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DEGRADATION OF ORGANIC COMPOUNDS IN PAPER AND TEXTILE INDUSTRIAL WASTEWATERS BY ADVANCED OXIDATION PROCESSES

Memòria presentada per optar al grau de Doctora en Enginyeria Industrial

Montserrat Pérez Moya

Terrassa 2001

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CERTIFIQUEM:

Que la present memòria, de títol : "*Degradation of organic compounds in paper and textile industrial wastewaters by advanced oxidation processes*", ha estat desenvolupada sota la nostra direcció per **Montserrat Pérez Moya**, Enginyera Industrial, per a optar al grau de Doctora en Enginyeria Industrial.

I per a què així consti, signem el present certificat en Terrassa a 20 de Setembre de 2001.

Torrades
Francesc Torrades Carné

José Peral
José Peral Pérez

Mému Manželovi

Only after the last tree has been cut down.
Only after the last river has been poisoned.
Only after the last fish has been caught.
Only then will you find that money cannot be eaten.

Cree Indian Prophecy

"Un libro, como un viaje, se comienza con inquietud y se termina con melancolía"
José de Vasconcelos

No sé precisar a que se parece más la experiencia de llevar a cabo una investigación con el objetivo de escribir una tesis doctoral, si a un libro o a un viaje. De todas formas, como casi todo en la vida, lo he empezado con inquietud y curiosidad y al ver cercano el final no puedo evitar una cierta tristeza, compensada con el agradecimiento que siento por todo lo recibido.

La realización de una tesis no es siempre fácil. Parece contradictorio, puesto que: se escoge libremente, te permite aprender día a día, interactuar con muchas personas diferentes, etc... Sin embargo, todos los doctorandos que conozco han pasado por etapas similares de desilusión, de alta autocrítica, de extravio, y muchas veces, incluso, de desamparo.

Gran parte de la dificultad de realizar una tesis reside, tristemente, en la precaria situación del doctorando-becario, así como los pocos medios con que cuentan algunos departamentos para desarrollar los trabajos de investigación. Nuestra sociedad, que se autodefine como progresista y desarrollada, sigue destinando muy pocos recursos a la educación en general y a la investigación en particular, a pesar de que nuestros dirigentes hablen de la incuestionable importancia de la investigación en sus discursos. Desafortunadamente, los doctorandos en este país, no sólo encuentran dificultades durante la realización de su tesis; al finalizar la misma empieza una nueva carrera de obstáculos.

¿Como proyección profesional se valora la realización de una tesis? En general, en el mundo industrial no se reconoce el trabajo y aprendizaje de este periodo formativo. Sorprendentemente, la respuesta de la comunidad universitaria es similar. En muchas ocasiones muestra lo poco que valora el potencial intelectual del doctorando.

Es justo admitir que este "breve" espacio de tiempo (algo más de cuatro años) no sólo me ha servido para mejorar académica y científicamente, también me ha permitido valorar la cercanía y complicidad de muchas personas a las que quiero. Su proximidad me ha ayudado en muchos momentos a seguir creyendo en mi trabajo, siendo un gran estimulo en los momentos de dificultad y haciéndome apreciar lo maravilloso de la vida.

Como bien dice Lonnie Barbach "Un libro nunca se escribe solo." Así pues quiero agradecer a mis padres su constante ayuda y cariño especialmente cuando no entendían mis decisiones. A mi familia su confianza y apoyo. A mi tío Antonio por su esfuerzo y dedicación (charlas hasta altas horas de la madrugada) para lograr despertar y renovar mi interés por aprender y hacerme sentir que puedo cambiar el mundo, al menos el mío. A mi tía Dolores por sus frecuentes llamadas para saber como me ha ido un examen, un viaje o cualquier cosa que presintiera importante para mi. A mis primos, muchos de ellos además amigos y hermanos, porque con su sola presencia en mi vida han hecho que todo se llenara de colores en los momentos en que yo sólo veía en blanco y negro. A Pavel, mi compañero de viaje y sobretodo mi amigo, por tanta paciencia, comprensión, ternura y amor. A mi familia checa, que a pesar de la distancia, saben hacerme llegar su cariño por ondas invisibles. A mis amigos, que provienen de muchos y variados lugares, pero su presencia en mi vida es incuestionable. Con ellos he reído, soñado, compartido e imaginado un mundo mejor.

A mis directores de tesis el Dr. Francesc Torrades y el Dr. José Peral por la oportunidad de realizar esta investigación con todo lo que ello ha conllevado a nivel profesional y personal. Con mi mayor deseo de éxitos para ellos.

A mis compañeros de la EUETIB, con los que he compartido la parte final de la tesis y el inicio de una nueva etapa que esperemos esté llena de éxito.

A los profesores, compañeros y personal de los distintos laboratorios en que se realizo este proyecto:

- Laboratorio de Química de la ETSEI de Terrassa, Universidad Politécnica de Cataluña. Por haberme permitido después de finalizar el proyecto de final de carrera iniciar la tesis.

- Laboratorio de la Unidad de Químico-Física del Departamento de Química de la Universidad Autónoma de Barcelona. Al Dr. Xavier Doménech por facilitar la parte experimental de este trabajo y por mantener el buen ambiente que siempre se respira en dicho laboratorio.

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- Water Chemistry Department de la Universidad de Wisconsin, Madison, USA. Al Dr. Marc Anderson y a la Dra. Isabel Tejedor-Tejedor, por permitirme la experiencia de trabajar por primera vez fuera de nuestras fronteras y conocer a aquellos que siempre me recordaran la belleza de los lagos de Madison. A Jon también agradecerle su ayuda en la redacción en inglés de este trabajo.

- Laboratorio de recursos Renovables de la Universidad de Concepción, Chile. Agradecerle al Dr. H.D. Mansilla la posibilidad de trabajar bajo su dirección y con su grupo de trabajo. Allí, he aprendido que el compartir los conocimientos hacen el trabajo mucho más grato y convierten la investigación en un ejercicio de creatividad que forma parte activa de la vida. Gracias a quienes hicieron que me enamorara de Chile y lo sienta como mi hogar.

DEGRADATION OF ORGANIC COMPOUNDS IN PAPER AND TEXTILE INDUSTRIAL WASTEWATERS BY ADVANCED OXIDATION PROCESSES

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1. ADVANCED OXIDATION PROCESSES

Water is the most essential element necessary for life to exist on earth. Today we are coming to understand that fresh water reserves, like all natural resources, are limited. Wherever, and whenever, people experience a lack of clean drinking water, human life is endangered. Today, in the 21st Century, over 1.2 billion people world-wide do not have access to safe drinking water. Additionally, over 80 % of all infectious diseases in the third world are caused by an insufficient supply of safe drinking water. Moreover the demand for water in agriculture, industry and human consumption is also a potential source of violence and warfare [Bauer and Fallmann, 1997].

The efficient treatment of industrial wastewaters and contaminated drinking water has become critically important in a world that is faced with an ever increasing population and even faster growing industrialization. The last 10 years have seen a rather fast evolution of research activities devoted to environmental protection as the consequence of the special attention paid to the environment. Social, political and legislative authorities, both domestic and international, are demanding laws and regulations that are what previous generations would have considered extreme [Legrini et al., 1993].

These new laws and regulations address many types of pollutants not amenable to conventional biological treatments [Kahmark and Unwin, 1998]. These compounds can be characterized as being highly stable and/or as being difficult to be completely mineralized. In these cases, chemical oxidation attempts to mineralize the contaminants to carbon dioxide, water and inorganics, or, transform them into harmless products [Andreozzi et al., 1999].

It should be noted that methods based on chemical destruction, when properly developed, solve the problem of pollutant abatement differently than those processes in which only a phase separation occurs with the consequent problem of final disposal.

Included among the more accepted techniques for wastewater treatments are the advanced oxidation processes (AOPs) [Hoffmann et al., 1995, Linsebigler et al., 1995, Matsumoto et al., 1996, Bauer and Fallmann, 1997, Balcioglu and Arslan, 1998, Andreozzi et al., 1999, Chen and Ray, 1999]. The AOPs are used to cause the pollutant to be completely mineralized without a waste stream being formed, whereby these technologies are more interesting than removal, accumulation and concentration techniques.

Traditionally, AOPs technologies are those which are based on the *in situ* formation of hydroxyl radicals (OH·) by means of different reacting systems [Bauer and Fallmann, 1997, Andreozzi et al., 1999, Yeber et al., 1999b, Pérez et al., 2001, Torrades et al., 2001]. The hydroxyl radical is an extraordinarily reactive species. The strong oxidative nature of this compound ($E^o = 2.8$ V), much greater than other oxidants (ozone 2.08 V, hydrogen peroxide 1.78 V, chlorine 1.36 V, chlorine dioxide 1.27 V, oxygen 1.23 V, etc.), is able to completely transform organic carbon to CO_2 [Serpone, 1997].

The role of the hydroxyl radical is still rather controversial in some of the advanced oxidation processes. For example, in the Fenton reactions, there are numerous studies attempting to provide evidence for the role of the hydroxyl radical in the system and numerous research dedicated to provided evidence of a role in the Fenton reaction for a oxidant other than the hydroxyl radical [Bossmann et al., 1998, Pignatello et al., 1999].

Among the most extensively known AOPs are:

- Heterogeneous photocatalytic oxidation [Ollis et al., 1991, Hoffmann et al., 1995, Linsebigler et al., 1995, Serpone, 1997, Pérez et al., 2001]
- Ozonation reactions and ozonation in combination with photocatalysis process or the addition of H_2O_2, UVA, iron, etc. to the system [Logager et al., 1992, Saunamäki and Sorvari, 1992, Hostachy et al., 1997, Sánchez et al., 1998, Yeber et al., 1999b, Torrades et al., 2001]
- H_2O_2/UV systems [Matsumoto et al., 1996, Rodríguez et al., 1999b]
- Fenton reaction [Ruppert et al., 1993, Augusti et al., 1998, Chamarro et al., 2001] and Photo-Fenton reactions [Kiwi et al., 1994, Benkelberg and Warneck, 1995, Safarzadeh-Amiri et al., 1996, Tang and Huang, 1996, Chen and Pignatello, 1997, Bossmann et al., 1998, Hislop and Bolton, 1999, Pignatello et al., 1999].

1.1. Photocatalysis

Photocatalysis can be defined as the acceleration of a photoreaction by the presence of a semiconductor catalyst that can be activated by the absorption of light of energy greater ($h\nu \leq 380$ nm) than its band-gap. The semiconductor accelerates the chemical process because of the existence of electron-hole pairs [Hoffmann et al., 1995]. The excited electrons are transferred to the reducible specimen while at the same time the catalyst accepts electrons from the oxidizable specimen which occupies the holes. In this way, the net flow of electrons is null and the catalyst remains unaltered as shown in Figure 1.1.

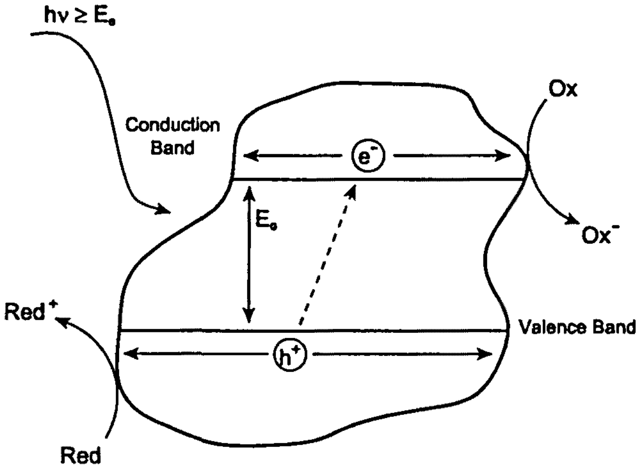


Figure 1.1. *Scheme of the radiation effect on a semiconductor material.*

Photocatalysis with irradiated semiconductors permits effective oxidation and reduction of organic and inorganic compounds. Titanimum dioxide particles have been demonstrated to be an excellent catalyst for photo-oxidation of a multitude of organic and inorganic compounds. Up to January 1999, over one thousand compounds have been treated using photocatalysis [Blake, 1999].

1.1.1. Brief description of the mechanism

On the basis of laser flash photolysis measurements, Hoffmann et al. proposed the following general mechanism for heterogeneous photocatalysis of TiO_2 [Hoffmann et al., 1995]. Characteristic times for various steps in the mechanism are given on the next page and Figure 1.2 summarizes the primary steps in the photoelectrochemical mechanism.

Primary Process	**Characteristic Times**	
✱ *Charge-carrier generation*		
$TiO_2 + h\nu \rightarrow h_{bv}^{+} + e_{bc}^{-}$	fast	I
✱ *Charge-carrier trapping*		
$h_{bv}^{+} + \rangle Ti^{IV}OH \rightarrow \{\rangle Ti^{IV}OH^{\bullet}\}^{+}$	fast (10 ns)	II
$e_{bc}^{-} + \rangle Ti^{IV}OH \leftrightarrow \{\rangle Ti^{III}OH\}$	shallow trap (100 ps)	III
$e_{bc}^{-} + \rangle Ti^{IV} \rightarrow \rangle Ti^{III}$	deep trap (10 ns) irreversible	IV
✱ *Charge-carrier recombination*		
$e_{bc}^{-} + \{\rangle Ti^{IV}OH^{\bullet}\}^{+} \rightarrow \rangle Ti^{IV}OH$	slow (100 ns)	V
$h_{bv}^{+} + \{\rangle Ti^{III}OH\} \rightarrow \rangle Ti^{IV}OH$	fast (10 ns)	VI
✱ *Interfacial charge transfer*		
$\{\rangle Ti^{IV}OH^{\bullet}\}^{+} + Red \rightarrow \rangle Ti^{IV}OH + Red^{\bullet +}$	slow (100 ns)	VII
$\{\rangle Ti^{III}OH\} + Ox \rightarrow \rangle Ti^{IV}OH + Ox^{\bullet -}$	very slow (ms)	VIII
$\rangle Ti^{III} + Ox \rightarrow \rangle Ti^{IV} + Ox^{\bullet -}$	very slow (ms)	IX

where

$\rangle Ti^{IV}OH$ represents the primary hydrated surface functionality of TiO_2, a titanol group
e_{bc}^{-} is a conduction-band electron
h_{bv}^{+} is a valence-band hole
Red is an electron donor
Ox is an electron acceptor
$\{\rangle Ti^{IV}OH^{\bullet}\}^{+}$ is the surface-trapped valence-band hole
$\{\rangle Ti^{III}OH\}$ and $\rangle Ti^{III}$ are the surface-trapped conduction band electron.

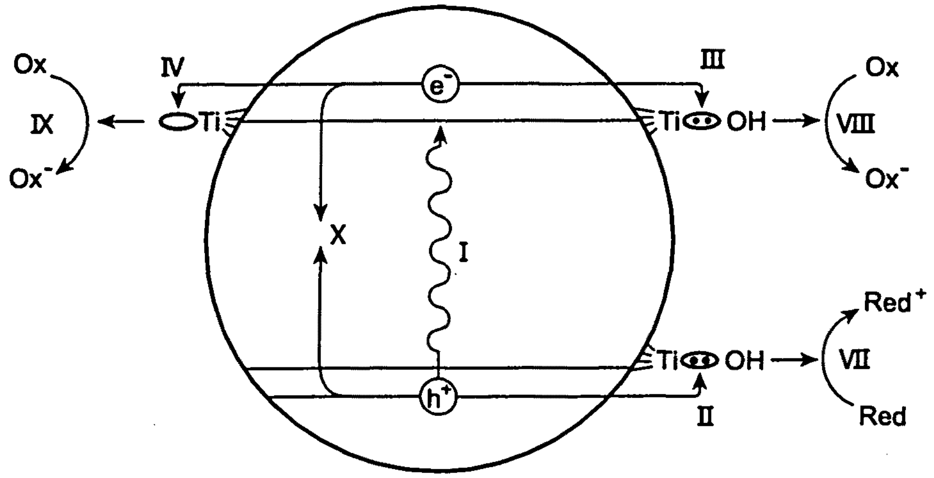


Figure 1.2. *Primary steps in the photoelectrochemical mechanism.*

The illumination of the semiconductor with light of energy greater than its band-gap (Eg) yields charge carrying electron-hole pairs (equation I). Both migrate quickly from the bulk to the surface of the semiconductor where the valence-band hole and the conduction-band electron are trapped at the surface titanol groups (equations II and III). The conduction-band electron is also trapped in a dangling surface bond to yield Ti(III) (equation IV).

After the charge-carrier trapping, two basic phenomena could take place:

1. Charge-carrier recombination with other charge-carriers from the bulk of the semiconductor (equations V and VI).
2. Interfacial charge transfer: redox reactions occur between the absorbed species (such as organic molecules and molecular oxygen) and the trapped charge carriers.

Equation III is a dynamic equilibrium (reversible process). Thus, there is a finite probability that the electron can be transferred back into the conduction band at room temperature.

It should be noted that even trapped electrons and holes can rapidly recombine

$e_{bc}^{-} + h_{bv}^{+} \rightarrow$ calor, hv (ps) **X**

This can be partially avoided through the capture of the electron by preabsorbed molecular oxygen and thus forming a superoxide radical:

$O_{2\,(ads)} + e_{bc}^{-} \rightarrow O_{2(ads)}^{-\bullet}$ **XI**

The overall rate of the reaction depends on the competition between charge carrier recombination and interfacial charge transfer. Various research efforts have been directed at increasing the overall reaction rate by inhibiting charge carrier recombination.

This general mechanism assumes that the substrate does not undergo any direct hole transfer and that the oxidative electron transfer occurs exclusively through a surface-bound hydroxyl radical $\{\rangle Ti^{IV}OH^{\bullet}\}^{+}$ or an equivalently trapped hole species. However, there is some controversy on the importance of the role played in the process by the valence-band holes before they are trapped either within the particle or at the particle surface [Terzian et al., 1991, Serpone, 1995]. Support of the hydroxyl radical as the principal reactive oxidant in the photoactivated TiO_2 derives from the observation that intermediates detected during the photocatalytic degradation of halogenated aromatic compounds are typically hydroxylated structures [Terzian et al., 1991, Hoffmann et al., 1995]. These intermediates are consistent with those found when similar aromatics are reacted with a known source of hydroxyl radicals.

In aromatic compounds, the aromatic part is hydroxylated and successive steps in oxidation/addition lead to ring opening. The resulting aldehydes and carboxylic acids are decarboxylated and ultimately produce CO_2 [Malato, 1999].

1.1.2. Application to the decontamination of water

As discussed previously, conventional water purification processes do not always achieve the complete removal of toxic organic compounds [Kahmark and Unwin, 1998]. In recent years, research into new, non-biological methods of water purification has lead to processes that actually destroy the pollutant instead of simply changing its phase.

Since Carey et al. [Carey et al., 1976] published their results with the photodechlorination of PCBS in the presence of TiO_2 in aqueous suspensions, numerous new studies have appeared using TiO_2 and UV irradiation. The degradation of organic pollutants present in wastewaters using the photocatalytic process appears very promising and the research in this field has grown very quickly the last few years. A review by Blake [Blake, 1999] compiled close to 3300 references on the photocatalytic destruction of compounds in water and air, of which 340 are considered highly toxic.

The most important features which make photocatalytic processes applicable to the treatment of contaminated aqueous effluents are:

- The process takes place at room temperature.
- The oxidation of the substances into CO_2 is complete.
- The oxygen necessary for the reaction is obtained from the atmosphere.
- The catalyst, TiO_2, is cheap, innocuous and can be reused.
- The catalyst can be attached to different types of inert matrices.
- The source of energy could be the sun, which is renewable and inexpensive.

1.1.2.1. Development and state of the art

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrodes [Fujishima and Honda, 1972], research efforts to understand the fundamental processes and to enhance the photocatalytic efficiency of TiO_2 have gradually increased. Figure 1.3 shows the references relating to these efforts collected by Blake [Blake, 1999] from 1970 until January 1999. Blake review clearly confirms that photocatalysis is now in a period of expansion, with new research groups continually appearing in the field.

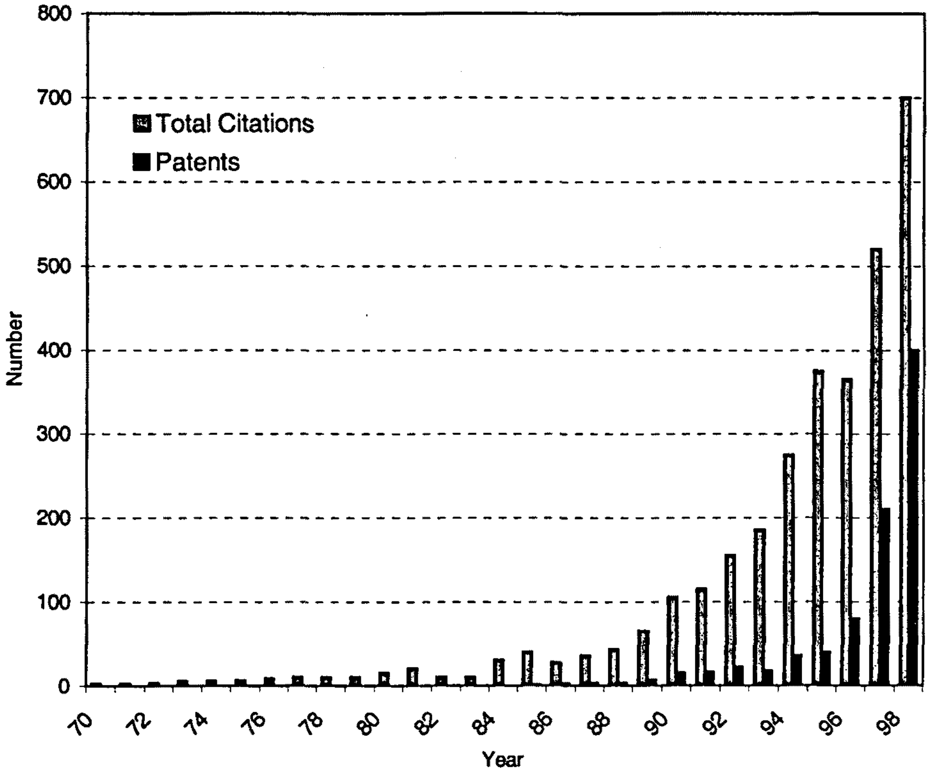


Figure 1.3. *Yearly distribution of the references and patents reviewed by Blake [Blake, 1999].*

The number of new publications, as well as patents, continues to grow each year, as shown in Figure 1.3. The growth in patents is primarily due to the high level of commercial interest in applications being developed in Japan.

Blake's bibliography data [Blake, 1999] on the publication frequency of different subject matters published between October 1996 and January 1999 reveals the following:

- Approximately 26 % of references are concerned with modification to the catalyst (TiO_2) by doping or metallization, the use of dye sensitizers, or the treatment of the catalyst itself with processes that modify its properties.
- 14 % were related to immobilization of the catalyst on a support to avoid the need to separate it from treated water after use.
- Only 2 % of the references used oxidants other than O_2 with the aim of improving the rate process.
- 12 % of the references are based in industrial reactors and systems designs that use this technology, as well as economic comparisons with alternative processes.
- Just 6 % references studied alternative catalysts to TiO_2.
- Bibliography reviews cover around 16 % references.

Articles on experiments with different compounds in aqueous suspensions of TiO_2 are not included, only those on advances that might improve process efficiency and recent bibliographic reviews.

The attempts to optimize the process have focused mostly on photocatalysis modification (26 % of references published between October 1996 and January 1999). In the last few years, surface catalyst characteristics, as well as semiconductor activity have improved, making it more sensitive to longer wavelengths and thereby allowing lower-cost radiation (e.g., sunlight) to be used for its activation.

Research on catalyst immobilization on an inert support has received special attention (over 75 % of the references between 1990 and 1995). Studies are based mainly on TiO_2 and it appears that there has not been much success in the search for alternative catalysts (just 6% of published papers between October 1996 and January 1999 attempted to study catalysts other than TiO_2).

A search for substances that aid in oxidation and thereby improve process performance has also been pursued by many research groups. No versatile product useful for all applications has yet been found.

It is also remarkable that in recent years, photocatalysis has emerged as an important technology for accelerating the oxidation and hence destruction of a wide range of organic compounds in polluted water and air [Linsebigler et al., 1995]. Hundreds of compounds have been the subject of degradation experiments using this technique. Water is the preferred medium since organic and inorganic pollution of ground water, rivers, lakes and even, at already detectable levels, in the sea, are a severe problem [Martinez et al., 1999]. Lately a large amount of useful information has been generated, not only on the processes themselves, but on the environmental behavior of the pollutant. Photocatalysis with TiO_2 was applied to nearly a thousand compounds from 1970 until January 1999: 93 % were organic compounds and just 7 % inorganic compounds such as heavy metals, cyanide, etc. Over 35 % of those organic compounds are included in the EPA list as priority pollutants [EPA, 1988]. In addition, other compounds not currently categorized as dangerous, but which could become dangerous in the future were also investigated.

Photocatalysis as a method of decontamination has acquired a high relevancy and it is possible that successful research on those aspects still to be resolved, together with the incidence of industrial facility design studies and their cost, could spread the application of photocatalysis to real problems in the very near future.

1.1.2.2. Photoreactors

An efficient photocatalytic system requires a large surface area of TiO_2 that is accessible to illumination and to reactant species. These obligatory conditions lead to difficulties with reactor design. Various reactor designs, such as slurry reactors, paked bed flow-through reactors and supported thin film flow-by reactors, meet the conditions of a high surface area irradiated TiO_2 in contact with the reactant. However, all of these systems have limitations related to getting UV light to the reacting surface in the photoefficient and cost effective manner.

A more promising design is one that employs supported, thin films of TiO_2. This design eliminates the problem of separating the catalyst from the reactant and allowing greater penetration of UV light into the reactor. The sol-gel synthesis method can be used to deposit thin (40 nm-500nm), porous, high surface area films of anatase TiO_2 onto a variety of substrates [Xu and Anderson, 1991, Aguado and Anderson, 1993].

Thin-film reactors do have some important limitations:

- A decrease in activated TiO_2 surface area in a specific reactor volume compared to the catalyst in suspension in the same volume.
- A considerable reflection loss from the catalyst support.
- The light must strike the supported TiO_2 films at near-normal incidence to maximize light absorption and reaction rates [Zeltner et al., 1995]. Consequently, there are difficulties in obtaining the correct illumination when the source of photons is not inside the reactor. This is especially a problem for solar radiation.
- Limitations in mass transfer at low flow rates [Ollis et al., 1991]. This effect is more intense when the illumination is increased since a good part of it cannot be used. When this occurs, the reaction rate does not increase with increased photon flow.
- An increase in reactor pressure drop [Pacheco et al., 1990]. The consequence of this effect is an increase in the cost of energy and capital since more powerful pumping systems must be installed.

Consequently, the challenge is to maximize the supported, illuminated thin film surface area within a given reactor volume while minimizing the cost of UV photon generation.

As a way to overcome the light distribution limitations inherent in conventional photoreactor design, the use of waveguides to support and illuminate photocatalysts was initially proposed more than twenty years ago [Marinangeli and Ollis, 1977]. It has been shown that UV light transmitted through a quartz fiber coated with a film of TiO_2 will photocatalytically degrade organic compounds in aqueous solution [Bauer and Hofstadler, 1994, Peill and Hoffmann, 1995]. It seems that a portion of the light is refracted through the catalyst coating with each internal reflection thus activating the catalyst.

Waveguide photoreactors would have several advantages:
- Fiber optic reactor would fix a large amount of supported catalyst with a minimal volume. Additionally, a large number of fibers can be bundled together, increasing the amount of catalyst per unit reactor volume [Hofstadler et al., 1994].
- The light propagation through the fibers to the catalyst should minimize losses due to scattering associated with reactor designs based on external illumination.
- It should also minimize power costs, as one light source can be used to illuminate many coated fibers.

However, waveguide photoreactors must solve still many problems to be successfully employed as commercial systems. Further research in sol-gel derivated TiO_2 film is required to overcome the delamination of the film from the fibers. Also, Peill and Hoffmann [Peill and Hoffmann, 1995] reported a maximum fiber length of 10 cm due to light loss through refraction out of the fiber.

At this point, it will be instructive to examine the fundamental concepts involved in light propagation through waveguides. This can be found in any optical physics text [Born and Wolf, 1980]. Also, some research groups has focused in this subject [Miller, 1998].

Generally, when light strikes the interface between two transparent media of different refractive indices, as Figure 1.4. shows, three distinct phenomena can occur:

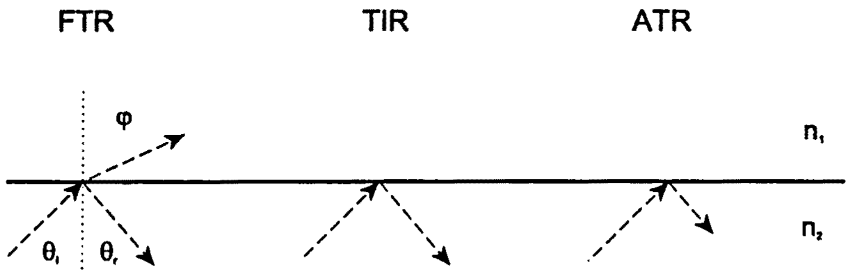


Figure 1.4. *Different modes of reflection at the interface between two transparent media.*

where
n_1, n_2, refractive indices of transparent media 1 and 2
θ_1, incident angle of light striking the interface
θ_r, angle of reflection (= θ_1)
θ_c, critical angle (= $\sin^{-1} n_1/n_2$)
φ , angle of refraction

The phenomena represented in Figure 1.4. are:

- Frustrated Total Reflection (FTR): Light can be partially reflected and partially refracted when $n_1 > n_2$ and/or $\theta_1 < \theta_c$.
- Total Internal Reflection (TIR): Light can be totally reflected into the initial medium of transmission, with no loss of energy, when $n_1 < n_2$ and $\theta_1 > \theta_c$.
- Attenuated Total Reflection (ATR): If the second medium (n_1) absorbs light, ATR occurs. In this case, reflection is total, but a portion of the light energy is lost into the second medium through absorption.

Based on Figure 1.5, optical theory predicts that TIR or ATR can occur only when $n_2 < n_1$ and $\theta_1 > \theta_c$. From other side Harrick [Harrick, 1967] describes a situation where a very thin film is present at the interface between two semi-infinite media. As Figure 1.5 shows, the character of the interface is determined largely by the two semi-infinite media, and ATR can occur despite the presence of a thin film with refractive index $n_2 > n_1$.

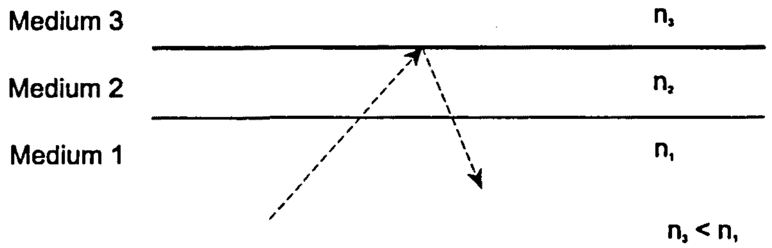


Figure 1.5. *Attenuated Total Reflection at the interface of two transparent media. A thin film is present at the interface.*

Experimental observations of thin-film ATR spectra account for the occurrence of ATR phenomena when a relatively high index thin film is present at the reflecting interface. In the Water Chemistry Program at the University of Wisconsin-Madison, they developed planar silica waveguides coated with TiO_2 that propagate UV light in an attenuated total reflection (ATR) mode [Miller et al., 1999]. These systems do not lose light through refraction at the waveguide surface and the TiO_2 coating absorbs a small portion of light at each reflection.

In Section 6 (Paper 8) we described the process and evaluation of a reactor design that demonstrates the advantages of TiO_2-coated acrylic waveguides for the scale-up of TiO_2-based photocatalytic processes.

1.2. Ozonation

Ozone, a well-known oxidative agent, has a reduction potential of 2.08V. In general, ozone treatment leads to a quick and thorough contaminant removal. The literature is replete with successful applications of ozonation on a wide range of contaminant compounds. Although ozone reacts very efficiently with aromatics compounds, [Larson and Weber, 1994] its production requires a large amount of electrical energy along with a significant consumption of chemical reagent [Bauer and Fallmann, 1997]. Both the generation of O_3, and the production of photons with an artificial light source, require a significant energy input. Consequently, the total cost of an ozonation process is usually high.

Fortunately, ozone treatment requires a UVA radiation less energetic and, thus, less expensive, than the usual irradiation at 254 nm. Solar light, which contains a non-disregardable UVA fraction is adequate for the activation of the photochemical mechanism involved in ozone treatment. The use of solar light would thus be a lower cost alternative.

1.2.1. Brief description of the mechanism

The half-life of ozone in water depends on the pH of the solution. The ozone decomposition mechanism is initiated with OH^- ions present in the aqueous medium. During the complex chain reaction mechanism, several radical species are formed, which act as reaction promoters; the hydroxyl radical being one of these species. Hoigné et al. [Hoigné, 1985, Staehelin and Hoigné, 1985, Hoigné, 1988] have set the standard in the study of the ozonation process with their thorough research of the reaction mechanism of aqueous ozone. Their research on the decomposition of ozone in the presence of organic solutes showed that organic solutes could act as initiators, promoters, or terminators of the chain reactions responsible for ozone decomposition. Figure 1.6. depicts the reaction scheme as proposed by Hoigné and coworkers, and describes the participation of organic solutes in the chain reaction.

Ozone reacts with the organic load present in wastewater by two different mechanisms: (a) Direct reaction with the O_3 molecule. This process could inactivate the ozone molecule (reaction between ozone and the organic molecule M_1 in Figure 1.6). Sometimes, however, the ozonide ion ($O_3{\cdot}^-$) is formed being M_2 the organic molecule acting as initiator. (b) Indirect reaction with OH radicals produced after O_3 degradation from the fragmentation of the $HO_3\cdot$. The $HO_3\cdot$ specie is the product of ozonide ion protonation. The OH radicals react with substrate M_4. As a result of that reaction, organic radicals are formed, which can act as chain propagators. In this case, a reaction path, complementary with the process which takes place in pure water, appears.

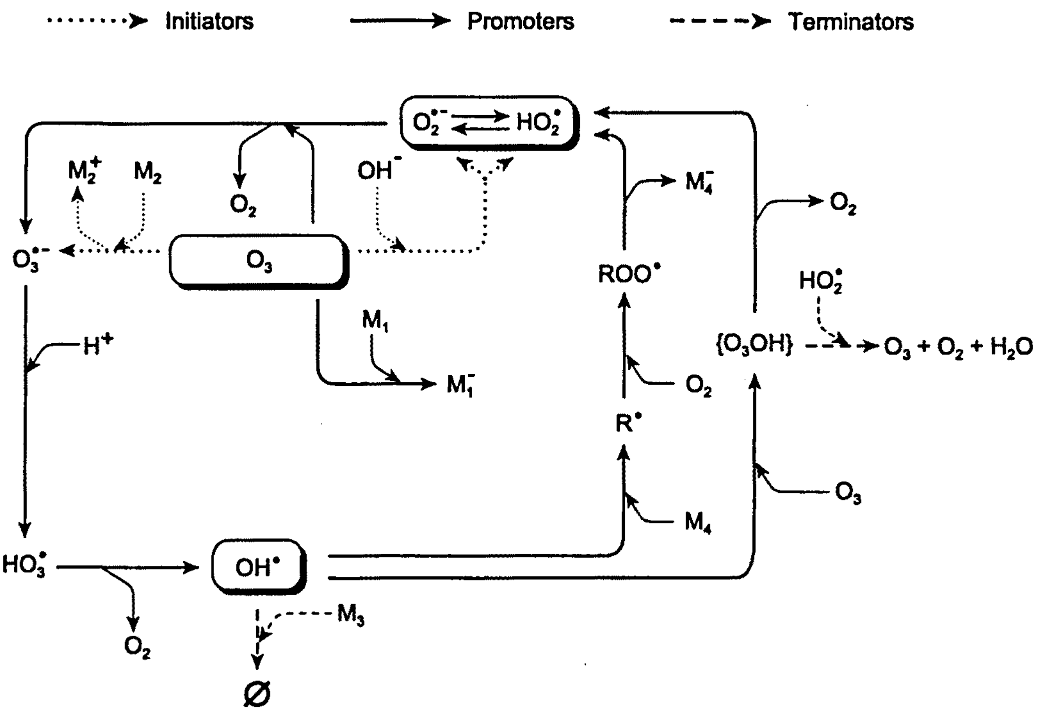


Figure 1.6. *Reactions of aqueous ozone, in the presence of solutes M, which react with ozone or which interact with OH radicals by scavenging and/or converting OH· into* $HO_2\cdot$.

Many common species encountered in natural waters and wastewaters may act as initiators (hydroxide ion, hydrogen peroxide, Fe^{2+}, dissolved organic matter), promoters (alcohols, aryl groups, dissolved organic matter), or chain terminators (alkyl groups, carbonate/bicarbonate, dissolved organic matter) for the free-radical chain reactions that convert ozone to the hydroxyl radical [Peyton, 1990].

The efficiency of the indirect reaction depends on the composition of the water, specifically, the rate at which ozone decomposes and the extent to which non-target solutes scavenge hydroxyl radicals.

The OH radical yield calculated by Hoigné et.al., is 0.65 molecules of OH· for every molecule of ozone decomposed. The decomposition of the O_3 molecule can be achieved in basic pH, under UV irradiation or with the use of additives like Fe(II), etc

Since the oxidative power of the OH radical (2.8 V vs. NHE) is higher than the oxidative power of ozone (2.08 V vs. NHE), O_3 is a more efficient oxidant when the experimental conditions favor its degradation to OH·.

1.2.2. Ozonation combined with: UVA, H_2O_2, Fe, Photocatalysis

Ozonation, combined with H_2O_2, UVA, or both, and even with heterogeneous photocatalytic processes, has been widely applied in wastewater treatments and consequently, it is a well-known process and has been extensively studied [Mao and Smith, 1995, Tanaka et al., 1996, Mansilla et al., 1997, Muller et al., 1998, Sánchez et al., 1998, Klare et al., 1999, Yeber et al., 1999a, Yeber et al., 1999b].

The mechanism of O_3 decomposition in presence of UVA light has been studied by Peyton et al. [Peyton et al., 1987]. Numerous investigators deal with the light-induced decomposition of ozone in aqueous systems [Peyton et al., 1987, Legrini et al., 1993]. O_3/UV is a complex oxidation process because OH radicals can be produced through different reaction pathways. Peyton and coworkers [Peyton and Glaze, 1988] developed a mass model for the photolytic ozonation (ozone/UV) treatment of organic compounds in water. The scheme used is shown in Figure 1.7. and its origins from the work of Staehelin and Hoigné [Staehelin and Hoigné, 1985] are obvious.

Initiation can occur with the reaction of ozone with OH^- or HO_2^-, or by peroxide photolysis. Peroxide is formed by ozone photolysis as well as from the reaction of ozone with many unsaturated organic compounds. Once hydroxyl radical generation begins, OH· reacts with organic substrates to produce an organic radical, which readily adds oxygen to form an organic peroxyl radical. Some peroxyl radicals formed in this way can rapidly eliminate superoxide which readily reacts with ozone to yield a hydroxyl radical. Peroxyl radicals may be considered the true propagators of thermal chain reactions. Moreover, it is clear that under these conditions the system has a chemical behavior of both O_3/H_2O_2 and H_2O_2/UV systems [Peyton and Glaze, 1988, Legrini et al., 1993, Andreozzi et al., 1999].

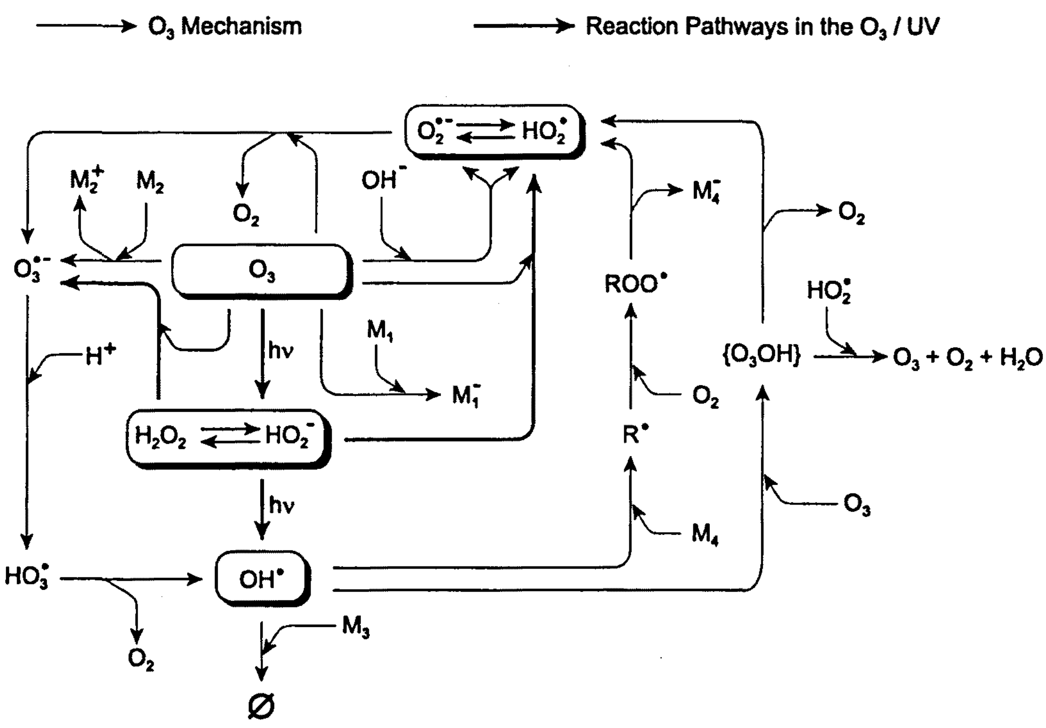


Figure 1.7. *Reaction pathways in the ozone/UV.*

As mentioned before, many current studies [Sánchez et al., submitted for publication] have found that sunlight produces a noticeable increase in the rate of ozone activation along with a complementary improvement in the rates of organic removal and reduced treatment costs. The simultaneous use of Fe (II) ions in solution, which are known to catalytically decompose ozone, and sunlight, have been recently studied [Sánchez et al., submitted for publication].

Transition metal ions, such as Fe(II), are capable of catalyzing the decomposition of ozone into hydroxyl radicals [Pérez et al., submitted for publication] following the mechanism proposed in the literature and described below:

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \qquad (1.1)$$

$$FeO^{2+} + H_2O \rightarrow Fe(OH)^{2+} + OH\cdot \qquad (1.2)$$

Fe(II) could also support the effect of ozonation by reacting with $HO_2\cdot$ [Kringstad and Lindstrom, 1984], one of the products of ozone decomposition, and when the pH is below 4.8, generating hydrogen peroxide as reaction 1.3 shows:

$$H^+ + HO_2\cdot + Fe^{2+} \rightarrow H_2O_2 + Fe^{3+} \qquad (1.3)$$

The presence of hydrogen peroxide and Fe (II) leads to the traditionally accepted Fenton and Fenton-like reactions:

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad k = 76.5\ l\cdot mol^{-1}\cdot s^{-1} \qquad (1.4)$

The application of light causes other reaction mechanisms, i.e., the photo-Fenton reaction, to produce additional OH radicals and leads to the recycling of Fe^{2+} as shown in the following reaction:

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH\cdot \qquad (1.5)$

This ozone mixture, with iron ions and irradiation, leads to a more complete treatment with ozone, Fenton, Fenton-like and Photo-Fenton reactions. The complex mechanism of these latter reactions will be more extensively explained in the following section.

Recently, the simultaneous application of both, the photocatalysis and the ozonation processes, and the sequential application of both techniques, has been described [Pérez et al., 1997, Sánchez et al., 1998, Torrades et al., 2001] and a synergy between the two processes has been detected. We analyzed the various combinations here for the degradation of organic matter in paper pulp bleaching effluents and for the identification of any cost reductions.

A mechanistic explanation of the synergetic effects detected when simultaneously applying ozonation and photocatalysis involves the formation of an ozonide radical anion ($O_3\cdot^-$) related to the conduction band electron scavenging ability of O_3. The following sequence of reactions have been proposed [Tanaka et al., 1996, Sánchez et al., 1998]:

$$O_3 + e^-(TiO_2\ cond.band) \rightarrow O_3^{\bullet -} \qquad (1.6)$$
$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \qquad (1.7)$$
$$HO_3^{\bullet} \rightarrow O_2 + OH^{\bullet} \qquad (1.8)$$

This pathway of OH· generation was highly effective at the low pH conditions we used for the experiments conducted for this study. Another possible reaction mechanism is shown in reaction 1.9. This reaction is undesirable and leads to a decrease of the compounds degradation. Reaction 1.9 can decrease the benefits of combining photocatalisis with ozone because ozone competes with the organic matter giving rise to a much less reactive radical species [Wittmann et al., 1996]:

$$OH^{\bullet} + O_3 \rightarrow O_2 + HO_2^{\bullet} \qquad (1.9)$$

1.2.3. Application to the decontamination of water

The use of ozone for the removal of pollutants has been widely investigated and is currently applied in those cases where classical treatments are inefficient or insufficient. Staehelin and Hoigné [Staehelin and Hoigné, 1985] were pioneers in investigating ozone decomposition in aqueous systems which contain model pollutants that are oxidized.

Ozone, in conjunction with UV light, is a tool used today in the decontamination of drinking water and for the treatment of strongly contaminated wastewaters. This technique, as a method of removing organic material, has undergone significant technical developments [Legrini et al., 1993]. The first studies on the ozonation of pulp and paper effluents were done in the 1970's [Bauman, 1974, Melnyk et al., 1977]. Since then, ozone has been extensively studied in the treatment of pulp effluents [Mao and Smith, 1995, Mansilla et al., 1997, Torrades et al., 2001] and is now a well recognized technique and an area of intensive research [Tanaka et al., 1996, Mansilla et al., 1997, Sánchez et al., 1998, Yeber et al., 1999a, Yeber et al., 1999b] because ozonizers are, in most cases, readily available in drinking water treatment facilities.

Even though ozonation is extensively used in water treatment and might be an alternative method used in the degradation of water contaminants, there is little accurate data on the ozonation of the various micropollutants. For instance, the literature related to ozonation as a method for destruction of chlorophenols is incomplete and sometimes contradictory [Trapido et al., 1997].

In this work, ozonation treatment will be applied to bleaching Kraft mill industry wastewaters. Bleaching effluents are an outstanding research subject because of some of the contaminants they might contain, [Balcioglu and Arslan, 1998], particularly chlorinated phenols and polyphenolic compounds. These compounds are difficult to eliminate by conventional wastewater treatment processes and are a source of environmental concern because of the risk they pose to aquatic environments [Earl and Reeve, 1990, Sierka and Bryant, 1993, Tsai et al., 1994]. Also, ozonation treatment is used in this study to decrease the contamination level of a synthetic 2,4-dichlorophenol sample.

1.2.3.1. Development and state of the art

Although ozone treatment is effective and reasonably quick, in the removal of contaminants and in color removal, the cost of the treatment is as much as ten times greater than other AOPs like Photocatalysis or Fenton and Photo-Fenton reactions [Pérez et al., submitted for publication]. Consequently, future research should be centered on the goal of reducing ozone demand without decreasing the efficiency of contaminant compounds removal.

There are still many questions relating to the mechanism involved in the production of radicals and the subsequent oxidation of organic substrates. In the literature, there are many conflicting reports on the efficiency of this oxidation method, which may be linked to mechanistic problems as well as to the difficulty of dissolving and photolyzing ozone with high efficiency. Other areas studied mainly concern secondary reactions of some of the oxidative intermediates that could be related to the particular experimental conditions of a water treatment project. These reactions could impair the efficiency of contaminant removal [Legrini et al., 1993].

On the other hand, a large number of papers have been published dealing with the oxidation of organic compounds in aqueous systems by ozone and UV radiation. Unfortunately, most of these studies omitted important parameters such as TOC values. The lack of this data makes comparison with pilot or semipilot plant data difficult.

Moreover, the poor solubility of ozone in water, and the consequent mass transfer limitations, represent a serious and specific problem in the technical development of this process. Several researchers have focused their studies in obtaining better results in mass transfer and in solving some of the remaining technical problems encountered in scale-up [Glaze et al., 1987].

1.3. Fenton, Fenton-like and Photo-Fenton reactions

The Fenton reagent, a mixture of hydrogen peroxide and an iron (II) salt, is another source of hydroxyl radicals (OH·) and has been in use for more than a century [Fenton, 1894]. Hence, the Fenton reagent and its combination with a light source have been used the last few years in the treatment of ground, surface, and wastewaters containing biocidal or nonbiodegradable organic compounds [Legrini et al., 1993].

Among AOPs, the Fenton reaction and especially the photochemically enhaced Fenton reaction are considered the most promising treatment for the remediation of highly contaminated waters [Bossmann et al., 1998]. A review of the literature [Eisenhauer, 1964, Barbeni et al., 1987, Pignatello, 1992, Goldstein et al., 1993, Ruppert et al., 1993, Kiwi et al., 1994, Safarzadeh-Amiri et al., 1996, Pignatello et al., 1999] reveals many successful applications, including a treatment of industrial wastewater on a large scale (500 L) with the use of the photochemically enhanced Fenton reaction [Oliveros et al., 1997].

The photochemically enhanced Fenton reaction can be driven using low energy photons, which are in the visible portion of the electromagnetic spectrum. The fact that the reaction can be driven by these low energy photons allows the process to operate using solar irradiation as a low cost alternative [Safarzadeh-Amiri et al., 1996, Bauer and Fallmann, 1997].

1.3.1. Brief description of the mechanisms

It is generally accepted the mechanism described by Haber and Weiss [Haber and Weiss, 1934], where the production of hydroxyl radicals (OH·) in the Fenton reaction, under dark conditions, is caused by the interaction of H_2O_2 with Fe(II) salts:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\bullet} + OH^{-} \qquad k = 76.5\ \mathrm{l{\cdot}mol^{-1}{\cdot}s^{-1}} \qquad (1.10)$$

Fe(III) can react with H_2O_2 in the so-called Fenton-like reactions:

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe-OOH^{2+} + H^{+} \qquad (1.11)$$

$$Fe-OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \qquad (1.12)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (1.13)$$

regenerating Fe(II) and supporting the Fenton process [Pignatello, 1992].

Dark reaction rates, after Fe(II) (in catalytic quantities) consumption, are controlled by the Fenton-like process between H_2O_2 and the Fe(III) formed in the first seconds of direct Fenton reaction. The Fenton-like process regenerates Fe(II) (see reactions 1.11-1.13) which, in presence of excess H_2O_2 is readily transformed giving Fe(III). Thus, an effective iron cycling takes place, with approximately constant Fe(III) concentration, traces of Fe(II) and a fairly constant oxidant intermediate production.

In the presence of light, the degradation rate of the organic pollutants by Fenton reaction would increase due to the photoreduction of Fe(III) to Fe(II) ions, a step that produces new OH· radicals and regenerates Fe(II) ions, that can further react with more H_2O_2 molecules. The photoreduction of Fe(III) follows the equation:

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \tag{1.14}$$

Photo-Fenton reactions can use photons with a wavelength of approximately 400 nm. The Fenton-like reactions have been shown to absorb photons up to 550 nm [Sun and Pignatello, 1993, Pignatello et al., 1999]. As mentioned previously, photo-Fenton reactions can be driven with low energy photons that belong to the visible part of the electromagnetic spectrum leading to a reduction in cost using solar radiation [Safarzadeh-Amiri et al., 1996].

With more than a century of research into the complex mechanism of the Fenton reaction, there is still intense controversy [Bossmann et al., 1998, Hislop and Bolton, 1999, Pignatello et al., 1999]. The most recent studies have presented further evidence suggesting more reactive intermediates and additional reactions which would complicate an already complex system.

Recent thermodynamic calculation have demonstrated that the classic mechanism proposed by Haber and Weiss (reaction 1.10) [Haber and Weiss, 1934] cannot take place because the formation of the intermediate $H_2O_2^{\cdot}$ is not favored [Goldstein et al., 1993]. In contrast, the formation of the hydrated iron(II)-H_2O_2 complex is thermodynamically favored. Figure 1.8 shows the reaction pathways proposed for Bossman et.al. [Bossmann et al., 1998] which may help our understanding of the mechanism of the Fenton reaction. The above mentioned Fenton-like reactions (reactions 1.11-1.13) are also included in the scheme. Simplified notations are used for the various iron complexes.

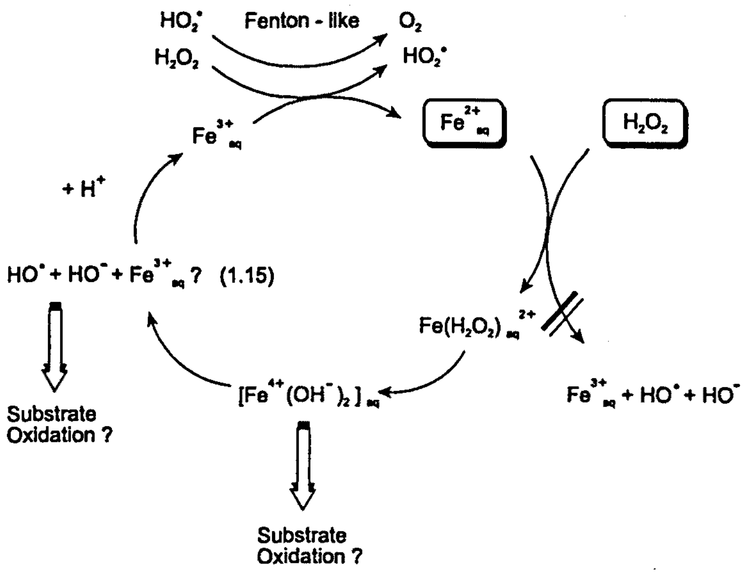


Figure 1.8. *Mechanistic presentation of possible reactions involved in the Fenton process without light irradiation.*

Until now, it was widely accepted that oxidations using the Fenton reaction, or the photochemically enhaced Fenton reaction, were initiated by free hydroxyl radicals [Pignatello, 1992, Safarzadeh-Amiri et al., 1996, Oliveros et al., 1997]. Recently the question whether OH production (reaction 1.15 in the Figure 1.8.) is too slow to compete with direct electron transfer between the substrate and an hydrated higher-valence iron species (most likely Fe^{4+}_{aq}) has raised [Bossmann et al., 1998].

Depending on the substrate, different reactive intermediates, other than the hydroxyl radical, have been proposed for the Fenton reaction. Additionally, hydroxyl radicals react with organic compounds through the reaction pathway summarized in Figure 1.9 :

1) by addition to double bonds possessing a sufficient electron density
2) by hydrogen abstraction from alkyl groups or hydroxyl groups (albeit with lower efficiency)
3) by electron transfer

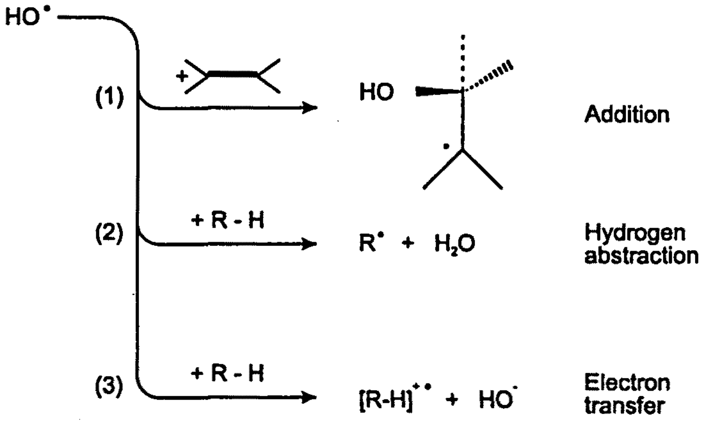


Figure 1.9. *Possible reactions pathways involving hydroxyl radicals.*

A second area of renewed interest concerns the mechanism of the photochemically enhanced recycling of $Fe^{2+}_{aq.}$ In studies concerning the photo-Fenton reaction (reaction 1.14), Pignatello et al. [Pignatello et al., 1999] obtained results that could possibly be explained by the formation of an alternative oxidant in place of, or more likely in addition to, OH·.

Previous researchers have demonstrated that the irradiation of Fe(III)+H_2O_2 (also called photo-Fenton reaction) enhances the rate of oxidant production through the involvement of high valence Fe intermediates responsible for the direct attack on organic matter [Bossmann et al., 1998, Pignatello et al., 1999]. Absorption of visible light by the complex formed between Fe(III) and H_2O_2 appears to cause the formation of such high valence Fe-based oxidants.

The use of light in the Fenton reaction leads to an improvement in reaction yields by:

a) Driving the photo-Fenton reaction by producing extra hydroxyl radicals and aiding in the recovery of Fe(II) needed in the Fenton reaction. The photo-Fenton reaction may involve direct photolysis of ferric ion (equation 1.14).
b) Causing the photolysis of Fe(III)-peroxy complexes or any of their potential intermediates [Pignatello et al., 1999]. The initial oxidation of organic pollutants generates oxygenated intermediates which can react with Fe^{3+} and form complexes. These complexes are also photoactive and regenerate ferrous ions and the oxidation of the organic pollutant on irradiation [Safarzadeh-Amiri et al., 1996].

$$Fe^{3+}(L^-) + h\nu \rightarrow Fe^{2+} + L^\bullet \quad (L = organic\ ligand) \tag{1.16}$$

In particular, this process has been demonstrated for the complexes formed between Fe(III) and the carboxylic acid moiety [Hislop and Bolton, 1999]. Large quantities of carboxylic acid are expected to be formed as degradation intermediates of the original organic substrate. In these cases, the complexes under irradiation also produce CO_2.

$$Fe^{3+}(LCO_2) + h\nu \rightarrow Fe^{2+} + CO_2 + L^{\bullet} \qquad (1.17)$$

The performance of such a complex reactive system is a function of pH, as expected from equations 1.10 to 1.14. However, each reaction has its optimal performance at distinct pH values: (a) Fenton reaction is nearly pH independent [Pignatello, 1992], (b) The Fenton-like reaction is optimal at pH 2.8 [Pignatello, 1992], and (c) The photo-Fenton reaction is clearly pH dependent [Pignatello et al., 1999]. For high pH values, low activity is detected due to the formation and precipitation of $Fe(OH)_3$, a process that hampers the development of photo-Fenton reaction. For pH values below the optimal, activity decrease because Fe (III) forms different species in solution and the quantum yield of light absorption by Fe(III) is directly dependent on the specific species responsible for the absorption.

The main Fe(III) species that exists at pH 2-3, $Fe(OH)^{2+}(H_2O)_5$, is the one with the largest light absorption coefficient and quantum yield for OH· production, along with Fe(II) regeneration, in the range 280-370 nm [Benkelberg and Warneck, 1995]. At a lower pH, $Fe^{3+}(H_2O)_6$ is more concentrated and the effectiveness of light absorption, regeneration of Fe(II) and, eventually, TOC degradation, is lower. At a higher pH, $Fe(OH)_2^{+}(H_2O)_4$ dominates, but the solution becomes unstable with $Fe(OH)_3$ precipitation [Benkelberg and Warneck, 1995]. On the other hand, the pH during the reactions evolves toward the optimal pH value (approximately 3).

Although the Fenton reaction has been widely studied, there is no agreement on the ratio of $[H_2O_2]$ to [Fe(II)] that leads to the best results. Different authors have reported different ratios of the two reactants. It has to be taking into account that large excesses of either H_2O_2 or Fe^{2+} could be detrimental since these species can react with some of the intermediates like OH· which is responsible for the direct oxidation of the organic load:

$$Fe(II) + OH^{\bullet} \rightarrow Fe(III) + OH^{-} \qquad (1.18)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (1.19)$$

Moreover, it has been reported that incorporation of a new oxidant into the complex reaction mechanism of the Fenton-photo-Fenton systems, such as molecular oxygen, can help the mineralization reactions [Utset et al., 2000]. O_2 consumption can be caused by three different processes [Pignatello, 1992]:

a) O_2 reacts with intermediate organoradicals [Kunai et al., 1986] to form photolabile Fe(III) complexes, thus promoting overall mineralization.
b) The reaction between O_2 and the intermediate organoradicals generates H_2O_2 by the "Dorfman" mechanism:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \xrightarrow{H_2O} ROH + HO_2^{\bullet} \qquad (1.20)$$

$$H^+ + HO_2^{\bullet} + e^- \rightarrow H_2O_2 \qquad (1.21)$$

with Fe(II) acting as electron source [Kunai et al., 1986].
c) the intermediate hydroperoxides and organoperoxides serve to oxidize Fe(II) to Fe(III)

$$RO_2^{\bullet} + Fe^{2+} \rightarrow RO_2^- + Fe^{3+} \qquad (1.22)$$

which is photoactive. In any case, direct oxidation of Fe^{2+} by O_2 (autoxidation) is too slow in acidic solution to be important [Pignatello, 1992].

1.3.2. Application to the decontamination of water

Over the last 30 years, attention has turned to the possible application of the Fenton reaction and the photoassisted reactions, in oxidative treatment of contaminated water. Since 1975, when Walling [Walling, 1975] presented further evidence of the involvement of hydroxyl radicals in the oxidation of various organic compounds by Fenton reagent, many contaminants have been studied using these reagents. The reactions produce powerful oxidizers capable of degrading highly contaminated wastewater [Bauer and Fallmann, 1997, Rodríguez et al., 1999a], many organic compounds and often extensive mineralization of target pollutants [Pignatello, 1992, Ruppert et al., 1993, Kiwi et al., 1994, Benkelberg and Warneck, 1995, Ansari et al., 1996, Li, 1996, Safarzadeh-Amiri et al., 1996, Tang and Huang, 1996, Chen and Pignatello, 1997, Augusti et al., 1998, Bossmann et al., 1998, Gallard et al., 1998, Hislop and Bolton, 1999].

In applications of the Fenton system to wastewaters, Lin and Peng [Lin and Peng, 1995] found that Fenton's treatment was economically competitive with conventional technologies for the removal of COD and color from textile wastewaters.

The use of Fenton reagent as an oxidant for wastewater treatment is attractive due to the fact that:

- Iron is a highly abundant and non-toxic element. Iron is the second most abundant metal and the fourth most abundant element found in the earth's crust where it is found as ferrous or ferric ions [Safarzadeh-Amiri et al., 1996].
- Hydrogen peroxide is easy to handle and is environmentally benign.
- Photo-Fenton reaction could be performed under solar irradiation which is a very promising, low-cost treatment [Safarzadeh-Amiri et al., 1996, Bauer and Fallmann, 1997].

1.3.2.1. Development and state of the art

The Fenton reagent has been studied since 1894 when H.J.H. Fenton reported that ferrous ions strongly promote the oxidation of malic acid by hydrogen peroxide [Fenton, 1894]. Since then, the importance and ubiquity of hydroxyl radicals have become increasingly apparent and they have been the major oxidants used in the photochemistry of water. Consequently, hydroxyl radicals are intensely studied.

Currently, the controversy concerning their role in Fenton and Photo-Fenton processes has lead to renewed vigor in understanding their roles [Walling, 1975, Logager et al., 1992, Pignatello, 1992, Goldstein et al., 1993, Sun and Pignatello, 1993, Benkelberg and Warneck, 1995, Chen and Pignatello, 1997, Bossmann et al., 1998, Pignatello et al., 1999].

As mentioned above, understanding the mechanism of this complex system and the reactions pathways which take place when a Fenton reagent is used under light irradiation, are areas where researchers are today focusing their work. Another important area of research is the question of the ratio [H_2O_2] to [Fe(II)] which leads to the optimal result. Different authors have reported different ratios of the two reactants. For instance, Eisenhauer [Eisenhauer, 1964] used 3:1:1 ratios (H_2O_2/Fe(II)/Phenol) for an efficient oxidation of phenol, while Sedlak et al. [Sedlak and Andren, 1991] used a 1:4:20 ratio (H_2O_2/Fe(II)/Chlorobiphenyls) in their oxidation experiments. Molar ratios of H_2O_2 as high as 100:1:16 (H_2O_2/Fe(II)/Clorophenols) were used by Barbeni et al. [Barbeni et al., 1987]. Tang et al. [Tang and Huang, 1996] reported an 11:1 ratio of H_2O_2/Fe(II) for 2,4-Dichlorophenol degradation. Ruppert et al. [Ruppert et al., 1993] used a 40:1:4 ratio of H_2O_2/Fe(II)/4-Chlorophenol in their studies. Bauer et al. [Bauer and Hofstadler, 1994] used 400:1 molar ratios (H_2O_2/Fe(II)) when treating real wastewaters. Chamarro et al. [Chamarro et al., 2001] used, in their experiments, (H_2O_2/Fe(II)) ratios from 5000:1 to 50:1 ppm, and the results presented so far in our research were obtained with 100:1:50 ppm ratios (H_2O_2 / Fe(II) / Wastewater). It seems difficult to reach an agreement in this matter when researchers such as Bossman et.al. [Bossmann et al., 1998] claim that depending on the substrate, reactive intermediates other than the traditionally accepted hydroxyl radical might be involved. Consequently, when the oxidative species, as well as the reaction pathways, are dependent upon the substrate, it may not be possible to find a universal ratio $[H_2O_2]/[Fe(II)]$ for all type of substrates.

A third topic of current investigation concerns the application of either the Fenton reaction or/and the photochemically enhanced reactions to the decontamination of wastewaters as mentioned in the Section 1.3.2.

Recent studies, which have concluded that photochemically Fenton-enhanced reactions can occur with solar irradiation [Safarzadeh-Amiri et al., 1996, Bauer and Fallmann, 1997], have opened a new research topic, specially interesting for the large scale application of this process.

References

Aguado, M. A. and Anderson, M. A., *Sol. Energ. Mat. Sol. C.*, 1993, **28,** 345.

Andreozzi, R., Caprio, V., Insola, A. and Marotta, R., *Catal. Today*, 1999, **53,** 51.

Ansari, A., Peral, J., Domènech, X., Rodríguez-Clemente, R. and Casado, J., *J. Mol. Catal. A-Chem.*, 1996, **112,** 269.

Augusti, R., Dias, A. O., Rocha, L. L. and Lago, R. M., *J. Phys. Chem. A*, 1998, **102,** 10723.

Balcioglu, I. A. and Arslan, I., *Environ. Pollut.*, 1998, **103,** 261.

Barbeni, M., Minero, C., Pelizzetti, E., Borgarello, E. and Serpone, N., *Chemosphere*, 1987, **6,** 2225.

Bauer, R. and Fallmann, H., *Res. Chem. Intermediat.*, 1997, **23,** 341.

Bauer, R. and Hofstadler, K., *Environ. Sci. Technol.*, 1994, **28,** 670.

Bauman, H. D., *Tappi J.*, 1974, **57,** 116.

Benkelberg, H.-J. and Warneck, P., *J. Phys. Chem. A*, 1995, **99,** 5214.

Blake, D. M., *Bibliography of work on the photocatalytic removal of hazardous compounds from water and air, Update number 3, to January, 1999* ,1999, National Technical Information Service., U.S. National Renewable Energy Laboratory.

Born, M. and Wolf, E., *Principles of Optics*, 1980, Pergamon Press, New York.

Bossmann, S. H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E. P., Payawan, L., Straub, M., Wörner, M. and Braun, A. M., *J. Phys. Chem. A*, 1998, **102,** 5542.

Carey, J. H., Lawrence, J. and Tosine, H. M., *B. Environ. Contam. Tox.*, 1976, **16,** 697.

Chamarro, E., Marco, A. and Esplugas, S., *Water Res.*, 2001, **35,** 1995.

Chen, D. and Ray, A. K., *Appl. Catal. B-Environ.*, 1999, **23,** 143.

Chen, R. and Pignatello, J. J., *Environ. Sci. Technol.*, 1997, **31,** 2399.

Earl, P. F. and Reeve, D. W., *Tappi J.*, 1990, **73,** 179.

Eisenhauer, H. R., *J. WPCF*, 1964, **36,** 1116.

EPA, *Notice of the second priority list of hazardous substances commonly found sites* ,1988, Environmental Protection Agency.

Fenton, H. J. H., *J. Chem. Soc.*, 1894, **65,** 899.

Fujishima, A. and Honda , K., *Nature*, 1972, **37,** 238.

Gallard, H., De Laat, J. and Legube, B., *New J. Chem.*, 1998, 263.

Glaze, W. H., Kang, J.-W. and Chapin, D. H., *Ozone-Sci. Eng.*, 1987, **9,** 335.

Goldstein, S., Czapski, G. and Meyerstein, D., *Free Radical Bio. Med.*, 1993, **15,** 435.

Haber, F. and Weiss, J. J., *Proc. R. Soc. London, Ser. A*, 1934, **147,** 332.

Harrick, N. J., *Internal Reflection Spectroscopy*, 1967, (Ed, Corporation, H. S.) New York, pp. 13.

Hislop, K. A. and Bolton, J. R., *Environ. Sci. Technol.*, 1999, **33,** 3119.

Hoffmann, M. R., Martin, S. T., Choi, W. and Bahnemann, D. W., *Chem. Rev.*, 1995, **95,** 69.

Hofstadler, K., Bauer, R., Novalic, S. and Heisler, G., *Environ. Sci. Technol.*, 1994, **28,** 670.

Hoigné, J., *Sci. Total Environ.*, 1985, **47,** 169.

Hoigné, J., *The Chemistry of Ozone in Water*, 1988, (Ed, Stucki, S.) Plenum Publishing Corp., New York.

Hostachy, J.-C., Lenon, G., Pisicchio, J.-L., Coste, C. and Legay, C., *Water Sci. Technol.*, 1997, **35,** 261.

Kahmark, K. A. and Unwin, J. P., *Water Environ. Res.*, 1998, **70,** 667.

Kiwi, J., Pulgarin, C. and Peringer, P., *Appl. Catal. B-Environ.*, 1994, **3,** 335.

Klare, M., Waldner, G., Bauer, R., Jacobs, H. and Broekaert, J. A. C., *Chemosphere*, 1999, **38,** 2013.

Kringstad, K. P. and Lindstrom, K., *Environ. Sci. Technol.*, 1984, **18,** 236A.

Kunai, A., Hata, S., Ito, S. and Sasaki, K., *J. Am. Chem. Soc.*, 1986, **108,** 6012.

Larson, R. and Weber, E., *Reaction mechanism in environmental organic chemistry* , 1994, Lewis Publishers.

Legrini, O., Oliveros, E. and Braun, A. M., *Chem. Rev.*, 1993, **93,** 671.

Li, Y.-S., *Arch. Environ. Con. Tox.*, 1996, **31,** 557.

Lin, S. H. and Peng, C. F., *Environ. Technol.*, 1995, **16,** 693.

Linsebigler, A. L., Guangquan, L. and Yates, J. T., *Chem. Rev.*, 1995, **1995,** 735.

Logager, T., Holcman, J., Sehested, K. and Pedersen, T., *Inorg. Chem.*, 1992, **31,** 3523.

Malato, S., *Solar photocatalytic decomposition of pentachlorophenol dissolved in water* ,Thesis 1999, Plataforma Solar de Almería, CIEMAT, Tabernas.

Mansilla, H. D., Yeber, M. C., Freer, J., Rodríguez, J. and Baeza, J., *Water Sci. Technol.*, 1997, **35,** 273.

Mao, H. and Smith, D. W., *Ozone-Sci. Eng.*, 1995, **17,** 205.

Marinangeli, R. E. and Ollis, D. F., *AIChE J.*, 1977, **23,** 1000.

Martinez, M., Campos, A., Garcia, A. and Gonzalez, C. L., *B. Environ. Contam. Tox.*, 1999, **62,** 0272.

Matsumoto, M. R., Jensen, J. N., Reed, B. E. and Lin, W., *Water Environ. Res.*, 1996, **68,** 431.

Melnyk, P. B., Judkins, D. and Netzer, A., *Tappi J.*, 1977, **60,** 97.

Miller, L., *Photocatalytic Oxidation of Organic Compounds via Waveguide-Supported Titanium Dioxide Films* ,1998, Water Chemistry Program, University of Wisconsin, Madison.

Miller, L., Tejedor-Tejedor, M. I. and Anderson, M. A., *Environ. Sci. Technol.*, 1999, **33,** 2070.

Muller, T. S., Sun, Z., Kumar, G., Itoh, K. and Murabayashi, M., *Chemosphere*, 1998, **36,** 2043.

Oliveros, E., Legrini, O., Hohl, M., Müller, T. and Braun, A. M., *Water Sci. Technol.*, 1997, **35,** 223.

Ollis, D. F., Pelizzetti, E. and Serpone, N., *Environ. Sci. Technol.*, 1991, **25,** 1523.

Pacheco, J., Prairie, M., Evans, L. and Yellowhorse, L., In *25th Intern. Society Energy Conversion engineering Conference*, 1990, Reno, Nevada.

Peill, N. J. and Hoffmann, M. R., *Environ. Sci. Technol.*, 1995, **29,** 2974.

Pérez, M., Torrades, F., Domènech, X. and Peral, J., *Quim. Anal.*, 1997, **16,** 211.

Pérez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J. and Mansilla, H. D., *Appl. Catal. B-Environ.*, 2001, **33/2,** 89.

Pérez, M., Torrades, F., Domènech, X. and Peral, J., Submitted for publication in *J. Chem. Technol. Biot.*

Peyton, G. R., *Oxidative treatment methods for removal of organic compounds from drinking water supplies*, 1990, (Ed, Ram, N. M.) Lewis Publishers, Chelsea, pp. 313.

Peyton, G. R. and Glaze, W. H., *Environ. Sci. Technol.*, 1988, **22,** 761.

Peyton, G. R., Smith, M. A. and Peyton, B. M., *Photolytic ozonation for protection and rehabilitation of ground water resources; A mechanistic study.*, 1987, University of Illinois, Water Resources Center, 206.

Pignatello, J. J., *Environ. Sci. Technol.*, 1992, **26,** 944.

Pignatello, J. J., Liu, D. and Huston, P., *Environ. Sci. Technol.*, 1999, **33,** 1832.

Rodríguez, J., Contreras, D., Parra, C., Freer, J., Baeza, J. and Durán, N., *Water Sci. Technol.*, 1999a, **40,** 351.

Rodríguez, J., Mutis, A., Yeber, M. C., Freer, J., Baeza, J. and Mansilla, H. D., *Water Sci. Technol.*, 1999b, **40,** 267.

Ruppert, G., Bauer, R. and Heisler, G., *J. Photoch. Photobio. A-Chem.*, 1993, **73,** 75.

Safarzadeh-Amiri, A., Bolton, J. R. and Cater, S. R., *J. Adv. Oxid. Technol.*, 1996, **1**, 18.

Sánchez, L., Peral, J. and Domènech, X., *Appl. Catal. B-Environ.*, 1998, **19**, 59.

Sánchez, L., Domènech, X., Peral, J. and Casado, J., Submitted for publication in *Environ. Sci. Technol.*

Saunamäki, R. and Sorvari, J., *Nord. Pulp Pap. Res. J.*, 1992, **3**, 113.

Sedlak, D. L. and Andren, A. W., *Environ. Sci. Technol.*, 1991, **25**, 777.

Serpone, N., *Sol. Energ. Mat. Sol. C.*, 1995, **98**, 369.

Serpone, N., *J. Photoch. Photobio. A-Chem.*, 1997, **104**, 1.

Sierka, R. A. and Bryant, C. W., *Biological Treatment of Kraft Wastewater Following Pretreatment of Extraction Waste Stream by Titanium Dioxide and Membranes*, 1993, (Eds, D.F.Ollis and H.Al-Ekabi) Elsevier Science Publishers B.V., Tucson, pp. 275.

Staehelin, J. and Hoigné, J., *Environ. Sci. Technol.*, 1985, **19**, 1206.

Sun, Y. and Pignatello, J. J., *Environ. Sci. Technol.*, 1993, **27**, 304.

Tanaka, K., Abe, K. and Hisanaga, T., *J. Photoch. Photobio. A-Chem.*, 1996, **101**, 85.

Tang, W. Z. and Huang, C. P., *Environ. Technol.*, 1996, **17**, 1371.

Terzian, R., Serpone, N., Draper, R. B., Fox, M. A. and Pelizzetti, E., *Langmuir*, 1991, **7**, 3081.

Torrades, F., Peral, J., Pérez, M., Domènech, X., García Hortal, J. A. and Riva, M. C., *Tappi J.*, 2001, **84**, 63.

Trapido, M., Veressinina, Y., Hentunen, J. K. and Hirvonen, A., *Environ. Technol.*, 1997, **18**, 325.

Tsai, T. Y., Renard, J. J. and Phillips, R. B., *Tappi J.*, 1994, **77**, 149.

Utset, B., Garcia, J., Casado, J., Domènech, X. and Peral, J., *Chemosphere*, 2000, **41**, 1187.

Walling, C., *Accounts Chem. Res.*, 1975, **8**, 125.

Wittmann, G., Ilisz, I. and Dombi, A., In *Regional Conference on Ozone, Ultraviolet Light, Advanced Oxidation Processes in Water Treatment*, 1996, International Ozone Association, pp. 441.

Xu, Q. and Anderson, M. A., *J. Mater. Res.*, 1991, **6**, 1073.

Yeber, M. C., Rodríguez, J., Baeza, J., Freer, J., Zaror, C., Durán, N. and Mansilla, H. D., *Water Sci. Technol.*, 1999a, **40**, 337.

Yeber, M. C., Rodríguez, J., Freer, J., Baeza, J., Durán, N. and Mansilla, H. D., *Chemosphere*, 1999b, **39**, 1679.

Zeltner, W. A., Fu, X. and Anderson, M. A., In *Proceedings of the 88th A&WMA Annual Meeting*, 1995, Vol. 4B Pittsburgh, PA.

2. LIGHT SOURCES

The constant research into AOPs has demonstrated that most of these processes are most effective in the presence of a light source [Peyton et al., 1987, Curcó et al., 1996, Safarzadeh-Amiri et al., 1996, Bauer and Fallmann, 1997, Mansilla et al., 1997, Pérez et al., 1997, Serpone, 1997, Chen and Ray, 1999, Hislop and Bolton, 1999, Malato, 1999]. However, the requirement of a light source leads to an important economic problem because the electrical demand. In consequence, the total cost of this process is clearly increased [Bauer and Fallmann, 1997].

It is important to note that not all photoassisted processes require light of the same wavelength and energy. While direct O_3 or H_2O_2 photolysis requires photons of a short wavelength (<310 nm), TiO_2 photocatalysis can take advantage of photons of wavelengths up to 380 nm [Hoffmann et al., 1995]. Photo-Fenton reactions can use photons with wavelength close to 400 nm. The mixtures Fe(III) + H_2O_2 (known as Fenton-like reactions [Pignatello, 1992]) have shown photon absorptions up to 550 nm [Pignatello et al., 1999]. Consequently, because photo-Fenton reaction can be driven with photons of low energy (photons that belong to the visible part of the spectrum), the photo-Fenton processes are a potential low cost AOP that can run under solar irradiation [Safarzadeh-Amiri et al., 1996].

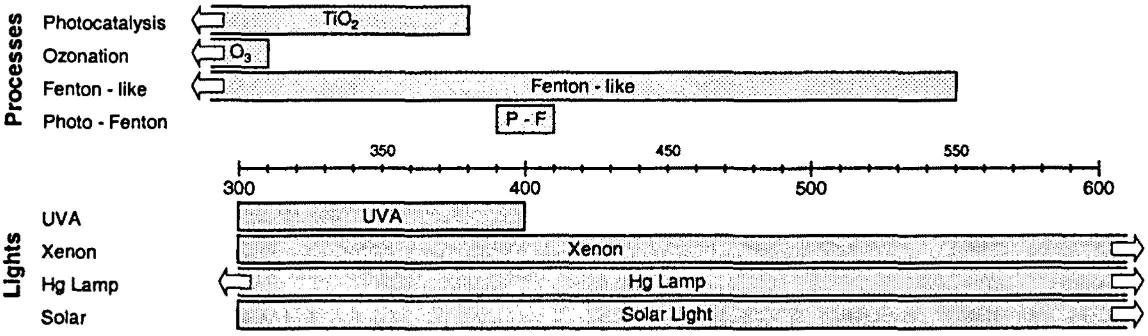


Figure 2.1. *Wavelength intervals of different light sources used in the current research and the more appropriated intervals for the AOP studied.*

Figure 2.1 shows that it is a small portion of the solar electromagnetic spectrum that is used in the photocatalytic process with TiO_2. But, because solar energy is so cheap and abundant, even under these limitations, it is still advantageous to use it [Wilkins, 1994].

One of the goals of this research is to find the most economically effective AOP for the wastewater studied. With this aim in mind, the use of solar energy may help to reduce the cost of the process without reducing its efficiency. Figure 2.1 is a depiction of the wavelength interval of different light sources used in the current research and the wavelength irradiation appropriated for the AOP studied. However, cataloging solar UV radiation values is a rather daunting task due to the variability from one location to another during the day and between seasons. Ultimately, it will be necessary to know this data at each location and in real time. With the aim to obtain comparative results from our studies, part of the research was carried out under artificial light sources:

- *UVA light:* a 6 W Philips black-light fluorescent lamp.
- *Xenon lamp:* a 250 W xenon lamp (Applied Photophysics).
- *High pressure mercury light:* a Philips 125 W high-pressure mercury lamp, ($\lambda > 254$ nm, energy flux 12 $mW \cdot cm^{-2}$). Total UV incident radiation flux was determined by potassium ferrioxalate actinometry ($5.9 \cdot 10^{-5}$ $Einstein \cdot L^{-1} \cdot s^{-1}$) [Murov, 1973]. The real output of the lamp in the 250-300 nm region was determined by actinometry using a Pyrex filter and it was 37 % of the total emission.

UVA and Xenon light were the most used in the present work. Table 2.1 summarizes the characteristic parameters of these two artificial light sources.

Table 2.1. *Characteristic parameters of UVA and Xenon lights.*

	UVA light	*Xenon lamp*
Wavelength interval (nm)	300-420	$\lambda > 300$
Intensity of the incident light ($Einstein \cdot s^{-1}$)	$1.38 \cdot 10^{-9}$	$7.55 \cdot 10^{-8}$
Energy flux (W)	$9 \cdot 10^{-4}$	$3.92 \cdot 10^{-2}$
Energy per surface ($W \cdot cm^{-2}$)*	$3.83 \cdot 10^{-5}$	$1.653 \cdot 10^{-3}$

*energy per surface of the wavelength up to 500 nm

In Annex 1 is summarized the irradiation spectrum of both artificial light sources and the calculation performed with the values obtained from the uranyl actiometer [Braun et al., 1991] to reach the data shown in the above-mentioned table.

Solar radiation

Yearly, the energy that the earth receives from the sun is $1.7 \cdot 10^{14}$ kW, or equivalently $1.5 \cdot 10^{18}$ kWh. This amount of energy is approximately 28000 times the total yearly energy usage by the world's six billion plus human beings. The radiation found outside of earth's atmosphere has a wavelength between 0.2 μm and 50 μm, which is reduced to a wavelength interval between 0.3 μm and 3 μm by the time it reaches the earth's surface, due to adsorption by different atmospheric components (ozone, oxygen, carbon dioxide, aerosols, steam, clouds).

The global solar radiation is divided into:
- direct radiation which reaches the surface without being absorbed or scattered.
- diffuse radiation which reaches the surface after being dispersed.

In general, the direct component of global radiation is at a minimum on cloudy days while the diffuse component is at a maximum. Likewise, on clear days, the opposite situation occurs.

The following figure shows the standard spectrum [ASTM, 1987] of direct solar radiation at ground level on a clear day and it reflects the substances which absorb part of the radiation and their absorption wavelength [Iqbal, 1983]. The dotted line corresponds to extraterrestrial radiation at the same interval of wavelength.

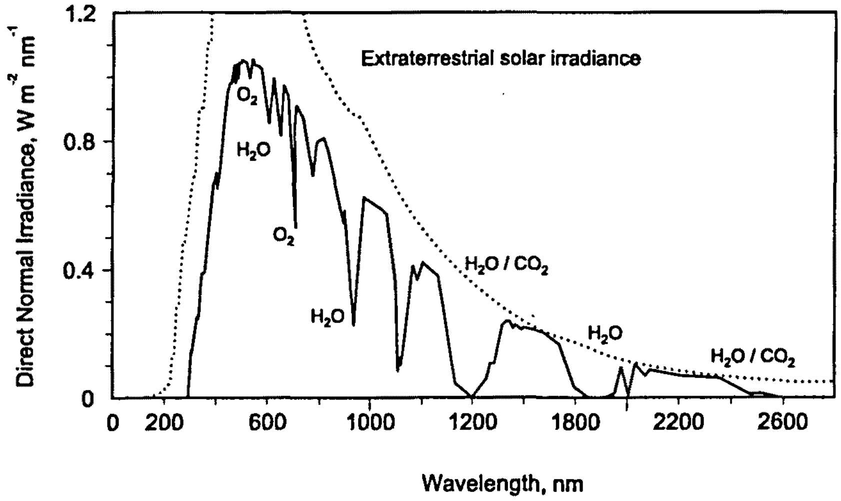


Figure 2.2. *Effect of atmospheric components on Solar spectrum.*

Measurements carried out have demonstrated that the UV part of the solar spectrum is between 3.5 and 8% of the total [Riordan et al., 1990]. Measurement of the energy input at wavelengths below 400 nm entering our reactor gave a value of $5 \cdot 10^{-3}$ W·cm^{-2}. The energy per surface area calculated for the artificial light sources consider a wavelength up to 500 nm. Thus, solar light energy per surface area for $\lambda<500$ nm should presumably give a larger photon input than our calculated value.

References

ASTM, 1987, **E891-87**.

Bauer, R. and Fallmann, H., *Res. Chem. Intermediat.*, 1997, **23**, 341.

Braun, A. M., Maurette, M.-T. and Oliveros , E., *Photochemical Technology*, 1991, (Ed, Wiley&Sons, J.) , pp. 75.

Curcó, D., Malato, S., Blanco, J. and Giménez, J., *Sol. Energ. Mat. Sol. C.*, 1996, **44**, 199.

Chen, D. and Ray, A. K., *Appl. Catal. B-Environ.*, 1999, **23**, 143.

Hislop, K. A. and Bolton, J. R., *Environ. Sci. Technol.*, 1999, **33**, 3119.

Hoffmann, M. R., Martin, S. T., Choi, W. and Bahnemann, D. W., *Chem. Rev.*, 1995, **95**, 69.

Iqbal, M., *An introduction to Solar radiation* , 1983, Academic Press, Canada.

Malato, S., *Solar photocatalytic decomposition of pentachlorophenol dissolved in water* ,Thesis 1999, Plataforma solar de Almería, CIEMAT, Tabernas.

Mansilla, H. D., Yeber, M. C., Freer, J., Rodríguez, J. and Baeza, J., *Water Sci. Technol.*, 1997, **35**, 273.

Murov, S. V., *Handbook of Photochemistry* , 1973, Marcel Dekker, New York.

Pérez, M., Torrades, F., García Hortal, J. A., Domènech, X. and Peral, J., *J. Photoch. Photobio. A-Chem.*, 1997, **109**, 281.

Peyton, G. R., Smith, M. A. and Peyton, B. M., *Photolytic ozonation for protection and rehabilitation of ground water resources; A mechanistic study.*, 1987, University of Illinois, Water Resources Center, 206.

Pignatello, J. J., *Environ. Sci. Technol.*, 1992, **26**, 944.

Pignatello, J. J., Liu, D. and Huston, P., *Environ. Sci. Technol.*, 1999, **33**, 1832.

Riordan, C. J., Hulstrom, R. L. and Myers, D. R., *Influences of atmospheric conditions and air mass on the ratio of ultraviolet to total solar radiation* ,1990, Solar Energy Research Institute (SERI), TP-215-3895.

Safarzadeh-Amiri, A., Bolton, J. R. and Cater, S. R., *J. Adv. Oxid. Technol.*, 1996, **1,** 18.

Serpone, N., *J. Photoch. Photobio. A-Chem.*, 1997, **104,** 1.

Wilkins, F. W., *Chem. Eng. Process*, 1994, 41.

3. ENVIRONMENTAL CONTAMINATION PROBLEMS

In every portion of the globe, toxic or hazardous chemicals are being found more and more in effluent streams. Added to the traditional contamination problems is the realization that permanent damage is happening to the environment because of compounds which are chemically stable. These types of chemicals lead to bioaccumulation and their permanence in an environmental ecosystem last for a long time [Rand, 1995].

Using the criteria of fresh water consumption and the volume of wastewater discharged, two industries, the paper pulp and textile industries, are considered especially polluting among all industrial sectors [Balcioglu and Arslan, 1998, Vandevivere et al., 1998].

3.1. Paper industry wastewaters

The Kraft process is normally used to obtain cellulosic pulps. The pulps from the Kraft process contain a variable percentage around 10 % of the original lignin, depending on their final use; and are colored, due to the presence of different conjugated structures such as quinines, chalcones and stilbenes [Bajpai and Bajpai, 1994] which absorb visible light.

The pulp obtained from the Kraft process quite often follows a bleaching sequence. Currently, the most relevant environmental problem in the cellulose pulp industry is related to the effluents discharged from the pulp bleaching process [Rodríguez et al., 1998]. In this process, the pulp is bleached in sequences of successive stages, where the most relevant stages are the chlorine/chlorine dioxide stage followed by an alkaline extraction. The effluents contain low molecular weight compounds with demonstrated toxic effects and high molecular weight chlorinated lignins with strong dark color which can be degraded in the environment giving rise more harmful compounds [Eriksson et al., 1985].

Most recently, the pulp and paper industry is facing more stringent regulations on the quality of effluent discharges allowed to enter into the receiving waters, and most especially from the bleach pulp mills. As the result of this increased surveillance, new bleaching sequences have appeared that are different from the more traditional bleaching sequences. It is possible to group them in two main categories:

- ECF (Elemental Chlorine Free): Elemental chlorine is totally replaced by other chlorine derivates, with chlorine dioxide being the favored derivate.

- TCF (Total Chlorine Free): Neither elemental chlorine, nor any other chlorine product, is used throughout the bleaching sequence.

ECF bleaching sequences are the more preferred and implemented today throughout the industry [Pryke and Mckenzie, 1996], due to:

- The quality of the bleaching pulp obtained is quite similar to the one produced in the conventional pulp bleaching process.
- The ECF process effluents contain less chlorine compounds.
- The organic chlorine compounds formed are less toxic than those in the conventional bleaching effluents.
- The investment required to transform a conventional bleaching process into an ECF is smaller than the investment required to transform that same process into a TCF process.

Although TCF sequences are implemented in several pulp mills all over the world, still is required additional research. In some cases, the bleaching pulp obtained is still far from the commercial quality demanded and it would necessarily be required a large investment to implement this new technology throughout the industry. Other recent studies [Ebeling and Meloni, 1997] show that there is no great differences in the ecological impacts of well treated modern ECF and TCF mill effluents.

Unfortunately, the toxic nature of pulp effluents because of the chlorinated organic substances released by the Kraft bleaching process led to the development of adaptive strategies to comply with the environmental regulations. The Kraft mill industry worldwide is preparing to meet the proposed regulations via two approaches [Sierka and Bryant, 1993, Hostachy et al., 1997]:

- In-plant process modifications such as extended cooking, oxygen delignification and substitution of chlorine dioxide for chlorine in the bleaching stage.
- The treatment of wastewaters by physical-chemical processing, AOPs (Advanced Oxidation Processes)

The cost of internal measures, which rises exponentially with the severity of the regulations, is becoming prohibitive and the external treatment of the wastewaters must be considered [Hostachy et al., 1997].

3.2. Textile industry wastewaters

Much like the pulp industry, the textile industry consume considerable amounts of water in their manufacturing processes and hence produce huge amounts of wastewaters. Textile effluents are also characterized by their low biochemical oxygen demand and high color content [Correia et al., 1994]. Additionally, textile effluents are highly variable in composition depending on which wet processes were employed [EPA, 1978], causing many problems in treatment with conventional methods [Balcioglu and Arslan, 1998, Vandevivere et al., 1998].

The main sources of wastewaters generated by the textile wet-processing industry originate from the washing (or scouring) and bleaching of natural fibers as well as from the dyeing and finishing steps. Contaminants from earlier, raw material preparation processes will ultimately end up in the textile effluent. Potentially problematic compounds are biocides which are used in the growing or storage of cotton or wool (e.g. chlorinated aromatics), finishing products (e.g. synthetic resins), surfactants (e.g. alkyl phenol ethoxylates), dye solvents, reducing agents, heavy metals, sulphate salts, oxidizing agents and bleaching agents (e.g. hypochlorite, hydrogen peroxide) [Delée et al., 1998].

In spite of all the complexity of textile pollutants, it should be said that the chemical composition of textile mill effluent is changing very rapidly as a result of shifting consumer preferences. The result is the emergence of US and European ecolabels which include considerations of emissions to the environment and chemicals used during the manufacture of textile products [Reid, 1996]. In Table 3.1 are summarized the major pollutant types identified in textile wastewaters [Delée et al., 1998].

The table shows that the main pollutants in bleaching effluents are pH and salt effects, toxicants and refractory organics.

Numerous large-scale studies have been conducted to assess the toxicity of textile effluents on aquatic life. Costan et. al. [Costan et al., 1993] found that textile effluents ranked second in toxicity, among eight industrial sectors represented, by using a series of bioassays assessing the acute, sublethal and chronic toxicity at various trophic levels.

Table 3.1. *Major pollutant types in textile wastewaters and their origin.*

Pollutants	*Major chemical types*	*Main processes of origin*
Organic load	Starches, enzymes, fats, greases, surfactants, waxes	Desizing Scouring Washing
	Acetic acid	Dyeing
Color	Dyes, scoured wool impurities	Dyeing Scouring
Nutrients (N,P)	Ammonium salts, phosphate-based buffers, urea and sequestrants	Dyeing
pH and salts effects	NaOH, mineral/organic acids, carbonate, silicate, sodium chloride, sulphate,	Scouring Desizing **Bleaching** Mercerising
Sulphur	Sulphate, sulphide and hydrosulphite salts, sulphuric acid	Dyeing
Toxicants	Heavy metals, reducing agents, oxidizing agents, biocides, quaternary ammonium salts	Desizing **Bleaching** Dyeing Finishing
Refractory organics	Surfactants, dyes, resins synthetic sizes, chlorinated organic compounds, carrier organic solvents	Scouring Desizing **Bleaching** Dyeing Washing Finishing

Inside the refractory organics, the surfactants play and important roll. A wide range of surfactants is currently employed in the wet textile operations to improve the wetability of the fibres [Delée et al., 1998]. The alkyl phenol ethoxylates are a large fraction of the non-ionic surfactants largest consumer in the textile industry [Naylor, 1995].

The issue is rather controversial in view of the fact that the discharge of alkyl phenol surfactants into sewers is often restricted. In Portugal, the discharge of alkyl phenol surfactants into sewers is restricted to 0.5 ppm of phenol equivalents or even banned as in Germany [Gähr et al., 1994]. These restrictions were established because alkyl phenol polyethoxylate surfactants biodegrade to alkyl phenol which tend to sorbs onto and accumulate in sewage sludge with concentrations up to 1000 ppm recorded [Brunner et al., 1988]. Alkyl phenols are, however, much more toxic than the ethoxylated forms, with maximum accepted concentration in the low ppb range [Naylor, 1995].

3.3. Chlorophenols

Chlorophenols are important contaminants which come principally from industry. These polluted compounds appear as intermediates in the chemical industry or are generated during the chlorination of effluents containing phenolic compounds. Chlorophenols are widely used as fungicides and in the synthesis and transformation of herbicides and insecticides. Due to their stability and bioaccumulation, they remain in the environment for long periods. Because they are highly toxic and carcinogenic, they have caused considerable damage and they are a threat to the ecosystem in water bodies and human health. Consequently, chlorophenols are ranked high among pollutants in the environment. An effective and economic treatment for eliminating these compounds in our water is in urgent demand [Sehili et al., 1989, D'Oliveira et al., 1990, Wang et al., 1999].

2,4-Dichlorophenol (2,4-DCP) was employed as environmentally relevant pollutant model. 2,4-Dichlorophenol is one of the 129 priority pollutants listed by the U.S. EPA [Keith and Telliard, 1979, Tang and Huang, 1996]. The major environmental problem caused by 2,4-DCP is its presence in drinking water [Tang and Huang, 1996]. Because of the persistence of chlorinated phenols in the environment, adverse effect of these pollutants on aquatic life is also an important environmental concern. 2,4-DCP can be degraded by either biological methods or physicochemical processes [Steiert et al., 1987]. However, biological methods usually take from several days to months to complete. Thus, physicochemical treatment processes for chlorinated phenols including 2,4-DCP have been actively investigated.

References

Bajpai, P. K. and Bajpai, J., *J. Biotechnol.*, 1994, **33,** 211.

Balcioglu, I. A. and Arslan, I., *Environ. Pollut.*, 1998, **103,** 261.

Brunner, P. H., Capri, S., Marcomini, A. and Giger, W., *Water Res.*, 1988, **22,** 1465.

Correia, V. M., Stephenson, T. and Judd, S., *Environ. Technol.*, 1994, **15,** 917.

Costan, G., Bermingham, N., Blaise, C. and Ferard, J. F., *Environ. Toxicol. Wat. Qual.* , 1993, **8,** 115.

Delée, W., O'Neill, C., Hawkes, F. R. and Pinheiro, M., *J. Chem. Technol. Biot.*, 1998, **73,** 323.

D'Oliveira, J.-C., Al-Sayyed, G. and Pichat, P., *Environ. Sci. Technol.*, 1990, **24,** 990.

Ebeling, K. and Meloni, E., *Tappi Proc. Env. Conf. Exhib.*, 1997, **1,** 437.

EPA, *Textile processing industry*, 1978, Environmental Protection Agency, EPA-625/778-002.

Eriksson, K. E., Kolar, M. C., Ljungquist, P. O. and Kringstad, K. P., *Environ. Sci. Technol.*, 1985, **19,** 1219.

Gähr, F., Hermanutz, F. and Oppermann, W., *Water Sci. Technol.*, 1994, **30,** 255.

Hostachy, J.-C., Lenon, G., Pisicchio, J.-L., Coste, C. and Legay, C., *Water Sci. Technol.*, 1997, **35,** 261.

Keith, L. H. and Telliard, W. A., *Environ. Sci. Technol.*, 1979, **13,** 416.

Naylor, C. G., *Text. Chem. Color*, 1995, **27,** 29.

Pryke, D. C. and Mckenzie, D. J., *Pulp Pap. Can.*, 1996, **97,** 27.

Rand, G. M., *Cap 1: Fundamentals of Aquatic Toxicology*, 1995, (Ed, Rand, G.) Hemisphere publishing Corporation, New York.

Reid, R., *J. Soc. Dyers Colour*, 1996, **112,** 142.

Rodríguez, J., Fuentes, S., Freer, J., Mansilla, H. D., Ferraz, A. and Baeza, J., *Environ. Technol.*, 1998, **19**, 75.

Sehili, T., Boule, P. and Lemaire, J., *J. Photoch. Photobio. A-Chem.*, 1989, **50**, 117.

Sierka, R. A. and Bryant, C. W., *Biological Treatment of Kraft Wastewater Following Pretreatment of Extraction Waste Stream by Titanium Dioxide and Membranes*, 1993, (Eds, D.F.Ollis and H.Al-Ekabi) Elsevier Science Publishers B.V., Tucson, pp. 275.

Steiert, J. G., Pignatello, J. J. and Crawford, R. L., *Appl. Environ. Microbiol.*, 1987, **53**, 907.

Tang, W. Z. and Huang, C. P., *Environ. Technol.*, 1996, **17**, 1371.

Vandevivere, P. C., Bianchi, R. and Verstraete, W., *J. Chem. Technol. Biot.*, 1998, **72**, 289.

Wang, K.-H., Hsieh, Y.H., Chou, M.-Y. and Chang, C.Y., *Appl. Catal. B-Environ.*, 1999, **21**, 1.

4. EXPERIMENTAL PROCEDURES

4.1. Description of the experimental systems

Most tests were conducted in a thermostatic cylindrical Pyrex cell that is 85 mm high with a diameter of 55 mm and a volume of 130 cm^3. A scheme of the reactor is shown in Figure 4.1.

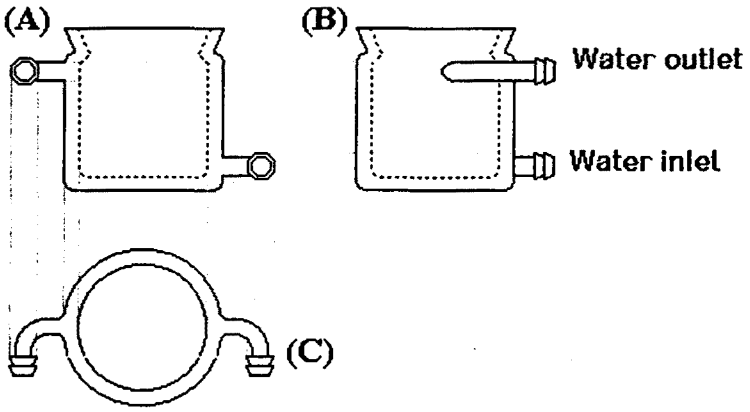


Figure 4.1. *Thermostatic batch photoreactor. (A): front view, (B): side view, (C): upper view.*

The reactor is surrounded by a water jacket that allowed us to control the reactor temperature. By adjusting water input through the water inlet and outlet, we were able to control reactor temperature within ± 0.1°C. The reactor has three ports lid that can be sealed. We used one port for introducing, when required, gas into the reactor. In those cases where compressed air was introduced into the reactor, we bubbled it into the cell through a porous metal diffuser after the compressed air was passed through 0.2 $mol{\cdot}L^{-1}$ NaOH solution in order to eliminate any CO_2 that the gas might contain. Excess gas left the reactor via the second port and then bubbled onto a gas stripping trap. The third port usually remained closed during the experiments and we only opened that port to take samples from the reactor.

Reaction mixtures consisting of either 100 mL of industrial effluent or synthetic samples, plus the required amount of reagents, were maintained homogeneous by magnetic stirring inside the cell.

As mentioned above, we used different light sources to carry out the experiments and each light source was directly related to the treatment under study. Every light source required a different setup. The majority of the experiments were performed using Xenon lamp irradiation. Figure 4.2 shows a diagram of the experimental setup. The distance from the light source to the reactor was 10 cm.

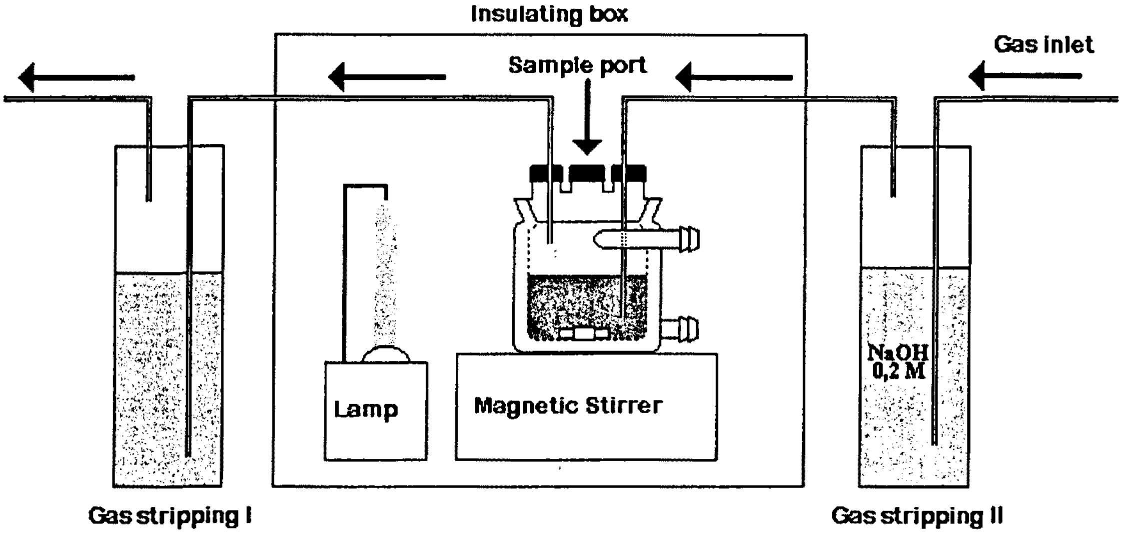


Figure 4.2. *Schematic representation of the experimental setup.*

Experiments that involved either black light or solar light sources were similar to the above mentioned except for the positioning of the light source For those experiments involving either black light or solar, the light source is over the reactor and the reactor is open for the duration of the experiment. For the artificial black-light, the lamp was placed 5 cm over the reactor.

On the other hand, the experiments described in Section 6 (Paper 7) consisted of a 1.1 L cylindrical photochemical glass reactor as shown in Figure 4.3. As is the case of the first reactor, this system is refrigerated with water to ensure a temperature control within ± 0.1°C. The reactor also has three sealable ports comparable to the first reactor. Pure oxygen was bubbled inside the cell through a fritted glass at the bottom of the reactor. A Philips 125 W high-pressure mercury lamp, ($\lambda > 254$ nm), placed in a quartz tube and immersed in the treated solution, was used as the irradiation source.

Reaction mixtures consisted of 1100 mL of Chilean industrial effluent, plus the required amount of reagents, maintained homogeneous by a magnetic stirrer inside the cell.

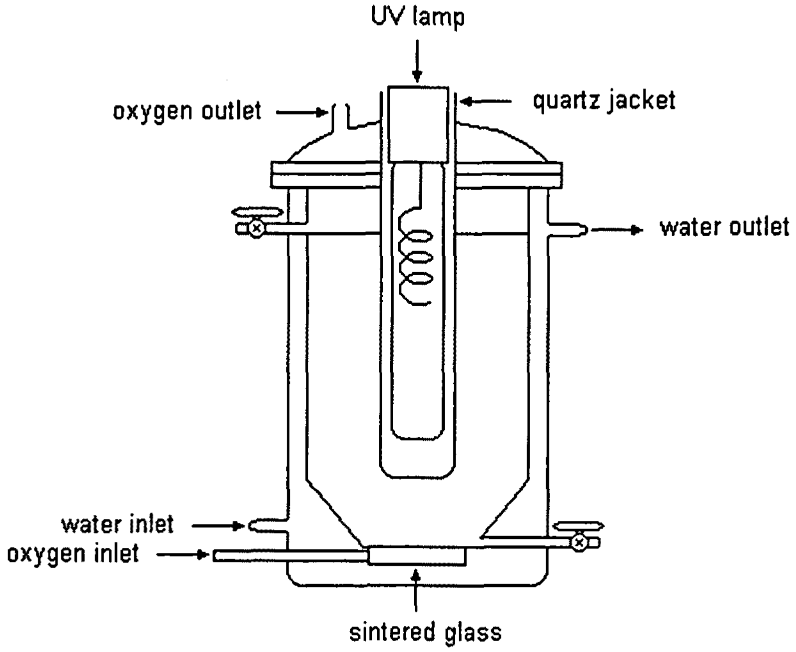


Figure 4.3. *Thermostatic batch photoreactor used in the experiments described in Section 6 (Paper 7).*

The treatment systems that used an artificial light source were placed inside an insulating box that had several ports to allow sampling and gas circulation.

4.2. Materials and reagents

Paper effluents

The contaminant organic load present in any bleaching pulp mill effluent mainly depends on the following:

- Raw material (the type of wood used in the pulping process): Generally, the lignin present in softwoods only contain the guaicil group; the syringol group is not present [Saunamäki and Sorvari, 1992]. On the other hand, hardwoods such as eucalyptus, beech tree, birch, black poplar, maple tree,... contain both guaiacol and syringol in ratios of 4:1 or 1:2, depending on the tree specie, its placement in the stem (secondary wall fiber or middle lamella, vessels, parenchyma cells, ...) and the age of the tree.
- Cooking conditions can lead to a different Kappa number and consequently a different bleaching agent demand.

- Bleaching conditions: The bleaching agent (for instance the percentage of dioxide chlorine substitution in the chlorination steps) used, will determine whether the reaction is a substitution or an oxidation reaction.

Effluents from Spain were obtained from Kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%) trees; consequently their lignin contains both syringol and guaiacol. Generally, after cooking, the methyl groups are lost and the main groups have turned into cathecols.

The Chilean effluent is from *Pinus radiata* Kraft pulp. Because this is softwood, we should not expect to find any syringol group.

The data from Annex 2 shows that a syringol compound was found in both first and second effluent, along with other organochlorated compounds such as guaiacols and cathecols. But in the Chilean effluent, no syringol group was found.

Cooking and bleaching processing conditions clearly affect the composition of the effluents. Annex 2 is a complete listing and characterization of the pulp bleaching wastewaters studied before any treatments of the industrial effluents were performed.

For purposes of this study, we worked with industrial effluents as well as effluents generated in our laboratory that simulated normal industrial processing. In a laboratory batch reactor we generated two different bleached Kraft mill effluents. The first effluent was obtained from the D stage (100 % chlorine dioxide) of an elemental chlorine free (ECF) AOD bleaching sequence (acid pretreatment (A) followed by an oxygen delignification (O) and chlorine dioxide bleaching (D)). The second laboratory generated effluent was obtained from the first D stage (100 % ClO_2) of a ECF sequence. The main difference between the two effluents is that the first one has an oxygen delignification step before the chlorination step.

We also studied two samples of industrial wastewater from Spain. Both were pulp effluents obtained from the chlorination step of bleaching conventional sequences applied to Kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%). The first effluent studied comes from the bleaching sequence $(D_{20}C_{80})(EO)D_1D_2$, while the second one came from the $O(D_{22}C_{78})(EO)D_1D_2$ sequence. The oxygen delignification stage of the second effluent is the main difference between the two effluents. Consequently, the first effluent will present a higher contaminant load than the second one. In order to reduce the level of organic contaminants of the first effluent, a hydrolysis of the wastewater with $Ca(OH)_2$ (pH=12, 1 hour) was carried out. After the hydrolysis step, the effluent was stored at – 4°C. The second effluent was also stored at – 4°C but the hydrolysis step was not done on it.

A third bleaching industrial pulp effluent from a Chilean wastewater was studied. In this case, the effluent was obtained from the first alkaline extraction stage in the bleaching sequence O(DO)(EOP)D_1D_2, *Elemental Chlorine Free* (ECF), of *Pinus radiata* Kraft pulp. The two main differences from the effluent from Spain are that, in this case, the bleaching sequence is an ECF and the effluent came from the alkaline extraction stage instead of the chlorinated one. The effluent was stored at – 4°C with no alteration or manipulation done.

Textile effluents

The textile effluents used in this study were obtained from the hydrogen peroxide bleaching sequence of a cotton substrate mixed with a very small amount of synthetic fibers and pretreated with hypochlorite. The wastewater was supplied by a Spanish textile manufacturer. In order to work with a lower organic contaminant load, a hydrolysis with $Ca(OH)_2$ (pH 12, room temperature, for 1 h) was carried out on the effluent following the procedure described by Dorica [Dorica, 1992].

Annex 2 contains a summary of the characterization of the textile effluent before treatments were performed.

2,4 - Dichlorophenol

Analytical grade 2,4-dichlorophenol was purchased from Aldrich and was diluted to a concentration of 100 $mg \cdot L^{-1}$. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Formic acid

In order to test the acrylic waveguide reactor design discussed in Section 6 (Paper 8), formic acid was used in the photocatalysts experiments. We chose formic acid for the following reasons [Aguado and Anderson, 1993]:

- Formic acid has a simple molecular structure. Its oxidation to carbon dioxide involves simple molecules. Consequently, one would expect relatively simple reaction mechanisms involved in the photocatalytic oxidation of this molecule.
- Problems associated with reactant and product diffusion inside the porous membrane are minimized because both molecules are small.
- The rate of photocatalytic degradation of formic acid is rapid. Consequently, it is possible to monitor the reaction evolution via changes in the formic acid concentration even if the photocatalyst is relatively ineffective.
- Solubility of formic in water is high.

- Titania is resistant to chemical attack by formic acid.
- While photochemical decomposition of formic acid is possible, it requires the use of radiation with wavelengths shorter than 260 nm.

Reagents

The semiconductor titanium dioxide, TiO_2 Degussa P-25 with an anatase-rutilo ratio of 80:20, is widely used because:

- It is highly absorptive of UV radiation. It becomes photoactive upon illumination by UV light of 380 nm or less and it has a band-gap energy of ca. 3.2 eV.
- It is sufficiently adsorptive of many organic contaminants of interest.
- It has high stability in a wide pH range.
- It has relatively strong oxidative power.
- It is highly resistant to photocorrosion during photocatalytic activity while in contact with water.
- It is inexpensive.

It is generally accepted that TiO_2 is the best photocatalyst to perform the degradation of organic micropollutants in an aqueous media [Minero et al., 1991, Herrmann et al., 1993]. Consequently, it is frequently used in photocatalytic decontamination research of real effluents [Sierka and Bryant, 1993, Pérez et al., 1997, Balcioglu and Arslan, 1998, Peralta-Zamora et al., 1998, Yeber et al., 2000, Torrades et al., 2001] and also of synthetic samples [D'Oliveira et al., 1990, Stafford et al., 1996, Trillas et al., 1996, Rideh et al., 1997, Wang et al., 1999, Dionysiou et al., 2000, Peiró et al., 2001].

The catalyst surface is one of the most important parameters in the degradation rate of samples treated by a photocatalysis process. It is interesting to note that the catalyst must present a high surface/volume ratio to achieve a large catalytic effect with the least amount of catalyst. The physical-chemical properties of TiO_2 used that make it such a good catalyst are [Sánchez, 1999]:

- The specific surface area of the semiconductor is 57.9 $m^2 \cdot g^{-1}$ as calculated by the nitrogen adsorption in a BET apparatus.
- The elemental particle average diameter of 27 nm was determined by SEM (scanning electron microscopy) images analysis. This technique also showed evidence of particle agglomeration.
- The ZCP (zero charge point) for the catalyst TiO_2 Degussa-P25 is approximately 6.25.

Ozone was derived from a Sander Labor-Ozonisator 301.7 fed with a pure oxygen stream. The resulting ozone and oxygen mixture was immediately bubbled through the studied sample by means of a metallic diffuser. The generator is equipped with a power control. A working current of 1 A and a pressure of 0.5 bar were used. An ozonized oxygen flow-rate of 330 $mL{\cdot}min^{-1}$ (1.5 g $O_3{\cdot}h^{-1}$) was employed to ensure ozone saturation of the system. The amount of ozone generated was determined by iodometry.

The aqueous solutions used in the laboratory were prepared with deionized water obtained from a Millipore Mili-Q system. This provides a typical conductivity lower than $6{\times}10^{-8}\ \Omega^{-1}{\cdot}cm^{-1}$ and a TOC (total organic carbon) of less than 0.1 ppm.

All the other reagents used in the experiments were, at least, of reagent grade. Analytical grade hydrogen peroxide was purchased from Panreac, heptahydrated ferrous (99%) from Aldrich, sulphuric acid (≥ 96%) from Aldrich, and pure oxygen (industrial quality) from Carburos Metálicos, S.A.

On the other hand, the reagents needed for the analytical methods are listed in Section 4.4.

4.3. Experimental Design

Without slighting the importance of statistical testing as a method of interpreting the results of a concluded experiment, it is necessary to be conscious that the application of a correct experimental design is required, in order to delimit the experimental dominion. Also, to obtain the maximum information from the studied system with the minimum number of well-chosen experiments accomplished [Pepió and Poló, 1990].

The studied system is considered as an unknown function, were the input parameters, factors, produce the output, answer. The end objective of the experimental design is to manufacture an approximation of the system function. The function allows us to know the main effects produced by the input parameters, the interaction between them and the extension of the experimental error. One factor that must be considered is the evaluation of the model quality when the answer function is obtained.

While the classical approximation used to find the answer for the system under study, is to studying the effect of each factor individually, the concept of developing an experimental design defines a group of experiences in order to study the influence of the chosen factors at different levels and the interaction between them, to arrive at an overall system answer. Also it is possible to calculate the optimal conditions to get the most desirable response.

Applications of this statistical methodology have been reported for pulp mill effluents treated with ozone [Rodríguez et al., 1998], photocatalysis [Pérez et al., 2001] and in the Fenton reaction of industrial wastewater's containing aromatic amines [Oliveros et al., 1997].

The experimental design applied in Section 6 (Papers 6 and 7) was used to chose the experiment which allowed us to correlate the results and to develop equations that provided an estimation of which parameters affected the contaminant load of the effluent and could be manipulated in order to reduce contaminant load. In all cases, a software previously developed [Barros Neto et al., 1995] was used. In both papers, a factorial experimental design (2^3) with repetition of the centrepoints was chosen. Factor levels and their coded values are summarized in the papers.

The answer obtained and evaluated was used to represent a surface answer of the system which allowed us to estimate the system answer in all the wide studied interval. Moreover, the best result could be assessed inside the delimitated studied system.

4.4. Methods of Analysis

The analyses were performed on the initial samples and on samples collected throughout the experiments. Several different analyses were performed on every set of samples because of different experimental treatment conditions and consequently different results. Parameters were chosen in order to maximize characterization of the experiments accomplished while still being simple enough to permit a large number of samples to be treated and, thereby, allowing us to perform the maximum number of experiments.

Our goal was to analyze all the chosen parameters on every sample immediately. In those cases where this was not possible, the samples were refrigerated at - 4°C for the least possible amount of time. In addition, we ran tests to determine the stability of the samples over time and we found no change in any of the values analyzed after an extended period of storage.

4.4.1. Organic compounds analysis

The effluents of the pulp and textile industries are characterized by their low biochemical oxygen demand (BOD) and their high toxicity because of the chlorinated organic substances released during the bleaching processes. Moreover, the textile effluents are also highly variable in composition [Balcioglu and Arslan, 1998]. Consequently, it is specially interesting the characterization of the wide variety of toxic and refractory organic compounds contained in such variable effluents, with the aim of determining the contamination load of the studied industrial wastewater and subsequently choosing the most appropriate treatment in order to mineralize these harmful compounds.

It is important to note that low molecular weight compounds have a large probability of bioaccumulation due to their ability to penetrate tissue. The most toxic compounds are those with the higher chlorine substitution.

The identification of the chemical constituents of the four studied industrial wastewaters, and the synthetic sample analysis (2,4-dichlorophenol), were done by means of liquid chromatography (HPLC) with UV detection and GC-MS.

For liquid chromatography analysis, we used an HPLC Mettrohm 690 equipped with a UV-Visible detector (model 795A) from Applied Biosystems and a Hewlett-Packard electronic integrator (model 3394A). A Shimadzu LC-10AT high pressure pump with the capability to administer four different solvents by means of a proportional system valve was used. This process was used on the bleaching pulp industrial effluents from Spain as well as the synthetic sample studied in this work.

The chromatographic conditions used for paper wastewaters and the 2,4-dichlorophenol samples were:

- Methanol (Riedel-de Häen HPLC gradient grade)/water (bidistilled) 0/100 volume percentage at initial time, and 100/0 at final time, 15 minutes.
- Hypersil ODS, 200 mm long, 4.6 mm diameter and 5 μm particle diameter
- Flow 1 $mL{\cdot}min^{-1}$.
- Detector wavelength, 254 nm

In order to eliminate TiO_2, or/and any other particle, that could damage the chromatographic column, we filtered the sample through a syringe with a 0.45 μm membrane filter (Schleicher&Schuell) before injection.

Additionally, the initial samples of all industrial effluents and some other samples that we collected throughout the processes, were also analyzed by means of GC-MS.

The first alkaline extraction effluent obtained from a Chilean pulp mill after the bleaching sequence $O(DO)(EOP)D_1D_2$, (ECF) of *Pinus radiata* Kraft pulp, and its treated samples, were analysed by the Laboratory of Renewable Resources, University of Concepción, Chile, by means of an HP 5890 Series II gas chromatograph equipped with a HP 5972 mass selective detector.

The samples obtained from a Spanish pulp mill, were analyzed by the Department of Chemistry of the Autonomous University of Barcelona, Spain, by means of a HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector.

In the Spanish and Chilean laboratories, GC-MS analyses were accomplished with an ionization of electronic impact of 70 eV. The spectra were recorded from a 40 – 600 amu interval in the Spanish laboratory and a 33-550 amu interval in the Chilean laboratory.

In all the cases, one liter of the sample was filtered through a Speedisk® membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 μL in dichloromethane and 1 μL was injected into the GC. Identifications were carried out with the aid of the WILEY (275,000 spectra) and NIST (130,000 spectra) database libraries.

The initial Chilean effluent sample was also diluted to 2 mL with dichloromethane and derivatised by methylation with diazometane and then 1 μL was injected into the GC. Results were identical whether or not the samples were derivatised.

The assays carried out in the Spanish laboratory were as follows:

A capillary column, HP-5MS (5% Phenyl Methyl Siloxane), with the dimensions of 30 m, 250 μm, 0.25 μm was used. We used helium with a flow rate of 1.3 $\mathrm{mL \cdot min^{-1}}$ as a carrier gas. The sample injection was carried out with a 0.6 min of splitless time, at 250 °C. The temperature program used for the GC-MS analysis ramped as follows: 70 °C (3 min), $5\mathrm{°C \cdot min^{-1}}$ until 270 °C, maintaining this temperature during 30 min.

The conditions of the assays done on the Chilean samples differ only in the splitless time and the carrier gas flow rate in the GC. Those values for the Chilean assays were set at 0.5 min and 0.9 $\mathrm{mL \cdot min^{-1}}$ respectively.

4.4.2. TOC analysis

Organic load is a key parameter in wastewaters control. For our analysis, we used both the total organic carbon (TOC) method, as well as the chemical oxygen demand (COD) method to determine the organic charge present. Basically, in the TOC analysis, the sample undergoes combustion until all carbon is in the CO_2 form. Next the carbon dioxide is quantified by IR detection.

The total organic carbon (TOC) technique is a quantification of all the carbon contained in the organic matter present in the water sample. The TOC analysis does not differentiate between the carbon of different organic compounds, but does distinguish between organic and inorganic carbon. Consequently, TOC does give a measure of the mineralization of the samples independent of the type of intermediates which appear. Additionally, TOC is more accurate than COD. COD quantification must be carried out under strict conditions in order to have comparative results and could present interferences from some non organic reducing species contained in the sample.

The total carbon analyses of the samples generated during the degradation experiments gave us the mineralization rate of the processes in a simple and quick analysis. Total organic carbon of initial and treated samples was determined with a Shimadzu 5000 TOC analyzer, according to the n° 5310B Standard Method [APHA, 1999b].

4.4.3. COD analysis

Chemical oxygen demand (COD) measures the oxygen equivalent of the organic and inorganic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. Reaction (4.1) is the basic reaction of the COD method and shows that the equivalent rate is 8 grams of oxygen for oxidation equivalent:

$$O_2 + 4H^+ + 4\,e^- \rightarrow 2\,H_2O \tag{4.1}$$

The COD is expressed as mg·L^{-1} of consumed oxygen and is a valuable parameter in the study of the organic matter present in the wastewaters.

COD testing was performed in accordance with EPA 00340 and following the closed reflux micro method commercially available from Hach Co.

According to the standard method, the quantity of dichromate is known and in excess. The analyzed samples are then added to a digestion solution obtained from Hach. After a 2 hours digestion period, the samples are allowed to cool. A colorimetric determination is done using a blank sample as reference in a Hach spectrophotometer (model DR/2000) with a wavelength of 620 nm. The Hach spectrophotometer gives the COD value in mg·L^{-1} O_2.

We validated our technique using the Standard Methods for the examination of water and wastewater, n° 5220C [APHA, 1999a]. The comparison between methods gave a relative deviation of less than 1 %. For this reason, we mainly used the procedure as describe by the Hach company due to its high reproducibility and simple operating procedure.

4.4.4. Color analysis

Color determination was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells according to the Canadian Pulp and Paper Association Standard [CPPA, 1993].

The color determination is made by comparison to a standard platinum-cobalt solution which has a similar dominant wavelength of transmitted light at 570-580 nm than the pulp mill effluents, and the complementary wavelengths of absorbed light range between 450-480 nm.

The standard color solution is equal to 500 color units (c.u.) or 0.146 absorbance units, measured in the above mentioned spectrophotometer at the wavelength of 465 nm and is commercially available.

The effluent, or diluted effluent, is adjusted to pH 7.6 ± 0.1. Because color is pH dependent, it increases when pH is higher. Any pH adjustment must not result in increasing the effluent volume more than 1 %. Thus, HCl and NaOH solutions of suitable concentration should be used. Because suspended material in an effluent causes the scattering and adsorption of light, it must be removed before measuring for color.

4.4.5. AOX analysis

Discharge of chlorinated organic matter from pulp and textile bleach plants is a subject of increasingly environmental and regulatory debates. However, these are not the only industries that discharge a large amount of adsorbable organic halogen (AOX) in their effluents. The majority of organic halogen compounds are synthetic substances used in disperse industries, and their environmental impact is not usually studied.

The presence of halogen in organic molecules makes them more resistant to the biodegradation and gives them a hydrophobic character, which leads to the accumulations of these compounds in the adipose tissue of animals.

Chlorinate organic matter in effluents is mainly comprised of high molecular weight material. On the low molecular weight side, over 200 individual compounds have so far been identified [Kringstad and Lindstrom, 1984]. Identification and quantification of individual compounds is exceedingly complex. Thus, a generic measurement was needed to quantify the total amount of chlorine bound to organic matter [Odendahl et al., 1990]. Since 1990, AOX has been the accepted group parameter [McCubbin and Folke, 1995]. There is still controversy concerning whether the AOX technique is an adequate method for the measurement of organically-bound chlorine in effluents.

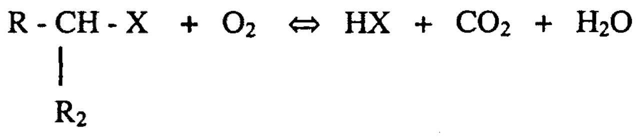
Swedish studies conflict with work done in United States [Odendahl et al., 1990]. Currently, AOX is restricted in some countries including Belgium, Sweden and Germany, with a discharge limit of 0.5 mg·dm^{-3} in the latter country. McCubbin et al. [McCubbin and Folke, 1995, Vandevivere, 1998 #50] report that the Environment Department of Canada has considered and rejected an AOX regulation with the assumption that all Kraft mills currently discharge less than 2 kg·t pulp^{-1} AOX, or will do so in the near future.

The AOX parameter measures the quantity of halogens present in a sample under specific experimental conditions. The parameter has an addition character and the results obtained are global values. The technique was developed in the late 1970s. The method was standardized in Germany in 1985 (**DIN 38409 H14**) and incorporated into legislation. Others techniques for determining AOX have been developed such as **ISO 9652, SCAN-W 9:89, CPPA H.6P and ONORM6275.** The quantitative technique is adequate for the direct analysis of an halogen-organic combinations, adsorbable in active carbon, and present in waters which contain more than 10 µg/l of organic halogens.

We used the AOX parameter only on analyses done on the laboratory generated paper pulp effluent and on the Chilean pulp mill effluent and its treated samples. The analyses done on the laboratory pulp effluents were performed in an EUROGLAS ECS-2000 AOX analyzer.

The AOX analyses on the Chilean pulp mill effluent allowed us to study the evolution of the parameter through the process and its relation to any toxicity measurements. The first alkaline extraction effluent from an ECF sequence had an initial AOX level of 60 ppm (0.54 kg·t pulp^{-1} AOX). Even though this value is a quarter of what Mc Cubbin et al. [McCubbin and Folke, 1995] expected, it is clearly higher than the 0.5 ppm discharge limit allowed in Germany. That analysis was performed in the Laboratory of Renewable Resources, University of Concepción, Chile, according to the recommended procedures of **SCAN-W 9:89 and DIN 38409 H14** in an EUROGLAS ECS-1000 AOX analyzer. Both AOX analyzers followed these three basic steps:

- **Adsorption onto activated carbon:** A batch adsorption method recommended by the German standard **DIN 38409,** mentioned above, was performed.
- **Pyrolysis of the organic halogens by an oxygen stream:** After the washing and filtrating operation, the sample was burned in oxygen in a sealed environment at a temperature of approximately 950 °C. See reaction (4.2) below.



$$R-\underset{\underset{R_2}{|}}{CH}-X + O_2 \Leftrightarrow HX + CO_2 + H_2O \qquad (4.2)$$

- **Microcoulometric titration:** A process based in a potentiostatic microcoulometric determination. The potentiostatic system is a combination of two electrodes wherein reactions (4.3) and (4.4) took place. The silver electrode generates Ag^+ ions in order to reestablish balance and this produces an increase in the intensity current which is measured by the analyzer equipment and relates to the AOX content expressed in ppm.

$$Ag \rightarrow Ag^+ + e^- \qquad (4.3)$$
$$AgCl + e^- \rightarrow Ag^+ + Cl^- \qquad (4.4)$$

The AOX parameter takes into account all the organic compounds with one or more halogens. This fact makes it difficult to interpret results because although we might know the total quantity of organic halogen present in a sample, we cannot directly relate the total halogen present with the toxicity or the contamination grade. Consequently, to ensure the correct interpretation of the AOX parameter, it is more accurate to compare results of the same wastewater with a fix composition.

4.4.6. Acute toxicity analysis

Acute toxicity analysis determines what concentration of the sample studied lead to an inhibition of development or to the mortality of the group of organism exposed to the toxic agent for a short period of time under controlled conditions [Cooney and Rand, 1995]. Because the death of the organisms is more easily detected, the more common acute toxicity test is the lethality one. Normally, it measures the lethal media concentration (CL50) which is the quantity that causes the mortality of 50% of the organisms. In this case, the mortality of the bacteria *Photobacterium phosphoreum* is used as the organism to quantify toxicity. Mortality is measured by the amount of luminescence inhibition caused by the death of *Photobacterium phosphoreum*, and it is defined as EC_{50} values, the effective media concentration.

The utilization of bioluminescence organism as a technique to quickly determine the acute toxicity in aqueous samples was settled in the late 1970's by the Microbics Corporation [Bullich, 1979].

Our acute toxicity tests were performed by MICROTOX® using the *Photobacterium phosphoreum* luminescence inhibition to assess the EC_{50} values following the procedures of AFNOR T 90-320 [AFNOR, 1991]. The results are expressed as Toxicity Units (TU) which are defined as $100/EC_{50}$.

4.4.7. Total phenol analysis

Phenols defined as hydroxiderivates of benzene, and its condensed nucleus, are measured colorimetrically by the 4-aminoantipirine method. This method determines, under adequate pH conditions, the phenols substituted in *orto* and *meta* positions. Acidification of the sample leads to the elimination of the main interferences and by means of distillation the nonvolatile interferences.

The distillated phenolic compounds react with the 4-aminoantipirine at pH 7.9 ± 0.1 in presence of potassium ferricyanide to form a colored sample, which is measured at the wavelength of 500 nm. The calibration curve, determined with a known phenol concentration, is compared to the results of the photometric sample to determine the quantity of phenol present in the studied sample. The direct photometric method follows the standard procedure [APHA, 1989a].

We applied this assay to the Chilean effluent without previous manipulation. The sample was analyzed in the Laboratory of Renewable Resources, University of Concepción, Chile, by means of a Shimadzu 1603A spectrophotometer.

Total phenol determinations of the treated samples of Chilean effluents were done using the standard procedure [APHA, 1989b] and represent the addition of simple phenols and high molecular weight phenolic compounds (lignin and tannins).

Both lignin and tannin contain aromatic hydroxyl groups that react with Folin phenol reagent (tungstophosphoric and molybdophosphoric acids) to form a blue compound suitable for the determination of concentrations up to at least 9 $mg{\cdot}L^{-1}$. However, the reaction is not specific for lignin or tannins, nor for compounds containing hydroxyl groups, as many other reducing materials, both organic and inorganic, respond similarly. The adsorption of the samples is measured at 700 nm with a light path of 1 cm by a Shimadzu 1603A spectrophotometer. A calibration curve was developed by using known phenol standards. The lower limit of detection phenol and tannic acid is around 0.025 $mg{\cdot}L^{-1}$ and around 0.1 $mg{\cdot}L^{-1}$ for lignin when using a 10 mm light path cells.

4.4.8. UV-visible spectra

It is well-known that some organic compounds commonly found in wastewaters, such as lignin, tannin, humic substances, and various aromatic compounds, strongly absorbs ultraviolet (UV) radiation. Strong correlations may exist between UV absorption and organic content and color [Edzwald et al., 1985].

UV absorption also has been used to monitor industrial wastewater effluents [Bramer et al., 1966] and to evaluate organic removal. Standard method n° 5910 [APHA, 1999c] is intended to be used to provide an indication of the aggregate concentration of UV-absorbing organic constituents.

UV-visible spectra determinations were carried out in a Shimadzu 1603A spectrophotometer. UV-visible spectra analysis between 200 and 600 nm in the initial and treated samples were carried out in order to study degradation that occurs in the samples at different irradiation times. A gradual decrease in the absorption spectra is indicative of degradation of the chromophoric groups. The most accurate data was observed at the absorption at the 280 nm wavelength because it is the wavelength commonly measured to detect the presence of phenolic compounds.

4.4.9. Ozone flux analysis

The quantity of ozone contained in the gas flow, which fed the reactor, was measured by iodometry [Beyer and Walter, 1987]. The gas was bubbled through 100 mL of KI 0.120 mol·L^{-1} buffered with Na_2HPO_4 (0,041mol·L^{-1})/$NaH_2PO_4 \cdot 2H_2O$ (0,026 mol·L^{-1}). The reaction between ozone and potassium iodide produces iodine as Reaction 4.5 shows

$$2H^+ + O_3 + 2I^- \rightarrow I_2 + O_2 + 2H_2O \qquad (4.5)$$

which is measured by tiosulfate titration:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (4.6)$$

4.4.10. Fe^{2+} analysis

The Fe (II) is determined in some of the Fenton and Photo-Fenton experiments in order to obtain more information on the reaction mechanism.

According to the n°3500-FeB standard method [APHA, 1999d], if the main goal is to determine total iron, the ionic iron is reduced to Fe (II) by boiling with acid and hydroxylamine. After that, the sample is treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of Fe (II) to form an orange-red complex as following reaction shows:

$$Fe^{2+} + 3\ PhH^{+} \leftrightarrow Fe(Ph)_3^{2+} + 3\ H^{+} \qquad (4.7)$$

A colorimetric determination is done using the 510 nm wavelength. Samples measurements are compared with the calibration curve previously created.

In those cases where it is desired to know the Fe (II) content, the determination is done at the sampling site because of the possibility of a change in the Fe (II)-Fe (III) ratio over time in acidic solutions. Samples should not be exposed to sunlight and hydroxylamine should not be added.

References

AFNOR, 1991, **T 90-320.**

Aguado, M. A. and Anderson, M. A., *Sol. Energ. Mat. Sol. C.*, 1993, **28,** 345.

APHA, 1989a, **n° 5530D,** 5.

APHA, 1989b, **n° 5550,** 5.68.

APHA, 1999b, **n° 5310 B.**

APHA, 1999c, **n° 5910.**

APHA, 1999d, **n° 3500-Fe B.**

APHA, 1999a, **n° 5220 C.**

Balcioglu, I. A. and Arslan, I., *Environ. Pollut.*, 1998, **103,** 261.

Barros Neto, B., Scarminio, I. S. and Bruns, R. E., *Planejamento e otimizaçao de experimentos*, 1995, UNICAMP, Campinas.

Beyer, M. and Walter, E., *Manual de Química Orgánica*, 1987, Reverté S.A.

Bramer, H. C., Walsh, M. J. and Caruso, S. C., *Water Sewage Works*, 1966, **113,** 275.

Bullich, A. A., *Use of Bioluminescent bacteria for determinating toxicity in aquatic environment*, 1979, (Eds, Markings and Kimerle) ASTM, Philadelphia, pp. 98.

Cooney, J. D. and Rand, G. M., *Chapter 2: Aquatic Toxicology*, 1995, (Ed, Taylor and Francis) Washington , DC USA,.

CPPA, 1993, **standard H.5.**

Dionysiou, D. D., Suidan, M. T., Bekou, E., Baudin, I. and Laîné, J.-M., *Appl. Catal. B-Environ.*, 2000, **26,** 153.

D'Oliveira, J.-C., Al-Sayyed, G. and Pichat, P., *Environ. Sci. Technol.*, 1990, **24,** 990.

Dorica, J., *J. Pulp Pap. Sci.*, 1992, **18,** 231.

Edzwald, J. K., Becker, W. C. and Wattier, K. L., *Journal American Water Works Association*, 1985, **77,** 122.

Herrmann, J. M., Guillard, C. and Pichat, P., *Catal. Today*, 1993, **17,** 7.

Kringstad, K. P. and Lindstrom, K., *Environ. Sci. Technol.*, 1984, **18,** 236A.

McCubbin, N. and Folke, J., *Pulp Pap. Can.*, 1995, **96,** 43.

Minero, C., Aliberti, C., Pelizzetti, E., Terzian, R. and Serpone, N., *Langmuir*, 1991, **7,** 928.

Odendahl, S. M., Weishar, K. M. and Reeve, D. W., *Pulp Pap. Can.*, 1990, **91,** 60.

Oliveros, E., Legrini, O., Hohl, M., Müller, T. and Braun, A. M., *Water Sci. Technol.*, 1997, **35,** 223.

Peiró, A. M., Ayllón, J. A., Peral, J. and Doménech, X., *Appl. Catal. B-Environ.*, 2001, **30,** 359.

Pepió, M. and Poló, C., *Planificación de Experiencias* , 1990, Publicaciones del Laboratorio de Estadística ETSEIT-UPC, Terrassa.

Peralta-Zamora, P., Gomes de Moraes, S., Pelegrini, R., Freire, M., Reyes, J., Mansilla, H. D. and Durán, N., *Chemosphere*, 1998, **36,** 2119.

Pérez, M., Torrades, F., García Hortal, J. A., Domènech, X. and Peral, J., *J. Photoch. Photobio. A-Chem.*, 1997, **109,** 281.

Pérez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J. and Mansilla, H. D., *Appl. Catal. B-Environ.*, 2001, **33/2,** 89.

Rideh, L., Wehrer, A., Ronze, D. and Zoulalian, A., *Industrial & Engineering Chemistry Research.*, 1997, **36,** 4712.

Rodríguez, J., Fuentes, S., Freer, J., Mansilla, H. D., Ferraz, A. and Baeza, J., *Environ. Technol.*, 1998, **19,** 75.

Sánchez, L., *Eliminación de la anilina mediante fotocatálisis heterogenea y combinaciones de esta con otras técnicas de oxidación avanzada* ,Thesis 1999, Chemistry Department, Universitat Autonoma de Barcelona, Bellaterra.

Saunamäki, R. and Sorvari, J., *Nord. Pulp Pap. Res. J.*, 1992, **3,** 113.

Sierka, R. A. and Bryant, C. W., *Biological Treatment of Kraft Wastewater Following Pretreatment of Extraction Waste Stream by Titanium Dioxide and Membranes*, 1993, (Eds, D.F.Ollis and H.Al-Ekabi) Elsevier Science Publishers B.V., Tucson, pp. 275.

Stafford, U., Gray, K. A. and Kamat, P. V., *Journal of Catalysis.*, 1996, **167,** 25.

Torrades, F., Peral, J., Pérez, M., Domènech, X., García Hortal, J. A. and Riva, M. C., *Tappi J.*, 2001, **84,** 63.

Trillas, M., Peral, J. and Domènech, X., *J. Chem. Technol. Biot.*, 1996, **67,** 237.

Wang, K.-H., Hsieh, Y.H., Chou, M.Y. and Chang, C.-Y., *Appl. Catal. B-Environ.*, 1999, **21,** 1.

Yeber, M. C., Rodríguez, J., Freer, J., Durán, N. and Mansilla, H. D., *Chemosphere*, 2000, **41,** 1193.

5. THE SCOPE OF THE WORK

The purpose of this study is to better understand the treatment of wastewaters by Advanced Oxidation Processes (AOPs). They are becoming everyday more important from the environmental point of view. Although these emerging technologies have been extensively studied, there is still many controversial issues to be solved before the AOPs can be applied at the industrial scale. The present work will look into some of the shortcomings involved in the processes. The main emphasis of this study is centered in the bleaching pulp mill effluent. However, bleaching industrial textile effluents were also included in this study.

Before studying AOPs on real industrial wastewaters there has been some studies carried out on bleaching pulp paper effluents generated in the laboratory *(Papers 1 and 2)*. Within the AOPs, we chose the photocatalysis and ozonation treatment processes to test the viability of treating effluent from laboratory generated chlorine bleaching pulp, that is toxic and has a high contaminant load, with the hydroxyl radical, the generally accepted oxidant for all AOPs. That test assumed that the hydroxyl radical was the proper oxidant for the contaminant load present in the laboratory generated effluents. Following that, an extensive study was planned using industrial wastewaters.

Industry demands an efficient, cost effective treatment of their wastewaters. A study of different AOPs (mainly Photochemistry, Photocatalysis, Ozonation, Fenton, Photo-Fenton and Fenton-like reactions) using industrial bleaching wastewaters was accomplished so that we could establish the benefits and problems of each treatment. TOC decay and treatment cost were the comparative parameters contrasted in the study *(Paper 3)*. The main benefits and shortcomings of each process were discovered. Every treatment was extensively studied and we attempted to find some way to solve those limitations in order to obtain a successful application. We found that the ozonation process should develop strategies to decrease the cost of the treatment *(Paper 4)*; and we also found that photocatalysis requires the proper processing conditions.

Additionally, we noticed that a powerful light source is necessary and/or an improvement of the light utilization efficiency of the TiO_2 catalyst *(Papers 7 and 8)*.

Although the Fenton reagent, in presence of solar light, seems to be a very promising process, much of the ongoing research on that treatment has not elucidated what is the mechanism of the process and what is the optimum ratio iron/hydrogen peroxide. Consequently, we felt it necessary to focus on bleaching pulp and textile effluents treatment with such a system *(Papers 5, 6, 9 and 10)*.

All the previously mentioned studies were organized and presented in paper format. The study was organized in the following manner:

Paper 1: ***"Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation":*** Photocatalytic treatment was tested on two different chlorine bleaching pulp effluents obtained in the laboratory. The effluents presented different contaminant loads in order to validate the applicability of photocatalysis on different contaminant load effluents and processing conditions. The treatment was applied under several work conditions. The parameters: catalyst loads, % light intensity, pH and temperature were studied and the conditions which led to the best results were chosen to be looked at more extensively in a long time experiment. This long experiment allowed us to study the treatment kinetics.

The paper provided evidence that the photocatalytic process can efficiently reduce the organic content of the effluents, and like in the case of most photocatalytic oxidations described in the literature, the contaminant load degradation followed a Langmuir-Hinshelwood kinetic equation.

Paper 2: ***"Removal of organic contaminants in bleached Kraft effluents using photocatalysis and ozone":*** Two different bleaching Kraft effluents were obtained in the laboratory. An extended photocatalytic treatment was performed on both effluents in order to observe the kinetic behavior of both treatments. A serial application of both treatments as well as the simultaneous application of photocatalysis and ozonation was carried out on one of the effluents. Combining both advanced oxidation processes simultaneously provided a synergistic effect that was superior in performance to that of applying the photocatalysis and ozonation processes sequentially.

Paper 3: ***"Removal of organic contaminants in paper pulp effluents by AOP's. Economic study.":*** The study was performed on a chlorine bleaching industrial pulp wastewater. Mainly, we performed the advanced oxidation processes under experimental conditions described in the literature. The main aim of our study was to compare the different treatments. The parameters we chose to base our comparison on were TOC decay and the treatment cost per kg TOC decay. Key findings of this study were developed in following papers.

Paper 4: ***"Treatment of bleached Kraft mill effluents and polychlorinated phenolic compounds with ozonation":*** The previous paper concludes that ozonation treatment is highly efficient in TOC removal but the cost per treatment is ten times higher than other advanced oxidation processes. Consequently, the study of ozonation was focused on ways to reduce the cost per treatment without sacrificing the higher TOC decay. Keeping this aim in mind, several strategies were tested. Ozone was combined with

UVA light and/or iron salts in sequential and simultaneous treatments. We developed interesting conclusions both with the pulp paper effluent and with the synthetic sample of 2,4-dichlorophenol.

Paper 5: ***"Removal of organic contaminants in paper pulp treatment effluents by Fenton and Photo-Fenton reactions":*** From our results in paper 3, we found the Fenton reagent, under light radiation, appeared to be a very promising treatment. This study enlarged the findings of paper 3 with the goal to figure out the right working conditions and the experimental setup for the specific wastewater treated. The effects of parameters such as pH and temperature were studied. Solar light energy was tested as light source for the process.

Paper 6: ***"Experimental design of Fenton and Photo-Fenton reaction of a cellulose bleaching effluent":*** Expanding on the work done on paper 5, we fixed an interval of working conditions where the main parameters which control the complex reaction system are near a relative optimum value. In this study, we used an experimental design that allowed us to study the influence of the chosen parameters and the interaction between them and how that affected the results. We approximate the function of the system and use that to find a system best answer for our specific studied interval. For the present study, solar energy was used after previous results had ensured its capability as a light activation source.

Paper 7: ***"Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent":*** From paper 3, we knew that we needed a more powerful light source. A new experimental set up was chosen and the study was performed using an experimental design. An estimative function for the system was assessed. The function allowed us to know the main effects produced by the input parameters, the interaction between them and the extension of the experimental error. AOX, acute toxicity, phenol and a GC-MS analysis lead us to conclude that the chlorine organic compounds were eliminated from the treated wastewater.

Paper 8: ***"Photocatalyst-coated acrylic waveguides for oxidation of organic compounds":*** An approach based on titanium dioxide (TiO_2)-coated waveguides for the enhancement of light utilization is discussed in the context of developing commercially viable applications of TiO_2 photocatalysis. Rather than attempting to chemically modify TiO_2 to improve oxidation rates, or to modify the reactant solution to minimize the impact of aforementioned limitations, this work assumes that the greatest strides toward the commercial viability of TiO_2 photocatalytic reactors can be made by improvements in reactor design. Specifically, overall enhancements of system performance are best achieved by improving the light utilization efficiency of the TiO_2 catalyst.

Paper 9: ***"Removal of organic contaminants in textile mill effluents by Fenton and Photo-Fenton reactions":*** Results of papers 5 and 6 encouraged us to apply the Fenton reagent, under light radiation, in the treatment of textile industrial wastewaters. We concentrated on the effect of temperature on the complex system and the possibility of using solar light. An economic study revealed the importance of the temperature parameter on the treatment of textile wastewaters, which usually present a high residual temperature. Moreover, the presence of solar energy increases the TOC decay and significantly decreases the cost of treatment.

Paper 10: ***"Fenton and Photo-Fenton oxidation of textile effluents":*** The study of Fenton reaction under light irradiation for textile industrial wastewaters was enlarged. Other important parameters such as reagent load were tested in order to approach the most suitable working conditions for treated wastewaters.

6. PAPERS

The study is summarized in the following publications:

I. ***Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation***
Pérez, M., Torrades, F., García Hortal, J.A., Domènech, X., Peral, J.
Journal of Photochemistry and Photobiology A: Chemistry, 1997, **109**, 281-286.

II. ***Removal of organic contaminants in bleached Kraft effluents using photocatalysis and ozone***
Torrades, F., Peral, J., Pérez, M., Domènech, X., Garcia-Hortal, J.A., Riva, M.C.
Tappi Journal, 2001, **84**, 63-72.

III. ***Removal of organic contaminants in paper pulp effluents by AOPs. Economic study***
Pérez, M., Torrades, F., Domènech, X., Peral, J.
Submitted for publication in *Journal of Chemical technology and Biotechnology*

IV. ***Treatment of bleached Kraft mill effluents and polychlorinated phenolic compounds with ozonation***
Pérez, M., Torrades, F., Domènech, X., Peral, J.
Submitted for publication in *Journal of Chemical technology and Biotechnology*

V. ***Removal of organic contaminants in paper pulp treatment effluents by Fenton and Photo-Fenton reactions***
Pérez, M., Torrades, F., García Hortal, J.A., Domènech, X., Peral, J.
Submitted for publication in *Applied Catalysis B: Environmental*

VI. ***Experimental design of Fenton and Photo-Fenton reaction of a cellulose bleaching effluent***
Pérez, M., Torrades, F., Peral, J., Mansilla, H. D.
Submitted for publication in *Applied Catalysis B: Environmental*

VII. ***Multivariate approach to photocatalytic degradation of a cellulose bleaching effluent***
Pérez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J., Mansilla, H. D.
Applied Catalysis B: Environmental, 2001, **33/2**, 89-96.

VIII. ***Photocatalyst-coated acrylic waveguides for oxidation of organic compounds***
Miller, L. W., Tejedor-Tejedor, M. I, Perez, M. Johnson, R., Anderson, M. A.
12th Internacional Congres on Catalysis, Granada 9-14th July 2000. Proceedings of the 12th ICC, Ed. Avelino Corma, et al. Elsevier, Amsterdam, ISBN: 0-444-50480-X, Vol.130, pp. 1925-1930.

IX. ***Removal of organic contaminants in textile mill effluents by Fenton and Photo-Fenton reactions***
Pérez, M., Torrades, F., Domènech, X., Peral, J.
International Textile Congress, Terrassa 18-20th June 2001. Conference Proceedings of the 2001 International Textile Congress, Ed. Arun Naik, UPC, Terrassa, ISBN: 84-600-9667-X, Vol.1, pp. 346-353.

X. ***Fenton and Photo-Fenton oxidation of textile effluents***
Pérez, M., Torrades, F., Domènech, X., Peral, J.
Submitted for publication in *Water Research*

Paper 1

Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation

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Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation

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Abstract

TiO_2 slurries under UV light irradiation were used for the oxidation and removal of the organic load of effluent from the bleaching of paper pulp. TOC was the main analytical parameter used to characterize the reaction progress, although COD, AOX and color also received periodic attention. Conditions such as the catalyst load, light intensity, pH, temperature, and concentration of O_2 and organic matter were changed through several series of experiments in order to determine their effect. A zero order kinetics accounts for the observed variation of TOC with time during most of the reaction, the rate constant being 0.25–0.40 ppm min^{-1} at 25 °C. This behavior is explained in terms of a Langmuir–Hinshelwood rate equation in a highly substrate concentrated system. © 1997 Elsevier Science S.A.

Keywords: Organic contaminants; Paper pulp

1. Introduction

The pulp and paper industry produces large quantities of spent bleach effluent. These liquors are highly colored and contain large concentrations of organic matter, in particular chlorinated organics, most of them being difficult to eliminate by conventional waste water treatment processes and, therefore, being accumulated in the environment [1–6].

Heterogeneous photocatalytic oxidation is a well known procedure for waste water treatment, which can be used to carry out the complete mineralization of a large number of organic compounds [7–10]. It has shown to be particularly efficient for the attack of chlorinated compounds [11] and, for that reason, it is potentially suited for the treatment of paper pulp bleaching effluents.

In the present study samples of bleaching effluents obtained after chlorine dioxide (ClO_2) oxidation of paper pulp were treated with TiO_2 in the presence of UV light and air bubbling. TOC was chosen as the most general parameter for the study of the detoxification and organic content removal, although other characteristics such as AOX (adsorbable organic halogen), COD (chemical oxygen demand) and color were controlled through the experiments. The conditions were varied systematically, so that information about the effect that the catalyst mass, organic load, pH, temperature and O_2 concentration have on the process could be collected. Special attention was paid to the reaction kinetics and the potential of the method for complete removal of TOC content.

2. Experimental section

The effluents used in the present research were obtained in the laboratory after bleaching sequences of a paper pulp made from *Eucaliptus globulus* chips. The Kappa index and viscosity of the resulting pulp were 20.6 and 650 $cm^3\ g^{-1}$ respectively. The bleaching sequence consisted of three steps: (i) acid pretreatment (2 mol l^{-1} H_2SO_4), (ii) bubbling with pressurized O_2 (to reduce the lignin content), and (iii) treatment with chlorine dioxide. The effluent from this last step formed the starting solution of the present research. Only in the experiments where a much higher organic matter content was needed were the acid pretreatment and O_2 bubbling steps avoided.

All chemicals used in this work were at least of reagent grade and were used as received. The titanium dioxide (Degussa P25) was predominantly anatase (80% anatase and

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20% rutile), as shown by X-ray diffraction. The BET surface area, determined from nitrogen adsorption at −196 °C (Accusorb 2100 E Micromeritics) was 59.1 $m^2 g^{-1}$. The average particle size, determined by scanning electron microscopy, was 27 nm.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of TiO_2, was maintained in suspension by magnetic stirring. As a light source, a 125 W Philips HPK medium pressure mercury vapor lamp was used. The intensity of the incident light inside the photoreactor, measured employing a uranyl actinometer, was 9.2×10^{-5} einstein $dm^{-3} min^{-1}$.

TOC of initial and irradiated samples was determined, after filtering the catalyst, with a Shimadzu TOC 5000 total organic carbon analyzer. COD was detected spectrophotometrically at 620 nm with a specific commercial reagent kit (Hach DR/2000). For AOX measurements a Euroglas analyzer, model ECS2000, was used. Color determination was carried out in a double beam spectrophotometer SP8-300 Pye Unicam at the wavelength of 465 nm using cuvettes of 10 mm light path, according to the standards of the CPPA (Canadian Pulp and Paper Association, Standard H.5, 1991).

3. Results and discussion

The paper pulp treatment effluent, produced as described in Section 2, contained the following contaminating load: 306 ppm TOC, 515 mg $O_2 l^{-1}$ COD, 27.7 ppm AOX, and 250 color units. TOC was chosen as the main parameter of study in the present work because it is the most general quantification of organic matter. Nevertheless determinations of COD, a more extensively used index for water pollution, were also carried out. AOX and color, both particularly important measurements in effluents coming from the paper mill industry, were also sporadically collected.

Blank experiments were carried out in order to ascertain whether photocatalytic oxidation takes place with such an organic content. When 100 ml of the effluent were mixed with 0.2 g TiO_2, a decrease of 9.8 ppm (3.2%) in TOC value after 15 min in the dark was noticed. For longer mixing times no further TOC removal took place. In contrast, the presence of UV light produced a reduction of 16.2 ppm (5.3%) TOC after 15 min, and longer reaction times involved larger reductions. The initial decrease in TOC in the dark is, thus, a consequence of pure adsorption and saturation of the catalyst surface. No appreciable TOC decay was noticed when the solution was irradiated during 1 h in the absence of TiO_2. The mass of TiO_2 suspended is expected to influence the reaction efficiency by providing a larger reactive surface. This point was tested, and the results for three different TiO_2 loads (1, 2 and 6 $g l^{-1}$) are shown in Fig. 1. As can be seen, in the three cases the reaction rates of TOC removal, which are the slope of the curves, are similar (approximately 0.25 ppm min^{-1}) and suffer no appreciable change with time. The only difference appears in the initial TOC decrease, which is clearly larger in the experiment with 6 $g l^{-1}$ catalyst. This observation agrees with the existence of an initial saturation of the solid surface which would be larger for larger amounts of suspended TiO_2. The other parameters studied follow similar behavior, with larger reductions for increasing mass of catalyst. In this way, after 8 h reaction under irradiation and in the presence of 6 $g l^{-1}$ TiO_2, reductions of AOX and COD of 80% and 64% respectively took place, the reductions obtained with 2 $g l^{-1}$ being 71% and 49%. The improvement in the color reduction was spectacular, going from 21% to 72% for the above mentioned values of mass in suspension and the same reaction time.

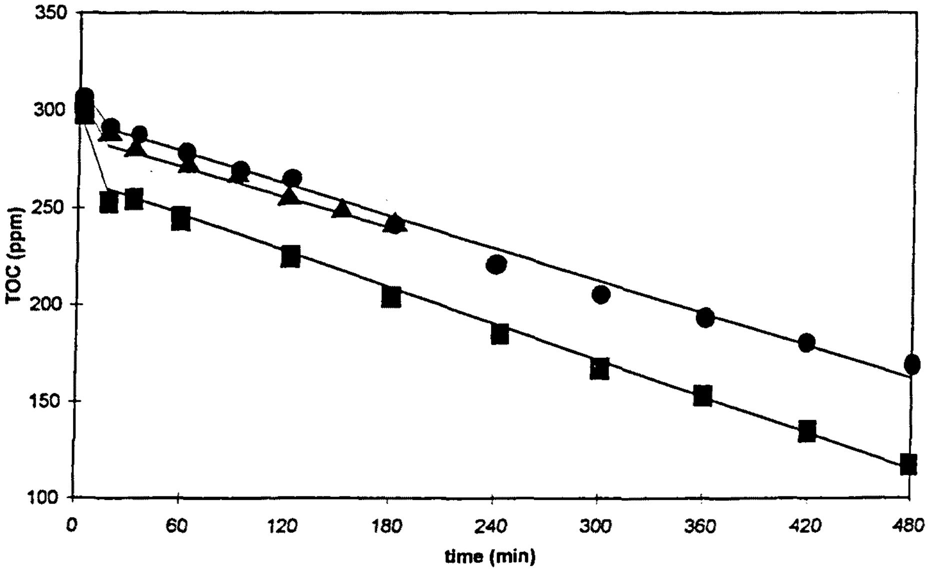

Fig. 1. TOC vs. reaction time for three different catalyst loads: 1 $g l^{-1}$ (▲), 2 $g l^{-1}$ (●), and 6 $g l^{-1}$ (■). AOD sequence effluent, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

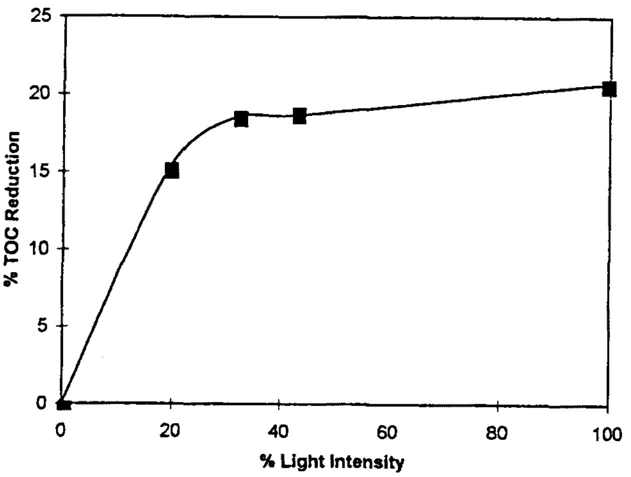

Fig. 2. Effect of relative light intensity on TOC removal. AOD sequence effluent, 2 g l^{-1} TiO_2, pH≈3, air flow 60 ml min^{-1}, 25 °C. Full light intensity 9.2×10^{-5} einstein min^{-1}.

The light intensity was also a variable studied. Fig. 2 presents the removal of TOC vs. the percentage of full lamp intensity used in different experiments. The results clearly indicate no important changes in TOC removal for light intensities going from 30% to 100%. Below 30% of full lamp power the efficiency of the reaction rapidly decreases. An excess of photons is being used in our standard experiments. Different behavior was noticed with AOX, a 35% larger reduction when moving from 100% to 43% light intensity. This fact might well indicate the existence of homogeneous photochemistry among halogen-containing reaction intermediates, which could, through direct activation by photons, react and lose the halogen without complete mineralization. In this way a change in photon flux could produce a decrease in AOX with no influence on the degree of mineralization owing to heterogeneous photochemistry.

The influence of initial pH was also studied. No variations in TOC values in the pH range studied and in the absence of catalyst were noticed, so phenomena such as organic matter precipitation or homogeneous hydrolysis could be ruled out. Fig. 3 presents the TOC-time course for several initial pH. The slope of the curves and, hence, the reaction rates are similar and constant in time, which indicates a lack of influence of pH on photocatalysis under the conditions used here. Nevertheless, the only differences occur again during the initial minutes of the reaction, with a larger TOC adsorption onto the catalyst for pH 6 and 10, which are above the point of zero charge (pzc) of TiO_2 which is 5.5. The behavior of COD and color is similar to that observed for TOC. AOX changes follow again a different direction. The removal of halogen containing species is clearly favored at acid pH (45% reduction after 3 h at pH 3 compared with 30% reduction at pH 6 and 10). The favored adsorptivity of these electronegative species onto the positively charged catalyst surface could explain these phenomena.

Experiments at two different temperatures (25 and 40 °C) were also carried out to detect any possible influence of that variable on the reaction rate. Fig. 4 shows the corresponding data. In this case there is a slight improvement for the higher temperature (0.40 ppm min^{-1} at 40 °C vs. 0.28 ppm min^{-1} at 25 °C). In any case the increase is too low if compared with typical Arrenhius behavior, and the global process could be considered as controlled by the charge transfer step, which is known to be very little affected by temperature [12,13].

As all oxidation processes, photocatalysis is based on the consumption of an oxidant, in the present case the O_2 in solution. O_2 reacts with the photogenerated conduction band electrons keeping the electrical neutrality in the TiO_2 particle. The concentration of O_2 could very well control the oxidation process and experiments were carried out in both air and pure O_2 atmospheres to look for such an effect. Fig. 5 shows very little difference when bubbling these two gases into the TiO_2 slurry, making clear that the amount of O_2 present in solution through all the experiments described so far was enough to

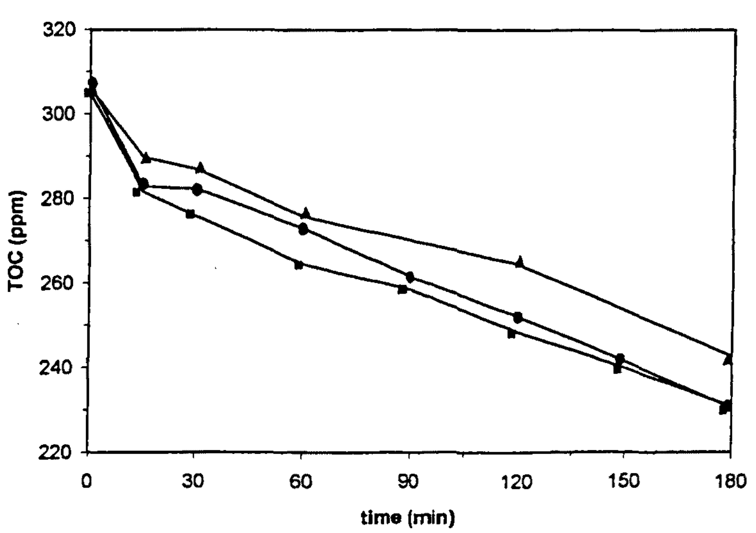

Fig. 3. Time course of TOC for three different initial pH values: pH 3 (▲), pH 6 (●), and pH 10 (■). AOD sequence effluent, 2 g l^{-1} TiO_2, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

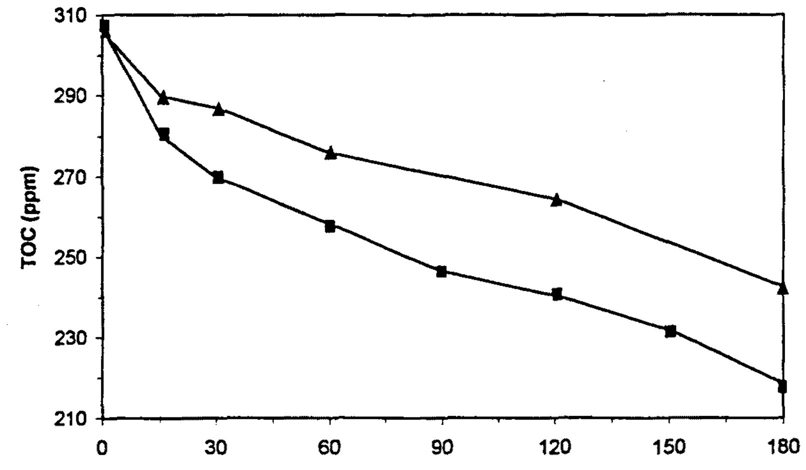

Fig. 4. TOC vs. reaction time data of experiments at 25 (▲) and 40 °C (■). AOD sequence effluent, 2 g l^{-1} TiO_2, pH ≈ 3, air flow 60 ml min^{-1}, $9.2\times10^{-}$ einstein min^{-1}.

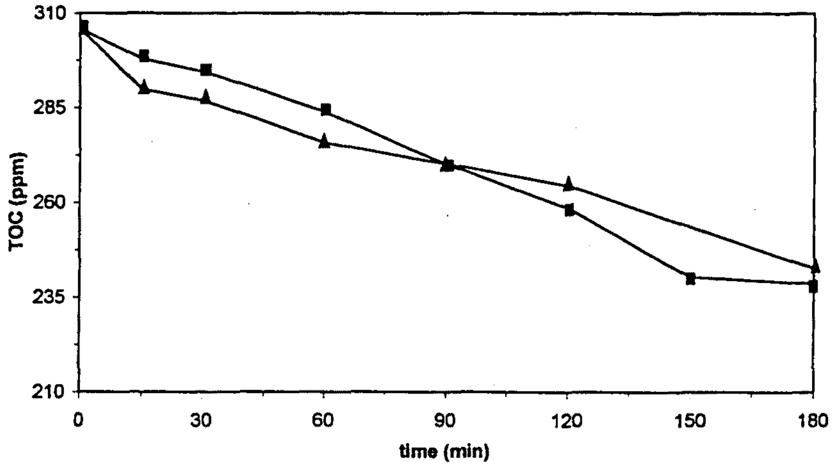

Fig. 5. TOC-time course under two different atmospheres: air (▲) and pure O_2 (■). AOD sequence effluent, 2 g l^{-1} TiO_2, pH = 3, gas flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

saturate the system so that O_2 reduction could not be considered a rate-limiting step. AOX and color reduction behave differently. 55% AOX reduction was attained after only 3 h reaction in the presence of pure O_2, 5 h being necessary to remove the same amount in air atmosphere. On the other hand, while 24% color reduction was obtained after 3 h in O_2 atmosphere, only 20% decrease in this parameter was detected within 8 h of reaction in air atmosphere.

The reaction efficiency for a higher initial contaminant load was examined. To accomplish this a new sequence of paper mill effluent generation was followed, which omits the acidification and O_2 treatment of the paper pulp. The values of the analytical parameters for this effluent were as follows: 1380 ppm TOC, 3700 mg O_2 l^{-1} COD, 69.8 ppm AOX, and 7030 color units. Fig. 6 shows the TOC-time course when two different amounts of TiO_2 (2 and 6 g l^{-1}) were used to prepare slurries for irradiation. Again, the slopes are similar and constant in time, indicating that for this contaminated solution no change is observed in the kinetics of heterogeneous photocatalysis. Only a small increase in reaction rate is noticed when comparing the slopes of these curves with those depicted in Fig. 1 (0.4 ppm min^{-1} and 0.25 ppm min^{-1} respectively).

Finally, a long term irradiation was carried out to ascertain whether the system could undergo complete mineralization and how that would take place. Fig. 7 shows the data collected during that experiment. As is indicated on the figure, three zones of different kinetic behavior are noticed. The narrow band of a few minutes at the beginning of the reaction is due, as previously indicated, to the existence of a dark adsorption onto the catalyst surface. The central zone, which includes the subsequent 500 min is characterized by a zero order. From that moment the reaction rate slows down, being difficult to assign a reaction order. The zero order behavior can be explained by considering that most water phase photocatalytic oxidations described in the literature so far follow the Langmuir–Hinshelwood (LH) equation [14]:

$$r=\frac{kK[\mathrm{A}]}{1+K[\mathrm{A}]} \qquad (1)$$

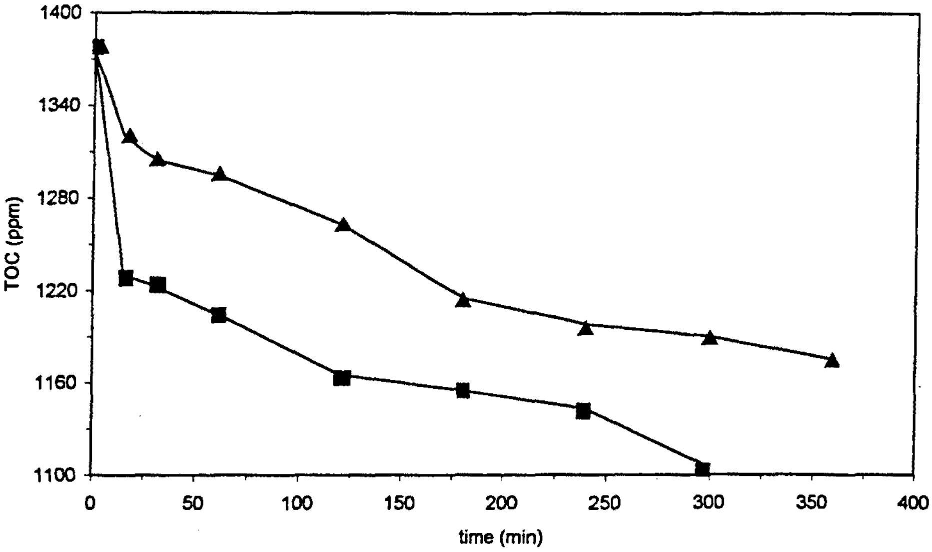

Fig. 6. TOC vs. reaction time for two different catalyst loads: 2 g l^{-1} (▲) and 6 g l^{-1} (■). D sequence effluent, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

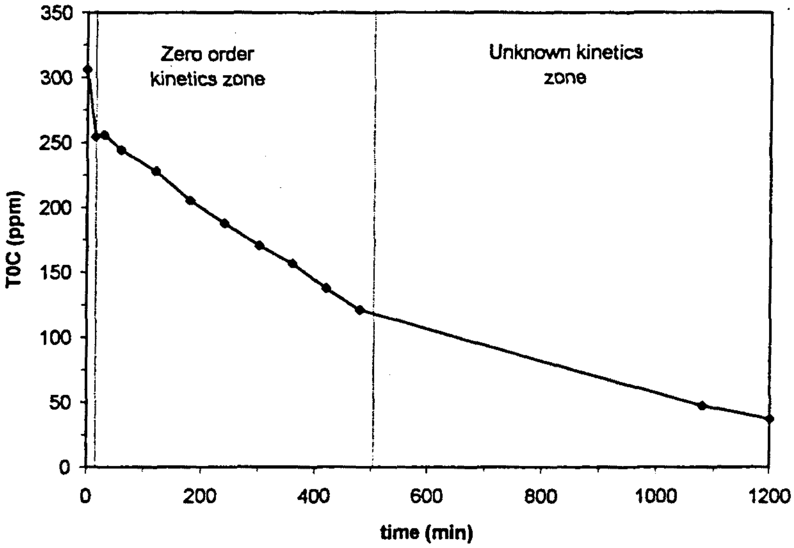

Fig. 7. TOC vs. time for a long term irradiation experiment. AOD sequence effluent, 2 g l^{-1} TiO_2, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

where [A] is the reactant concentration (in the present case a mixture of species which is summarized as TOC), K is the adsorption constant of that species onto the TiO_2, and k is the rate constant of the charge transfer reaction itself. If the $K[A]$ product is large enough then $1+K[A]\approx K[A]$ and

$$r=k \qquad (2)$$

This can be the situation when treating paper pulp bleaching effluents: a large concentration of organics (most cases where the LH equation has been applied correspond to a few ppm of organics in solution) and a noticeable adsorption constant. The TiO_2 is rapidly saturated by the TOC containing species so that the surface reaction sees a nearly constant concentration of organics during the central part of the process.

Several reasons can explain the decrease in reaction rate for long irradiation times: the decrease in TOC itself, which would cancel the condition of a large $K[A]$ mentioned above, competition for the surface active sites between reactant and intermediate species, aging of the catalyst surface, agglomeration of particles, changes in pH, etc.

4. Conclusions

Photocatalytic oxidation can efficiently reduce the organic content of contaminated water generated during the pulp bleaching step of the paper making process. During the initial minutes of the reaction the decrease in TOC is due purely to dark adsorption onto the surface of the TiO_2 solid catalyst. The extent of this adsorption depends on the amount of catalyst in contact with the solution, but no important influence of such an experimental parameter was noticed during the photocatalytic process. The light intensity reaching the reaction vessel has an effect on the reaction rate only when levels of photons below 30% of the lamp full output are considered. Neither pH nor temperature have a remarkable influence on the photocatalytic process after the initial dark adsorption has taken place. A 4–5 fold increase in organic content produces only a slight improvement in the reaction rate, and the kinetics of TOC removal during the central part of the process follows a zero order equation; this behavior has been explained as a particular case of the most general Langmuir–Hinshelwood equation. Other interesting contamination indexes, such as COD, AOX and color are systematically reduced during photocatalysis. However, some quantitative divergences arise when comparing the uniformity of these reductions for the different parameters along the experiments.

Acknowledgements

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References

[1] P.F. Earl, D.W. Reeve, Tappi J. (1990) 179.
[2] C. Rappe, S. Swanson, B. Glas, K.P. Kringstad, F. DeSousa, L. Johansson, Z. Abe, Pulp Paper Canada 90 (1989) T273.
[3] T.Y. Tsai, J.J. Renard, R.B. Phillips, Tappi J. 77 (1994) 149.
[4] S.A. Heimburger, D.S. Blevins, J.H. Bostwick, G.P. Donnini, Tappi J. (1988) 51.
[5] S.A. Heimburger, D.S. Blevins, J.H. Bostwick, G.P. Donnini, Tappi J. (1988) 69.
[6] D.G. Wilson, M.F. Holloran, Pulp Paper Canada 93 (1992) T372.
[7] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[8] D.F. Ollis, in E. Pelizzetti and M. Schiavello (eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht, 1991.
[9] N. Serpone, E. Pelizzetti, H. Hidaka, Solar Energy Meet. IPS-9, Beijing, China, 1992.
[10] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[11] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1523.
[12] J. Kiwi, J. Phys. Chem. 89 (1985) 2437.
[13] J.S. Curran, J. Domènech, N. Jaffrezic-Renault, R. Phillipe, J. Phys. Chem. 89 (1985) 957.
[14] D.F. Ollis, E. Pelizzetti, N. Serponne, in: N. Serpone, E. Pelizzetti (eds.), Photocatalysis Fundamentals and Applications, Wiley, 1989, p. 603.

Paper 2

Removal of organic contaminants in bleached Kraft effluents using photocatalysis and ozone

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REMOVAL OF ORGANIC CONTAMINANTS IN BLEACHED KRAFT EFFLUENTS USING HETEROGENEOUS PHOTOCATALYSIS AND OZONE

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ABSTRACT

Heterogeneous photocatalysis and ozone treatment have been successfully used to remove low concentrations of organic and halo-organic contaminants in water. This study examines the use of ozone and the photocatalytic treatment for the destruction of organic pollutants in bleached kraft mill effluents (BKME). Reductions in the levels of AOX (adsorbable organic halogen), TOC (total organic carbon), COD (chemical oxygen demand), and color were used as indicators of organic contaminant removal. Two different BKMEs were obtained in a laboratory bench reactor under optimal conditions for the preparation of bleached hardwood pulp from Eucalyptus globulus. *One BKME was obtained from the D stage (100% ClO_2) of an elemental-chlorine-free (ECF) AOD bleaching sequence, while the other was obtained from the first D stage (100% ClO_2) in a conventional ECF sequence.*

INTRODUCTION

Nearly all of the environmental loading from a modern sulfate pulp mill originates during the first chlorination and the caustic extraction stages of the bleaching process *(1)*. These are responsible for the high levels of TOC (total organic carbon), COD (chemical oxygen demand), color, and chlorinated organics found in bleached kraft mill effluents (BKME). The presence of chlorinated organics in BKME has been recognized as an important environmental issue *(2–6)*. The chlorinated organic compounds are quantified by the surrogate parameter AOX (adsorbable organic halogen). AOX includes compounds that are mutagenic, toxic, and not readily biodegradable. Despite of the controversy about the use of AOX as an effluent quality parameter, the regulatory agencies are setting discharge limits for AOX.

In anticipation of pollution control legislation, kraft mills worldwide are preparing to meet the proposed regulations via two approaches:

1. In-plant process modifications such as extended delignification and substitution of chlorine in the bleaching stage by molecular oxygen, ozone, or hydrogen peroxide
2. Treatment of wastewaters by physical-chemical processes, including chemical oxidation (i.e., ozone).

Both aerobic and anaerobic biological treatment schemes have been applied to individual processes and total plant wastewaters. Indeed, the pulp industry is making a concerted effort to improve the applicability of physical-chemical treatments.

In this paper, we study the application of heterogeneous photocatalysis and ozone to destroy organic contaminants in BKMEs from the first D stage (100% ClO_2) of two ECF (elemental chlorine free) bleach sequences applied to kraft pulp from *Eucalyptus globulus*:

1. An AOD bleach sequence (acid pretreatment (A) followed by an oxygen delignification (O) and chlorine dioxide bleaching (D))
2. A conventional ECF bleach sequence (D(EO)D sequence)

These effluents were chosen because of their increasing prevalence in the production of bleached pulps *(7)*. In addition, the contaminant loads from these ECF bleach sequences are amenable to treatment, which will help pulp mills to comply with increasingly strict environmental regulations *(8)*.

Heterogeneous photocatalysis with TiO_2 has been successfully used in the laboratory to destroy low concentrations of organic and halo-organic contaminants in water. Many works concerning the treatment of organic synthetic samples can be found in the literature *(9–15)*. Other works have demonstrated the effectiveness of the photocatalysis procedure in removing organic BKME contaminants in the laboratory *(16–20)*. Sierka *et al. (20)* reported a combination of photocatalysis and ozone. Other techniques, such as filtration and biological treatment, have also been studied.

The aim of this work, and that of several recently published papers *(21–23)*, is to enhance the biodegradability of BKMEs by means of various combined advanced oxidation processes (AOP). An early work by Tanaka *et al. (24)*, dealing with samples of agricultural chemicals, reports the sequential application of photocatalysis and ozonation. More recently, several authors have demonstrated the beneficial effect of a combined ozone and photocatalytic treatment using synthetic samples at low concentrations *(25–32)*.

Heterogeneous photocatalysis involves the irradiation of a semiconductor such as titanium dioxide (TiO_2) with ultraviolet light below 390 nm. Natural (sunlight) or artificial (UV lamps) photon sources can be applied. The radiation stimulates electrons in the valence band of the TiO_2 particles suspended in the wastewater. The excited electrons jump to the conduction band, leaving holes in the valence band. Once formed, the electron (e^-) – hole (h^+) pairs can recombine to generate heat, or they can migrate to the TiO_2 surface and react with dissolved organic or inorganic species in water.

It has been postulated *(20, 21, 33–35)* that holes react with water and OH^- to produce hydroxyl radicals. The latter can completely oxidize organics (including halogenated organics) to water, carbon dioxide, and mineral acids. Electrons can react with dissolved oxygen to form superoxide anions (O^{-}_2) that eventually produce hydroxyl radicals ($OH^{\bullet}$). Electrons may also react with metals, causing their precipitation on the TiO_2 surface *(36–39)*. The external addition of oxidants such as ozone is expected to enhance the net production of radicals, a fact that would be sustained by increased rates of organic destruction, although the effectiveness of ozone by itself for oxidizing organic compounds is widely documented *(23, 37–44)*. Mansilla *et al. (21)* claim that addition of ozone to heterogeneous systems such as ZnO/UV minimizes the recombination of electron–hole pairs. The electron-withdrawing capacity of ozone can promote the generation of holes.

In this work, photocatalysis alone and in combination with ozonation has been applied to the previously described bleach-plant effluents. Fairly concentrated samples of BKME were treated by sequences of photocatalysis and ozonation or by simultaneous application of both techniques. In the case of the most contaminated effluent (from the first D stage of a (D(EO)D) bleach sequence), hydrolysis in basic media was carried out before the application of photocatalysis. Dorica *(45)* has reported the removal of organic chlorine from bleach-plant effluents using alkaline hydrolysis. In addition, Milosevich *et al. (46)* demonstrated that neutralization of bleach-plant effluent with lime mud, followed by the addition of an alkaline sulfide process liquor, was a practical, cost-effective method of reducing mill AOX discharge.

EXPERIMENTAL

The experiments were performed with laboratory effluents obtained from two ECF bleaching sequences:

- BKME1: collected from the D stage (100% ClO_2) of an AOD bleaching sequence
- BKME2: obtained from the first D stage (100% ClO_2) in a conventional (D(EO)D) bleaching sequence.

Both BKMEs (bleached kraft mill effluents) were obtained in a laboratory bench reactor under optimal conditions for the preparation of bleached hardwood pulp from *Eucalyptus globulus*.

We also worked with a modified BKME2 that was treated to reduce the load of organic contaminants. The modified effluent was obtained by subjecting the BKME2 to hydrolysis with $Ca(OH)_2$ (pH 12, during 1 h), which reduced TOC by 70%. This process — carried out at room temperature — has been described elsewhere *(42)*.

The semiconductor used was titanium dioxide (Degussa P. 25). It was predominantly anatase (80% anatase and 20% rutile), as shown by X-ray diffraction. The BET surface area of TiO_2, determined from nitrogen adsorption (Accusorb 2100 E Micromeritics), was 57.9 m^2/g. The average particle size, measured by scanning electron microscopy, was 30 nm.

The ozone generator — supplied by Carburos Metálicos S.A. — was equipped with power control via current settings. A working current of 1 A and a pressure of 0.5 bar were used. To ensure saturation of the system, an ozonized oxygen flow rate of 330 mL/min (1.5 g O_3/h) was employed.

Experiments were conducted in a thermostatic Pyrex cell with a capacity of 130 cm^3. The reaction mixture inside the cell was maintained in suspension by magnetic stirring. A 125-W

Philips HPK mercury vapor lamp was used as a light source. The IR fraction of the beam was removed by the water in the double jacket of the photoreactor. The intensity of the incident light inside the photoreactor, measured with a uranyl actinometer, was 9.2×10^{-5} Einstein/min.

In each experiment, a 100-mL volume of effluent of known pH was placed in the reactor, where the temperature and bubbling gas flow rate had previously been set. Air at an approximate flow rate of 60 mL/min was used. The flow rate was periodically controlled by using a Varian digital flowmeter. The required amount of semiconductor was weighed to the third decimal place on a Bosch S-2000 analytical balance and suspended in the reactor solution. Agitation and light source were switched on, and samples were periodically taken from the reactor by means of an ICO sterile 5-mL syringe and centrifuged on a Centromix S-549 centrifuge. The resulting sample was used to determine TOC. Then AOX, COD, and color were determined after passing the sample through a disposable membrane filter (Schleicher & Schuell) of 0.45-µm pore size. The membrane filter was tested to ensure that it was not reacting with or holding any of the products we were attempting to measure.

All AOX tests were performed according to SCAN W 9:89 and the method outlined by Torrades *et al.* *(47)* using a Euroglass ECS 2000 apparatus. The Hach COD test apparatus was used to measure all COD. We validated the Hach results based on results obtained using CPPA Standard Method H.3 (1991).

Total organic carbon (TOC) concentrations were measured on a Shimadzu TOC 5000. All color measurements were conducted in a double-beam spectrophotometer (SP8-300 Pye Unicam) at the wavelength of 465 nm using cuvettes of 10-mm light path, according to CPPS Standard Method H.5 *(48)*.

RESULTS AND DISCUSSION

The BKME1, obtained as described in the experimental section, had the following global parameter values: TOC = 306 mg/L; COD = 515 mg/L; AOX = 27.7 mg/L; and color = 250 c.u. (color units).

Figure 1 shows the changes in TOC after prolonged (20 h) photocatalytic treatment of BKME1 effluent in the presence of TiO_2. As can be seen, an 88% TOC reduction (from 306 to 36.9 mg/L) was obtained. A detailed analysis of the data shows three different zones of TOC removal. In the first minutes, an important decrease in TOC (100 mg/L, approx.) is noticed, largely due to dark adsorption of the organic contaminants onto the TiO_2 surface. Two experiments were carried out to verify that the initial decrease of TOC is a consequence of adsorption and saturation of the catalyst surface. A decrease of 3.2% in TOC was obtained after 15 min of stirring our effluent with TiO_2 in the dark. Longer reaction times did not produce further reduction. The same experiment under light irradiation produced an initial reduction of 5.3% of TOC values, followed by low decrease of TOC for longer reaction times.

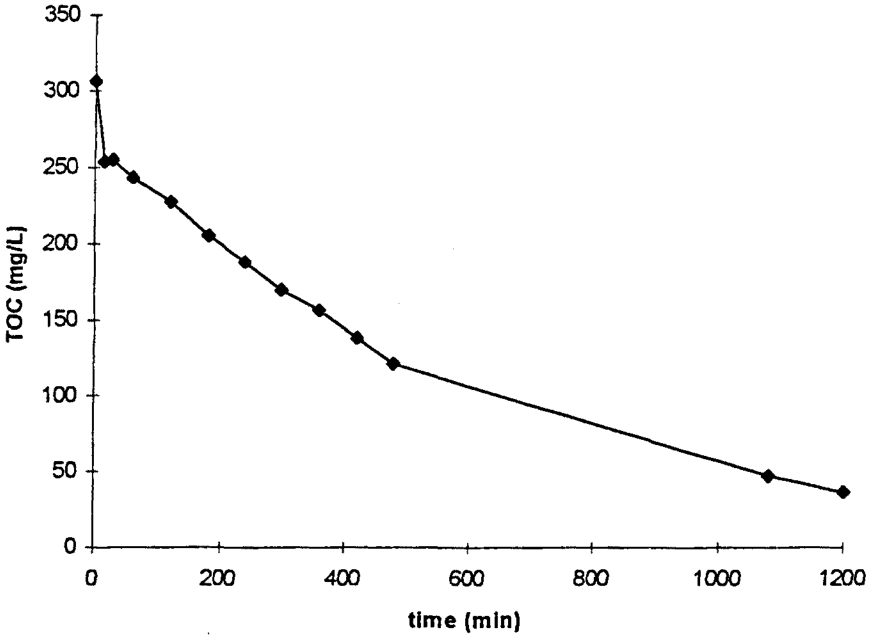

Figure 1. Decrease of total organic carbon (TOC) with run time for photocatalytic treatment of BKME1 effluent (run time = 20 h, [TiO₂] = 6 g/L, pH = 3, UV irradiation, air flow rate = 60 mL/min, T *= 25°C)*

After this initial TOC reduction, zero-order kinetics is observed. The zero-order behavior can be explained by considering the Langmuir–Hinshelwood mechanism of heterogeneous reactions in the presence of a large concentration of reactants *(49)*. For sufficiently long reaction times, the reaction slows down, and removal of the final remnants of TOC becomes difficult. The reductions obtained for the other reaction indicators were 100% in color, 92.5% in AOX, and 85% in COD. Thus, the TOC reduction is associated with a complete removal of colored compounds and a drastic degradation of the toxic halogenated compounds.

The BKME2, obtained as described in the experimental section, had the following global parameter values: TOC = 1380 mg/L; COD = 3700 mg/L; AOX = 69.8 mg/L; and color = 7030 c.u. Note that the BKME2 effluent is clearly more contaminated than BKME1.

The BKME2 effluent was also subjected to a prolonged (52 h) photocatalytic treatment with TiO_2. **Figure 2** shows changes in TOC during the reaction. A moderate 38% reduction in TOC (from 1380 to 857.3 mg/L) is observed over the 52-h reaction time. As in the case with BKME1, there is a large initial decrease in TOC (more than 200 mg/L) during the first 500 min, indicating the adsorption of dark organic matter onto the catalyst surface. Afterwards, the reaction slows down, and complete TOC removal from BKME2 seems too difficult to accomplish. The large differences in reactivity can be explained by the difference in initial TOC content for the two BKMEs. The high TOC content in BKME2 produces a large concentration of organic intermediates that remain on the TiO_2 surface and inhibit the degradation of the original compounds. The same should happen with the less-loaded BKME1, but almost complete TOC removal is obtained before the system is inhibited. The other reaction indicators — AOX, COD, and color — showed reductions of 50%, 57.5%, and 65%, respectively. These reductions are noticeably larger than the TOC reduction, demonstrating that color and AOX are mainly present in the compounds initially existing in solution.

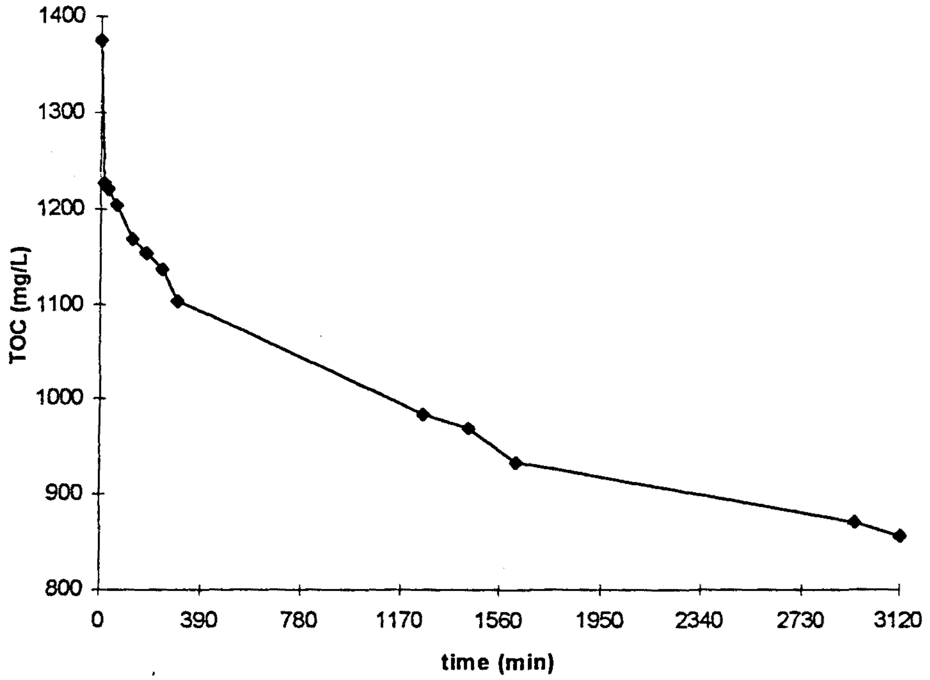

Figure 2. Decrease of total organic carbon (TOC) with run time for photocatalytic treatment of BKME2 effluent (run time = 52 h, [TiO_2] = 6 g/L, pH = 3, UV irradiation, air flow rate = 60 mL/min, T = *25°C)*

While the extent of TOC degradation in the BKME2 effluent is noticeable, photocatalytic treatment alone would be inadequate to comply with future environmental regulations *(8)*. Consequently, a combination of treatments is needed to ensure adequate degradation of the effluent.

Hydrolysis of BKME2 effluent followed by photocatalysis resulted in a 70% reduction of TOC (from 1380 to 417 mg/L). Alkaline hydrolysis involves a precipitation process that has a significant impact on contaminant removal, with precipitation accounting for about 50% of TOC reduction. The removal of the remaining TOC was assayed by simultaneous use of ozonation and photocatalysis. As pointed out earlier, recent works have shown that this combination can improve removal of TOC through the synergetic effects between the two oxidation techniques *(22–29)*. The beneficial consequences of such a combination can be envisaged from another perspective: O_3/UV (simultaneous use of O_3 and ultraviolet light) is a well-proven technique of BKME treatment, but the use of 254-nm UV light increases its running cost. The addition of TiO_2 (a cheap and stable catalyst) improves the ozonation yields while using less-energetic UVA photons.

In this way, after filtration of the precipitate and adjustment of the remaining aqueous phase to pH 3, the following sequences of treatment were tested on BKME2 effluent after alkaline hydrolysis:

- Photocatalysis followed by ozonation (Ph–O_3)
- Ozonation followed by photocatalysis (O_3–Ph)
- Simultaneous ozonation and photocatalysis (O_3+Ph).

The photocatalytic treatment in sequences Ph–O_3 and O_3–Ph lasted 150 min, and the ozonation treatment was 180 min. The simultaneous treatment (O_3+Ph) lasted 150 min. The results obtained in these experiments are shown in **Figure 3**. As can be seen, reductions of more than 80% of TOC are readily attainable with the three sequences, and the slopes of the curves suggest no difficulties in attaining further TOC reduction at longer reaction times. Data in Figure 3 show a major synergistic effect. The O_3+Ph sequence resulted in the same reduction of the contaminant load obtained in the sequences Ph–O_3 and O_3–Ph, but in a shorter time (150 min for O_3+Ph vs. 330 min for Ph–O_3 and O_3–Ph). This behavior has not been reported previously, and it seems of obvious interest from an applications point of view. It is also remarkable that previous photocatalytic treatment of the polluted samples favors the subsequent ozonation, as can be inferred from the difference of slopes of the ozonation curves in sequences O_3–Ph and Ph–O_3. The reduction of the reaction time implies less ozone demand and a consequent reduction in the cost of the global process.

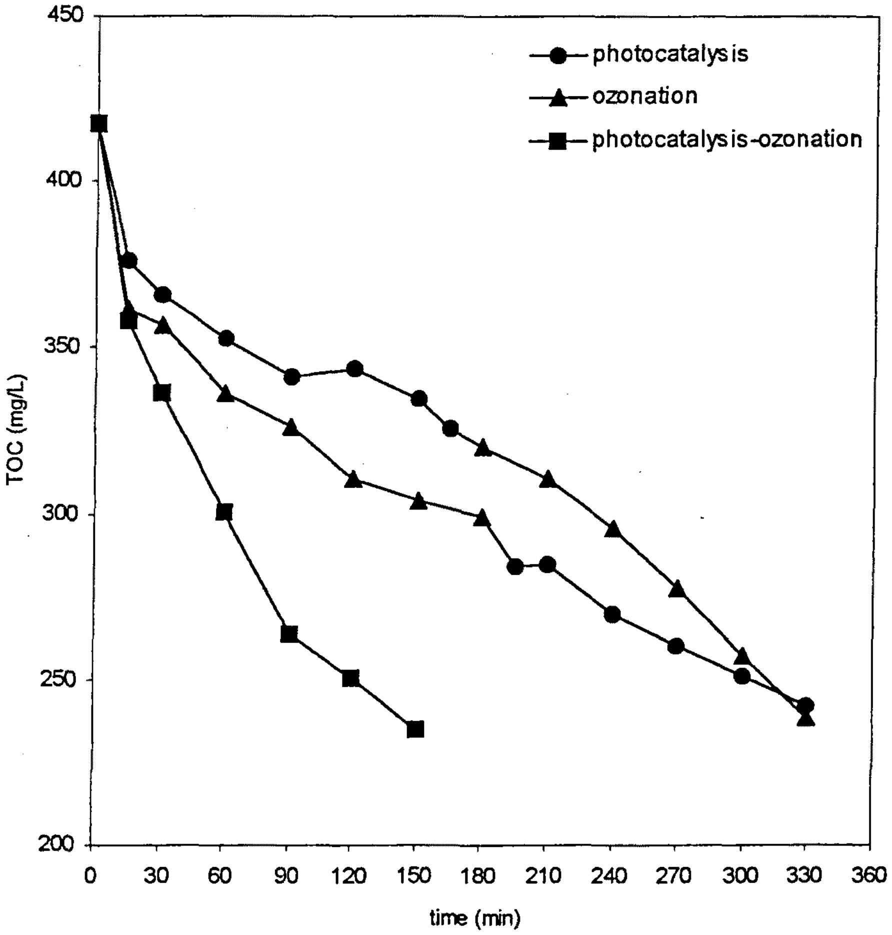

Figure 3. Decrease of total organic carbon (TOC) with run time for combined photocatalytic and ozonation treatments of BKME2 effluent (run time = 6 h, $[TiO_2]$ = 6 g/L, pH = 3, UV irradiation, 1.5 g O_3/h, air flow rate = 330 mL/min, T = ***25°C)***

The values of AOX and COD after the different treatments are given in **Table I**. In all cases, the reduction exceeded 85%. A fully decolorized effluent was obtained with each of the three sequences (O_3–Ph, Ph–O_3, and O_3+Ph).

	TREATMENTS [a]					
	Hydrolysis	O_3 (175 min)	O_3 – Ph (330 min)	Ph (150 min)	Ph – O_3 (330 min)	Ph + O_3 (150 min)
AOX, mg/L	23	10.33	8.59	14	7.81	9.87
Reduction [b], %	...	...	88	...	89	86
COD, mg/L	905	626	485	751	402	440
Reduction [b], %	...	...	87	...	89	88

[a] Ph: photocatalytic treatment; O_3: ozone treatment

[b] Including previous hydrolysis

Table I. Reduction of AOX and COD for various treatments of BKME2 effluent

CONCLUSIONS

Heterogeneous photocatalysis and ozone are known to be effective techniques for destroying low levels of organic pollutants in aqueous systems. This paper examines the capability of these techniques to destroy organic contaminants in bleached kraft mill effluents (BKME). A 20-h photocatalytic treatment removed all of the color and most of the TOC, AOX, and COD in a lightly loaded effluent obtained from the D stage (100% ClO_2) of an AOD bleach sequence. For an effluent with a higher contaminant load — like the one (BKME2) obtained from the chlorine dioxide (bleaching) stage (D) in a conventional ECF sequence — the best treatment is the one that takes advantage of a previous hydrolysis and the synergistic effect of simultaneous photocatalysis and ozonation. Similar levels of TOC removal were obtained in the sequences hydrolysis–Ph–O_3 and hydrolysis–O_3–Ph, although for larger reaction times. The TOC, COD, and AOX reductions in the treated effluents were above 80% in all cases, and the effluents were always fully decolorized.

LITERATURE CITED

1. Välttilä, O., "Discharges from a modern kraft pulping process and their treatability with aerobic biological methods," *Proceedings of International Conference on Bleached Kraft Mills*, [PUBLISHER], [LOCATION OF PUBLISHER], Feb. 4–7, Melbourne, Australia, 1991.
2. Bonsor, N., McCubbin, N., and Sprague, J. B., "Kraft mill effluents in Ontario," Report to Technical Advisory Committee, Pulp and Paper Section of MISA, Ontario Ministry of Environment, Toronto, 1988.
3. Reeve, D. W. and Earl, P. F., *Pulp Paper Can.* 90(4): T128(1989).
4. Stromdahl, I. and Lovblad, R., *Svensk Papperstid.* 90(6): 52(1987).
5. Norrstrom, H., "Reducing the discharges to water — technical objectives," *Proceedings 2nd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1987.
6. Huber, L. and Baumung, H., "Requirements for the treatments of effluents from pulp mills in the FRG," *Proceedings 2nd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1987.
7. Pryke, D. C. and Mckenzie, D. J., *Pulp Paper Can.* 97(1): 27(1996).
8. Lescot, J. C. and Jappinen, H., *Appita* 47(4): 330(1994).

9. Hoffmann, M. R., Martin, S. T., Choi, W., and Bahnemann, D. W., "Environmental applications of semiconductor photocatalysis," *Chem. Rev.* 95: 69(1995).
10. Ollis, D. F., "Solar-assisted photocatalysis for water purification: Issues, data, questions," in *Photochemical Conversion and Storage of Solar Energy* (E. Pelizzetti and M. Schiavello, Eds.), Kluver Academic Publishers, Dordrecht, The Netherlands, 1991.
11. Serpone, N., Pelizzetti, E., and Hidaka, H., "Heterogeneous photocatalysis: Issues, questions, answers and successes," *Proceedings of 9th International Conference on Solar Energy, IPS-9* (Z. W. Tian and Y. Cao, Eds.), International Academic Publishers, Beijing, China, 1992, pp. 33–73.
12. Ollis, D. F., Pelizzetti, E., and Serpone, N., *Envir. Sci. Technol.* 25: 1523(1991).
13. Fox, M. A. and Dulay, M. T., *Chem. Rev.* 93: 341(1993).
14. Matthews, R. W., *Solar Energy* 38: 405(1982).
15. *Homogeneous and Heterogeneous Photocatalysis* (E. Pelizzetti and N. Serpone, Eds.), Dordrecht Reidel, Amsterdam, 1986.
16. Ollis, D. F., *Envir. Sci. Technol.* 19(6): 480(1985).
17. Okamoto, K., Yamamoto, H., Tanaka, M., and Itaya, A., *Bull. Chem. Soc. Japan* 58: 2015(1985).
18. Matthews, R. W., *Water Res.* 20(5): 569(1986).
19. Turchi, C. S., Edmundson, L., and Ollis, D. F., *Proceedings of 5th International Symposium on Wood and Pulping Chemistry*, TAPPI PRESS, Atlanta, 1989.
20. Sierka, R. A. and Bryant, C. W., *Photocatalytic Purification and Treatment of Water and Air* (D. F. Ollis and H. Al-Ekabí, Eds.), Elsevier Science, New York, 1993, p. 275.
21. Mansilla, H. D., Yeber, M. C., Freer, J., Rodríguez, J., and Baeza, J., *Water Sci. Technol.* 35(4): 273(1997).
22. Yeber, M. C., Rodríguez, J., Freer, J., Baeza, J., Durán, N., and Mansilla, H. D., *Chemosphere* 39(10): 1679(1999).
23. Yeber, M. C., Rodríguez, J., Baeza, J., Freer, J., Zaror, C., Durán, N., and Mansilla, H. D., *Water Sci. Technol.* 40(11): 337(1999).
24. Tanaka, K., Abe, K., Sheng, C. Y., and Misanaga, T., *Envir. Sci. Technol.* 26(12): 2534(1992).
25. Sánchez, L., Peral, J., and Domènech, X., *Appl. Catal., B* 19(1): 59(1998).
26. Tanaka, K., Abe, K., and Misanaga, T, *J. Photochem. Photobio. A* 101: 85(1996).
27. Muller, T. S., Sun, Z., Kumar, G., Itoh, K., and Murabayashi, M., *Chemosphere* 36: 2043(1998).
28. Klare, M., Waldner, G., Bauer, R., Jacobs, H., and Broekaert, J. A. C., *Chemosphere* 38: 2013(1999).
29. Hay, S. and Obee, T. N., *J. Adv. Oxidation Technol.* 4: 209(1999).
30. Krapfenbauer, K. and Getoff, N., *Radiat. Phys. Chem.* 55: 385(1999).
31. Rivas, L., Bellobono, I. R., and Ascari, F., *Chemosphere* 37: 1033(1998).
32. Gratson, D. A., Nimlos, M. R., and Wolfrum, E. J., "Photocatalytic oxidation of gas-phase BTEX-contaminated waste streams," *Air Waste Management Association Annual Meeting Proceedings*, 4B(88): 11(1995).
33. Prairie, M. R., Evans, L. R., and Martinez, S. L., "Destruction of organics and removal of heavy metals in water via TiO_2 photocatalysis," *Chemical Oxidation: Technology for the Nineties, Second International Symposium*, Technomic, Lancaster, PA, 1994, pp. 428–441.
34. Fox, M. A., *Acc. Chem. Res.* 16: 314(1983).
35. Matthews, R. W., *J. Catalysis* 111: 264(1988).
36. Clark, W. C. and Vonjijidis, A. G., *J. Catalysis* 4: 691(1965).
37. Mollers, F., Tolle, H. J., and Memming, R., *J. Electrochem. Soc.* 121: 1160(1974).

38. Netzer, A. and Bowers, A., *1st International Symposium on Ozone for Water and Wastewater Treatment*, International Ozone Assn., Vienna, 1975.
39. Prengle, H. W., *Hydrocarbon Proc.* 10: 82(1975).
40. McGuire, M. L., *Ozone Technology Symposium Proceedings*, International Ozone Institute, Los Angeles, 1978.
41. Macur, G. J., *35th Industrial Waste Conference Proceedings*, [PUBLISHER], [LOCATION OF PUBLISHER], West Lafayette, 1981.
42. Coburn, L. A., Englande, A. J., Lockwood, M. P., and Collins, T., "Kraft bleach plant effluent by ultraviolet/oxidation process," *TAPPI 1984 Environmental Conference Proceedings*, TAPPI PRESS, Atlanta, p. 277.
43. Herberl, R., Urban, W., Gehringer, W., and Szinovatz, W., "Research on biological and advanced treatment of pulp-bleaching effluents," *Proceedings 3rd IAWPRC Symposium on Forest Industry Wastewaters*, Pergamon Press, Oxford, UK, 1991.
44. Saunamaki, R. and Sorvari, J., *Nordic Pulp Paper Res. J.* 7(3): 113(1992).
45. Dorica, J., *J. Pulp Paper Sci.* 18(6): 231(1992).
46. Milosevich, G. M. and Hill, D. A., *Pulp Paper Can.* 93(3): 61(1992).
47. Torrades, F., Riva, M. C., Torres, S., Garcia Hortal, J. A., Domènech, X., Peral, J., and Pérez, M., *Anal. Chim. Acta* 333: 139(1996).
48. CPPA Standard Method H.5, "Color of pulp mill effluents" (revised Aug. 1993), Canadian Pulp and Paper Association, Montreal.
49. Ollis, D. F., Pelizzetti, E., and Serpone, N., in *Photocatalysis Fundamentals and Applications* (N. Serpone and E. Pelizzetti, Eds.), Wiley, New York, 1989, p. 603.

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Paper 3

Removal of organic contaminants in paper pulp effluents by AOPs. Economic study

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Abstract

The degradation of the organic content of a bleaching Kraft mill effluent was carried out by using Advanced Oxidation Processes (AOPs). The study was focused in the identification of the AOP, or combination of AOP's, that exhibit the higher efficiency along with the lower economical requirements. Direct UV photolysis (UV), TiO_2 assisted-photocatalysis (TiO_2/UV), Fenton, Fenton-like, and photo-Fenton reactions (Fe(II)/H_2O/UV), UV-assisted ozonation (O_3/UV) and addition of Fe^{2+} and/or H_2O_2 to the TiO_2/UV and the O_3/UV systems, were used for the degradation of a cellulose conventional bleaching effluent. The effluent was characterized by the general parameters TOC, COD and color, and analyzed for chlorinated low molecular weight compounds using GC-MS. The costs of the above mentioned systems per unit of TOC reduction were compared.

***Keywords*:** Cellulose bleaching effluent, Chlorinated phenols, Photocatalisis, Ozonation, Fenton reaction.

Introduction

Kraft mill industry generates large quantities of wastewaters. Paper pulp bleaching effluents contain high concentrations of organic matter,[1] in particular chlorinated phenols and polyphenolic compounds, most of them difficult to eliminate by conventional wastewater treatment processes.[2-3] Due to their toxicity, bioaccumulation and carcinogenic potential,[4] these compounds are a serious threat to the environment.

An effluent coming from the chlorination stage (Cl_2/ClO_2, 20% of ClO_2 sustitution) of the conventional bleaching sequence applied to kraft pulp from 90% of *Eucalyptus globulus* and 10 % of *Eucalyptus grandis* was chosen.

Recent progress in chemical water treatment has lead to the development of Advanced Oxidation Processes (AOP's). These processes involve the generation and use of the highly oxidative OH radical (2.8 V vs. NHE), in order to oxidize almost all organic pollutants present in cellulose mill effluents. The most widely known AOPs include: heterogeneous photocatalytic oxidation,[5-8] treatment with ozone (often combined with H_2O_2, UVA, or both and even with heterogeneous photocatalytic processes),[9-12] Fenton,[13-15] Fenton-like,[16] and Photo-Fenton reactions.[17-22]

The high electrical energy demand and the consumption of chemical reagents are common problems among all the AOPs.[3] Either generation of O_3 or the production of photons with artificial light sources require an important energy input. Therefore the total costs of these processes are usually high.

The purpose of this research is to apply the different AOPs and its combinations to the treatment of bleaching kraft mill effluents in order to reduce the amount of organic contaminants presents in the industrial wastewater at the minimum cost. One factor that must be considered is that treatment of the effluent is required to comply with environmental legislation.[23]

Photocatalysis

Photocatalysis is based on the production of electron-hole pairs (equation (1)) by illumination with light of band gap energy ($\lambda < 380$ nm for TiO_2) of a semiconductor powder dispersed in an aqueous medium.

$$TiO_2 + h\upsilon \rightarrow h^+_{bv} + e^-_{bc} \qquad (1)$$

These charge carriers migrate to the particles surface and react with adsorbed species of suitable redox potential. The main reactions of this process are summarized in equations (2)-(4):

$$h_{bv}^{+} + H_2O_{ads} \rightarrow OH^{\bullet} + H^{+} \qquad (2)$$
$$h_{bv}^{+} + OH_{ads}^{-} \rightarrow OH^{\bullet} \qquad (3)$$
$$e_{bc}^{-} + O_2 \rightarrow O_2^{\bullet -} \qquad (4)$$

Despite photocatalysis has shown to be adequate for the degradation of a wide variety of compounds, the process is only efficient for rather diluted effluents, and involves large energy consumptions.[5, 24] Many authors try to enhance the process adding reagents with different chemical roles such as H_2O_2, O_3, Fe (II), Fe (III).[25-26]

Ozonation

The application of ozone in wastewater treatment is a well-known technique and research field.[9-12] The mechanism of organic matter oxidation by O_3 has been carefully studied by Hoigne et al.[27-29]

Ozone could react with the organic load present in the wastewater in two different ways: (a) direct reaction with the O_3 molecule, (b) indirect reaction with OH radicals produced after O_3 degradation. The decomposition of the O_3 molecule can be achieved in different ways: at basic pH, under UV irradiation, with the use of additives like Fe(II), etc.

The OH radicals yield calculated by Hoigné et.al., is 0.65 molecules of $OH^{\bullet}$ for every molecule of ozone decomposed. Since the oxidative power of OH radical (2.8 V vs. NHE) is higher than the oxidative power of ozone (2.08 V vs. NHE), O_3 is a more efficient oxidant when the experimental conditions favor its degradation to $OH^{\bullet}$.

The mechanism of O_3 decomposition in presence of UV light has been studied by Peyton et al.[30]

Fenton and Photo-Fenton reactions

The Fenton reaction is a combination of Fe^{2+} and H_2O_2 with production of $HO^{\bullet}$, and is a well-known technique of organic matter degradation that has experienced an important growth in the number of practical applications in recent years.[13-15] The generally accepted reaction for $HO^{\bullet}$ formation is:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \qquad k = 76.5\ l\cdot mol^{-1}\cdot s^{-1} \qquad (5)$$

If H_2O_2 is in excess, it can react with Fe(III) species to regenerate Fe(II) (Fenton-like reaction):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad (6)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (7)$$

giving rise to a catalytic process for H_2O_2 degradation and $HO^{\bullet}$ formation.

The presence of UV-Vis light can enhance the recovery of Fe^{2+} through the photo-Fenton process:

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + HO^{\bullet} \qquad (8)$$

Light can also favour organic matter degradation by driving direct photolysis processes of the complexes formed between Fe^{3+} and organic intermediates (most probably carboxylic acids). Nevertheless, recent works have shown that the species responsible for organic matter attack in the Fenton process and for light absorption in the photo-Fenton process is a high valence iron transient.[18-19]

Experimental

The effluents were the aqueous refuse of the chlorination step of the bleaching sequence $(D_{20}C_{80})(EO)D_1D_2$ applied to Kraft paper pulp of *Eucalyptus globulus* (90%) and *Eucalyptus grandis* (10%), which was supplied by an Spanish paper manufacturer. In order to reduce the level of organic contaminants hydrolysis of the wastewaters with $Ca(OH)_2$ (pH=12, 1 hour) was carried out. After hydrolysis the effluent was stored at - 4°C.

The semiconductor used was titanium dioxide (Degussa P. 25). It was predominantly anatase (80% anatase and 20% rutile), as shown by X-ray diffraction. The BET surface area of TiO_2, determined from nitrogen adsorption (Accusorb 2100 E Micromeritics), was 57.9 $m^2 \cdot g^{-1}$. The average particle size, measured by scanning electron microscopy, was 30 nm.

The rest of the chemicals used were, at least, of reagent grade. Analytical grade hydrogen peroxide and heptahydrated ferrous sulfate were purchased from Aldrich and Panreac, respectively, and were used as received. Solutions were prepared with deionized water obtained from a Millipore Mili-Q system.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of reagents, was continuously stirred with a magnetic bar. In the main experiments the temperature was maintained at 25.0±0.1°C. A 6 W Philips black-light fluorescent lamp was used as light source. The intensity of the incident light inside the photoreactor, measured employing am uranyl actinometer, was $1.383 \cdot 10^{-9}$ Einstein·s^{-1}.

Ozone was produced by a Sander Labor-Ozonisator 301.7, fed with a pure oxygen stream. The resulting ozone and oxygen mixture was immediately bubbled through the bleaching effluent by means of a metallic diffuser. The generator is equipped with power control via current settings. A working current of 1 A and a pressure of 0.5 bar were used. An ozonized oxygen flow-rate of 330 mL·min^{-1} (1.5 g $O_3 \cdot h^{-1}$) was employed to ensure saturation of the system. The amount of ozone generated was determinated by iodometry.

Total organic carbon (TOC) of initial and irradiated samples was determined with a Shimadzu 5000 TOC analyzer. Color determination was carried out in a double beam SP8-300 Pye Unicam spectrophotometer at the wavelength of 465 nm, using 10 mm light path cells and referenced to a Pt-Co standard solution, according to the H.5 standard of the CPPA.[31] Chemical Oxygen Demand (COD) was determined by a standardized methodology (EPA 00340).

For the analysis of low molecular weight compounds dissolved in the effluent, a HP 6890 gas chromatograph equipped with a quadrupole HP 5973 mass selective detector was used. The GC-MS analysis was carried out with ionization of electronic impact (70 eV), and the spectra were recorded in the interval 40 – 600 amu. One liter of the sample was filtered with a Speedisk® membrane (J.T. Baker) following the EPA 525 procedure. Samples were reconstituted to 100 μL in dichloromethane and 1 μL was injected in the GC. Identifications were carried out with the aid of the data base library WILEY (275,000 spectra) and NIST (130,000 spectra) and with a customized database generated in our laboratory. A capillary column HP-5MS (5% Phenyl Methyl Siloxane) with the dimensions of 30 m, 250 μm, and 0.25 μm was used. The carrier was helium with a flow rate of 1.3 mL·min^{-1}. The temperature program used during the GC-MS analysis ramped as follows: 70 °C (3 min), 5°C·min^{-1} until 270 °C (30 min). The sample injection was carried out with a 0.6 min of splitless time at 250°C.

Results and discussion

High values of COD and TOC were found in the bleaching effluent after hydrolysis (see table 1). GC-MS analysis of the effluent allowed determination of the structure of some low molecular weight compounds. The mass spectra and the identified structures are shown in Table 2 and Figure 1, respectively. All the substances found show a high degree of chlorination, in good agreement with structures found and reported by other authors.[8,32] A large number of unidentified compounds and long chain acids also appeared in the chromatograms (not shown in table 2).

Table 1. *Initial characterization parameters of the bleaching Kraft mill effluent after hydrolysis pretreatment.*

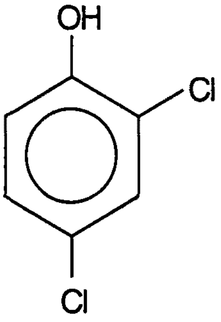
Parameter	Value
TOC (ppm)	441±8*
COD ($mg{\cdot}L^{-1}O_2$)	1384±24*
Color ($mg{\cdot}L^{-1}Pt$)	197±25*

*($n = 4$, $\alpha = 0.05$)

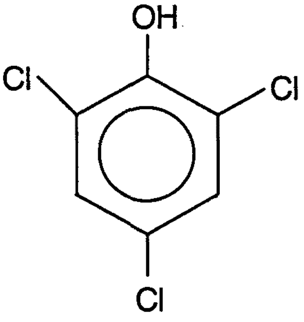
Table 2. *Low molecular weight compounds identified in the bleaching Kraft mill effluent after hydrolysis pretreatment.*

#[a]	rt[b]	mol wt	main fragments m/z (relative abundance)
1	10.09	162	166 (10), 164 (61), 163 (8), 162 (100), 126 (8), 100 (14), 99 (16), 98 (32), 63 (33), 62 (13), 61 (7)
2	15.03	196	200 (15), 198 (49), 196 (51), 162 (7), 160 (7), 158 (5), 132 (12), 99 (15), 97 (31)
3	18.25	192	196 (14), 194 (50), 192 (78), 181 (15), 179 (75), 177 (100), 151 (42), 149 (75), 113 (46)
4	20.60	226	230 (16), 228 (48), 226 (52), 215 (31), 213 (96), 211 (100), 187 (13), 185 (45), 183 (51), 149 (34), 147 (54), 121 (13), 119 (20)
5	24.88	260	266 (8), 264 (34), 262 (70), 260 (55), 251 (11), 249 (49), 247 (100), 245 (81), 223 (18), 221 (24), 219 (48), 217 (33), 185 (7), 183 (28), 181 (30)
6	25.16	256	260 (29), 258 (95), 256 (100), 245 (19), 243 (63), 241 (67), 215 (27), 213 (30), 202 (19), 200 (60), 198 (65), 197 (28), 195 (28)

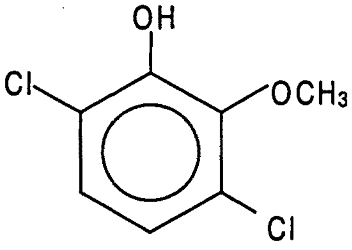
[a]compound number. [b]retention time, min.



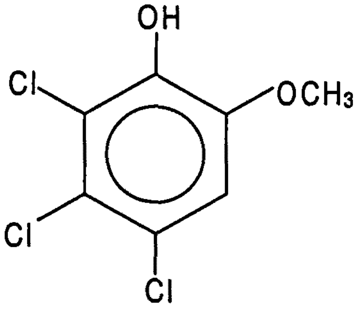
1: 2,4-dichlorophenol



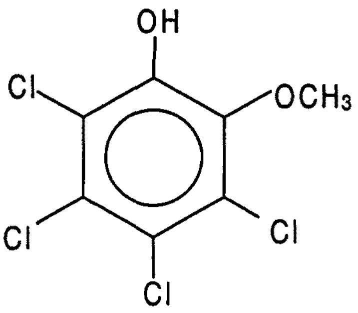
2: 2,4,6-trichlorophenol



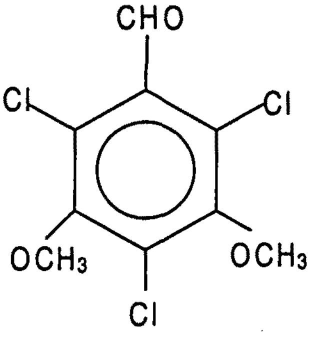
3: 3,6-dichloroguaiacol



4: 4,5,6-trichloroguaiacol



5: tetrachloroguaiacol



6: trichlorosyringol

Figure 1. *Structures of some low molecular weight compounds identified by CG-MS analysis of the bleaching effluent after hydrolysis treatment.*

The main purpose of this study is to compare the relative cost of treatment of bleaching efluents by different AOP's, in order to identify the best price/performance ratio. Due to inherent differences between the several AOP's compared here, the following conventions and considerations were taken:

1. The estimated cost of each process was assessed by the costs per kg TOC removed after 3 hours of treatment, and it will be accompanied with the percentage of TOC removal after that reaction time.
2. Only chemical and energy costs (retail dealer prices) were considered in the estimation. All other running costs and capital investments were simply ignored. Energy costs of running pumps and process control were also neglected.
3. The costs of additional operations like neutralization, filtration, required in some of the treatments were not included in the cost assessment.
4. Costs were obtained with non-optimized reactors. Fast reaction rates involve shorter residence times or smaller reactor volumes, as residence time is inversely proportional to the reactor volume. The same reactor volume was used for all AOP's.
5. Energy consumption at the laboratory scale is higher than at an optimized large-scale plant. However, this should no affect relative costs between AOP's.
6. In the Photocatalytic treatment the catalyst cost was neglected due to the fact that TiO_2 could be reutilized (at least a moderated number of times).[33]

All the processes studied in the present paper could be run under solar irradiation,[3,15] turning the irradiation cost into zero. Solar irradiation was not used in our experiments, but this should be an aspect of further research if costs are to be reduced.

Photocatalytic process

Figure 2 shows the time course of TOC for three different TiO_2 loads: 1, 2 and 6 $g{\cdot}L^{-1}$. After 3 hours of irradiation the TOC removal with the 6 $g{\cdot}L^{-1}$ TiO_2 load almost double the removal obtained with the 1$g{\cdot}L^{-1}$ load, but it is only slightly larger that the one obtained with the 2 $g{\cdot}L^{-1}$ load. The same behavior was observed when COD was determined. Color degradation after 3 hours of reaction was around 60 % in the three cases.

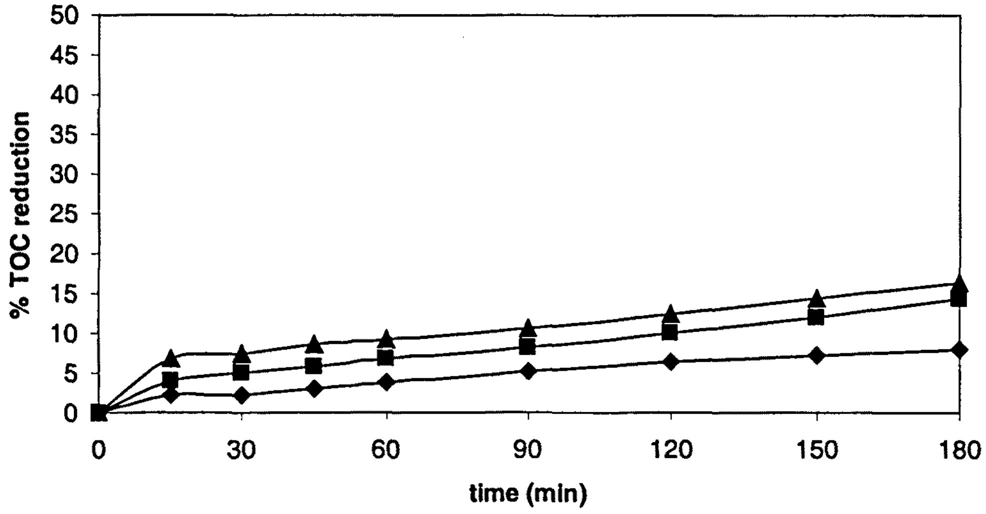


Figure 2. *Percentage of TOC reduction vs. time in a photocatalytic treatment with several TiO_2 loads: 1 g·L^{-1} (◆); 2 g·L^{-1} (■); 6 g·L^{-1} (▲).pH=3, T=25 °C, UVA irradiation*

The estimated treatment costs are shown in figure 3. As can be seen, the treatment with 2 g·L^{-1} of TiO_2 is the cheapest one.

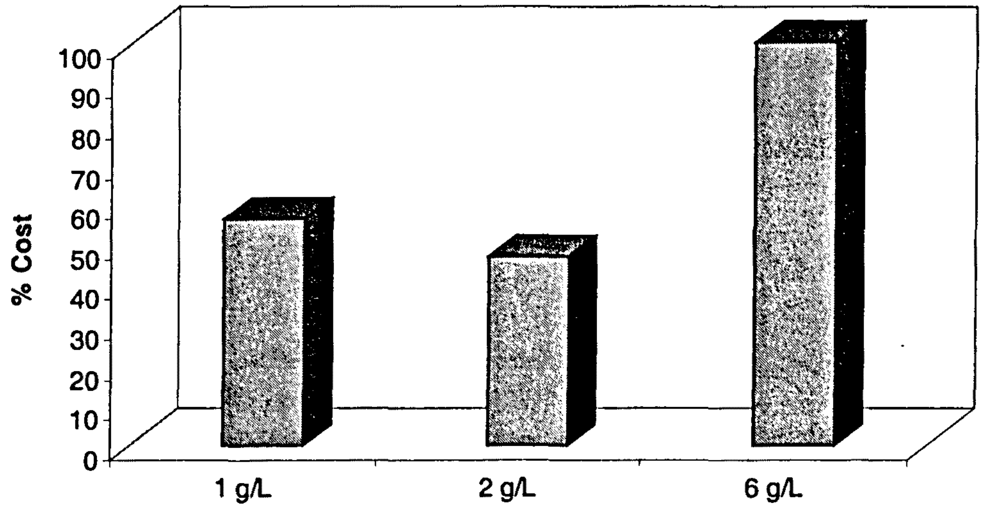


Figure 3. *Comparison of energy and chemical costs of photocatalytic process with several TiO_2 load.*

However, it has to be said that the TiO_2 catalyst can be recovered after treatment and reutilized a large number of runs. In that case, the costs of the two treatment with the larger amounts of catalyst would converge, being even more convenient in that case to use 6 g·L^{-1} of TiO_2 load because it renders a slightly higher reaction yield. As it has been pointed out above, from now on, when comparing photocatalysis with other treatment processes the price of the catalyst is not included in the cost estimation. An important aspect not considered here is the price of catalyst separation after the treatment. It is most likely that, for a large-scale plant, this cost would be lower the lower the catalyst load.

Direct Photolysis in presence of Fe(II)

Since the wastewaters treated in this work absorb light in the UVA region, direct photolysis could also lead to organic matter degradation. Direct photolysis in presence of several Fe(II) concentrations was tested. Iron species are known to form a variety of light absorbing complexes with organic matter, especially with carboxylic acid groups and, thus, their presence might potentially help the degradation process. The addition of Fe^{2+} to the solutions does improve the yield of TOC removal (data not shown).

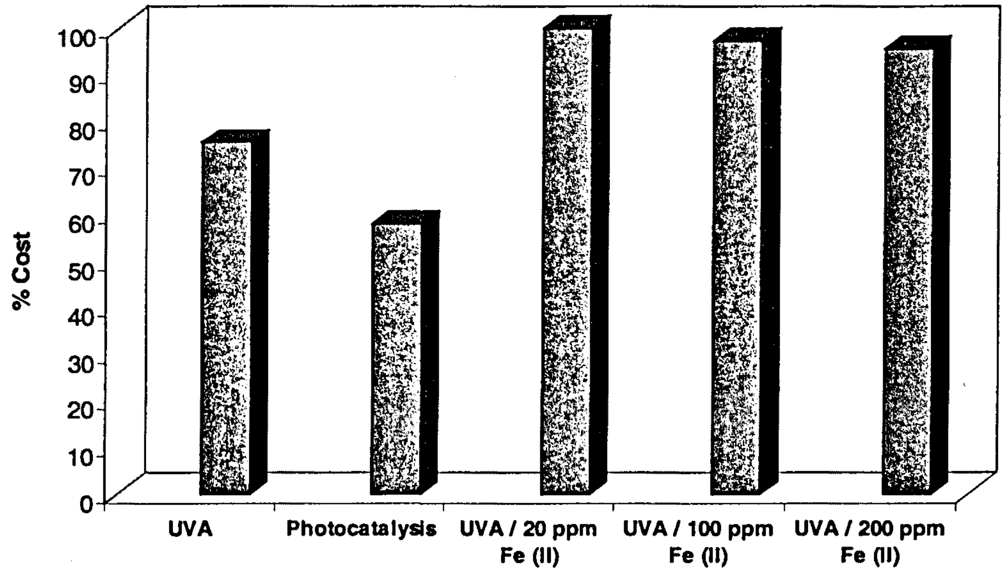


Figure 4. *Comparison of energy and chemical costs of photocatalytic, photolysis, and photolysis with different iron load.*

However, the comparison of the costs (figure 4) indicates that the use of Fe^{2+} is not worth it, since the improvement on TOC removal do not compensate the extra cost of the iron salt. It is worth to note that photocatalysis is cheaper (if the price of TiO_2 is not considered) than photolysis or photolysis in presence of Fe^{2+}.

Figure 5 compares the percentage of reduction of different parameters between photocatalysis and photolysis (no Fe^{2+} present). TOC and COD reduction are slightly higher for Photocatalysis, but the most marked difference between treatments is observed for the wastewater color. Photocatalysis reached around 50% reduction of this parameter after 3 hours of treatment, while photolysis produced more colored samples, as other author has previously noticed.[34] This fact is indicative of different reaction pathways and reaction intermediates that give different color to the treated samples.On the other hand, Fe^{2+} treated samples were highly colored, due to the complex species formed between organic matter and iron.

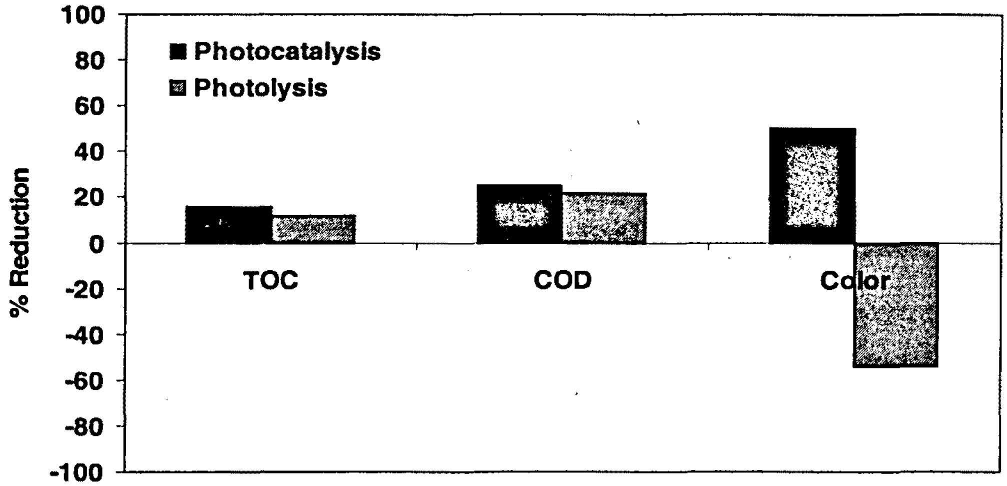


Figure 5. *Percentage of TOC, COD and color reduction after 3 hours photocatalytic or photolysis treatment.*

Effect of adding H_2O_2 on Photocatalysis

Several additives have been used to improve the yield of photocatalysis, among them H_2O_2. The reported role of H_2O_2 changes with concentration: at low concentrations H_2O_2 plays a beneficial role, while at high concentrations it becomes detrimental.[26,35] H_2O_2 is a better electron acceptor than O_2, it may be photo-split to directly produce $HO^{\bullet}$, but it may also absorb photons without producing reaction, thus competing with the photocatalyst for light absorption. It can also compete with the organic substrates for adsorption at the catalyst surface sites.

Figure 6 summarizes the results obtained during illumination of bleaching wastewater with 2 $g{\cdot}L^{-1}$ TiO_2 and in presence of H_2O_2 at several concentrations: 0, 10, 100, and 500 ppm. As can be seen, the increase of H_2O_2 initial concentration showed little effect upon long term TOC removal with only minor improvements of the initial reaction rate, especially for the higher H_2O_2 charge. The estimated costs are almost the same in the four cases. The mildly improvement achieve with the hydrogen peroxide addiction cannot compensate the increasing cost of the treatment.

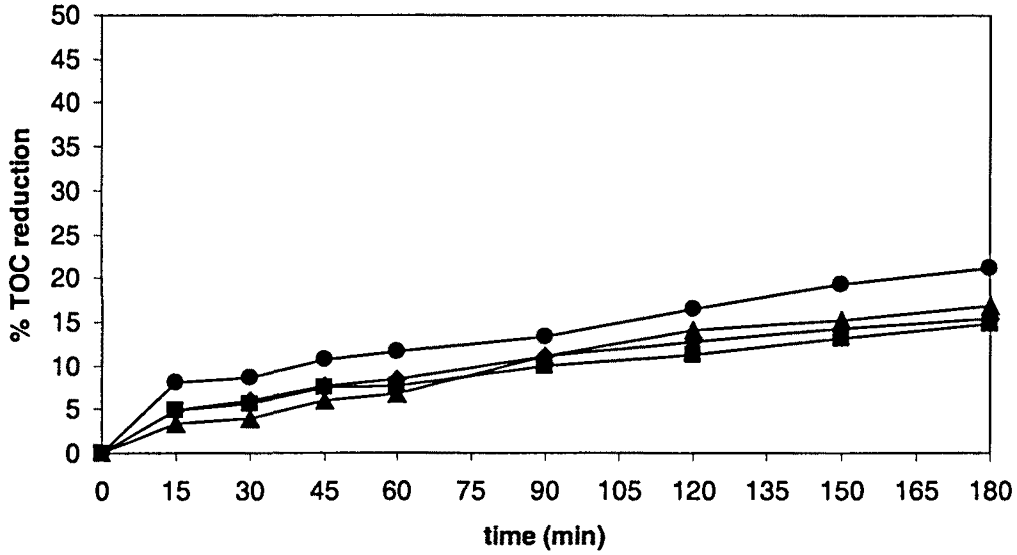


Figure 6. *Percentage of TOC reduction vs. time in a photocatalytic treatment in presence of 2 g·L^{-1} TiO$_2$ and several hydrogen peroxide charge: 0 mg·L^{-1} (◆); 10 mg·L^{-1} (■); 100 mg·L^{-1} (▲); 500 mg·L^{-1} (●); pH=3, T=25 °C, UVA irradiation*

Effect of adding Fe^{2+} and H_2O_2 on Photocatalysis

Another additive frequently used in several AOP's is Fe^{2+}. The Fe^{3+}/Fe^{2+} couple is formed by readily exchangeable redox species that can act as charge relay in many charge transfer processes. In the case of photocatalysis Fe^{2+} can also have a beneficial effect derived from its dopant role. Thus, experiments were carried out where photocatalysis of the paper pulp bleaching wastewaters in presence of Fe^{2+} and H_2O_2 was undertaken. Figure 7 shows gradual increase in TOC removal with increasing hydrogen peroxide load.

In all cases there is fast initial TOC decrease, most probably due to the occurrence of a Fenton reaction, a fast process if compared to photocatalysis alone time scales. The larger the initial H_2O_2 the fastest the initial TOC decrease. After such noticeable initial degradation the rate of TOC removal decreases and becomes almost constant.

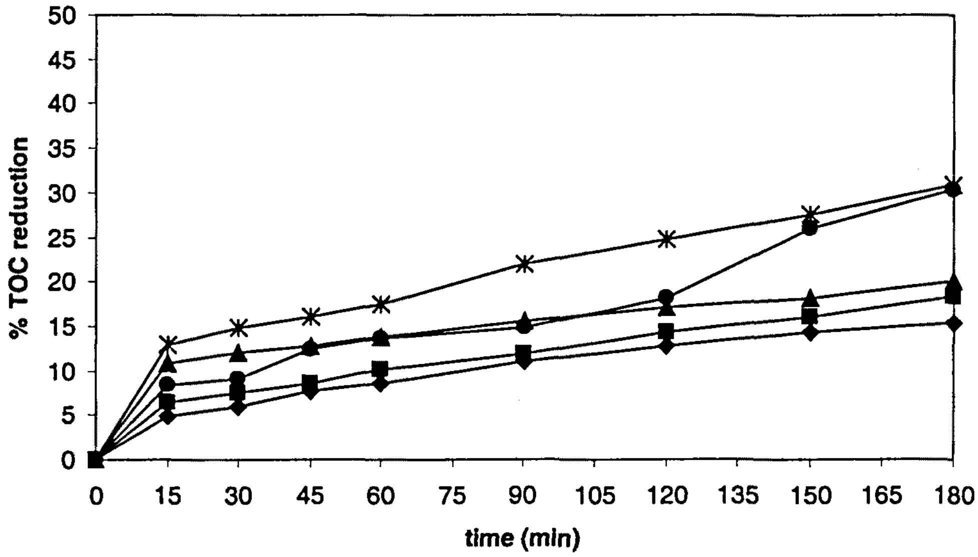


Figure 7. *Percentage of TOC reduction vs. time in the following treatments: Photocatalytic treatment in presence of 2 g·L^{-1} TiO$_2$ (◆). Photocatalytic treatment in presence of 2 g·L^{-1} TiO$_2$, 20 mg·L^{-1} of Fe^{2+} and several hydrogen peroxide loads: 10 mg·L^{-1} (■); 100 mg·L^{-1} (▲); 500 mg·L^{-1} (✳). Fenton and Photo-Fenton reaction with 20 mg·L^{-1} of Fe^{2+} and 500 mg·L^{-1} of H$_2$O$_2$ (●); pH=3, T=25 °C, UVA irradiation*

When comparing slopes in figure 7 with slopes in figure 2 it is clear that photocatalysis in presence of Fe^{2+} and H_2O_2 proceeds faster. The more plausible explanation of this improvement is the occurrence of Fenton-like and photo-Fenton processes, that lead to the regeneration of Fe^{2+} (the limiting reagent), and that in presence of an excess of H_2O_2 can sustain the Fenton reaction. In conclusion, from the experimental data no evidences exist for Fe^{2+} supported photocatalysis, and the observed TOC decrease seem to be the result of photocatalysis and Fenton system working in parallel.

When estimating the cost of the process (figure 8) there is an improvement due to the addition of Fenton reagent to photocatalysis, an improvement that is maximum when using the larger H_2O_2 concentration. However, figure 8 also shows the existence of minimal differences in cost between the system composed by simultaneous photocatalysis and Fenton and the Fenton system alone (see bellow for description of these experiments), i.e., photocatalysis brings no noticeable improvement to the reaction rate of the Fenton system (being precise the Fenton, Fenton-like, and photo-Fenton complex system).

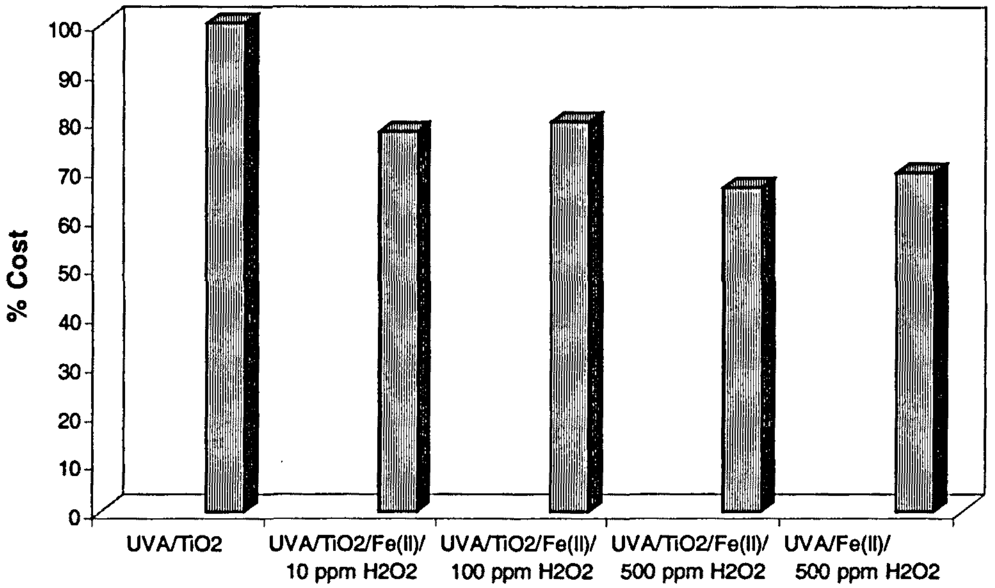


Figure 8. *Comparison estimative costs of various AOP's after 3 hours treatment per kg TOC removal.*

A comparison of bleaching effluent TOC removal within different AOP's treatments (TiO_2 / UV, TiO_2 / UV / H_2O_2, TiO_2 / UV / H_2O_2 / Fe^{2+}, UV / H_2O_2 / Fe^{2+}) is showed in figure 9.

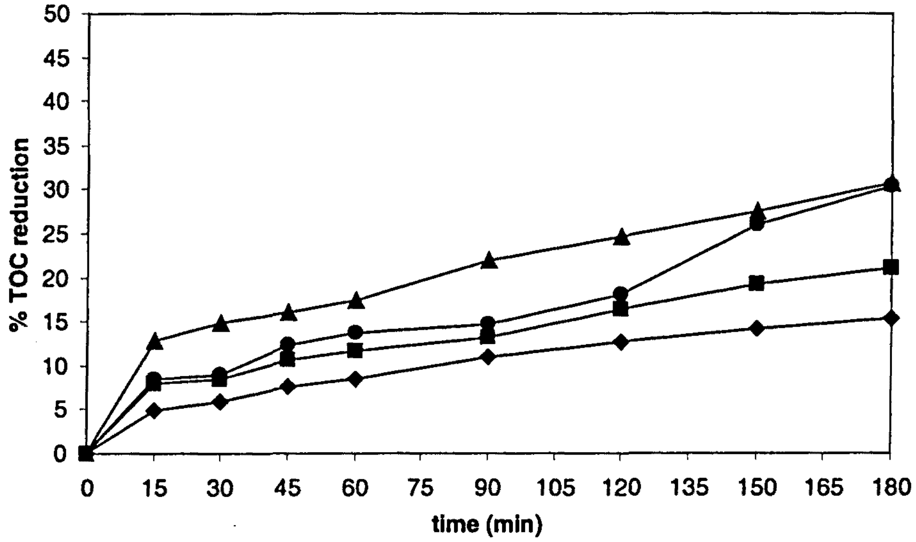


Figure 9. *Percentage of TOC reduction vs. time in the following treatments: photocatalytic treatment, 2 g·L^{-1} TiO_2 (◆). Photocatalytic treatment with 2 g·L^{-1} TiO_2 and in presence of 500 mg·L^{-1} hydrogen peroxide load (■); Photocatalytic treatment with 2 g·L^{-1} TiO_2, 20 mg·L^{-1} of Fe^{2+} and 500 mg·L^{-1} hydrogen peroxide load (▲); Fenton and Photo-Fenton reaction with 20 mg·L^{-1} of Fe^{2+} and 500 mg·L^{-1} of H_2O_2 (●); pH=3, T=25 °C, UVA irradiation*

As can be seen, for long-term reaction the best results are always obtained in presence of the Fenton reagent, although at shorter times some differences may arise when using Fenton reaction in presence or absence of TiO_2. It is clear that some of the reaction intermediates are better handled in presence of the photocatalyst.

Ozone and its combination with UV, Fe^{2+} and heterogeneous photocatalysis

In general, ozone treatment is able to reach high and fast TOC removal. However, it is a process that involves a high electrical demand along with an important consumption of chemicals. For this reason the estimated relative cost of ozonation is more than ten times higher than the rest of treatment costs assessed in this paper.

On the other hand, ozonation is highly effective: TOC reduction of the bleaching effluents reached with ozonation ranges from 50 to 80% after 3 hours. Meanwhile, for the same reaction time treatments like phototocatalysis achieve around 15 % of TOC degradation, as can be seen in figure 10 where the photocatalytic treatment is compared with ozonation in the dark and under UVA irradiation. The gradual decrease of TOC concentration with time observed for ozonation in the dark slows down at low organic loads, indicating the existence of a concentration dependent kinetics. On the contrary, ozonation in presence of irradiation produces a steady removal of TOC that seems to follow zero order kinetics.

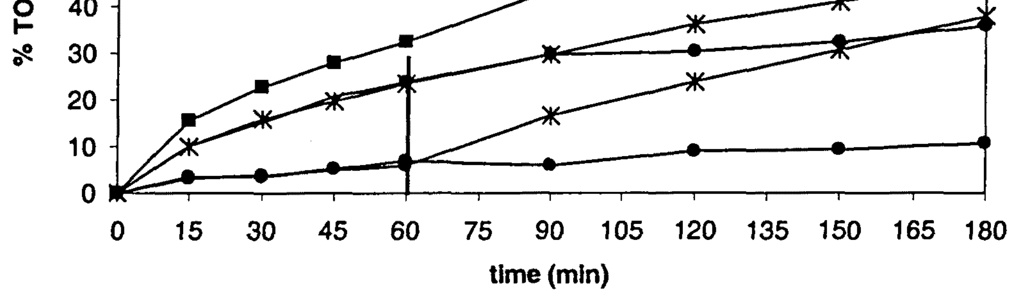


Figure 10. *Percentage of TOC reduction vs. time in the following treatments: photocatalytic treatment in presence of 2 $g \cdot L^{-1}$ TiO_2 (●); Ozonation under dark conditions (✳); Ozonation under UV irradiation (■). pH=3, T=25 °C.*

The combined effect of simultaneous photocatalysis and ozonation or the sequential application of both techniques has been recently studied[7, 9] and synergy between them has been detected. These combinations have been tested here for the degradation of organic matter in paper pulp bleaching effluents, trying to identify potential cost decreases associated with them.

A mechanistic explanation of the synergic efects detected when simultaneously combining ozonation and photocatalysis involves the formation of an ozonide radical anion ($O_3^{\bullet -}$) due to the conduction band electron scavenging ability of O_3. The following sequence of reactions have been proposed:[9-10]

$$O_3 + e^- (TiO_2\ cond.band) \rightarrow O_3^{\bullet -} \qquad (9)$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \qquad (10)$$

$$HO_3^{\bullet} \rightarrow O_2 + OH^{\bullet} \qquad (11)$$

This way of generating $OH^{\bullet}$ is highly effective at low pH, i.e., under the experimental conditions present in this study. Nevertheless, the experiments with simultaneous combination of O_3 and photocatalysis, data non shown here, did not show any noticeable improvement in TOC removal if compared to the ozonation under irradiation. A possible explanation of such result is that ozone could react with $OH^{\bullet}$[36] in competition with the organic matter, giving rise to a much less reactive radical species:

$$OH^{\bullet} + O_3 \rightarrow O_2 + HO_2^{\bullet} \qquad (12)$$

On the other hand, comparison of the reduction of other analytical parameters between the ozonation in absence or in presence of photocatalysis, shows similar COD reduction (around 80% in both treatments), and minor differences in color (more efficient the combined process), probably due to the role played by TiO_2 as adsorbent.

It is known that ozone reacts very efficiently with aromatic compounds.[37] This fact suggests that an ozonation pretreatment in the dark would be a convenient way to iniciate organic degradation, leaving wastewaters of lower organic content and amenable for photocatalytic treatment. Figure 10 shows that ozonization in the dark gives faster rates of TOC removal than photocatalysis alone, but when ozonation is interrupted (after one hour) and photocatalysis begins no improvement in the reaction rate is observed, i.e., similar behaviors are shown during the photocatalytic degradation with and without pretreament. When the inverse order is explored (one hour of photocatalys followed by ozonation in absence of UVA light) it appears again that no important differences arise between ozonation (in the dark or under UVA irradiation) with and without photocatalytic pretreatment.

In order to check whether the improvement of TOC removal when combining ozonation and photocatalysis has direct consequences in the estimation of the relative treatment cost of theses processes, they have been calculated and presented in figure 11.

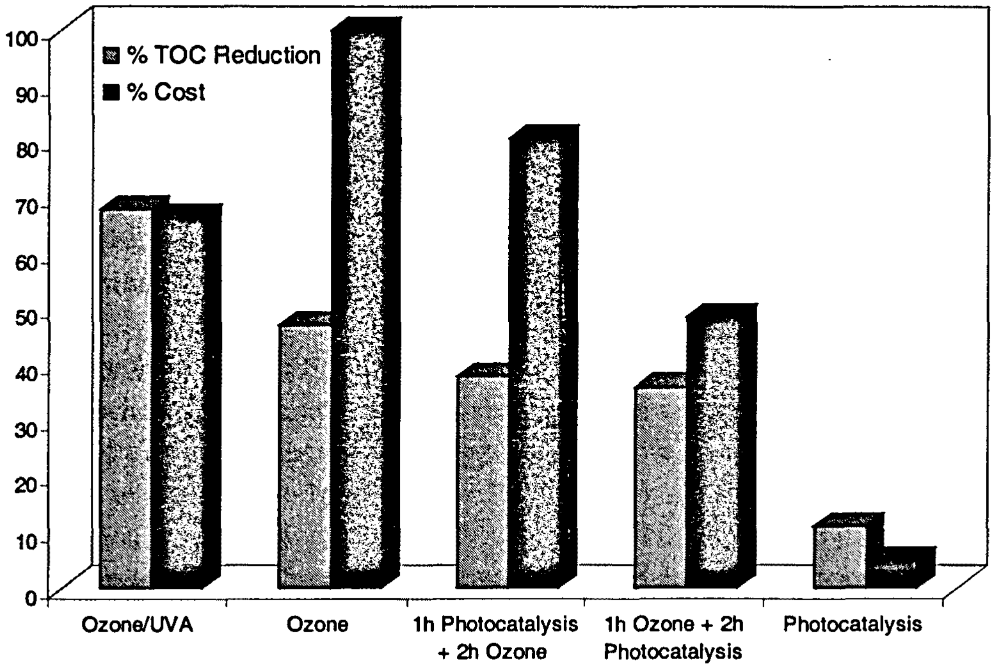


Figure 11. *Comparison of TOC decay and estimated costs per kg TOC removed for various AOPs after 3 hours treatment.*

Ozonation in dark condition clearly is the most expensive treatment. When carrying out ozonation under UVA irradiation there is a 20 % increase of TOC removal and a 30 % decrease of the estimated relative cost. It is important to notice that UVA irradiation of ozone is less energetic and, thus, less expensive, than the usual irradiation at 254 nm, and it can be done by using solar light, because it contains a non-disregardable UVA fraction (a rough estimation indicates that the UVA fraction of solar light at the earth surface have one order of magnitude more photons that the UVA lamp used in these experiments). The potential use of solar light could produce a further cost decrease.

Photocatalysis treatment is the cheapest one: 85 % cost reduction if compared to ozonation, but it involves the lower TOC removal, being this an important backdraw for the practical implementation of the technique.

Interesting remarks can be made from the results of combined ozonation and photocatalysis. In both cases a noticeable cost reduction is obtained with only differences of 10 % in TOC removal if compared to the performance of ozonation in the dark. The combined experiment with one hour ozonation in the dark followed by two hours of photocatalytic treatment gives a cost reduction of 50% in comparison of the three hours ozone treatment without light irradiation.

Conclusions

Treatment of paper pulp bleaching effluents with several AOP's has been carried out, paying attention to practical considerations like reaction yields and relative treatment cost. TiO_2 Photocatalysis has proven to be the cheapest option, although the rate of TOC removal is the lowest one, making the technique inadequate for practical applications. Direct photolysis, even in presence of Fe^{2+}, is less cost effective than photocatalysis, and differences in wastewater color during the treatment point toward differences in reaction mechanisms and intermediates between the two techniques. Addition of H_2O_2 to the photocatalytic reaction produces minor improvements of TOC reduction that are not compensated by the cost increase.

No evidences of Fe^{2+} supported photocatalysis are found, and the TOC decrease produced in the systems containing TiO_2, Fe^{2+} and H_2O_2 seems the consequence of photocatalysis and Fenton reaction working in parallel.

On the other hand ozone treatment gives large TOC removals, especially under UVA light irradiation, and the use of light during ozonation produces a noticeable decrease of the treatment cost. Besides, an ozonation pretreatment followed by photocatalysis step implies similar rates of TOC reduction than any of the separated treatment techniques, but at a 50 % cost reduction respect to ozonation process after only three hours treatment.

The best choice of AOP for paper pulp bleaching effluent has to balance the more efficient techniques in terms of reaction rate, that usually are the most expensive, with the low cost of the slower processes.

Acknowledgements

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References

1. Välttilä O, Discharges from a modern kraft pulping process and their treatability with aerobic biological methods. *Proceedings of the International Conference on Bleached Kraft Mills* Melbourne, Australia (1991).
2. Sierka RA and Bryant CW, Photocatalytic Purification and Treatment of Water and Air, in *Biological Treatment of Kraft Wastewater Following Pretreatment of Extraction Waste Stream by Titanium Dioxide and Membranes,* ed by Ollis DF, and Al-Ekabi H, pp 275-290 (1993).
3. Bauer R and Fallmann H, The Photo-Fenton Oxidation-a cheap and efficient wastewater treatment method. *Res Chem Intermed* **23**: 341-354 (1997).
4. Earl PF and Reeve DW, Chlorinated organic matter in bleached chemical pulp production. Part 6: Chlorinated compounds in effluents. *Tappi J* **73**:179-183 (1990).
5. Hoffmann MR, Martin ST, Choi W and Bahnemann DW, Environmental applications of semiconductor photocatalysis. *Chem Rev* **95**:69-96 (1995).
6. Blake DM, Technical review: Bibliography of work on the photocatalytic removal of hazardous compounds from water and air, Update number 3, to January, 1999. *National Technical Information Service, U.S. National Renewable Energy Laboratory* (1999).
7. Torrades F, Peral J, Pérez M, Domènech X, García Hortal JA and Riva MC, Removal of organic contaminants in bleached Kraft effluents using heterogeneous photocatalysis and ozone. *Tappi J* **84**:63-72 (2001).
8. Pérez M, Torrades F, Peral J, Lizama C, Bravo C, Casas S, Freer J and Mansilla HD, Multivariate approach to photocatalytic degradation of cellulose bleaching effluent. *Appl Catal B-Environ* **33/2**:89-96 (2001).
9. Sánchez L, Peral J, Domènech X, Aniline degradation by combined photocatalysis and ozonation. *App Catal B- Environ* **19**:59-65 (1998).
10. Tanaka K, Abe K and Hisanaga T, Photocatalytic water treatment on immobilized TiO_2 combined with ozonation. *J Photochem Photobiol A-Chem* **101**:85-87 (1996).
11. Klare M, Waldner G, Bauer R, Jacobs H and Broekaert JAC, Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation. *Chemosphere* **38**:2013-2027 (1999).
12. Mao H and Smith DW, Influence of ozone application methods on the efficacy of ozone decolorization of pulp mill effluent. *Ozone Sci Eng* **17**:205-236 (1995).
13. Peyton GR, Oxidative treatment methods for removal of organic compounds from drinking water supplies in *Significance and Treatment of Volatile Organic Compounds in Water Supplies,* Lewis Publishers, Chelsea, pp 313 (1990).
14. Chamarro E, Marco A and Esplugas S, Use of Fenton reagent to improve the biodegradability of effluents *Water Research* **35**:1995-1999 (2001).

15. Pérez M, Torrades F, Domènech X and Peral J, Removal of organic contaminants in textile mill effluents by Fenton and Photo-Fenton reactions. *Conference Proceedings of the 2001 International Textile Congress*, ed by Naik A. Terrassa, **1**:346-353 (2001).
16. Pignatello J, Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ Sci Technol* **26**:944-951 (1992).
17. Sun Y and Pignatello JJ, Photochemical reactions involved in the total mineralization of 2,4-D by $Fe^{3+}/H_2O_2/UV$. *Environ Sci Technol* **27**:304-310 (1993).
18. Pignatello JJ, Liu D and Huston P, Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ Sci Technol* **33**:1832-1839 (1999).
19. Bossmann SH, Oliveros E, Göb S, Siegwart S, Dahlen EP, Payawan L, Straub M, Wörner M and Braun AM, New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. *J Phys Chem* **102**:5542-5550 (1998).
20. Kiwi J, Pulgarin C and Peringer P, Effect of Fenton and photo-Fenton reactions on the degradation biodegradability of 2 and 4-nitrophenols in water treatment. *Appl Catal B-Environ* **3**:335-350 (1994).
21. Tang WZ and Huang CP, 2,4-dichlorophenol oxidation kinetics by Fenton's reagent. *Environ Technol* **17**:1371-1378 (1996).
22. Safarzadeh-Amiri A, Bolton JR and Cater SR, The use of Iron in Advanced Oxidation proceses. *J Advan Oxid Technol* **1**:18-26 (1996).
23. Lescot JC and Jappinen H, Effluent treatment in pulp and paper mills: present technology and development trends. *Appita J* **47**:330-332 (1994).
24. Legrini O, Oliveros E and Braun AM, Photochemical processes for water treatment. *Chem Rev* **93**:671-698 (1993).
25. Sánchez L, Peral J and Domènech X, Degradation of 2,4-dichlorophenoxyacetic acid by in situ photogenerated Fenton reagent. *Electrochim Acta* **41**:1981-1985 (1996).
26. Dionysiou DD, Suidan MT, Bekou E, Baudin I and Laîné J-M, Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water. *Appl Catal B-Environ,* **26**:153-171 (2000).
27. Hoigné J, The Chemistry of Ozone in Water, in *Process Technologies for Water Treatment,* ed by Stucki, S. Plenum Publishing Corp, New York, (1988).
28. Hoigné J, Organic micropollutants and treatment processes: Kinetic and final effects of ozone and chlorine dioxide. *Sci Total Env* **47**:169-185 (1985).
29. Staehelin J and Hoigné J, Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environ Sci Technol* **19**:1206-1213 (1985).
30. Peyton GR, Smith MA and Peyton BM, Photolytic Ozonation for Protection and Rehabilitation of Ground Water Resources; A Mechanistic Study. *Research Report No. 206* University of Illinois, Water Resources Center, (1987).
31. Canadian Pulp and Paper Association Standard Method H.5 – *Color of Pulp Mill Effluents* (Approved method, December 1991; Revised, August 1993)

32. Tsai TY, Renard JJ and Phillips RB, Formation of polychlorinated phenolic compounds during high chlorine dioxide substitution bleaching. *Tappi J* 77:149-157 (1994).
33. D'Oliveira JC, Al-Sayyed G and Pichat P, Photodegradation of 2- and 3- chlorophenol in TiO_2 aqueous suspensions. *Environ Sci Technol* 24:990-996 (1990).
34. Yeber MC, Rodríguez J, Freer J, Durán N and Mansilla HD, Photocatalytic degradation of cellulose bleaching effluents by supported TiO_2 and ZnO. *Chemosphere* 41:1193-1197 (2000).
35. Ollis DF, Pelizzetti E and Serpone N, Destruction of water contaminants. *Environ Sci Technol* 25:1523-1529 (1991).
36. Wittmann G, Ilisz I and Dombi A, Mechanism of catalysed ozone decomposition in aqueous solutions in *Regional Conference on Ozone, Ultraviolet Light, Advanced Oxidation Processes in Water Treatment*, International Ozone Association, p.441 (1996).
37. Larson R and Weber E, *Reaction mechanism in environmental organic chemistry* Lewis Publishers, 316-331 (1994).