580	211
DCOD (mg O_2/l)	336	118
DOC (mg/l)	87	13
diss. lignin (mg/l)	55	36
absorbance	1.43	0.56
transmittance (%)	4	28
turbidity (n.t.u.)	120	37
TS (mg/l)	302	204
TSS (mg/l)	58	50
TDS (mg/l)	245	154
TVS (mg/l)	232	-
TVSS (mg/l)	80	-
TVDS (mg/l)	152	62
pH	4.84	3.81
H_2O_2 (% w/v)	0.150	0.039

Table 5.2. Characteristics of 50% diluted heat condensate before and after photooxidation. Initial concentration of H_2O_2 = 0.15%. Reaction time = 3 hrs. T = 25°C.

Characteristic	H.C. (undil.)	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6
TCOD (mg O_2/l)	1161	844	1029	842	531	603
DCOD (mg O_2/l)	672	408	593	401	294	298
DOC (mg/l)	174	90	132	108	103	85
diss. lignin (mg/l)	110	75	83	69	61	61
absorbance	2.84	2.15	3.02	1.94	-	1.67
transmittance (%)	0.14	0.71	0.10	1.15	-	2.14
turbidity (n.t.u.)	285	170	212	152	-	124
TS (mg/l)	637	397	497	362	-	318
TSS (mg/l)	115	56	47	36	-	14
TDS (mg/l)	489	341	450	326	-	304
TVS (mg/l)	464	156	286	163	-	118
TVSS (mg/l)	160	≈ 0	30	32	-	≈ 0
TVDS (mg/l)	304	156	256	195	-	118
pH	4.70	3.02	3.21	3.05	3.56	3.00
H_2O_2 (% w/v)	-	0.092	0.082	0.092	0.057	0.076

Table 5.3. Characteristics of pure heat condensate before and after photooxidation. Exp. 2: Initial concentration of H_2O_2 = 0.20%, reaction time = 3 hrs, T = 25°C. Exp. 3: Initial concentration of H_2O_2 = 0.15%, reaction time = 3 hrs, T = 25°C. Exp. 4-6: Initial concentration of H_2O_2 = 0.20%. Exp. 4: reaction time = 3 hrs, T = 45°C. Exp.5: reaction time = 3 hrs, T = 25°C, 0.5 mM CuO. Exp.6: reaction time = 4 hrs, T = 25°C.

The highest difference in Dissolved Organic Carbon (DOC) before and after the photooxidation treatment was obtained in experiment 1 by using a 50% solution of heat condensate effluent. A percentage DOC removal as high as 81.1 % was obtained. However, for all other experiments the DOC differences are in the range of approximately 40 to 50 %, except for experiment 3 which was less successful with a

DOC difference of 24 %. These results are in accordance with COD results. This makes sense, since both parameters are proportional to the organics concentration of the wastewater.

A contaminant of great interest found in a pulp and paper mill effluent is definitely dissolved lignin, since it is an organic compound that is rather difficult to eliminate in a conventional wastewater treatment process (see materials and methods). The best results for elimination of dissolved lignin were obtained in experiments 5 and 6, both giving a 45 % removal of dissolved lignin. This performance cannot be really compared to results in the literature, since the analytical method used to determine the concentration of dissolved lignin might differ from one researcher to another. However, this performance is better than the one obtained by Stenberg and Horberg with a biological treatment process, where they had a 35 % reduction in acid soluble lignin of their effluent. This comparison holds true if it is assumed that acid soluble lignin is similar to dissolved lignin.

Lignin is one of the main organic compounds which account for the colour of a pulp and paper effluent. Unfortunately, it was rather difficult to obtain reproducible results for colour measurements in these experiments, so this characteristic parameter had to be abandoned due to technical difficulties. However, a difference in absorbance of the effluent before and after photooxidation treatment is closely related to an elimination of colour. The differences in absorbance for each experiment go in accordance with the differences in dissolved lignin concentration. The lowest absorbance after treatment, among the experiments using a pure effluent, was obtained with experiment 6, with a value of 1.67. It was impossible to find a comparative value for experiment 5 since the presence of CuO in suspension caused a large increase in the absorbance of the wastewater solution. The lowest absorbance obtained with experiment 6 corresponds to the highest final transmittance (2.14 %) since these parameters are inversely proportional, as demonstrated by equation 5.3.

In experiments with pure heat condensate solutions, results demonstrating the differences in turbidity and solids generally have the same pattern. The experiment which produced the highest removal of turbidity and overall solids was number 6. This performance is followed, in decreasing order of turbidity and solids removal, by experiments 4, 2 and 3. This trend goes in accordance with previously obtained results. However, these parameters could not be considered for experiment 5, due to the presence of suspended CuO which would have possibly lead to large analytical errors in turbidity and solids measurement.

In general, for an oxidation experiment, a change in pH would normally express the extent of a reaction. The final pH observed in experiments 2, 4 and 6 is practically the same, i.e. approximately 3.00 - 3.05. However, the final pH resulting from experiment 5 is relatively high, 3.56. This is unexpected, since this experiment produced some of the most noticeable results in the removal of COD as well as other characteristic parameters, which showed that oxidation was very effective during the treatment process.

Moreover, it would be normal to assume that the experimental conditions that gave the best results would also be the ones that consumed hydrogen peroxide most efficiently. A high difference in hydrogen peroxide concentration indicates a large production of hydroxyl radicals, which are the main oxidizing agents in a UV/H_2O_2 photooxidation process. The experiment which consumed the most H_2O_2 is number 5, with a difference in concentration of 0.143 % w/v, followed closely by experiment 6, with a H_2O_2 consumption of 0.124 % w/v. This makes sense, since these experiments were very efficient for the oxidation of the wastewater. Experiments 2 and 4 consumed the same amount of hydrogen peroxide, 0.108 % w/v, and experiment 3 is the one where the H_2O_2 consumption was the least efficient, with a difference of only 0.068 % w/v between the initial and final concentrations of H_2O_2. Therefore the efficiency of H_2O_2 consumption is closely related to the efficiency of oxidation of the wastewater. The experiment which started with a 50 % diluted heat condensate solution also had a relatively high H_2O_2 consumption efficiency, with a difference in H_2O_2 of 0.111 % w/v. This is approximately twice the H_2O_2 consumption obtained in experiment 3, where the initial H_2O_2 concentration was the same but the heat condensate solution was undiluted.

This is due to the higher light absorption of the diluted effluent solution, thereby facilitating the photolysis of H_2O_2.

In summary, experiments 5 and 6 generally produced similar results. This indicates that CuO can be greatly beneficial to the photooxidation process. By adding 0.5 mM of this catalyst to the H_2O_2/effluent mixture, the time of reaction is reduced by one hour when compared to the time of reaction necessary to obtain similar results with only the H_2O_2/effluent mixture getting irradiated with UV light. There was no significant difference between the results obtained in experiments 2 and 4. This contradicts previous results which showed that an increase in temperature significantly improved the photooxidation process (figure 5.9). The poorest results were produced by experiment 3 in which the initial H_2O_2 concentration was reduced to 0.15 % w/v, instead of the usual 0.20 % w/v used for all other experiments with pure heat condensate. This means that a concentration of 0.15 % H_2O_2 is insufficient for an efficient photooxidation of a pure heat condensate solution. The results obtained in experiment 1 can not really be compared to the ones obtained in the other experiments, since the initial effluent concentration is different. However, they confirm the previous observation that a diluted effluent can be more easily photooxidized due to its higher light transmittance.

Experimental conclusions

The results obtained from the numerous experiments performed during the scope of this research work lead to a series of conclusions:

- When UV light and H_2O_2 are used separately to treat the effluent, each individual process slowly and partially oxidizes the organics from the wastewater. However, when these two processes are combined and form hydroxyl radicals (•OH) in solution, the rate of oxidation is greatly accelerated.

- There was an optimal concentration of H_2O_2 that had to be determined experimentally. When the wastewater was 50 % diluted, a concentration of 0.15

% w/v H_2O_2 produced the best results. When the wastewater was pure, the optimal H_2O_2 concentration was 0.20 %. This means that the optimal H_2O_2 concentration increases with an increasing effluent concentration.

- Changes in the initial pH of the effluent did not have an effect on the efficiency of the photooxidation process. This could be considered beneficial for the process, since it would not be affected by pH variations of the effluent.

- An increase in the operating temperature from 25°C to 45°C proved to accelerate the rate of photooxidation of the wastewater. However, this effect was not observed in a second similar experiment where the temperature was also raised to 45°C.

- The concentration of the wastewater had an effect on the photooxidation process in terms of percentage DCOD eliminated. A more concentrated effluent has a higher absorbance and therefore blocks UV light away from H_2O_2, thus affecting its photolysis potential and hydroxyl radicals production.

- Cupric oxide (CuO) was very successful in accelerating the rate of photooxidation of the effluent. When exposed to UV light, CuO gets photolyzed to generate a cupric ion (Cu^{+2}), which can then act as a catalyst for the decomposition of hydrogen peroxide into OH radicals.

- The UV/H_2O_2 process was successful in considerably reducing the amount of dissolved lignin and organics responsible for colour in the heat condensate. This is very useful, since lignin and other organics greatly contribute to the toxicity of the effluent.

CHAPTER 6 CONCLUSION

Contributions to knowledge

Photooxidation of a TMP mill effluent with hydrogen peroxide has never been attempted before. This experimental research has proved that photooxidation with H_2O_2 is applicable for the partial degradation of a "heat condensate", a typical effluent generated by TMP mills.

Experimental results support many previous observations made by other researchers. For instance, that there is an optimal H2O2 concentration that has to be determined for each new set of experimental conditions. Additionally, an increase in operating temperature accelerates the rate of oxidation of the effluent. The process is also affected by changes in the concentration of the effluent, since an increase in effluent concentration leads to a higher absorbance and thus a blocking of UV light.

The assumption that the rate of oxidation of the effluent varies with its transmittance, or that its reaction rate constant is a function of the effluent transmittance, is an innovative idea brought up by the author as an attempt to understand the shape of curves expressing the rate of disappearance of the effluent DCOD. An initially low transmittance of the effluent would probably slow down the rate of reaction, and as the oxidation process advances with time, color-producing organics are destroyed, and a decrease in effluent color is proportional to an increase in its transmittance. This allows a higher amount of UV light to enter the effluent solution and photoactivate the remaining H_2O_2. This way the photooxidation is a continuous process characterized by a relatively slow degradation of an initially-colored effluent.

Using CuO as a photocatalyst in an advanced oxidation process has not been widely investigated by other researchers, since very few information on the subject is available in the literature. A series of experiments done during this experimental work have showed that it is a very efficient catalyst for photooxidation with H_2O_2, since it accelerates the rate of oxidation of the effluent considerably when added to the reacting mixture.

Finally, an important observation made during this experimental work is the elimination of color and dissolved lignin by the UV H2O2 photooxidation process. Lignin is one of the most toxic compounds of pulp and paper mill effluent and is usually difficult to be taken care of by conventional, biological secondary treatment processes.

Feasibility study

Throughout this experimental work, it has been demonstrated that the photooxidation process combining hydrogen peroxide with UV light has some interesting potential for the treatment of a pulp and paper mill effluent. The photooxidation process was not only effective in decreasing the COD of the effluent, but it was also successful in the partial destruction of dissolved lignin and decolorization of the heat condensate, two actions usually difficult to achieve with a conventional biological treatment process.

However, the implementation of a photooxidation process as an alternative to biological treatment might be neither practical nor economical. This advanced oxidation process would be subject to design limitations which would make it rather difficult to use in a real-size effluent treatment plant.

First, it was demonstrated that the transmittance and/or colour of the effluent play a major role in the efficiency of the photooxidation process. The wastewater has to be clear enough in order to absorb a sufficient amount of UV light for an efficient photoactivation of H_2O_2. This is generally not true for a typical pulp and paper mill effluent coming out of a primary treatment stage which usually consists of a simple decantation of settleable solids. In fact, most pulp and paper effluents contain a high concentration of dissolved solids and color-producing organic compounds which would block UV light out. In the course of this research work, the heat condensate effluent was the clearest type of effluent that could be found at the investigated mill, and its dilution in pure water proved to be very beneficial to the process. However, diluting the effluent is definitively out of the question in the operation of a pulp and paper mill, since one of the main objectives of an environmental strategy is to reduce the consumption of fresh water by the mill. For a photooxidation process to be efficient a secondary treatment process, the primary stage of treatment would need to, along with a reduction in solids concentration, eliminate some of the color-producing organic constituents of the effluent.

Within the batch experimental conditions that were used, the photooxidation process required a very long time (≥ 3 hrs) to significantly decrease the DCOD of the heat condensate. A slow reaction time means that a high retention time would be required by the effluent in a continuous flow photooxidation system. The wastewater would need an extensive amount of time to get sufficiently oxidized. In the design of a typical wastewater treatment plant, hydraulic retention time is a very important parameter to consider, since a high retention time means larger tank volume and higher surface area requirements. This leads to an increase in the cost of infrastructures, possible design complications and more functional problems, etc.

The flowrate of a pulp and paper mill total effluent is usually very large since the operations of a typical mill require massive amounts of water. A large photooxidation system would then have to be built in order to take care of all the generated wastewater. An additional complication is the fact that UV light can penetrate the wastewater only up to a certain extent of depth. This would have to be taken into consideration for the design of a UV/H_2O_2 system, since it signifies that a large number of UV lamps would be required to treat a pulp and paper mill effluent. These lamps require a lot of energy and some maintenance, which lead to an increase in operating costs. If the adopted design is a continuously-stirred tank reactor, intense mixing would also be required. However, despite all these design complications, a large UV/H_2O_2 system might still be feasible, since there are already some domestic wastewater treatment plants which use large systems with UV lamps for the disinfection of their water.

In a pulp and paper mill, the total effluent is usually a combination of many different effluents generated by various processes. An interesting alternative for the use of a UV/H_2O_2 system would be to apply it only onto a certain effluent which would be better suited for a photooxidation process, instead of applying it onto the total combined effluent of the mill.

Suggestions for future work

Photooxidation has received a lot of attention from researchers in the past few years, since it is considered to be a technology with an enormous potential for the treatment of polluted effluents. During this project, a real pulp and paper mill effluent was photooxidized with UV and H_2O_2. Even though the produced results were very interesting from a research point of view, there are other avenues that could be taken in further experiments to complement those results and investigate the process more fully.

A photooxidation process such as the one that was investigated should be tested as a tertiary treatment alternative. Since actual secondary treatment processes such as biological reactors or aerated lagoons do not fully eliminate all organics and lignin from the effluent, and therefore do not allow recycling of the treated wastewater back into the mill, there is a need for a tertiary treatment process which would be in charge of polishing the effluent. Photooxidation could be well suited for that, since in theory it could destroy all the remaining organics of the wastewater and thus allow its recycling back into the mill. In fact, the future of photooxidation technologies probably lies in the elimination of toxic trace elements present in contaminated waters.

In this research work it was decided to test the UV/H_2O_2 process on a real pulp and paper mill effluent to study the applicability of this process in a real mill operation. However, in many effluent treatment studies, the investigated wastewater is generally a simulated one. First, the researcher finds and isolates the main toxic constituents of the effluent of interest, and he make solutions of these constituents in laboratory, so that he can investigate the effect of the process on each constituent individually. In our case, it would have been interesting to simulate in laboratory a wastewater containing solely dissolved lignin, for instance. Even though this is less representative than real field effluent, it allows more flexibility to the researcher to investigate the effect of the process on the toxic compound he is most interested in.

This experimental study was very much engineering oriented in the sense that it investigated the effect of operational parameters on the efficiency of a photooxidation process. It would be a good idea, however, to also study the chemistry of the process and its kinetics in more details. This can lead to a better understanding of the treatment process and possibly create original ideas on how to optimize it.

Additional heterogenous photocatalysts could be investigated, or at other wavelengths. TiO_2 should be definitively investigated at a photonic wavelength of 400 nm, for instance, since experiments from other researchers have many times proved its efficiency as a heterogeneous photocatalyst at that wavelength.

Finally, other advanced oxidation processes could be investigated for the secondary or tertiary treatment of a pulp and paper mill effluent. For example, ozone with UV light, ozone with hydrogen peroxide, or a combination of ozone and hydrogen peroxide with UV light. These processes are all known to be producers of hydroxyl radicals, and their efficiency regarding the treatment of polluted waters has been proved many times by various researchers.

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