UNIVERSITAT DE BARCELONA
FACULTAT DE QUÍMICA
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WET OXIDATION PROCESSES FOR WATER POLLUTION REMEDIATION

Doctoral Thesis

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Barcelona, Mayo 2006

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CERTIFICA:

Que el presente trabajo de investigación titulado "Wet Oxidation Processes for Water Pollution Remediation", constituye la memoria que presenta la Ingeniera Química **Verónica García Molina** para aspirar al grado de Doctor en Ingeniería Química y ha sido realizado dentro del programa de Doctorado "Ingeniería del Medio Ambiente y del Producto", bienio 2001-2003, en el Departamento de Ingeniería Química de la Universidad de Barcelona bajo mi dirección.

Y para que así conste, firmo el presente certificado, a veintidós de Marzo de dos mil seis.

Dr. Santiago Esplugas Vidal

ACKNOWLEDGEMENTS

First of all I would like to thank Professor Santiago Esplugas for being the director of this work and for giving me the opportunity to work in his research group. I am also grateful to Professor Juha Kallas, Head of the Department of Chemical Engineering of Lappeenranta University of Technology and to Professor Thomas Melin, Head of the IVT-RWTH Aachen, for their support and priceless advices during my stays in Finland and Germany respectively.

Special thanks to Dr. Svelana Verenich who was my first guide in the researching world.

I am also indebted to those with whom I have shared the time of this Doctoral Thesis, specially Kati Roosalu from Finland and the big group of the IVT. Among the latter, I would like to emphasize the help and support that I have received from Thomas Wintgens and Rita Hochstrad. I am thankful as well to Johannes Meier and Jens Hoppe for their friendship and for making me smile and laugh even in the not so good moments.

I am also especially thankful to Beata Janosova, for all the time we spent together, for all her support and for being one of the nicest persons I have ever met.

I thank as well all my colleagues in the Department of Chemical Engineering, for being a strong team and especially to Jordi, Renato and Óscar, because without them it would have been much harder to develop this Doctoral Thesis. Among them, I would like to emphasize the priceless support that I received from Jordi.

Most of all, I am indebted to many people, family and friends, especially to Esteri, Mikko and my parents, for being always there giving me not only their love and friendship in good and bad moments, but also their support while doing this Thesis. To all of them my sincere warmest thanks.

Finally, I would like to thank all the members of the Panel for accepting being examiners of this work.

To my aunt

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1 INTRODUCTION

In the beginning of the 21st century, the mankind is facing the problem of wastewaters as an important challenge. According to the WHO (World Health Organization), the shortage or even lack of water affects more than 40 % of the world population due to political, economical and climatological reasons (*WHO, 2000*). Besides, more than 25 % of the world population suffers from health and hygienic problems related to water. Despite the plans carried out by the UN (United Nations) in recent years, 1100 million people around the world lack safe water and 2.4 billion people have no access to sanitation, especially in developing countries of Africa, Asia and Latin America (*UN, 2005*). On the other hand, the domestic use of water and industrial activities, of special impact among developed countries, generate high amounts of wastewater, which's direct disposal to natural channels causes considerable negative effects in the environment. This fact, together with the need to restore wastewaters for new uses, makes the search and development of suitable water treatment processes of vital importance.

Advanced Oxidation Processes (AOPs) appear to be a promising field of study as wastewater treatments, for the reason that the organic components that are thermodynamically unstable to the oxidation are eliminated and not transferred from one phase to another. AOPs include several techniques such as ozonation, Fenton, photo-Fenton, photocatalysis, wet oxidation…etc

In this work, the efficiency of two of these Advanced Oxidation Processes, i.e., wet oxidation and wet peroxide oxidation, have been studied for the treatment of single and multi-component wastewaters. On one side, the degradation of solutions containing 4-chlorophenol by these techniques has been studied. On the other hand, and regarding multi-compound solutions, an investigation of wet oxidation of concentrated solutions has been implemented. Two different pulp and paper mill wastewater have been treated by this mechanism. The first one was a debarking wastewater previously concentrated by evaporation and was supplied by a Finnish company. The second wastewater was a model solution of a Termo-mechanical Pulp (TMP) process waster, which was firstly nanofiltrated and then treated by wet oxidation.

In addition, due to the growing importance of membrane technologies in several wastewaters fields, a research concerning ultrafiltration of solutions containing organic compounds has been conducted.

1.1 TREATMENT TECHNOLOGIES

The need to restore contaminated sites to avoid further damage to the environment has arisen in the last years the development of effective methods for pollutants removal. The main goal is to attain complete mineralization to CO_2 and H_2O in addition to small amounts of some ions, e.g. chloride anions, or at least to produce less harmful intermediates. An ideal waste treatment process must completely mineralize the toxic species present in the waste streams without leaving behind any hazardous residues and should be cost-effective as well *(Stoyanova, 2003)*.

The conventional pollutant destructive technologies include biological, thermal and physic-chemical treatments (*Jardim et al., 1997*). On most occasions, biological treatments require a long residence time for microorganisms to degrade the pollutant because they are affected by toxicity; thermal treatments present considerable emission of other hazardous compounds; some other techniques such as flocculation, precipitation, adsorption on granular activated carbon (GAC), air stripping or reverse osmosis (RO) require a post-treatment to remove the pollutant from the newly contaminated environment (*Danis et al., 1998*).

Alternative methods to these well-established techniques are the so-called **Advanced Oxidation Processes (AOPs)** (*Glaze et al., 1987, Glaze, 1994*) which have been reported to be effective for the near ambient degradation of soluble organic contaminants from waters and soils providing an almost total degradation (*Peyton et al., 1982)*. AOPs are based on the initial formation of radicals, i.e., hydroxyl radicals (**$OH^{\cdot}$**) that later act as non-selective oxidation agents. Several technologies are included in the AOPs like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis…etc. and the main difference between them is the manner to form the radicals. Even though these techniques can provide the conversion of contaminants to less harmful compounds, on most occasions, oxygenated organic products and low molecular weight acids are formed throughout the process (*Gilbert, 1987; Heinzle et al., 1995; Ledakowicz, 1998*); in addition, Advanced Oxidation Processes are limited to treat waters which contain low concentrations of organic or inorganic scavenging substances (*Glaze et al.,* 1992). Experiences with different oxidation technologies and substrates have shown that a partial oxidation of toxic water may increase its biodegradability up to high levels (*Kiwi et al., 1994; Scott and Ollis, 1995*).

1.1.1 ADVANCED OXIDATION PROCESSES

Advanced Oxidation Processes were defined in 1987 by Glaze (*Glaze et al., 1987*) as "*near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effective water purification*". Hydroxyl radical is then, traditionally thought to be the active specie responsible for the destruction of pollutants (*Peyton et al., 1988; Glaze and Kang, 1989; Haag and Yao, 1992; Braun et al., 1993*). It is a powerful, non-selective oxidant, which acts very rapidly with most organic compounds oxidizing them into carbon dioxide and water thanks to its high standard reduction potential (see table 1.1.1-1).

Once the hydroxyl radicals are generated, they virtually attack all organic compounds. Depending on the nature of the organic species, two types of initial attack are possible. According to the first one, the radical abstracts a hydrogen atom to form water as with alkanes or alcohols. The second possibility consists of an electrophylic addition of the radical to double bonds, as in the case of olefins or aromatic compounds. After the addition of the radical, free organic radicals are generated ($R^{\cdot}$) that react with oxygen molecules generating a peroxiradical and allowing the initiation of a chain reaction system that ends in the complete mineralization of the contaminant (*Buxton et al, 1988*).

Table 1.1.1-1 Relative oxidation power of some oxidizing species (*Munter, 2001)*.

Oxidizing species	**Relative oxidation power**
Chlorine	1.00
Hypochlorous acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO_2^+	2.35

Advanced Oxidation Processes are suited for destroying dissolved organic contaminants such as halogenated hydrocarbons (trichloroethane, trichloroethylene), aromatic compounds (benzene, toluene, ethylenzene, xylene), pentachlorophenol (PCP), nitrophenols, detergents, pesticides, etc... Finally, they can be also used to oxidize inorganic contaminants such as cyanide, sulphide and nitrite. (*Munter, 2001*)

There are several technologies included in the AOPs and each one is at a different level of development and commercialization. Figure 1.1.1-1 shows the application range of some wastewater treatments depending on the flow rate and organic matter content of the effluent to be treated. According to this illustration, technologies based on UV radiation and ozonation should be preferred at low flow rates and low organic loads in the incoming effluent. When the incoming effluent contains a high organic load, processes such as incineration and wet oxidation should be employed depending on the flow rate of the effluent. On the other hand, biological treatments appear to be suitable when the flow rate of the feed is high and it has a low content of organic matter.

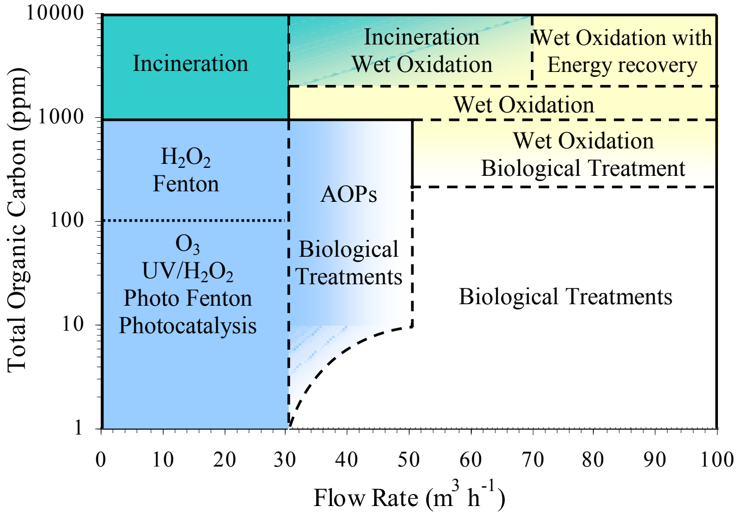


Figure 1.1.1-1 Application range of different oxidation technologies. Adapted from *Hancock 1999* and *Blesa, 2001*.

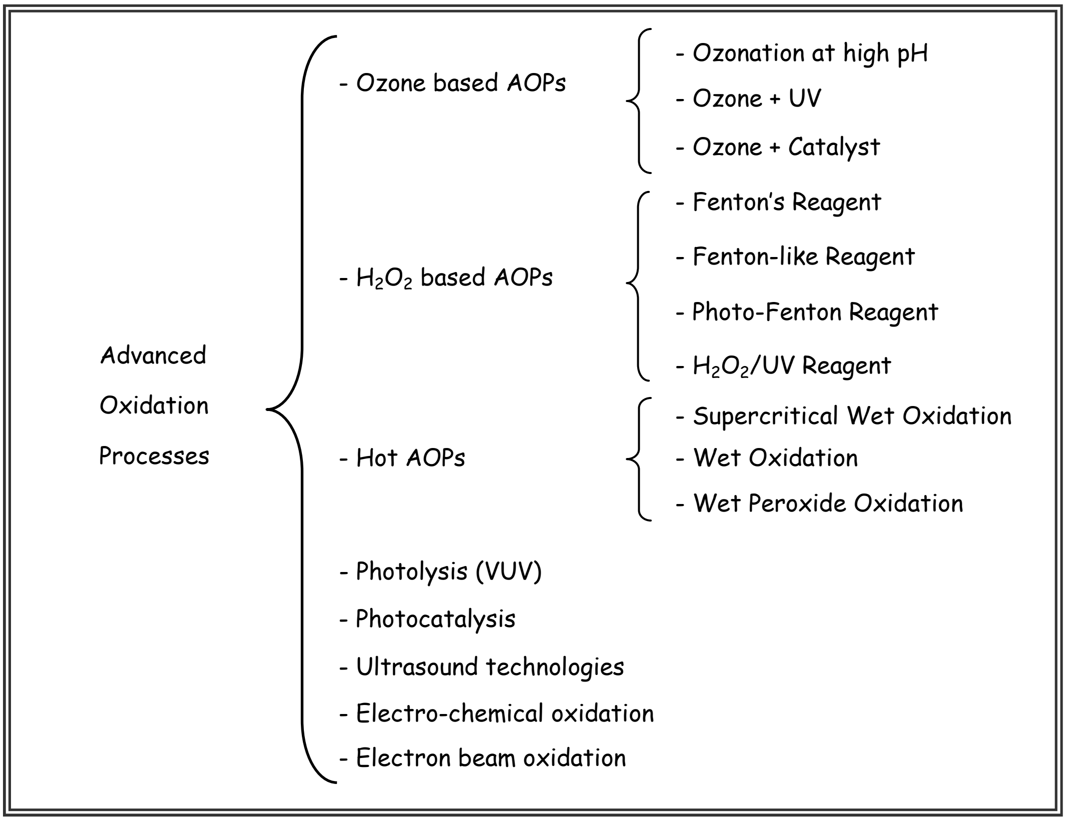


Figure 1.1.1-2 Advanced Oxidation Processes classification.

One commonly accepted classification of the AOPs consists of dividing these techniques depending on the source to form the radicals. This classification is shown in figure 1.1.1-2 and it distinguishes: AOPs based on ozone, AOPs based on hydrogen peroxide, photocatalysis, “Hot” AOPs, ultrasound technologies, electro-chemical oxidation and electron beam oxidation. This work is focused in the “Hot” Advanced Oxidation Processes, which includes three technologies depending on the oxidation agent used to produce the radicals and the operating conditions at which the reaction is carried out: wet peroxide oxidation, wet oxidation and supercritical wet oxidation.

1.1.2 OZONE BASED ADVANCED OXIDATION PROCESSES

Since the beginning of the 20th century, the disinfection properties of Ozone have been well known. However, it has been in the past 20 years when ozone has acquired an important role in the field of wastewater treatments. Thanks to its high electrochemical oxidation potential of 2.1 V (*Hunsberger et al, 1977*) and also due to the absence of hazardous decomposition products over the duration of the process, ozone is a potential treatment agent to transform refractory compounds into substances that can be further removed by conventional methods (*Hu and Yu, 1994*).

1.1.2.1 Ozonation at Alkali conditions

The ozonation process commences with the generation of ozone from oxygen, which is normally implemented by an electrical discharge in presence of air or pure oxygen. This step consumes high amounts of energy involving certain difficulties in the scaling up of the process (*Malato et al., 2001b; Munter, 2001*).

Once the ozone is generated, the oxidation of the organic matter can occur through two different reaction pathways, i.e., direct and indirect (free radical) ozonation, leading to different oxidation products and different types of kinetics. When the direct ozonation takes place, ozone is the main oxidizing agent of the process. On the other hand, the indirect ozonation is based on the formation of hydroxyl radicals that later act as main oxidizing agent. At this point, it has to be noted that ozonation can only be considered as an Advanced Oxidation Process when the $OH^{\cdot}$ radicals are the oxidizing agents of the process. Due to the different oxidation power between molecular ozone and hydroxyl radical, the rate of the attack by indirect ozonation (i.e. $OH^{\cdot}$) is typically 10^6 to 10^9 times faster than the corresponding reaction rate for direct ozonation (i.e. O_3) (*Munter, 2001*).

In table 1.1.2-1 the reaction rates of ozone and hydroxyl radical with different organic compounds are given. It can be seen that chlorinated alkenes react faster than the saturated molecules such as alkanes because the double bond is very susceptible to the hydroxyl attack.

Table 1.1.2-1 Reaction rate constants (k, $M^{-1}s^{-1}$) of ozone versus hydroxyl radical (*Munter, 2001*).

Compound	**O_3**	**$OH^{\cdot}$**
Chlorinated Alkenes	10^3-10^4	10^9-10^{11}
Phenols	10^3	10^9-10^{10}
N-containing organics	10-10^2	10^8-10^{10}
Aromatics	1-10^2	10^8-10^{10}
Ketones	1	10^9-10^{10}
Alcohols	10^{-2}-1	10^8-10^9

Importance of the pH

The supremacy of one of the reaction pathways (direct or indirect) versus the other is deeply related to the pH of the solution to be treated (*Hoigné, 1998*). At low pH, ozone is the main oxidizing agent and it exclusively reacts with compounds with specific functional groups through selective reactions such as electrophilic, nucleophilic or dipolar addition reactions (i.e. direct pathway) (*Langlais et al., 1991*). On the other hand, at high pH and under the presence of certain substances such as hydroxyl ion and transition metal cations, ozone decomposes yielding hydroxyl radicals (i.e. indirect ozonation) which react non-selectively with the organic matter (*Legrini et al., 1993*).

Normally, under acidic conditions (pH<4) the direct ozonation dominates the process, in the range of pH= 4-9 both are present, and above pH 9 the indirect ozonation prevails. This can be explained taking into account that the decomposition rate of ozone in water increases as the pH rises, and at pH 10, the half-life of ozone in water can be less than 1 minute (*Munter, 2001*). The use of the direct or the indirect way to remove the organic compounds depends on the nature of the pollutants, the pH of the media and the doses of ozone (*Malato et al., 2001b*).

Indirect Reaction Pathway

The indirect reaction pathway involves radicals and the first step of the process is the decay of the ozone molecules, accelerated by initiators HO^- ions, to form secondary oxidants i.e. $HO^{\cdot}$ radicals, which react non-selectively and immediately with solutes. The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical $O_2^{\cdot-}$ and hydroperoxyl radical $HO_2^{\cdot}$. By the reaction between ozone and the super-oxide anion radical the ozonide anion radical $O_3^{\cdot-}$ is formed, which decomposes immediately giving $OH^{\cdot}$ radicals. In few words, three molecules of ozone produce two $OH^{\cdot}$ radicals according reaction 1.1.2-1 (*Gottschalk, 2000)*:

$3O_3 + OH^- + H^+ \rightarrow 2\ OH^\bullet + 4\ O_2$ Reaction 1.1.2-1

The radical pathway is very complex and influenced by many substances, however, a mechanism based on three different stages: initiation, propagation and termination reactions can be suggested. The mechanism commences with the reaction between O_3 and OH^- to from $O_2^{\cdot-}$ and $HO_2^{\cdot}$ (reaction 1.1.2-2). Subsequently, $O_2^{\cdot-}$ reacts with O_3 (reaction 1.1.2-3) to form some other radicalary species that finally form $OH^{\cdot}$ radicals (reaction 1.1.2-5). (*Pera-Titus et al., 2004*)

Initiation	$O_3 + HO^- \rightarrow O_2^{\bullet-} + HO_2^\bullet$	$k_1 = 70\ M^{-1}\ s^{-1}$	Reaction 1.1.2-2

Propagation:	$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$	$k_2 =$ 1.[illegible] $*10^9\ M^{-1}\ s^{-1}$	Reaction 1.1.2-3
	$O_3^{\bullet-} + H^+ \leftrightarrow HO_3^\bullet$	pKa = [illegible].2	Reaction 1.1.2-4
	$HO_3^\bullet \rightarrow HO^\bullet + O_2$	$k_3 = 1.1 *10^8\ M^{-1}\ s^{-1}$	Reaction 1.1.2-5
	$HO^\bullet + O_3 \rightarrow HO_4^\bullet$	$k_4 = 2.0 *10^9\ M^{-1}\ s^{-1}$	Reaction 1.1.2-[illegible]
	$HO_4^\bullet \rightarrow HO_2^\bullet + O_2$	$k_5 = 2.8 *10^4\ M^{-1}\ s^{-1}$	Reaction 1.1.2-7
	$HO_2^\bullet \leftrightarrow O_2^{\bullet-} + H^+$	pKa = 4.8	Reaction 1.1.2-8

In presence of bicarbonate, carbonate and tert-butyl alcohol, new passive radicals are formed which do not interact any more with ozone or organic compounds, leading to termination reactions.

Termination:	$HO^\bullet + CO_3^{2-} \rightarrow HO^- + CO_3^{\bullet-}$	k[illegible] $= 4.2 *10^8\ M^{-1}\ s^{-1}$	Reaction 1.1.2-9
	$HO^\bullet + HCO_3^- \rightarrow HO^- + CO_3^\bullet$	$k_7 = 1.5 *10^7\ M^{-1}\ s^{-1}$	Reaction 1.1.2-10

1.1.2.2 Ozonation coupled with Ultraviolet light

Ozonation of many pollutants in aqueous effluent can be enhanced by Ultraviolet (UV) illumination (*Glaze et al., 1987*), which is an alternative method to reduce the residence time and consequently the high costs of the simple ozonation. In the O_3/UV system, the oxidation of the organic matter is carried out by the $OH^{\cdot}$ as it occurred in simple ozonation at alkali pH. The main difference between these two processes is the manner followed to generate the radicals. In this process, the solution is irradiated with UV light and according to Peyton (*Peyton, 1990*), depending on the wavelength of the irradiated light, the generation of the hydroxyl radical may occur throughout two different ways. In the event that the irradiated light has a wavelength (λ) lower than 300 nm the generation of $OH^{\cdot}$ occurs as follows:

Ozone photolysis: $O_3 + H_2O + h\nu \rightarrow H_2O_2$ Reaction 1.1.2-11

Photodissotiation of H_2O_2: $H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet}$ Reaction 1.1.2-12

However, if the irradiated light has a wavelength $\lambda \geq 300$ nm, ozone reacts directly with the H_2O_2 generated in reaction 1.1.2-11:

$O_3 + H_2O_2 \rightarrow OH^{\bullet} + HO_2^{\bullet} + O_2$ Reaction 1.1.2-13

When the wavelength is higher than 300 not only $OH^{\cdot}$ radicals are formed but also weaker oxidizing hydroperoxyl radicals ($HO_2^{\cdot}$) (*Pera-Titus et al., 2004*).

1.1.2.3 Ozonation coupled with catalysts

Some approaches have been taken into account in order to improve the oxidizing power of ozone or ozone/UV leading to the reduction of the required time for the reaction and hence, decreasing its energy costs. The addition of hydrogen peroxide, which actually acts as a homogeneous catalyst, to ozonized solutions causes rapid decomposition of ozone with high output of $OH^{\cdot}$ radicals (*Langlais et al., 1991).* In this case, in addition to the general pathway for ozonation exposed in section 1.1.2.1, ozone reacts with H_2O_2 when present as anion HO_2^- and the direct reaction of ozone with the non-dissociated H_2O_2 is negligible due to a very low kinetic constant (*Pera-Titus et al, 2004*):

$H_2O_2 + O_3 \rightarrow H_2O + O_2 \quad k < 0.01\ M^{-1}\ s^{-1}$ Reaction 1.1.2-14

According to the hypothesis suggested by Staehelin and Hoigné (*Staehelin and Hoigné, 1982)*, the decomposition of ozone in water solutions may be described by the following reaction sequences:

$O_3 + HO^- \rightarrow HO_2^-$ Reaction 1□1□2-15

$H_2O_2 \rightarrow HO_2^- + H^+$ Reaction 1□1□2-1□

$O_3 + HO_2^- \rightarrow OH^\bullet + O_2^{\bullet -} + O_2$ Reaction 1□1□2-17

$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$ Reaction 1□1□2-18

$O_3^{\bullet -} + H_2O \rightarrow OH^\bullet + OH^- + O_2$ Reaction 1□1□2-19

As it can be deduced from the previous reaction scheme, the addition of hydrogen peroxide to ozonized solutions may cause a significant enhancement in the reaction rate and the specific ozone consumption may be reduced *(Preis et al, 1995).* In most cases the optimum ratio H_2O_2/O_3 is considered to be 0.5 mol/mol or even higher. Chamarro et al. (*Chamarro et al., 2001*) found the stoichiometric coefficients for 4-CP degradation in the range 0.601 ± 0.044 (mol removed/mol active reagent).

Another possibility related to this field of research comprises the use of a catalysts based on ferrous/ferric ions or alumina. Promising experiments involving ferrous or ferric ion homogeneous catalysis together with ozonation in presence or in absence of radiation are reported in the literature (*Abe and Tanaka, 1997*).

1.1.3 HYDROGEN PEROXIDE BASED ADVANCED OXIDATION PROCESSES

Hydrogen peroxide is a safe, efficient and easy to use chemical oxidant suitable for a wide usage on contamination prevention. Discovered by Thenard in 1818, it was first used to reduce odor in wastewater treatment plants, and from then on, it became widely employed in the field of the wastewater technologies (*EPA, 2002*). However, since hydrogen peroxide itself is not an excellent oxidant for many organic pollutants, it must be combined with UV light, salts of particular metals or ozone to produce the desired degradation results.

1.1.3.1 Fenton’s reagent (H_2O_2/Fe^{2+})

The Fenton reaction is a widely used and studied catalytic process based on an electron transfer between H_2O_2 and a metal acting as a homogeneous catalyst (*Safarzadeh-Amiri et al., 1996; Lücking et al., 1998*). By far, iron is the most commonly used catalyst for this kind of reactions. The reactivity of this system was first observed in 1894 by its inventor Fenton (*Fenton, 1894*), but it was not until the 1930s when its utility was recognized once a mechanism based on hydroxyl radicals was suggested (*Prousek, 1995*).

A mechanistic pathway based on hydroxyl radicals is commonly accepted for the description of the degradation of organic compounds by Fenton reaction. The main stages involved in the process are the following (*Pera-Titus et al., 2004*).

Initial reactions:

H_2O_2	→	$H_2O + \frac{1}{2} O_2$	Reaction 1□1□3-1
$H_2O_2 + Fe^{2+}$	→	$Fe^{3+} + OH^- + OH^\bullet$	Reaction 1□1□3-2
$H_2O_2 + Fe^{3+}$	→	$Fe(OOH)^{2+} + H^+ \leftrightarrow Fe^{2+} + HO_2^\bullet + H^+$	Reaction 1□1□3-3
$OH^- + Fe^{3+}$	→	$Fe(OH)^{2+} \leftrightarrow Fe^{2+} + OH^\bullet$	Reaction 1□1□3-4

Propagation reactions:

$OH^\bullet + H_2O_2$	→	$HO_2^\bullet + H_2O$	Reaction 1□1□3-5
$HO_2^\bullet + H_2O_2$	→	$HO^\bullet + H_2O + O_2$	Reaction 1□1□3-□
$HO_2^\bullet + HO_2^-$	→	$HO^\bullet + HO^- + O_2$	Reaction 1□1□3-7

Termination reactions:

$Fe^{2+} + HO^\bullet$	→	$Fe^{3+} + HO^-$	Reaction 1□1□3-8
$HO_2^\bullet + Fe^{3+}$	→	$Fe^{2+} + H^+ + O_2$	Reaction 1□1□3-9
$HO^\bullet + HO_2^\bullet$	→	$H_2O + O_2$	Reaction 1□1□3-10
$HO^\bullet + HO^\bullet$	→	H_2O_2	Reaction 1□1□3-11

1.1.3.2 Fenton's-like reagent

Even thought Fenton processes appear to be a promising field of research in the degradation and/or removal of organic compounds, it has a disadvantage related to the catalyst, i.e., iron salts. The fact is that the homogeneous catalyst, added as iron salt, cannot be retained in the degradation process, involving thus high reactive costs. Some attempts have been made in order to replace the homogeneous catalyst by a heterogeneous metal supported one, where the iron ions are placed on a support material (*Al-Hayek and Doré, 1990; Fajerweg and Debellefontaine, 1996; Lin and Gurol, 1998*). Therefore, the hydroxyl radicals are generated from the hydrogen peroxide, as it occurs in the Fenton's process, activated by the iron ions simultaneously leached from the support material.

Among the various catalysts studied, *goethite* (α-FeOOH) is one of the most efficient catalysts for Fenton-like degradation of organics compounds due to the characteristics of its surface and the ferrous ion generation. It is thought to be suitable for the removal of hazardous pollutants since it exists in soil and can be recycled to further uses (*Ravikumar and Gurol, 1994; Lin and Gurol, 1998*). Ferrous ions can be regarded to be produced from the reductive dissolution of goethite as shown below in reaction 1.1.3-12 (*Zinder et al., 1986*):

$$\alpha\text{-FeOOH(s)} + 3H^{+} + e- \quad \leftrightarrow \quad Fe^{2+} + 3H_2O \qquad \text{Reaction 1.1.3-12}$$

On the other hand, the following reaction provides electrons:

$$H_2O_2 \quad \rightarrow \quad 2H^{+} + O_2 + 2e^{-} \qquad \text{Reaction 1.1.3-13}$$

Combining reactions 1.2.3-12 and 1.2.3-13 the following reaction is obtained:

$$2\alpha\text{-FeOOH}(s) + 4H^{+} + H_2O_2 \quad \leftrightarrow \quad 2Fe^{2+} + O_2 + 4H_2O \qquad \text{Reaction 1.1.3-14}$$

Hydroxyl radicals are therefore produced by Fenton reaction:

$$Fe^{2+} + H_2O_2 \quad \rightarrow \quad Fe^{3+} + HO^{\bullet} + HO^{-} \qquad \text{Reaction 1.1.3-15}$$

As it is widely assumed, the dissolution of goethite plays an important role in the goethite/H_2O_2 Fenton's-like process. It can interact chemically with H^+, HO^-, cations, and anions, followed by a series of dissolution reactions.

1.1.3.3 Photo-Fenton´s reagent (H_2O_2/Fe^{2+}/UV)

The photo-Fenton process is an efficient and inexpensive method for wastewater and soil treatment (*Ruppert et al., 1994; Bauer and Fallmann, 1997*). Photo-Fenton is known to be able to improve the efficiency of dark Fenton or Fenton-like reagents by means of the interaction of radiation (UV or Vis) with Fenton's reagent (*Sundstrom et al., 1989; Pignatello, 1992*). This technique has been suggested to be feasible and promising to remove pollutants from natural and industrial waters and to increase the biodegradability of waters containing toxic organic pollutants, being used as a pre-treatment method to decrease the toxicity of water (*Miller et al., 1988; Maletzky and Bauer, 1998;Fallmann et al., 1999*).

As for the mechanistic pathway, all initial, propagation and termination steps are the same as the ones exposed for the reactions with Fenton's reagent. Nevertheless, another step for initial reactions related to the radiation must be added (*Chen and Pignatello, 1997*):

$$H_2O_2 + Fe^{2+} + h\nu \rightarrow Fe^{3+} + HO^- + HO^\bullet$$

Reaction 1□1□3-1□

1.1.3.4 Photo-oxidation with Hydrogen Peroxide

This Advanced Oxidation Process is based on the formation of $HO^\cdot$ radicals by means of the photolysis of hydrogen peroxide and the subsequent propagation reactions.

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet$$

Reaction 1□1□3-17

The molar absorptivity of hydrogen peroxide at 253.7 nm is low, about 20 M^{-1} cm^{-1} and $OH^\cdot$ radicals are formed per incident photon absorbed (*Glaze et al., 1987)*. Compared to ozone, at this wavelength, the rate of photolysis of aqueous hydrogen peroxide is about 50 times slower. Thus, this technique requires a relatively high dose of H_2O_2 and/or a much longer UV-exposure time than, for example, the UV/O_3 process. On the other hand, the rate of photolysis of hydrogen peroxide has been found to be pH dependent. It increases when increasing the alkalinity of the medium, in view of the fact that at 253.7 nm peroxide anions HO_2^- may be formed, which display a higher molar absorptivity than hydrogen peroxide, 240 M^{-1} cm^{-1} (*Glaze et al., 1987)*, by the following reaction:

$HO_2^- + h\nu \rightarrow HO^\bullet + O^{\bullet -}$ Reaction 1.1.3-18

In the event that there are other strong UV absorbers different than hydrogen peroxide, the observed effect will be the same as if the incident flux were decreased, i.e. there is less radiation intensity available for the photolysis of hydrogen peroxide, or the amount of radiation transformed into $HO^\bullet$ radicals will be lower if such absorbents are present.

The absorptivity of hydrogen peroxide may be increased by using UV lamps with output at lower wavelengths. The main reactions of the system are the following ones (*Benítez et al, 2000b; Glaze et al. 1992*):

Initial reaction:
$H_2O_2 + h\nu \rightarrow 2HO^\bullet$ Reaction 1.1.3-19
$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$ Reaction 1.1.3-20

Propagation:
$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$ Reaction 1.1.3-21
$HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2$ Reaction 1.1.3-22
$HO_2^\bullet + HO_2^- \rightarrow HO^\bullet + HO^- + O_2$ Reaction 1.1.3-23

Termination:
$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ Reaction 1.1.3-24
$HO^\bullet + HO^\bullet \rightarrow H_2O_2$ Reaction 1.1.3-25

1.1.4 Photocatalysis

Photocatalytic degradation has proven to be a promising technology for degrading refractory chlorinated aromatics (*Calza et al., 1997; Chu, 1999; Davis and Green, 1999*) and more than 1700 references have been recently collected on this discipline (*Blake, 1999*). Compared with other conventional chemical oxidation methods, photacatalysis may be more effective due to the fact that semiconductors are inexpensive and capable of mineralizing various refractory compounds (*Ku et al, 1996*), however this technique is still in the developmental stage for many cases (*Dionysiou et al, 2000*).

Photocatalytic reactions occur when charges separation is induced in a large band gap semiconductor by excitation with ultra band gap radiations (*Rideh et al, 1997*). The absorption of light by the photocatalyst greater than its band gap energy excites an electron from the valence band of the irradiated particle to its conduction band, producing a positively charged hole in the valence band and an electron in the conduction band (*Izumi et al, 1980)* as shown in figure 1.1.4-1.

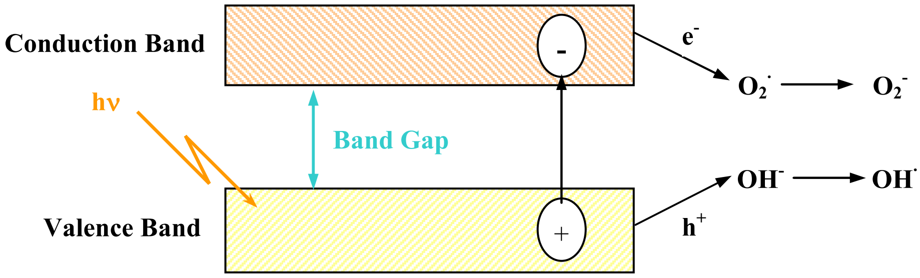


Figure 1.1.4-1 Conduction and valence bands and electron–hole pair generation in semiconductors.

The hole in the valence band may react with water absorbed on the surface to form hydroxyl radicals and on the other hand, the conduction band electron can reduce absorbed oxygen to form peroxide radicals anions that can further disproportionate to form $HO^{\cdot}$ through various pathways (*Al-Ekabi et al, 1992*). In the course of the photocatalytic process, other oxygen containing radicals are also formed including superoxide radical anion and the hydroperoxide radical (*Dionysiou et al, 2000*). In addition, the band electron may also react directly with the contaminant via reductive processes (*Jones and Watts, 1997*). It is not clear under which experimental conditions, one reaction pathway is more important than the other. It is generally accepted that the substrate adsorption on the surface of semiconductors plays an important role in photocatalytic oxidation (*Duonghong et al., 1982*). Therefore, if the surface of the catalyst is covered with the organic substance to be degraded, the direct oxidation by positive holes could be the major oxidation pathway since the adsorption on the surface of the catalyst is the pre-requisited step for direct charge transfer. On the other hand, indirect oxidation by hydroxyl radicals requires the adsorption of water or hydroxide ions on the surface to form the hydroxyl radicals (*Tang and Huang, 1995*).

1.1.4.1 Direct photocatytic pathway

The literature suggests two different direct photocatalytic reaction mechanisms, the Langmuir-Hinshelwood process and the Eley-Rideal process.

The Langmuir–Hinshelwood process

This mechanism is based on the production of electrons and holes by the photoexcitation of the catalyst. The hole is then trapped by the adsorbed molecule (RH) to form a reactive radical state. On one side, this reactive specie (RH_{ads}^{+}) can decay when recombination with an electron occurs and on the other hand, its chemical reaction yields to the products and regenerates the original state of the catalyst surface (S). Reactions 1.1.4-1 to 1.1.4-6 show the reaction mechanism of the Langmuir–Hinshelwood process adapted from Serpone and Emelie (*Serpone and Emelie, 2002*).

$RH + S \rightarrow RH_{ads}$ (adsorption/desorption Langmuir equilibrium)	Reaction 1.1.4-1
$RH_{ads} \rightarrow RH + S$ (adsorption/desorption Langmuir equilibrium)	Reaction 1.1.4-2
$Cat + hv \rightarrow e^{-} + h^{+}$ (photoexcitation of the catalyst)	Reaction 1.1.4-3
$RH_{ads} + h^{+} \rightarrow RH_{ads}^{+}$(hole trapping by adsorbed molecule)	Reaction 1.1.4-4
$RH_{ads}^{+} + e^{-} \rightarrow RH_{ads}$ (decay of the reactive state)	Reaction 1.1.4-5
$RH_{ads}^{+} \rightarrow product + S$ (chemical reaction)	Reaction 1.1.4-6

The Eley–Rideal process

This process starts with the photogeneration of free carriers and the subsequent trapping of the holes by surface defects (i.e. “potential” surface active centers) S to produce surface active centers S^{+}. These surface active centers can then react with the RH (chemisorption) to form species $(S–RH)^{+}$ that further decompose yielding the photoreaction products or can recombine with electrons, which represents their physical decay. The reactions involved in the process are shown below (adapted from *Serpone and Emelie, 2002*).

$Cat + h\nu \rightarrow e^- + h^+$ (photogeneration of free carriers) Reaction 1.1.4-7
$S + h^+ \rightarrow S^+$ (hole trapping by surface defects) Reaction 1.1.4-8
$S^+ + e^- \rightarrow S$ (physical decay of active centers) Reaction 1.1.4-9
$S^+ + RH \rightarrow (S\text{–}CP)^+$ (chemisorption) Reaction 1.1.4-10
$(S\text{–}RH)^+ \rightarrow S\ ^+$ products (reaction to form photoreaction products) Reaction 1.1.4-11

1.1.4.2 Indirect photocatalytic pathway

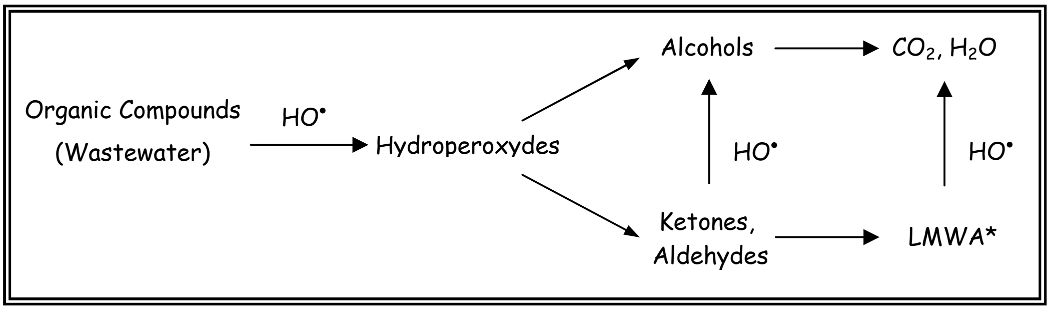
The radical photodegradation mechanism is shown in reactions 1.1.4-12 to 1.1.4-18 adapted from *Yue et. al, 2002*. The process commences with the photogeneration of electron–hole pairs on the surface of the catalyst particles when irradiated by the light in the region of absorption charge-transfer bands (reaction 1.1.4-12). The hole is trapped by the water molecules leading the formation of $HO^\cdot$ radicals and H^+ (reaction 1.1.4-13) and the electrons allow the formation of H_2O_2 which further decomposes in more $OH^\cdot$ radicals by means of its reaction with the oxygen supplied in the medium (reactions 1.1.4-14 to 1.1.4-17). Finally, the radicals formed during this mechanism are responsible for the oxidation of organic compound "RH" yielding some intermediate compounds and mineralization products.

$h\nu \rightarrow e^- + h^+$ Reaction 1.1.4-12
$h^+ + H_2O_{(ads)} \rightarrow HO_{(ads)}^\bullet + H_{(ads)}^+$ Reaction 1.1.4-13
$O_2 + 2e^- \rightarrow O_{2\ (ads)}^{\bullet -}$ Reaction 1.1.4-14
$O_{2\ (ads)}^{\bullet -} + H^+ \leftrightarrow HO_{2\ (ads)}^\bullet$ Reaction 1.1.4-15
$HO_{2\ (ads)}^\bullet \rightarrow H_2O_{2\ (ads)} + O_2$ Reaction 1.1.4-16
$H_2O_{2(ads)} \rightarrow 2HO_{(ads)}^\bullet$ Reaction 1.1.4-17
$2HO_{(ads)}^\bullet + RH \rightarrow$ Intermediates $\rightarrow ?? \rightarrow CO_2 + H_2O$ Reaction 1.1.4-18

1.1.5 HOT ADVANCED OXIDATION PROCESSES

Hot Advanced Oxidation Processes include *Supercritical Water Oxidation (SCWO)*, *Subcritical Oxidation or Wet Oxidation (WO)* and *Wet Peroxide Oxidation (WPO)*. These processes differ from the rest of the Advanced Oxidation Processes not only in terms of operating conditions but also in the concentration of the pollutants present in the wastewater. Thus, hot Advanced Oxidation Processes are mainly used for concentrated wastewaters. Supercritical wet oxidation takes place above the critical point of water (T≥ 374 ºC and P ≥ 22.1 MPa) (*Ding et al., 1996*) and wet oxidation engages with oxidation at a temperature range of 125-300 ºC and pressures of 0.5-20 MPa. The use of oxygen as the oxidizing agent is common to WO and SCWO processes. Finally, there is one mores process, which involves oxidation with hydrogen peroxide and which uses temperatures and pressures both below the critical point of water, i.e., wet peroxide oxidation (*Sanger et al., 1992; Debellefontaine et al., 1996*).

Despite starting from different oxidizing agents, these processes are based on the same principles: The generation of hydroxyl radicals that later act as oxidizing agents. The understanding of the reaction mechanisms is essential for the development of kinetics models. Nowadays, a free-radical reaction mechanism appears to be accountable for WO of organic compounds in both sub-critical and supercritical water (*Li et al., 1991*). Figure 1.1.5-1 shows a simplified scheme of the basic free radical mechanism of WO reaction.



* LMWA: Low Molecular Weight Acids

Figure 1.1.5-1 Wet Oxidation process simplified diagram. (Adapted from *Debellefontaine and Foussard, 2000*)

According to Li et al., the reaction mechanism can be divided into the following stages:

1. ***Initial radical formation.*** Two radical formation reactions are included:

- The production of hydroxyl radical is the first step in this sequence of reactions. The mechanism starts when oxygen reacts with the weakest C-H bonds of the organic compounds and as a result of the reaction, hydroxyl radicals ($HO_2^{\cdot}$) and organic radicals are formed (reaction 1.1.5-1). $HO_2^{\cdot}$ also reacts with C-H bonds (reaction 1.1.5-2) forming more organic radicals and hydrogen peroxide.

$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$ Reaction 1.1.5-1

$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O_2$ Reaction 1.1.5-2

- The second radical formation reaction occurs when the hydrogen peroxide decomposes generating hydroxyl radicals ($HO^{\cdot}$) (reaction 1.1.5-3). This stage can be understood in two different ways depending on the process. In the case of a WO system, this stage is the second radical formation step, however, in the case of a wet peroxide system, this is the main radical formation reaction. The decomposition of the hydrogen peroxide takes place on the surface of the reactor and other heterogeneous or homogeneous species (M). At this range of temperatures, thermal decomposition of hydrogen peroxide should be also taken into account (reaction 1.1.5-4).

$H_2O_2 + M \rightarrow 2\ HO^{\bullet}$ Reaction 1.1.5-3

$H_2O_2 \rightarrow H_2O + \frac{1}{2}\ O_2$ Reaction 1.1.5-4

2. ***Chain reactions, oxidation of the organic compounds:*** At this stage of the reaction mechanism, organic compounds (RH) are oxidized by means of the hydroxyl radical. As it can be observed in reaction 1.1.5-5, the hydroxyl radical abstracts one hydrogen from the organic molecule generating an organic radical ($R^{\cdot}$) and water.

$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$ Reaction 1.1.5-5

Then, the organic radical ($R^{\cdot}$) reacts with oxygen (reaction 1.1.5-6) producing a peroxy radical ($ROO^{\cdot}$).

$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ Reaction 1.1.5-□

This peroxy radical ($ROO^{\cdot}$) rapidly abstracts a hydrogen atom from an organic compound (reaction 1.1.5-7) to generate the unstable hydroperoxide (ROOH) and another organic radical ($R^{\cdot}$).

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$ Reaction 1.1.5-7

3. ***Final Reactions:*** The chain reactions end when the hydroperoxide reacts with organic compounds to yield alcohol (reaction 1.1.5-8) or when it decomposes to ketones and eventually acids (reaction 1.1.5-9).

$ROOH \rightarrow 2ROH$ (alcohol) Reaction 1.1.5-8

$ROOH \rightarrow$ Ketones $\rightarrow$ Acids Reaction 1.1.5-9

These scissor reactions proceed until the formation of low molecular weight acids, which are more difficult to oxidize, and therefore, which have a longer existence time. These low molecular weight organic acids will be eventually converted to end products (CO_2 and H_2O) (reaction 1.1.5-10).

Low molecular weight acids $\rightarrow CO_2 + H_2O$ Reaction 1.1.5-10

In order to estimate which of the stages is the one that controls the whole mechanism, it is of major importance to analyze the activation energy involved in each reaction. Li et al. (*Li et al. 1991*) reported the pre-exponential factors and the activation energies of the reactions involved in the process for the degradation of methane (see table 1.1.5-1).

Table 1.1.5-1 Initiation mechanism associated with hydroxyl radicals (*Li et al., 1991*).

Reaction	**Pre-exponential Factor (A)****	**Activation Energy* (kJ/mol)**	**Reference**
Radical Formation			
$H_2O_2 \rightarrow 2HO^{\cdot}$	$1.00\ 10^{13}$	200.83	Giguere & Liu, 1957
	$3.00\ 10^{14}$	207.94	Bedeneev et al., 1988
	$1.58\ 10^{14}$	201.89	Webley & Tester, 1991
$H_2O + O_2 \rightarrow HO_2^{\cdot} + HO^{\cdot}$	$8.07\ 10^{10}$	287.03	Rofer & Streit, 1989
$H_2O + O_2 \rightarrow 2HO_2^{\cdot}$	$5.42\ 10^{10}$	166.20	Tsang & Hampson, 1986
$CH_4 + O_2 \rightarrow CH_3^{\cdot} + HO_2^{\cdot}$	$4.04\ 10^{10}$	283.00	Tsang & Hampson, 1986
	$6.02\ 10^{10}$	234.30	Bedeneev et al., 1988
	$3.98\ 10^{10}$	237.84	Webley & Tester, 1991
Hydrogen Abstraction			
$CH_4 + HO^{\cdot} \rightarrow CH_3^{\cdot} + H_2O$	$7.95\ 10^{3}$	11.25	Bedeneev et al., 1988
	$1.58\ 10^{4}$	11.70	Webley & Tester, 1991
$CH_4 + HO_2^{\cdot} \rightarrow CH_3^{\cdot} + H_2O_2$	$1.81\ 10^{8}$	77.70	Tsang & Hampson, 1986
	$1.81\ 10^{9}$	89.96	Bedeneev et al., 1988
	$2.00\ 10^{8}$	77.75	Webley & Tester, 1991
$RH^{\tau} + HO^{\cdot} \rightarrow R^{\cdot} + H_2O$	$2.90\ 10^{10}$	12.80	Khar'kova et al., 1989
Radical Shift			
$HO^{\cdot} + H_2O_2 \rightarrow H_2O^{\cdot} + HO_2^{\cdot}$	$1.75\ 10^{9}$	1.33	Tsang & Hampson, 1986
	$2.23\ 10^{9}$	2.16	Bedeneev et al., 1988
	$1.58\ 10^{9}$	1.25	Webley & Tester, 1991
$HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + HO^{\cdot}$	$3.39\ 10^{9}$	137.36	Rofer & Streit, 1989

*The reaction rate constant (k)= AT^{n}exp(-E/RT), where A is pre-exponential factor, n= 0 for the all reactions in this table, E is the activation energy (kJ/mol), R is the gas constant 8.314 J/(mol K), and T is the temperature.

** The dimensions of the pre-exponential factors of the rate constants are: s^{-1} for monomolecular reactions, L/(mol s) for bimolecular reactions.
RH^{τ} = Cyclohexane

A more accurate analysis of the before mentioned reactions concerning the wet oxidation of methane can be carried out taking into consideration the kinetic values shown in the previous table. From this data it can be noted that the reactions involved in the radical OH$^\cdot$ formation i.e., reactions 1.2.5-1, 1.2.5-2 and 1.2.5-3 have higher activation energies than the hydrogen abstraction reaction 1.2.5-5. This could indicate that the radical formation is the rate-controlling step of the process. However, despite the fact that the radical formation rate constants appear to be lower than the propagation rate constants, hydrogen abstraction is considered as the rate-controlling step in view of the fact that the concentration of both HO$_2^\cdot$ and HO$^\cdot$ is much lower than those of molecular oxygen or hydrogen peroxide. (*Li et al., 1991*).

Reaction 1.1.5-1	$CH_4 + O_2 \rightarrow CH_3^\bullet + HO_2^\bullet$	Pre-exponential factor[*]	Activation Energy[**]
		$4.04\ 10^{10}$	283.00
		$6.02\ 10^{10}$	234.30
		$3.98\ 10^{10}$	237.84

Reaction 1.1.5-2	$CH_4 + HO_2^\bullet \rightarrow CH_3^\bullet + H_2O_2$	Pre-exponential factor[*]	Activation Energy[**]
		$1.81\ 10^{8}$	77.70
		$1.81\ 10^{9}$	89.96
		$2.00\ 10^{8}$	77.75

Reaction 1.1.5-3	$H_2O_2 + M \rightarrow 2\ HO^\bullet$	Pre-exponential factor[*]	Activation Energy[**]
		$1\ 10^{13}$	200.83
		$3\ 10^{14}$	207.94
		$1.58\ 10^{14}$	201.89

Reaction 1.1.5-5	$CH_4 + HO^\bullet \rightarrow CH_3^\bullet + H_2O$	Pre-exponential factor[*]	Activation Energy[**]
		$7.95\ 10^{3}$	11.25
		$1.58\ 10^{4}$	11.70

[*] The dimensions of the pre-exponential factors of the rate constants are: s^{-1} for monomolecular reactions, L/(mol s) for bimolecular reactions.

[**] The dimensions of the activation energy are kJ/mol

1.1.6 ULTRASOUND TECHNOLOGIES

Ultrasound systems are definitely one of the less studied AOPs. However, some information has been collected, and since 1990 there has been an increasing interest in the use of ultrasound to destroy organic contaminants present in water or/and wastewater (*Hao et al., 2004*). In figure 1.1.6-1 a scheme of the process is depicted. In it, the three phases involved in this technology can be distinguished: the aqueous phase, the gas-liquid shell and the gas cavitation bubble.

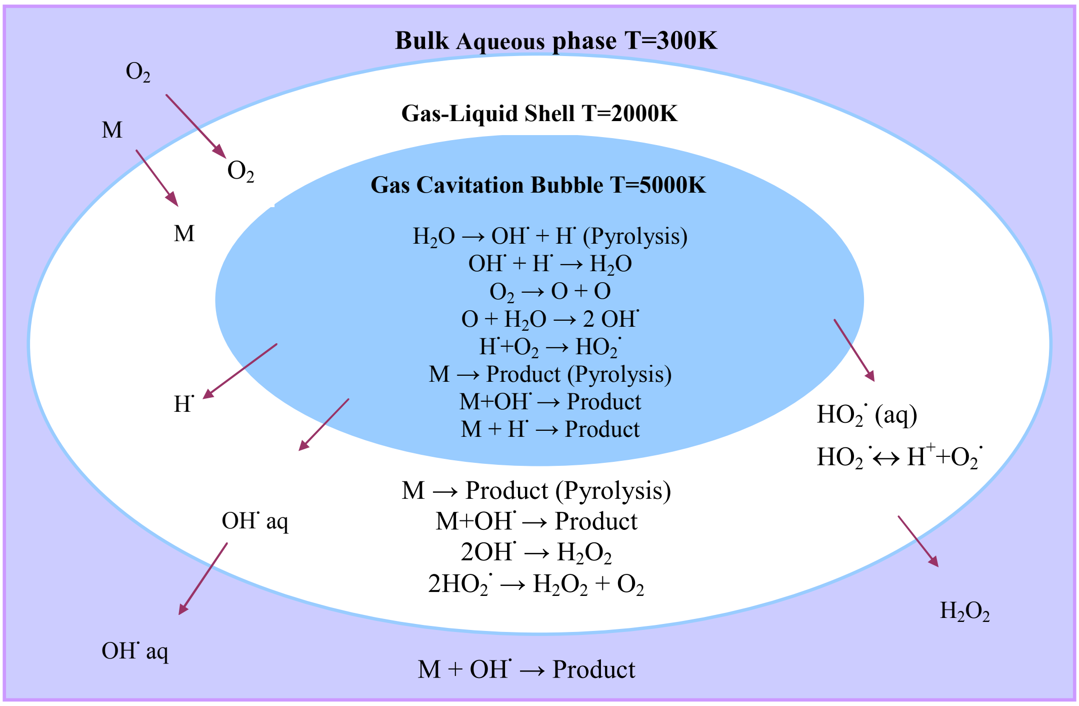


Figure 1.1.6-1 Ultrasound technology process.

When water is exposed to ultrasound above an intensity threshold, cavitations (stable and transient) are produced within the aqueous medium and the absorbed energy makes chemical changes of profound interest. The principles of cavitation are based on the formation and growth of microbubbles during rarefaction phase of acoustic waves and their subsequent violent collapse over the duration of compression cycle of the waves. As a result of the collapse of the microbubbles, the temperature and pressure in the cavity may even exceed 3000 K and 1000 bar (1 bar ≈ 100 kPa ≈ 1 atm), sufficiently high to break any chemical bond

(*Bernstein et al, 1996*). There are two important effects of cavitation, and sonochemical reactions can be categorized according to them as follows:

- Pyrolysis reactions involving thermal decomposition of solvent, solute or gases present as a result of the high pressure and temperature upon bubble collapse.

- Radical reactions which occur in three distinct regions within the hot bubble cavity, at the interface between the bubble and liquid bulk and in the bulk media.

According to the previous figure, the $OH^{\cdot}$ are produced during the ultrasound process as follows. Apolar volatile compounds (represented by M in the figure) are able to vaporize into the cavities and undergo pyrolysis. Consequently, water vapor in the cavity can be decomposed to hydroxyl free radicals and hydrogen radicals.

$H_2O + \text{Ultrasound} \rightarrow OH^{\bullet} + H^{\bullet}$ Reaction 1□1□-1

In the event that O_2 is present in the vapor phase of the bubble, it scavengers $H^{\cdot}$ by the following reaction:

$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$ Reaction 1□1□-2

O_2 can also undergo thermolysis, producing excited oxygen atoms:

$O_2 \rightarrow O + O$ Reaction 1□1□-3

then more $OH^{\cdot}$ are formed:

$O + H_2O \rightarrow 2\ OH^{\bullet}$ Reaction 1□1□-4

What is of major importance to notice is that subjecting an aqueous solution containing pollutants to ultrasonic waves will cause their degradation by hydroxyl radicals (oxidation mechanism) and/or by high temperature (pyrolysis mechanism). Only in the event that the substrate is volatile and hydrophobic, it will flux into a cavitation bubble and decompose by pyrolysis and oxidation reactions simultaneously (*Jennings and Townsend, 1961*).

1.2 WET OXIDATION PROCESSES

Among the Advanced Oxidation Processes, which are carried out at high temperature and pressure conditions, wet oxidation processes can be distinguished. Various oxidation techniques are suited for the elimination of organic aqueous wastes and because of the environmental drawbacks of incineration, enclosed processes, as liquid phase oxidation should be preferred. Wet oxidation is a promising technology to treat such liquid wastes and various catalysts, including iron, cadmium, hydrogen peroxide etc…, can be used in order to increase the efficiency without increasing the temperature and the pressure at which the reaction is performed. Wet peroxide oxidation is a similar process but uses hydrogen peroxide as oxidizing agent instead of oxygen or air and requires lower operating conditions of temperature and pressure. As opposed to wet oxidation, which is capital intensive, wet peroxide oxidation needs limited capital but generates higher running costs. (*Debellefontaine et al, 1996*)

1.2.1 BACKGROUND AND CURRENT SITUATION OF THE TECHNOLOGY

The first wet oxidation patent was obtained in 1950 by Zimmermann (Zimpro, US), althought it was already discovered in 1935. It was first used as a completely new method of obtaining vanillin directly from pulping liquor by partial oxidation of the ligno-sulphonic acids. The technology was introduced to the pulp and paper market in 1955, and to the municipal sewage sludge market in the late '50s and early '60s. The process can treat any kind of waste, produced by various branches of industrial activity or sludge produced by conventional treatment processes (*Debellefontaine et al., 1996*). Nowadays, the main uses of this technology are (www.usfilters.com):

1- Treatment of spent caustic liquors that typically come from plants of ethylene production (from the scrubbing of cracked gas with aqueous sodium hydroxide) or from oil refining plants (from the extraction or treatment of acidic impurities, such as hydrogen sulfide, mercaptans and organic acids in hydrocarbon streams).

2- Treatment of high strength waste streams in order to make them more suitable to conventional treatments such as biological polishing, or as pretreatment for product recovery. Wet oxidation destroys the large molecules in waste, converting them predominantly to carbon dioxide with some formation of low weight carboxylic acids such as acetic acid, which is highly biodegradable. The purpose of this treatment is to condition a waste that is: toxic, reactive, refractory to biotreatment or hazardous.

3- Treatment of sludge that includes:

- Sludge dewatering: Low pressure/temperature oxidation is used for sludge conditioning to allow its dewatering.
- Sludge destruction: At higher temperatures, volatiles in sludge can be destroyed.
- Wet Air Regeneration: Wet air oxidation is used in conjunction with a biological process referred to as the powdered activated carbon treatment (PACT®) system for both regeneration of carbon and destruction of biological sludge.

According to manufactures information, currently there are more than 200 wet oxidation plants in the world that are operated for the treatment of different types of waste, such as effluents from pulp and paper mills, wastes from petrochemical plants, textile wastewaters, thermo-mechanical pulp sludge, paper mill sludge, sewage sludge, activated sludge, blow down effluents from crystallizers and so forth. Wet air oxidation also finds its application in the petrochemical and textile industries, where ultrasonic irradiation in the presence of Cu^{2+} ions is employed as an effective pretreatment of the process. (*Papadaki et al, 2004*).

1.2.2 THE WET OXIDATION PROCESS

Wet oxidation involves the liquid phase oxidation of organic or oxidizable inorganic components at elevated temperatures and pressures using a gaseous source of oxygen. This technology is commonly named Wet Oxidation (WO) when pure oxygen is used and Wet Air Oxidation (WAO) when air is supplied to the system. This process has a very limited interaction with the environment and when the oxidation is not complete it can be coupled with a biological treatment to eliminate or to treat any kind of waste, even toxic (*Debellefontaine and Foussard, 2000*).

The following schematic reactions represent the fundamental transformations of organic matter over the duration of the wet oxidation process (*Mishira et al., 1995; Kolaczkowski et al. 1999*)

Organics + O_2	→	$CO_2 + H_2O + RCOOH$	Reaction 1.2.2-1
Sulphur Species + O_2	→	SO_4^{-2}	Reaction 1.2.2-2
Organic Cl	→	$Cl^- + CO_2 + RCOOH$	Reaction 1.2.2-3
Phosphorous + O_2	→	PO_4^{-3}	Reaction 1.2.2-4
Organic N + O_2	→	$CO_2 + H_2O + NH_3$ (or/and N_2, NO_3^-)	Reaction 1.2.2-5

From the previous scheme it can be noted that over the duration of the WO, the organic compounds are reduced to CO_2 or other innocuous components, nitrogen is transformed into NH_3, NO_3 or elementary nitrogen and finally, halogen compounds and sulfurs are transformed into halides and sulphates (*Perkow and Steiner, 1981; Levec, 1995*). It should be mentioned that WO presents an important advantage compared with other processes, since no NO_x, SO_2, HCl, dioxides or other harmful products are generated within the process.

Two parameters commonly used to characterize the efficiency of the wet oxidation process are the TOC (Total Organic Demand) and the COD (Chemical Oxygen Demand). The comparison between these values, measured at the commencement and at the end of the reaction, allows the knowledge of the degree of mineralization of the process or in other words, the amount of organic matter transformed into CO_2, which is normally one of the main objectives to be accomplished.

A typical COD removal achieved after a wet oxidation reaction oscillates between 75 % and 90 % (*Li et al., 1991*). The oxidation of the initial matter is not always complete and the result of the reaction is a mixture of biodegradable products of low molecular weight such as organic acids, aldehydes and alcohols (*Scott, 1997*). The non-complete oxidation can be explained taking into account that the oxidation rate increases along with the increase in the molecular weight/carbon number (*Mishira et al., 1995*). As a consequence, low molecular weight acids, which are the last organic intermediates formed throughout the process previous to the formation of carbon dioxide, are the most refractory compounds for the oxidation process and remain in the solution. The formation of these carboxylic acids causes on one side the decrease of the pH over the duration of the process and on the other hand an increase in the biodegradability of the wastewater.

In figure 1.2.2-1 the evolution of some parameters such as COD, BOD (Biochemical Oxygen Demand) and Volatile Acids is depicted versus the TOD (Total Oxygen Demand) reduction.

It can be observed that the BOD of the solution firstly increases, then reaches a maximum and finally decreases. The initial increase is due to the degradation of the non-biodegradable organic compounds and the formation of biodegradable intermediates. This period of time is characterized by having an increasing ratio: biodegradable matter / non-biodegradable matter. At some point, the non-biodegradable matter present in the solution reaches its minimum because it has been widely oxidized. This moment coincides with the maximum biodegradability. After reaching this maximum, the oxidation of the biodegradable intermediate compounds takes place and since the amount of biodegradable matter decreases, the biodegradability of the solution also decreases until the end of the reaction. Another fact to point out from figure 1.2.2-1 is that in the wet oxidation process a continuous decrease of the Chemical Oxygen Demand (COD) occurs, since as soon as the oxidation commences, there is less and less matter remaining in the solution, and thus less oxygen is necessary to oxidize this remaining matter.

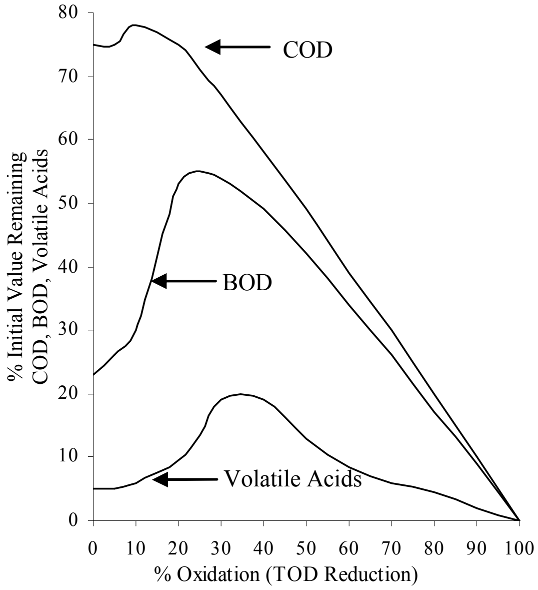


Figure 1.2.2-1 COD, BOD and Volatile Acids versus percentage of oxidation (*Wilhelmi and Knopp, 1979*).

Regarding the resistance that the different compounds offer to the oxidation, two groups of substances can be distinguished: *Easily oxidized compounds* and *non-easily oxidized compounds*. Typically, aliphatic and aromatic compounds containing non-halogen functional groups, e.g., phenols and anilines are easily oxidized by wet air oxidation. On the other side, compounds which are resistant to wet air oxidation include aromatic containing electron withdrawing groups such as halogen and nitro groups (*Scott, 1997*).

1.2.3 OPERATING CONDITIONS

The degree of oxidation depends, on one side on the operating conditions i.e. temperature, pressure and residence time and on the other side, on the organic compounds resistance to chemical oxidation. The range of temperature and pressure at which the reaction is carried out is not strictly limited. However, the pressure should be always maintained well above the saturation pressure corresponding to the operating temperature, so that the reaction occurs in the liquid phase (*Li et al., 1991*). Table 1.2.3-1 shows some of the conditions of pressure and temperature found in the literature. The usual times of reaction are between 15 and 120 minutes (*Li et al., 1991*).

Table 1.2.3-1 Operating Conditions in WAO systems.

Reference	**Temperature (ºC)**	**Pressure (bar)***
Li et al.,1991	150–350	20-200
Mishira et al., 1995	125-320	5-200
Beyrich et al., 1979	150-300	50-200
Escalas et al., 1997	175-320	22-208
Debellefontaine and Foussard., 2000	200-325	Up to 150
Perkow et al., 1981	150-330	30-250
Foussard et al., 1989	197-327	20-200

*The pressure in the reactor is the sum of the pressure of the steam generated at this temperature and the pressure of the air or oxygen supplied to maintain an elevated oxygen concentration in the liquid phase.

When evaluating the effluent to be treated it has to be noted that wet oxidation is a reaction accompanied by a release of energy (*Debellefontaine et al., 1996*) and, thus, in order for the process to be energy self-sufficient, the COD of the waste should be high. Several authors have reported an optimum value between 10 and 20 kg/m^3 of COD in the entry stream.

Compared with other treatments such as incineration, wet oxidation requires much less energy. The fact is that for WO the only energy required is the difference in enthalpy between the incoming and outcoming, whereas, for incineration, not only the sensible enthalpy is to be provided but also the heat for the complete evaporation of water (*Wilhelmi and Knopp, 1979; Mishira et al., 1995*). These differences can be observed in figure 1.2.3-1, where incineration, even with heat recovery shows higher energy requirements. In this figure, the autogenous point of the processes can be noted. This point corresponds to the conditions under which the process can be run without any contribution or recovery of energy. It can be seen that the autogenous point for wet oxidation corresponds to a stream inlet of 10 g/L of organic matter, whereas a feed stream of more than 200 g/L is necessary in order to reach autogenous conditions in incineration. At this point, where incineration becomes autogenous, wet oxidation is already extensively exothermic.

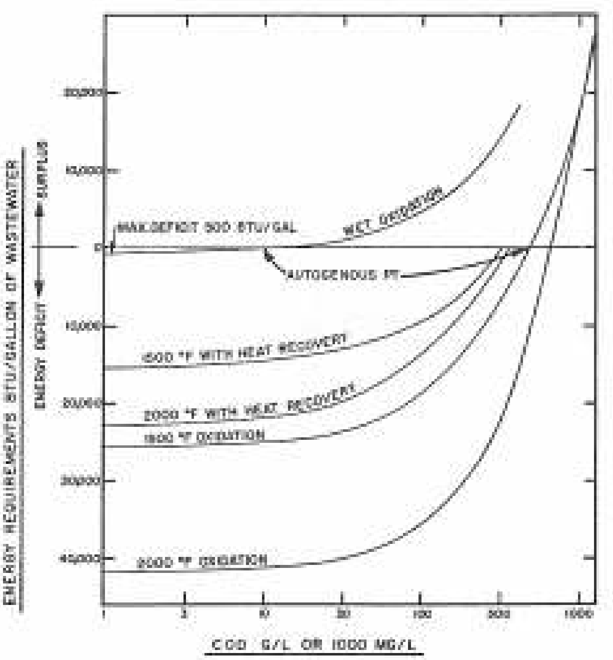


Figure 1.2.3-1 Thermal energy requirements vs. organic content: thermal and wet oxidation (*Wilhelmi and Knopp, 1979*). (1 BTU/Gallon = 16 kJ/m^3; ºC= (ºF-32)/1.8).

On the other hand, the capital costs of a WO system are high and depend on the flow and oxygen demand of the effluent, severity of the oxidation conditions, and the required construction materials. The reactor itself can account for a significant fraction (50 %) of the total equipment cost. (*Mishira et al., 1995*).

1.2.4 REACTION ENGINEERING

The reaction engineering of WO when working with a gaseous source of oxygen as oxidizing agent is specially complicated due to the fact that three phases are involved in the process:

- ✓ *Liquid phase*: is the phase where the reaction takes place.
- ✓ *Solid phase:* contains all the suspended solids and other particles. At high temperatures, these solids, mainly formed by organic compounds are partially dissolved into the liquid.
- ✓ *Gaseous phase*: is composed basically by the oxidizing agent which should diffuse from this phase to the liquid phase. This mass transfer could cause an important physical resistance to the process depending on the operating conditions.

Mechanisms of the WO reaction:

1. *Oxygen diffusion from gaseous to liquid phase.* In this step of the process the oxygen contained in the gaseous phase crosses the G-L interface. However, this interface offers certain resistance to be crossed and it is necessary to reduce the thickness of the layer as much as possible. By keeping turbulence in the liquid phase the layer becomes thinner and the oxygen mass transfer improves. Despite the efforts to increase the efficiency of this mechanism, it is usually the responsible for the physical resistance in the whole process.

2. *Diffusion of organic compounds from solid to liquid phase.* Within the solids and colloids of the solid phase cross the S-L interface and dissolve into the bulk of water. Normally this step does not present an important resistance to the whole process in view of the fact that the high temperature provokes a fast diffusion and dissolution of the solids.

3. *Reaction.* WO reaction takes place in the liquid phase. The rate of the reaction depends on many factors such as temperature, pressure and catalyst.

4. *Desorption of gaseous products.* The CO_2 formed in the course of the reaction is transfered from the liquid to the gaseous phase. This step does not suppose an important resistance to the whole process, notwithstanding the fact that high pressure conditions complicate the diffusion of the gas from one phase to the other.

Figure 1.2.4-1 shows a scheme of the mechanisms present in the reaction engineering. As it can be observed, oxygen is transferred from the gaseous phase to the liquid phase (1), meanwhile organics diffuse from the solid phase to the liquid phase (2). The third step in the reaction mechanism is the oxidation of the organics by means of the oxygen (3). As a result of the reaction CO_2 is formed which diffuses from the liquid phase to the gaseous phase (4).

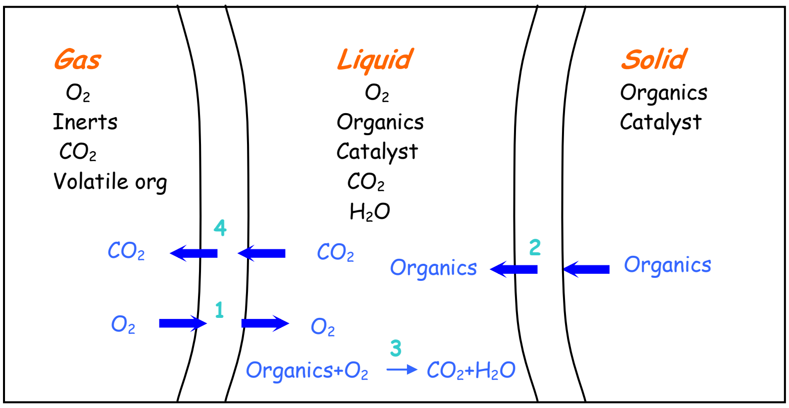


Figure 1.2.4-1 Scheme of the main mechanisms involved in wet oxidation processes.

Attending to the previous description of the mechanisms, it can be deduced that the controlling stages of the WO process are the *diffusion of the oxygen from the gaseous phase* (physical resistance) and the *chemical reaction* (chemical resistance). According to this, and depending on the rates of these mechanisms three extreme cases are conceivable (*Beyrich et al., 1979*):

Case I Reaction Rate >> Diffusion Rate.

The oxygen [A] diffusing through the film is completely consumed in the film by a very rapid reaction. The rapid disappearance of the dissolved gas gives rise to a high concentration gradient at the interface and consequently, the oxygen is not present in the bulk of the liquid.

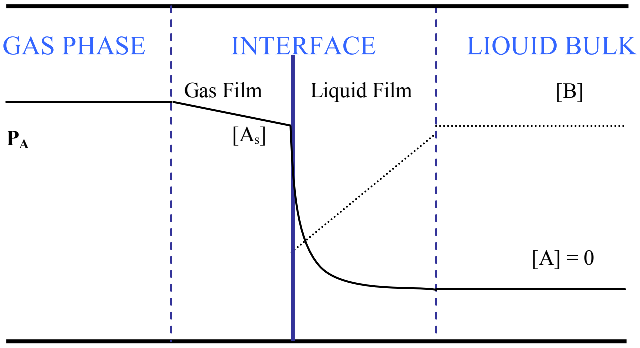


Figure 1.2.4-2 Reaction Regime I.

Case II Reaction Rate ≈ Diffusion Rate.

The reaction takes place essentially in the bulk of the liquid but the liquid dissolved gas concentration is low due to the reaction. In this case, the transfer of oxygen from the gas to the liquid phase controls the process.

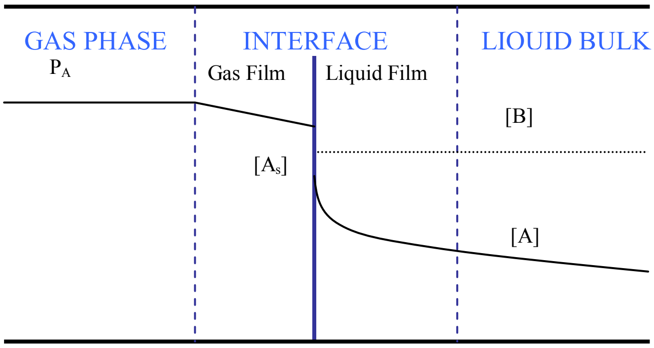


Figure 1.2.4-3 Reaction Regime II.

Case III Reaction Rate <<< Diffusion Rate.

The reaction is so slow that the concentration of the dissolved gas in the bulk of the liquid attains approximately the interface concentration or even the saturation concentration. In this situation, the reaction controls the whole process.

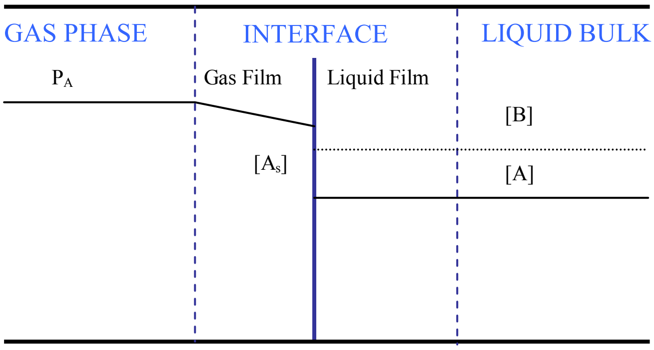


Figure 1.2.4-4 Reaction Regime III.

According to Beyrich (*Beyrich et al., 1979*), only the two last cases are of major importance for Wet Air Oxidation. However, at this point it is important to distinguish between an industrial reactor and a laboratory reactor. There are many aspects such as the hydrodynamics that strongly affect the conditions in an industrial reactor. On the other hand, in a laboratory, only a high mixing efficiency (corresponding to the third case) will allow unbiased kinetic rates to be determined (*Debellefontaine et al., 1996*).

Considering only the two extreme cases above explained, the reaction can be controlled by the mass transfer of oxygen from the gas phase to the liquid or by the chemical reaction. The mass transfer of oxygen rate can be express as:

$$r_{mt} = k_L a \ c_{O,L}^S \ E$$ Equation 1□2□4-1

where :

$k_L a$	is the liquid side volumetric mass transfer coefficient
$c_{O,L}^S$	is the saturation concentration of oxygen
E	is an enhancement factor

On the other hand, the chemical reaction for this system can be described as follows:

$$- r_{chem} = k_{chem} c_{org} c_{O,L}$$ Equation 1□2□4-2

Considering this, and that the oxidative process takes places under quasi-steady-state conditions, the preceded equations for the rates of oxygen disappearance due to the reaction and its mass transfer to the liquid phase can be combined with the mass balance across the reactor to obtain the overall oxidation rate (*Verenich, 2003*). Thus, in the event that the process is controlled by the chemical reaction then,

$$\frac{1}{k_{chem} c_{org}} \quad >> \quad \frac{1}{k_L aE} \qquad \text{and } -r = r_{chem}$$ Equation 1□2□4-3

Or, if the oxidation is controlled by the mass transfer then,

$$\frac{1}{k_L aE} \quad >> \quad \frac{1}{k_{chem} c_{org}} \qquad \text{and } -r = r_{mt}$$ Equation 1□2□4-4

To know whether the oxidative reactions take place in the bulk of the liquid phase, which requires a large volume of liquid, or in the boundary layer of water phase and, therefore, involve a large interfacial area, the Hatta number, Ha, has been elaborated to check the interfacial conditions.

$$Ha = \frac{\sqrt{k_{chem} c_{org} D_{O,L}}}{k_L}$$ Equation 1□2□4-5

Where $D_{O,L}$ is the diffusivity of oxygen in aqueous solutions and it can be found either in literature or can be computed using the formula shown below (*Reid et al., 1996*)

$$D_{O,L} = 7.4 \times 10^{-10} \frac{(2.6 \times M_{H_2O})^{1/2} T}{v_o^{0.6} \mu_{H_2O}}$$ Equation 1□2□4-□

Where: M_{H_2O} is the molecular mass of water

μ_{H_2O} is the dynamic viscosity of water

ν_o is the molecular volume of the solute

The value of the Hatta number for slow chemicals reactions is very small (Ha<<1), but for fast reactions, it has large values (Ha>>1). The computation of Hatta number in the course of the WO of different water solutions revealed values of Ha lower than 0.02, which corresponds to a chemically controlled process with rather slow reactions. (*Verenich, 2003*).

1.2.5 KINETICS OF THE REACTION

Many kinetics models for multi-compound solutions have been suggested in the literature. One of first ones was the General Lumped Kinetic Model (GLKM) suggested by Li et al. in 1991. After some predictions and considerations, the mathematical model leads to equation 1.2.5-1, which allows the prediction of the Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) or Total Oxygen Demand (TOD) over the duration of the reaction:

$$\frac{[A+B]}{[A+B]_o}=\frac{[A]_o}{[A]_o+[B]_o}\left[\frac{k_2}{k_1+k_2-k_3}e^{-k_3t}+\frac{(k_1-k_3)}{k_1+k_2-k_3}e^{-(k_1+k_2)t}\right]+\frac{[B]_o}{[A]_o+[B]_o}e^{-k_3t} \qquad \text{Equation 1.2.5-1}$$

Where A represents all initial and relatively unstable intermediate organic compounds except acetic acid and B contains the refractory intermediates represented by acetic acid. The model assumes a scheme of the reaction pathways as shown in figure 1.2.5-1.

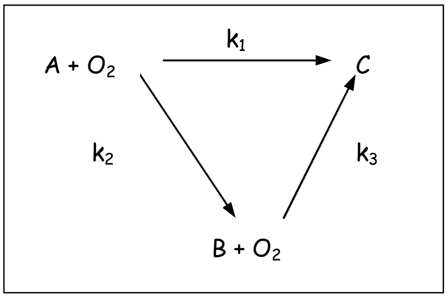


Figure 1.2.5-1 Scheme of the reaction pathways

In addition, the model assumes the following considerations:

1- The concentration of the groups A or B may be expressed in forms of Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) or Total Oxygen Demand (TOD).
2- Based on the bibliography, the reaction rate may be assumed to be first order to group A or B, and nth order to oxygen.
3- The reactor is supposed to follow the model of an isothermal and ideal batch reactor or plug-flow reactor with constant volumetric flow rate.

Some other models have been found in the literature, such as the Lumped kinetic Model (LKM) by *Zhang and Chuang* (1999), the Multi-component Kinetic Model suggested by *Escalas et al.*, (1997), the Extended kinetic Model (ELKM) by *Belkacemi et al.*, (2000) and the Lumped kinetic Model for Oil Waters (LKM-OW) by *López Bernal et al.*, (1999).

This investigation includes not only a study about wet oxidation of multi-compound solutions but also about solutions containing one compound, i.e., 4-chlorophenol. For this reason, it seems also interesting to determine some data regarding the kinetics of the wet oxidation of single-compound solutions. Related to this, the data published in 1995 by Mishira et al. results significant to this study, especially chapter 2.2 (pages 9-11), which includes a description of wet oxidation of Phenols and substituted Phenols. Based on the literature collected until that moment, they affirmed that Phenols and Chlorophenols exhibit an induction period, the length of which depends on the oxygen partial pressure, followed by a fast reaction step. Thus, the reaction can be divided in two separate parts. In the first one, i.e. **induction period**, the radicals are formed and in the second part, the oxidation takes place. The orders of these reactions are assumed to be 1 respect the chlorophenol and between 0 and 1 for oxygen (*Verenich, 2003*), thus the reaction rate can be expressed as follows:

$$-\frac{d[4-CP]}{dt} = k_i^o e^{\left(\frac{-Ea_i}{RT}\right)}[4-CP]^m[O_L]^n \qquad \text{Equation 125-1}$$

where m= 1 and 0<n<1

On the other hand, it has been found in the literature that the kinetics of the induction period followed and equation of the Arrhenius type that includes a pressure term (Verenich, 2003) and therefore, the duration of the induction period can be expressed as:

$$t_i = \frac{k'_i}{P} e^{\left(\frac{Ea'_i}{RT}\right)}$$ Equation 1.2.5-2

Combining equations 1.2.5-1 and 1.2.5-2, and assuming a pseudo-first order reaction (n= 0), the kinetics of the wet oxidation reaction of solutions containing 4-chlorophenol can be expressed as follows:

$$\ln\frac{[4-CP]}{[4-CP]_o} = k_i^o e^{\left(\frac{-Ea_i}{RT}\right)}\left[t - \frac{k'_i}{P} e^{\left(\frac{Ea'_i}{RT}\right)}\right]$$ Equation 1.2.5-3

It seems that the presence of the induction period is acquiring more and more importance and it has been studied as well for the catalytic wet oxidation of phenol (*Santos et al., 2006*) and for the wet peroxide oxidation of the same compound (*Nikolopoulus et al., 2005*).

Some data has been found in the literature regarding the kinetic parameters of the wet oxidation of 4-CP. Yang and Ekert (1988) found that the order with respect to 4-CP and oxygen was 1 and 0 respectively, and that the activation energy was 33 kJ/mol when working in the range of temperatures of 310-340 ºC and 7.5 MPa of Po_2. These results are not in agreement with the ones found by Joglekar et al. 1991, who found order 1 for oxygen and 4-CP working at 150-180 ºC and 0.3-1.5 MPa of Po_2. In addition they also found the activation energy and pre-exponential factors values of the induction period and the steady state: Induction step: A= 1.29 10^{14} and Ea= 134.5 kJ/mol and Steady Step: A= 2.21 10^{8} and Ea= 77 kJ/mol.

1.2.6 CATALYTIC WET OXIDATION

Catalytic Wet Oxidation (CWO) is an upgraded wet oxidation with the incorporation of a suitable catalysts. The CWO process can be carried out at much milder temperature and pressure conditions, thus reducing not only the capital costs and the corrosion but also the safety implications. The process of CWO and WO are considered to be very similar, since at the end of the reaction acetic acid, besides CO_2 can be identified (*Debellefontaine et al., 1996*).

The importance of free radicals in this mechanism encourages researchers to find catalyst and promoters for radical reactions. Homogeneous catalysts were first investigated, especially with copper and iron salts, which are known to give high conversion of organic pollutants. However, their use induces a separation step to remove the salts from the clean water. Because of this, heterogeneous catalysts have been widely developed (*Levasseur et al., 2006*). Even though heterogeneous catalysts are used, the composition should be carefully chosen in order to avoid a significant leaching of the metal. Transition metal oxides have been proved to be very effective for organics removal, however they are characterized by leaching. Currently, it seems that the future of catalytic wet oxidation is based on the combination of a noble metal such as Pt, Ru, Ir, Rh, Pd… over supports like CeO_2, ZrO_2 or TiO_2, which have been proved to be very stable in aqueous solutions under high temperature and pressure conditions (*Zhao et al.,2005; Minh et al. 2006; Goi et al. 2006; Posada et al. 2006*) .

Many heterogeneous metal oxide catalysts, such as alumina supported CuO, Fe_2O_3, MnO, ZnO, NiO and TiO_2 supported Ru, etc, have been studied for oxidation of model organic compounds such as phenol, chlorophenol and carboxylic acids *(An et al., 2001).* However, the studies on wet oxidation of Chlorophenols are scarce and only few references of this topic have been found in the literature. Okitsu et al., (1994) studied the degradation of p-chlorophenol by wet oxidation in presence of Pt. They found out that the decomposition of the target compound after 30 minutes was 90.9 %, 60.9 % and 46.0 % for 1.2 μm size catalyst, 69 μm size catalyst and 80 μm size rutile support catalyst respectively.

Another research group (*Chang et al., 1997*) carried out wet oxidations of p-chlorophenol catalyzed by MnO_2, Co_2O_3 and $CuSO_4.5H_2O$. The latter was demonstrated to be the most effective in reducing the concentration of the chlorophenol in water. Quin et al., (2001), also studied this field and the catalysts employed were Tetra-amine platinum (II) nitrates solutions, palladium chloride and ruthenium chloride, manganese (II) acetate over the following supports ultrafine γ-alumina, cerium (III) acetate, and activated carbon. They concluded that supported noble catalysts are effective catalysts for wet oxidation of 4-chlorophenol and that the activity of the noble metal on alumina or activation carbon decreases in the order of Pt>Pd>Ru. They found as well, that the order was the opposite when cerium was the support.

1.2.7 WET PEROXIDE OXIDATION

Wet oxidation is a very efficient process but it involves high temperature and pressure conditions. In order to lower this constraint, more efficient oxidizers can be employed. The first idea developed was to use homogeneous catalyst such as transition metal salts or hydrogen peroxide in order to promote air oxidation at a lower temperature. The second attempt was to use hydrogen peroxide as the oxidizer instead of molecular oxygen, leading to the development of another process, wet peroxide oxidation (*Debellefontaine et al., 1996*).

As opposed to WAO-WO, which employ a gaseous source of oxidizing agent (air or oxygen) and which is a two-step process (mass transfer plus oxidation), wet peroxide oxidation uses a liquid oxidizing agent (hydrogen peroxide) which eliminates the mass transfer problems. Wet peroxide oxidation can be understood as well as an adaptation of the Fenton process in the event that iron salts are used as catalyst. Under these circumstances, the only difference between both processes would be the temperature at which the reactions are conducted.

The mechanistic pathway the wet peroxide oxidation follows is considered to be similar to the one of the Fenton's processes and the $OH^{\cdot}$ radicals are of main importance. The radical can react either with an organic, leading to oxidized organic species, or with itself, leading in this case to inactive molecular oxygen. Then, it is easily understood that the efficiency for oxidation of organics will strongly depend on the concentration of $OH^{\cdot}$ radicals. The best results are obtained when all the radicals produced are trapped by the organic species, then the peroxide concentration within the reactor must be kept at a value as low as possible above the concentration of organics. This results in a step by step addition of the peroxide, during the run of a batch process, and throughout the reactor in the course of a continuous process. (*Debellefontaine et al., 1996*).

The literature about this technology is scarce, however the good efficiency lately proved by wet peroxide oxidation has attracted researchers attention and investigations in this field are currently being conducted. Wet peroxide oxidation has been proved to be effective under mild conditions for the treatment of phenolic compounds (*García-Molina et al. 2004; Okawa et al.,2005*). The use of catalysts during the wet peroxide oxidation is also acquiring more and more importance and promising results about the degradation of phenol and p-coumaric acid over several catalysts, such as iron aluminium combinations and Fe-Zeolites respectively have been obtained (*Najjar et al., 2005; Kurian and Sugunan, 2006; Niikolopoulus, 2006*).

1.3 MEMBRANE TECHNOLOGY

Opposite to Advanced Oxidation Processes, which main characteristic is the fact that they are able to destroy the pollutants and to achieve nearly complete mineralization, membrane technology appear to be a promising field of study in terms of separation strategies. In the last years, membrane technology applied to wastewater has overcome one of the fields in which more research is being developed. The principle of this technology is based on the separation of solids or non-miscible particles of a liquid or gaseous effluent. The applications of the membrane technology can be analyzed from two different points of view. In some cases, the aim of the process is to recover or concentrate some valuable substances from a solution. This is common practice in the chemical and pharmaceutical industries. Another application, related to this, is the concentration of a wastewater stream for further treatment where a higher concentration is required, as seen in some advanced oxidation processes. The second principal application comprises the removal of undesirable products such as particles, colloids, high molecular weight materials, bacteria and viruses from an effluent stream in order to obtain more purified water. Another example is the utilization of membrane systems for potable water treatment, which are already in use in several countries. (*García-Molina et al., 2006*)

The two most important components of these processes are membranes and modules. Membranes are planar, semi-permeable structures which let permeate some components of a fluid while other components are held back. On the other hand, modules are the close spatial arrangement where membranes are placed. In figure 1.3-1 a scheme of a tangentially fed membrane process can be observed. It should be noted that over the duration of the process, two currents are generated, the permeate and the concentrate. The *permeate* is composed of those substances that manage to cross the membrane and the *concentrate* consists of those compounds that are rejected by the membrane.

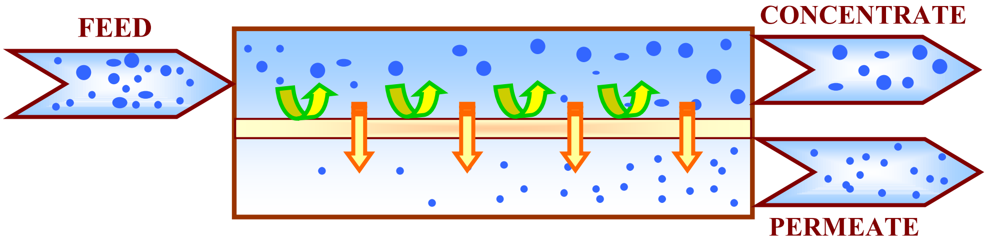


Figure 1.3-1 Cross-flow model Filtration.

Membranes can be classified according to two different criteria:

1- by the size or molar mass of the largest particles or molecules that can permeate the membrane.
2- by the separation principle employed and the aggregation state of the fluids contacting the membrane.

Regarding the first criteria, *porous* and *dense* membranes can be distinguished. For the retention of macroscopic particles and of molecules with a molar mass higher than 2000 kg/mol “porous” membranes are employed. On the other hand, separation of smaller particles is carried out by dense membranes, i.e., membranes that do not present a microscopically porous structure. The transport mechanism through porous membranes is the so-called sieving mechanism. In dense membranes the mechanism of transport is on most occasions modeled as a sequence of steps that includes sorption, diffusive transport and desorption. For this reason, dense membranes are commonly known as “sorption diffusion membranes”.

Paying attention now on the second criteria, i.e. classification according to the separation mechanism, two groups can be distinguished. On one hand, one finds the *processes based on the transmembrane pressure difference* and on the other hand, the *processes with similar pressures in both permeate and concentrate chambers*. Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) are processes whose driving force is the transmembrane pressure. On the other hand, the separation in other processes such as Diffusion Dialysis (DD) and Electrodialysis (ED), occurs due to other driving forces, and thus, the pressure in both sides of the membrane is similar. In Diffusion Dialysis mass transport follows the concentration gradient of dissolved components. In Electrodialysis, the separation process takes place due to the different permeability of membranes for cations and anions.

Gas Permeation (GP) and Vapor Permeation (VP) form another particular group of membrane processes. Both processes are based on the partial pressure difference i.e., fugacity between feed and permeate side, however, and as a difference from processes such as ultrafiltration, in this case the permeate is a gas or a vapor.

1.3.1 PROCESSES BASED ON THE TRANSMEMBRANE PRESSURE DIFFERENCE

As it was previously mentioned, these processes depend on the application of an external pressure in order to deal with the filtration mechanism. In the case of working with liquid-liquid systems on both sides of the membrane, the processes to be employed, depending of the particle size and the applied pressure, are: ultrafiltration and microfiltration which employ porous membranes and nanofiltration and reverse osmosis which use dense membranes. In figure 1.3.1-1 a wide range of different size substances and the most suitable membrane process for the retention of each of them are depicted.

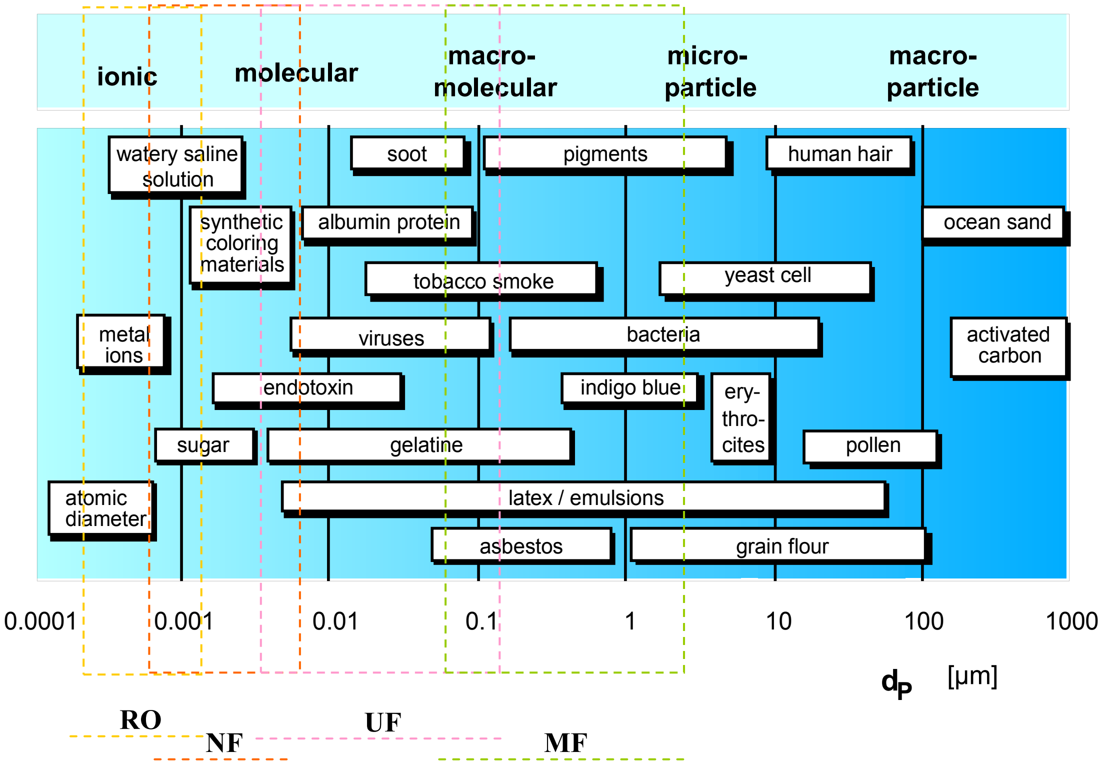


Figure 1.3.1-1 Particles sizes and membrane processes applicability range (adapted from *Melin, 2004*).

In terms of applied pressure, microfiltration usually requires a pressure increment between 0.5 and 3 bar, ultrafiltration an increment between 1 and 10 bar, nanofiltration between 10 and 30 bar and finally, reverse osmosis between 10 and 200 bar. Microfiltration membranes have the biggest pore diameter and the lowest increment of pressure between both sides of the membrane; consequently, almost all micro-solids contained in the original effluent are able to cross the membrane, provoking a low selectivity of the membrane. In general terms, only suspended particles can be separated from the original liquid when using MF membranes. The opposite case corresponds to RO membranes, whose pore diameter is the smallest and the pressure applied the highest. This implies that almost only water is able to cross the membrane while even mono-valent salts and non-dissociate acids are rejected by the membrane. RO membranes accomplish the highest selectivity and allow the total purification of the water. The selectivity of UF and NF membranes is located between MF and RO membranes.

Working with this kind of membrane processes implies the application of hydraulic pressure. In the event that the flux is perpendicular to the membrane, accumulation of particles on the surface of the membrane are likely to happen, producing the obstruction of the membrane and the consequently dramatic diminution of the permeate flow rate. In order to avoid or to reduce these accumulations, the input stream should be fed tangentially (*Tanninen, 2000b*). However, even when working in a tangential or cross-flow mode, reduction of the permeate flux in the course of the process eventually occurs. The main reasons for this flux decline are the concentration polarization and the fouling of the membrane (*Mänttäri and Nyström, 2000*). In figure 1.3.1-2 these two operation modes are depicted. In it, it can be observed that the accumulation of particles or molecules is more likely to happen when the inlet stream in fed perpendicularly to the membrane.

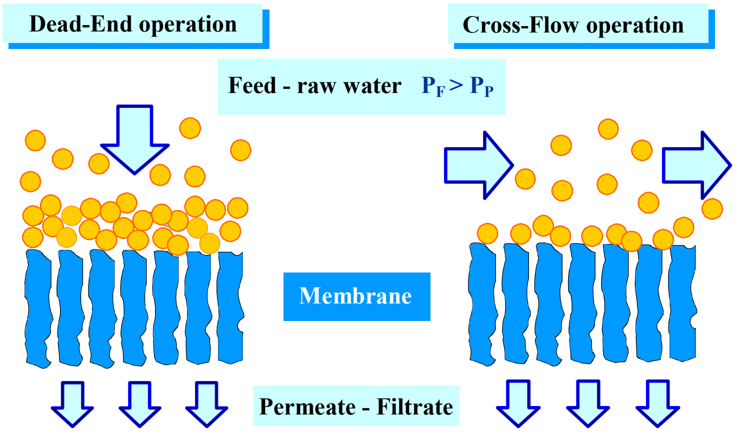


Figure 1.3.1-2 Dead-End and Cross-Flow operation in membrane processes. (adapted from *Melin, 2004*).

Concentration polarization is a reversible phenomenon also named “reversible cake layer formation” caused by the accumulation of some solids on the surface of the membrane in the concentrate chamber. It is an inherent phenomenon of pressure driven membrane processes. This problem commences with an initial accumulation of solids on the membrane surface that hinders the pass of the water through it and enhances the continuous accumulation of new solids. This leads to the formation of a solids layer adjacent to the membrane surface that totally avoids the pass of the water. This problem is commonly solved by using tangential flow circulation units. Therefore, accumulation on the surface of the membrane is reduced or even avoided. (*Ullmann's, 1991*)

On the other hand, membrane fouling consists of the adsorption of feed constituents on the membrane surface. This contamination of the membrane is the consequence of interactions of the type particle-particles or particle-membrane and it can be influenced by the hydrodynamics of the system, the membrane material, the feed pre-treatments and the operating parameters. This phenomenon is often observed when solutions containing biological materials have to be processed (*Ullmann's, 1991*). In many cases concentration polarization promotes fouling. Thus, fouling can be significantly reduced by minimizing concentration polarization (*Mänttäri and Nyström, 2000*). Once fouling is detected in the system, the only way to minimize and control it consists of applying special module back-flushing and chemical cleaners. These chemicals should not only be effective against several foulants, but gentle in repairing the membranes to preserve and restore their characteristics. The optimal choice of the cleaning agent is a function of the membrane material and the kind of foulant in a complex manner (*Liikanen et al., 2002*). These choices to avoid fouling, i.e. back-flushing and chemical cleaners, implies extra operating costs.

In figure 1.3.1-3 the influence of fouling and concentration polarization on membranes performance is represented. It should be noted that the permeate flux decreases when the membrane suffers from concentration polarization. However, the decrease in the flux is drastically much higher when fouling of the membrane occurs. Due to the importance of having always an optimum permeate flux, it is of major importance to have these two phenomena under control.

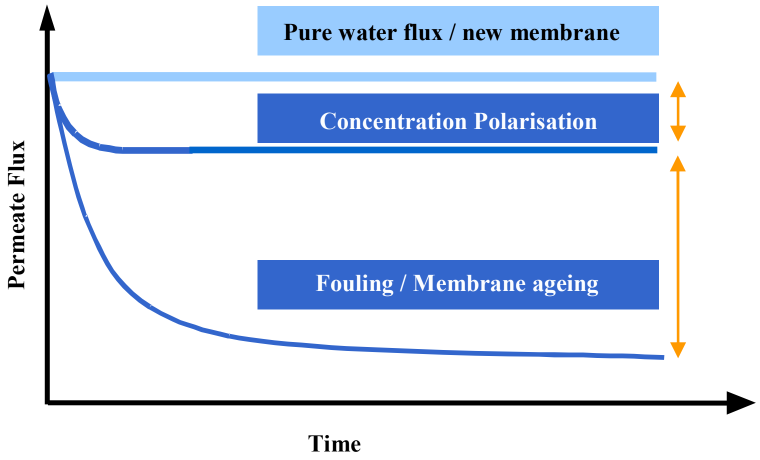


Figure 1.3.1-3 Impact of fouling on membrane performance. (*Melin, 2004*).

1.3.2 COMBINATION MEMBRANE TECHNOLOGY - OXIDATION

Membrane and oxidation processes are well known processes in the field of wastewater treatments by their capacity to eliminate discoloration and odor from water. In many cases their effectiveness and efficiency are very similar and in fact, it is very common to find units where these processes are combined to treat color and odor of wastewater (*Rosa and Pinho, 1995; Jin and Fan, 1996*). The combination of these two processes appears to be of special interest due to the different properties that these techniques present. On one side, membrane technology is able to separate the undesired substances from a wastewater and to obtain extra-pure water. On the other side, oxidation techniques allow the destruction of this undesired matter. A remarkable characteristic of the combination of these processes is that both can serve as pre- or post-treatment for the other. This way, some solids precipitated in the oxidation can be later easily separated by membrane filtration. Under these circumstances, the oxidation is the first stage of the process. On the other hand, when the membrane process acts as pretreatment, its mission consists of removing substances that can inhibit the oxidation or concentrating the wastewater in order to diminish the amount of water to be oxidized. (*Tanninen, 2000a*)

One application of this hybrid technology is a system where oxidation is employed as pre and post-treatment for the membrane process, thus the system is formed by three units: pre-ozonation, membrane filtration and wet oxidation (figure 1.3.2-1). The clarified effluent of a paper mill is dealt by means of ozonation with the purpose of eliminating or reducing the lignin content. In the second stage, the effluent is nanofiltrated and two new effluents are obtained. The permeate presents a lower inorganic load than the original effluent and it is recirculated to the process. The concentrate from the membrane unit is sent to a WO unit where the organic compounds are eliminated.

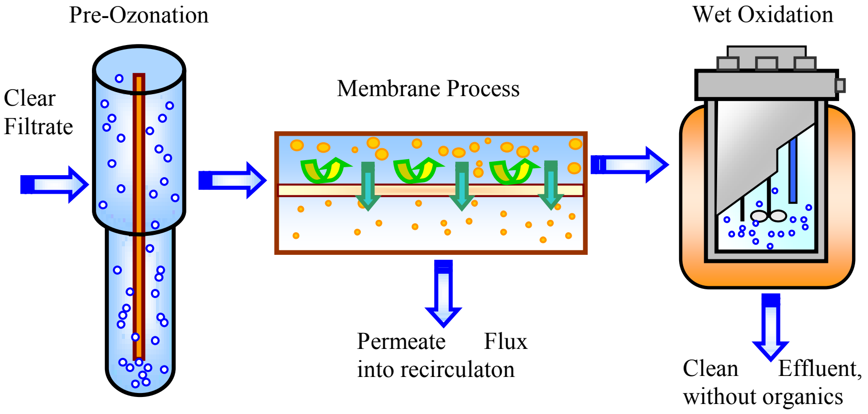


Figure 1.3.2-1 Pre-ozonation- nanofiltration-oxidation process (adapted from *Munter, 1998*).

Another application of this combination of processes, where the membrane process acts as pre-treatment, is based on a Japanese patent (*Sumita et al., 1999*) for the elevated organic and manganese content waters processing (figure 1.3.2-2).

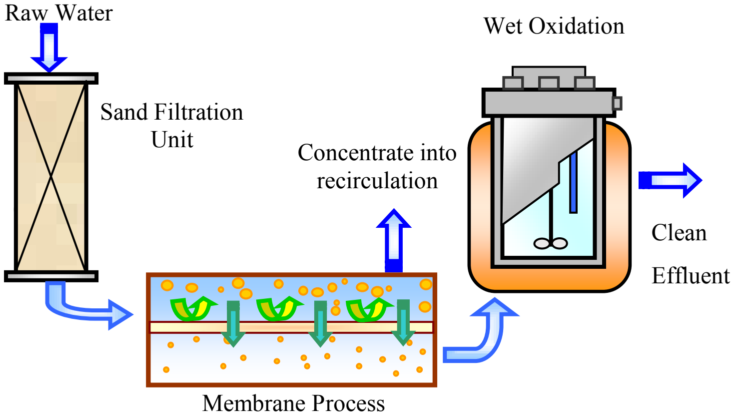


Figure 1.3.2-2 Combination of filtration, nanofiltration and oxidation (adapted from *Tanninen, 2000a*).

In this particular application, the effluent is made to pass through a stuffed column of sand where the filtration of suspended particles is carried out. In the following stage, the water is treated by membrane filtration, where most of the organic matter and manganese are retained. The obtained permeate is put under oxidation in a catalytic column in presence of hydrated manganese, with the purpose of transforming soluble manganese into insoluble. As a result of the process, water of excellent quality that solely contains rests of organic matter and manganese is obtained.

In some cases, the oxidation is also used as a pre-treatment. One of these applications is a German patent (*Patzlaff et al.,1999*), based on an oxidation followed by a membrane unit (figure 1.3.2-3). The aim is to mix the wastewater, of elevated organic content, with hydrogen peroxide, that acts as oxidant. The resulting mixture is then treated by membrane filtration and from this unit, a high purified permeate is obtained.

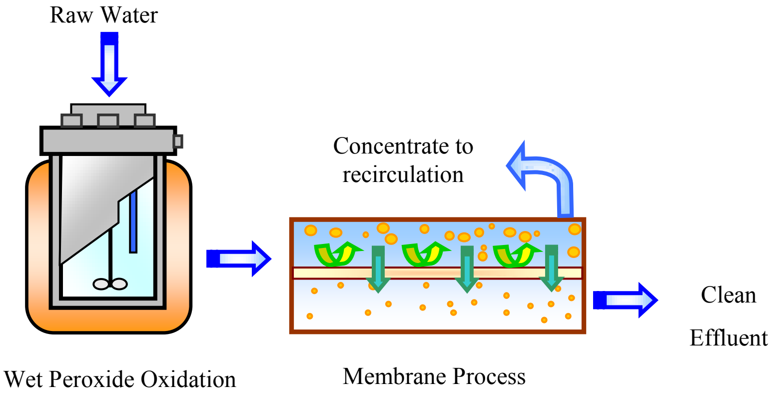


Figure 1.3.2-3 Hybrid process Oxidation-Nanofiltration (adapted from *Tanninen, 2000a*).

Another German patent (*Kotowski, 1999*) describes a process based on a combination membrane filtration-catalytic oxidation for the treatment of highly polluted wastewaters. The waste effluent is firstly treated by membrane filtration, where two currents are originated: the concentrate and the permeate. The concentrate is further treated by a catalytic oxidation by means of H_2O_2 and ferrous or titanium salts.

1.4 MODEL COMPOUND: 4-CHLOROPHENOL

Chlorophenols[1] (CPs) make up a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act (*Keith and Telliard, 1979; Hayward, 1999; EPA, 2002*) and by the European Decision 2455/2001/EC, in view of the fact that most of them are toxic and hardly biodegradable. The need to restore contaminated sites to avoid further risks to the environment has promoted in the last years the development of effective methods for CPs removal.

Chlorophenols are chemical derivatives of phenol which contain from one to five chlorine atoms. They were discovered in 1836 when Laurent chlorinated coal tar (*Ullmann's, 1991*). There are 19 different chlorophenols, formed by replacing from one to five of the non-hydroxyl hydrogens of the phenol molecule with chlorine atoms. These include three monochlorophenols (MCP), six dichlorophenols (DCP), six trichlorophenols (TCP), three tetrachlorophenols (TTCP) and one pentachlorophenol (PCP). In figure 1.4-1 the chemical structure of all these compounds is depicted.

Chlorophenols are compounds of special interest because of their high toxicity and low biodegradability. Their persistence in the environment is due to their chlorinated nature *(Takeuchi, 2000)* and they are considered to act as uncoupleers of oxidative phosphorylation *(Terada, 1990).* Due to their numerous origins, they can be found in ground waters, wastewater and soils (*Wegman and van den Broek, 1983*) and even in the trophic chain of places with very low pollution levels (*Paasivirta et al., 1980; WHO, 1989a*).

Regarding the guideline values for chlorophenols concentration in the aquatic environment, the first edition of the "Guidelines for Drinking-water Quality", published in 1984 by the World Health Organization (WHO), suggested an individual chlorophenol maximum concentration of 1 μg/L. The same concentration was suggested in the Directive 98/83/CE.

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[1] As generally submitted in the literature, the general nomenclature used for CPs is the following one: monochlorophenol (CP), dichlorophenol (DCP), trichlorophenol (TCP), tetrachlorophenol (TTCP) and pentachlorophenol (PCP)

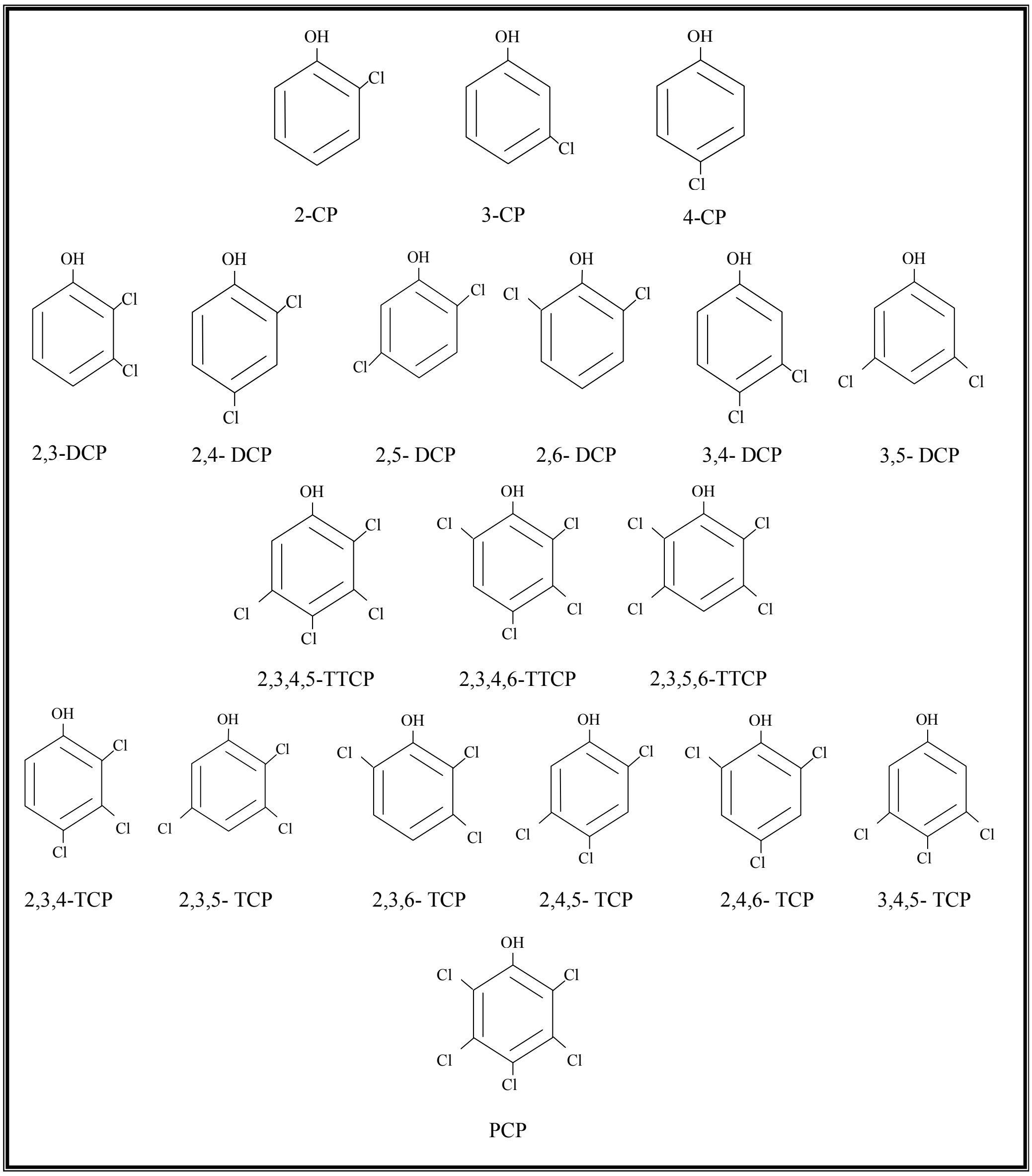


Figure 1.4-1 Chlorophenols family.

1.4.1 PROPERTIES OF 4-CHLOROPHENOL

Parachlorophenol is a phenol with a chlorine atom in the 4th or para position (see figure 1.4-1). Some other accepted names of this compound are 4-chlorophenol, phenol-4-chloro-, phenol- p-chloro-, 4-chlorophenol, 4-hydroxychlorobenzene and p-chlorphenol (*http://chemfinder.cambridgesoft.com*).

As a member of the chlorophenols family, 4-CP is characterized by producing disagreeable taste and odor to drinking water at concentrations below 0.1 $\mu g \cdot L^{-1}$ (*Veschueren, 1983*) and adverse effects on the environment (*Folke and Birklund, 1986*). It is a white needle-like crystalline solid at ambient temperature with a boiling point well above the boiling point of water. It has a low vapor pressure, but not negligible, and it is slightly soluble in water but highly soluble in alcohols (*Warrington, 1996*). Low solubility in water may be increased by the formation of the sodium or potassium salt congeners. In table 1.4.1-1 the boiling and melting points, the relative density to water and, the solubility in water of 4-CP are given. In order to be able to establish a comparison between different Chlorophenols, the same physical properties of some compounds of the family are also given.

Table 1.4.1-1 Physical properties of some Chlorophenols (*International Occupational Safety and Health Information Centre, 1999*).

CP	Boiling Point (ºC)	Melting Point (ºC)	Relative density (water = 1)	Solubility in water, g/100 mL at 20 ºC
2-CP	175	9.3-9.8	1.3	2.85
3-CP	214	33	1.245	2.6
4-CP	220	43	1.3	2.7
2,4-DCP	210	45	-	0.5
2,5-DCP	211 at 99.2 kPa	59	-	Poor
3,5-DCP	233 at 100.9 kPa	68	-	Poor
2,3,6-TCP	253	58	-	None
2,4,5-TCP	253	67	1.68	0.1
2,4,6-TCP	246	69	1.5 at 58ºC	None
2,3,5,6-TTCP	288 decomposes	115	1.6 at 60ºC	Poor
PCP	309 decomposes	191	1.98	0.001

In the table it can be noted that 4-CP has higher boiling and melting points than the rest of monochlorophenols and that all of them have similar densities and solubilities in water. Compared to 2,4-DCP, 4-CP has a higher boiling point, nevertheless, the most significant difference between them as for physical properties is the solubility in water. Comparing 4-chlorophenol with trichlorophenols, tetrachlorophenols and pentachlorophenol, it can be easily noted that 4-CP melts and boils at a lower temperature and that has higher solubility in water than the rest of these compounds.

As a compound of the chlorophenols' family, 4-CP is flammable but does not actually burn; rather it decomposes on heating to form toxic, volatile, chlorinated gases (*WHO, 1989c*). It is a weak acid and a versatile intermediate in chemical syntheses in view of the fact that both the hydroxyl group and the aromatic ring can react by both electrophilic and nucleophilic substitution.

1.4.2 ORIGINS AND USES OF 4-CHLOROPHENOL

Parachlorophenol is manufactured by direct chlorination of phenol (*Ullmann's, 1991*) and it is introduced into the environment as a result of discharges from manufacturing plants, discharges from factories using the compound as intermediate in the production of higher chlorinated phenols and other products such as phenoxy herbicides or through the degradation of other chemicals (e.g. phenolxyalkanoic acids). It can be also found in the aquatic medium as a result of the chlorination of humic matter or natural carboxylic acids in the course of the chlorination of municipal drinking water (*Exon, 1984*).

Indirect sources of entry of 4-CP to the aquatic environment include discharges from paper mills, where it is formed as by-product of the bleaching process, as a result of the disinfection of sewage, industrial wastes and drinking water with chlorine, and from the microbial breakdown of agricultural herbicides such as 2,4-D and subsequent run-off/leaching of the products *(www.ukmarinesac.org.uk).* Finally, fly ash from incinerators, power stations, fireplaces and forest fires also contribute to the widespread distribution of chlorophenols in the environment. (*Warrington, 1996*).

Grinmwood and Mascarenhas (1997) found that reliable data on the production levels of chlorophenols other than pentachlorophenol were not available in open literature. In 1975, the combined global production of all chlorophenols was estimated to approach 200 million kilograms, where more than half consisted of chlorophenols other than PCP, with 2,4-DCP, 2,4,5-TCP and 2,3,4,5-TCP predominating *(WHO 1989a).*

In general, Chlorophenols are employed as agricultural chemicals, pharmaceuticals, biocides and dyes (*Ullmann's, 1991*). Due to their biocidal activity Clorophenols are used to prevent growth of microorganism in the manufacture of some industrial products such as photographic chemicals, paints, oils, textiles, glues, starches, cellulosic wood fillers, rubber, protein-based products and shampoos, in industrial cooling and process waters in mills (*Warrington, 1996*). Among these, the main uses of 4-CP are the following (*EPA, 1980a,b*): extraction of sulphur and nitrogen from coal, intermediate in the synthesis of dyes and drugs, denaturant in alcohol, solvent in the refining of oils, production of the herbicide 2,4-D, the germicide 4-CP-o-cresol and 2,4-CP

1.4.3 ENVIRONMENTAL CONSIDERATIONS

The half-life of most Chlorophenols is short under most natural conditions: half-lives range from days to weeks or, on occasion months. Accumulation of high levels of Chlorophenols in organisms and the maintenance of such high levels is the result of constant input to the environment. If such input were to cease, the Chlorophenol levels would be expected to drop quickly in sediments, water and organisms. Bacteria are able to break down Chlorophenols by two different mechanisms: ring cleavage to yield aliphatics instead of aromatics and dechlorination. (*Warringon, 1996*)

All the substitutions sites on the phenol molecule are not equal in their effect of toxicity to organisms since the location of the chlorines affects the efficiency of microbial breakdown. Among the monochlorophenols, 4-chlorophenol is much more toxic than either 2- or 3-chlorophenol because, within any isomeric group of congeners, those with chlorine in the 4th or para position, are more toxic than the others. (*Warrington, 1996*)

1.4.3.1 Toxicity to animals and plants

All Chlorophenols have bactericidal activities and are highly toxic to algae. They also possess a phytotoxicity that increases with the degree of chlorination. The absorption of Chlorophenols by plants depends on the solubility of the product and pH of the environment.

Terrestrial and aquatic plants can in certain cases absorb, transform and eliminate Chlorophenols without harm, but most often these plants are very sensitive to the phytotoxicity of these aromatic compounds. Fish and other aquatic organisms absorb Chlorophenols either through their gills, gastrointestinal tract, or skin. Acute toxicity for invertebrates, crustacean and freshwater and seawater fish increases with the level of chlorination. These compounds also have a long-term toxic effect at low concentrations (*Ullmann's, 1991*). The 50 % Lethal Doses (LD_{50}) values for rats, the Maximum Acceptable Concentrations (MAC) and Aesthetic Objectives (AO) of some Chlorophenols in drinking water are shown in table 1.4.3-1. It can be observed that as for the Oral Lethal Doses available, PCP is the most toxic compound and trichlorophenols the less harmful.

Table 1.4.3-1 LD_{50} of Chlorophenols for rats (*Registry of Toxic Effects of Chemical Substances, 1983*), MAC and AO of some chlorophenols in drinking water (*EHP, 1987*; *Warrington, 1996*).

Chlorophenol	**LD_{50} (mg/Kg)**		**MAC (µg/L)**	**AO(µg/L)**
	Oral	**Percutaneous**		
2-chlorophenol	670	950		
3-chlorophenol	570	1030		
4-chlorophenol	261	1390		
2,4-dichlorophenol	580	1730	900	≤ 0.3
2,4,5-trichlorophenol	820	2260		
2,4,5-trichlorophenol, sodium salt	1620			
2,4,6-trichlorophenol	820		5	≤ 2
2,3,4,6-tetrachlorophenol	140	210	100	≤ 1
pentachlorophenol	50	100	60	≤ 30
pentachlorophenol, sodium salt	210	72		

1.4.3.2 Health Effects

Chlorophenols are readily absorbed when administered by the oral, inhalation or dermal routes (*WHO, 1989a,b*). These compounds were found to accumulate mostly in the liver and kidneys of experimental animals and to a lesser degree in the brain, muscle or fat (*WHO, 1984*). They are bound to glucuronide or sulphate in the liver. Chlorophenols are eliminated primarily in the urine in both free and bound forms, with lesser amounts in faecal matter. Four human volunteers who ingested PCP at a concentration of 0.1 mg/Kg bw (bw= body weight) eliminated 74 % and 12 % of the administrated dose as PCP and PCP-glucuronide respectively, in the urine within eight days (*Braun et al., 1978*). The hazardous biological effects of 4-CP and some other compounds of the same family are given in table 1.4.3-2.

Table 1.4.3-2 Hazardous biological effects of Chlorophenols. Adapted from *CESARS, 1989*.

Chlorophenol	**Hazardous Biological Effects**
2-CP 3-CP 4-CP	- Unpleasant and penetrating odor (3 and 4-CP) - Toxic by skin adsorption, ingestion or inhalation - Tissue irritant - When heated to decomposition, it emits highly toxic fumes
2,4–DCP	- Slight fire hazard - Reacts strongly with oxidizing agents - Emission of toxic fumes when heated or in contact with strong acids - Strong eye and tissue irritant - Inhaled fumes provokes irritation of the respiratory track - Toxic when ingested and when absorbed through the skin - Chloracne and porphyria have been reported in manufacturing personnel
2,4,5-TCP	- Non-flammable and no serious health hazard occurs with normal industrial use - Harmful when ingesting large amounts - High amounts of dust of fumes provoke eye and nose membranes irritation - Skin absorption causes irritation, redness and edema but no danger of poisoning - Prolonged skin contact will result in mild to moderate chemical burns
2,4,6-TCP	- non- flammable - heating the salt to 280ºC produces dibenzo-p-dioxins - Dust causes eye, nose and pharynx irritation and may injure the cornea - Irritation, redness and chemical burn can be caused by skin absorption
2,3,4,5 and 2,3,5,6 TTCP	- Emission of toxic chlorine fumes when heated to decomposition
2,3,4,6-TTCP	- Non-flammable - Strong skin irritant - Pungent odor
PCP	- Strong and Pungent smell - Non-flammable but emits toxic fumes when heated to decomposition - Vapors and dust irritates skin and mucous membranes

In this table it can be observed that the major hazardous effects of 4-chlorophenol are its unpleasant and penetrating odor, its toxicity by skin adsorption, ingestion or inhalation, its tissue irritating nature and the emission of toxic fumes when it is heated to decomposition.

The toxic effects of Chlorophenols are directly proportional to the degree of chlorination (*Department of National Health and Welfare, 1986)* due mainly to higher fat solubility as indicated by higher octanol/water coefficients values, resulting in greater uptake by organisms *(Warrington, 1996)*. Acute exposure to lesser chlorinated phenols in humans results in muscular twitching, spasms, tremors, weakness, ataxia, convulsions and collapse. Acute poisoning by PCP is characterized by general weakness, fatigue, ataxia, headache, anorexia, sweating, hyperpyrexia, nausea, vomiting, tachycardia, abdominal pain, terminal spasm and death.

In humans, the minimum lethal oral dose of PCP has been estimated to be 29 mg/kg bw (*EHP, 1987*). Soft issues sarcomas, Hodgkin's disease and leukemia have been reported in epidemiological studies and phenoxy acids. The World Health Organization examined data for 2,4,5-TCP, 2,4,6-TCP and PCP and concluded that, at the time of the review, the data was inadequate for an evaluation of carcinogenicity (*WHO, 1984*).

1.5 PULP AND PAPER INDUSTRY WASTEWATER

Industrial activity has been recognized as causing water pollution through atmospheric depositions and wastewater discharge. The pulp and paper industry is the world's sixth largest polluter (after the oil, cement, leather, textile, and steel industries), as it discharges a variety of liquid wastes, including chlorinated derivates of phenol, into the environment (*Ali and Sreekrishnan, 2001*).

Pulp and paper mills employ and generate materials that may be harmful to the air, water, and land: pulp and paper processes generate large volumes of wastewaters which might adversely affect freshwater or marine ecosystems, residual wastes from wastewater treatment processes may contribute to existing local and regional disposal problems, and air emissions from pulping processes and power generation facilities may release odors, particulates, or other pollutants. Major sources of pollutant releases in pulp and paper manufacture are at the pulping and bleaching stages respectively. As such, non-integrated mills (i.e., those mills in the absence of pulping facilities on-site) are not significant environmental concerns when compared to integrated mills or pulp mills.

The pulp and paper industry is the largest industrial process water user in the U.S. In 1988, a typical pulp and paper mill employed 60 to 65 m^3 of water per ton of pulp produced. General water pollution concerns for pulp and paper mills are effluent solids, biochemical oxygen demand, toxicity, and color. Toxicity concerns arise from the presence of chlorinated organic compounds such as dioxins, furans, and others (collectively referred to as adsorbable organic halides, or AOX) in wastewaters after the chlorination/extraction sequence (*EPA, 1995*).

Papermaking is a branch of the industry that requires large amounts of water; nevertheless, the fresh water demand and the emission of wastewater can be remarkably reduced with the incorporation of closed water circuits (*Elvers et al., 1991*). During the manufacturing processes no water is produced or consumed, so that, the wastewater in a paper mill is only a result of the intake and use of fresh water. The water problem in a pulp and paper mill can be undertaken from two different points of view. On one side, the effluent from the industry can cause an environmental damage due to the properties of the wastewater. In this sense, it is necessary to treat the water before its deposal. On the other hand, in order to reduce the fresh water consumption, the wastewater should be treated in order to make feasible its reuse. What it is of major importance to notice is that from both points of views, it is necessary to treat the wastewater.

Within a paper mill, the fresh water is used for the following purposes (*Elvers et al., 1991*):

- As cleaning water for the paper machine (wire and felt cleaning).
- As sealing water and confining water in stuffing boxes, suction boxes and cleaners.
- As a solvent and dispersant for fillers and additives.
- As raw material in the operations of whitening, washing and in hydrolysis reactions.

1.5.1 PULP AND PAPER MILL MAIN CHARACTERISTICS

The chosen raw materials and the processes of manufacturing employed, determine the characteristics, not only of the pulp and paper produced but also of the wastewater effluent. One of the aims of this Thesis is to treat this kind of wastewater by wet oxidation, however, before starting this research it is necessary to analyze the factors that determine and modify the quality of the wastewater (i.e., raw materials and processes) in the course of the manufacturing.

1.5.1.1 Raw materials

The study of the raw materials is specially significant when analyzing the wastewater in view of the fact that at the end of the process the water contains part of these materials.

Nowadays, the great majority of paper is manufactured from wood, notwithstanding the fact that in some occasions, even certain remainders of agriculture and some plants are used as raw materials (*Mc. Ketta and Cunnigham, 1995*). The wood, as raw material, is a source of cellulose fibers; cellulose is the main material for paper production and it is commonly considered that the quality of a paper is higher, the higher is its content in cellulose and the longer are its fibers (*Mitjà, 1995; Gullichen and Paulapuro, 2000*). It is noticeable that cellulose is such a valuable product in this kind of industries that currently manufacturers are trying to recover and reuse the cellulose accumulated in the wastewater effluents.

The composition of wood varies a lot depending on the specie of the tree, the geographic location where it has grown and it even varies with the time of the year. The main components of wood are shown in figure 1.5.1-1.

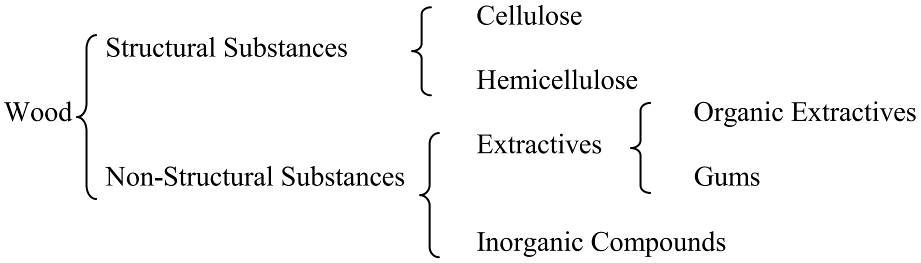


Figure 1.5.1-1 Wood structure main components.

The characteristics of each one of the main components of wood are described more in detail as follows.

- ***Structural Substances:***

  The main chemical constituents of all wood species are *cellulose, hemicellulose and lignin.*

  - *Cellulose and hemicellulose* are carbohydrates and the difference between them is that cellulose is a polydispersed linear homopolysaccharide whereas hemicellulose is a heteropolysaccharide. It is considered that on average two-thirds of the dry matter of wood is composed of polysaccharides, i.e., cellulose and various hemicelluloses. The cellulose content varies between 40 % and 45 % of the wood dry solids, whereas the content of hemicellulose is typically in the range of 25 % to 35 % of the wood dry solids. (*Gullichen and Paulapuro, 2000*).

  - *Lignin* is an amorphous polymer with a high content of functional groups that allows a widely range on linkages between the lignin and some carbohydrates. Although it is evident that physical and chemical interactions (i.e., hydrogen bonds, van der Waals forces and chemical bonding) occur between lignin and carbohydrates, it has been difficult to verify the precise type and amount of chemical linkages. However, lignin not only interacts with some carbohydrates, but also with cationic chemicals employed in paper making, causing a negative effect on the brightness and strength of the paper. The content of lignin in the dry matter is estimated between 20 % and 30 % of the wood dry solids (*Elvers et al., 1991; Gullichen and Paulapuro, 2000*).

- ***Nonstructural Substances:***

  This group includes certain less common substances of low molecular weight. The most significant representatives are ***extractives*** and ***inorganic compounds***.

  - *Extractives* comprise a large number of substances that normally impart color, odor, and taste to wood. Wood extractives can be classified into two groups: *organic extractives and water-soluble polysaccharids* called *"gums"*. Table 1.5.1-1 shows a classification of organic extractives in wood. In paper mills with a high degree of white-water system closure, wood extractives can have a negative impact on paper machine run-ability and on the paper and wastewater quality. In fact, specks in the paper, decreased wet strength, interferences with cationic process chemicals, impaired sheet brightness and paper strength are often caused by lipophilic extractives.

Moreover, effluents from pulp and paper mills can be acutely toxic to fish, mainly due to the presence of resin acids. (*Örsa and Holmbon, 1994*).

- *Inorganic compounds* occupy between 0.1 and 5 % of the dry solids and can affect the wastewater quality in the way that they involve an increase in the quantity of suspended solids, and consequently an increase of the turbidity. The most representative compounds of this group are salts (carbonates, silicates, oxalates, phosphates and sulphates) and oxides (*Elvers et al., 1991a*).

Table 1.5.1-1 Classification of organic extractives in wood (*Elvers et al., 1991a*).

Aliphatic and Alicyclic Compounds	Phenolic Compounds	Other Compounds
Terpenes and terpenoids	Simple phenols	Sugars
(Including resin* acids and steroids)	Stilbenes	Cyclitols
Ester or fatty acids (fats and waxes)	Lignans	Tropolones
Fatty acids and alcohols	Isoflavones	Amino acids
Alkanes	Condensed tannins	Alkaloids
	Flavonoids	Coumarins
	Hydrolysable tannins	Quinones

* The term *resin* is often used as a collective name for the lipophilic extractives (with the exception of the phenolic compounds), which can be extracted from a wood sample by nonpolar organic solvents but are insoluble in water. Most resin compounds protect the wood against microbiological or insect attack.

1.5.1.2 Main Processes

There are many processes involved in the paper manufacturing, these go from the initial wood debarking until the refining of the paper. The main representative steps of this type of industries are briefly described below:

- ***Pulp manufacturing***

There are two different stages in the pulp manufacturing, the Processing of Raw Materials and the Pulping Processes.

1. *Processing of Raw Materials* includes following processes (*Elvers et al., 1991b*):
   - The Storage of Wood
   - Wood debarking
   - Production of Chips

2. *Pulping Processes* accomplish the separation of the source material into fine fibers with more or less removal of lignin or other non-fibrous adjuncts. There are many different manufacturing processes involved in the conversion of wood to pulp. These range from mechanical processes, by which only mechanical energy is used to separate the fiber from the wood matrix, to chemical processes, by which the bonding materials, i.e., lignin, are removed chemically. Pulp properties are determined by the raw material and manufacturing process, and must be matched to the needs of the final paper product. According to the chemical, mechanical or semi-chemical pulping processes employed in this point, the following types of pulp are obtained (*Elvers et al., 1991b; Kirk-Othmer, 1997*):

   - *Chemical Pulp:* At elevated temperatures lignin, a large proportion of the hemicelluloses, and some of the cellulose are dissolved by the action of pulping chemicals on wood. As lignin is removed, much less mechanical energy is needed to separate the fibers from the wood matrix, and the resulting pulp fibers are undamaged and strong. The yield of this process (considering mass of pulp obtained from original matter) varies between 45 and 90 % depending on the intensity of the chemical process. Therefore, when the intensity of the chemical process is elevated, not only lignin is dissolved, but also hemicellulose. In this case, the yield of the process can be less than 45 %, but the obtained fibers have an elevated content in cellulose.

   - *Semi-chemical Pulp***:** This type of pulp is obtained from a chemical digestion, carried out at less extreme conditions than the previous one and followed by a mechanical processing. The yield of this process is between 60 and 90 % and is greater than the chemical processing because the amounts of matter removed by the chemical action are smaller.

   - *Mechanical Pulp:* In this case the separation of fibers is carried out by means of mechanical energy and since there is no elimination of matter by chemical agents, the composition of fibers at the end of the process is very similar to the original wood. For this reason, the content of lignin and hemicellulose is higher compared with both of the previous types of pulp and as a result of the small elimination of matter, the yield of the process is around 95 %.

- ***Paper manufacturing***

Once the pulp is prepared, several processes take part in order to manufacture the paper. These processes may be subdivided into the following operations (*Mc. Ketta and Cunnigham, 1995*):

- *Stock Preparation:* This operation includes the preparation of a thick slurry of pulp in water, “beating”, hydropulping or refining to reduce the thickness of fibers, addition of various chemicals to modify properties of the finished paper, a final cleaning to remove dirt, sand, lumps, etc., and dilution with additional water.

- *Sheet Formation:* In this step a very dilute slurry (less than 1 % in solids content) is run onto the forming fabric, and water is rapidly drained through the support to yield a sheet of somewhat interlocked fibers. The gravity dewatering action is aided by vacuum, pressure from an adjacent sheet, or even centrifugal forces.

- *Drying and Calendering:* At this point, the sheet is dried from an initial moisture of 70-80 % by weight to approximately 4 to 10 % by weight. The wet sheet is transferred to a series of heated steel rolls, where moisture is removed by evaporation.

- *Finishing:* This operation may include several different steps along the process. It may include the special additives such as dyes and pigments added to the pulper or beater to enhance color and opacity, or strength additives and fillers, also added in the stock preparation area. It might also include resin or latex dipping or spraying steps included part way along the drying train, or the application of finish coatings at the calendaring stage.

1.5.2 DEBARKING WASTEWATER

The primary wood treatment process or wood debarking is almost totally ignored in environmental studies. However, the effluent produced in this process is currently one of the most toxic wastewaters in the papermaking industry. The wastewaters from the debarking process are heavily contaminated by fatty and resin acids, tannins, lignins and their derivatives. The presence of lignins and their derivatives, as well as of polymerized tannins, causes these wastewaters to be also highly colored. Tannins are highly toxic polar phenolic polymers, which contribute as much as up to 50 % of the chemical oxygen demand (COD) of the wastewater (*Field et al., 1988*). Previously, the treatment of debarking process water using ozone (*Korhonen and Tuhkanen, 2000*) and a combination of chemical flocculation and activated sludge (*Saunamäki and Savolainen, 1999*) led to a large dose of the oxidant being consumed or to a decrease in the efficiency of the treatment with the increase in the concentration of the organic matter. Oxidative polymerization is a way of neutralizing the toxicity of the debarking effluent constitutes, but it does not, however, eliminate the pollutants from the aqueous solution. In this work, wet oxidation (WO) is considered as a suitable method for the elimination of contaminants from such effluents.

1.5.3 TERMO-MECHANICAL PULP PROCESS WATER

When considering the problem of fresh water consumption minimization within plants, industries face the problem of the build-up of substances that have drastic effects on the whole manufacturing process. The closure of water cycles in order to meet environmental protection legislation leads to an increase in the amount of dissolved and colloidal substances (DCS), such as lipophilic wood extractives (LWEs), in the process waters of paper mills. Approximately 1 –5 % of wood is lost due to its dissolution in process waters and because mechanical pulp is not on most occasions washed, the dissolved substances are transferred to the paper machine where they can interfere with the papermaking process (*Sjostrom,1990*). The presence of LWEs, commonly known as pitch compounds, can cause production downtime and the need for extra cleaning. These substances also impair product quality by causing dirt, holes, scabs etc. in the final sheet (*Karlsson et al.,2001; Zhang,2000; Zhang et al.,1999*).The LWEs that are present in process waters are mainly triglycerides, fatty and resin acids, waxes, sterols , steryl esters and lignans (*Dorado et al.,2001*).

2 OBJECTIVES OF THE WORK

The main objective of this work was to test the efficiency of wet oxidation processes when treating several types of aqueous wastes. On one side its performance for the abatement of chloro-organic aromatic toxic pollutants, such as 4-chlorophenol and 2,4-dichlorophenol has been studied. On the other hand, wastewater from pulp and paper mills, which has been reported to be an indirect source of entry of chlorophenols in the aquatic environment, has been investigated. More in detail, it has been taken as feed stream for the wet oxidation unit in order to investigate whether this type of waste streams can be treated by this technology or not.

Regarding Chlorophenols, special attention was drawn to the degradation of 4-chlorophenol by means of **wet oxidation** and w**et peroxide oxidation**. This aromatic compound was taken into investigation due to its harmful properties against the environment and due to its wide presence in the environment. Once it was clear that it could be degraded by these technologies, a research focused on the influence of the operating conditions in the result of the oxidation was carried out. The influence on the wet peroxide oxidation and wet oxidation reactions of the following parameters, initial concentration of the pollutant, temperature and amount of oxidizing agent (oxygen or hydrogen peroxide depending on the process) has been taken under study.

The identification and quantification of the intermediate compounds involved in the wet oxidation of 4-chlorophenol, together with a suggested mechanistic pathway, allowed the obtaining of a kinetic model, which appeared to be a useful tool for the prediction of these compounds throughout the reactions. The evolution of the free chlorine released to the solution from the degraded chlorophenol was also a useful tool when determining the kinetic pathway of the reaction.

Another objective of the work comprised the investigation of the variations of the biodegradability of the samples during the process. The knowledge of evolution of this parameter during the wet oxidation was thought to be of major importance, since high biodegradability enhancements allow the combination of a wet oxidation unit with a biological post-treatment, which is an effective and inexpensive technology to couple the oxidation.

The establishment of a comparison between wet oxidation and the wet peroxide oxidation for the removal of 4-chlorophenol was investigated as well.

Concerning wastewaters from pulp and paper mills, debarking and termo-mechanical pulp process wastewater have been treated by wet oxidation. Both waters were concentrated before oxidation in order to favor the economy of the process. Debarking wastewater was concentrated by evaporation and pulp process water by nanofiltration. The influence of the operating conditions, such as temperature and partial pressure of oxygen, on the results achieved at the end of the wet oxidation were studied and evaluated in order to find the optimum working conditions for each type of wastewater. Special attention was drawn to the evolution of Lipophilic Wood Extractive Compounds throughout the reactions. In addition, kinetic models suggested in the literature were tested to find a suitable one, which allowed the prediction of for instance, the organic load, over the duration of the reactions.

Due to the fact that wet oxidation is more economically viable when the initial waste stream is highly concentrated, a final chapter dedicated to a emerging technique, i.e., membrane technology has been included in this thesis. An investigation regarding the parameters affecting its performance, as well as the general aspects of the process has been conducted.

3 MATERIALS AND METHODS

The equipments used to effectuate oxidation and ultrafiltration experiments as well as the materials and procedures used to analyze the samples are described in this section, which is divided into three part: wet oxidation, wet peroxide oxidation and ultrafiltration.

3.1 WET OXIDATION

The equipments and methods employed to develop the experimental part concerning the study of wet oxidation reactions are explained in this chapter. In the first part of this section, the experimental devices are described in detail. The second, third and fourth parts include the methodology followed to carry out the WO experiments with chlorophenol solutions and of the two wastewaters from the pulp and paper mills.

3.1.1 EQUIPMENT

Two different equipments have been used to carry out wet oxidation reactions. Both devices comprised the same elements and the only difference between them was the volume of the reactor. The first WO system, hereafter R1-300, included a 300 mL stainless-steel high-pressure autoclave reactor (Parr Instrumental Co, USA). The second one, hereafter

R2-450, was furnished by the same company but had a volume of 450 mL. Both reactors are made of stainless steel (T316SS), which permits to conduct experiments at neutral or close to acidic pH and are capable of performing batch experiments at pressures of up to 5 MPa and temperatures of up to 350 ºC. A drop band with one screw and a split ring pair with screws allow the use of these reactors under the before mentioned conditions. The reactors are also equipped with heating, refrigeration and agitation systems. An electronic controller (GWB, Instrumental Parr Co, USA) is used to maintain temperature and stirring speed constant and monitor the pressure of the reactor. A scheme of the WO equipment used to effectuate the reactions is illustrated in figure 3.1.1-1.

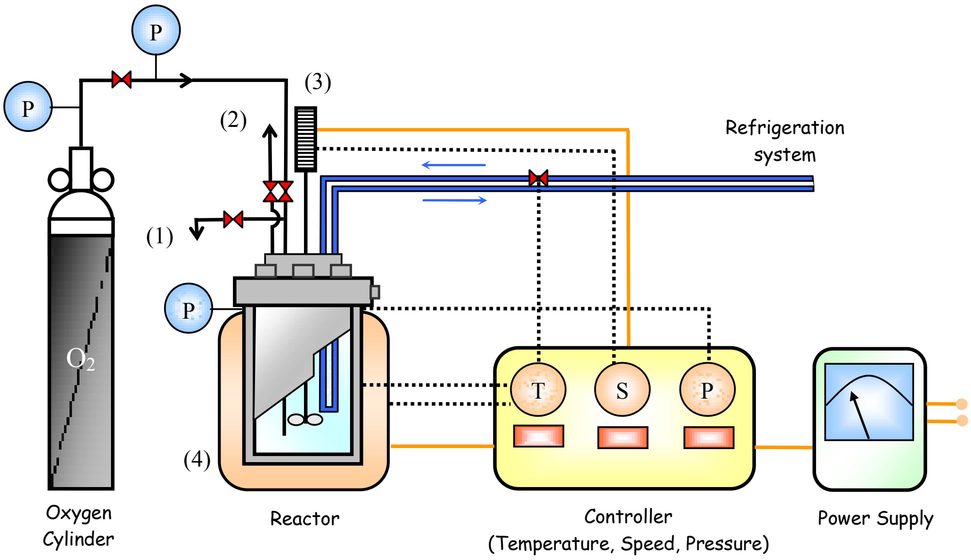


Figure. 3.1.1-1 Wet Oxidation equipment: 1) Sample Extraction, 2) Gas Draining, 3) Stirrer, 4) Heater.

3.1.2 WET OXIDATION REACTIONS OF CHLOROPHENOL SOLUTIONS

Wet oxidation reactions of 4-chlorophenol and 2,4-dichlorophenol solutions were carried out in the equipment R2-450, meaning that the volume of the reactor was 450 mL. The first stage of the experimental procedure comprised the preparation of the chlorophenol solutions to be treated. Millipore water was used to prepare the solutions. Parachlorophenol and 2,4-dichlorophenol were supplied by Sigma-Aldrich Chemicals (Germany). The concentration of these solutions ranged from 500 to 1000 ppm and they were prepared in an extractor due to the inherent properties of these substances. Some other chemicals, which were thought to be probable intermediates of the process, such as quinone, hydroquinone and phenol were provided by Sigma-Aldrich Chemicals (Germany) as well.

Once the solutions were ready, 300 mL were introduced into the reactor, which was then properly closed and the refrigeration system was switched on. The following step consisted of fixing the desired temperature on the controller and waiting until the temperature of the reactor reached the set value. Depending on the selected temperature, the preheating period lasted from 30 to 60 min. Once the temperature was reached, the oxygen valve was opened and the oxygen partial pressure was then adjusted to the designated value for the experiment. At this point, the reaction was assumed to commence. Each reaction lasted 1.5 hours and during this period of time several samples were withdrawn from the reactor and analyzed for Total Organic Carbon (TOC), pH, High Pressure Liquid Chromatograph (HPLC) and Ion Chromatograph (IC). Some of the samples were also analyzed for Biochemical Oxygen Demand (BOD).

Once the reaction was finished, the reactor was depressurized and the treated aqueous solution was removed. The operating conditions are described in table 3.1.2-1.

Table 3.1.2-1 Wet oxidation reactions operating conditions.

Reactor	R2-450
Oxidizing agent	Pure oxygen
Initial concentration of CP	500 or 1000 ppm depending on the experiment
Rate of agitation	750 rpm
Partial Pressure of O_2	5, 7.5, 10 or 15 bar depending on the experiment
Temperature	150, 160, 175 or 190 ºC depending on the experiment
Volume	300 mL of Chlorophenol solution
Duration of the reactions	1.5 hours after preheating period

In the course of the wet oxidation reactions, the following samples were withdrawn from the reactor in order to determine the reaction extent:

- ***Original sample:*** corresponded to the solution fed into the reactor.
- ***Sample at time t = 0*:** consisted of few milliliters of solution taken directly from the reactor when the desired temperature was reached. The analysis of this sample allows the evaluation of the influence of the preheating period, when some decomposition in the wastewater could occur.
- ***Samples at time t = 5, 15, 30, 45, 60, 75 and 90 minutes:*** were taken directly from the reactor at different periods of reaction time.
- ***Last sample:*** consisted of the oxidized solution that remained in the reactor after cooling down the reactor. By comparing the analysis of this sample and the last sample of the reaction (i.e. t= 90 minutes) the probable influence of the cooling period can be determined.

3.1.3 WET OXIDATION OF NANOFILTRATION CONCENTRATE OF TMP PROCESS WATER

The first step in the experimental procedure consisted of obtaining water with similar properties to the one produced directly from the tertiary circuit of paper mills. To produce the model wastewater, 3 kg of pulp with a humidity of 45 % were added to 38 kg of distilled water, previously warmed up to 70 ºC. At this composition of pulp and water, the mixture contained only 4 % of dry solids. It was then maintained at 70 ºC for 40 minutes and after this, the pulp was partially separated from the water by filtration. The amount of water obtained from this process was 33 kg and it was then directed to the NF unit, where two effluents were obtained: the concentrate and the permeate. The concentrate was then treated by WO.

3.1.3.1 Nanofiltration Equipment

The equipment used for the NF was a membrane filtration unit Labstak M20 (DSS company, Denmark). It comprised a variable number of series of membranes, membrane supporting plates and spacer plates, fixed and compressed by means of an outer support. In this type of modules the membranes are located at both sides of the supporting plates, and when more than 2 membranes are used, a spacer plate should be placed between the different series of membranes.

The membrane module was made of stainless steel and could house from 2 to 40 individual membranes. In this equipment, the permeate was stored in a container and its weight was measured by means of a balance, whereas the concentrate was recycled to the feed tank. In order to pump the feed, a gear pump was used and the pressure remained constant by means of its control and monitorization. The equipment had four manometers, two of them were located in the feed and the other two in the concentrated flow. The equipment also had thermometers in the feed and in the permeate effluents that allowed the determination of possible temperature changes due to an overheating of the pump. Finally, a flow-meter installed in the permeate effluent allows its measurement.

In order to nanofiltrate the prepared wastewater the minimum of one support plate with a filtration area of 0.036 m^2 was used. The membranes consisted of a mixture of polyamide and polysulfite with pore diameter of 1.5 nm. The NF was carried out for three hours and the temperature of the feed was maintained at 40 ºC.

3.1.3.2 Wet Oxidation Experiments

Reactor R1-300 was used for these experiments. The operating procedure was similar to the one explained in section 3.1.2 (WO of Chlorophenol solutions). The main difference remained in the volume treated and the preheating period. In the present case, a volume of 175 mL of the nanofiltration concentrate TMP process wastewater was treated due to the smaller size of the reactor. The preheating period was longer, between 50 to 90 minutes due to the lower power of the heater. The reaction lasted 2 hours and during this period of time several samples of wastewater were taken from the reactor. COD, TOC, content of Lignin, BOD, and pH of the samples were analyzed in order to evaluate the evolution of the reaction. Once the reaction was finished, the reactor was depressurized and the treated water solution was removed. The variables to be studied were the effect of the pressure and temperature. In table 3.1.3-2 the operating conditions at which these reactions were carried out are described.

Table 3.1.3-2 Wet oxidation of TMP nanofiltration concentrated wastewater operating conditions.

Reactor	R1-300
Oxidizing agent	Pure oxygen
Solution	Pulp and paper mill TMP process water nanofiltration concentrate
Rate of agitation	750 rpm
Partial Pressure of O_2	5, 7.5, 10 or 15 bar depending on the experiment
Temperature	150, 160, 175 or 190 ºC depending on the experiment
Volume	175 mL of solution
Duration of the reactions	2 hours after preheating period

The samples withdrawn from the reactor over the duration of the process were: original, t= 0, 10, 30, 60, 90 and 120 minutes and a residual sample corresponding to the oxidized solution that remained in the reactor after the cooling down period.

3.1.4 WET OXIDATION OF EVAPORATION CONCENTRATE OF DEBARKING WATER

The original wastewater of these experiments was provided by a Finnish Pulp and Paper mill. It had a dark brown color and the dry solid-content was about 20-25 %. About 61 % of the solid matter present in this concentrated consisted of organic compounds. The COD content was between 47-60 g/L, 30-40 % of biodegradability and 5.5-9 g/L of soluble tannin/lignin. The pH of this water was 5.5-7.

The R2-450 reactor was used for these experiments and the procedure followed was different from the other wet oxidation reactions. The main difference is that in these experiments, only water was preheated in the reactor and when the desired temperature was reached, the concentrated wastewater was introduced in the reactor. The advantage of the new procedure is that it attempts to ensure that the properties of the tested solution are not modified before the reaction starts, as it could happen when operating normally (i.e., during the preheating period).

The first step consisted of introducing 250 mL of distilled water into the reactor. On the other hand, 50 mL of the debarking evaporation concentrated solution was introduced into a pipette. The pipette was then connected to the reactor and to a cylinder with Nitrogen, which was used to ensure a higher pressure in the pipette in order to be able to insert the concentrate solution into the reactor. Once the desired temperature was reached, the valve on the pipette was opened and consequently the debarking concentrate solution was introduced into the reactor. After this, a decrease in the temperature of the reactor as a result of the lower temperature of the concentrate was observed. When the temperature of the reactor reached again the set one the oxygen valve was opened and the oxygen partial pressure was then adjusted to the designated for the experiment. At this point, the reaction was assumed to be started.

The reaction lasted 2 hours and within this time samples at 0, 10, 30, 60, 90 and 120 minutes were taken from the reactor. The Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and Volatile Acids of the samples were later analyzed in order to evaluate the evolution of the reaction. Once the reaction was finished, the reactor was depressurized and the treated water solution was removed. In table 3.1.4-1 a summary of the operating parameters is given.

Table 3.1.4-1 Wet oxidation of evaporation concentrated debarking wastewater operating conditions.

Reactor	R2-450
Oxidizing agent	Pure oxygen
Solution	Evaporation concentrate debarking wastewater from pulp and paper mills
Rate of agitation	750 rpm
Partial Pressure of O_2	10 bar
Temperature	Between 170 and 200 ºC depending on the experiment
Volume	50 mL of concentrate solution and 250 mL of distilled water
Duration of the reactions	2 hours after preheating period

3.2 WET PEROXIDE OXIDATION

The devices and procedures used to carry out the wet peroxide oxidation experiments of solutions containing chlorophenols are described in this chapter.

Wet peroxide oxidation reactions were carried out in a high-pressure tank reactor Autoclave Eng., model EZE-SEAL, hereafter R3-300, with a capacity of 300 mL and produced by IBERFLUID S.A. (Spain). The reaction cell is made of stainless steel ALSI 316 and due to a split ring pair with 6 screws the reactor is capable to work under severe conditions of pressure (max. 227 bar at 454 ºC). The reactor is equipped with a heating jacket made of ceramic elements, a cooling system and an agitation system (electric motor, maximal working rate of 3000 rpm.). The experimental equipment also comprises an electronic controller that allows control and monitoring of both temperature and stirrer (IBERFLUID, SA). See figure 3.2-1.

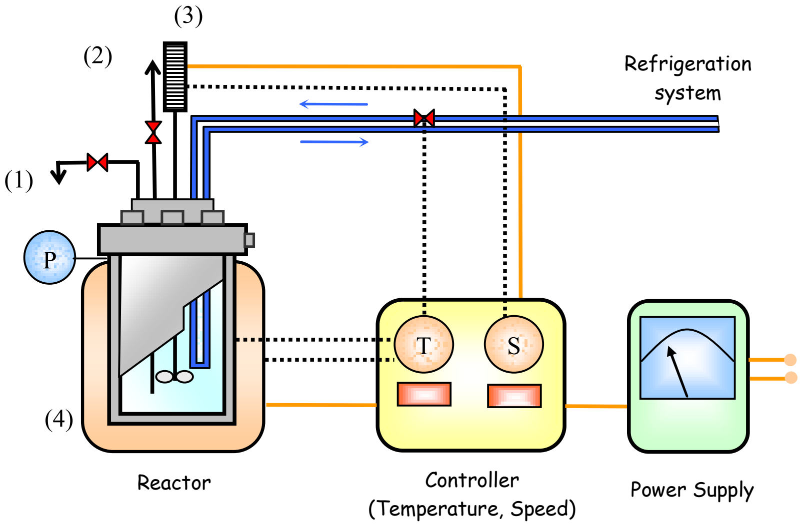


Figure 3.2-1 Wet Peroxide Oxidation equipment: 1) Sample Extraction, 2) Gas Draining, 3) Stirrer, 4) Heater.

It is necessary to point out that one of the most noticeable differences between the experimental equipments used for WO and WPO is the need of having an oxygen bottle in the case of wet oxidation experiments, since oxygen is the oxidizing agent. Another difference remains in the digital controller, since in this equipment it does not monitor the pressure. In this case, a manometer located above the reactor provides the value of the pressure. Finally, in the wet oxidation installations, the tube to withdrawn the samples is placed in the oxygen line and the gas drain is on a separated line. However, in the wet peroxide oxidation equipment, the gas drain is located in the same line as the manometer and the tube used to withdrawn the samples.

Wet Peroxide Oxidation reactions of solutions containing 4-chlorophenol

Wet peroxide oxidation reactions commenced with the preparation of parachlorophenol solutions and the addition of the oxidizing agent, hydrogen peroxide. These two reactants were furnished by Panreac Quimica, S.A. (Spain). For each reaction, 200 mL of the solution were introduced into the reactor. The chosen parachlorophenol concentrations for this study were 300, 500, 750 and 1000 ppm. Once the parachlorophenol solution was introduced into the reactor, the hydrogen peroxide (i.e. the oxidizing agent) (30 % w/v) was added. The amounts of the oxidizing agent added to the 200 mL of parachlorophenol were 1, 2.5 and 5 mL, or in other words, 1.5, 3.7 and 7.31 ppm in the reactor. After this, the reactor was closed, the cooling water pump was turned on and the temperature and stirrer speed were programmed to the controller. Once the temperature was reached, between 30 or 40 minutes after it had been programmed, the system reacted for 1.5 hours and during this period of time several samples were withdrawn from the reactor and analyzed for Total Organic Carbon (TOC), pH, High Pressure Liquid Chromatograph (HPLC) and COD (Chemical Oxygen Demand). The operating conditions of these experiments are shown in table 3.2.1-2.

Table 3.2.1-2 Wet Peroxide Oxidation reactions operating conditions.

Reactor	R3-300
Oxidizing agent	Hydrogen Peroxide (30 %), volumes of 1, 2.5 or 5 mL depending on the reaction
Initial concentration of CP	300, 500, 750 or 1000 ppm depending on the experiment
Rate of agitation	750 rpm
Pressure	The corresponding to the vapor pressure of the solutions
Temperature	100, 130 or 160 ºC depending on the experiment
Volume	200 mL of CP solution
Duration of the reactions	1.5 hours after preheating period

3.3 ULTRAFILTRATION

This section includes a description of the equipment employed and the methodology followed when carrying out the ultrafiltration experiments.

A Low Pressure Filtration Cell GN 10-400 provided by Berghof (Germany) was used as a test cell in order to study the ultrafiltration of aqueous solutions containing organic compounds. It consists of a PTFE support disk where two cylinders are placed. The inner cylinder is made of glass and it contains the feed solution. The external cylinder is made of plexiglass and serves as burst shield. The plexiglass cylinder has a security valve to ensure an immediate pressure reduction in case of overpressure. On the surface of the PTFE support disk, a Tyvec paper should be laid in order to protect the membrane (76 mm).

The test cell is capable of working with a feed solution volume of 400 mL and at a maximum pressure and temperature of 10 bar and 100°C, respectively. Experiments were carried out at room temperature and the cell was pressurized by air. In order to reduce the probable fouling of the membrane, the test cell is also equipped with a stirrer, which was used at a stirring rate of 300 rpm. Figure 3.3-1 illustrates the experimental equipment.

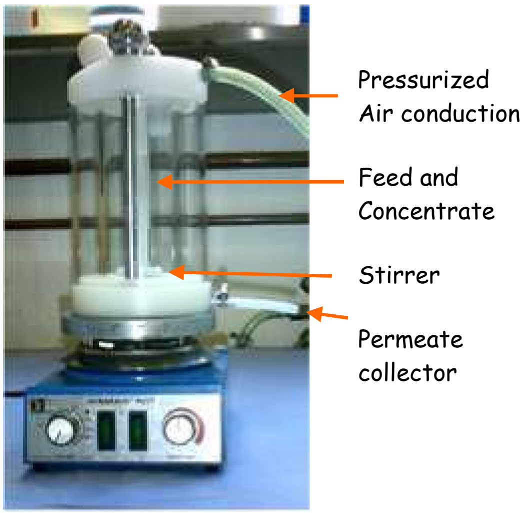


Figure 3.3-1 Ultrafiltration test unit

The three membranes used for this study were supplied by MICRODYN-NADIR (Wuppertal, Germany). The first one was a C030FM membrane with a Molecular Weight Cut Off (MWCO) of 30 kiloDalton (kDa) and made of Cellulose. It can be used in a pH range from 1 to 12 and until a maximum temperature of 55 °C. The second and third membranes were a P020F membrane with a MWCO of 20 kDa and a P005F with a MWCO of 5 kDa. Both of them are made of Polyethersulfone, can be used in all pHs and until a maximum temperature of 95 °C.

Ultrafiltration experiments

The first step of the experimental procedure was the preparation of the membranes. The day before the experiment, the membrane was washed for a couple of minutes with tap water. It was then kept submerged in distilled waster for the whole night. Once the membrane was placed in the test cell, 400 mL of distilled water were introduced into the cell. Then the pressure was adjusted (from 1 to 3 bar depending on the experiment) and the permeate was collected. These experiments with water were carried out in order to ensure stationary conditions.

The feed solution of part of the tests consisted of stock solutions containing dextran FP40 research grade furnished by Serva (Heidelberg, Germany) with a molecular weight range between 36000 and 44000 Dalton. Fig. 3.3.1-1 shows a scheme of a dextran molecule. Solutions containing Suwanee River humic acid Standar II, Suwanee River fulvic acid Standar, 1R101 Natural Organic Matter (NOM) RO isolation and 1R108N Nordic reservoir NOM RO isolation, were used as feed solutions as well. These chemicals, humic acids, fulvic acids and two different NOM were supplied by the International Humic Substances Society (Minnesota, USA). In addition, cellulose powder microcrystalline and alginic acid, both purchased from MP Biochemicals, LLC (Eschwege, Germany) were employed as feed solutions in part of the experiments.

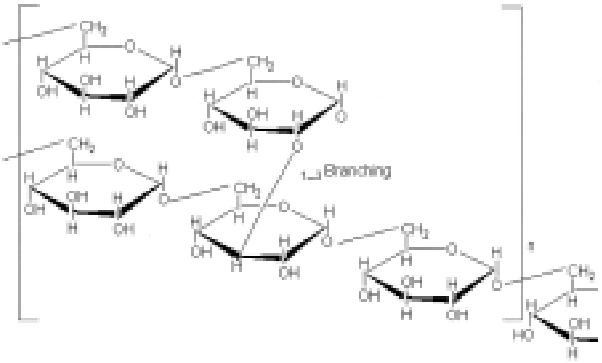


Figure 3.3.1-1 Chemical structure of Dextran

The rest of the chemicals used were supplied by Merck (Dermstadt, Germany): KH_2PO_4 (crystalline, extra pure), Na_2HPO_4 (for analysis), Na_2CO_3 (for analysis), $NaHCO_3$ (extra pure) and $CaCl_2.2H_2O$ (crystalline grade for analysis)

In the course of each experiment the time to collect a certain volume of permeate was measured in order to know the evolution of the flux and the permeability throughout the filtration. After the test with water, the same procedure was done with the solutions containing dextran, NOM, cellulose alginic, humic or fulvic acid depending on the experiment. A final sample named retentate was withdrawn from the test cell after the filtration.

COD was measured spectrophotometrically and Cuvette Tests LCK 114 provided by Dr. Bruno Lange GMBH & Co. (Düsseldorf, Germany) were used for the preparation of the samples. The pH was measured by means of a pH meter 761 Calimatic from Knick (Dülmen, Germany) and a Conductivity meter 703 supplied by Knick (Dülmen, Germany) was used to measure the conductivity of the samples.

The experimental part of this project can be divided into four different sections. The first part comprises a study about the influence of the initial concentration of the different compounds on the ultrafiltration performance. For this purpose, experiments with test solutions with different concentrations were carried out. The second part investigates the influence of the transmembrane pressure. The third part analyzes the possible effect of the pH of the initial solution, while part four examines the influence of the Ca content in the feed.

3.4 CHEMICAL ANALYSES

Wet oxidation samples were analyzed for Total Organic Carbon (TOC), pH, High Pressure Liquid Chromatograph (HPLC), Ion Chromatograph (IC) and in some cases for Biochemical Oxygen Demand (BOD). On the other hand, the samples collected from the wet peroxide oxidations were analyzed for TOC, pH, HPLC and Chemical Oxygen Demand (COD). TOC and COD were analyzed because when working with wastewaters it is of special interest to know the percentage or the amount of the organic matter that is converted into CO_2, i.e., the mineralization accomplished during the process. The pH is also important in view of the fact that it indicates the formation of acids. A sharp decrease in the pH then, indicates a fast degradation of the initial compound. The HPLC was used to identify and quantify not only the target compound but also the intermediates formed over the duration of the reaction. In order to quantify the amount of ion chloride released from the organic molecules, the IC was used.

BOD analysis were carried out in order to observe the evolution of the biodegradability during the reaction.

3.4.1 TOTAL ORGANIC CARBON

Total Organic Carbon (TOC) in water and wastewater is composed by a variety of organic compounds in various oxidation states. Some of this carbon compounds can be also oxidized chemically and/or biologically, for this reason the Chemical Oxygen Demand (COD) or the Biochemical Oxygen Demand (BOD) can be used to characterize these fractions as well. However, TOC is a more convenient and direct expression of the total organic content than either BOD or COD. Another difference between TOC, BOD and COD is that the first one is independent of the oxidation state of the organic matter and does not measure other organically bonded elements, such as nitrogen and hydrogen, and inorganic compounds. (*Greenberg, 1985*)

The analysis is carried out by injecting a small amount of sample into a furnace at high temperature and oxidizing atmosphere. Aided by a catalyst, the organic carbon is oxidized to CO_2. The amount of CO_2 produced is analyzed by an infrared method (*Tchobanoglous and Burton, 1991*). For wet oxidation reactions the used equipment was a Shimadzu 5050 TOC Analyzer, meanwhile a Shimadzu 5055 TOC analyzer was employed to analyze the samples from the wet peroxide oxidation reactions. These equipments analyzed the Total Carbon and then the Inorganic Carbon. The amount of TOC is then obtained from the difference between these two parameters. As mention previously, TOC values are of major importance in view of the fact that they show the level of mineralization (i.e. conversion to CO_2 and H_2O) of the samples, which is a way to measure the efficiency of the process.

Samples from ultrafiltration experiments were analyzed for Total Organic Carbon in an external laboratory, ALA Analytisches Labor GmbH (Aachen, Germany).

3.4.2 CHEMICAL OXYGEN DEMAND

The determination of the Chemical Oxygen Demand is used to indicate the amount of oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant, dichromate in this case. The test was carried out according to the dichromate reflux method suggested in the Standard Methods for the determination of Water and Wastewater (*Greenberg et al., 1985*). This test is preferred over procedures using other oxidants because of superior oxidizing ability and applicability to a wide variety of samples. The analysis requires two solutions to be prepared:

- **Digestion Solution 0.2 N $K_2Cr_2O_7$** prepared by adding to 500 mL of distilled water 10.216 g of $K_2Cr_2O_7$ (previously dried at 104 ºC for 2 hours), 167 mL of concentrated H_2SO_4 and 33.3 $HgSO_4$. The mixture must be well dissolved, then cooled down to room temperature and finally diluted to 1000 mL. The $HgSO_4$ is added to form $HgCl_2$, avoiding therefore, the oxidation of the chlorine by the chromate (reaction 3.4.2-1), which might cause an interference in the results.

$$6\ Cl^- + Cr_2O_7^{-2} + 14\ H^+ \xrightarrow{\text{Catalyst, heat}} 3\ Cl_2 + 2\ Cr^{+3} + 7\ H_2O \qquad \text{Reaction 3.4.2-1}$$

- **Catalyst Solution** prepared by adding Ag_2SO_4, which acts as a catalysts for the oxidation of certain organic compounds, to concentrated sulfuric acid in a proportion of 5.5 g Ag_2SO_4/kg H_2SO_4. The solution was left for 2 days to ensure complete dissolution of the reagents.

The analytical part comprises the heating to an elevated temperature (150 ºC) of a known sample volume (2.5 mL) with an excess of potassium dichromate (1.5 mL of digestion solution) in presence of sulphuric acid (3.5 mL catalyst solution) for a period of time of two hours in sealed glass tubes. During this time, the organic matter is oxidized and dichromate (yellow) is replaced by chromic ions (green). The reaction takes place as follows (*Tchobanoglous and Burton, 1991*):

$$\text{Organic matter } (C_aH_bO_c) + Cr_2O_7^{-2} + H^+ \xrightarrow{\text{Catalyst, heat}} Cr^{+3} + CO_2 + H_2O \qquad \text{Reaction 3.4.2-2}$$

After keeping the samples in the block digester at 150 ºC for two hours they are cooled down and then, the absorbency, previously calibrated for COD values, was measured by spectrophotometry at a wavelength of 585 nm.

A spectrophotometer DR/2000 Hach Company (USA) was used to analyze the samples from wet oxidation reactions. The ones from wet peroxide oxidation reactions were measured in an ODDYSEY DRI2500 HACH Company (USA). Finally, the COD of the samples from ultrafiltration experiments was measured spectrophotometrically and Cuvette Tests LCK 114 supplied by Dr. Bruno Lange GMBH & Co. (Düsseldorf, Germany) were utilized.

3.4.3 HIGH PRESSURE LIQUID CHROMATROGRAPH

High Pressure or Performance Liquid Chromatography was used in order to identify and quantify certain compounds. For wet oxidation reactions of solutions containing 4-CP and 2,4-DCP, a High Pressure Liquid Chromatograph (HPLC) system Hewlett-Packard series 1100 was used to quantify the target compounds also to be able to identify and quantify the intermediates of the reaction. The column used was a YMC-Pack Pro C18 provided by YMC, Inc, c/o Waters (USA) with a length of 150 mm and 4.6 mm of inner diameter. The analysis was carried out under a wavelength of 254 nm and the solution used consisted of a 50 % mixture of Millipore water and Acetonitrile (Sigma-Aldrich Chemicals, Germany).

Samples from wet peroxide oxidation of solutions containing 4-CP and 2,4-DCP were analyzed with a HPLC supplied by Waters Corporation (Massachusetts, USA). The column used was a TR-016059 furnished by Tecknokroma S. Coop. C. Ltda (Barcelona, Spain) with a length of 250 mm and an inner diameter of 4.6 mm. The mobile phase was a mixture of Acetonitrile (Panreac Quimica, S.A., Spain) and water in proportion of 40:60 % in volume. The pH of the mixture was acidified to a pH of 3 by the addition of phosphoric acid (Panreac Quimica, S.A., Spain). The wavelength used was 267.3 nm.

Prior to the analysis of the samples it was necessary to calibrate the HPLC. For this purpose, several samples with a known concentration of the studied compounds were analyzed and with the results, a calibration line was made based on the areas of the picks observed. These analysis are considered of special importance because they allow the determination of the concentration (and consequently level of degradation) of the target compound at each moment of the reaction and of the main intermediates, allowing the prediction of the pathways of the reaction.

3.4.4 ION CHROMATOGRAPH

To determine the free chloride ion concentration in each sample, a Dionex, DX-120 Ion Chromatograph (IC) from Dionex Corporation (USA) was used. The solution employed consisted of a 0.5 M of $HNaCO_3$ and 0.5 M Na_2CO_3. Acetonitrile (one drop) was added into 1 liter of the previous mixture to avoid the growth of microorganisms inside the equipment.

The knowledge of the chloride ion concentration during the reaction is important in view of the fact that it shows the level of degradation of the target compound. A high concentration of ion chloride in the solution involves high degradation of the initial compound. Moreover, this information also plays an important role when predicting the intermediates of the reaction. The 4-CP is the only source of chloride ion in the system, for this reason, in the event that the amount of ion present in the system is lower than the one corresponding to the 4-CP degraded, some other intermediates containing chloride might be formed in the course of the reaction.

3.4.5 BIOCHEMICAL OXYGEN DEMAND

The Biochemical Oxygen Demand (BOD) is the oxygen required by an aqueous sample to biochemically degrade the organic material, to oxidize the inorganic material such as sulfides and ferrous iron and to oxidize reduced forms of nitrogen, unless their oxidation is prevented by an inhibitor. Traditional dilution method is based on the measurement of dissolved oxygen (DO) in an initial probe and in the same sample after incubation period of 5 days. This is the minimum time that the bacteria need to digest the organic molecules, specially long and complex ones (*Escalas et al., 1997; Gullichen and Paulapuro, 2000*). In order to reduce the duration of these analysis a digestion set LCW917 (DR. LANGE, Germany) was used. Its task was to break long molecules in smaller pieces, so that they can be quickly digested by the bacteria.

The bacteria used in this equipment were *Issatchenkia orientalis* and *Rhodococcus erythropolis* and they are placed in the interior of the BOD Sensor. The breakage of the organic chains takes place in a reactor LT100 (DR. LANGE, Germany) maintained at 148 ºC for an hour. Before introducing the samples in this reactor some HCl was added to the samples, and once the reaction was finished the assays were neutralized by adding NaOH, after which the samples were ready to be analyzed with the BOD Sensor (DR. LANGE, Germany).

Figure 3.4.5-1 BOD sensor and thermostat (DR. LANGE, Germany).

3.4.6 TANNIN AND LIGNIN

The following test was used in order to measure all the hydroxylated aromatic compounds, including tannin, lignin, phenol and cresol; however, the results are reported as total tannin and lignin and expressed as mg/L tannic acid. The procedure followed the one suggested in the literature (*Kloster, 1974*; *Hach 2001*). According to this, 0.5 mL of a tannin-lignin reactive (Hach Company, USA) were added to 25 mL of each filtrated samples. This mixture was then swirled in order to ensure homogeneity. 5 mL of Sodium Carbonate Solution (Hach Company, USA) was added to the samples. Then a 25-minute reaction began and the samples developed a blue color if tannins and/or lignins were present. After the reaction, the blue-colored solutions were analyzed by means of a spectrophotometer DR/2000 (Hach Company, USA) at a wavelength of 700 nm.

3.4.7 VOLATILE ACIDS

The volatile acids test is based on the esterification of the carboxylic acids present and determination of the esters by the ferric hydroxamate reaction (*Montgomery et al., 1962*). All the volatile organic acids present are reported as their equivalent of mg/L of acetic acid. The first stage of the method consists of mixing 0.2 mL of the centrifuged sample with 0.6 mL of Ethylene Glycol. After mixing, 80 μL of 19.2 N Sulfuric Acid Standard Solution is added into the tube and the new solution is mixed again. The tube is then placed into a boiling water bath during three minutes. After this, the sample is cooled and 0.2 mL of Hydroxylamine Hydrochloride Solution is added into the tube and mixed. The next steps consist of adding, 0.8 mL of 4.5 N Sodium Hydroxide Standard Solution, 4 mL of Ferric Chloride Sulfuric Acid Solution and 4 mL of Demineralized Water. After this, a three-minute reaction period begins. The sample is then analyzed in a spectrophotometer DR/2000 (Hach Company, USA) at a wavelength of 495 nm.

3.4.8 LIPOPHILIC WOOD EXTRACTIVES

The content of extractives was measured by making extractions to the samples; previously prepared and then analyzed and quantified by Gas Chromatography (GC). Firstly, the pH of the samples was adjusted to 3.5 by adding sulphuric acid; then, they were centrifuged in order to separate fibers, fines and other non-colloidal particles from dissolved and colloidal substances. Once the samples were ready, three extractions were carried out. In the first one, 2 mL of extraction agent (solution of MTBE) was added to 4 mL of the clarified sample. Afterwards, the samples were shaken vigorously to enhance the homogeneity and then centrifuged again for 5 minutes at 1500 rpm. After centrifugation, the organic phase was pipetted off with care and the extractive process was repeated again but now pure MTBE was used. The extraction agent obtained after each extraction of each sample was mixed and dried under nitrogen atmosphere.

The following stage consisted of preparing the samples to be analyzed in the Gas Chromatographer (HP 6890) with automatic on-column injection (Restek RTX-1) of silylated samples. To prepare the silylated samples, 100 μL of bis-(trimethylsilyl)-trifluoro-acetamide and 50 μL of trimethylchlorosilane were added to each sample before keeping them in a furnace at 70 ºC for 40 minutes. The Gas Chromatograph provided direct determination of free fatty acids, resin acids, sterols, steryl esters, triglycerids and lignans.

4 EXPERIMENTAL RESULTS AND DISCUSSION

This chapter contains three different parts. In the first one, the results related to the degradation of 4-chlorophenol and 2,4-dichlorophenol by wet oxidation and wet peroxide oxidation are included. The second part shows the results obtained from the wet oxidation of multi-component wastewaters coming from the pulp and paper industry. Two raw waters were taken under investigation, on one side thermo-mechanical pulp wastewater (synthetic), previously nanofiltralted, and on the other side, real evaporation concentrate debarking wastewater. Finally, the third section includes the results of the experiments carried out to check the parameters that are though to have an influence on the membrane processes.

4.1 WET OXIDATION AND WET PEROXIDE OXIDATION OF SINGLE-COMPOUND SOLUTIONS

Five different parts are included in this chapter. In the first one some preliminary tests made to check the effect of the pre-heating period and the speed of the stirrer during the process are explained. The second part comprises the study of the results about the influence of the temperature, initial concentration of 4-CP and H_2O_2 on the duration of the wet peroxide oxidation of solutions containing parachlorophenol. In addition, some of these results are compared to the ones obtained when using 2,4-dichlorophenol as feed solution. In the third part, the influence of the temperature, partial pressure of oxygen and initial concentration of 4-CP during the wet oxidation reactions is studied. In the fourth section, a comparison between these two technologies, i.e., wet oxidation and wet peroxide oxidation for the removal of 4-CP is established. Finally, last part of this chapter comprises an investigation about the mechanistic pathway of the wet oxidation of 4-CP and the suggestion of a feasible kinetic model.

4.1.1 PRELIMINARY TESTS

These experiments were carried out to study possible variations of the initial solution in the course of the pre-heating and to determine the influence of the stirring speed, which plays an important role in the process due to possible mass transference problems.

Study of the pre-heating period

Wet oxidation and wet peroxide oxidation are techniques included in the so-called *Hot Advanced Oxidation Processes*, which are processes that work under high pressure and temperature. The need to reach the desired reaction temperature makes inevitable the existence of a period of time, in which the temperature of the reactor increases from room temperature to the temperature of the reaction. This period of time is known as *preheating period* and it normally lasts from 20 to 40 minutes depending on how high the desired temperature is. The study of the influence of this period of time is thought to be significant because during this time the solution is under high temperature and changes in its properties and composition are likely to happen.

For this study several experiments at different concentrations of the pollutant were carried out in the wet peroxide oxidation reactor. These experiments consisted of introducing the initial solution of 4-CP at different concentrations (from 300 to 1000 ppm) in the reactor, heating it up until 200 ºC and then cooling down. Samples were taken at fixed temperatures (20, 100, 130, 150, 175 and 200 ºC) and then they were analyzed for pH, TOC, COD and HPLC. The results of these experiments are shown in tables 4.1.1-1 to 4.1.1-8 of Appendix I. In figure 4.1.1-1 the variation of the 4-CP concentration with the increase of the temperature for different initial concentrations is depicted. It can be observed that in none of the experiments the 4-CP was degraded while increasing the temperature.

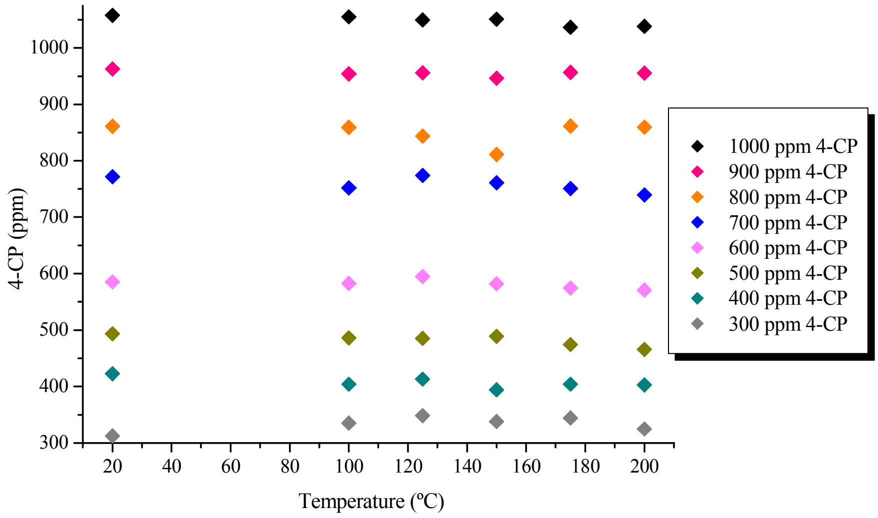


Figure 4.1.1-1 Effect of the preheating period on the 4-CP concentration.

The same conclusion can be reached when looking at the results of the TOC, shown in figure 4.1.1-2, since no variations of the TOC values were observed while heating the solution up to 200 ºC.

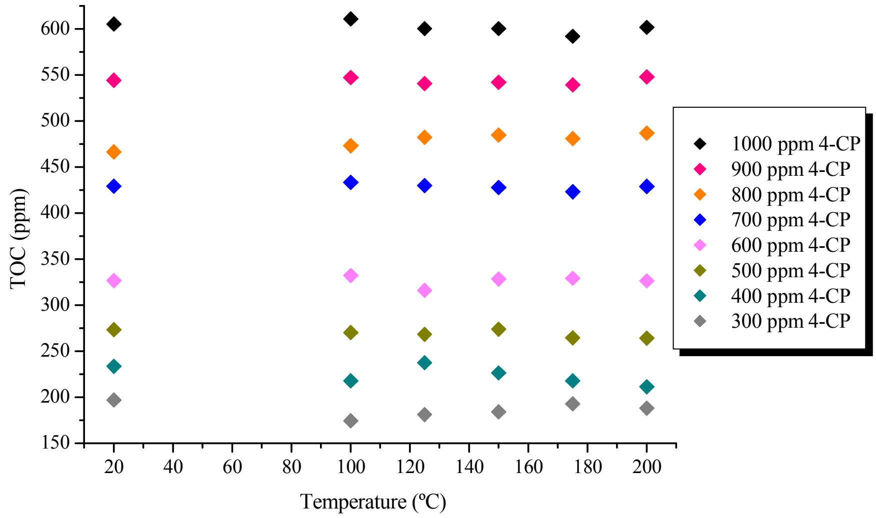


Figure 4.1.1-2 Effect of the preheating period on the TOC.

According to the previous results, it can be affirmed that in absence of oxidizing agent, 4-chlorophenol is not degraded in the range 20-200 ºC. This fact complies with the chromatographs obtained from the High Pressure Liquid Chromatograph, since no other peak than the one of the 4-CP was observed when analyzing the samples withdrawn from the reactor in the course of these experiments.

It was also thought to be interesting to compare the results of the TOC of each sample with the TOC related to the 4-CP and calculated from its concentration. This is of major importance in view of the fact that if both TOC values are equal or at least similar we will able to affirm that in the solution there are no other compounds than the target compound. On the other hand, in the event that the TOC measured is higher than the TOC related to the 4-CP then in the solution there might be some other compounds a part from the 4-CP. The TOC related to the 4-CP can be calculated as follows; considering that the molecular weight of 4-CP is 128.5 g/mol, the one of Carbon is 12 g/mol and that every mol of 4-CP contains 6 mols of Carbon:

$$\mathrm{X\ mg/L\ \ 4-CP} \times \frac{\mathrm{1\ mmol\ 4-CP}}{\mathrm{128.5\ mg\ 4-CP}} \times \frac{\mathrm{6\ mmol\ C}}{\mathrm{1\ mmol\ 4-CP}} \times \frac{\mathrm{12\ mg\ C}}{\mathrm{1\ mmol\ C}} = \mathrm{TOC\ (mg\ C/L)\ or\ (ppm)}$$

These calculations have been made for all the samples taken throughout all the experiments and they are included in table 4.1.1-9 and 4.1.1-10 of Appendix I. In figure 4.1.1-3 the comparison between the experimental TOC (measured) points, designated as “exp” and the TOC related to the 4-CP, designated as “theor”, can be observed.

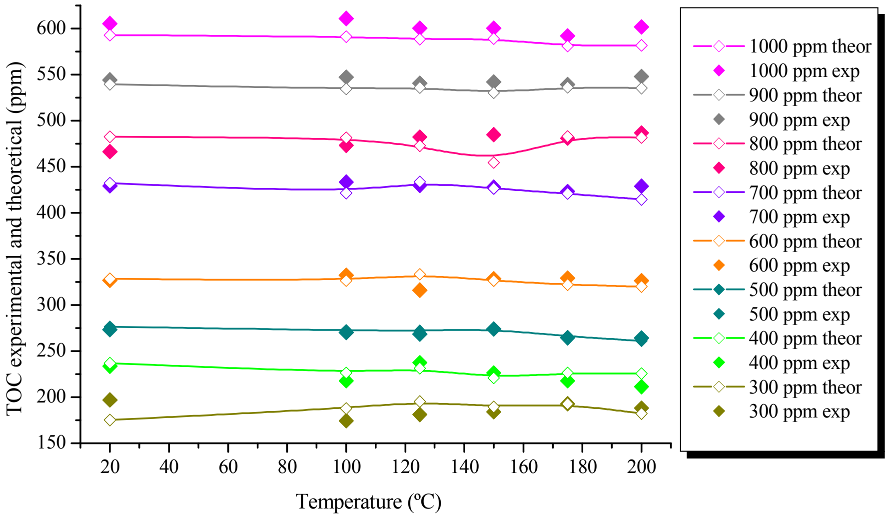


Figure 4.1.1-3 Experimental and theoretical values of TOC versus temperature.

From figure 4.1.1-3 it can be concluded that the measured TOC of the samples and the values of the TOC calculated from the 4-CP coincided in almost all the points. This shows, on one hand the reliability of these measurements, both TOC and HPLC; on the other hand, and most significant, it shows that all the organic carbon present in the solution came from the 4-CP and that no other intermediates are formed while heating the reactor in absence of oxidizing agents.

According to these results, it is clear that when heating the reactor, any changes as for the solution composition are likely to happen.

Study of the stirring speed

As it was explained in section 1.2.4 on page 35 and so on, the controlling stages of the wet oxidation process can be the *diffusion of the oxygen from the gaseous phase* (physical resistance) and the *chemical reaction* (chemical resistance). Several authors have demonstrated by calculating the Hatta number that wet oxidation is a chemical reaction controlled process (*Verenich, 2003*). Despite this fact, it was considered relevant to study the effect of the stirrer speed in order to avoid any kind of mass transfer resistance. It is also necessary to point out that this study only affects the wet oxidation part of the research, since when hydrogen peroxide is used as oxidizing agent, mass transfer problems are totally avoided.

To study the influence of the stirring speed on the degradation of 4-CP during the wet oxidation process several reactions were carried out. These experiments consisted of introducing 350 mL of a solution containing 500 ppm of parachlorophenol, fixing the temperature at 160 ºC, the partial pressure of oxygen at 10 bar and varying the speed of the stirrer. According to the data found in the literature, working at 500, 750 and 900 rpm was thought to be the most appropriated for this preliminary study. Samples were analyzed for TOC, pH and concentration of 4-CP. The results of these experiments are shown in tables 4.1.1-11 to 4.1.1-13 of Appendix I. In figure 4.1.1-4 the pH variations and the evolution of the TOC in the course of these three reactions are depicted. It can be observed that all the reactions presented similar pH tendency, it started from a value close to 5 and decreased until reaching a final value around 2.5. The only difference that can be noted between these three experiments belongs to the reaction at 500 rpm, in which the decrease of the pH was slightly smaller. This fact indicates that the reaction is a bit slower when the stirring speed is the lowest, most likely due to interferences in the mass transfer step. Same conclusions can be reached from the TOC results. The TOC measured at the end of the reaction is higher when working at 500 rpm, meaning thus, that higher TOC removals are reached when operating at the highest stirring speeds.

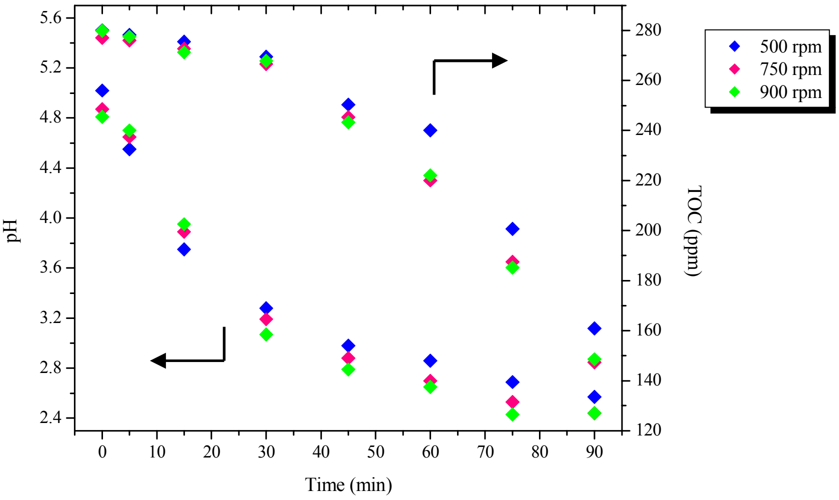


Figure 4.1.1-4 pH and TOC vs. time. WO at 500 ppm of 4-CP, 10 bar of Po_2 and 160 ºC; varying the speed of the stirrer 500, 750 and 900 rpm.

According to these results, and in order to avoid mass transfer problems it was decided to carry out the wet oxidation reactions at a stirring speed of 750 rpm.

4.1.2 WET PEROXIDE OXIDATION OF 4-CHLOROPHENOL

In this section the influence of several parameters such as temperature, initial concentration of 4-CP and dosage of peroxide added, on the wet peroxide oxidation reaction is studied. The experimental research plan was divided into 3 different parts depending on the temperature at which the reaction was carried out (100, 130 and 160 ºC). Once the temperature was fixed, the rest of the parameters were studied varying the initial concentration of chlorophenol in the range 300-1000 ppm and the dose of hydrogen peroxide from 1 to 5 mL.

4.1.2.1 Wet Peroxide Oxidation at 100 ºC

The aim of this section is to evaluate the influence of the initial concentration of 4-CP and the dosage of hydrogen peroxide over the duration of the wet peroxide reaction at 100 ºC. The chosen concentrations of the initial solutions were 300, 500, 750 and 1000 ppm and the amounts of the oxidizing agent were 5, 2.5 and 1 mL. The following sections are divided according to the hydrogen peroxide dose used in each set of experiments.

Reactions with 5 mL of Hydrogen Peroxide

Wet peroxide oxidation reactions of 300, 500, 750 and 1000 ppm 4-CP solutions were carried out at 100 ºC with 5 mL of H_2O_2. Samples were analyzed for pH, TOC and HPLC. The results of these experiments are shown in tables 4.1.2-1 to 4.1.2-4 of Appendix I and also depicted in figures 4.1.2-1 to 4.1.2-3. These figures, apart from the pH, TOC and 4-CP values throughout the reactions, show also the tendency of the temperature (designated by an orange line) in order to be able to distinguish between the preheating period, the reaction itself and the cooling down period.

Before discussing the pH results of these experiments it is necessary to point out that normally in all Advanced Oxidation Processes the pH tends to decrease as soon as the reaction commences. This fact is due to the formation of Low Molecular Weight Acids (LMWA) as a result of big organic molecules abatement. Thus, the drop of the pH normally indicates that the "big" organic molecules are being degraded.

According to the results depicted in figure 4.1.2-1 it can be affirmed that the oxidation of the target compound occurred in all the cases since the pH tended to decrease and that its degradation happened already during the preheating period when the temperature increased from 20 to 100 ºC (time 0 to 14 min). In this figure, it can be also noted that throughout the reaction, the lowest pH corresponded to the highest concentrated solution and on the other hand, the highest pH corresponded to the less concentrated. This fact can be explained taking into account that under the same operating conditions, high 4-CP concentrated solutions form higher amounts of Low Molecular Weight Acids than low concentrated solutions. The low pH can be explained then, considering the acidic nature of these compounds, or in other words, high amounts of LMWA in the solution involves low pH.

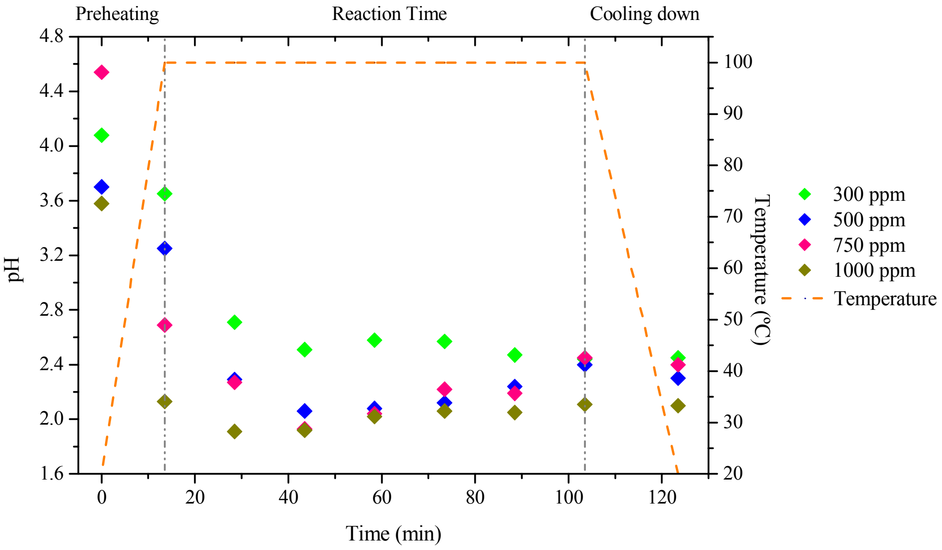


Figure 4.1.2-1 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 5 mL of H_2O_2.

In figure 4.1.2-2 and 4.1.2-3 the variation throughout the reactions, of the TOC and the concentration of 4-CP respectively can be observed. As it was expected and according to the decrease of the pH observed in all the experiments, the TOC and the 4-CP concentration decreased throughout the reaction. Focusing on the end of the reactions, it can be affirmed that complete mineralization was not accomplished in any of the experiments and that the lowest TOC values at the end of the reaction were performed by the less concentrated solutions. Paying attention now at the preheating period, it seems of special interest the fact that the preheating period affected in a different way depending on the initial concentration of 4-CP in the solution. This way, when working with the lowest concentrations, i.e. 300 and 500 ppm, any variation of the TOC was observed within the first 14 minutes (figure 4.1.2-2). On the other hand, the most concentrated solutions (750 and 1000 ppm) presented a TOC removal of 10 % and 15 % respectively during the preheating period.

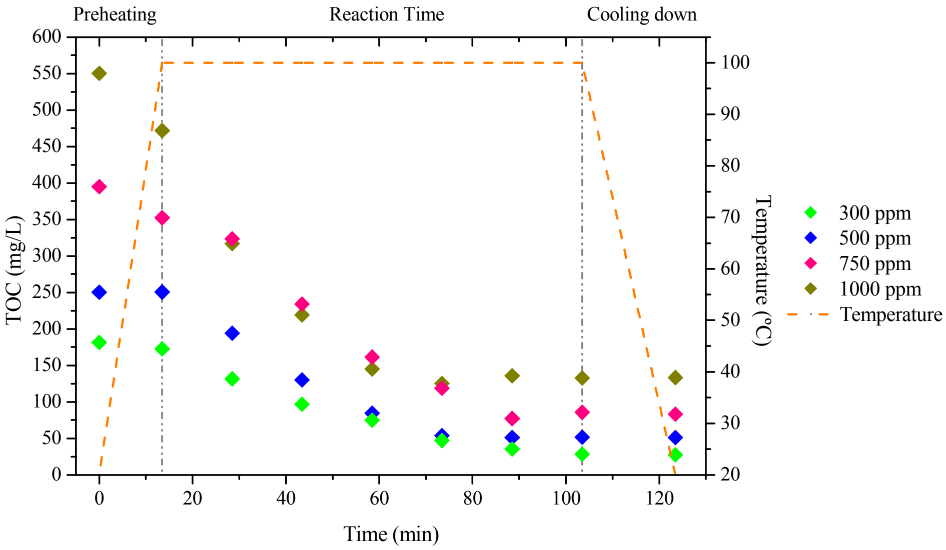


Figure 4.1.2-2 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 5 mL of H_2O_2.

As for the 4-CP, in figure 4.1.2-3 it can be seen that after 44 minutes it was completely removed from the solution in all the experiments (only few ppm were detected in the experiment at 500 ppm). In addition, it can be seen that in all the experiments the 4-CP concentration began to decrease already in the preheating period. This fact, together with the results of the TOC allows the discussion of some interesting results:

- High concentrated solutions presented a decrease in the TOC and 4-CP in the course of the preheating period. This indicates that the 4-CP was transformed into some intermediates compounds that were further oxidized to CO_2 and H_2O.

- Low concentrated solutions presented a 4-CP decrease during the preheating period but, the TOC remained constant during this time. This fact shows that the 4-CP was degraded into some intermediate compounds that were not further oxidized allowing a constant TOC within the first 14 minutes.

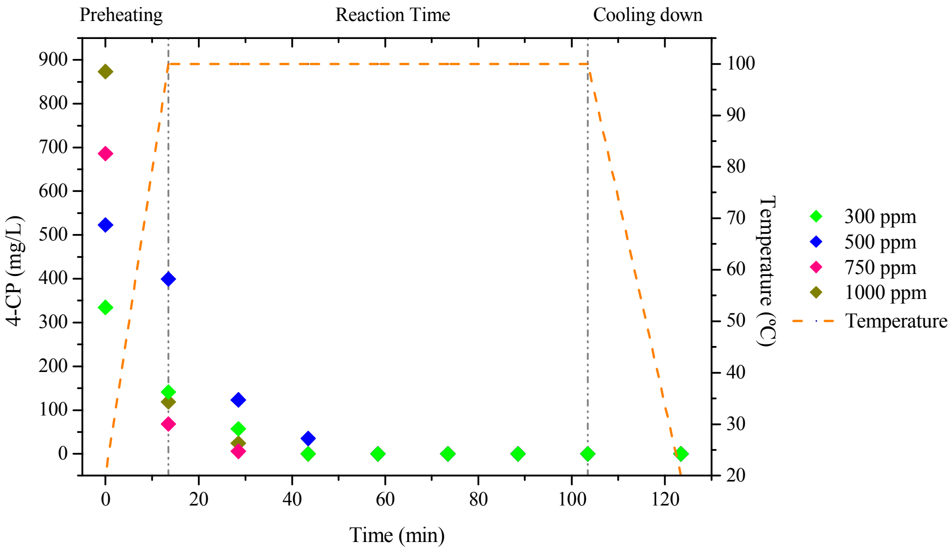


Figure 4.1.2-3 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 5 mL of H_2O_2.

Despite the fact that the previous figures are of great interest since they show the values of pH, TOC and 4-CP throughout the reactions, it is difficult to see the influence of the 4-CP concentration in the indicial solution. For this reason new values are needed in order to be able to establish comparisons between the reactions studied. These new values are the TOC and 4-CP removal that can be calculated as follows:

$$4-\text{CP removal}=\frac{\text{Initial Concentration of CP}-\text{Concentration of CP at any time}}{\text{Initial Concentration of CP}}=1-\frac{\text{CP}}{\text{CP}_o}$$

$$\text{TOC removal}=\frac{\text{Initial TOC}-\text{TOC at any time}}{\text{Initial TOC}}=1-\frac{\text{TOC}}{\text{TOC}_o}$$

The results of these calculations for the wet peroxide oxidation reactions included in this section are depicted in figures 4.1.2-4 and 4.1.2-5. In the former the TOC removal for the experiments carried out with an initial charge of 300, 500, 750 and 1000 ppm throughout the reactions are shown. It can be observed that at the end of the reaction the highest TOC removal (85 %) corresponded to the less concentrated experiment and the most concentrated one presented the smallest degradation (75.6 %). These results showed that high concentrations involve faster mineralization rates. Opposite conclusions can be reached from the 4-CP removals shown in figure 4.2.1-5, where the most concentrated solutions (1000 and 750 ppm) showed a faster 4-CP removal rate than the lowest concentrated (300 and 500 ppm).

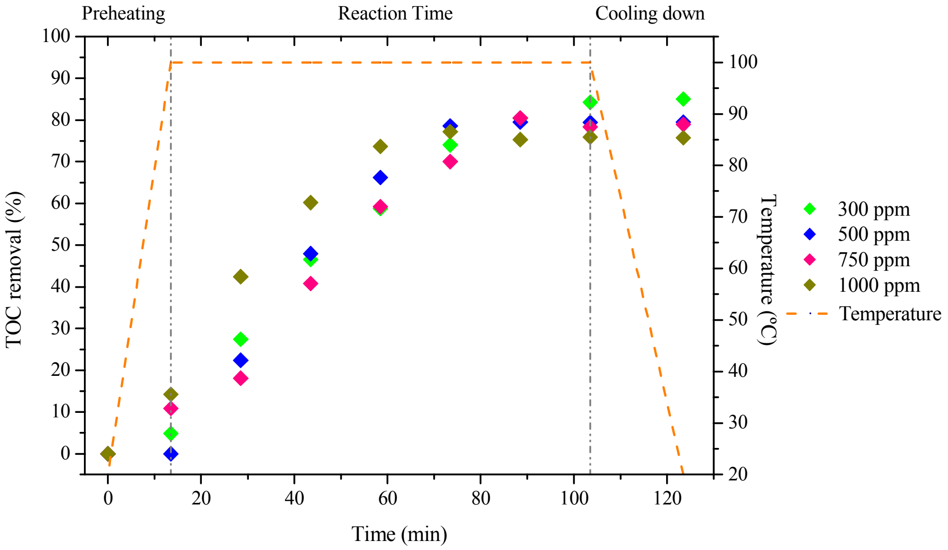


Figure 4.1.2-4 TOC removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 °C, 750 rpm and 5 mL of H_2O_2.

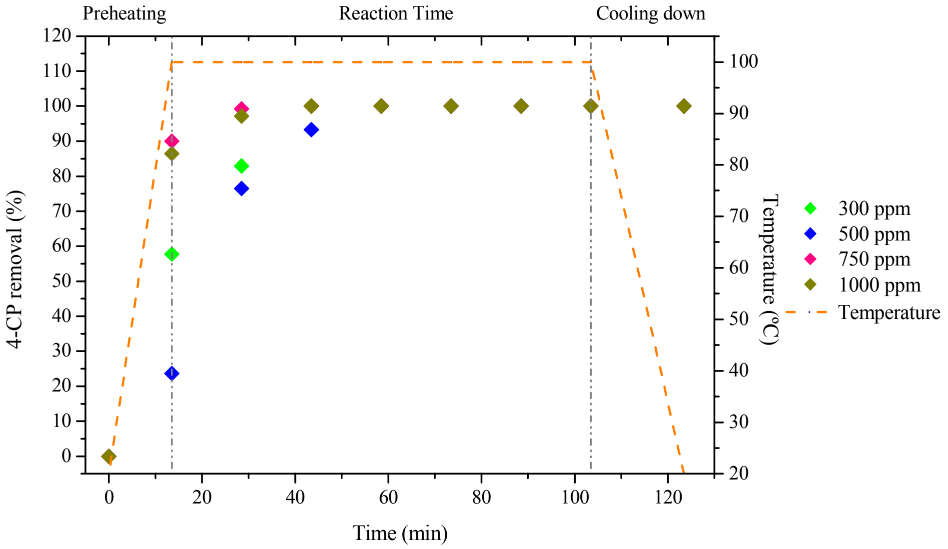


Figure 4.1.2-5 4-CP removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 °C, 750 rpm and 5 mL of H_2O_2.

In order to complement to some extent the results above presented, some extra experiments were carried out with another compound of the same family, i.e., 2,4-DCP. These experiments comprise wet peroxide oxidations of solutions containing 500 and 1000 ppm of this compound. In order to make feasible the establishment of comparisons between both organics, the same operating conditions as the experiments with 4-CP were selected, i.e., 100 ºC and 5mL of H_2O_2. The results of these two experiments are included in Appendix I, tables 4.1.2-5 and 4.1.2-6.

In figures 4.1.2-6 and 7, the TOC and Chlorophenol removals of the above mentioned experiments are depicted throughout the reactions. From the TOC results it seemed that 4-chlorophenol was more easily degraded than 2,4-dichlophenol, since the TOC removals of the monochlorophenol are higher during the reactions, especially, the ones belonging to the highest concentrated solutions. However, when focusing on both chlorophenol removals (fig. 4.1.2-7), remarkable differences were not observed, meaning that both compounds were degraded at a similar reaction rate. According to this, the observed differences concerning the TOC removal could be only understood taking into consideration the intermediate compounds formed over the duration of the reactions. Consequently, the intermediates formed from the 2,4-DCP appeared to be more refractory to the oxidation than the ones formed from the 4-CP.

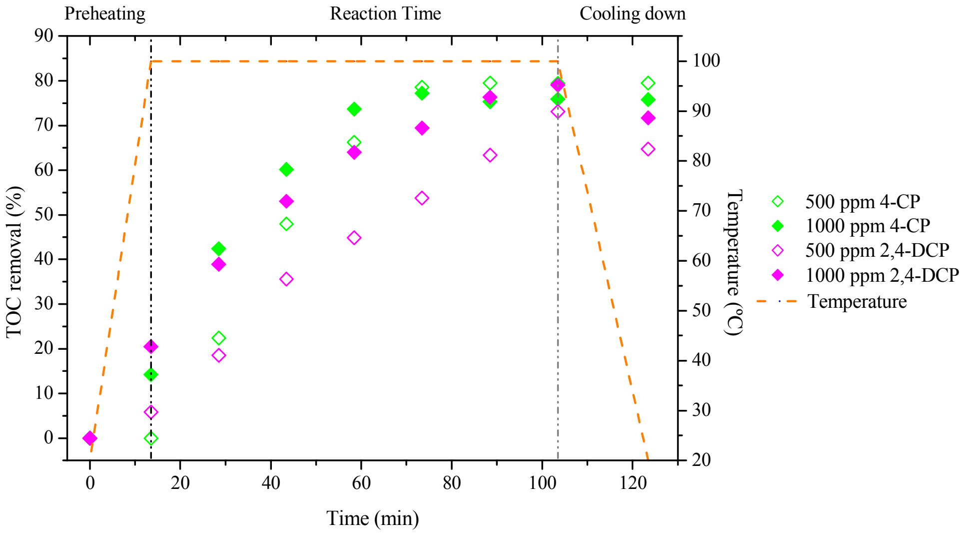


Figure 4.1.2-6 TOC removal vs. Time. Wet Peroxide Oxidation of 500 and 1000 ppm solutions of 4-CP and 2,4-DCP at 100 ºC, 750 rpm and 5 mL of H_2O_2

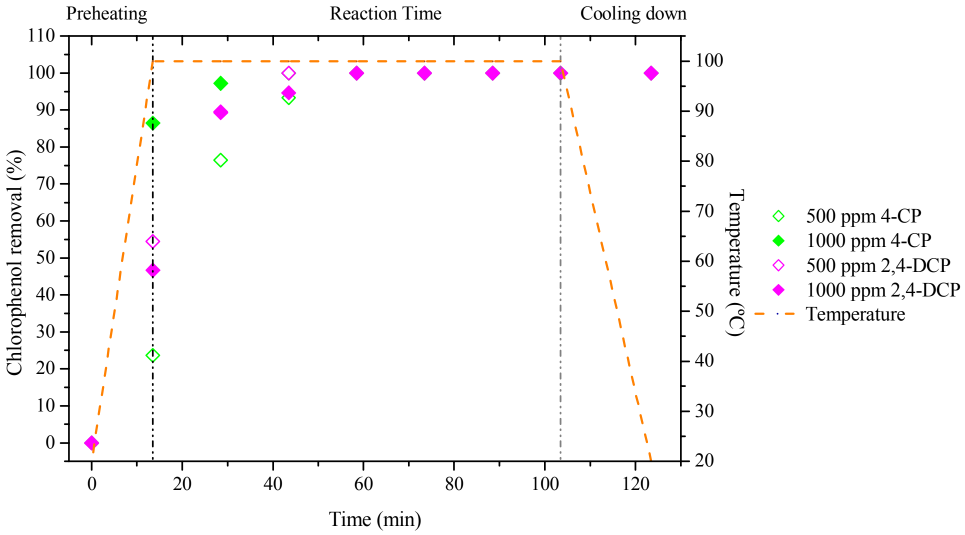


Figure 4.1.2-7 Chlorophenol removal vs. Time. Wet Peroxide Oxidation of 500 and 1000 ppm solutions of 4-CP and 2,4-DCP at 100 ºC, 750 rpm and 5 mL of H_2O_2.

Reactions with 2.5 mL of Hydrogen Peroxide

In order to study the influence of the concentration of the 4-CP in the initial solution when working at 100 ºC, 750 rpm and 2.5 mL of H_2O_2, reactions at 300, 500, 750 and 1000 ppm were carried out. In this case, samples were taken and analyzed in the same way as in the previous section, when working with 5 mL of oxidizing agent. The results of these experiments can be found in Appendix I tables 4.1.2-7 to 4.1.2-10 and are depicted in figures 4.1.2-8 to 4.1.2-12.

In figure 4.1.2-8 the pH variations throughout the reaction are shown. It can be observed that the pH decreased in all the cases from the beginning of the reaction until minute 28, remaining then constant until the end of the experiment. Its decrease, even in the preheating period (until minute 13), indicated a 4-CP degradation already in the first minutes of the reaction (when the temperature was still increasing). Comparing the tendency of the different reactions it can be noted that the most concentrated reactions (1000 and 750 ppm) performed lower pH values at the end of the reaction than the reactions with an initial concentration of 300 and 500 ppm. The higher acidity attained at the end of the reactions by the highest concentrated solutions is a consequence of the higher formation of low molecular weight acids.

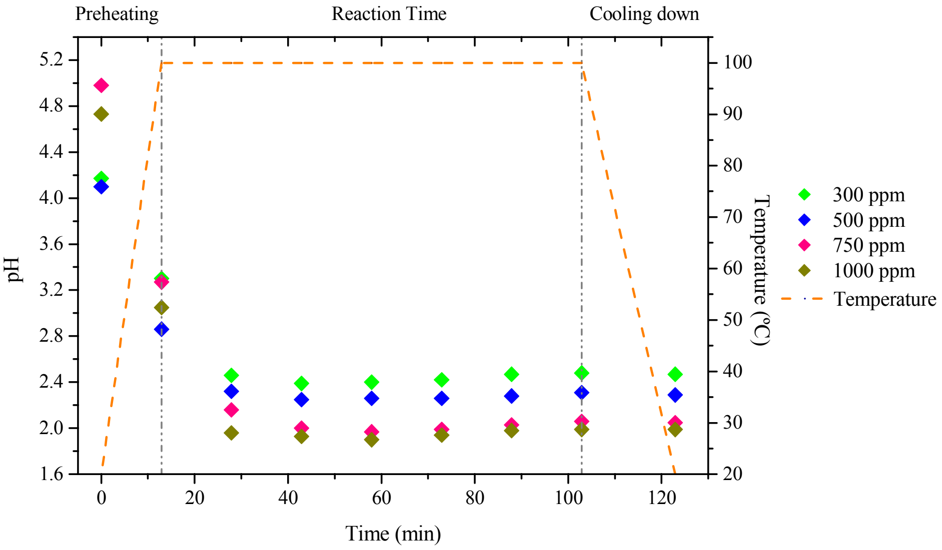


Figure 4.1.2-8 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

In figures 4.1.2-9 and 4.1.2-10 the TOC and 4-CP concentration values throughout the reactions are shown. As for the TOC (figure 4.1.2-9), it can be seen that complete mineralization (TOC= 0) at the end of the reaction was not reached under any of these operating conditions. In addition, the lowest TOC values were accomplished by the experiment carried out at 300 ppm and the highest by the one at 1000 ppm. It can be also appreciated that in all the reactions the TOC varied slightly during the preheating period (i.e., until time 13 min) and then it started to decrease gradually until the end of the reactions. Moving now on to the 4-CP concentrations throughout the reactions (figure 4.1.2-10) it can be observed that in all the experiments, after 43 minutes all the 4-CP was degraded. In addition and paying attention to the preheating period, it can be observed that the concentration of 4-CP started to decrease at the beginning of the preheating period. Taking into account that during this time the TOC remained constant and that the 4-CP concentration decreased, it can be affirmed that the 4-CP was degraded into some intermediates but only a slight mineralization occurred until the desired temperature was reached.

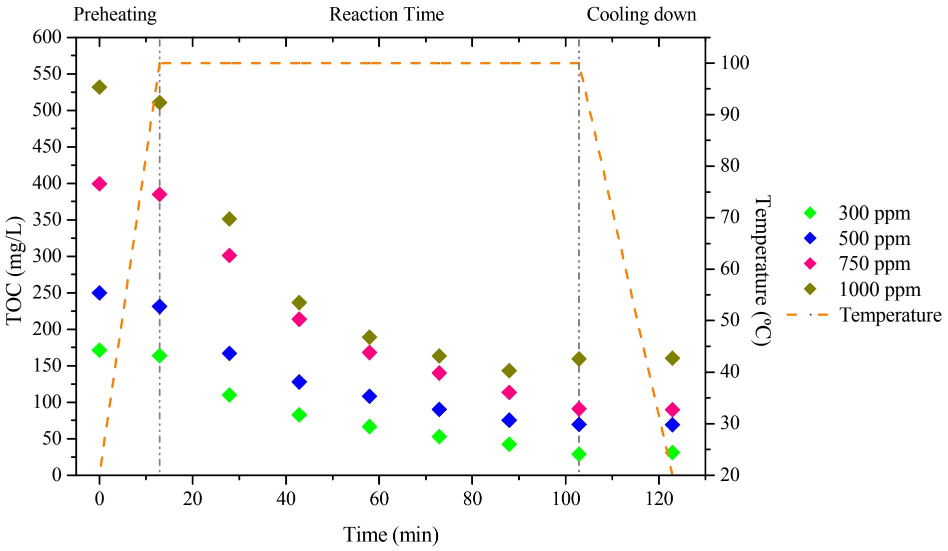


Figure 4.1.2-9 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

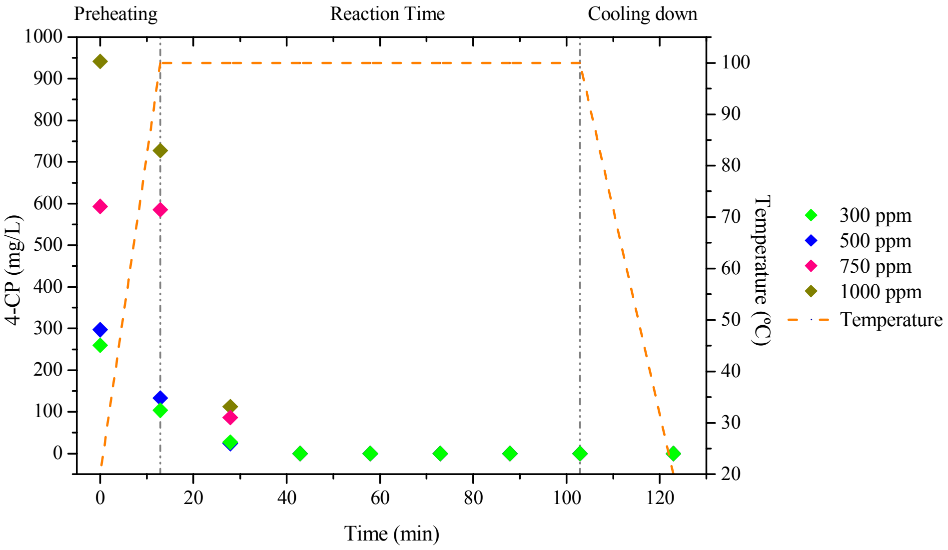


Figure 4.1.2-10 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

As it was explained in the previous section, figures 4.1.2-8 to 4.1.2-10 are useful because they show the value of the studied parameters (pH, TOC and 4-CP concentration) at any time of the reaction. However, these figures do not allow the establishment of a comparison between the test solutions with different initial concentration. For this purpose, it is necessary to calculate the TOC and the 4-CP removal, which are values independent of the initial concentration that allow the comparison between the experiments. Figures 4.1.2-11 and 4.1.2-12 show the TOC and the 4-CP removal of these reactions. As mention before, in figure 4.1.2-11 it can be observed that in any experiment complete mineralization was reached under these operating conditions. In this figure it can be also seen that the highest TOC removal at the end of the reaction was reached when working with an initial solution of 300 ppm and the lowest when working at 1000 ppm. As for the 4-CP removal, in figure 4.1.2-12 it can be observed that the 300 ppm experiment attained the fastest 4-CP degradation.

What has been observed after carrying out wet peroxide oxidations maintaining the temperature fixed at 100 ºC and using two different doses of oxidizing agent (i.e., 2.5 and 5 mL) is that, the target compound is degraded within 60 minutes of reaction meanwhile complete mineralization is not attained by any of the experiments. This fact suggests the refractory to oxidation nature of the intermediate compounds formed during the reactions. In order to get more information about this aspect, the following wet peroxide oxidation reactions were carried out varying the dose of hydrogen peroxide and the temperature.

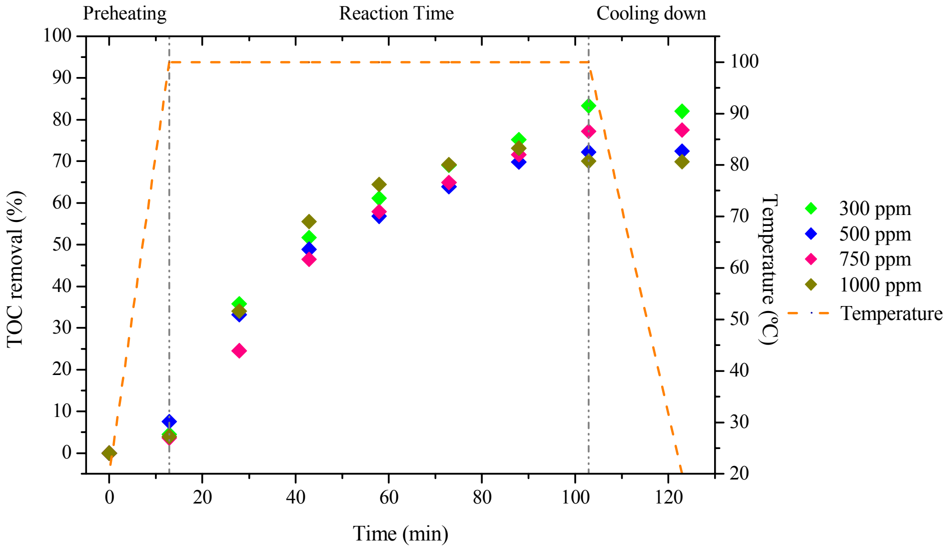


Figure 4.1.2-11 TOC removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

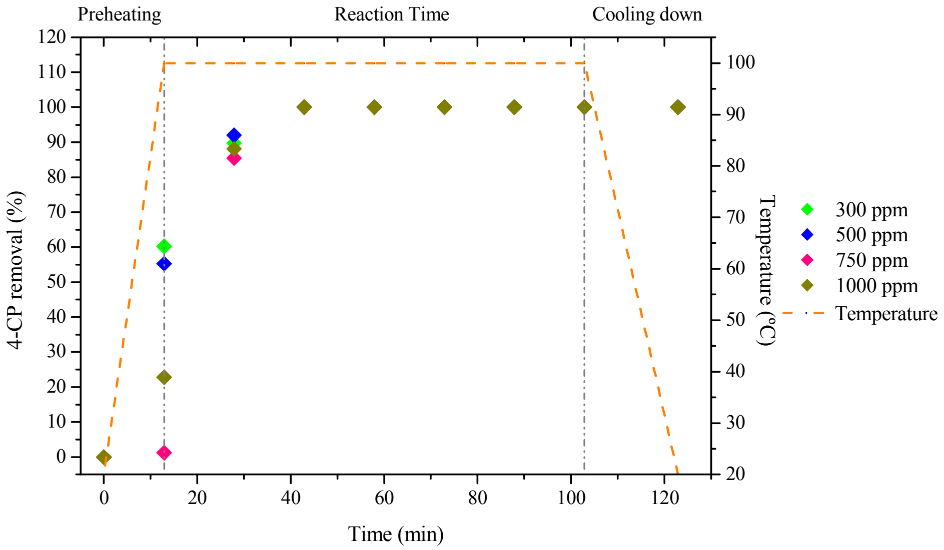


Figure 4.1.2-12 4-CP removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

However, before continuing the research varying the operating parameters, some extra experiments with 2,4-DCP were carried out in order to establish comparisons between these two chlorophenols. These wet peroxide oxidation were done with an initial charge of 500 and 1000 ppm of 2,4-DCP. The operating conditions were: 100 ºC of temperature and 2.5 mL of H_2O_2. The results of these experiments can be found in Appendix I, tables 4.1.2-11 and 4.1.2-12. In figures 4.1.2-13 and 14 the TOC and Chlorophenol removals throughout these reactions with 2,4-DCP and 4-CP are depicted. In the first place, it should be noted the difference between the TOC and Chlorophenol removals in these plots. On one side both chlorophenols disappeared within the first hour of reaction, being slower the 2,4-DCP degradation. On the other hand, the two chlorophenols presented different behaviors as for TOC removals. The solutions containing 4-chlorophenol achieved a final TOC removal of about 75 %. On the other hand, the TOC coming from the 2,4-DCP was removed slower, reaching a final value between 50 and 60 % depending on the initial concentration. This fact can be explained taking into account the different intermediates formed from these two chlorophenols. According to these results it can be affirmed that the intermediates formed in the course of 2,4-DCP oxidation are more difficult to degrade than the ones formed during the WPO of 4-CP.

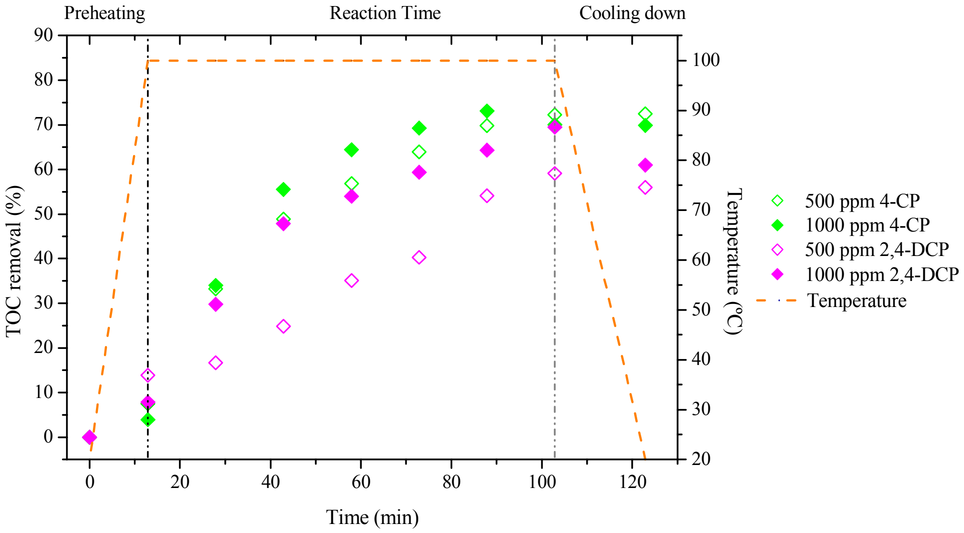


Figure 4.1.2-13 TOC removal vs. Time. Wet Peroxide Oxidation of 500 and 1000 ppm solutions of 4-CP and 2,4-DCP at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

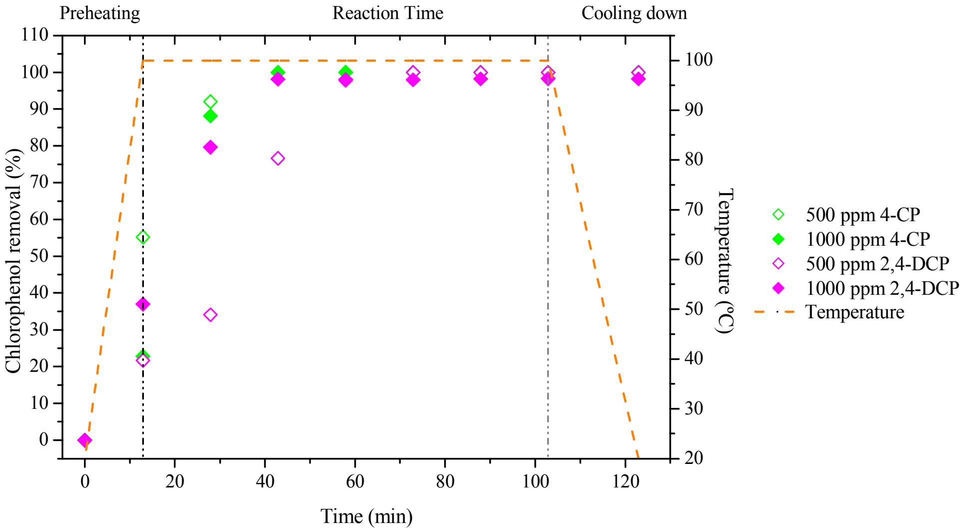


Figure 4.1.2-14 Chlorophenol removal vs. Time. Wet Peroxide Oxidation of 500 and 1000 ppm solutions of 4-CP and 2,4-DCP at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

Reactions with 1 mL of Hydrogen Peroxide

Wet peroxide oxidation reactions with initial solution concentrations of 4-CP of 300, 500, 750 and 1000 ppm, keeping the rest of parameters constant: 100 ºC, 750 rpm and 1 mL of hydrogen peroxide were carried out in order to study the influence of the initial concentration in the reaction. The results of these experiments are shown in tables 4.1.2-13 to 4.1.2-16 of Appendix I and depicted in figures 4.1.2-15 to 4.1.2-16.

In figure 4.1.2-15 the evolution of the pH throughout the reactions can be seen. It should be noted that the pH decreased already over the duration of the preheating period (0-13 min), then it continued decreasing until time 28 minutes, remaining then approximately constant until the end of the reaction. In the figure it can be also noted that the lowest pH at the end of the reaction corresponded to the highest concentrated experiments, meanwhile the highest pH was reached by the lowest concentrated one. As it was explained in previous sections this fact is due to the major generation of carboxylic acids when working with high concentrated solutions.

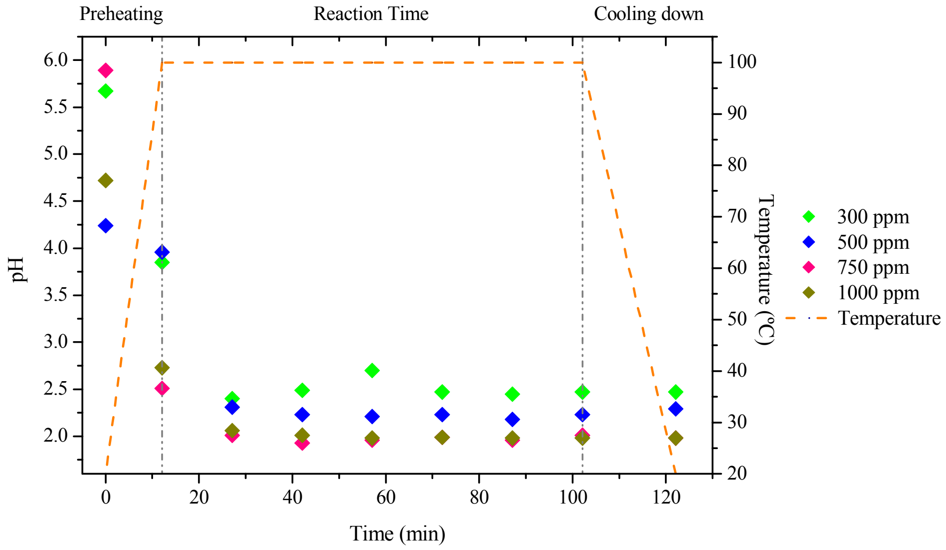


Figure 4.1.2-15 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

In figures 4.1.2-16 and 4.1.2-17 the TOC and 4-CP concentration evolution during the reaction can be observed. In figure 4.1.2-16 it can be seen that complete mineralization was not attained by any of these experiments and that, the TOC values at the end of the reactions were proportional to the initial concentrations. Therefore, the highest concentrated solutions had the highest TOC values at the end of the reaction and vice versa. Looking now at the preheating period it seems of special interest the fact that during this time the TOC remained constant in all the experiments, involving null mineralization. In addition, it can be also seen that for the most concentrated solutions, once reached the set temperature (t= 12 min), the TOC decreased until time 27 and then it remained constant. This fact involves, that after 27 minutes of reaction all the hydrogen peroxide was consumed when working with 1000 and 750 ppm. However, the experiments at 500 and 300 ppm, presented a progressive TOC decrease throughout the reaction.

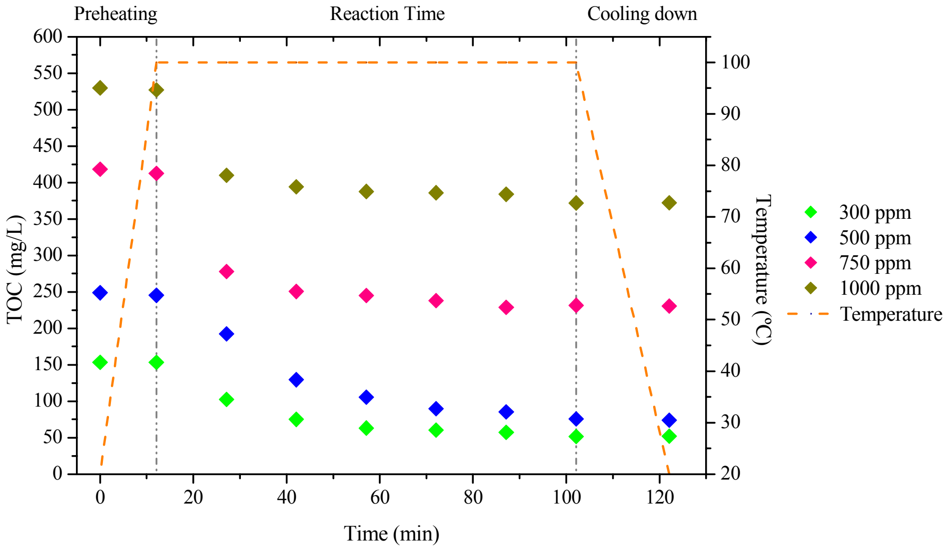


Figure 4.1.2-16 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

As for the 4-CP concentration (figure 4.1.2-17) it can be noted that 4-CP was completely degraded in almost all the experiments within the first 42 minutes of the reaction. In fact, only a small percentage of the initial concentration remained in the final solution when working with the highest concentration, i.e. (1000 ppm).

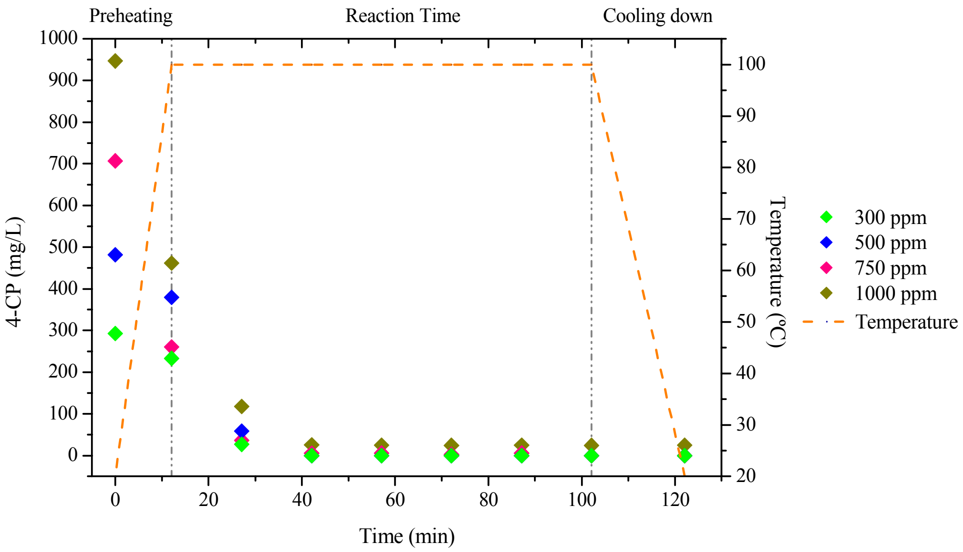


Figure 4.1.2-17 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 °C, 750 rpm and 1 mL of H_2O_2.

In figures 4.1.2-18 and 4.1.2-19 the TOC and 4-CP removal of this set of experiments can be observed. In figure 4.1.2-19 it can be seen that the 4-CP was partially degraded during the first 12 minutes of reaction. The 300 ppm experiment had a 4-CP removal in the vicinity of 20 % in the course of the preheating period; approximately the same removal was observed in the experiment at 500 ppm, and finally the most concentrated solutions, 750 and 1000 ppm presented a removal of 63 % and 52 % respectively after the first 12 minutes. According to this, it can be affirmed that under this operating conditions (100 ºC, 1 mL H_2O_2 and 750 rpm) the 4-CP removal rate is faster when working with concentrated initial solutions. In these figures it can be also seen that after 42 minutes of the reaction there was no 4-CP present in the solution.

Having a look at figure 4.1.2-18 it can be seen that at this time (42 min) in all the experiments there was still TOC in the solution, involving the presence of organic intermediates compounds. Another fact that should be mention from the TOC removal is that the highest removals were attained by the less concentrated solutions. This can be explained taking into account that the more concentrated the initial solution, the higher the amount of refractory intermediates compounds are formed. Since these compounds are more refractory to the oxidation, they provoke a lower degree of mineralization.

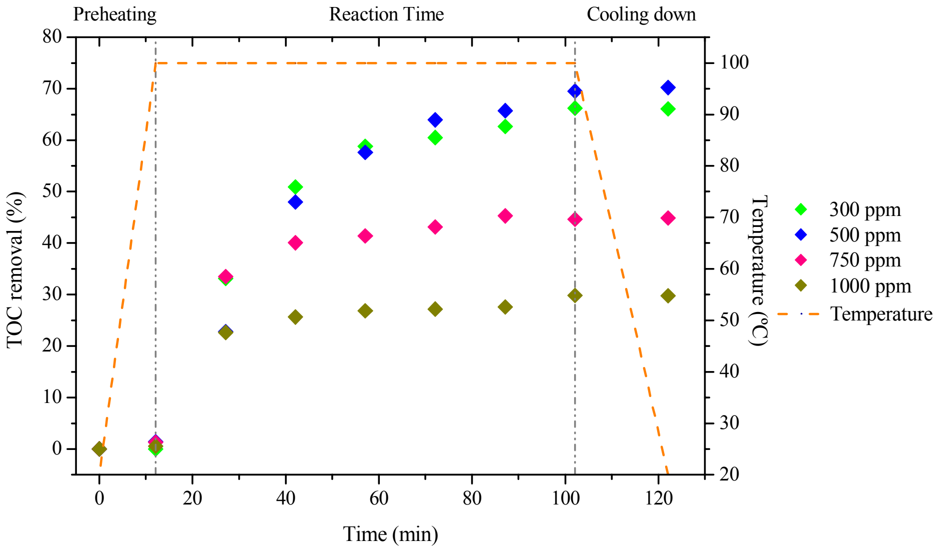


Figure 4.1.2-18 TOC removal vs. Time. WPO of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

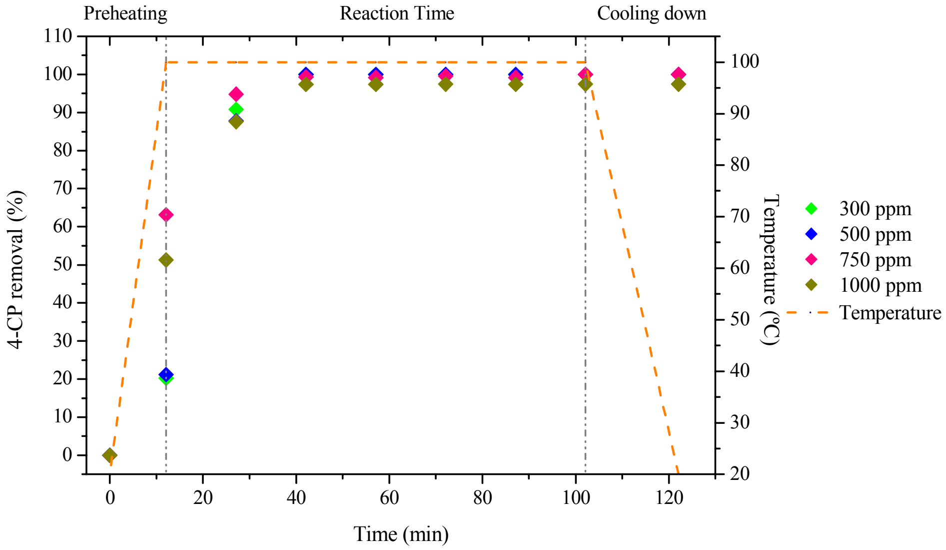


Figure 4.1.2-19 4-CP removal vs. Time. WPO of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

In order to complement to some extent the results above presented, some extra experiments were carried out with another compound of the same family, i.e., 2,4-DCP. These experiments include wet peroxide oxidations of solutions containing 500 and 1000 ppm of this compound. The reactions were carried out at 100 ºC using 1 mL of H_2O_2. These are the same operating conditions as the experiments with 4-CP included in this section, in order to make feasible the establishment of comparisons between the two compounds. The results of these two experiments are included in Appendix I, tables 4.1.2-17 and 4.1.2-18.

In figures 4.1.2-20 and 21, the TOC and Chlorophenol removals of the above mentioned experiments are depicted throughout the reactions. In the first place and regarding the TOC removal of the two compounds (4-CP and 2,4-DCP), it can be affirmed that the highest differences between them occurred at the highest concentration. It can be seen in figure 4.2.1-20 that meanwhile at the highest concentration (1000 ppm) the difference between the two compounds is not so noticeable, when working at the lowest concentration (500 ppm) the difference in TOC removal is around 20 %. The fact that when working at 500 ppm of initial concentration, the TOC removal for 4-CP solutions is 70 % and 55.1 % for 2,4-DCP solutions, can be justified considering that 2,4-DCP and its intermediates are more difficult to be degraded than 4-CP. Having a look at figure 4.1.2-20, it can be appreciated that the chlorophenol removal in these cases is complete already after 40 minutes of reaction, meaning thus, that after this point the intermediate compounds play an important role in the process. This fact leads us to the conclusion, that the intermediate compounds formed during 2,4-DCP degradation are more difficult to degrade than the ones formed from 4-CP.

On the other hand, taking into account how the system evolves when working with the highest concentrations, it can be seen that the oxidizing agent (H_2O_2) is the limitant reagent of these reactions. The TOC removal when working with 2,4-DCP and 4-CP are 20 and 27 % respectively. In this case, the highest TOC removal of 4-CP solutions can be explained in the same way as above. In addition, and taking into consideration the Chlorohenol removals throughout the reactions, it can be affirmed that 2,4-DCP needs a highest amount of oxidizing agent than 4-CP. The 2,4-DCP and 4-CP removals when working at 1000 ppm of initial concentration were 74 and 97 % respectively.

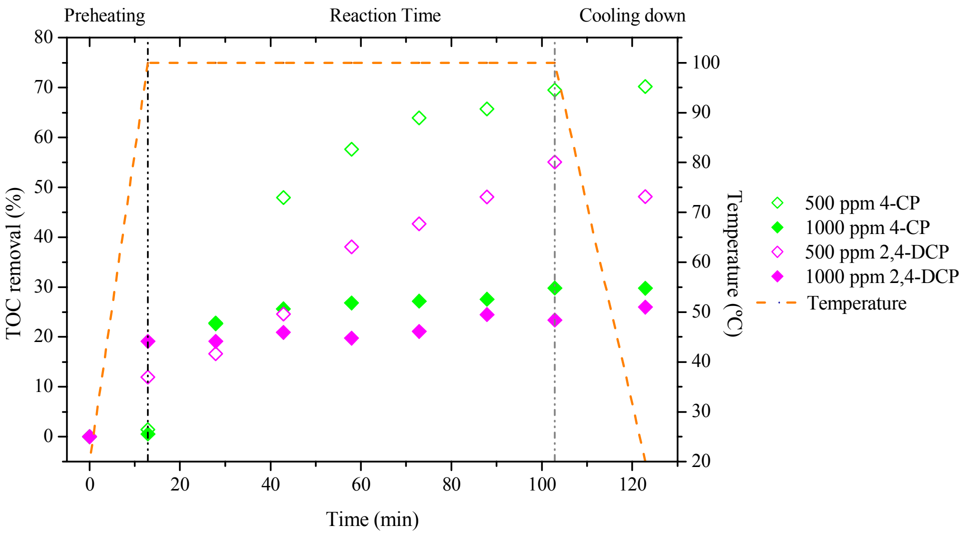


Figure 4.1.2-20 TOC removal vs. Time. WPO of 500 and 1000 ppm 4-CP and 2,4-DCP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

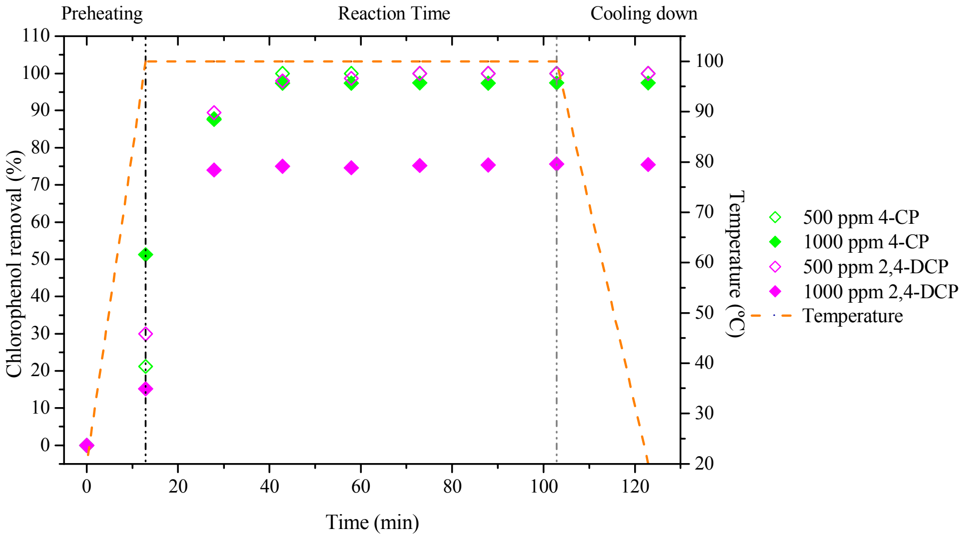


Figure 4.1.2-21 4-CP and 2,4-DCP removal vs. Time. WPO of 500 and 1000 ppm 4-CP and 2,4-DCP solutions at 100 ºC, 750 rpm and 1 mL of H_2O_2.

4.1.2.2 Wet Peroxide Oxidation at 130 ºC

This chapter includes the study of the influence of the initial concentration of 4-CP in the course of the wet peroxide oxidation of solutions containing this compound at 130 ºC and using different amounts of the oxidizing agent, hydrogen peroxide. For this purpose, reactions with 5 and 2.5 mL were carried out.

Reactions with 5 mL of Hydrogen Peroxide

Wet peroxide oxidations reactions of solutions containing 300, 500, 750 and 1000 ppm of 4-CP, keeping the rest of the parameters constant (750 rpm, 130 ºC and 5 mL of H_2O_2) were carried out. As when working at 100 ºC, samples were analyzed for pH, TOC and HPLC. The results of these experiments are included in Appendix I, tables 4.1.2-19 to 4.1.2-22 and depicted in figures 4.1.2-22 to 4.1.2-24. In these figures, the evolution of the temperature during the experiments, designated by an orange line, can be observed as well. In figure 4.1.2-22 the evolution of the pH values of the solution throughout the reaction is depicted.

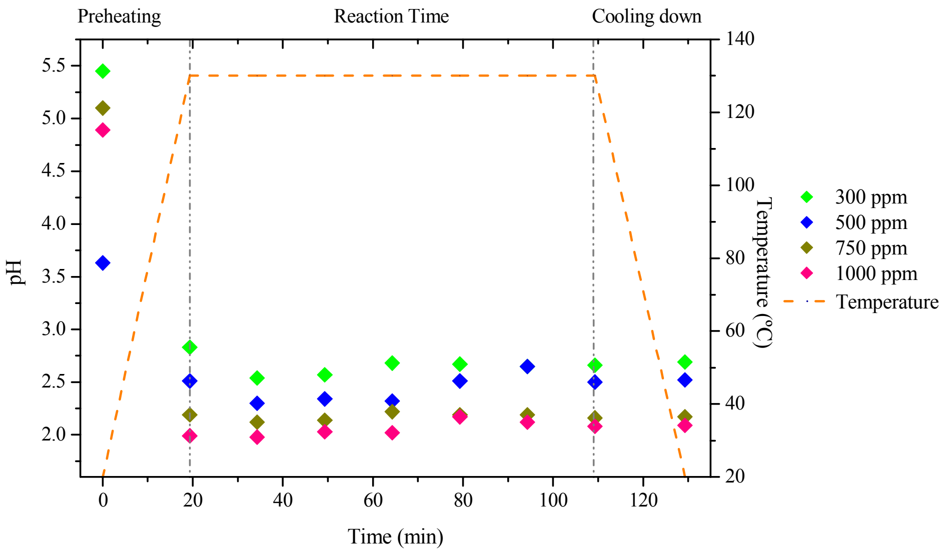


Figure 4.1.2-22 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 5 mL of H_2O_2.

It can be noted that the pH dropped drastically over the duration of the preheating period (first 20 minutes) remaining then constant until the end of the reaction. As it was observed in previous experiments, the pH at the end of the reaction was lower the higher the initial concentration, due to the different amounts formed of low molecular weight acids.

In figures 4.1.2-23 and 4.1.2-24 the TOC and 4-CP values throughout the reaction are represented. In the first figure, it can be observed that almost complete mineralization was accomplished at the end of the reaction when working with the solution at 300 ppm. In addition, it can be seen that the highest concentrated experiment shows the highest TOC value at the end of the experiment. On the other hand, as shown in figure 4.1.2-24 the 4-CP was completely removed during the first 35 minutes in all the experiments. Another fact to mention, related to the preheating period, is that there were noticeable changes as for TOC and 4-CP in all the reactions during this period of time. It can be observed that after approximately 20 minutes of reaction almost all the 4-CP had already disappeared. However, the values of the TOC showed that at that point there were still some organic compounds in the solutions, giving importance or relevance to their role in the mechanistic pathway.

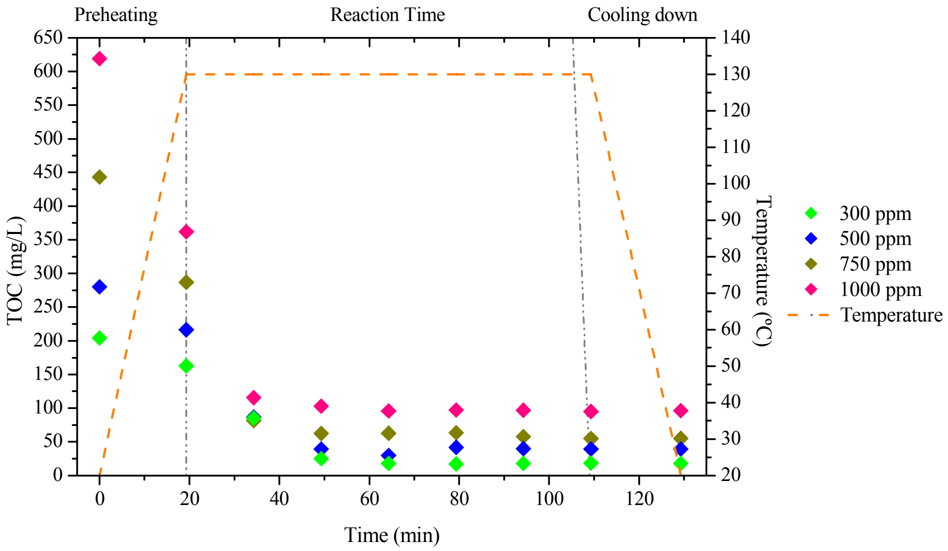


Figure 4.1.2-23 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 5 mL of H_2O_2.

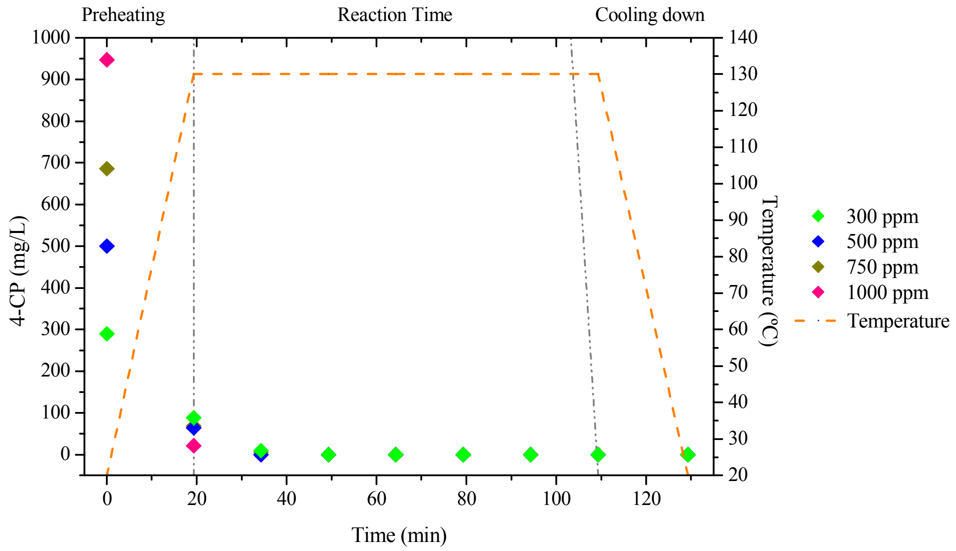


Figure 4.1.2-24 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 5 mL of H_2O_2.

To study the influence of the initial concentration of 4-CP in the reaction, the TOC and 4-CP removals were calculated and are depicted in figures 4.1.2-25 and 4.1.2-26 respectively. It can be observed that an increase in the initial concentration of the solution implied higher 4-CP and TOC removals during the preheating period. The 4-CP removals attained at the end of the preheating period of these experiments were: 300 ppm: 70 %, 500 ppm: 87 %, 750 ppm: 90 % and 1000 ppm: 98 %. These results proved that the 4-CP abatement is faster the higher the concentration. On the other hand, TOC removals after the preheating period were: 300 ppm: 20 %, 500 ppm: 22 %, 750 ppm: 35 %, 1000 ppm: 42 %. According to these results, the most concentrated solutions presented the highest TOC and 4-CP removal rates in the course of the pre-heating period. Another fact to point out is that at the end of the reaction all the experiments presented similar values of TOC removal; however, the less concentrated solutions had a slightly higher removal.

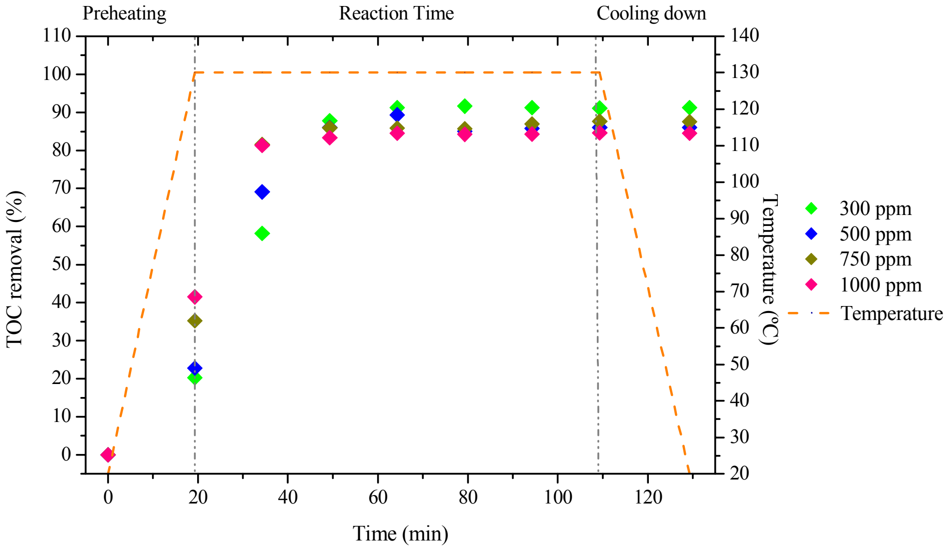


Figure 4.1.2-25 TOC removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 5 mL of H_2O_2.

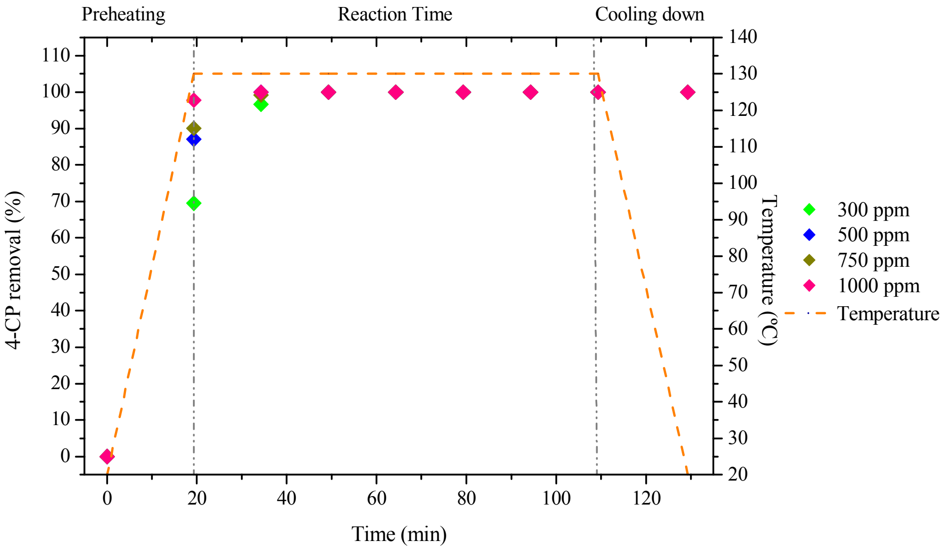


Figure 4.1.2-26 4-CP removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 5 mL of H_2O_2.

Reactions with 2.5 mL of Hydrogen Peroxide

To study the influence of the initial concentration of 4-chlorophenol over the duration of the wet peroxide oxidation process when working with 2.5 mL of hydrogen peroxide at 130 ºC, reactions with an initial solution of 300, 500, 750 and 1000 ppm were carried out. TOC, pH and HPLC results are shown in Appendix I, in tables 4.1.2-23 to 4.1.2-26 and also depicted in figures 4.1.2-27 to 4.1.2-29. Figure 4.1.2-27 shows the evolution of the pH throughout these reactions. It can be observed that the pH dropped rapidly in the course of the preheating period and then remained constant until the end of the reaction. This fact indicated that the major changes in the reactor occur within the 17 first minutes of the reaction. It is also necessary to point out that the highest concentrated solutions had the lowest pH values at the end of the reaction, due to the major formation of low molecular weight acids.

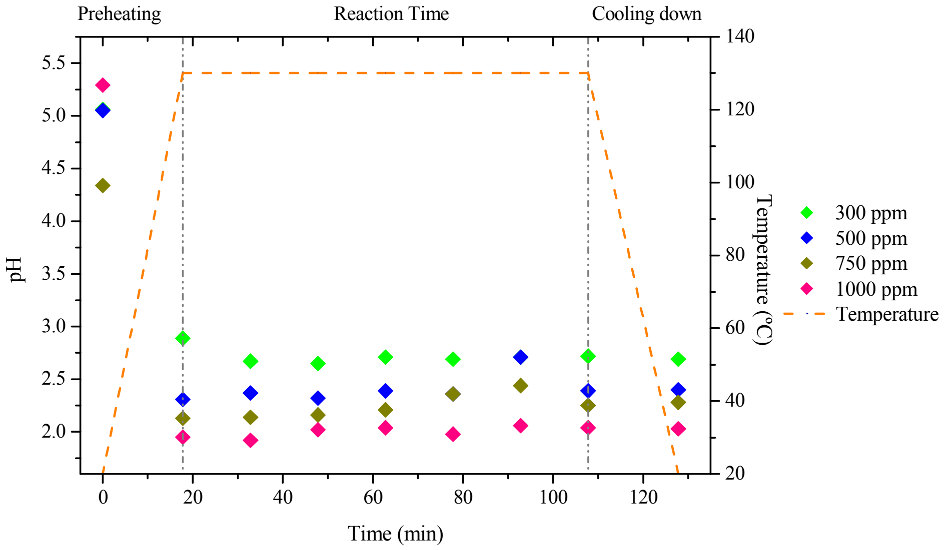


Figure 4.1.2-27 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 2.5 mL of H_2O_2.

In figures 4.1.2-28 and 4.1.2-29 the TOC and the 4-CP content in the solution is represented versus the time of the reaction. It seems of special importance the fact that after 32 minutes of reaction there was no 4-CP remaining in the solution. However, in figure 4.1.2-28 it can be observed that in any experiment complete TOC removal was achieved. This fact indicates that some of the intermediate compounds formed during the reaction were refractory to the oxidation. In the same figure, it can also be observed that the lowest TOC values at the end of the reaction were reached when working with the lowest initial concentrations and vice versa. This fact is in agreement with the tendency of the pH since low molecular weight acids are considered to be refractory to oxidation by means of AOPs.

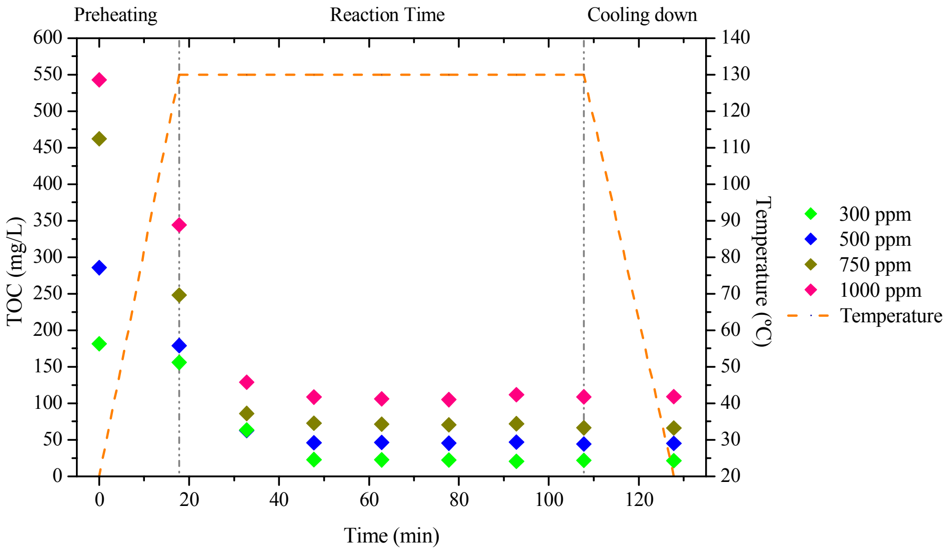


Figure 4.1.2-28 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 2.5 mL of H_2O_2.

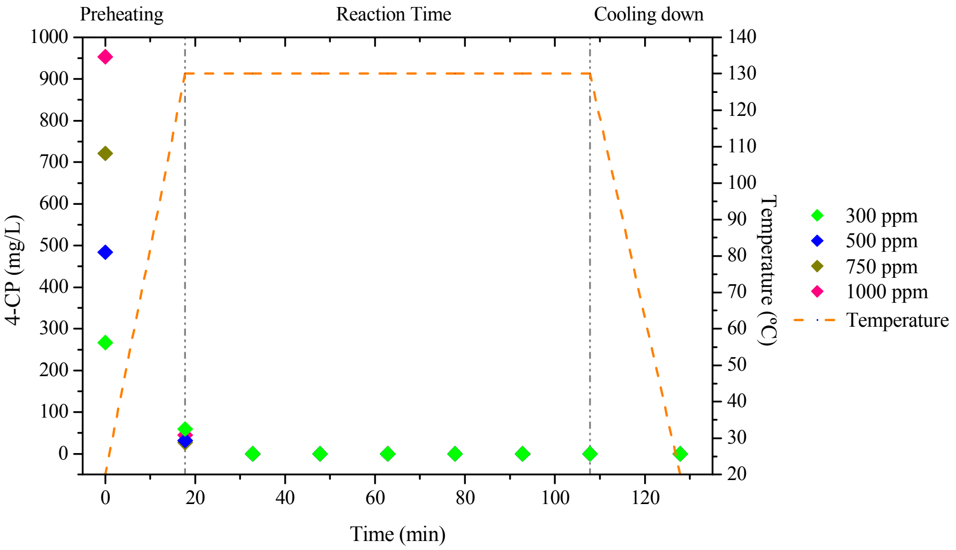


Figure 4.1.2-29 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 100 ºC, 750 rpm and 2.5 mL of H_2O_2.

As in previous sections, the TOC and 4-CP removals throughout the reactions have been calculated in order to estimate the influence of the initial concentration of 4-CP in the solution to be treated. In figures 4.1.2-30 and 4.1.2-31 the results of these calculations are depicted. In them, it can be observed that within the preheating period the removals of 4-CP and TOC of the less concentrated solution (300 ppm) were smaller than for the rest of the experiments. It can be also seen that after 47 minutes the TOC remained constant in all the experiments until the end of the reaction. Another fact to point out is that at the end of the reaction the highest TOC removal (88 %) was attained when working with an initial solution of 300 ppm and the lowest (80 %) when working with the most concentrated one (1000 ppm).

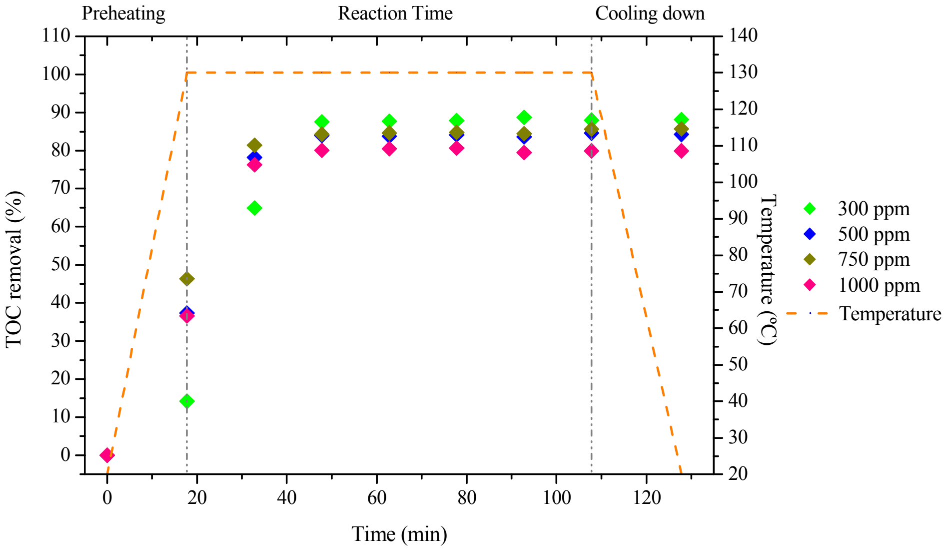


Figure 4.1.2-30 TOC removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 °C, 750 rpm and 2.5 mL of H_2O_2.

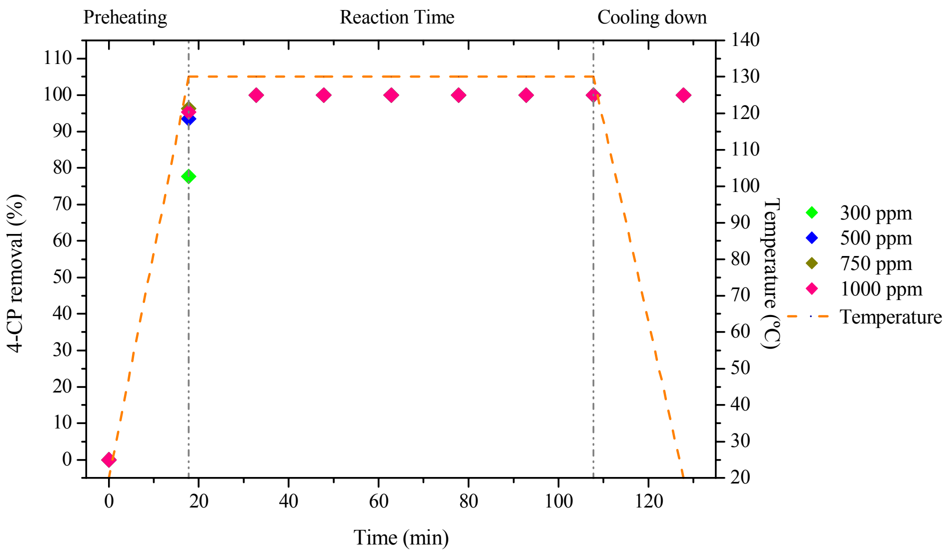


Figure 4.1.2-31 4-CP removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 130 ºC, 750 rpm and 2.5 mL of H_2O_2.

4.1.2.3 Wet Peroxide Oxidation at 160 ºC

This chapter includes the study of the influence of the initial concentration of 4-CP in the course of the wet peroxide oxidation reactions at 160 ºC and using different amounts of the oxidizing agent, hydrogen peroxide. For this purpose, reactions with 5 and 2.5 mL of H_2O_2 and keeping the rest of the operating parameters constant (160 ºC and 750 rpm) were carried out.

__Reactions with 5 mL of Hydrogen Peroxide__

Wet peroxide oxidations reactions of solutions containing 300, 500, 750 and 1000 ppm of 4-CP under the following conditions: 750 rpm, 160 ºC and 5 mL of H_2O_2 were carried out. As it happened when working at 100 ºC and 130 ºC, samples were analyzed for pH, TOC and HPLC. The results of these experiments are included in Appendix I, tables 4.1.2-27 to 4.1.2-30 and depicted in figures 4.1.2-32 to 4.1.2-34. In these figures, the tendency of the temperature, designated by an orange line, throughout the reactions can be also observed.

In figure 4.1.2-32 the pH values, measured over the duration of these reactions, are displayed versus time of the experiments. It can be noted that the pH variations occurred in the 25 first minutes of the reaction and from this moment on it remained constant until the end of the experiment. It can be also noted that the lowest pH was reached when working with the highest concentration solutions as a result of the fast degradation of the parent compound and the high generation of acids.

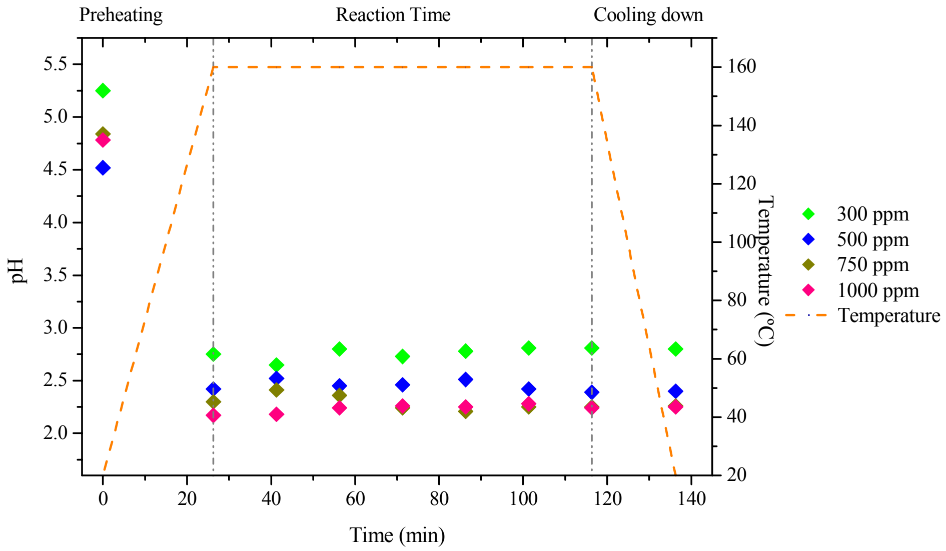


Figure 4.1.2-32 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 5 mL of H_2O_2.

In figures 4.1.2-33 and 4.1.2-34 the TOC and 4-CP concentration values throughout the reaction can be observed. As it was observed when analyzing the pH tendencies, all the changes as for TOC and 4-CP concentration occurred during the preheating period. It can be also noted that in all the experiments complete 4-CP removal was accomplished within the 25 first minutes of the reaction. On the other hand and regarding the TOC values achieved at the end of the experiments, it should be pointed out that the lowest concentrated solutions reached the lowest TOC values. In these three plots (pH, TOC and 4-CP vs. time) two areas can be differentiated. In the first part, a sharp decreased in these values occurred after which, these parameters remained approximately constant. This fact gives an indication that all the oxidizing agent was consumed before the desired temperature is reached, ending thus, the reaction after the first 25 minutes.

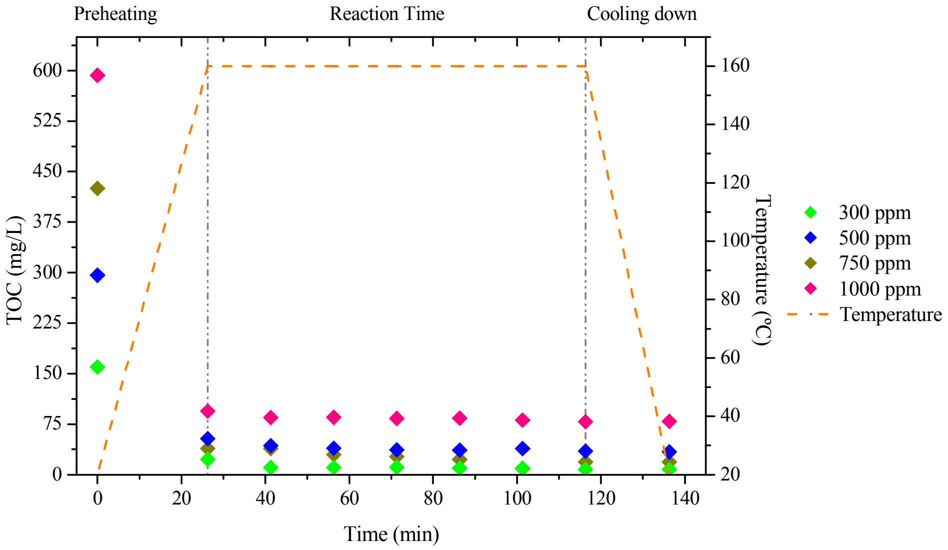


Figure 4.1.2-33 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 5 mL of H_2O_2.

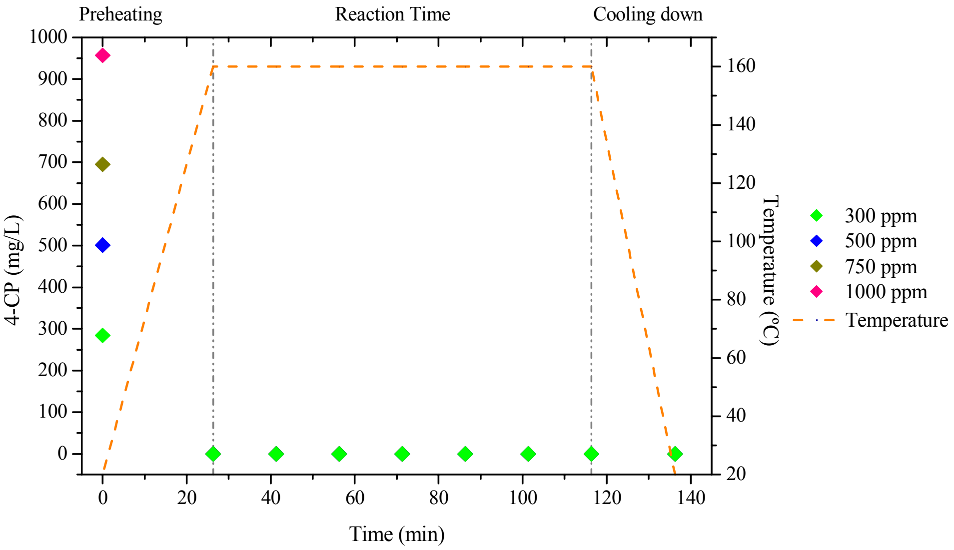


Figure 4.1.2-34 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 5 mL of H_2O_2.

The values of the TOC and 4-CP removals at any time of the reaction are depicted in figures 4.1.2-34 and 4.1.2-35. As for the 4-CP removal, all the experiments presented the same tendency since after 25 minutes of reaction there was no 4-CP left in the solution. Something similar happened when analyzing the TOC removal; after 40 minutes of reaction, no changes in the value of the TOC were observed. What seems of special importance is the fact that the highest TOC removals were achieved by the less concentrated solutions. Once again, this fact is explained taking into account the formation of refractory to oxidation carboxylic acids. The generated amount of these acids is proportional to the initial concentration of 4-CP. Therefore, high initial concentration of monochlorophenol involves high concentrations of acids and higher values of TOC remaining the end of the reaction.

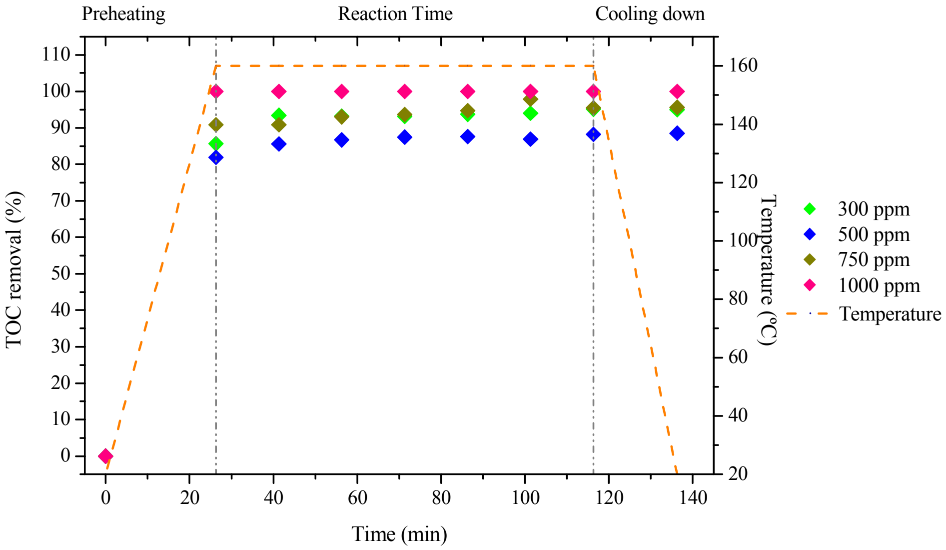


Figure 4.1.2-35 TOC removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 °C, 750 rpm and 5 mL of H_2O_2.

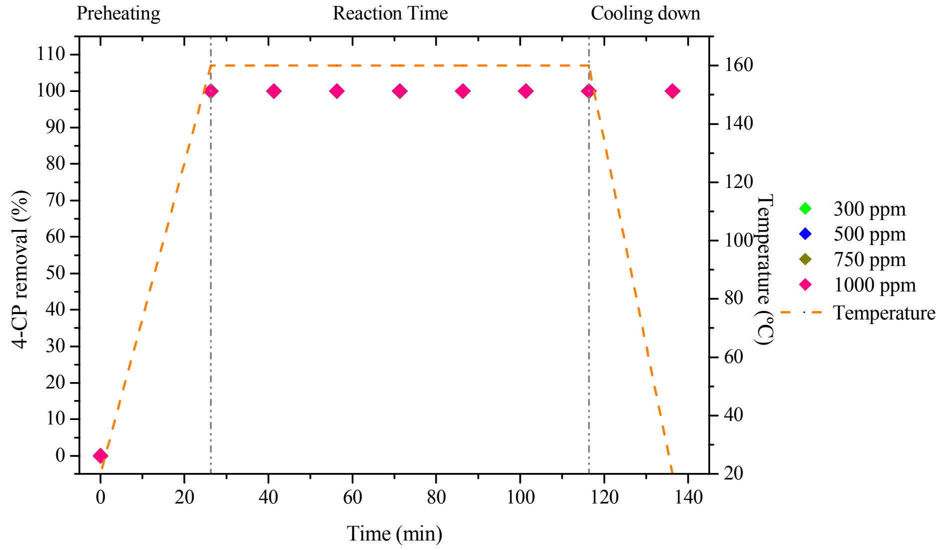


Figure 4.1.2-36 4-CP removal vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 °C, 750 rpm and 5 mL of H_2O_2.

Reactions with 2.5 mL of Hydrogen Peroxide

Wet peroxide oxidations reactions of solutions containing 300, 500, 750 and 1000 ppm of 4-CP, maintaining the rest of the operating parameters constant (750 rpm, 160 ºC and 2.5 mL of H_2O_2) were performed. Samples were analyzed for pH, TOC and HPLC. The results of these experiments are included in Appendix I, tables 4.1.2-31 to 4.1.2-34 and depicted in figures 4.1.2-37 to 4.1.2-39. The former illustrates the values of the pH of throughout the reactions. As it happened when carrying out the reactions at the same temperature but with 5 mL, the pH decreased rapidly in the first 28 minutes of the reaction (preheating period) and then it remained constant until the end of the reaction.

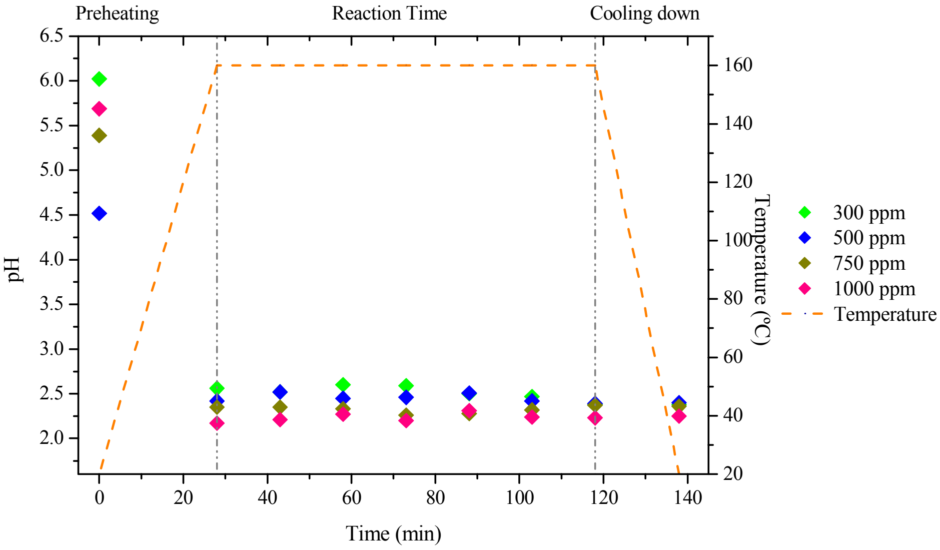


Figure 4.2.1-37 pH vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 2.5 mL of H_2O_2.

In figures 4.1.2-38 and 4.1.2-39 the values of the TOC and 4-CP concentration throughout the reactions are depicted. It can be seen that during the preheating period (from time 0 to 28 minutes) the 4-CP is completely degraded in all the experiments. In figure 4.1.2-38, it can be seen that TOC presented an analogous behavior, since its values in all the experiments decreased sharply during the preheating period and then they remained constant until the end of the reaction. The 4-CP and TOC tendencies can be explained if we consider that in the course of the first minutes of the reaction (preheating period) all the hydrogen peroxide is consumed; In fact, after 160 ºC are reached in the reactor there is no oxidizing agent in the medium and thus, the TOC does not further decrease.

In addition, it can be seen that the highest TOC value at the end of the experiment corresponded to the reaction at the highest concentration i.e., 1000 ppm. This fact is in agreement with the observed tendency of the pH (1000 ppm experiment showed the lowest pH) and can be explained taking into account that at the commencement of the reaction this experiment has the highest amount of 4-CP. During the reaction 4-CP is transformed into intermediates of the reaction (low molecular weight acids) and a high 4-CP concentration involves a high amount of acids generated, which at the same time involves a sharp drop of the pH.

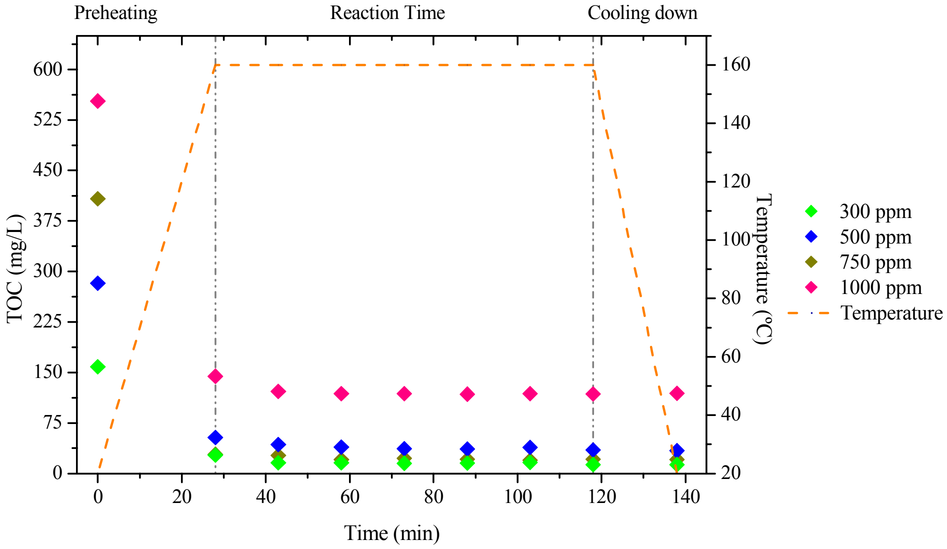


Figure 4.1.2-38 TOC vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 2.5 mL of H_2O_2.

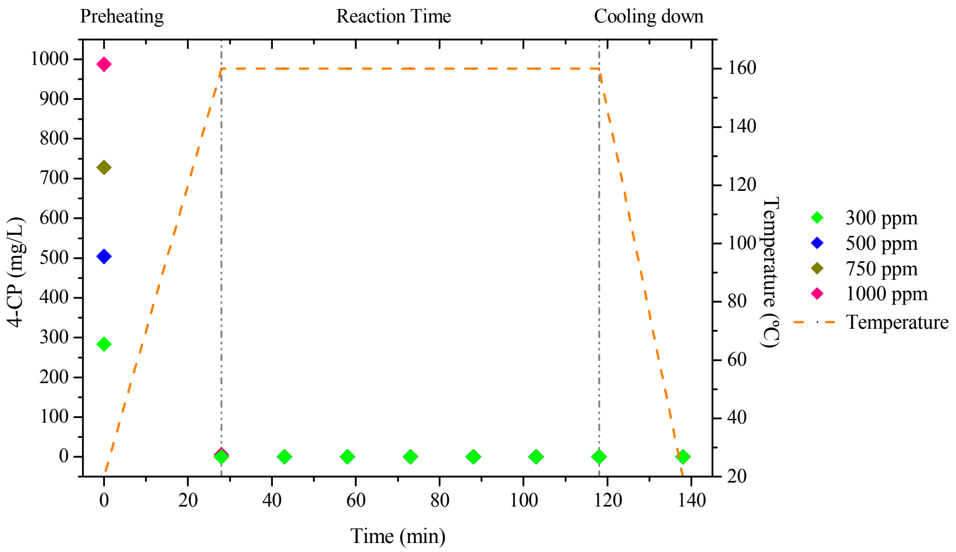


Figure 4.1.2-39 4-CP vs. Time. Wet Peroxide Oxidation of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 2.5 mL of H_2O_2.

In order to be able to decide under which concentration the 4-CP and TOC removals were faster, they have been calculated for all the samples throughout the reactions. The results of these calculations are depicted in figures 4.1.2-40 and 4.1.2-41. As for the 4-CP removal, it can be seen that any difference is presented between the experiments, since after 28 minutes of reaction complete removal is accomplished by all the experiments. On the other hand, differences as for the TOC were observed between the different initial concentration experiments and the lowest TOC removal was performed when working at 1000 ppm.

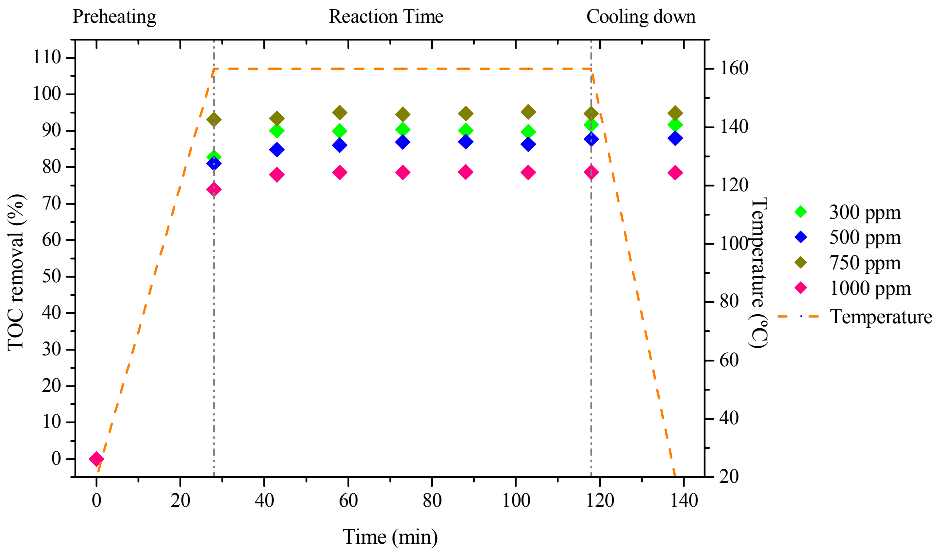


Figure 4.1.2-40 TOC removal vs. Time. WPO of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 2.5 mL of H_2O_2.

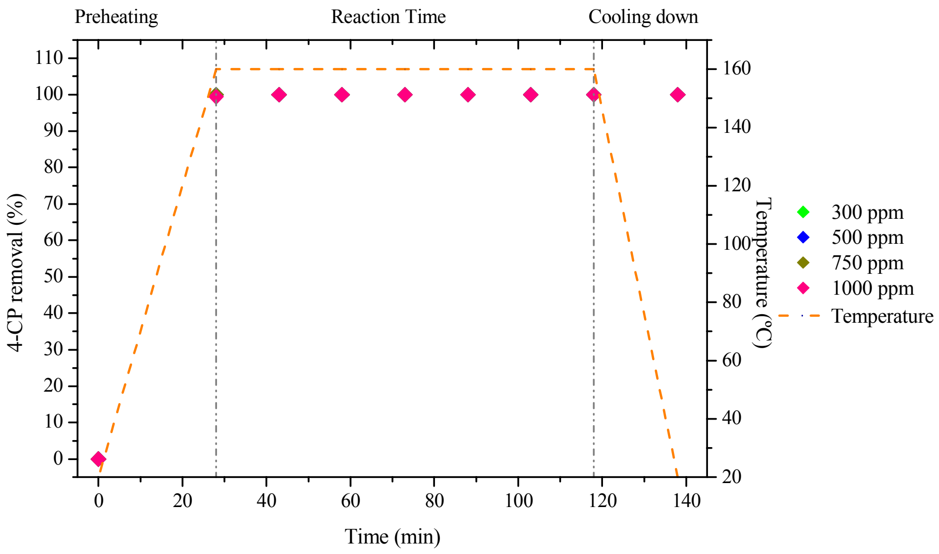


Figure 4.1.2-41 4-CP removal vs. Time. WPO of 300, 500, 750 and 1000 ppm 4-CP solutions at 160 ºC, 750 rpm and 2.5 mL of H_2O_2.

4.1.2.4 Wet Peroxide Oxidation reactions results summary

In this chapter the influence of the temperature, dose of hydrogen peroxide and concentration of 4-CP in the initial solutions in the course of the wet peroxide oxidation process has been studied by means of carrying out reactions at different operating conditions. The purpose of this section is to summarize these results and to give some clues, so that the reader can easily see the influence of the studied parameters. Figures 4.1.2-42, 43 and 44 show the TOC removals attained at the end of the wet peroxide oxidations at 100, 130 and 160 ºC by the following experiments: 300ppm of 4-CP with 5 mL of H_2O_2, 300 ppm of 4-CP with 2.5 mL of H_2O_2, 1000 ppm of 4-CP with 5 mL of H_2O_2 and 1000 ppm of 4-CP with 5 mL of H_2O_2. These experiments were selected in view of the fact that they performed with the extreme concentrations 300 ppm and 1000 ppm so that differences can be clearly observed.

The most important points to be discussed from these results are the following:

1-The highest TOC removals at the end of the reaction were achieved when working with the less concentrated solutions. This fact is explained taking into account that a high initial concentration of 4-CP involves a high formation of organic intermediates compounds which are more refractory to the oxidation than the 4-CP. According to this, when working with an initial solution of 1000 ppm, a high amount of intermediates are formed, provoking thus a smaller removal of the TOC.

2-When working with higher amounts of oxidizing agent, higher TOC removals are reached at the end of the reaction. However complete mineralization was not attained, meaning that under these operating conditions the H_2O_2 is not in excess respect the organic compounds.

3-High operating temperatures favors the TOC removal. It can be observed in the above mentioned figures that when increasing the temperature (especially from 100 to 130 ºC) a higher TOC removal is obtained at the end of all the reactions. The decomposition of 4-CP was studied by single H_2O_2 at room temperature by Benítez et al. (*Benítez et al., 2000a, 2001*) and it was concluded that no significant degradation was obtained. Therefore, H_2O_2 does not oxidize the studied organic compounds at low temperatures. This effect has been already observed by several authors with some refractory pollutants.

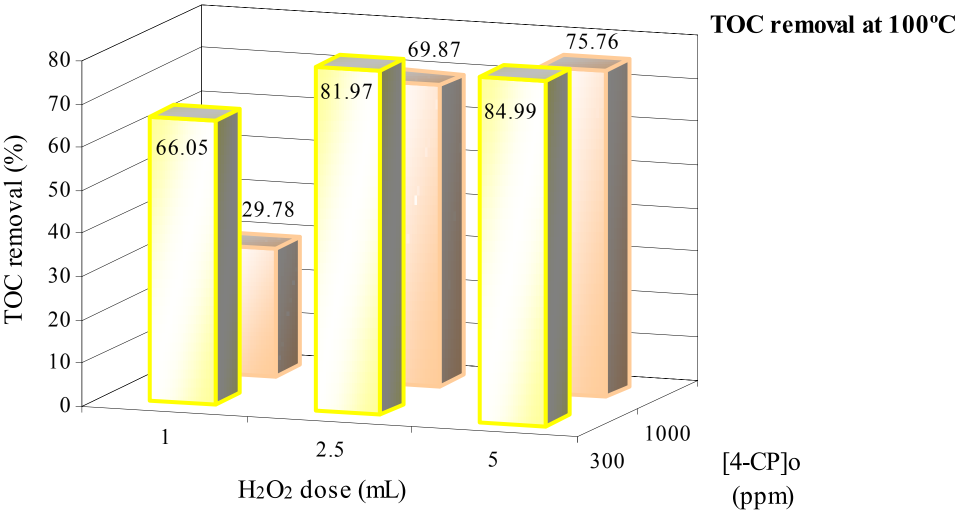


Figure 4.1.2-42 TOC removal at the end of the experiments vs initial concentration of 4-CP and vs H_2O_2 dose. Wet peroxide oxidation reactions carried out at 100ºC, 1, 5 or 2.5 mL of H_2O_2 and 300 or 1000 ppm of initial concentration of 4-CP.

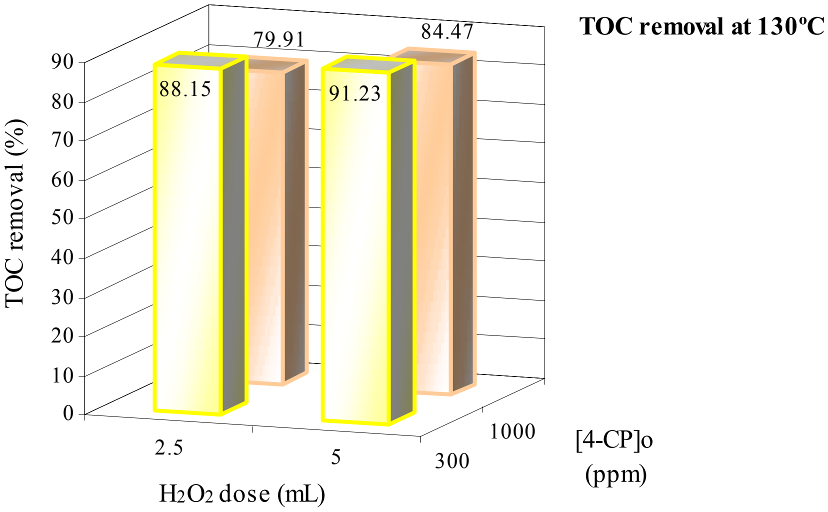


Figure 4.1.2-43 TOC removal at the end of the experiments vs initial concentration of 4-CP and vs H_2O_2 dose. Wet peroxide oxidation reactions carried out at 130ºC, 1, 5 or 2.5 mL of H_2O_2 and 300 or 1000 ppm of initial concentration of 4-CP.

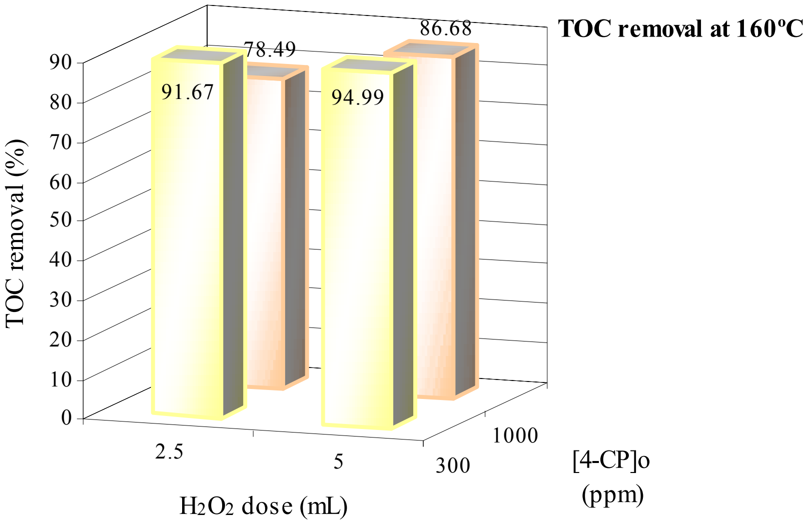


Figure 4.1.2-44 TOC removal at the end of the experiments vs initial concentration of 4-CP and vs H_2O_2 dose. Wet peroxide oxidation reactions carried out at 160ºC, 1, 5 or 2.5 mL of H_2O_2 and 300 or 1000 ppm of initial concentration of 4-CP.

4.1.3 WET OXIDATION OF 4-CHLOROPHENOL

This chapter contains four different parts. The first one comprises the study of the influence of the temperature on the wet oxidation process and the second one includes the study of the influence of the initial concentration of 4-chlorophenol throughout the reaction. The influence of the partial pressure of oxygen is taken under evaluation in the third one and finally, in the last part, some information about the evolution of the biodegradability of the solution to be treated is given.

4.1.3.1 Study of the influence of the temperature

To study the influence of the temperature in the wet oxidation of solutions containing 4-CP, two different series of experiments were carried out. In the former, the initial concentration was set at 1000 ppm, 750 rpm of stirring speed, partial pressure of oxygen of 10 bar and four different experiments were carried out varying the temperature: 150, 160, 175 and 190 ºC. In the second series of experiment, the pressure and temperature were the same as in the previous experiments but the initial concentration was set at 500 ppm. Thus, not only the influence of the temperature could be studied but also its influence at different initial concentrations.

Wet Oxidation Reactions at 1000 ppm of 4-CP initial concentration

This series of experiments includes four experiments that were carried out at 150, 160, 175 and 190 ºC, keeping the rest of parameters constant: Po_2= 10 bar, stirring speed of 750 rpm and initial concentration of 4-CP= 1000 ppm. The samples of these experiments were analyzed for TOC, pH, HPLC and IC. The results are shown in tables 4.1.3-1 to 4.1.3-4 of Appendix I and are depicted in figures 4.1.3-1 to 4.1.3-5.

In figure 4.1.3-1 the pH values of the samples withdrawn from the reactor throughout the experiments are shown. From these results, it can be seen that the pH at the end of the reaction of the experiment carried out at 150 ºC was much higher than the rest of the reactions. This fact implies that fewer low molecular weight acids were formed during the reaction at 150 ºC, thus, fewer intermediates were formed and lower 4-CP degradation occurred. On the other hand, the rest of the reactions (at 160, 175 and 190 ºC) reached at the end of the reaction a pH around 2.5, involving an analogous composition in the residual solution. In addition, it can be observed that the pH decreased faster when the reaction was carried out at the highest temperature, showing a higher generation of acids and a faster degradation of the parent compound.

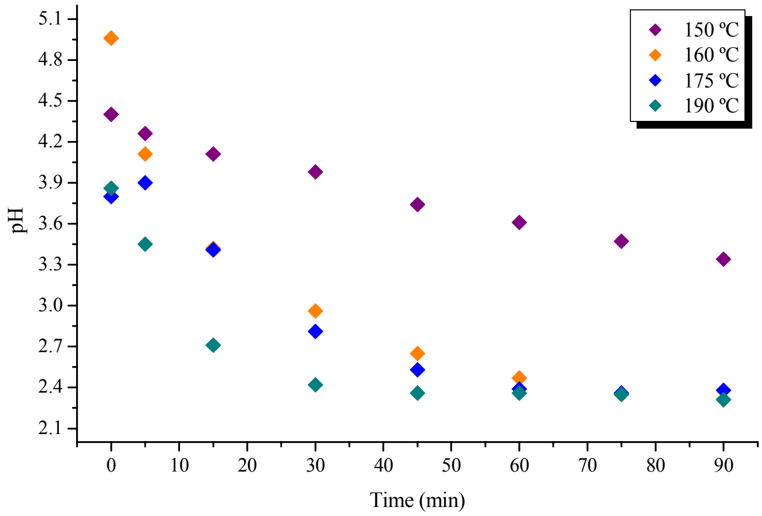


Figure 4.1.3-1 pH versus time. WO conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

In figure 4.1.3-2 the variations of the free chloride ion concentration in the solution throughout the reaction can be observed. These values were measured by means of an Ion Chromatograph and they were compared with the chloride released to the solution from the 4-CP decomposed. These values are named in figure 4.1.3-2 as “150-190 ºC theor” and were determined as follows: in every point the difference between the initial concentration of 4-CP and the 4-CP at that point was calculated and then the chloride associated to this destroyed 4-CP was calculated as in the following equation:

$$Cl^-(ppm) = ([4-CP]_o - [4-CP]_t) \times \frac{1\ mmol\ 4-CP}{Molecular\ weight\ 4-CP} \times \frac{1\ mmol\ Cl^-}{1\ mmol\ 4-CP} \times \frac{Molecular\ weight\ Cl^-}{1\ mmol\ Cl^-}$$

Where the concentration of 4-CP is expressed in mg/L (or ppm), the molecular weight of 4-CP is 128.5 g/mol and molecular weight of Cl^- is 35.5 g/mol.

The comparison between the measured Cl^- concentration and the one released from the degraded 4-CP results of special interest because it gives information about the intermediates formed in the course of the process.

- In the event that both values are similar no intermediates containing chlorine are formed during the reaction.

- If the measured Cl^- concentration is smaller than the calculated from the degraded 4-CP then intermediates containing chlorine atoms are formed during the process. In this case part of the chlorine released from the degraded 4-CP partly remains in the solution and can be measured by the Ion Chromatograph and partly is used to form new intermediates compounds.

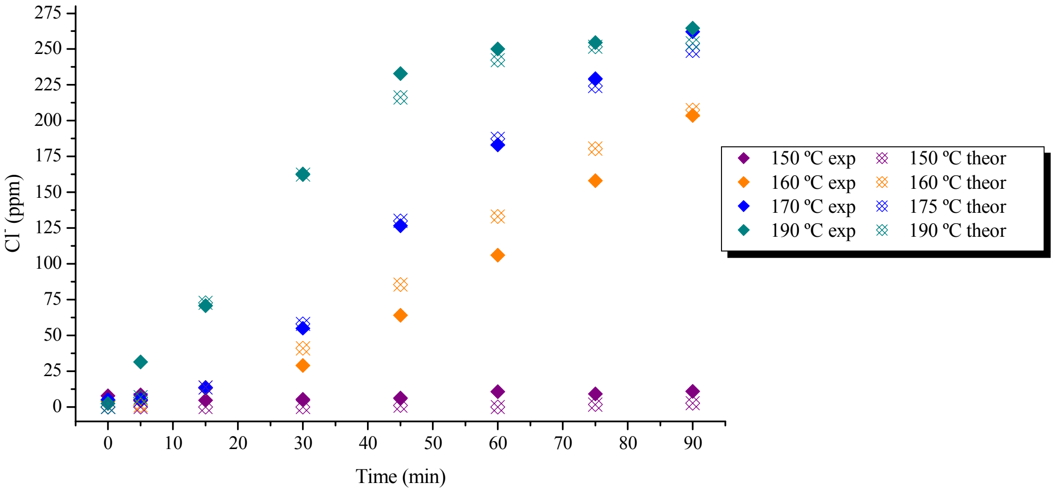


Figure 4.1.3-2 Experimental and calculated Cl^- concentration versus time. WO conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

Analyzing figure 4.1.3-2 it can be observed that the measured values coincided approximately with the calculated ones, meaning that any intermediate containing chlorine was formed during the reactions. Moving now on to the study of the influence of the temperature, it can be seen that the highest concentrations of chloride at the end of the experiments were accomplished when working at the highest operating temperatures. This fact means that at the end of the reaction, higher values of 4-CP degradation were attained when working at the highest temperatures.

Another fact to mention from this figure is that at the end of the reaction similar chloride concentration was measured when working at 175 and 190 ºC. However, even thought the final results were similar it should be mentioned that the concentration of free chloride ion in the solution was higher during the reaction at 190 ºC than at 175 ºC, involving a faster reaction rate at 190 ºC. This fact is in agreement with the results of the pH, where the fastest decrease of the pH was observed at 190 ºC.

As an example and with the aim of providing information about ion chromatographs, the results of the analysis of three samples taken from the WO at 175 ºC at times, 0, 15 and 30 minutes are included in figure 4.1.3-3. From the three plots of this figure, it can be observed that in each chromatograph two peaks appeared at different retention times. The first peak with a retention time of 2.23 minutes was an unidentified compound and was supposed to be either one interference of pollutant of the sample or some ion coming from the deterioration of the reactor, for example free ions Fe^{2+}/Fe^{3+}. In order to identify this first peak, patrons of common metallic and non-metallic compounds were analyzed, however the peak was not successfully identified. On the other hand, peak number 2, which appeared at a retention time about 2.5 min, was clearly identified as Cl^-. Its content in the samples from the WO were quantified, thanks to patrons previously prepared with a known amount of chloride ions.

As it was previously mentioned, samples were analyzed for pH, Cl^-, TOC and 4-CP concentration. Cl^- and pH have been above described and now instead of studying the TOC and 4-CP values throughout the reactions, their removals are going to be shown (since they are more representatives of the whole process). 4-CP and TOC removals in the course of the process are depicted in figures 4.1.3-4 and 4.1.3-5. In the former, it can be observed that the highest TOC removals at the end of the experiments were attained when working with the highest temperatures, ranging from 70 % of TOC removal at 190 ºC and 0 at 150 ºC. In this figure, it can be also observed that not only the highest removal was attained at the highest temperature, but also a faster removal throughout the reaction. This way, at time= 60 minutes, the TOC degraded at 190 ºC was already 60 % of the initial whereas at 175 ºC was around 30 %, at 160 ºC 15 % and 0 at 150 ºC

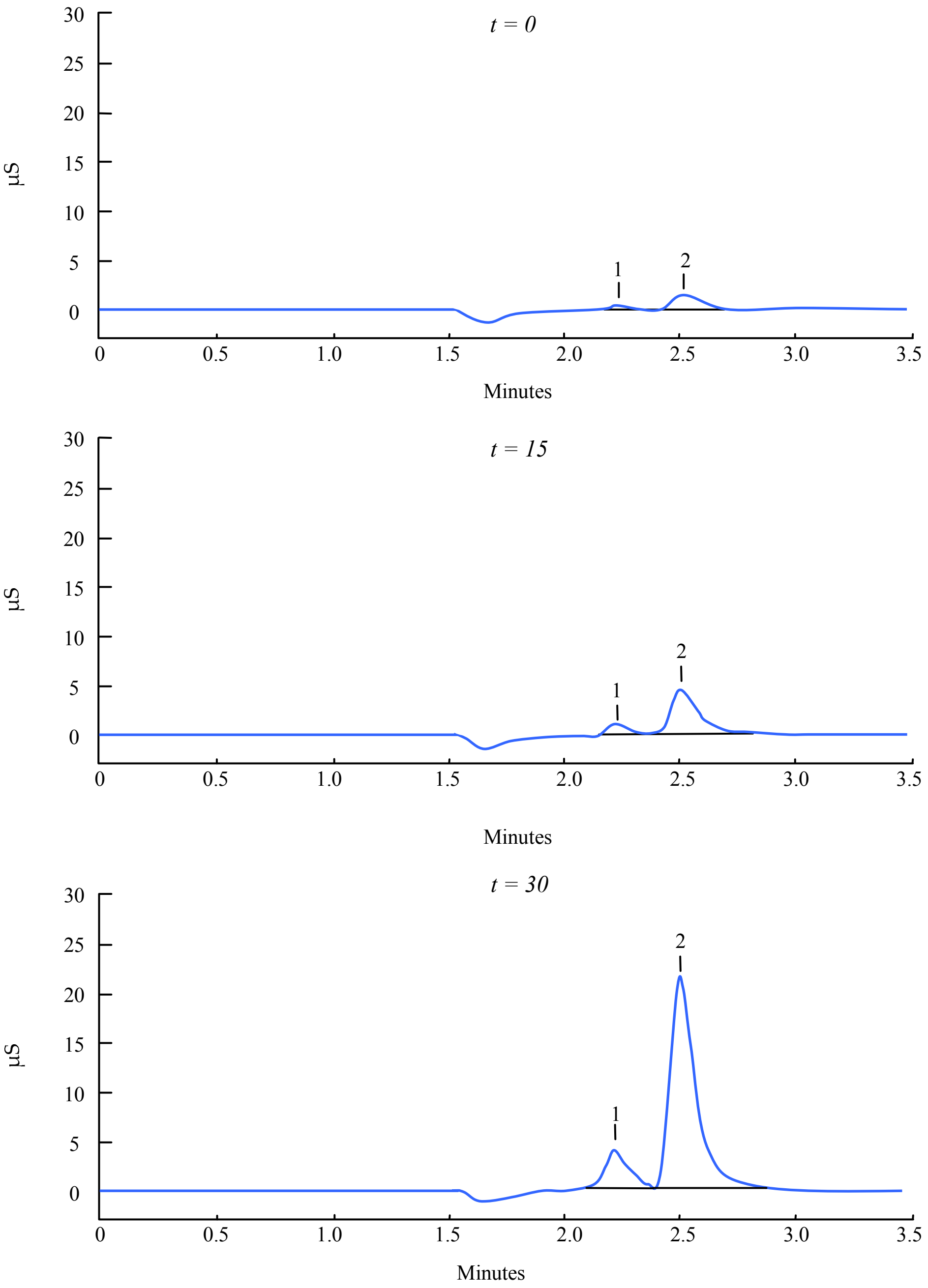


Figure 1.4.3-3 Ion Chromatograph results. Samples at times 0, 15 and 30 minutes. WO at 175 ºC and 10 bar. Initial solution containing 1000 ppm of 4-CP.

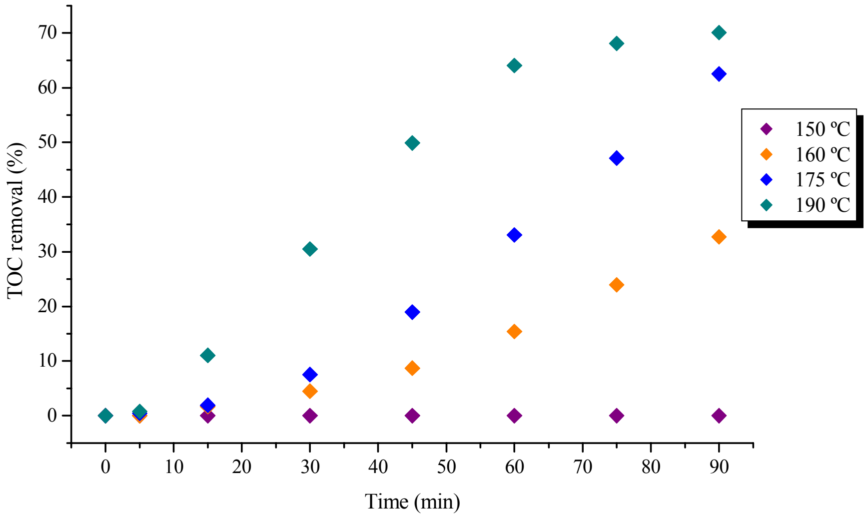


Figure 4.1.3-4 TOC removal versus time. WO conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

As for the 4-CP removal, it can be observed in figure 4.1.3-5 that the highest removals were achieved when working at 175 and 190 ºC. In fact both reactions attained analogous final removal values, however the reaction at 190 ºC showed the fastest removals throughout the experiment. In addition, and as it was expected from previous analysis, it can be concluded that when working at 150 ºC the temperature was not high enough to degrade our target compound.

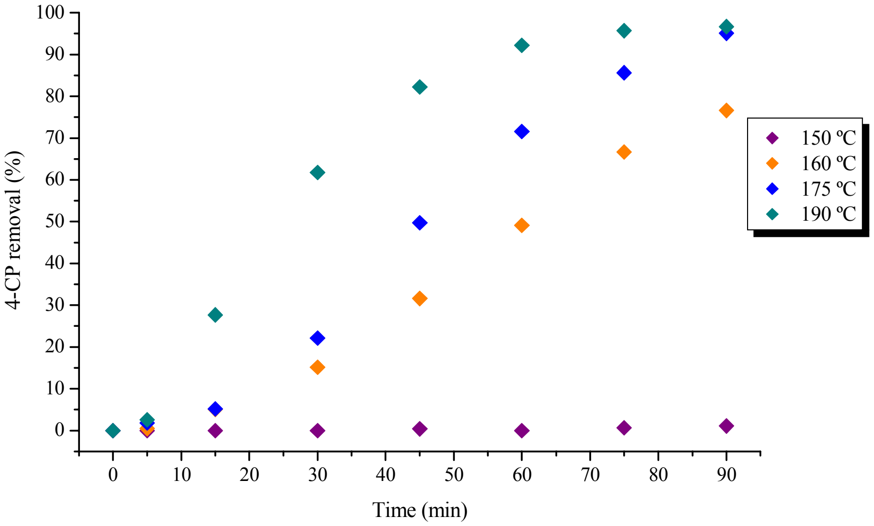


Figure 4.1.3-5 4-CP removal versus time. WO conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

To sump up, when carrying out WO at 10 bar of Po_2 and 1000 ppm of 4-CP, an increase of the temperature favors the reaction rate and whereas at 150 ºC almost no degradation is observed, at 190 ºC nearly complete degradation and high mineralization are accomplished.

Wet Oxidation Reactions at 500 ppm of 4-CP initial concentration

To study the influence of the temperature in the WO process when working with an initial solution of 500 ppm of 4-chlorophenol, four experiments at 150, 160, 175 and 190 ºC and keeping the rest of parameters constant: Po_2= 10 bar and stirring speed= 750 rpm were carried out. The samples of these experiments were analyzed for TOC, pH, HPLC and IC. The results are available in tables 4.1.3-5 to 4.1.3-8 of Appendix I and depicted in figures 4.1.3-6 to 4.1.3-9.

In figure 4.1.3-6 the variations of the pH throughout these reactions can be observed. These results were similar to the ones obtained when working with an initial solution of 1000 ppm of 4-CP. In essence, at the end of the reaction at 150 ºC the pH was higher than for the rest of the experiments involving fewer degradation of the target compound. It can be also observed that the reactions at 160, 175 and 190 ºC had analogous pH at the end of the reaction notwithstanding the fact that faster pH decrease during the experiments was observed when increasing the temperature.

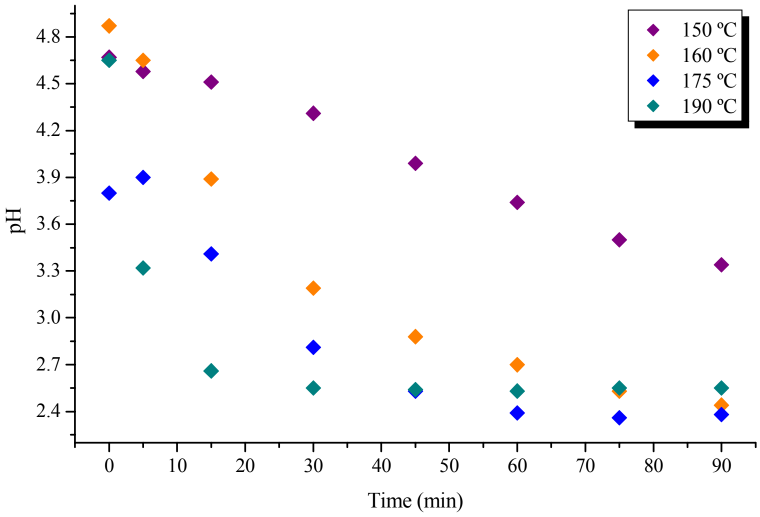


Figure 4.1.3-6 pH versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

In figure 4.1.3-7 the values of the measured chloride concentration and the one calculated from the degraded 4-CP throughout the reactions are depicted. As it was observed in the previous section it can be affirmed that any intermediate containing chlorine was formed during the process since both, the measured chloride and the chloride related to the 4-CP degradation were approximately the same in all the experiments. In addition, it can be also observed that the reaction at 150 ºC showed only a slight increase of the free chloride in the solution, meaning a low degradation of chlorophenol. Another fact to mention is that at the end of the reaction the experiments at 160, 175 and 190 ºC had a similar content of chloride in the solution, however, as it happened with the pH, the rate of appearance of the chloride was higher the higher the temperature of the reaction. This way, the reaction at 190 ºC reached its final chloride concentration after 30 minutes of reaction, whereas the experiment at 160 and 175 ºC had less than one half of the final amount. This means that from minute 30 until the end of the reaction no changes as for the amount of chloride occurred when working at 190 ºC, however at the lowest temperatures the amount of chloride progressively increased until the end of the experiment.

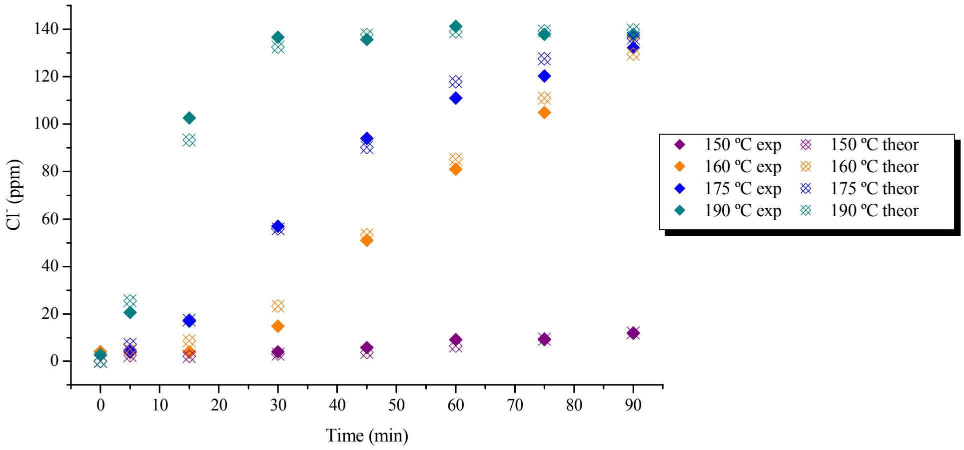


Figure 4.1.3-7 Measured and calculated Cl^- concentration versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

In figures 4.1.3-8 and 4.1.3-9, the TOC and 4-CP removals can be observed. As for the TOC removals at the end of the reactions it should be noted that there was any TOC removal when working at 150 ºC, and that the rest of the experiments presented an increase in the TOC removal as the temperature increased. Another fact to be mentioned is that the reactions at 160 and 175 ºC showed a progressive increase in the TOC removal until the end of the reactions; however in the reaction at 190 ºC, the TOC removal increased rapidly in the first 30 minutes of the reaction and then remained almost constant (at around 70 %) until the end of the experiment.

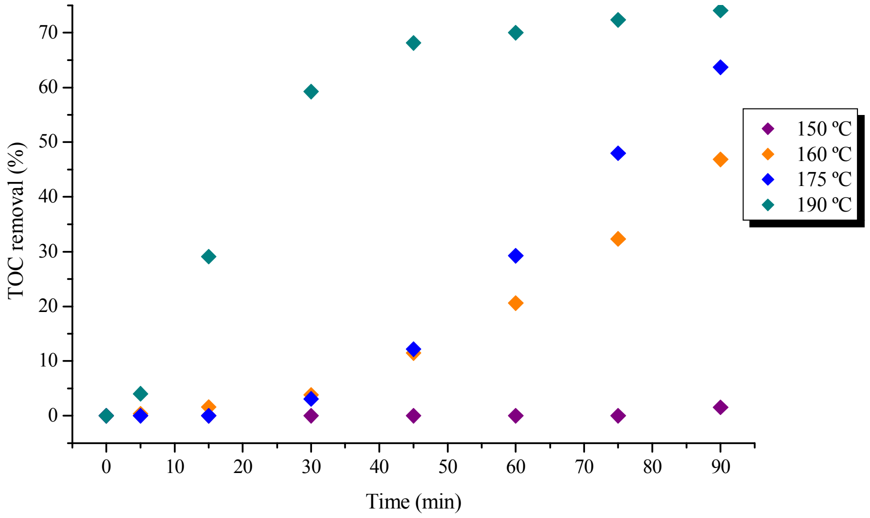


Figure 4.1.3-8 TOC removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

This fact was also observed when analyzing the 4-CP removals, shown in figure 4.1.3-9, since after 30 minutes of reaction all the 4-CP had been already degraded when working at the highest temperature. In this plot, it can be also noted that when carrying out the wet oxidation reaction at 150 ºC and under these operating conditions, only a slight 4-CP removal was achieved at the end of the reaction. The rest of the experiments reached a complete removal after 90 minutes of reaction, however it should be noted that higher temperatures involved faster removal rates. For example, after 30 minutes of reaction and working at 160 ºC the 20 % of the 4-CP was removed, at 175 ºC 40 % and at 190 ºC almost 100 % of the compound had been already degraded.

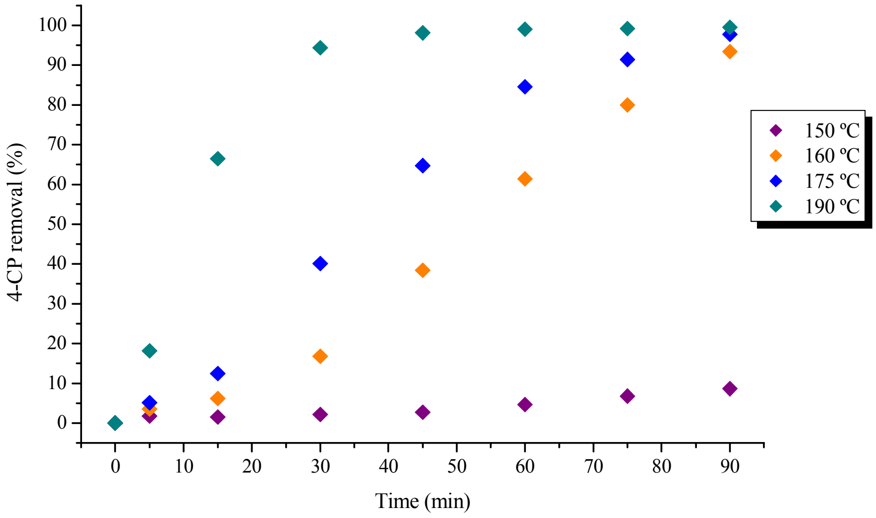


Figure 4.1.3-9 4-CP removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and different temperatures 150, 160, 175 and 190 ºC.

The conclusion reached from these experiments is the same as when the initial concentration was 1000 ppm: an increase in the temperature of the reaction results in an increase of the reaction rate.

Another fact to point out from these experiments is that, as it can be observed in the previous figures, the reactions can be divided into two different parts. In the first one, i.e., Induction Period the TOC and 4-CP removals were low and in the second part, the TOC and the 4-CP removals increased rapidly throughout the reaction. These results are in agreement with *Mishira et al. (1995)* who pointed out the existence of an initial period of time, i.e. induction period, when the radicals are formed and a second part, when the oxidation takes place. From these results it can be affirmed that the length of the “Induction Period” depended on the temperature at which the reaction was carried out.

4.1.3.2 Influence of the Initial Concentration of 4-CP

Having a look at the previous experiments, i.e. wet oxidation reactions of a solution containing 500 and 1000 ppm of 4-CP at 150, 160, 175 and 190 ºC and preserving the rest of operating conditions constant, a comparison can be established to evaluate the influence of the initial charge in the WO process. For this purpose, the TOC and 4-CP removals attained at the end of these reactions are depicted in figures 4.1.3-10 and 4.1.3-11.

It can be observed that at 150 ºC neither TOC nor 4-CP removals were accomplished at the end of the experiments when working with an initial solution of 1000 ppm. When performing the reaction with an initial charge of 500 ppm any TOC removal was observed, however, around 10 % of the initial 4-CP was degraded throughout the reaction. When carrying out the wet oxidation reaction at 160 ºC it was observed a higher TOC and 4-CP removal when the initial solution contained 500 ppm than when it had 1000 ppm of 4-CP. Moving now on to the experiments carried out at 175 ºC, it can be noted that the differences between both concentrations were not as evident as when working at 160 ºC, however slight higher removals were accomplished again by the less concentrated experiment. Finally, when working at the highest temperature (190 ºC) it was observed the same tendency as when working at 175 ºC, since the differences between the different concentrations were not remarkable. However, it is necessary to point out that the highest TOC and 4-CP removals were reached when working with the solution at 500 ppm.

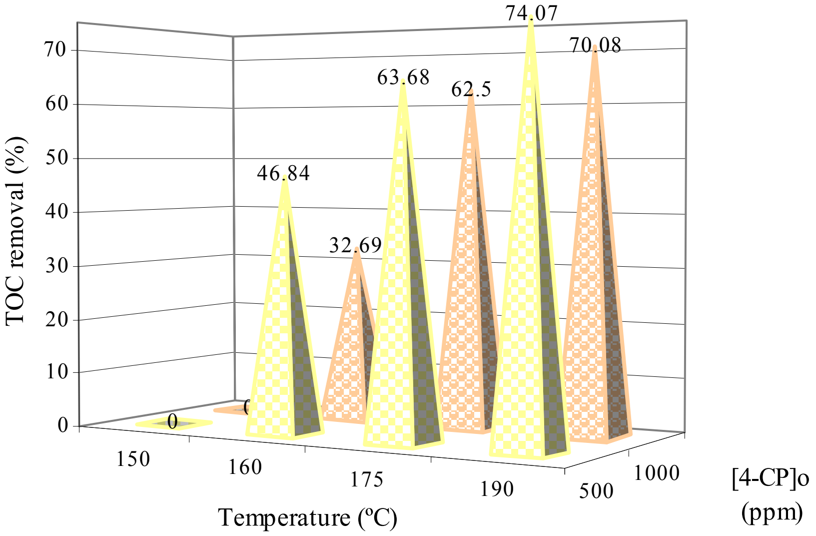


Figure 4.1.3-10 TOC removals versus temperature of the reaction. WO conditions: inicial 4-CP concentration 500 and 1000 ppm, 10 bar Po_2, 750 rpm and temperatures of 150, 160, 175 and 190 ºC.

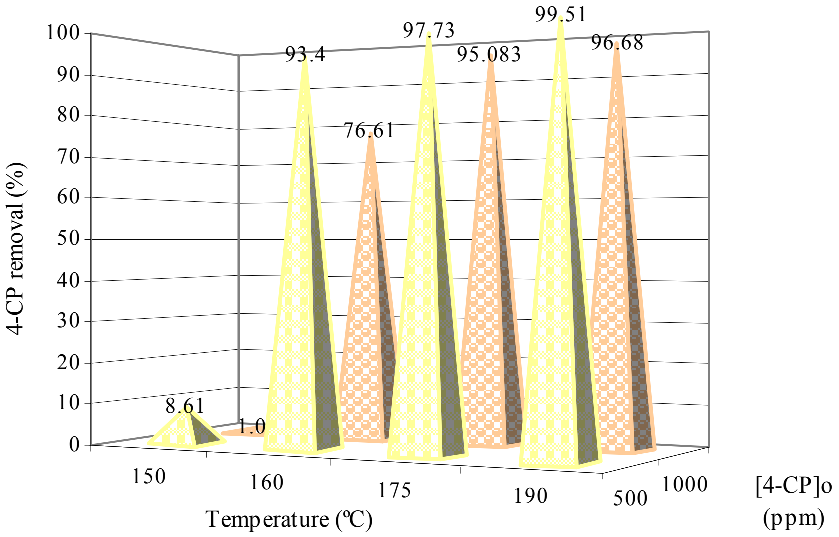


Figure 4.1.3-11 4-CP removals versus temperature of the reaction. WO conditions: inicial 4-CP concentration 500 and 1000 ppm, 10 bar Po_2, 750 rpm and temperatures of 150, 160, 175 and 190 ºC.

From these results it can be concluded that wet oxidation reactions of monochlorophenol containing solutions should be carried out at temperatures above 150 ºC in order to achieve the degradation, not only of the target compound but also of the intermediate compounds generated throughout the process.

4.1.3.3 Study of the influence of the Partial Pressure of Oxygen

To study the influence of the partial pressure of oxygen in the wet oxidation process two sets of experiments were carried out at different temperatures. In the first set of experiments the temperature was kept at 160 ºC and the partial pressure of oxygen was set at 5, 7.5, 10 and 15 bar. In the second set of experiments, the pressures were the same as in the previous ones but the temperature was set at 190 ºC. Samples withdrawn from these experiments were analyzed for pH, TOC, HPLC and IC.

Influence of the Partial Pressure of Oxygen at 160 ºC

Wet oxidation reactions of a solution containing 500 ppm of 4-chlorophenol were carried out at 160 ºC varying the partial pressure of oxygen from 5 to 15 bar. The results of these experiments are shown in tables 4.1.3-9 to 4.1.3-11 of Appendix I and depicted in figures 4.1.3-12 to 4.1.3-15. The pH values of these reactions throughout the reactions are illustrated in figure 4.1.3-12. It can be observed that the lowest pH values at the end of the reaction were attained by the experiments carried out at the highest partial pressures of oxygen and vice versa. These results were expectable since high oxidizing agent amounts implies high oxidation and thus, high generation of low molecular weight acids, fact that at the same time provokes a noticeable decrease of the pH. Another fact to mention from the pH tendencies is that the results obtained when carrying out the reactions at 10 and 15 bar of partial pressure of oxygen were practically the same. This indicates that under these conditions the oxygen was already in excess compared to the organic matter present in the solution.

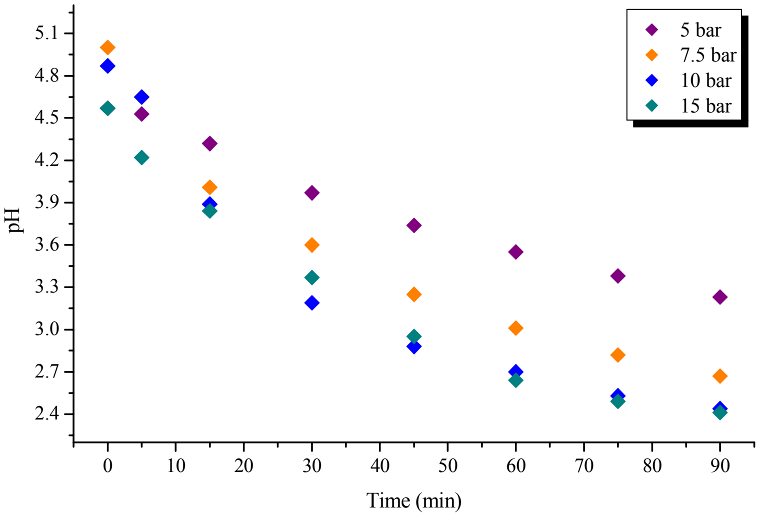


Figure 4.1.3-12 pH versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 160 ºC and different Po_2: 5, 10, 7.5 and 15 bar.

In figure 4.1.3-13 the chloride concentration presented in the solution during the course of the reactions can be observed. As in previous sections, this figure shows on one hand the chloride measured by means of the Ion Chromatograph and on the other hand, the chloride released to the solution by the degraded monochlorophenol at any time. The first fact to mention from the chloride results is that the measured and the calculated concentration coincided, thus no intermediate compounds containing chloride atoms were formed throughout the reactions. Besides this, it should be also noted that when working at 5 bar the concentration of chloride increased slightly over the duration of the experiment, meanwhile considerable changes were observed when carrying out the experiments at 7.5 and so on. Consequently, major degradation of our target compound was attained when increasing the percentage of oxidizing agent in the system. Finally, it seems of special importance the fact that the experiments at 10 and 15 bar showed similar tendencies. This fact is in agreement with the results of the pH and indicates an excess of oxygen under this operating conditions.

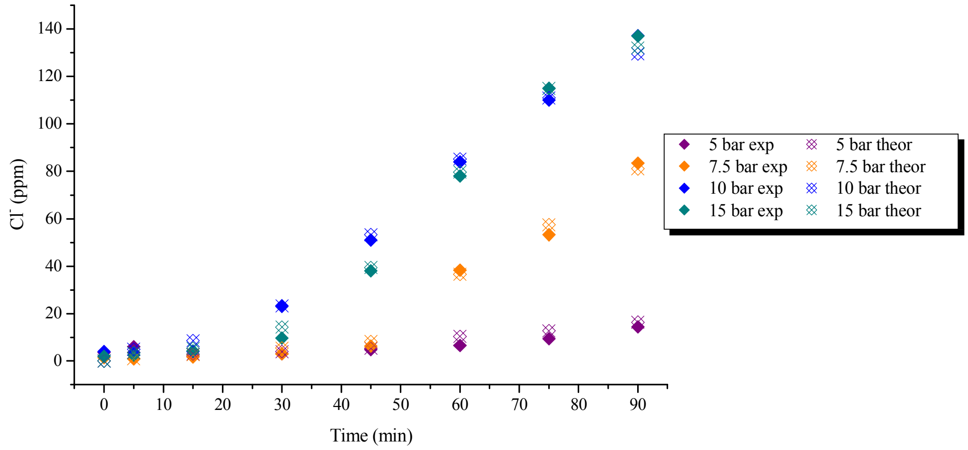


Figure 4.1.3-13 Measured and calculated Cl^- concentration versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 160 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

In figures 4.1.3-14 and 4.1.3-15, the TOC and 4-CP removals are represented versus the time of the reactions. From these figures, it can be observed that when the wet oxidation was carried out at 160 ºC and 5 bars, the degradation of 4-CP occurred in a remarkable slow way and thus, after 1.5 hours of reaction only 12 % of the initial amount was removed from the system. On the other hand, as soon as the partial pressure of the oxygen was increased, not only the degradation of the 4-CP but also the mineralization of the solution increased. This way, at 7.5 bar the TOC removal was 22.65 % whereas the 4-CP was 63.5 %; another fact that can be observed from these figures is that the differences between the experiments carried out at 10 and 15 bar were slight, confirming that at 10 bar the oxygen was already in excess with respect to the organic load.

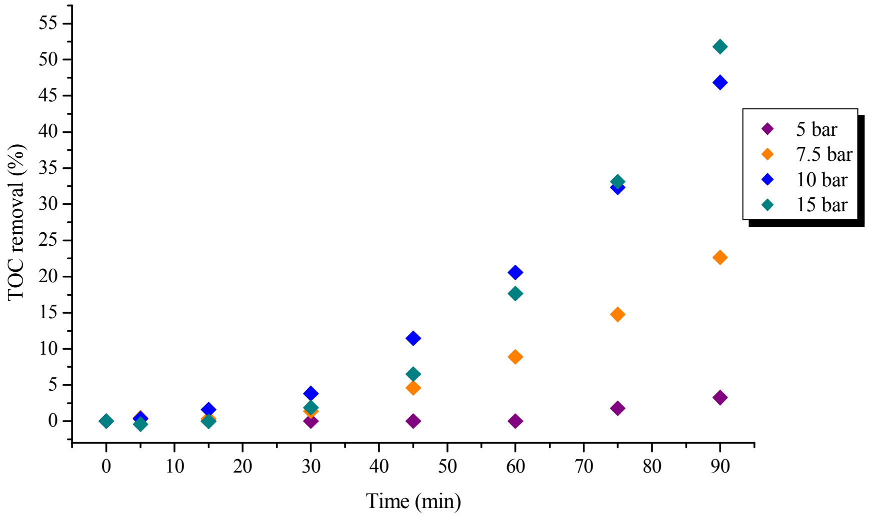


Figure 4.1.3-14 TOC removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 160 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

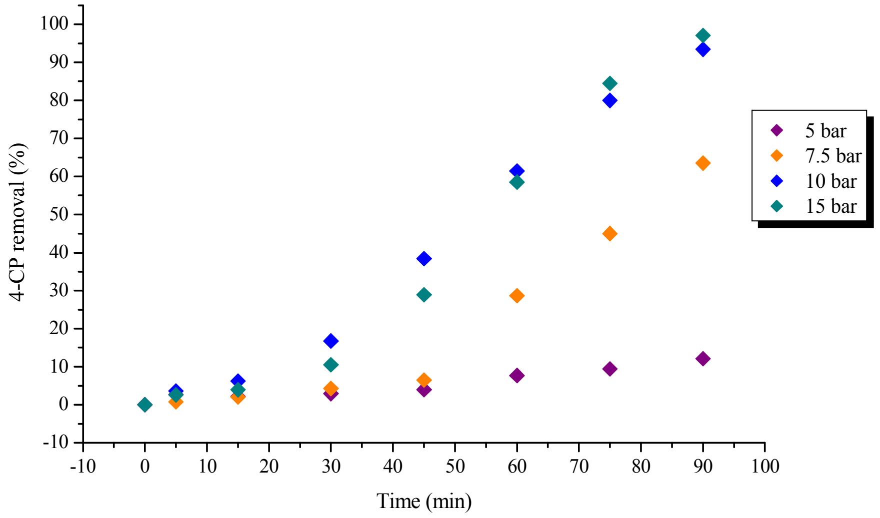


Figure 4.1.3-15 4-CP removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 160 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

Influence of the Partial Pressure of Oxygen at 190 ºC

To study the influence of the partial pressure of oxygen during the wet oxidation process at 190 ºC of a solution containing 500 ppm of 4-CP, reactions at different conditions of pressure: 5, 7.5, 10 and 15 bar were performed. Samples were analyzed for pH, TOC, HPLC and IC. The results are shown in tables 4.1.3-12 to 4.1.3-14 of Appendix I and are depicted in figures 4.1.3-16 to 4.1.3-19.

In figure 4.1.3-16, the pH values throughout these reactions are illustrated. It can be observed that in all the experiments a final pH value of around 2.7 was reached. However it should be also noted that this final value was faster reached by the experiments with the highest partial pressure, involving a faster reaction rate under these operating conditions. Another fact to be mentioned is the similarity between the pH values of the reactions carried out at 10 and 15 bar.

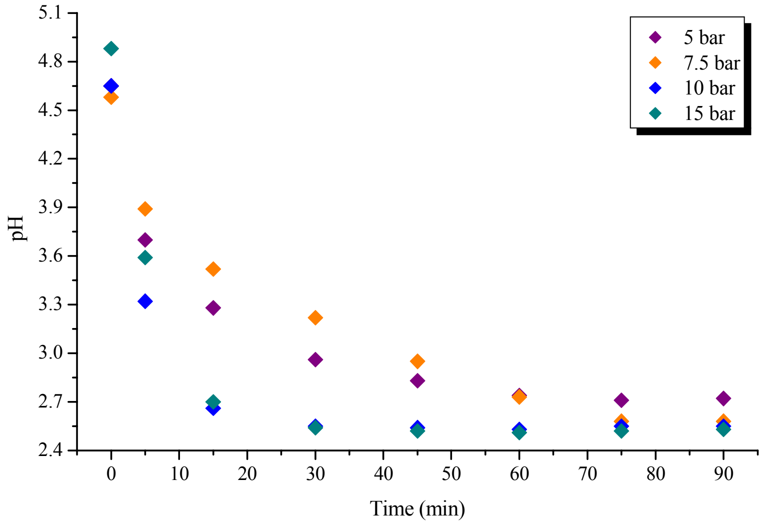


Figure 4.1.3-16 pH versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 190 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

In figure 4.1.3-17 the variations of the free chloride concentration in the solution throughout the reactions are depicted. In addition, the chloride released from the degraded monochlorophenol at every moment of the reaction can be observed. The experiments carried out at the highest partial pressures accomplished the highest chloride concentration at the end of the reaction and vice versa. In addition, the concentrations measured by the Ion Chromatograph coincided with the values calculated from the destroyed monochlorophenol at every point, involving the null formation of intermediate compounds containing chlorine atoms. Finally, it should be pointed out that experiments at 10 and 15 bar showed similar values of free chloride concentration throughout the reaction as it happened with the pH tendencies.

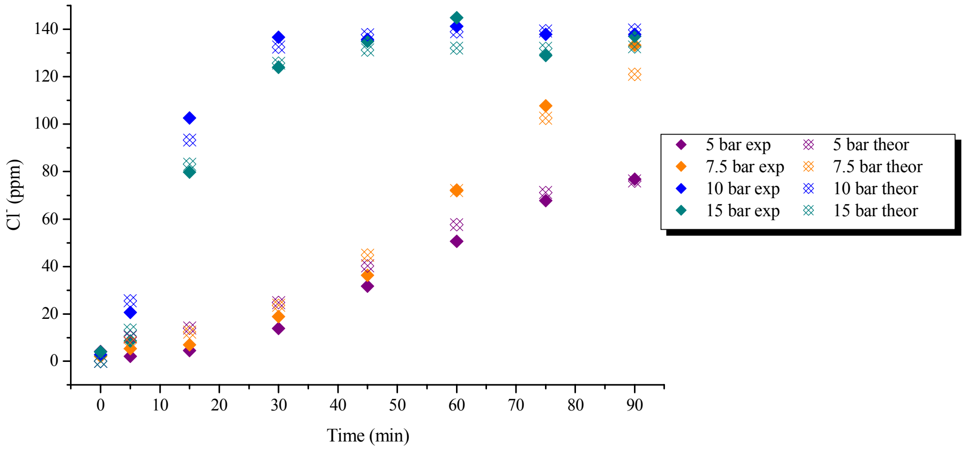


Figure 4.1.3-17 Measured and calculated Cl^- concentration versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 190 ºC and different Po_2: 5, 10, 7.5 and 15 bar.

In figures 4.1.3-18 and 4.1.3-19 the TOC and 4-CP removals throughout these experiments are depicted. One of the first conclusions to be reached from these plots is that as it was observed at 160 ºC, there were no relevant differences between the experiments carried out at 10 and at 15 bar, which means that under these conditions the oxygen was in excess with respect to the organic compounds. As for the degree of mineralization and 4-CP degradation it can be mentioned that the highest removals were achieved when working at the highest partial pressures and vice versa.

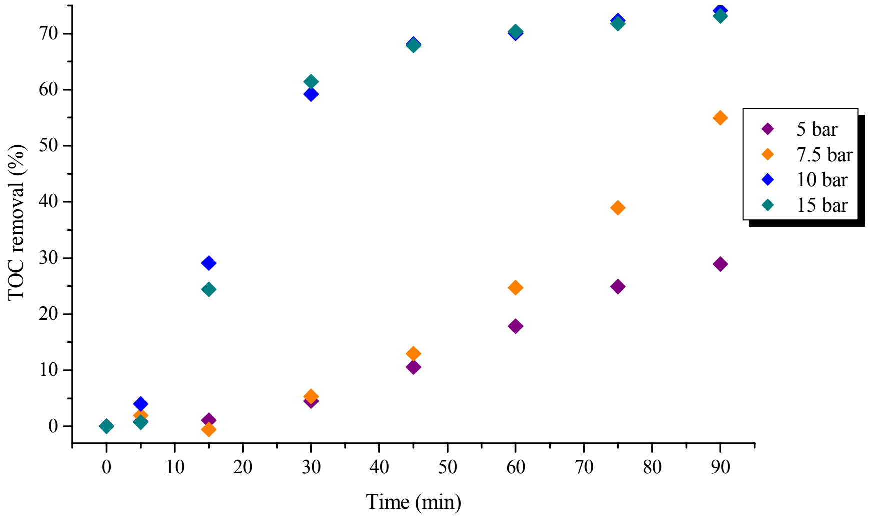


Figure 4.1.3-18 TOC removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 190 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

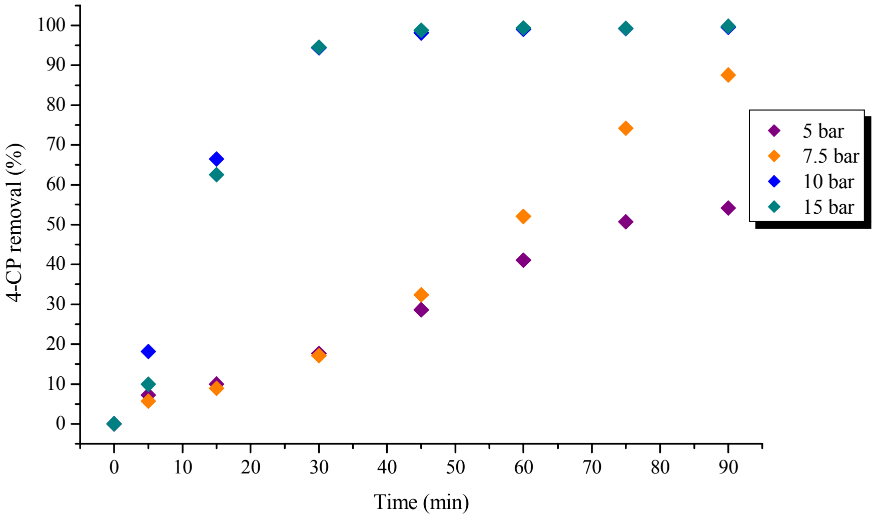


Figure 4.1.3-19 4-CP removal versus time. WO conditions: 500 ppm 4-CP, 750 rpm, 190 ºC and different $Po_{2:}$ 5, 10, 7.5 and 15 bar.

The conclusion reached from this study is that when working at 10 bars of partial pressure of oxygen the oxidizing agent is already in excess and thus, no differences are observed between experiments carried out at 10 and 15 bars.

Influence of the Partial Pressure of Oxygen at different temperatures

Once the study of the influence of the partial pressure of oxygen has been evaluated at different temperatures during the wet oxidation reaction of a solution containing 500 ppm of 4-chlorophenol, it seemed of special interest to compare the synergistic influence of both parameters, i.e., temperature of the reaction and partial pressure of oxygen. For this purpose, the results of the TOC and 4-CP removal obtained at the end of the reaction when working at 160 and 190 ºC were depicted versus the partial pressure of oxygen as it can be observed in figure 4.1.3-20. In this figure, it can be seen that when increasing the partial pressure of oxygen from 5 to 10 bar, a progressive increase in the TOC and 4-CP was attained at both temperatures. However, when increasing the pressure from 10 to 15 any significant variation was observed, involving thus, an excess of oxygen when working at 10 bar under these operating conditions.

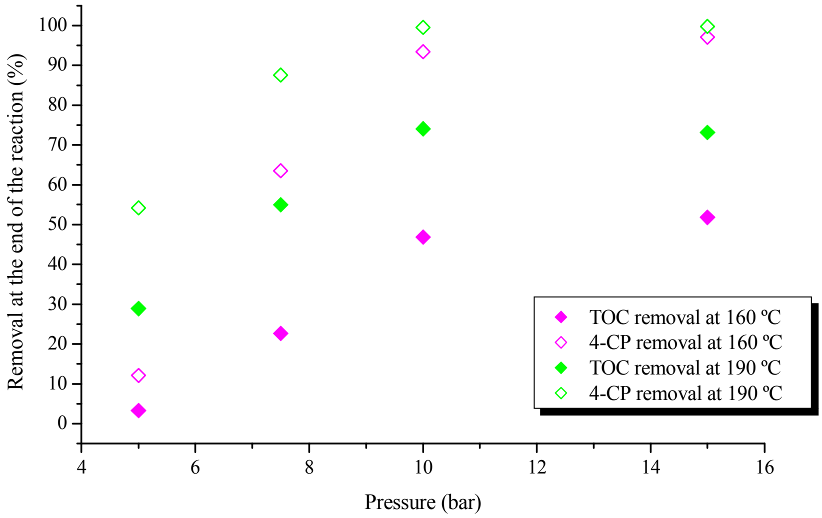


Figure 4.1.3-20 TOC and 4-CP removals versus Partial Pressure of Oxygen. Values obtained at the end of the WO reactions at 160 and 190 ºC of a solution containing 500 ppm of 4-CP.

Another fact to mention from these results is the difference between the 4-CP and TOC tendencies of the two temperatures studied. The difference between the TOC removal accomplished at the end of the reactions at 160 and 190 ºC was approximately constant when varying the partial pressure of oxygen. On the other hand, the difference between the 4-CP removal at the end of the reactions at 160 and 190 ºC decreased when increasing the partial pressure of oxygen. This means that an increase of the partial pressure of oxygen affected in a similar way the TOC removal of the experiments carried out at 160 and at 190 ºC. However, it affected in a different way the 4-CP removals of the reactions carried out at 160 and at 190 ºC since when increasing the partial pressure of oxygen from 5 to 15 bar at 190 ºC the 4-CP removal increased from 54.2 to 99.8 %, and at 160 ºC it increased from 12.1 to 97.1 %. Therefore, it can be concluded that an increase of the partial pressure resulted in a faster increase of the 4-CP removal when working at 160 ºC.

This fact can be explained taking into account that when working at 190 ºC and 10 or 15 bar, the 4-CP was eliminated from the medium within the 40 first minutes of reaction. On the other hand, when working at 160 ºC and 10-15 bar the total degradation of the 4-CP was not reached until the end of the reaction and thus, the results were similar than when working at 190 ºC but the reaction rate was much slower. According to this, the increase in the TOC removal is proportional to the increase of the partial pressure for both temperatures because a 100 % TOC removal was not reached in any of the experiments.

4.1.3.4 Biodegradability enhancement by Wet Oxidation

As it was observed in the previously discussed results, the main problem when working with this kind of solutions, i.e., solutions containing low biodegradable organic compounds, is not the degradation and elimination of the target compounds but the total mineralization of the compounds formed throughout the reaction. This way, 4-chlorophenol is characterized by being not biodegradable but it can be removed by means of wet oxidation and wet peroxide oxidation in a reasonable period of time and under reasonable operating conditions. However, the final intermediate compounds formed during the Advanced Oxidation Processes are characterized by being easily biodegradable and difficult to oxidize by means of oxidation processes. For this reason, a combination wet peroxide oxidation or wet oxidation with a biological post-treatment seems to be a promising choice to accomplish complete mineralization of the solution.

In order to study the evolution of the biodegradability within the wet oxidation process, the samples withdrawn from the experiments carried out at 500 ppm of 4-CP, 10 bar of Po_2, 750 rpm and at the following temperatures 150, 160, 175 and 190 ºC were also analyzed for the Biochemical Oxygen Demand (BOD). The results of the BOD values measured are shown in table 4.1.3-1.

Table 4.1.3-1 Biochemical Oxygen Demand values throughout WO reactions.

Samples	BOD (mg O_2/L)			
	WO at 150 ºC	WO at 160 ºC	WO at 175 ºC	WO at 190 ºC
Original	0	0	0	0
t = 0 min	5	10	5	20
t = 5 min	0	10	5	25
t = 15 min	0	30	46	110
t = 30 min	0	35	100	190
t = 45 min	7	60	153	230
t = 60 min	12	75	175	245
t = 75 min	12	82	183	240
t = 90 min	9	85	187	210
Residue	10	70	170	210

These BOD values are illustrated in figure 4.1.3-20. According to these results it can be affirmed that the wet oxidation process, carried out under these operating conditions, of a solution containing 4-chlorophenol enhances the biodegradability of the wastewater.

Another interesting tendency showed by these results was the fact that at the highest temperature the biodegradability first increased, then reached a maximum at minute 60 and then decreased until the end of the reaction. On the other hand, the rest of the experiments showed an increasing tendency throughout the reaction. Firstly, the experiment at 190 ºC is going to be analyzed. The initial increase in the biodegradability was due to the decrease in the 4-CP concentration that took place until minute 45 approximately, when the maximum removal (100%) was reached. Thus, a decrease in the less biodegradable compounds implied an increase of the total biodegradability of the solution. From minute 60 on the biodegradability started to decrease. This fact can be explained taking into account that during this period of time the TOC of the solution is also decreasing; consequently, the biochemical oxygen demand was fewer since less organic matter was present in the wastewater.

Moving on now to the rest of the experiments carried out at 150, 160 and 170 ºC, it can be observed that the biodegradability increased throughout the reactions in all the cases. This can be explained taking into account that the concentration of the 4-CP decreased progressively throughout the experiments. Consequently, in the course of the reactions, the amount of the less biodegradable compounds decreased and the amount of the biodegradable compounds increased, implying then an increase in the biodegradability.

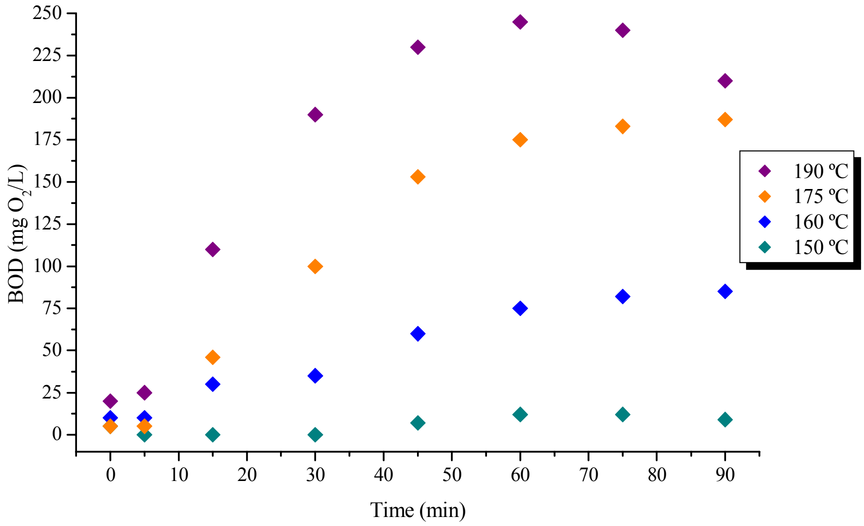


Figure 4.1.3-21 BOD versus time. WO reactions carried out with an inicial concentration of 500 ppm of 4-CP at 10 bar of Po_2, 750 rpm and 150, 160, 175 and 190 ºC.

4.1.4 WET OXIDATION AND WET PEROXIDE OXIDATION

After studying separately the wet oxidation and the wet peroxide oxidation processes for the treatment of effluents containing 4-chlorophenol it seems interesting to compare these two technologies in order to determine which one is more suitable and economical viable. For this purpose the following two experiments were chosen:

- Wet oxidation: 500 ppm of 4-CP in the initial solution, 750 rpm, 10 bar of partial pressure of oxygen and 160 ºC. (results available in table 4.1.3-6 of Appendix I)

- Wet peroxide oxidation: 500 ppm of 4-CP in the initial solution, 2.5 mL of H_2O_2, 750 rpm and 160 ºC. (results available in table 4.1.2-32 of Appendix I)

These experiments were selected in view of the fact that they had the same operating temperature and initial concentration of 4-CP.

The ratios between the TOC at different times of the reactions and the initial TOC presented in the solution for these two experiments are shown in figure 4.1.4-1. The ratios between the 4-CP throughout the experiments and the initial concentration throughout the reactions are depicted in figure 4.1.4-2. The first fact to be noted from these plots is that the wet peroxide oxidation reaction was faster and plus it reached higher 4-CP and TOC removals. According to this, it would be appropriated to suggest that WPO is a more suitable process to treat this kind of wastewater effluents. However, it should be pointed out that the operating costs play a significant role in this discussion since the price of hydrogen peroxide is higher than the one of oxygen. However, even more important than the difference of prices between the oxidizing agents is the possibility of recovering part of the energy used to heat up the reactor. This is usually done in the industry taking profit of the high temperature and pressure of the effluent after the reaction. According to this, and having a look at the operating conditions of both processes it should be mentioned that WO normally works under higher pressures than WPO processes since in WPO the pressure of the reaction is due to the vapor pressure of the solution and in WO the total pressure is the sum between the vapor pressure of the solution and the oxygen added. Thus, more energy could be recovered from the WO system than from the WPO.

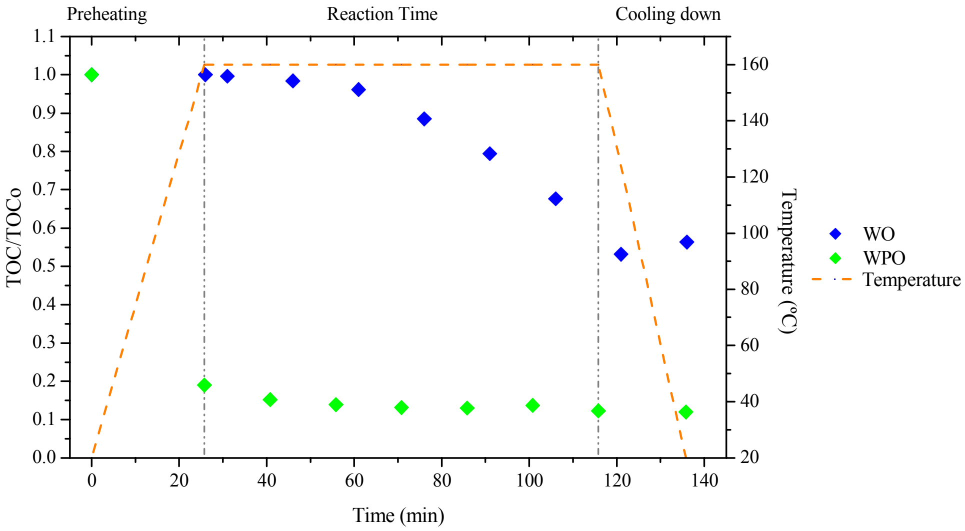


Figure 4.1.4-1 TOC/TOCo versus time. WO at 500 ppm of 4-CP, 750 rpm, 10 bar of PO_2 and 160 ºC. WPO at 500 ppm of MCP, 2.5 mL of H_2O_2, 750 rpm and 160 ºC.

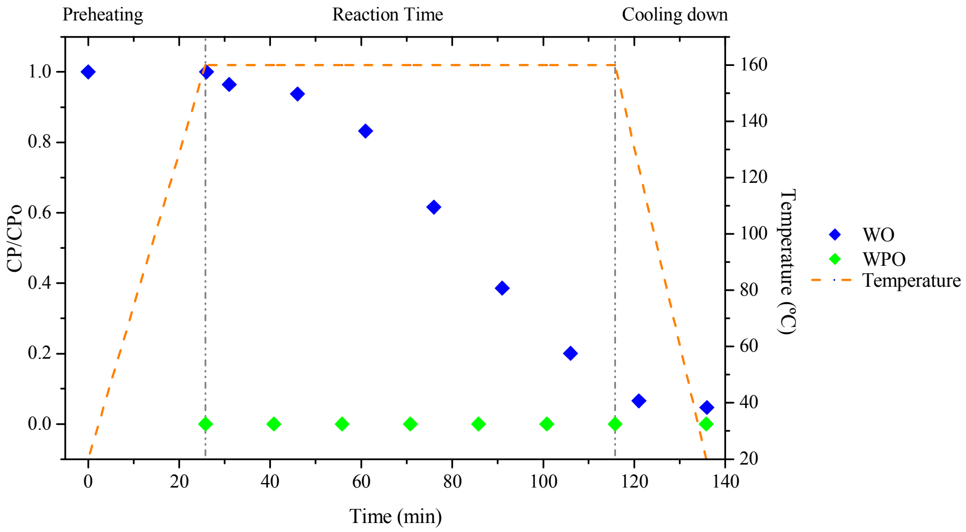


Figure 4.1.4-2 [4-CP]/[4-CPo] versus time. WO at 500 ppm of 4-CP, 750 rpm, 10 bar of PO_2 and 160 ºC. WPO at 500 ppm of MCP, 2.5 mL of H_2O_2, 750 rpm and 160 ºC.

4.1.5 KINETICS OF 4-CHLOROPHENOL DEGRADATION BY WET OXIDATION

The knowledge of the reaction mechanism and the kinetic model of any system is an important tool due to the fact that it allows the prediction of any of the compounds present in the system at any time of the reaction. This statement is of special importance when the system contains toxic or not desirable compounds, in view of the fact that the model will provide information about the moment when these compounds appear or disappear. In the case of the degradation of 4-chlorophenol by wet oxidation, the modeling of the reactions is interesting because it will give information about the optimum moment when the oxidation should be stopped and a post-biological treatment should continue with the abatement of the organic load.

In order to establish the reaction mechanism and the kinetic model, the results of the wet oxidation reactions carried out with an initial solution containing 1000 and 500 ppm of 4-CP, at 10 bar of partial pressure of oxygen and at different temperatures (160, 175 and 200 ºC) were evaluated.

The results of the HPLC allowed the identification and quantification of phenol (hereon PhOH), hydroquinone (hereon HQ) and quinone (hereon Q) as the most important intermediates. Two low molecular weight acids were identified as well: maleic and oxalic acids. As an example, the chromatographs of samples at time 0, 5 and 45 minutes of the WO carried out at 160 ºC, 10 bar and with an initial concentration of 500 ppm are shown in figure 4.1.5-1. Every analysis was run for about 10 minutes since all the compounds of the solution were expected to have a shorter retention time. In fact, 4-CP had a retention time of 4.2 minutes whereas phenol, hydroquinone and quinone last 2.93, 2.52 and 2.6 minutes to be detected by the equipment. In general terms, chromatographs are a useful tool to understand the evolution of the reaction. Focusing on the first chromatograph, belonging to the sample previous to the oxidation, it can be observed that initially the solution contains solely 4-CP. Moving on to the second chromatograph, it can be observed that after 5 minutes of reaction some hydroquinone has been already formed. In addition, compounds with a small retention time, most likely, low molecular weight acids have been generated. Finally, the third chromatograph shows that after 45 minutes of reaction, phenol, hydroquinone and quinone as well as low molecular weight acids have been formed. On the other hand, when comparing the height of the 4-CP peak, it can be observed that it decreased throughout the reaction, showing thus, the reduction in the 4-CP concentration in the reactor.

Even though, the target compound, i.e. 4-chlorophenol, tended to disappear throughout the reactions, it is important to emphasize that may be, some of the generated intermediate compounds are more toxic than the parent substance. This is especially interesting when thinking in a combination wet oxidation with a post biological treatment. Obviously, special care should be paid in destroying not only the target compound but also the toxic intermediates (in the case these last ones are as toxic as the parent compound or even more). Data concerning the level of toxicity of 4-chlorophenol, phenol, hydroquinone and quinone has been found in the literature. In table 4.1.5-1, the values of the EC_{50} reported in the literature, corresponding to 4-chlorophenol, hydroquinone, quinone and phenol are shown. The EC_{50} is defined as the contaminant concentration that produces a decrease in the light emitted by the microorganism of 50 % after 15 minutes of contact between the microorganism and pollutant. In other words, the EC_{50} is the pollutant concentration that provokes the death of 50 % of the microorganism after 15 minutes of contact with the contaminant.

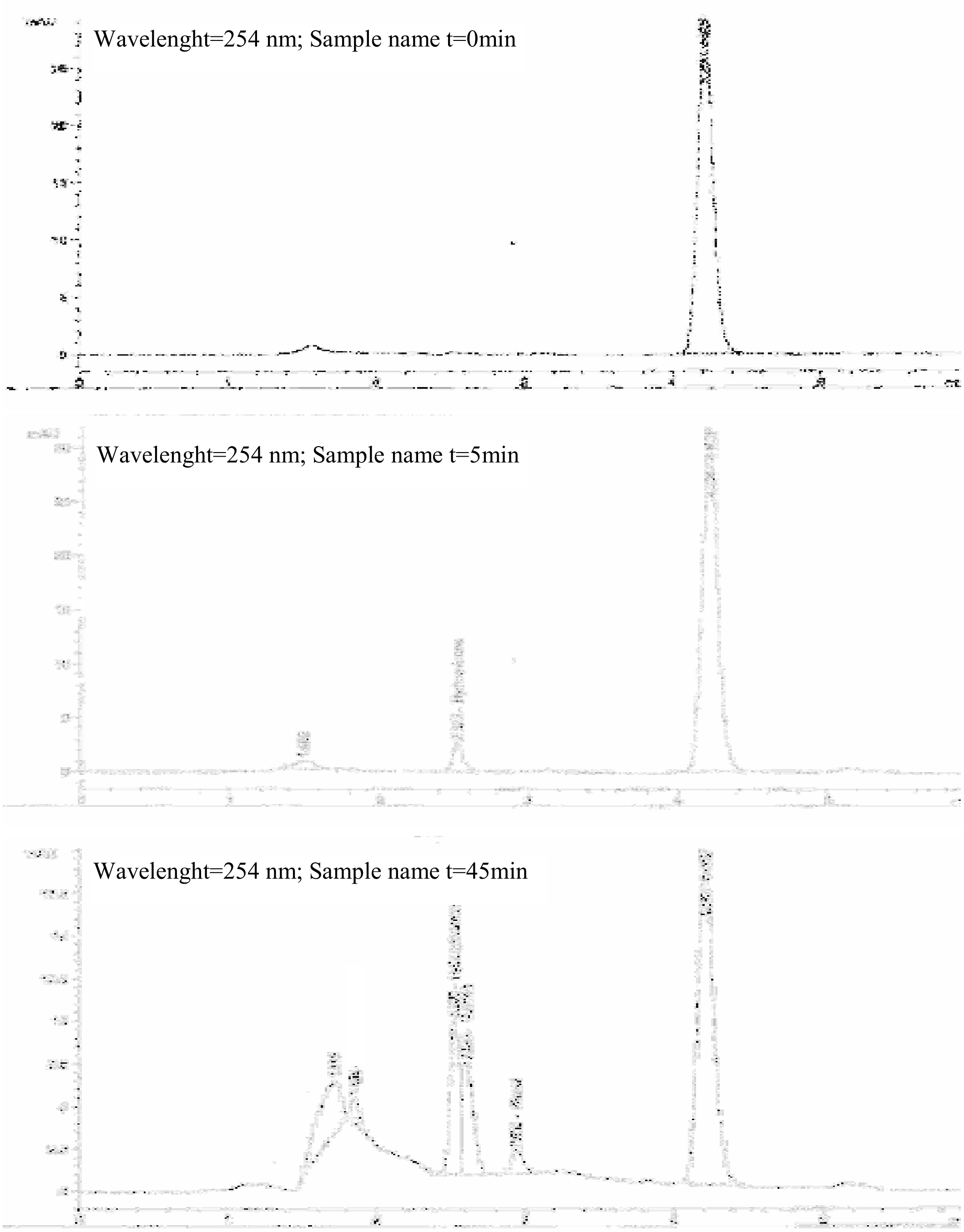


Figure 4.1.5-1 HPLC results. WO reaction at 160 ºC, 10 bar of Po_2 and 500 ppm of initial concentration of 4-CP.

Table 4.1.5-1 EC_{50} values of 4-chorophenol, phenol, hydroquinone and quinone.

Compound	**EC_{50} 15 minutes**	**Reference**
4-chlorophenol	20.88^a 14.75^b 8.29^c	Chen and Lin, 2006 Chen and Lin, 2006 Shannon et al. 1991
phenol	25.93^a 20.90^b 35.7^c	Chen and Lin, 2006 Chen and Lin, 2006 Shannon et al. 1991
hydroquinone	$0.0382\text{-}0.0798^c$ $0.042\text{-}0.079^c$	Kaiser and Palabrica, 1991 Hoeben, 2000
quinone	$0.022\text{-}0.08^c$ $0.0085\text{-}1.4^c$	Kaiser and Palabrica, 1991 Hoeben, 2000

[a] Measurements from Dissolved Oxygen
[b] Measurements from microorganism growth rate
[c] Microtox®

From the above EC_{50} values, it can be concluded that hydroquinone and quinone are much more toxic than phenol and 4-chlorophenol. Actually, the concentration of quinone and hydroquinone needed to kill half of the microorganism population is about three orders of magnitude smaller than the corresponding of 4-chlorophenol and phenol. For this reason, it seems of major importance to be able to predict the concentration of these toxic intermediate compounds over the duration of the reaction.

Taking into consideration the HPLC results of all the reactions, an initial mechanistic pathway was suggested. According to this mechanism, the hydroxyl radicals may attack the chlorophenol, giving rise to the formation of hydroquinone and phenol. Phenol would then decompose producing more hydroquinone, which at the same time would decompose into quinone. Quinone might be further oxidized giving rise to low molecular weight acids (see figure 4.1.5-2).

The modeling of this kinetic pathway was made assuming that the reactor behaves as an ideal batch reactor. It was considered as well, that all the substances followed a pseudo-first order kinetic model, leading thus, to the following equations for the prediction of 4-chlorophenol (4-CP), phenol (PhOH), hydroquinone (HQ) and quinone (Q).

$$\frac{d[4-CP]}{dt} = [4-CP](-k_1 - k_2)$$ Equation 4.1.5-1

$$\frac{d[PhOH]}{dt} = [4-CP]k_2 - [PhOH]k_5$$ Equation 4.1.5-2

$$\frac{d[HQ]}{dt} = [PhOH]k_5 - [HQ]k_3$$ Equation 4.1.5-3

$$\frac{d[Q]}{dt} = [HQ]k_3 - [Q]k_4$$ Equation 4.1.5-4

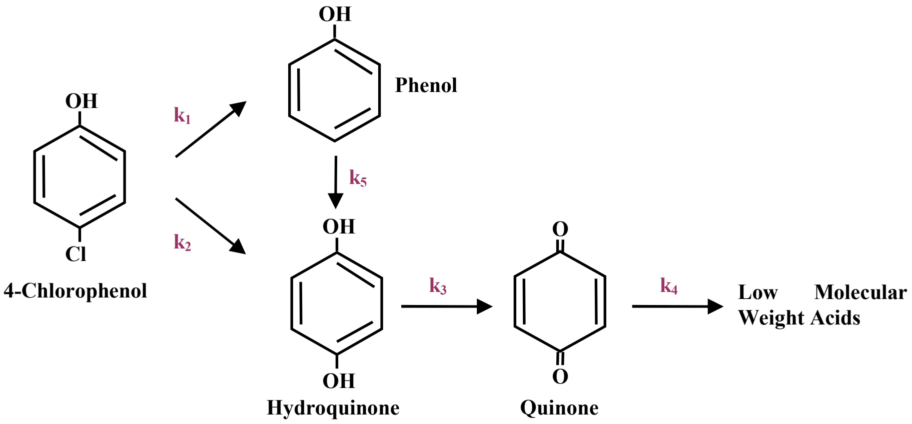


Figure 4.1.5-2 Suggested mechanistic pathway of the degradation of 4-chlorophenol by wet oxidation.

The kinetic constants were then found by minimizing the squared difference between the experimental and the calculated values (according to the integration of equations 4.1.5-1 to 5) of 4-chlorophenol, phenol, hydroquinone and quinone. However, the modeling of the previous kinetic scheme was not possible to be obtained without a high level of error. The non-accuracy of the model was thought to be due to the presence of phenol. In fact, any model containing phenol has been reported in the literature, and in addition, the measured concentration of phenol throughout the reactions was found to be in the vicinity of one hundred times lower than the respective concentrations of hydroquinone and quinone. For these reasons, phenol was considered hereon as a product of a non-relevant secondary reaction or the result of a contamination of the samples or the HPLC during the process of analyzing. According to this, a second kinetic model without including phenol is suggested and shown in figure 4.1.5-3.

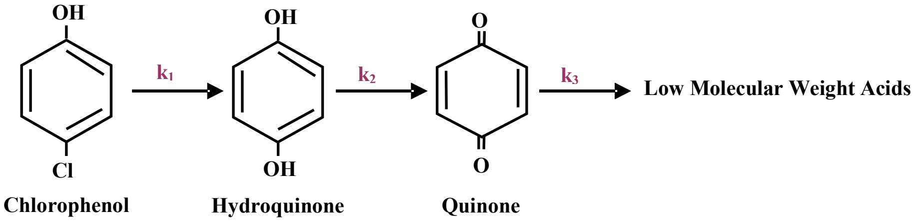


Figure 4.1.5-3 Suggested mechanistic pathway of the degradation of 4-chlorophenol by wet oxidation without taking into consideration the phenol formation.

It can be seen that 4-chlorophenol is firstly oxidized to hydroquinone, which was the first intermediate detected by the HPLC. In order to describe this first attack of the 4-chlorophenol by the hydroxyl radical, it is important to point out that hydroxyl radical can react with organic substances by electron transfer, $H^{\cdot}$ abstraction or $^{\cdot}OH$ addition to the aromatic ring (*Suffet and MacCarthy, 1989; Mopper and Zhou, 1990*). As a first stage of the degradation of 4-CP, the cleavage of the bond C-Cl occurs, leading to the formation of a triplet state. *Czaplicka (2005)* claimed that the increase in the reaction rate between OH radicals and 4-CP, resulting from the presence of a chlorine atom in the para-position of the phenyl rings, proved that the first stage of the 4-CP degradation was the C-Cl bond cleavage, and subsequently, the decomposition of the intermediate ionic or radicalary forms occurs. A 4-hydroxypenyl radical is the resultant product of this reaction, which gives rise to hydroquine after the addition of the OH radical to the molecule. As a second stage of the suggested kinetic mechanism, hydroquine is oxidized into quinone, which corresponds to a Hydrogen abstraction by the hydroxyl radical. Quintanilla (2004) studied the intermediate compounds of the catalytic wet oxidation of phenol. In this investigation, catalytic wet oxidation of hydroquinone was developed, reaching the conclusion that it was oxidized directly to quinone without giving rise to the formation of further compounds. The same author reported that the wet oxidation of quinone results in the formation of several acids of low molecular weight, such as maleic, malonic, oxalic, acetic and formic acid. Maleic acid might be formed as the product of the oxidation of quinone. The further oxidation of maleic acids (considering both isomers) will lead to the production of malonic, formic and oxalic acids. On one side, the oxidation of malonic acid will give rise to acetic acid, which is widely reported as a refractory to oxidation compound. Secondly, formic acid oxidation produces mineralization compounds and oxalic acid. Finally, the oxidation of oxalic acid ends in CO_2 and H_2O (see figure 4.1.5-4).

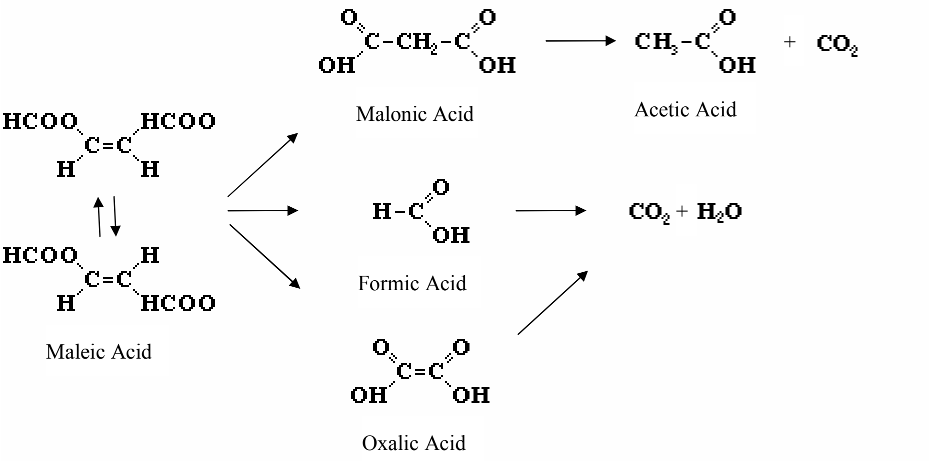


Figure 4.1.5-4 Suggested mechanistic pathway of the Low Molecular Weight Acids formed during wet oxidation (adapted from *Quintanilla, 2004*).

Focusing in the kinetics of the system, in the first place the reactor was assumed to behave as an ideal batch reactor. Secondly, the reactions between the radicals and the organic compounds were described as pseudo-first order reactions, considering thus, high ratios oxidant-to-organic as widely reported in the literature (*Shen et al., 1993; Hügul et al, 2000; Ghaly et al., 2001;Antonaraki et al., 2002*). The variation of the concentration of 4-CP along the time can be written as in equation 4.1.5-5.

$$\frac{d[4-CP]}{dt} = (-k_1)[4-CP] \qquad \text{Equation 4.1.5-5}$$

The integration of the previous equations was made using the Mathematica 4.1.2.0 (Wolfram Research, Inc.) software which allowed the obtaining of the following expression:

$$[4-CP] = f(t,k_1) = [4-CP]_0 e^{[-k_1(t-j)]} \qquad \text{Equation 4.1.5-6}$$

where j is the induction period of time and k_1 is the pseudo-first order reaction rate constant of reaction 1. k_i follows an Arrhenius type equation and can be described as equation 4.1.5-7.

$$k_i = k_i^o e^{\left(-E_i/RT\right)} \qquad \text{Equation 4.1.5-7}$$

On the other hand, the induction time, i.e., time needed for the hydroxyl radicals to be formed can be expressed as in equation 4.1.5-8.

$$j = k'_i \, e^{\left({Ea'_i}/{RT} \right)} \qquad \text{Equation 4.1.5-8}$$

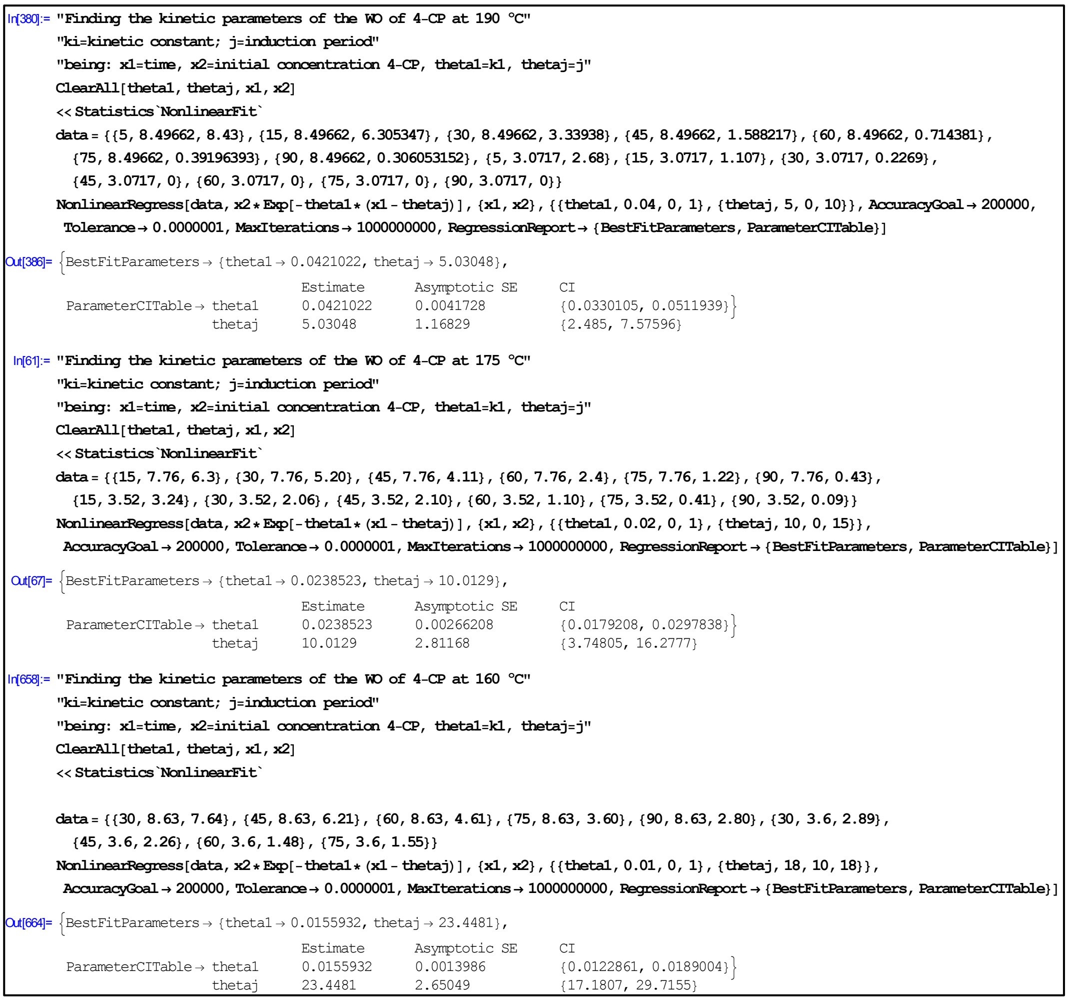
Once the equations related to the 4-CP degradation were known, the modeling of the kinetics was made in order to calculate the first kinetic parameters i.e., k_1 and j. The intermediate compounds were later evaluated, once these first parameters, related to 4-CP were obtained. Equation 4.1.5-6 was taken as starting point for the modeling of 4-CP abatement.

The simulation was developed by assuming initial values of k_1 and j at each temperature. The concentration of 4-CP at each time of each reaction was calculated by means of equation 4.1.5-6. An initial solution of the system was found using excel tool solver by minimizing the squared difference between the calculated and the experimental concentrations of 4-CP. This initial solution was then used by Mathematica 4.1.2.0 Software in order to find the optimum solution. In figure 4.1.5-5 the Mathematica code for the model fitting algorithm at each temperature is shown. The values of the kinetic constant "k_1" and the induction period "j" are given in table 4.1.5-2. Mathematica tool "NonlinearRegress" was used in order to find the optimum values of the kinetic parameters. The simulation methods employed was "LevenbergMarquardt", which gradually shifts the search for the minimum of nonlinear functions from the steepest descent to quadratic minimization (*Wolfram, 1999*).

Table 4.1.5-2 Values of kinetic constant "k_1" and induction period "j" at each temperature

	160 ºC	**175 ºC**	**190 ºC**
k_1 (L min^{-1})	$1.15\ 10^{-2} \pm 1.4\ 10^{-3}$	$2.38\ 10^{-2} \pm 2.6\ 10^{-3}$	$4.2\ 10^{-2} \pm 4.17\ 10^{-3}$
j (min)	23.4 ± 2.65	10.01 ± 2.81	5.02 ± 1.17

These results proved that the higher the temperature at which the reaction is carried out, the higher the kinetic constant, and consequently the faster the reaction. These values are in agreement with the experimental observations since 4-CP was faster degraded at the highest temperatures. On the other hand and regarding the induction period, it can be affirmed that the lower the temperature of the reaction, the longer the induction period, or in other words, the lower the temperature, the longer the time needed for the radicals to start attacking the 4-chlorophenol.



```
In[380]:= "Finding the kinetic parameters of the WO of 4-CP at 190 °C"
          "ki=kinetic constant; j=induction period"
          "being: x1=time, x2=initial concentration 4-CP, theta1=k1, thetaj=j"
          ClearAll[theta1, thetaj, x1, x2]
          << Statistics`NonlinearFit`
          data = {{5, 8.49662, 8.43}, {15, 8.49662, 6.305347}, {30, 8.49662, 3.33938}, {45, 8.49662, 1.588217}, {60, 8.49662, 0.714381},
            {75, 8.49662, 0.39196393}, {90, 8.49662, 0.306053152}, {5, 3.0717, 2.68}, {15, 3.0717, 1.107}, {30, 3.0717, 0.2269},
            {45, 3.0717, 0}, {60, 3.0717, 0}, {75, 3.0717, 0}, {90, 3.0717, 0}}
          NonlinearRegress[data, x2 * Exp[-theta1 * (x1 - thetaj)], {x1, x2}, {{theta1, 0.04, 0, 1}, {thetaj, 5, 0, 10}}, AccuracyGoal → 200000,
           Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

Out[386]= {BestFitParameters → {theta1 → 0.0421022, thetaj → 5.03048},
                                   Estimate     Asymptotic SE    CI
           ParameterCITable → theta1   0.0421022    0.0041728        {0.0330105, 0.0511939}}
                              thetaj   5.03048      1.16829          {2.485, 7.57596}

 In[61]:= "Finding the kinetic parameters of the WO of 4-CP at 175 °C"
          "ki=kinetic constant; j=induction period"
          "being: x1=time, x2=initial concentration 4-CP, theta1=k1, thetaj=j"
          ClearAll[theta1, thetaj, x1, x2]
          << Statistics`NonlinearFit`
          data = {{15, 7.76, 6.3}, {30, 7.76, 5.20}, {45, 7.76, 4.11}, {60, 7.76, 2.4}, {75, 7.76, 1.22}, {90, 7.76, 0.43},
            {15, 3.52, 3.24}, {30, 3.52, 2.06}, {45, 3.52, 2.10}, {60, 3.52, 1.10}, {75, 3.52, 0.41}, {90, 3.52, 0.09}}
          NonlinearRegress[data, x2 * Exp[-theta1 * (x1 - thetaj)], {x1, x2}, {{theta1, 0.02, 0, 1}, {thetaj, 10, 0, 15}},
           AccuracyGoal → 200000, Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

 Out[67]= {BestFitParameters → {theta1 → 0.0238523, thetaj → 10.0129},
                                   Estimate     Asymptotic SE    CI
           ParameterCITable → theta1   0.0238523    0.00266208       {0.0179208, 0.0297838}}
                              thetaj   10.0129      2.81168          {3.74805, 16.2777}

In[658]:= "Finding the kinetic parameters of the WO of 4-CP at 160 °C"
          "ki=kinetic constant; j=induction period"
          "being: x1=time, x2=initial concentration 4-CP, theta1=k1, thetaj=j"
          ClearAll[theta1, thetaj, x1, x2]
          << Statistics`NonlinearFit`

          data = {{30, 8.63, 7.64}, {45, 8.63, 6.21}, {60, 8.63, 4.61}, {75, 8.63, 3.60}, {90, 8.63, 2.80}, {30, 3.6, 2.89},
            {45, 3.6, 2.26}, {60, 3.6, 1.48}, {75, 3.6, 1.55}}
          NonlinearRegress[data, x2 * Exp[-theta1 * (x1 - thetaj)], {x1, x2}, {{theta1, 0.01, 0, 1}, {thetaj, 18, 10, 18}},
           AccuracyGoal → 200000, Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

Out[664]= {BestFitParameters → {theta1 → 0.0155932, thetaj → 23.4481},
                                   Estimate     Asymptotic SE    CI
           ParameterCITable → theta1   0.0155932    0.0013986        {0.0122861, 0.0189004}}
                              thetaj   23.4481      2.65049          {17.1807, 29.7155}
```

Figure 4.1.5-5 Mathematica code for the model fitting algorithm according to the suggested mechanistic pathway for the 4-CP degradation by WO.

In figure 4.1.5-6 the experimental values of the 4-CP concentration of each reaction are depicted together with the theoretical values calculated from the estimated kinetic parameters. In these plots it can be observed that the theoretical values (designated by lines) fit the experimental ones (designated by points) to a great extent.

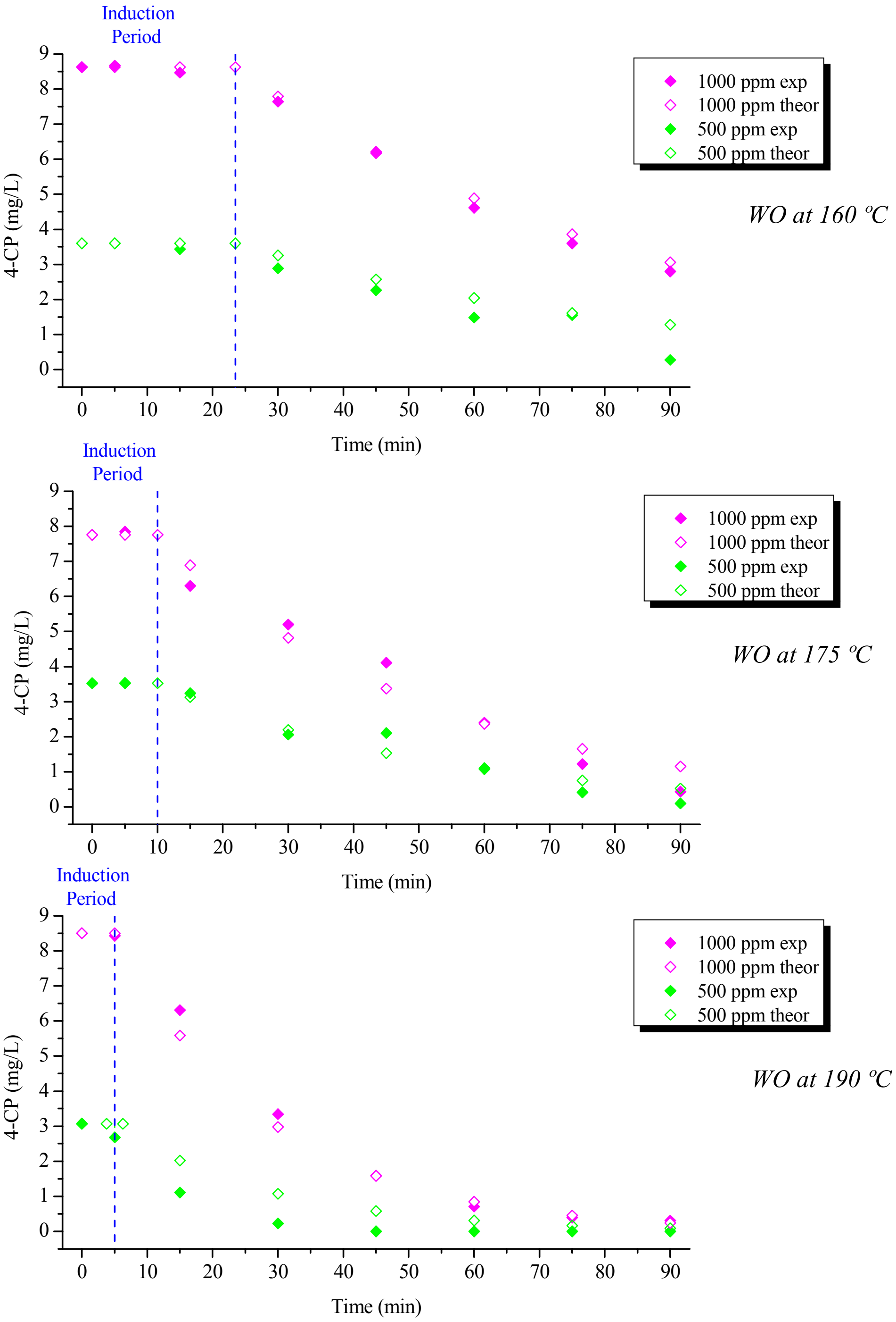


Figure 4.1.5-6 Experimental and calculated values of 4-CP throught wet oxidation at 160, 170 and 190 ºC.

Once the first kinetic parameters, i.e., k_1 and induction period, were determined, a similar procedure was followed in order to determine the rest of the kinetic parameters (related to hydroquinone and quinone). Taking into account the mechanistic pathway suggested and assuming that hydroquinone reacts according to a pseudo-first order kinetic model, its reaction rate can be expressed as in equation 4.1.5-9. The integration of this equation with the incorporation of the 4-CP concentration defined as in equation 4.1.5-5 was made using Mathematica Software, leading to equation 4.1.5-10 for the prediction of the hydroquinone concentration throughout the wet oxidation reaction. For the modeling of the system, the values of the variables j (induction time) and k_1 were used, so that, the only unknown parameter to be determined was k_2. The simulation of the hydroquinone concentration was made following a similar way as for the 4-CP degradation. Firstly, initial values of k_2 were assumed at each temperature in order to minimize the square difference between the real and the calculated concentrations of hydroquinone by means of Excel tool Solver. This initial solution was taken then as starting point for the simulation with Mathematica Software. In addition, and as in the case of the 4-CP, the simulation was made independently at each temperature, so that values of the kinetic constants at each temperature were obtained.

$$\frac{d[HQ]}{dt} = -k_2[HQ] + k_1[4-CP] \qquad \text{Equation 4.1.5-9}$$

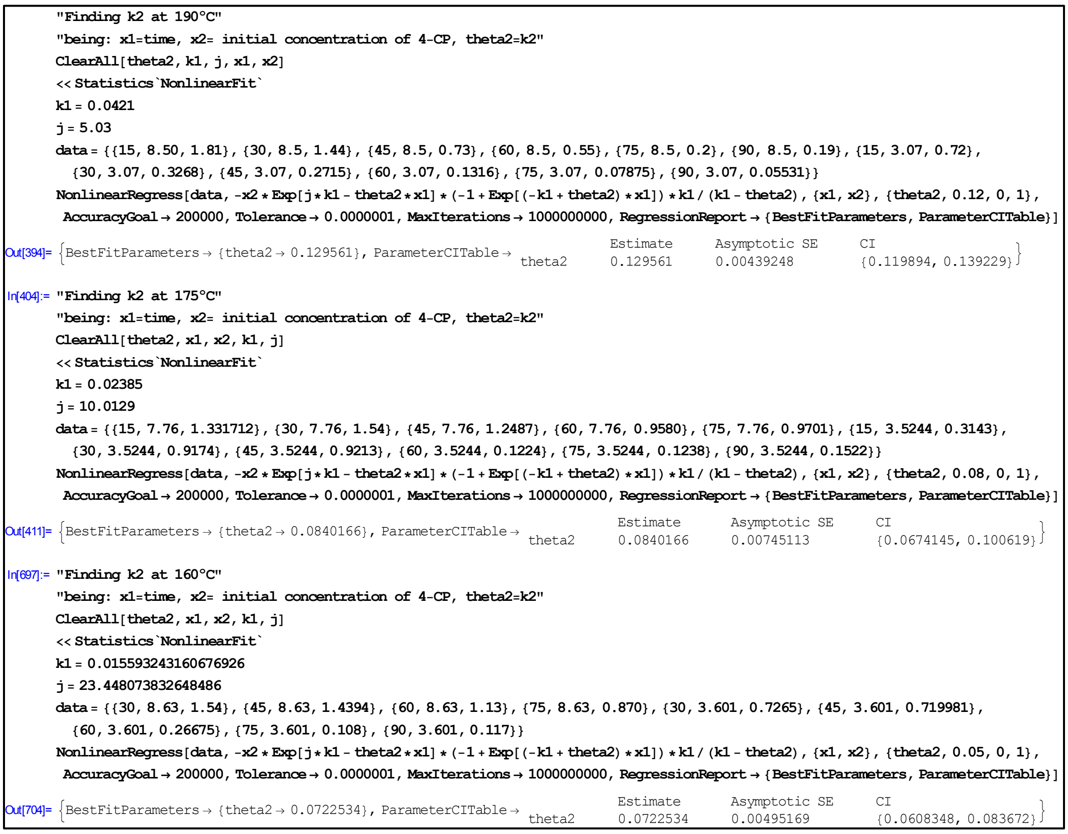
$$[HQ] = f(t,j,k_1,k_2) = \frac{-[4-CP]_o e^{(jk_1+k_2t)}(-1+e^{(-k_1+k_2)t})k_1}{k_1-k_2} \qquad \text{Equation 4.1.5-10}$$

The results of the Mathematica's simulation is shown in figure 4.1.5-7 and the values of the kinetic constants k_2 at each temperature are summarized in table 4.1.5-3.

Table 4.1.5-3 Values of kinetic constant "k_2" at each temperature

	160 ºC	**175 ºC**	**190 ºC**
k_2 (L min^{-1})	$7.72\ 10^{-2} \pm 4.95\ 10^{-3}$	$8.40\ 10^{-2} \pm 7.45\ 10^{-3}$	$12.95\ 10^{-2} \pm 4.39\ 10^{-3}$

The values of the kinetic constants belonging to the oxidation of hydroquinone into quinone appeared to the higher the higher the temperature of the reaction. This means that the reaction has a higher rate at the highest temperatures. When comparing the values of k_1 and k_2, it was found out that the second reaction is slightly faster than the first one, meaning that the formation of hydroquinone is slower than its disappearance. This fact would explain the low concentrations of hydroquinone observed and the non-accumulation of this specie in the system.



```
        "Finding k2 at 190°C"
        "being: x1=time, x2= initial concentration of 4-CP, theta2=k2"
        ClearAll[theta2, k1, j, x1, x2]
        << Statistics`NonlinearFit`
        k1 = 0.0421
        j = 5.03
        data = {{15, 8.50, 1.81}, {30, 8.5, 1.44}, {45, 8.5, 0.73}, {60, 8.5, 0.55}, {75, 8.5, 0.2}, {90, 8.5, 0.19}, {15, 3.07, 0.72},
          {30, 3.07, 0.3268}, {45, 3.07, 0.2715}, {60, 3.07, 0.1316}, {75, 3.07, 0.07875}, {90, 3.07, 0.05531}}
        NonlinearRegress[data, -x2 * Exp[j * k1 - theta2 * x1] * (-1 + Exp[(-k1 + theta2) * x1]) * k1 / (k1 - theta2), {x1, x2}, {theta2, 0.12, 0, 1},
         AccuracyGoal → 200000, Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]
                                                                          Estimate      Asymptotic SE      CI
Out[394]= {BestFitParameters → {theta2 → 0.129561}, ParameterCITable →  theta2   0.129561      0.00439248         {0.119894, 0.139229}}

In[404]:= "Finding k2 at 175°C"
        "being: x1=time, x2= initial concentration of 4-CP, theta2=k2"
        ClearAll[theta2, x1, x2, k1, j]
        << Statistics`NonlinearFit`
        k1 = 0.02385
        j = 10.0129
        data = {{15, 7.76, 1.331712}, {30, 7.76, 1.54}, {45, 7.76, 1.2487}, {60, 7.76, 0.9580}, {75, 7.76, 0.9701}, {15, 3.5244, 0.3143},
          {30, 3.5244, 0.9174}, {45, 3.5244, 0.9213}, {60, 3.5244, 0.1224}, {75, 3.5244, 0.1238}, {90, 3.5244, 0.1522}}
        NonlinearRegress[data, -x2 * Exp[j * k1 - theta2 * x1] * (-1 + Exp[(-k1 + theta2) * x1]) * k1 / (k1 - theta2), {x1, x2}, {theta2, 0.08, 0, 1},
         AccuracyGoal → 200000, Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]
                                                                           Estimate      Asymptotic SE      CI
Out[411]= {BestFitParameters → {theta2 → 0.0840166}, ParameterCITable →  theta2   0.0840166     0.00745113         {0.0674145, 0.100619}}

In[697]:= "Finding k2 at 160°C"
        "being: x1=time, x2= initial concentration of 4-CP, theta2=k2"
        ClearAll[theta2, x1, x2, k1, j]
        << Statistics`NonlinearFit`
        k1 = 0.015593243160676926
        j = 23.448073832648486
        data = {{30, 8.63, 1.54}, {45, 8.63, 1.4394}, {60, 8.63, 1.13}, {75, 8.63, 0.870}, {30, 3.601, 0.7265}, {45, 3.601, 0.719981},
          {60, 3.601, 0.26675}, {75, 3.601, 0.108}, {90, 3.601, 0.117}}
        NonlinearRegress[data, -x2 * Exp[j * k1 - theta2 * x1] * (-1 + Exp[(-k1 + theta2) * x1]) * k1 / (k1 - theta2), {x1, x2}, {theta2, 0.05, 0, 1},
         AccuracyGoal → 200000, Tolerance → 0.0000001, MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]
                                                                           Estimate      Asymptotic SE      CI
Out[704]= {BestFitParameters → {theta2 → 0.0722534}, ParameterCITable →  theta2   0.0722534     0.00495169         {0.0608348, 0.083672}}
```

Figure 4.1.5-7 Mathematica code for the model fitting algorithm of hydroquinone formation and degradation by WO.

In figure 4.1.5-8 the experimental and the calculated values of the hydroquinone versus the time of the reaction are depicted. The three plots illustrate the three wet oxidations at 160, 175 and 190 ºC. From these representations, it can be observed that the concentration of hydroquinone increased sharply after the induction period, reaching afterwards the peak of maximum concentration. In the case of the WO at 160 ºC, the peak was observed experimentally and theoretically in the vicinity of 30 minutes after the initiation of the reaction. On the other hand, at 175 ºC discrepancy was found between the experimental and the theoretical time of this peak. Whereas during the experiments the maximum concentration was observed at 30 minutes, theoretically it was found closer to the end of the induction period, more specifically after 15 minutes of reaction. These differences can be attributed to a low accuracy of the model when describing the real system or to experimental error. Finally, the results obtained at 190 ºC proved that the maximum concentration was observed after 15 minutes of oxidation both theoretically and experimentally.

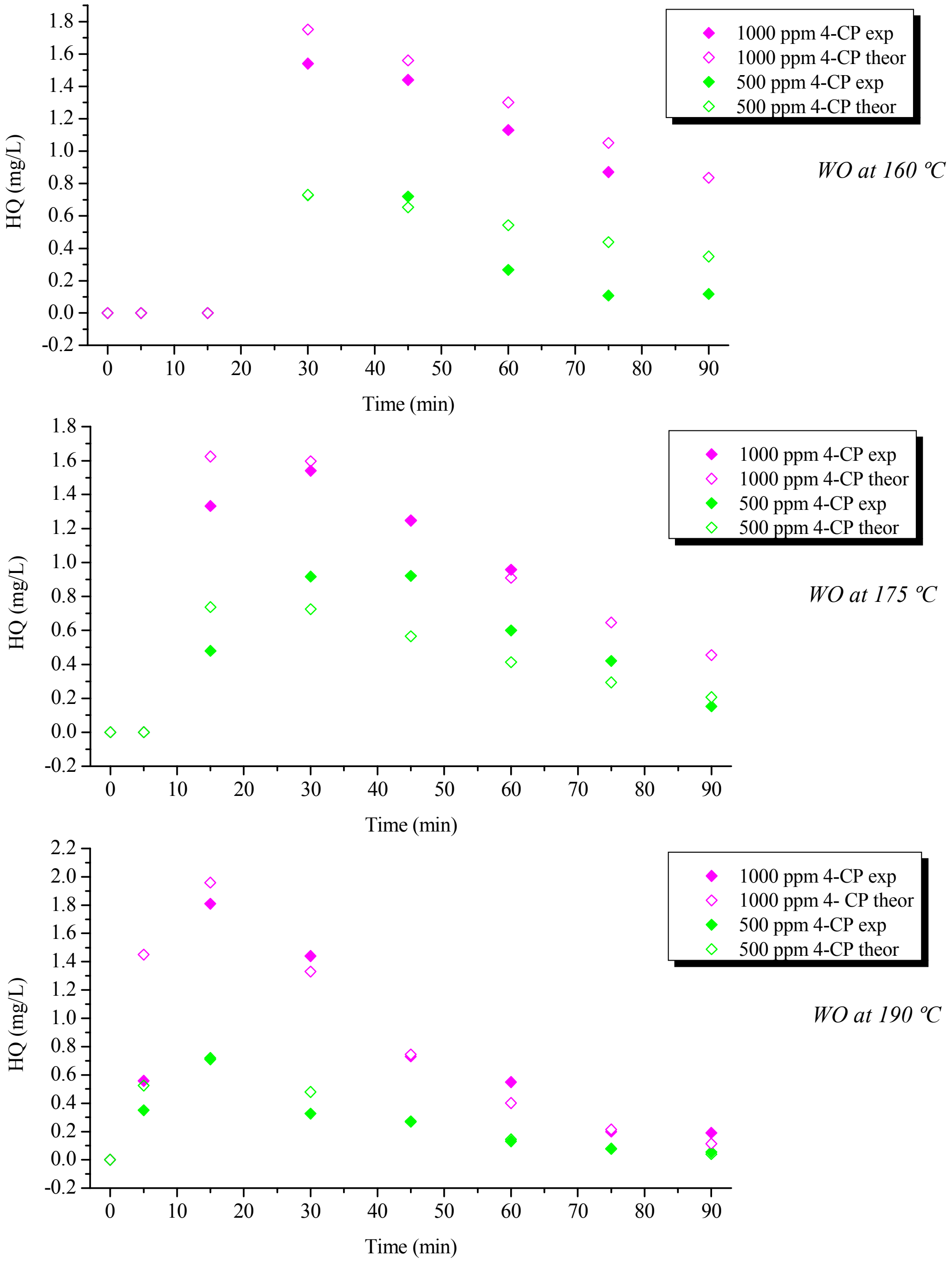


Figure 4.1.5-8. Experimental and theoretical values of hydroquinone concentration throughout WO reactions.

Regarding the degree of hydroquinone removal achieved at the end of these reactions it can be affirmed that only at the highest temperature (190 ºC) almost a complete removal was reached with both initial concentrations of 4-chlorophenol. It was also observed that a higher initial concentration of 4-CP resulted in higher HQ concentrations, and that under this conditions, the lower the temperature of the reaction, the lower the HQ removal.

With the values of the induction period and the kinetic constants k_1 and k_2 already determined, the simulation was continued by finding the value of the kinetic constant k_3, which belongs to the oxidation of quinone to low molecular weight acids. According to the suggested model and assuming that quinone reacts as a pseudo-first order kinetic model, its reaction rate can be described as in equation 4.1.5-11

$$\frac{d[Q]}{dt} = k_2[HQ] - k_3[Q]$$

Equation 4.1.5-11

The integration of this equation was made using Mathematica Software in order to obtain one expression which allowed the prediction of quinone concentration throughout the reactions.

Equation 4.1.5-12

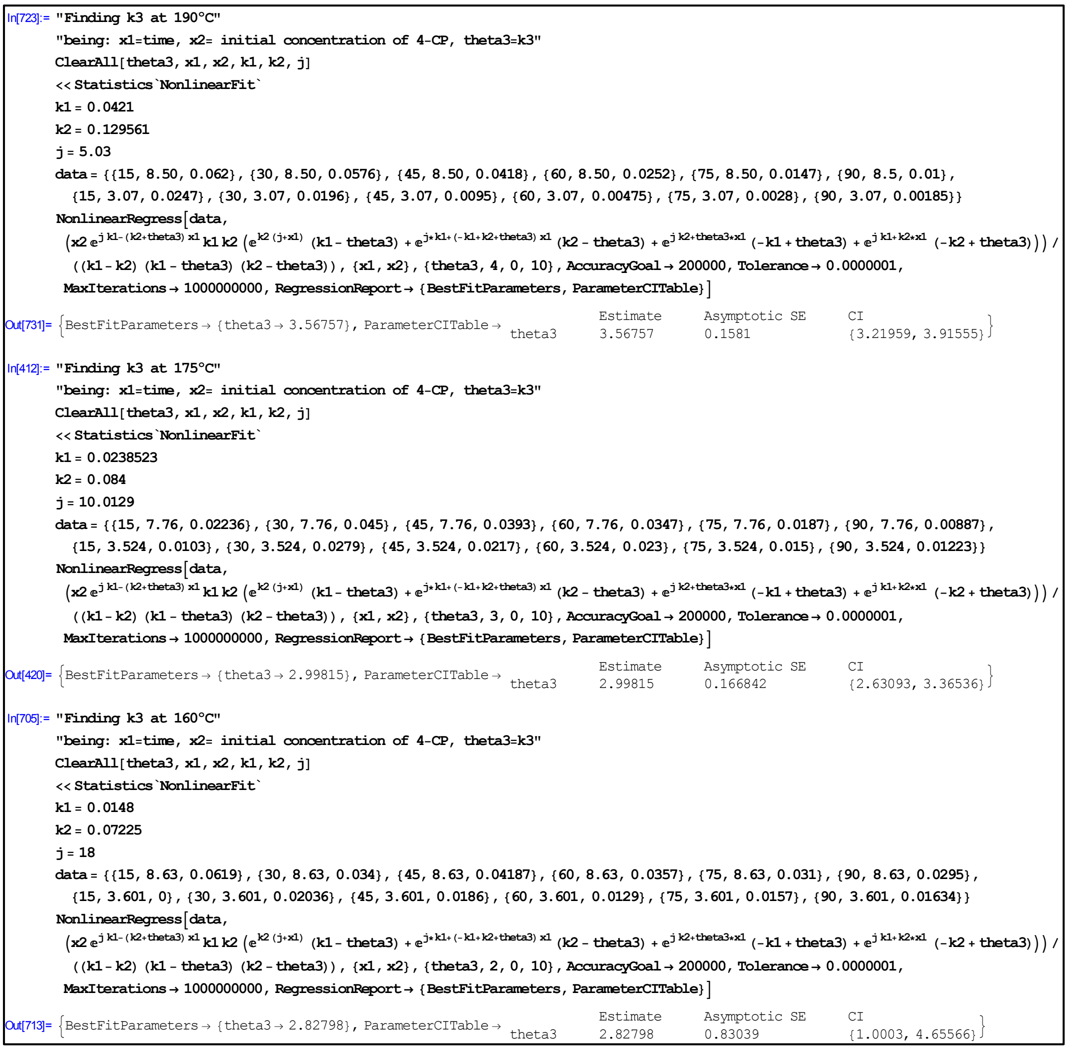
$$[Q] = \frac{k_2 e^{(jk_1-(k_2+k_3)t)} k_1 k_2 (e^{k_2(j+t)}(k_1-k_3) + e^{jk_1+(-k_1+k_2+k_3)t}(k_2-k_3) + e^{(jk_2+k_3t)}(-k_1+k_3) + e^{(jk_1+k_3t)}(-k_2+k_3))}{(k_1-k_2)(k_1-k_3)(k_2-k_3)}$$

The modeling of the system was made, in the first place by assuming initial values of k_3. It should be noted that from equation 4.1.5-12 the only unknown parameter is k_3 and consequently the concentration of quinone can be calculated, once k_3 is know. Excel tool Solver was used to find an initial solution of k_3 by minimizing the squared difference between the experimental and calculated concentrations of quinone. The initial value of k_3 was used as a starting point for the optimization with Mathematica Software. The results from Mathematica are shown in figure 4.1.5-9 and in table 4.1.5-4 the values of k_3 at each temperature are given.

Table 4.1.5-4 Values of kinetic constant "k_3" at each temperature

	160 ºC	**175 ºC**	**190 ºC**
k_3 (L min^{-1})	2.83 ± 1.58 10^{-2}	3.00 ± 1.67 10^{-2}	3.57 ± 1.58 10^{-2}

From these results, it can be concluded that the degradation of quinone into low molecular weight acids is faster the higher the temperature. On the other hand and comparing the values of k_3 with the previously obtained values of k_1 and k_2, it can be deduced that the degradation of quinone follows a faster reaction rate than its parents compounds (hydroquinone and 4-chlorophenol). This fact indicates that quinone is removed from the system faster than produced, which also proves the fact of the non-accumulation of quinone found in the system.



```
In[723]:= "Finding k3 at 190°C"
          "being: x1=time, x2= initial concentration of 4-CP, theta3=k3"
          ClearAll[theta3, x1, x2, k1, k2, j]
          << Statistics`NonlinearFit`
          k1 = 0.0421
          k2 = 0.129561
          j = 5.03
          data = {{15, 8.50, 0.062}, {30, 8.50, 0.0576}, {45, 8.50, 0.0418}, {60, 8.50, 0.0252}, {75, 8.50, 0.0147}, {90, 8.5, 0.01},
            {15, 3.07, 0.0247}, {30, 3.07, 0.0196}, {45, 3.07, 0.0095}, {60, 3.07, 0.00475}, {75, 3.07, 0.0028}, {90, 3.07, 0.00185}}
          NonlinearRegress[data,
           (x2 e^(j k1- (k2+theta3) x1) k1 k2 (e^(k2 (j+x1)) (k1 - theta3) + e^(j*k1+ (-k1+k2+theta3) x1) (k2 - theta3) + e^(j k2+theta3*x1) (-k1 + theta3) + e^(j k1+k2*x1) (-k2 + theta3))) /
            ((k1 - k2) (k1 - theta3) (k2 - theta3)), {x1, x2}, {theta3, 4, 0, 10}, AccuracyGoal → 200000, Tolerance → 0.0000001,
           MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

                                                                       Estimate     Asymptotic SE     CI
Out[731]= {BestFitParameters → {theta3 → 3.56757}, ParameterCITable →  theta3   3.56757      0.1581            {3.21959, 3.91555}}

In[412]:= "Finding k3 at 175°C"
          "being: x1=time, x2= initial concentration of 4-CP, theta3=k3"
          ClearAll[theta3, x1, x2, k1, k2, j]
          << Statistics`NonlinearFit`
          k1 = 0.0238523
          k2 = 0.084
          j = 10.0129
          data = {{15, 7.76, 0.02236}, {30, 7.76, 0.045}, {45, 7.76, 0.0393}, {60, 7.76, 0.0347}, {75, 7.76, 0.0187}, {90, 7.76, 0.00887},
            {15, 3.524, 0.0103}, {30, 3.524, 0.0279}, {45, 3.524, 0.0217}, {60, 3.524, 0.023}, {75, 3.524, 0.015}, {90, 3.524, 0.01223}}
          NonlinearRegress[data,
           (x2 e^(j k1- (k2+theta3) x1) k1 k2 (e^(k2 (j+x1)) (k1 - theta3) + e^(j*k1+ (-k1+k2+theta3) x1) (k2 - theta3) + e^(j k2+theta3*x1) (-k1 + theta3) + e^(j k1+k2*x1) (-k2 + theta3))) /
            ((k1 - k2) (k1 - theta3) (k2 - theta3)), {x1, x2}, {theta3, 3, 0, 10}, AccuracyGoal → 200000, Tolerance → 0.0000001,
           MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

                                                                       Estimate     Asymptotic SE     CI
Out[420]= {BestFitParameters → {theta3 → 2.99815}, ParameterCITable →  theta3   2.99815      0.166842          {2.63093, 3.36536}}

In[705]:= "Finding k3 at 160°C"
          "being: x1=time, x2= initial concentration of 4-CP, theta3=k3"
          ClearAll[theta3, x1, x2, k1, k2, j]
          << Statistics`NonlinearFit`
          k1 = 0.0148
          k2 = 0.07225
          j = 18
          data = {{15, 8.63, 0.0619}, {30, 8.63, 0.034}, {45, 8.63, 0.04187}, {60, 8.63, 0.0357}, {75, 8.63, 0.031}, {90, 8.63, 0.0295},
            {15, 3.601, 0}, {30, 3.601, 0.02036}, {45, 3.601, 0.0186}, {60, 3.601, 0.0129}, {75, 3.601, 0.0157}, {90, 3.601, 0.01634}}
          NonlinearRegress[data,
           (x2 e^(j k1- (k2+theta3) x1) k1 k2 (e^(k2 (j+x1)) (k1 - theta3) + e^(j*k1+ (-k1+k2+theta3) x1) (k2 - theta3) + e^(j k2+theta3*x1) (-k1 + theta3) + e^(j k1+k2*x1) (-k2 + theta3))) /
            ((k1 - k2) (k1 - theta3) (k2 - theta3)), {x1, x2}, {theta3, 2, 0, 10}, AccuracyGoal → 200000, Tolerance → 0.0000001,
           MaxIterations → 1000000000, RegressionReport → {BestFitParameters, ParameterCITable}]

                                                                       Estimate     Asymptotic SE     CI
Out[713]= {BestFitParameters → {theta3 → 2.82798}, ParameterCITable →  theta3   2.82798      0.83039           {1.0003, 4.65566}}
```

Figure 4.1.5-9 Mathematica code for the model fitting algorithm of quinone formation and degradation by WO.

In figure 4.1.5-10 the values of the quinone concentration obtained experimentally and theoretically are depicted versus the time of the reaction at each temperature. The first fact to be mentioned from this plot is that the model fitted the experimental data with quite accuracy.

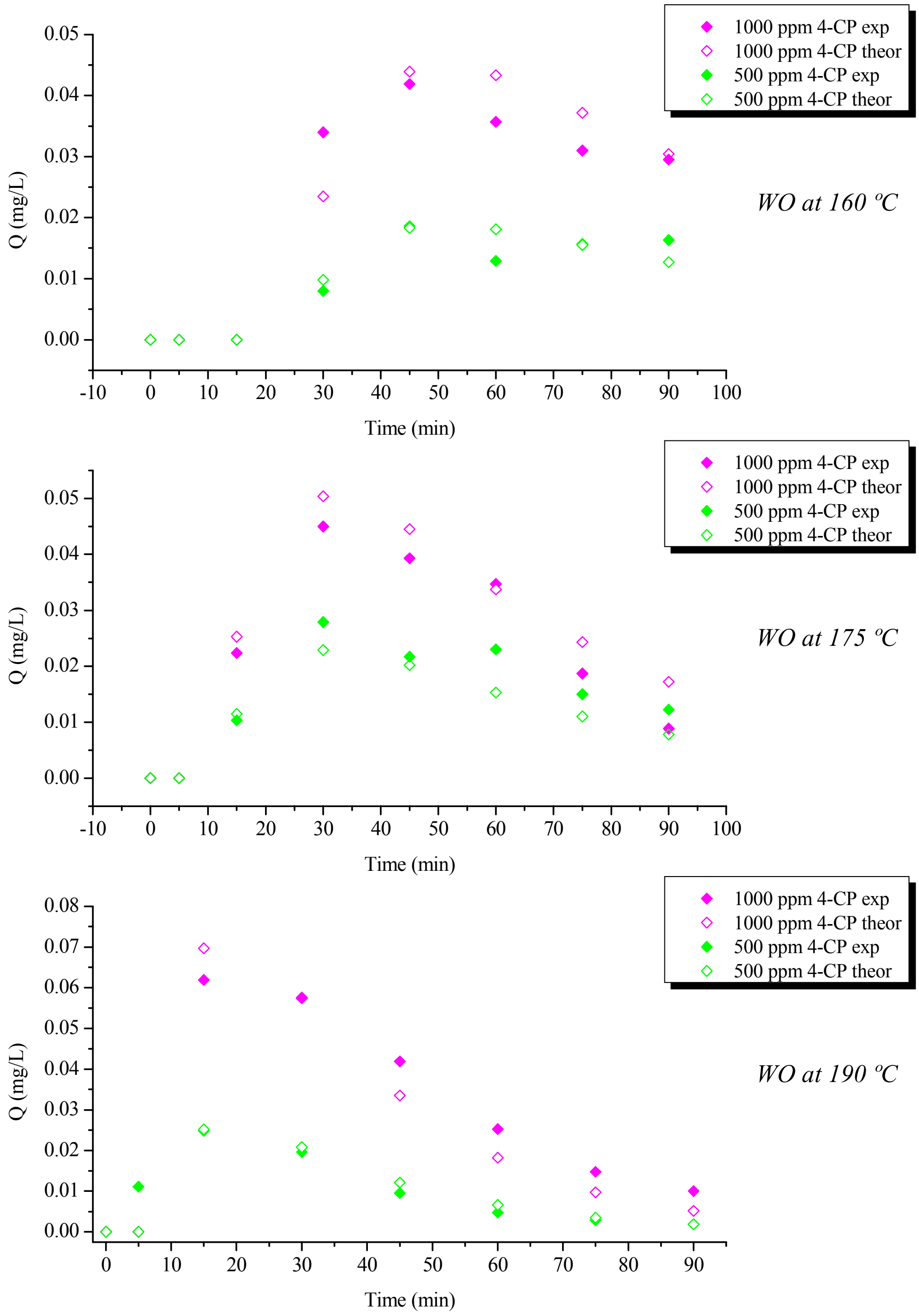


Figure 4.1.5-10 Experimental and theoretical values of quinone throughout wet oxidation at 160, 175 and 190 ºC.

Concerning the tendency of the points, it should be noted that the concentration of quinone tended to increase after the induction period, reaching a maxim peak afterwards. This tendency was more pronounced at the highest temperatures, where both theoretical and experimental maximum concentration coincides. At 190 ºC the maximum concentration was found after 15 minutes of reaction, whereas at 175 ºC it appeared after 30 minutes of the initiation of the reaction. The tendency of the experiment carried out at 160 ºC with the lowest initial concentration of 4-CP appear to be different from the other experiments. In this case, the quinone reached a maximum concentration, located after 30 minutes of reaction, and then it tended to remain approximately constant.

4.2 WET OXIDATION OF MULTI-COMPOUND WASTEWATERS

In this section wet oxidation reactions were tested in order to degrade wastewaters coming from pulp and paper mills. On one side, wastewater from the debarking process, previously concentrated by thermal evaporation, was oxidized by this technique. On the other side, water from the thermo-mechanical pulping, previously concentrated by nanofiltration, was treated as well. At this stage of the investigation, it should be pointed out that meanwhile the first one was an original wastewater from the pulp and paper mill, the second one was a synthetic water generated in one of the laboratories of “Lappeenranta University of Technology”.

4.2.1 NANOFILTRATION CONCENTRATE OF TERMO-MECHANICAL PULP PROCESS WATER

Model pulp and paper mill wastewater was prepared as explained in chapter 3.1.3 in order to simulate termo-mechanical pulp process water. The same chapter contains all the required information concerning the pretreatment (nanofiltration) as well as the procedure followed to conduct the wet oxidation reactions. In addition, data about the initial conditions or properties of the wastewater before and after the nanofiltration is given.

The first objective of this chapter was to check whether this type of wastewater could be successfully treated by WO. For this purpose, reactions at different temperatures and pressures were carried out. According to the literature and taking into account the economical restrictions that working at high conditions of temperature and pressure involves, a temperature between 120 and 200 ºC and pressures in the range of 5 to 15 bar were selected as operating conditions for this study. Special interest was drawn to the evolution of some compounds so called lipophilic wood extractives during the reactions.

With some of the obtained results, kinetic models found in the literature have been tested. One of the model allows the prediction of parameters such as the total organic carbon or the chemical oxygen demand throughout the reaction. The second model, on the other hand, allows the prediction of the chemical oxygen demand and the biochemical oxygen demand.

4.2.1.1 Influence of the Temperature

To study the influence of the temperature when treating this kind of wastewater reactions varying the temperature and maintaining the rest of the operating parameters constant were performed. According to this, the study was started by running one experiment at 120 ºC and increasing the temperature in 10 degrees in subsequent reactions until reaching 200 ºC. The rest of the operating parameters, i.e., partial pressure of oxygen and stirring speed were kept constant in all the experiments at 10 bar and 900 rpm respectively. The experimental measures of the samples from these experiments concerning COD, pH, TOC, BOD and content of Lignin are shown in tables 4.2.1-1 to 4.2.1-9 of Appendix II. In figure 4.2.1-1 the COD removal measured throughout all these reactions is depicted.

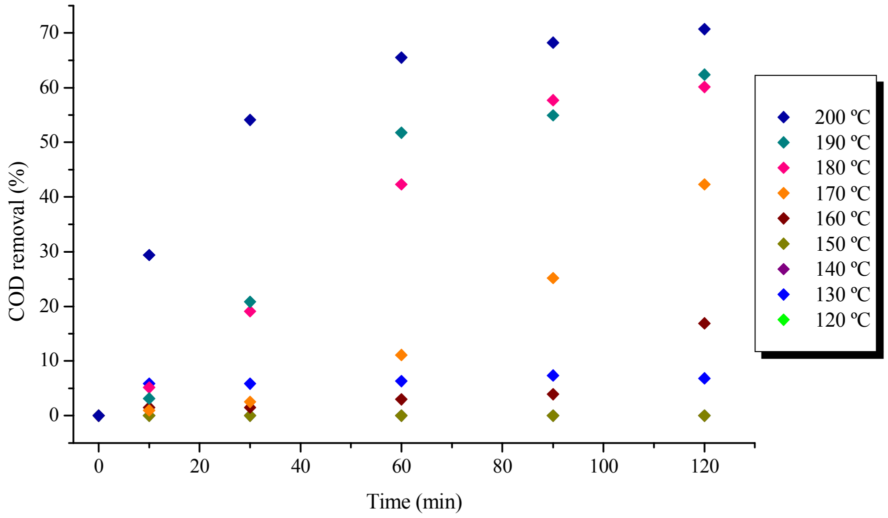


Fig. 4.2.1-1 COD removal vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

In this plot, it can be observed that up to 160 ºC the COD removal attained at the end of the reaction was lower than 20 % and consequently, higher temperatures are needed in order to have significant organic load removals. In the same figure, it can be seen that when carrying out the reactions at higher temperatures higher COD removals were achieved. In fact, at 160, 170, 180, 190 and 200ºC, COD removals of 16.87, 42.31, 60.05, 62.39 and 70.73 % were respectively obtained.

Concerning the TOC removals attained during the course of these experiments, it is necessary to point out that similar results to those from the COD were observed. In fact, in figure 4.2.1-2, it can be seen than an increase in the temperature gives rise to higher TOC removals. In fact, it seems remarkable that working under 160ºC, results in TOC removals lower than 10 % were attained. When comparing the COD and TOC removals, it can be seen that the COD removals are higher than the TOC removals. This fact can be explained taking into account that the TOC only represents the organic matter that contains carbons meanwhile the COD includes all the oxidizable species contained in the wastewater stream.

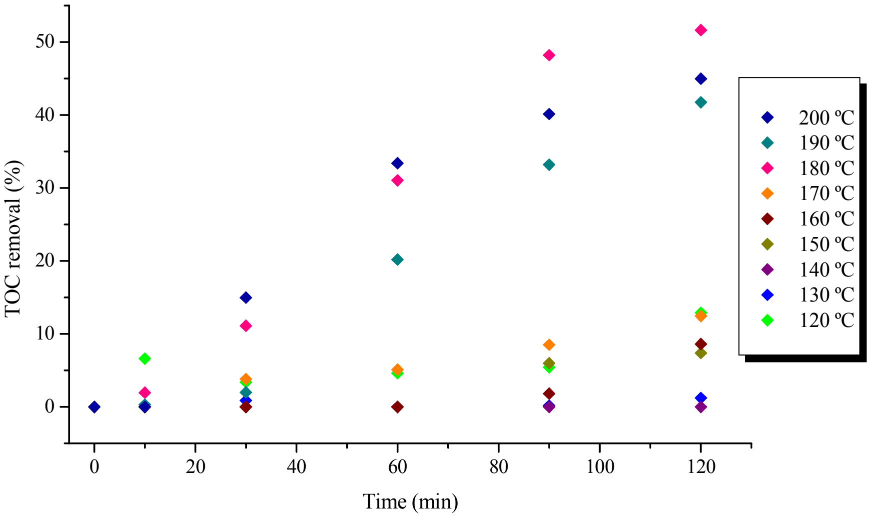


Fig. 4.2.1-2 TOC removal vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

From this set of experiments, the BOD_5 was measured as well throughout the reactions in order to know or to follow the tendency of the biodegradability. In figure 4.2.1-3 the values of the ratio BOD_5/COD, i.e., biodegradability, during the reactions is shown. The results proved that biodegradabilities lower than 0.4 were attained at the end of the reactions when carrying out WO at temperatures lower than 170 ºC, which means, that a biological treatment would not be suggested as a post-treatment. On the other hand, when increasing the temperature of the reactions, higher biodegradabilities were reached. More precisely, values of 0.62, 0.88, 0.74 and 0.98 were obtained when working at 170, 180, 190 and 200 ºC respectively. Attention must be paid at the results of the reaction at the highest temperature, i.e., 200 ºC. At the end of this reaction the value BOD/COD was close to 1, which means that almost all the oxidizable matter contained in the waste stream was readily biodegradable, which gives an indication of the high suitability of a biological post-treatment. This suggestion might be applicable as well to the WO carried out at temperatures higher than 170ºC because the BOD/COD levels are high enough to make feasible the use of a biological treatment.

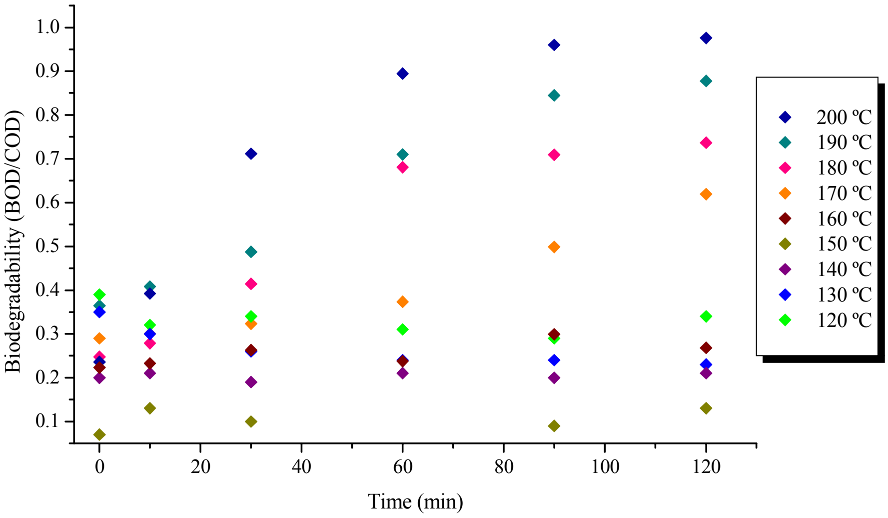


Fig. 4.2.1-3 Biodegradability vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

Another parameter that was measured from these experiments was the Lignin content. It is necessary to emphasize that the Lignin present in the water during the paper manufacturing processes affects the quality of the final product, decreasing it brightness and strength. For this reason, and when thinking in recycling the process water in order to achieve a closed water cycle, the Lignin content should be if not eliminated at least minimized to a maximum extent. In figure 4.2.1-4 the Lignin removals attained during the course of the reactions are depicted versus the time. Paying attention first to the reactions at the lowest temperatures it seems advisable that even thought during these experiments the COD removal was low, part of the Lignin was eliminated. According to these results, more than 20 % of the Lignin can be destroyed at 130 ºC. Another fact of special importance is that a removal close to 90 % was reached when performing the reactions at the highest temperatures.

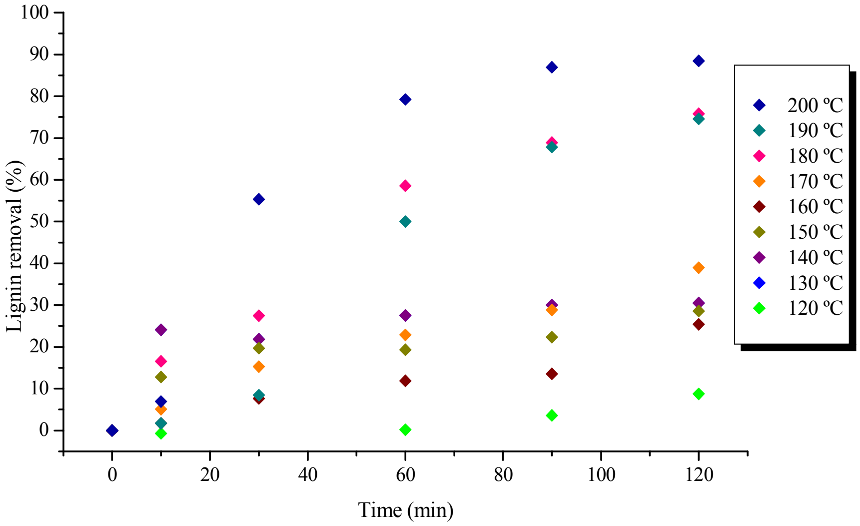


Fig. 4.2.1-4 Lignin removal vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

4.2.1.2 Influence of the Partial Pressure of Oxygen

The influence that the quantity of oxygen might have in the process of wet oxidation was tested by carrying out experiments maintaining the rest of the operating conditions constant and varying the partial pressure of oxygen. This set of experiments was developed at 170 ºC and at 4 different pressures of oxygen, i.e., 5, 7.5, 10 and 15 bar. Tables 4.2.1-10 to 4.2.1-12 of Appendix II comprise the experimental values measured during these reactions. The results of the reaction at 10 bar were already shown in table 4.2.1-6 in the same Appendix. In figure 4.2.1-5 the COD removal achieved during the course of these experiments is depicted. It can be concluded that an increase in the partial pressure of oxygen results in a higher COD removal. According to the results, at pressures lower than 10 bar the COD removals after two hours of oxidation were lower than 25 % and when the pressure of oxygen was 10 and 15 bar, the removals achieved were 42 and 53 % respectively. These results prove then, that the oxidizing agent of these reactions, i.e., molecular oxygen is not in excess respect the oxydizable matter and, consequently, the higher the amount of dissolved oxygen in the media, the higher the oxidation rate.

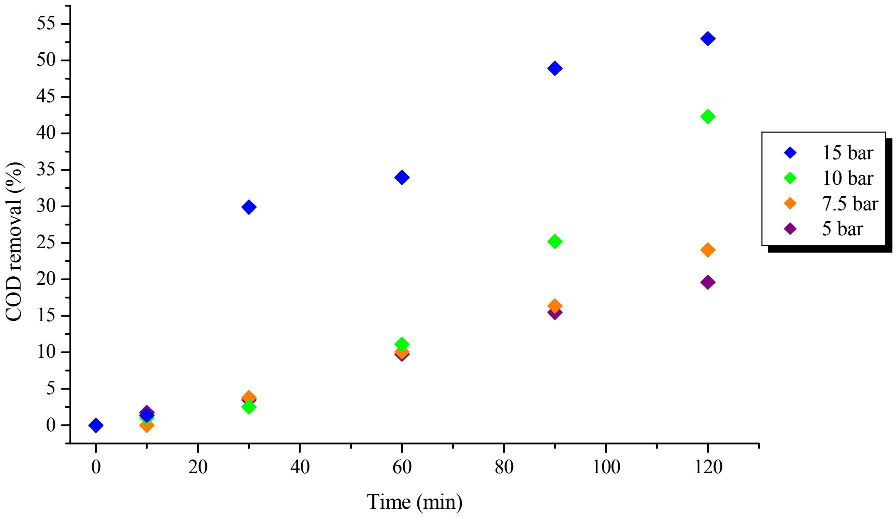


Fig. 4.2.1-5 COD removal vs. Time. WO reactions at 170 ºC and different Po_2.

Similar conclusions can be reached when paying attention to the TOC removals attained during the same reactions. The TOC removal achieved after two hours of wet oxidation at 5 bar of Po_2 was 3.74 %, at 7.5 bar 10.86 %, at 10 bar 12.44 % and finally, at 15 bar 18.56 %.

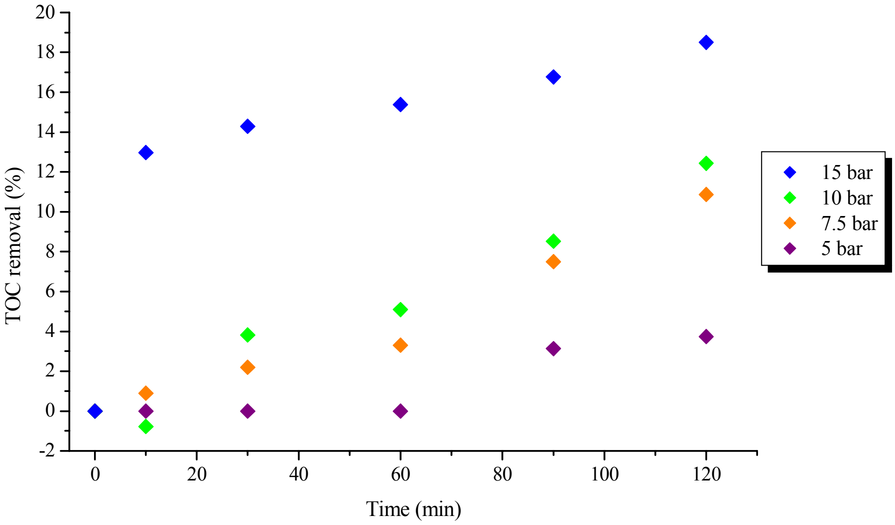


Fig. 4.2.1-6 TOC removal vs. Time. WO reactions at 170 ºC and different Po_2.

Concerning the ratio BOD/COD, or in other words, the biodegradability, it was observed that an increase in the partial pressure of oxygen resulted in a higher biodegradability of the treated stream. The results of the measured biodegradability throughout these reactions can be seen in figure 4.2.1-6. In this plot it can be noted that under 10 bar of partial pressure of oxygen the biodegradability attained is lower than 65 %, however, when increasing the Po_2 up to 15 bar, the biodegradability increased reaching a maximum in the vicinity of 90 %, which means that almost all the oxidizable matter contained in the waste stream is biodegradable.

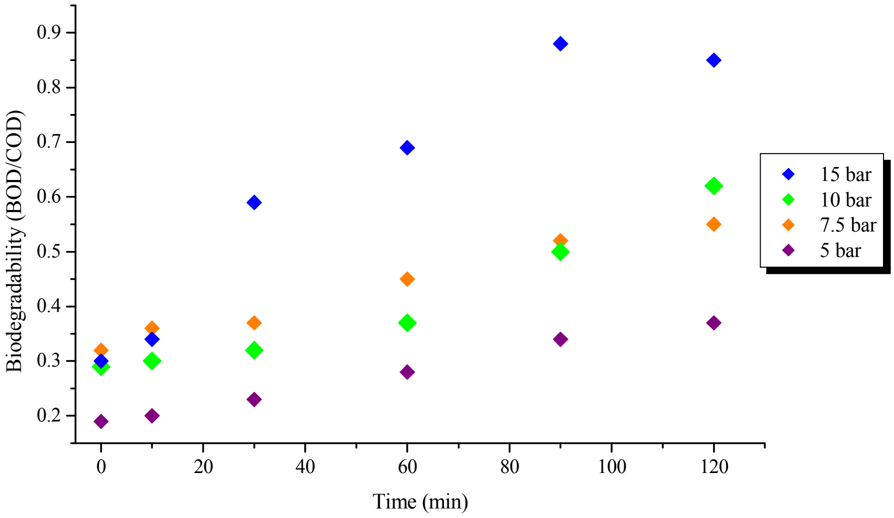


Fig. 4.2.1-6 BOD/COD vs. Time. WO reactions at 170 °C and different Po_2.

4.2.1.3 Lipophilic Wood Extractives

The presence of Lipophilic Wood Extractive compounds in the water cycles of a pulp and paper mill can cause production downtime and the need of extra cleaning (among other adverse effects) (*Verenich et al., 2004*). This group of substances is also known as pitch compounds and suitable techniques for removing them from the water effluents are needed. In this investigation, the concentration of these compounds was monitored during the wet oxidation reactions at different operating conditions. The knowledge of their concentration during the course of wet oxidations was found to be of prior importance due to the adverse influence that they have on the quality of the final product in the pulp and paper industry. It is especially interesting to know how the concentration of these compounds varies throughout the reactions at the lowest temperatures, where the COD and the TOC of the waste stream remained almost constant after two hours of reaction. Because of this, the samples from WO at 120 to 150ºC were analyzed as well by Gas Chromatography after a previous extraction. In tables 4.2.1-13 to 18 of Appendix II, the concentration of Fatty and Resin Acids, Lignans, Sterols, Steryl Acids as well as Triglycerids measured over the duration of the above mentioned reactions are shown. In addition figures 4.2.1-7 to 12 illustrate the removal of these compounds versus the time of the reaction. In this plots the preheating period, i.e., the time needed for the reactor to reach the desired temperature, is indicated by a vertical line. According to this, in the figures two different parts can be distinguished, on one side the preheating period (from 0 to 60 minutes) and the wet oxidation (from 60 to 180 minutes).

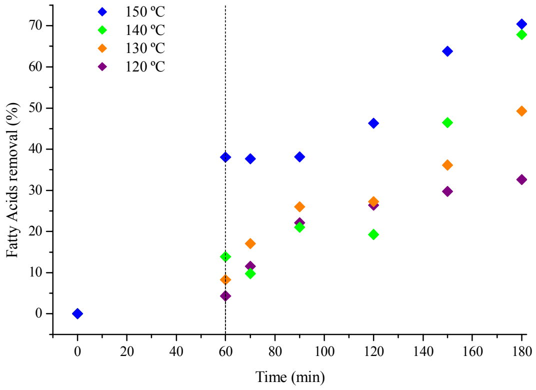


Fig. 4.2.1-7 Fatty Acids removal vs. Time.

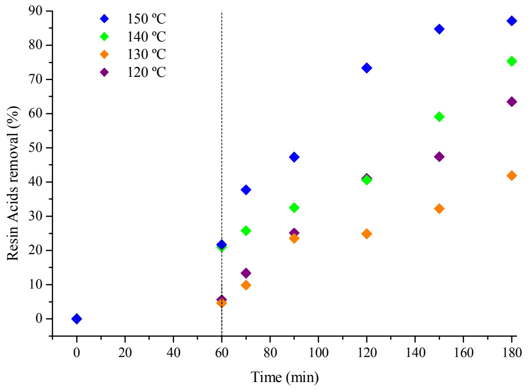


Fig. 4.2.1-8 Resin Acids removal vs. Time.

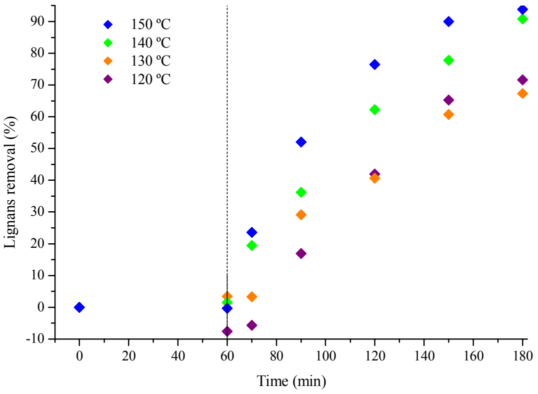


Fig. 4.2.1-9 Lignans removal vs. Time.

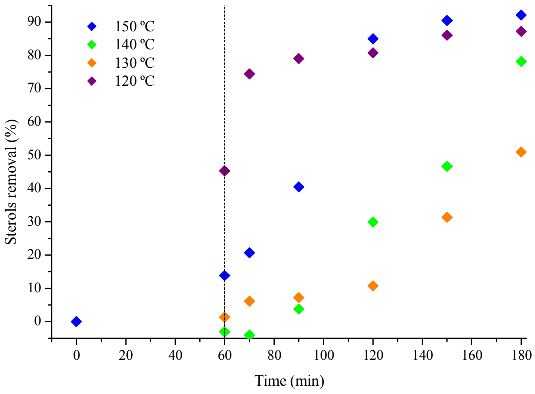


Fig. 4.2.1-10 Sterols removal vs. Time.

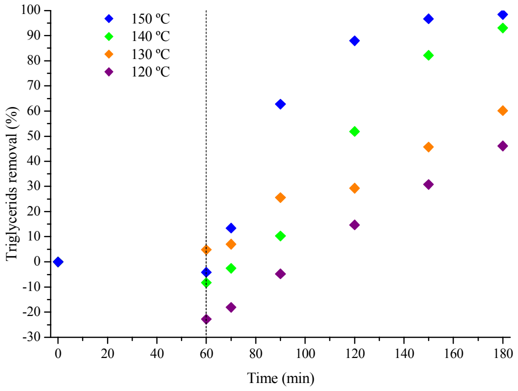


Fig. 4.2.1-11 Steryl Acids removal vs. Time.

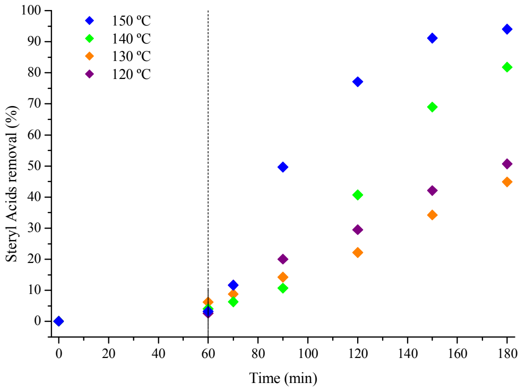


Fig. 4.2.1-12 Triglycerids removal vs. Time.

The first conclusion that can be reached from these results is that even thought under these operating conditions the COD removal attained is considerably low, LWEs are destroyed or removed to a high extent. In fact, when considering the total concentration of LWEs, table 4.2.1-1, the rather low temperatures of WO significantly affected its concentration in the water solution. At 150 ºC, only a small fraction, 8%, of the extractives remained in the treated water. However, the strong influence of polymeraritazion reactions, which occurred in the treated wastewater at 130 ºC, might have a negative impact on the LWEs removal and, therefore, extractive destruction fell at this temperature. The polymeration reactions, that are assumed to occur significantly, decreased the amount of the biodegradable compounds, the BOD values, in the treated solution. Owing to this fact, the biodegradability of the wastewater was not found to have improved during the course of the oxidation.

Table 4.2.1-1 Lipophilic Wood Extractives concentration after two hours of Wet Oxidation at 10 bars of Partial Pressure of Oxygen.

LWEs Removal (%)			
120 ºC	130 ºC	140 ºC	150 ºC
57.8	51.4	85.0	92.0

It was observed as well, that different types of extractives reacted at different rates. Hydrophilic Lignans demonstrated faster reactivity than the rest of LWEs. As the reaction proceeded, and the pH of the wastewater started to become more acidic, Steryl Esters, and

Triglycerids also began to undergo hydrolysis with the formation of Fatty Acids and alcohols. Consequently, the removal of Steryl Esters and Triglycerids increased more rapidly at higher temperatures due to the faster acidification of the water by the carboxylic acids that are formed. The higher the temperature, the stronger the effect of hydrolysis was in destroying Steryl Esters and Triglycerids along with the action of oxygen. The Fatty and Resin acids that remained in colloid state reacted with oxygen more slowly.

As a conclusion of these analyses, it can be emphasized than even thought high organic load removals were not attained at this range of temperatures, the degradation of lipophilic wood extractives compounds occurred to a high extent, especially at 150 ºC.

4.2.1.4 Kinetic Modeling

Most of the kinetic models suggested in the literature for multi-compound solutions follow the evolution of the reaction by controlling general parameters such as the COD, the BOD (Biochemical Oxygen Demand), the TOD (Total Oxygen Demand) or the TOC (Total Organic Carbon). These models are especially useful because when properly applied they are capable of predicting the evolution of these parameters throughout the reactions. One of these models is the "Generalized Kinetic Model for Wet Oxidation of Organic Compounds" suggested by Li et al. in 1991. Another model, which seems of special interest because it allows not only the prediction of the COD but also the BOD, is the "Lumped Kinetic Model for Wastewater Organic Burden Biodegradability Prediction" proposed by Verenich and Kallas (2000).

Generalized Kinetic Model for Wet Oxidation of Organic Compounds (Li et al, 1991)

This model is based on a simplified reaction scheme involving the formation and destruction of rate-controlling intermediates. As it normally occurs in WO, part of the organic compounds are destroyed to form the final oxidation products, while others are transformed to relatively stable intermediates, such as acetic acid, methanol and ethanol. The global rate of WO depends on the final product formation rate as well as the formation and destruction rates of stable intermediates. The activation energies of these intermediates (170-350 kJ/mol) are greater than those of higher-molecular-weight organic compounds (20-100 kJ/mol). Therefore, the rate of formation and destruction of these stable intermediates must be included in the global rate expression. (*Li et al., 1991*).This model classifies the substances present in the WO process into three groups, A, B and C:

- *Group A* includes all initial and relatively unstable intermediate organic compounds except acetic acid.
- *Group B* contains the refractory intermediates represented by acetic acid.
- *Group C* comprises the oxidation end products: CO_2 and H_2O.

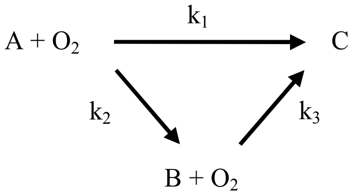


Figure 4.2.1-8 Scheme of the reaction pathways.

According to figure 4.2.1-8, the compounds included under the letter A can follow two pathways of reaction. By the former, they are oxidized and the formed products are the typical ones of the oxidation (H_2O and CO_2). By the second way, intermediate compounds are obtained, which are further oxidized producing CO_2 and H_2O by means of reaction 3. If k_2 is much smaller than k_1, means that the organic compounds of the current feed are easily oxidizable and have little tendency to form stable intermediates. However, when k_2 is more elevated, the acetic acid (or other low molecular weight acids) formation is more remarkable and the oxidation is not complete.

In addition, the model assumes the following considerations:

- The concentration of the groups A and B may be expressed in forms of Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), or Total Oxygen Demand (TOD).
- Based on the bibliography, the reaction rate may be assumed to be first order to group A or B, and nth order to oxygen.
- The reactor is supposed to follow the model of an isothermal and ideal batch reactor or plug-flow reactor with constant volumetric flow rate.

According to the previous description, the kinetics of the reaction for compounds A and B can be expressed by means of equations 4.2.1-1 and 4.2.1.-2

$$-\frac{d[A]}{dt} = k_1^o e^{-Ea_1/RT}[A][O_2]^{n1} + k_2^o e^{-Ea_2/RT}[A][O_2]^{n2}$$ Equation 4.2.1-1

$$-\frac{d[B]}{dt} = k_3^o e^{-Ea_1/RT}[B][O_2]^{n3} + k_2^o e^{-Ea_2/RT}[A][O_2]^{n2}$$ Equation 4.2.1-2

These equations can be rewritten as equations 4.3.1.3 and 4.3.1.4.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A]$$ Equation 4.2.1-3

$$-\frac{d[B]}{dt} = k_3[B] - k_2[A]$$ Equation 4.2.1-4

Where:

$$k_1 = k_1^o e^{-Ea_1/RT}[O_2]^{n1}$$ Equation 4.2.1-5

$$k_2 = k_2^o e^{-Ea_2/RT}[O_2]^{n2}$$ Equation 4.2.1-6

$$k_3 = k_3^o e^{-Ea_3/RT}[O_2]^{n3}$$ Equation 4.2.1-7

In many cases, n1, n2 and n3 are either near zero, or excess of oxygen is used. Consequently, the oxygen terms in eq. 4.2.1-5 to 4.2.1-7 may be assumed as a constant. In addition, at time t= 0, [A]= $[A]_o$ and [B]= $[B]_o$ and equations 4.2.1-3 and 4.2.1-4 can be solved analytically as shown in eq. 4.2.1-8 and 4.2.1-9:

$$[A] = [A]_o e^{(k_1+k_2)t}$$ Equation 4.2.1-8

$$[B] = [B]_o e^{-k_3 t} + \frac{k_2[A]_o}{k_1 + k_2 + k_3}\left[e^{-k_3 t} - e^{-(k_1+k_2)t}\right]$$ Equation 4.2.1-9

Combining equations 4.2.1-8 and 4.2.1-9, equation 4.2.1-10 is obtained:

$$\frac{[A+B]}{[A+B]_o} = \frac{[A]_o}{[A]_o + [B]_o}\left[\frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{(k_1 - k_3)}{k_1 + k_2 - k_3} e^{-(k_1+k_2)t}\right] + \frac{[B]_o}{[A]_o + [B]_o} e^{-k_3 t}$$ Equation 4.2.1-10

If $[B]_0$= 0, equation 4.2.1-10 can be further simplified giving rise to equation 4.3.1-11:

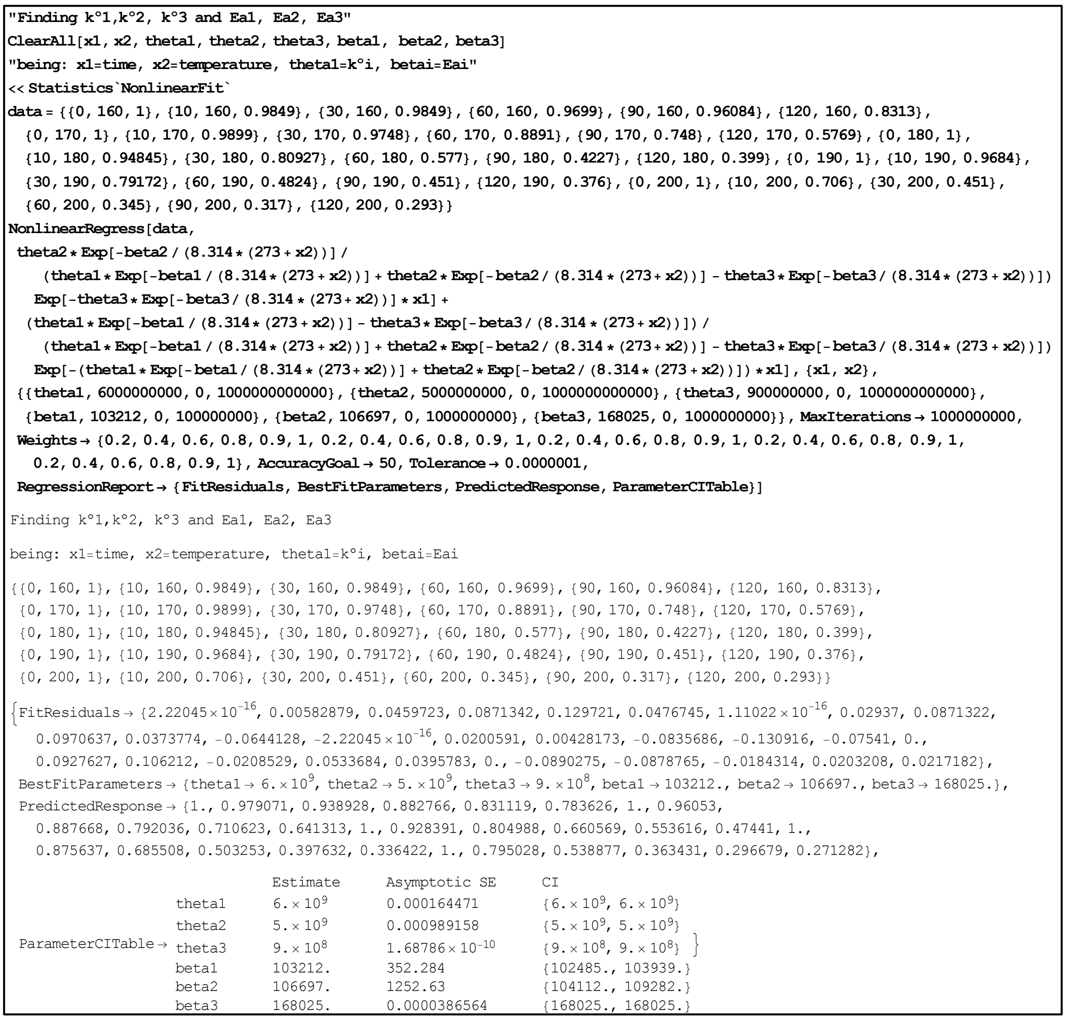
$$\frac{[A+B]}{[A+B]_o}=\left[\frac{k_2}{k_1+k_2-k_3}e^{-k_3t}+\frac{(k_1-k_3)}{k_1+k_2-k_3}e^{-(k_1+k_2)t}\right]$$ Equation 4.2.1-11

The simulation of these data was made according to equation 4.2.1-11 and using the experimental data of the COD measured throughout the WO at 160, 170, 180, 190 and 200 ºC in order to find the kinetic constants k_i, the frequency factors k^o_i and the activation energies Ea_i. The particular aim of this simulation was then, to calculate the kinetic parameters of the reactions in order to be able to predict the evolution of the reaction to some extent. For this purpose Mathematica 4.1.2.0 software purchased from Wolfram Research, Inc. was employed. This program was used to find the minimum squared difference between the calculated and the experimental values of the ratio $[COD]/[COD]_o$ by iterating the values of the three frequency factors and activation energies. According to the suggested model, six parameters are to be determined using the results of five experiments (WO at five temperatures), consisting each experiment of six values of the ratio COD/COD_o at different times. Before showing the results of the simulations it is necessary to point out that an initial solution of the parameters was previously found with Excel tool Solver using the following specifications: linear estimation, progressive derivation, method of Newton, precision of 1 10^{-6}, tolerance of 2 %, convergence 1 10^{-6}, time 10000 seconds and 10000 iterations. On the other hand, Mathematica tool “NonlinearRegress” was used in order to find the optimum values of the kinetic parameters. The simulation methods employed was “LevenbergMarquardt”, which gradually shifts the search for the minimum of nonlinear functions from the steepest descent to quadratic minimization (*Wolfram, 1999*).

The values of the kinetic parameters obtained from this simulation are shown in table 4.2.1-2. In addition, the results as obtained from Mathematica are shown in figure 4.2.1-9. From these data, it can be concluded that the parameters were calculated with small values of standard error, which confirm the validation of the suggested kinetic model.

Table 4.2.1-2 Frequency Factors and Activation Energies of reactions 1, 2 and 3 for WO of pulp and paper mill nanofiltration concentrate wastewater according to Li et al model determined by simulation using Mathematica software.

	Frequency Factors "ki" (L mol^{-1} min^{-1})	
k^o_1	k^o_2	k^o_3
$6\ 10^9 \pm 2\ 10^{-4}$	$5\ 10^9 \pm 1\ 10^{-3}$	$9.33\ 10^8 \pm 2\ 10^{-10}$
	Activation Energies "Eai" (kJ mol^{-1})	
Ea_1	Ea_2	Ea_3
$103.2\ 10^3 \pm 3\ 10^3$	$106.7\ 10^3 \pm 1\ 10^4$	$168.0\ 10^3 \pm 4\ 10^{-5}$



```
"Finding k°1,k°2, k°3 and Ea1, Ea2, Ea3"
ClearAll[x1, x2, theta1, theta2, theta3, beta1, beta2, beta3]
"being: x1=time, x2=temperature, theta1=k°i, betai=Eai"
<< Statistics`NonlinearFit`
data = {{0, 160, 1}, {10, 160, 0.9849}, {30, 160, 0.9849}, {60, 160, 0.9699}, {90, 160, 0.96084}, {120, 160, 0.8313},
  {0, 170, 1}, {10, 170, 0.9899}, {30, 170, 0.9748}, {60, 170, 0.8891}, {90, 170, 0.748}, {120, 170, 0.5769}, {0, 180, 1},
  {10, 180, 0.94845}, {30, 180, 0.80927}, {60, 180, 0.577}, {90, 180, 0.4227}, {120, 180, 0.399}, {0, 190, 1}, {10, 190, 0.9684},
  {30, 190, 0.79172}, {60, 190, 0.4824}, {90, 190, 0.451}, {120, 190, 0.376}, {0, 200, 1}, {10, 200, 0.706}, {30, 200, 0.451},
  {60, 200, 0.345}, {90, 200, 0.317}, {120, 200, 0.293}}
NonlinearRegress[data,
 theta2 * Exp[-beta2 / (8.314 * (273 + x2))] /
    (theta1 * Exp[-beta1 / (8.314 * (273 + x2))] + theta2 * Exp[-beta2 / (8.314 * (273 + x2))] - theta3 * Exp[-beta3 / (8.314 * (273 + x2))])
   Exp[-theta3 * Exp[-beta3 / (8.314 * (273 + x2))] * x1] +
  (theta1 * Exp[-beta1 / (8.314 * (273 + x2))] - theta3 * Exp[-beta3 / (8.314 * (273 + x2))]) /
    (theta1 * Exp[-beta1 / (8.314 * (273 + x2))] + theta2 * Exp[-beta2 / (8.314 * (273 + x2))] - theta3 * Exp[-beta3 / (8.314 * (273 + x2))])
   Exp[-(theta1 * Exp[-beta1 / (8.314 * (273 + x2))] + theta2 * Exp[-beta2 / (8.314 * (273 + x2))]) * x1], {x1, x2},
 {{theta1, 6000000000, 0, 1000000000000}, {theta2, 5000000000, 0, 1000000000000}, {theta3, 900000000, 0, 1000000000000},
  {beta1, 103212, 0, 100000000}, {beta2, 106697, 0, 1000000000}, {beta3, 168025, 0, 1000000000}}, MaxIterations → 1000000000,
 Weights → {0.2, 0.4, 0.6, 0.8, 0.9, 1, 0.2, 0.4, 0.6, 0.8, 0.9, 1, 0.2, 0.4, 0.6, 0.8, 0.9, 1, 0.2, 0.4, 0.6, 0.8, 0.9, 1,
   0.2, 0.4, 0.6, 0.8, 0.9, 1}, AccuracyGoal → 50, Tolerance → 0.0000001,
 RegressionReport → {FitResiduals, BestFitParameters, PredictedResponse, ParameterCITable}]

Finding k°1,k°2, k°3 and Ea1, Ea2, Ea3

being: x1=time, x2=temperature, theta1=k°i, betai=Eai

{{0, 160, 1}, {10, 160, 0.9849}, {30, 160, 0.9849}, {60, 160, 0.9699}, {90, 160, 0.96084}, {120, 160, 0.8313},
 {0, 170, 1}, {10, 170, 0.9899}, {30, 170, 0.9748}, {60, 170, 0.8891}, {90, 170, 0.748}, {120, 170, 0.5769},
 {0, 180, 1}, {10, 180, 0.94845}, {30, 180, 0.80927}, {60, 180, 0.577}, {90, 180, 0.4227}, {120, 180, 0.399},
 {0, 190, 1}, {10, 190, 0.9684}, {30, 190, 0.79172}, {60, 190, 0.4824}, {90, 190, 0.451}, {120, 190, 0.376},
 {0, 200, 1}, {10, 200, 0.706}, {30, 200, 0.451}, {60, 200, 0.345}, {90, 200, 0.317}, {120, 200, 0.293}}

{FitResiduals → {2.22045×10^-16, 0.00582879, 0.0459723, 0.0871342, 0.129721, 0.0476745, 1.11022×10^-16, 0.02937, 0.0871322,
   0.0970637, 0.0373774, -0.0644128, -2.22045×10^-16, 0.0200591, 0.00428173, -0.0835686, -0.130916, -0.07541, 0.,
   0.0927627, 0.106212, -0.0208529, 0.0533684, 0.0395783, 0., -0.0890275, -0.0878765, -0.0184314, 0.0203208, 0.0217182},
 BestFitParameters → {theta1 → 6.×10^9, theta2 → 5.×10^9, theta3 → 9.×10^8, beta1 → 103212., beta2 → 106697., beta3 → 168025.},
 PredictedResponse → {1., 0.979071, 0.938928, 0.882766, 0.831119, 0.783626, 1., 0.96053,
   0.887668, 0.792036, 0.710623, 0.641313, 1., 0.928391, 0.804988, 0.660569, 0.553616, 0.47441, 1.,
   0.875637, 0.685508, 0.503253, 0.397632, 0.336422, 1., 0.795028, 0.538877, 0.363431, 0.296679, 0.271282},

                              Estimate       Asymptotic SE       CI
                     theta1   6.×10^9        0.000164471         {6.×10^9, 6.×10^9}
                     theta2   5.×10^9        0.000989158         {5.×10^9, 5.×10^9}
 ParameterCITable →  theta3   9.×10^8        1.68786×10^-10      {9.×10^8, 9.×10^8}   }
                     beta1    103212.        352.284             {102485., 103939.}
                     beta2    106697.        1252.63             {104112., 109282.}
                     beta3    168025.        0.0000386564        {168025., 168025.}
```

Figure 4.2.1.9 Matemática 4.1 code for model fitting algorithm according to Li et al. model. $Theta_i$ represent the values of the frequency factors k^o_i and $beta_i$ are the Activation Energies Ea_i of the reactions involved in the mechanism.

In figure 4.2.1-10 the experimental points of the COD/COD$_o$ measured during the WO carried out within a temperature range of 160-200 ºC are depicted. In the same plot but marked with lines, the values of the ratio calculated from the results of the simulation applied to equation 4.2.1-11 are shown. From the plot it can be observed that the calculated values presented the same tendency as the experimental ones throughout the duration of the reaction. However, differences can be noted for example at the lowest temperature, 160 ºC, where the model and the posterior simulation give rise to values of the COD/COD$_o$ lower than the ones observed experimentally. The opposite tendency can be seen from the results at 180 ºC, where the calculated values of the ratio are higher than the experimental ones. This leads to the conclusion that the model can predict to some extent the evolution of the COD removal but with some lack of precision.

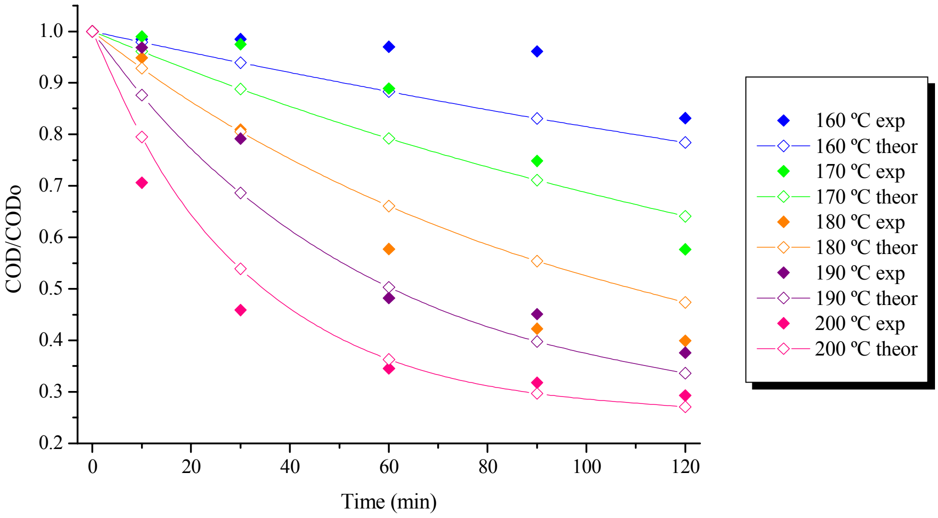


Figure 4.2.1-10 Experimental and Calculated values of the ratio COD/CODo. WO at different temperatures maintaining the Po$_2$ at 10 bar. Values obtained experimentally and theoretically using simulation software Mathematica and kinetic model of *Li et al. (1991)*.

An additional calculation was made to determine which reaction was apparently the fastest and which one the slowest. This was made taking into account the values of the kinetic parameters (k^o_i and Ea_i) of every reaction at each temperature. The kinetic constants were then calculated on the basis of the frequency factors and activation energies of the model and considering that they follow an Arrhenius equation as shown in equations 4.2.1-5, 6 and 7. In table 4.2.1-3 the values of the kinetic constants at each temperature are shown. In this table, it can be seen that the highest value corresponds to reaction 1 (direct mineralization of the initial matter to CO_2 and H_2O) and that the lowest is reaction 3 (mineralization of the intermediate compounds). This means, that when treated by wet oxidation the matter contained in this type of wastewater tends, in the first place to be oxidized directly and completely and in the second place it tends to form intermediate compounds which are more difficult to oxidize ($k_1 < k_2 < k_3$).

Table 4.2.1-3 Kinetic Constants of reactions 1, 2 and 3 for WO of pulp and paper mill nanofiltration concentrate wastewater according to Li et al. model.

T **k_i**	**160 ºC**	**170 ºC**	**180 ºC**	**190 ºC**	**200 ºC**
k_1 (min^{-1})	$2.12\ 10^{-3}$	$4.11\ 10^{-3}$	$7.53\ 10^{-3}$	$1.36\ 10^{-2}$	$2.4\ 10^{-2}$
k_2 (min^{-1})	$6.72\ 10^{-4}$	$1.31\ 10^{-3}$	$2.49\ 10^{-3}$	$4.58\ 10^{-3}$	$8.23\ 10^{-3}$
k_3 (min^{-1})	$5\ 10^{-12}$	$1.44\ 10^{-11}$	$3.93\ 10^{-11}$	$1.03\ 10^{-10}$	$2.59\ 10^{-10}$

Due to the fact that the model of Li et al., allowed only an estimated prediction of parameters such as the TOC, TOD or COD (being the COD the parameter used for the previous simulation), the model of Verenich and Kallas was also taken under study in order to determine kinetic parameters that will allow the prediction of the biodegradability tendency throughout the reactions.

Lumped Kinetic Model for Wastewater Organic Burden Biodegradability Prediction Verenich and Kallas (2000).

This model, proposed by Verenich and Kallas (*Verenich and Kallas, 2000*), is characterized, mainly, because it evaluates the changes in the biodegradability of the wastewater during the oxidation. These changes are important for the applicability of further biological processing, which is an economic way to reduce the organic load of the water. The present model, based on these qualities, assumes the WO mechanism depicted in figure 4.2.1-11.

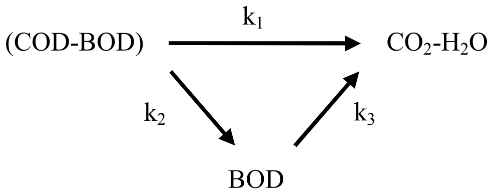


Figure 4.2.1-11 Scheme of the WO reaction mechanism suggested by the model of Verenich and Kallas.

According to this reaction pathway, the difference between the total organics measured via COD and biodegradable compounds described by BOD represents the refractory initial organic compounds. Their oxidation is assumed to proceed in two parallel ways: through the first one, they are oxidized to the end products of the reaction; through the second one, the matter contained in the waste stream is partially oxidized and turns into biodegradable. The biodegradable compounds are further oxidized to end products, i.e. carbon dioxide and water. When comparing this model with the one proposed by Li et al. (previously explained) it is important to notice that both kinetics models are based on a three-reaction scheme, however they differ in the description of the compounds contained in each one of the reactant groups and consequently, the equations describing both models are similar but not equal. Assuming that the reactor follows the model of an isothermal and ideal batch reactor Verenich and Kallas suggested the rate equations for the oxidation of each category of organics, see equations 4.2.1-12 and 4.2.1-13. It is necessary to emphasize that the rate of the reaction for the organic matter is considered of first order, in agreement with the models presented by Li et al. (1991) and Zhang and Chuang (1999).

$$-\frac{d[(\mathrm{COD}-\mathrm{BOD})]}{dt}=(k_1+k_2)[(\mathrm{COD}-\mathrm{BOD})] \tag{Equation 4.2.1-12}$$

$$-\frac{d[\mathrm{BOD}]}{dt}=k_3[\mathrm{BOD}]-k_2[(\mathrm{COD}-\mathrm{BOD})] \tag{Equation 4.2.1-13}$$

Where k_1, k_2 and k_3 are described as follows:

$$k_1=k_1^o\, e^{\frac{-Ea_1}{RT}}[O_2]^{n1} \tag{Equation 4.2.1-14}$$

$$k_2=k_2^o\, e^{\frac{-Ea_2}{RT}}[O_2]^{n2} \tag{Equation 4.2.1-15}$$

$$k_3=k_3^o\, e^{\frac{-Ea_3}{RT}}[O_2]^{n3} \tag{Equation 4.2.1-16}$$

At time *t= 0* the initial concentration of the refractory and the biodegradable compounds are $[(\mathrm{COD\text{-}BOD})]_o$ and $[\mathrm{BOD}]_o$, respectively. The integration of differential equations 4.2.1-12 and 4.2.13 produces expressions 4.2.1-17 and 4.2.1-18, respectively.

$$[(COD - BOD)] = [(COD - BOD)]_o e^{-(k_1+k_2)t} \qquad \text{Equation 4.2.1-17}$$

$$[BOD] = [BOD]_o e^{-k_3 t} + \frac{k_2[(COD - BOD)]_o}{k_1 + k_2 - k_3}\left(e^{-k_3 t} - e^{-(k_1+k_2)t}\right) \qquad \text{Equation 4.2.1-18}$$

Combining equations 4.2.1-17 and 4.2.1-18 the COD content of the water can be expressed as follows:

$$[COD] = [BOD]_o e^{-k_3 t} + [(COD - BOD)]_o \left(\frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{(k_1 - k_3)}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)} \right) \qquad \text{Equation 4.2.1-19}$$

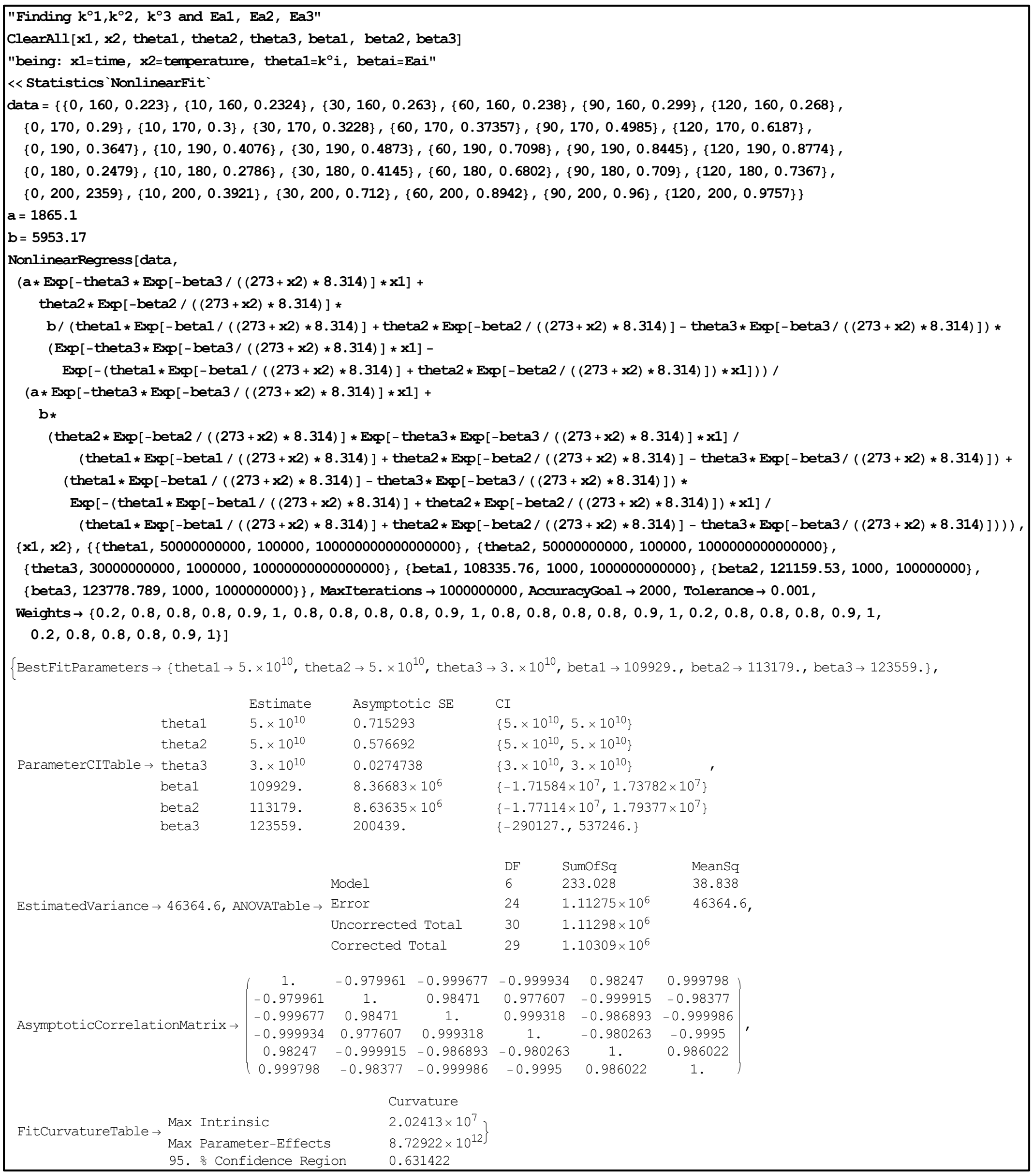
The simulation was in this case made by using equations 4.2.1-18 and 19 and calculating the ratio BOD/COD. The values of the ratio obtained experimentally and the theoretical ones were calculated in order to find the values of the kinetic parameters, activation energies and frequency factors. As in the previous model, the modeling was based on finding the minimum square difference between the experimental and calculated data. A first initial solution was found with Excel tool Solver, which was employed as a starting point for the simulation with Mathematica 4.1 software. The statistic parameters of Solver and Mathematica were the same as the ones used for the simulation with Li et al. model.

After running the simulation with Mathematica, the values of the frequency factors and activation energies shown in table 4.2.1.4 were obtained. From these results, it can be affirmed that even though the standard error related to the frequency factor is rather small, the ones related to the activation energies are much higher and consequently, considerable differences can be observed when comparing the experimental and the calculated values of the ratio BOD/COD.

Table 4.2.1-4 Frequency Factors and Activation Energies of reactions 1, 2 and 3 for WO of pulp and paper mill nanofiltration concentrate wastewater according to Verenich and Kallas model determined by simulation using Mathematica software.

	Frequency Factors “ki” (L mol^{-1} min^{-1})	
k^o_1	k^o_2	k^o_3
$5\ 10^{10} \pm 0.72$	$5\ 10^{10} \pm 0.58$	$3\ 10^{10} \pm 0.03$
	Activation Energies “Eai” (kJ mol^{-1})	
Ea_1	Ea_2	Ea_3
$110\ 10^3 \pm 8.3\ 10^6$	$113.1\ 10^6 \pm 8.6\ 10^6$	$123.6\ 10^3 \pm 2\ 10^{-6}$

Figure 4.2.1-12 shows the Mathematica code for the model fitting algorithm. It can be observed that a maximum number of iterations of 10^{10}, an accuracy goal of 2000 and a tolerance close to 0.001 were established. In addition, an in order to obtain more precise results, different weight was given to the different points of the experiments.



```
"Finding k°1,k°2, k°3 and Ea1, Ea2, Ea3"
ClearAll[x1, x2, theta1, theta2, theta3, beta1, beta2, beta3]
"being: x1=time, x2=temperature, theta1=k°i, betai=Eai"
<< Statistics`NonlinearFit`
data = {{0, 160, 0.223}, {10, 160, 0.2324}, {30, 160, 0.263}, {60, 160, 0.238}, {90, 160, 0.299}, {120, 160, 0.268},
  {0, 170, 0.29}, {10, 170, 0.3}, {30, 170, 0.3228}, {60, 170, 0.37357}, {90, 170, 0.4985}, {120, 170, 0.6187},
  {0, 190, 0.3647}, {10, 190, 0.4076}, {30, 190, 0.4873}, {60, 190, 0.7098}, {90, 190, 0.8445}, {120, 190, 0.8774},
  {0, 180, 0.2479}, {10, 180, 0.2786}, {30, 180, 0.4145}, {60, 180, 0.6802}, {90, 180, 0.709}, {120, 180, 0.7367},
  {0, 200, 2359}, {10, 200, 0.3921}, {30, 200, 0.712}, {60, 200, 0.8942}, {90, 200, 0.96}, {120, 200, 0.9757}}
a = 1865.1
b = 5953.17
NonlinearRegress[data,
 (a * Exp[-theta3 * Exp[-beta3 / ((273 + x2) * 8.314)] * x1] +
    theta2 * Exp[-beta2 / ((273 + x2) * 8.314)] *
     b / (theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] + theta2 * Exp[-beta2 / ((273 + x2) * 8.314)] - theta3 * Exp[-beta3 / ((273 + x2) * 8.314)]) *
     (Exp[-theta3 * Exp[-beta3 / ((273 + x2) * 8.314)] * x1] -
       Exp[-(theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] + theta2 * Exp[-beta2 / ((273 + x2) * 8.314)]) * x1])) /
  (a * Exp[-theta3 * Exp[-beta3 / ((273 + x2) * 8.314)] * x1] +
    b *
     (theta2 * Exp[-beta2 / ((273 + x2) * 8.314)] * Exp[-theta3 * Exp[-beta3 / ((273 + x2) * 8.314)] * x1] /
         (theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] + theta2 * Exp[-beta2 / ((273 + x2) * 8.314)] - theta3 * Exp[-beta3 / ((273 + x2) * 8.314)]) +
       (theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] - theta3 * Exp[-beta3 / ((273 + x2) * 8.314)]) *
        Exp[-(theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] + theta2 * Exp[-beta2 / ((273 + x2) * 8.314)]) * x1] /
         (theta1 * Exp[-beta1 / ((273 + x2) * 8.314)] + theta2 * Exp[-beta2 / ((273 + x2) * 8.314)] - theta3 * Exp[-beta3 / ((273 + x2) * 8.314)]))),
 {x1, x2}, {{theta1, 50000000000, 100000, 100000000000000000}, {theta2, 50000000000, 100000, 1000000000000000},
  {theta3, 30000000000, 1000000, 10000000000000000}, {beta1, 108335.76, 1000, 10000000000000}, {beta2, 121159.53, 1000, 100000000},
  {beta3, 123778.789, 1000, 1000000000}}, MaxIterations → 1000000000, AccuracyGoal → 2000, Tolerance → 0.001,
 Weights → {0.2, 0.8, 0.8, 0.8, 0.9, 1, 0.8, 0.8, 0.8, 0.8, 0.9, 1, 0.8, 0.8, 0.8, 0.8, 0.9, 1, 0.2, 0.8, 0.8, 0.8, 0.9, 1,
   0.2, 0.8, 0.8, 0.8, 0.9, 1}]

{BestFitParameters → {theta1 → 5. × 10^10, theta2 → 5. × 10^10, theta3 → 3. × 10^10, beta1 → 109929., beta2 → 113179., beta3 → 123559.},

                              Estimate      Asymptotic SE     CI
                    theta1    5. × 10^10    0.715293          {5. × 10^10, 5. × 10^10}
                    theta2    5. × 10^10    0.576692          {5. × 10^10, 5. × 10^10}
 ParameterCITable → theta3    3. × 10^10    0.0274738         {3. × 10^10, 3. × 10^10}          ,
                    beta1     109929.       8.36683 × 10^6    {-1.71584 × 10^7, 1.73782 × 10^7}
                    beta2     113179.       8.63635 × 10^6    {-1.77114 × 10^7, 1.79377 × 10^7}
                    beta3     123559.       200439.           {-290127., 537246.}

                                                              DF     SumOfSq           MeanSq
                                          Model               6      233.028           38.838
 EstimatedVariance → 46364.6, ANOVATable → Error              24     1.11275 × 10^6    46364.6,
                                          Uncorrected Total   30     1.11298 × 10^6
                                          Corrected Total     29     1.10309 × 10^6

                                   (    1.      -0.979961  -0.999677  -0.999934   0.98247    0.999798 )
                                   ( -0.979961     1.       0.98471    0.977607  -0.999915  -0.98377  )
 AsymptoticCorrelationMatrix →     ( -0.999677   0.98471      1.       0.999318  -0.986893  -0.999986 ) ,
                                   ( -0.999934   0.977607   0.999318      1.     -0.980263  -0.9995   )
                                   (  0.98247   -0.999915  -0.986893  -0.980263     1.       0.986022 )
                                   (  0.999798  -0.98377   -0.999986  -0.9995     0.986022      1.    )

                                             Curvature
                    Max Intrinsic            2.02413 × 10^7  }
 FitCurvatureTable → Max Parameter-Effects   8.72922 × 10^12 }
                    95. % Confidence Region  0.631422
```

Figure 4.2.1-12 Mathematica code for the model fitting algorithm according to Verenich and Kallas model. Theta$_i$ represent the values of the frequency factors k^o_i and beta$_i$ are the Activation Energies Ea$_i$ of the reactions involved in the mechanism.

As done with the first model studied, i.e., the model of Li et al., the experimental and calculated values concerning the model of Verenich and Kallas are represented in figure 4.2.1-13. In this plot, it can be observed that the experimental and the theoretical values follow a similar tendency. For instance, the lowest predicted biodegradability coincides with the lowest values obtained experimentally, and the highest values obtained theoretically coincide as well with the highest observed when carrying out the experiments. However, a certain level of precision can not be ensured when estimating the values of the biodegradability throughout the reactions. When comparing both models it is difficult to discern which one fits better the experimental data, or in other words, which one is able to give a better prediction of the reality. However, what can be observed at first sight is that both models show a bad prediction at the lowest temperature, i.e., 160 ºC and unfortunately it can not be affirmed whether this error is due to lack of experimental precision or as a consequence of an intrinsic problem of the model.

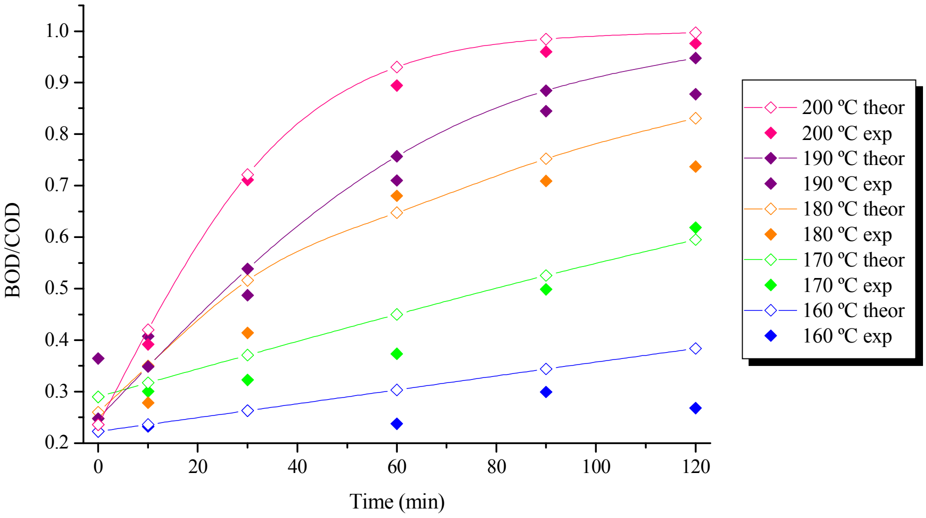


Figure 4.2.1-13 Experimental and Calculated values of the ratio BOD/COD. WO at different temperatures maintaining the Po_2 at 10 bar. Values obtained experimentally and theoretically using simulation software Mathematica and kinetic model of Verenich and Kallas.

The error that both models presented at each point of each experiment was calculated according to equation 4.2.1-20. The maximum individual error found in the prediction given from the model of Li et al. was found at time 90 min of the WO carried out at 180 ºC. This maximum error had a value in the vicinity of 25 %. On the other hand, the maximum individual error found from the Verenich and Kallas model was circa 30 % and was obtained at 90 minutes of reaction at 190 ºC. However, the individual errors are not enough to decide which model fits better the experimental data and, for this purpose, an average error was calculated for both models according to equation 4.2.1-21.

$$\text{Individual Error (\%)} = \text{Abs}\left[\frac{(\text{Experimental Value} - \text{Theoretical Value})}{\text{Experimental Value}}\right] * 100$$

Equation 4.2.1-20

$$\text{Average Error (\%)} = \sum \frac{\text{Individual Error (\%)}}{\text{number of experiments}}$$

Equation 4.2.1-21

The error showed by the Li et al model was 7.68 %, meanwhile the model of Verenich and Kallas had an average error of 11.61 %. Consequently, the model of Li et al., appears to give a more precise reproduction of what happens in the reactor concerning the COD removal. However, it should be emphasized that the model of Verenich and Kallas provides more information about the system since it predicts not only the COD but also the BOD.

4.2.2 EVAPORATION CONCENTRATE OF DEBARKING WATER

As explained in section 3.1.4, the operating procedure used in this experimentation differed to some extent from the one followed when implementing the rest of the experiments. These differences consisted mainly of the use of an external pipette, which allowed the introduction of the wastewater into the reactor just when the desired temperature was reached, avoiding this way the pre-heating period. The wastewater then, was mixed with the 250 mL of warm distilled water of the reactor and, as a consequence of the differences in the temperature of both solutions, some more minutes were needed in order to reach the desired temperature again. After opening the oxygen line, the reaction was allowed to evolve for two hours and during this period of time several samples were withdrawn from the reactor at times: 10, 30, 60, 90 and 120 minutes. These samples were analyzed for COD, BOD and Volatile Acids. The results of the analysis of the samples of the reactions at each temperature are shown in tables 4.2.2-1 to 4.2.2-4 of Appendix II.

In figure 4.2.2-1 the COD removal measured throughout the reaction is depicted versus the time. In this plot it can be observed that the higher the temperature the higher the COD removal. This is explained taking into account that the oxidation reaction rates follows an Arrehnius type equation and consequently they are favored by the increase of the temperature.

Another remarkable fact is that in none of the experiments a COD removal higher than 30 % was achieved. Actually, a 21.7 %, 24.07 %, 26.78 % and 28.8 % of COD removals were obtained when carrying out the reactions at 170, 180, 190 and 200 ºC respectively. Due to the low organic load removal achieved it is necessary to analyze the evolution of the biodegradability over the duration of the reaction in order to be able to discern whether the range of temperatures studied was appropriate or if higher temperatures or some catalyst might be necessary.

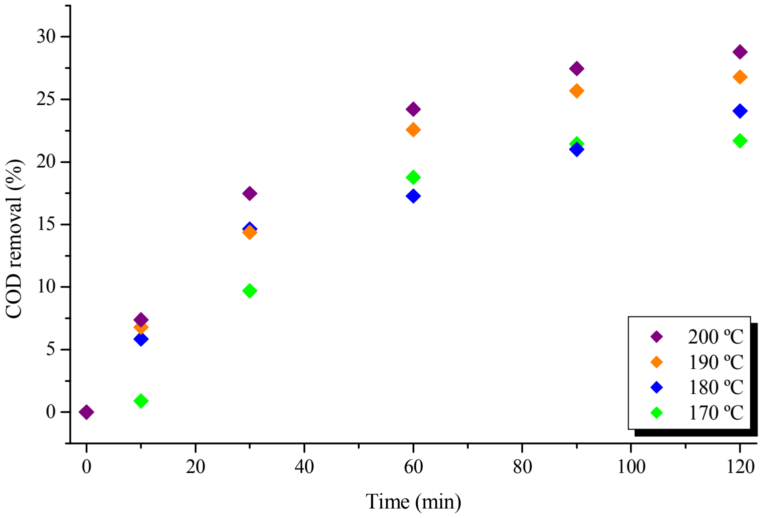


Fig. 4.2.2-1 COD removal vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

The results of the biodegradability, calculated as the ratio between the BOD_5 and the COD, are depicted in figure 4.2.2-2. In this plot, it can be observed that all the series of experiments followed the same tendency. From the first minutes of the reaction, the biodegradability tended to increase, then it reached a maximum and finally it started decreasing. The initial increase in the biodegradability is explained by assuming that at the beginning of the reaction there is a continuous formation of intermediate compounds which are highly biodegradable. In addition, and as it can be seen from picture 4.2.2-1, during the first hour of the reaction the COD diminished in a range between 15 and 25 %. What was observed after the first hour of reaction was the decrease in the biodegradability. This fact is explained by taking into account that from this time on, the oxidizing agent started to attack the biodegradable intermediates transforming them into less complex compounds or directly to CO_2 and H_2O. The decrease in the biodegradability can be thus explained by the degradation of the intermediate compounds.

Two different aspects should be evaluated, when trying to decide which temperature is more favorable to treat this type of wastewater, the COD and the biodegradability. It was previously discussed that the highest COD removal was attained when working at 200 ºC, so, according to the first criteria this temperature would be the most appropriate. However, the highest biodegradability was observed at 170 ºC. Usually it would be expected to attain the highest biodegradability at the highest temperature, however the refractory properties of the intermediate compounds to be oxidized must be taken into consideration. As it has been reported in the literature, the intermediate compounds generated during the oxidation are more difficult to be oxidized than the original components. According to this, the higher the temperature of the reaction, the faster the degradation of the intermediates, and thus, the lower the biodegradability. Consequently, the highest biodegradability was attained by the WO at 170 ºC because at this temperature it took longer to degrade the intermediate compounds and thus, they remained longer in the reactor.

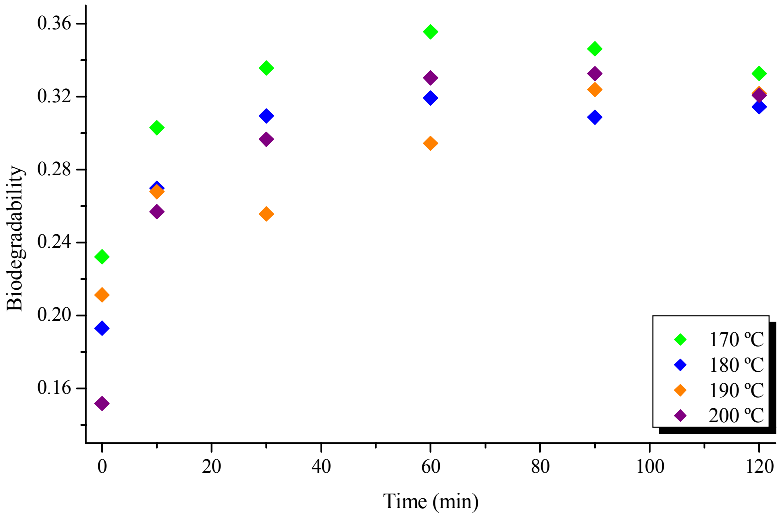


Fig. 4.2.2-2 Biodegradability vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

At this point, it is interesting to mention that according to the literature (*Tchobanoglous and Burton, 1991*) a municipal wastewater can be considered biodegradable when the biodegradability is higher or equal than 0.4. It is obvious that this value is not applicable for this case because in here industrial wastewaters are being treated. However, it is important to notice that when working at 170 ºC the biodegradability attained is close to 0.4.

The generation of volatile acids was calculated from the measured values of the volatile acids concentration. The generation of these acids is defined as the ratio between the difference in the concentration of the acids at time 0 and at any time and the initial concentration (equation 4.2.2-1).

$$\text{Generation of Volatile Acids} = \frac{[\text{Volatile Acids}]_t - [\text{Volatile Acids}]_o}{[\text{Volatile Acids}]_o} \qquad \text{Equation 4.2.2-1}$$

The volatile acids concentration measurement appeared to be an interesting tool because it provides information about the evolution of the final intermediates formed during the reaction and also about the biodegradability throughout the oxidation. The relationship between the formation of Low Molecular Weight Acids (LMWA) and the biodegradability is due to the biodegradable nature of these compounds. In figure 4.2.2-3 the evolution of the volatile acids generation versus the time of the reaction is depicted.

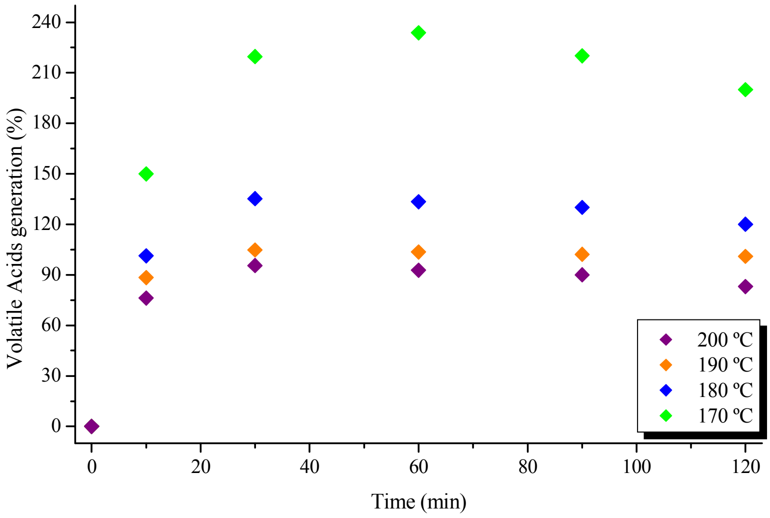


Fig. 4.2.2-3 Generation of Volatile Acids vs. Time. WO reactions at 10 bar of Po_2 and different temperatures.

In this plot, it can be observed that the volatile acids concentration values are in agreement with the measured biodegradability since the highest acid concentration was achieved once more at the lowest temperature. Consequently, it has been proved that the most suitable temperature to treat this type of concentrated wastewater is 170 ºC since the incorporation of a biological post-treatment is most favored and the difference in the COD removal achieved at the end of the reaction when comparing with higher temperatures is only about 15 % lower.

4.3 ULTRAFILTRATION OF MODEL SOLUTIONS

This section about ultrafiltration was thought to be interesting for this thesis because one of the possible industrial applications of the wet oxidation technology remains in the use of a membrane process previous to the oxidation. By means of this combination of processes, the concentrated effluent obtained from the membrane unit is treated by wet oxidation, which is more economically viable when treating concentrated solutions, favoring this way the economy of the whole process.

This investigation was specially focused on the parameters that can influence the good performance of the membrane units, i.e., the parameters that are thought to cause the deterioration of the membrane and flux decline, as a consequence of phenomenon known as concentration polarization and membrane fouling. Concentration polarization can be minimized by introducing the feed effluent tangentially to the membrane and by maintaining a high agitation on the surface of the membrane, so that accumulations on it are unlikely to happen. Among fouling, membrane surface fouling and internal pore fouling can be distinguished. The former is usually reversible and can be remedied with the use of chemical cleaners or back flushing. On the other hand, pore fouling might be irreversible and therefore, efforts should concentrate in avoiding it or at least minimizing it.

Due to the importance of fouling, before starting an ultrafiltration process design, emphasis should be put on studying all the parameters affecting its performance. These can be divided into the factors related to the membrane itself and the factors related to the filtration process conditions. Membrane parameters can be classified into two categories: physical-chemical parameters (pore size, porosity, skin thickness, surface roughness and charge, zeta potential and contact angle) and functional parameters such as membrane permeability, solute sieving and mechanical strength (*Cuperus and Smolders, 1991*). From a practical perspective, the functional parameters determine the suitability of a membrane for a particular application (*Mulherkar and Reis, 2004*). On the other hand, the main filtration parameters are the applied pressure and the initial concentration and molecular weight of the substances contained in the feed solution, all of which affect the permeability and the retention of the membrane process.

Regarding the properties of the feed solution, a classification of the fouling provoked can be establish depending on the compounds it contains. Thus, organic fouling, biological fouling, inorganic fouling or scaling and particulate fouling can be distinguished. Inorganic fouling is attributed to precipitate formations on the membrane surface, while particulate fouling is due to colloidal deposition in sub-micron size ranges. Biological fouling is caused by growth and adhesion of microorganisms, while organic fouling is thought to be caused by NOM including humic and fulvic acids as well as proteins and polysaccharides associated with microbial activity (*Tu et al. 2005*). Inherent characteristics of the feed solution, such as the pH and the ionic strength also appear to play a significant role in the process (*Cho et al., 2000; Müller et al, 2003*). In this sense, calcium and phosphates have been directly implicated with membrane fouling due to the formation of insoluble calcium salts, and as possible catalysts or bridging agents between the membrane and solutes (*Matzinos and Álvarez, 2002*). On the other hand, the pH of the solution can have an influence in both, the structure of the molecules contained in the aqueous solution and the surface membrane charge. Ghosh and Schnitzer (*Ghosh and Schnitzer, 1980*) pointed out that while at high pH and low ionic strength, humic acids have a large, flexible and linear shape, at low pH and high ionic strength they turn into a small, rigid and spherical shape. Regarding the effect of pH on the membrane, in the case of a membrane consisting of amine groups, at low pH it will become positively charged, while a membrane containing carboxylic acids will be negatively charged at mid to high pH conditions (*Texeira and Rosa, 2002*).

As mentioned in chapter 3.3.1, solutions containing dextran, cellulose, alginic, humic and fulvic acids, and two different NOM were used as feed effluents for this investigation. Dextran was chosen as a model compound, whereas NOM was taken under investigation because it is considered to be a significant precursor for the formation of mutagenic disinfection by-products (*Petala and Zouboulis, 2006*). NOM is mainly composed from humic substances, such as humic and fulvic acids, which are heterogeneous organic constituents with high molecular weight (*Stevenson, 1982*). Humic acids (HA) consist of a variety of molecular structures, such as alcylaromatic, quinoid and aliphatic in the core, as well as aminoacid or carbohydrate-like structures and carbonyl, carboxyl, phenyl and hydroxyl groups in the periphery (*Stevenson, 1982*).

Regarding the membranes employed for the experiments, the first one had a MWCO of 30 kDa and was made of cellulose, whereas the second and third ones were made of polyethersulfone and had a MWCO of 20 and 5 kDa respectively. One important feature of membranes is the zeta potential since it gives information about the charge of the membrane. When it is lower than zero, the membrane is negatively charged, and when it is higher than zero, the membrane is positively charged. The zeta potential of the 30 and

20 kDa membranes vs. the pH is depicted in Fig. 4.3.1. From this chart it can be concluded that both membranes are negatively charged, and that the charge becomes more negative with the increase of the pH.

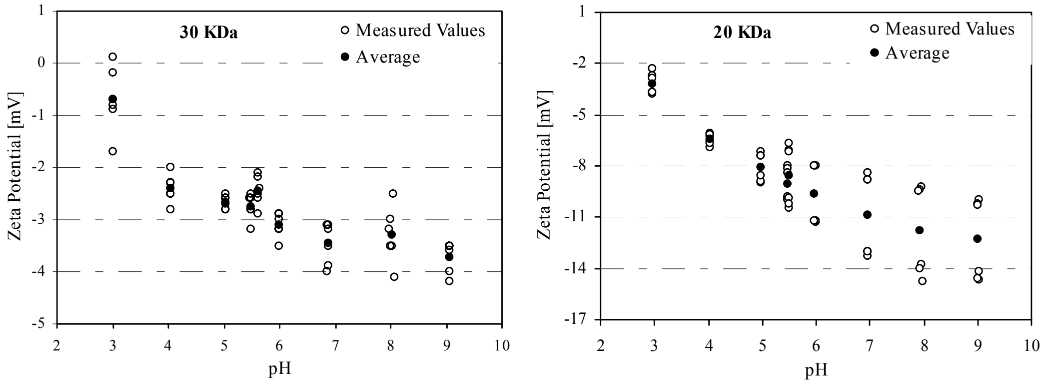


Figure 4.3.1 Zeta Potential vs. pH. 30 kDa and 20 kDa membranes.

4.3.1 INFLUENCE OF THE FEED STREAM CONCENTRATION

To study the influence of the initial concentration, solutions containing 1, 3, 5, 8 and 10 mg/mL of dextran were prepared and ultrafiltrated with 2 different membranes 30 and 20 kDa. The pressure applied in this set of experiments was 1 bar.

From the data measured in each experiment the evolution of the flux, the permeability, and the retention were calculated as follows:

$$\text{Flux} \quad (\text{L}/(\text{m}^2\text{h})) = \frac{\text{Volume of Permeate}}{\text{time} \times \text{Membrane Area}}$$ Equation 4.3.1-1

$$\text{Permeability} \quad (\text{L}/(\text{m}^2\text{hbar})) = \frac{\text{Flux}}{\Delta \text{p}}$$ Equation 4.3.1-2

$$\text{Retention} = 1 - \frac{\text{COD}_{\text{permeate}}}{\text{COD}_{\text{feed}}}$$ Equation 4.3.1-3

The results of the permeability vs. the volume of permeate collected are shown in figures 4.3.1-1 and 2. From these pictures it can be concluded that the flux is higher when working with the 30 kDa membranes since the pores offer a lower resistance than the 20 kDa membrane pores. However, the results of the experiments at the highest concentration, i.e. 10 mg/mL, appear to be of special interest since the flux (or permeability) follows a similar tendency when working with both membranes. This suggests that an increase in the concentration reduces the differences between the two membranes, mainly due to the formation of a fouling layer which controls the filtration.

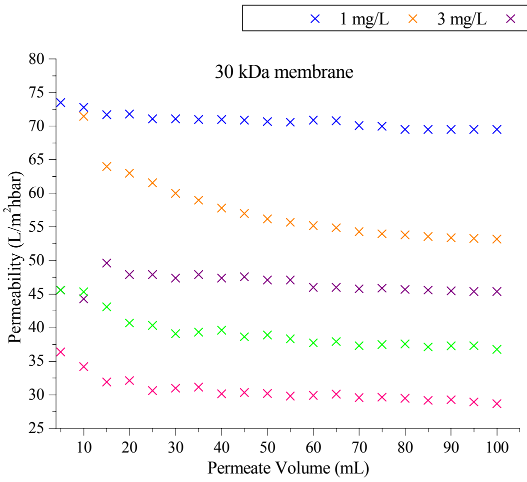


Figure 4.3.1-1 Permeability vs. volume of permeate. 30 kDa membrane.

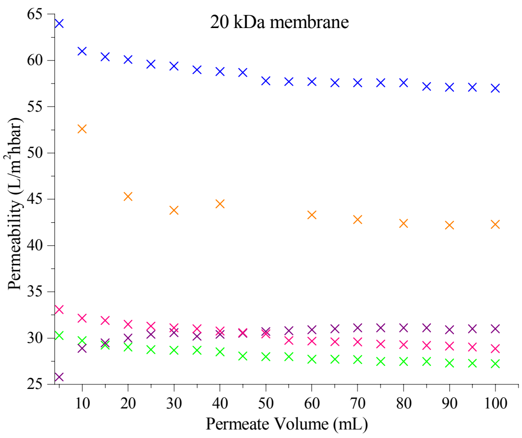


Figure 4.3.1-2 Permeability vs. volume of permeate. 20 kDa membrane.

The results also show an inverse relationship between concentration and flux, as the concentration increases the flux decreases. This is because the higher the concentration, the higher the amount of particles in the solution and therefore, the greater chance that a deposition layer on the surface of the membrane will form. It was also noted that the flux in the 20 kDa membrane decreased when increasing the concentration from 1 to 3 mg/mL, however, when increasing the concentration from 5 to 10 mg/mL no significant differences were observed. This is because when a solution containing 5 mg/mL is ultrafiltrated the 20 kDa membrane is already fouled due to a cake layer formed on the surface. On the other hand, the 30 kDa membrane did not illustrate this behaviour due to the larger membrane pores. From these experiments the retention was calculated according to equation 4.3.1-3.

The values of the retention vs. the concentration of dextran used in each experiment are depicted in Fig. 4.3.1-3. From these results the different tendencies of the 30 kDa and 20 kDa membrane can be seen. The retention of the 30 kDa membrane increased when increasing the concentration of the feed solution, while the retention of the 20 kDa membrane decreased when increasing the initial concentration. The increase in the retention when increasing the initial concentration (as occurs with the 30 kDa membrane) can be explained taking into account that some particles that are able to pass through the pores can get stuck there, provoking a decrease in the pore diameter and thus, making the membrane more selective. The decrease in the retention when increasing the concentration, as seen with the 20 kDa membrane, can be explained by assuming that when the initial concentration increases, a cake layer formation is more likely to happen. When this cake layer forms not only do the particles have difficulties to cross but also the water. This implies that the amount of water in the permeate phase decreases and thus the percentage of particles increases, i.e. the retention decreases.

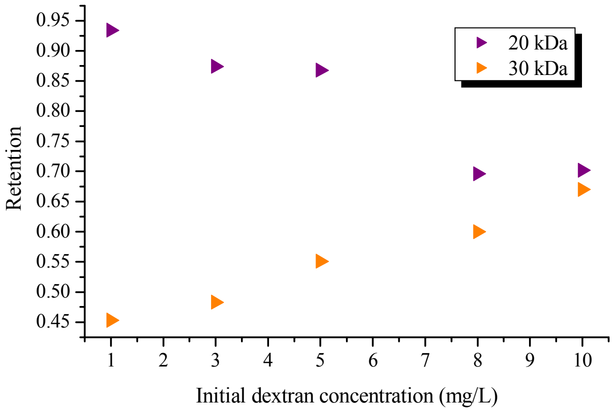


Figure 4.3.1-3 Retention vs. dextran concentration in the initial solution. 30 and 20 kDa membranes.

Similar tests were carried out but using solutions containing cellulose and alginic acid instead of dextran. In both cases the membrane used was the 30 kDa. On one hand and regarding the effect of the cellulose concentration on the membrane performance, it was found out that when working within a range of initial concentration from 1 to 10 mg/L, the membrane behaves in a similar way. However, attention must be drawn to the fact that during the course of the filtration (independently of the chosen initial concentration) the permeability decreased from an initial value in the vicinity of 340 $Lm^{-2}h^{-1}bar^{-1}$ to a final value between 240 and 260 $Lm^{-2}h^{-1}bar^{-1}$. This can be explained by taking into account the small size of the cellulose molecules compared to the pores of the membrane. Solutions containing alginic acid were also evaluated concerning the influence of its initial concentration in the feed solution on the UF process. The selected concentrations for these experiments were 3 and 0.3 mg/mL. The results of these tests are depicted in Fig. 4.3.1-4. As opposite to UF of cellulose solutions, differences regarding the permeability were observed. In this case, a remarkable decrease in the permeability was observed when increasing the concentration of the feed solution from 0.3 to 3 mg/mL. This fact can be explained considering that the phenomenon called concentration polarization, i.e. cake layer formation, is more probable to happen when working with highly concentrated solutions. According to this, the more concentrated solutions, the more pronounced decay in the flux. The retention attained when working with the highest concentrated solution was in the vicinity of 100% whereas with the lowest, the retention was 96%. The increase in the retention when increasing the initial concentration can be explained taking into account that some molecules adsorb at the membrane material, provoking a decrease in the pore diameter and consequently, making the membrane more selective.

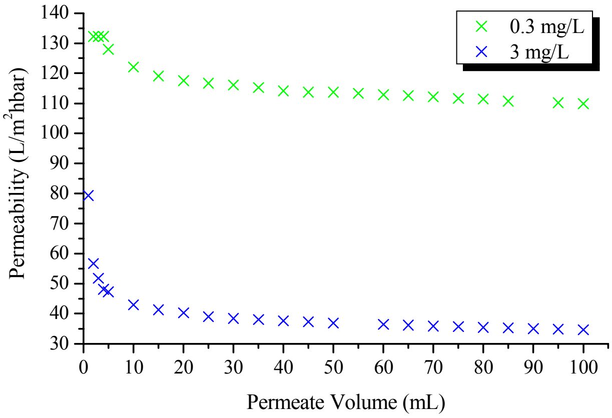


Figure 4.3.1-4 Permeability vs. volume of permeate. Initial solutions containing 3 and 0.3 mg/L of alginic acid. 30 kDa membrane.

4.3.2 INFLUENCE OF THE TRANSMEMBRANE PRESSURE

To conduct an investigation about the effect of the transmembrane pressure, UF experiments of solutions containing dextran, humic and fulvic acids, NOM 1R101N and NOM 1R108N were performed. The membrane used was the 30 kDa when working with dextran solutions and 5 kDa when working with the other polymers. The chosen initial concentration of dextran was 3mg/mL whereas for the rest of the compounds an initial solution containing 10 mg/L was employed. Transmembrane pressures ranging from 1 to 3 bar were applied to these feed solutions. After carrying out these UF experiments it was observed that the flux tended to increase as the applied pressure increased. This can be understood by considering that the transmembrane pressure is the driven force of the process and consequently, the higher the pressure, the higher the amount of solution which is able to pass through the membrane per unit of time. However, the permeabilities decreased when increasing the applied pressure. This fact can be explained by taking into account that the permeability is defined as the ratio between the flux and the transmembrane pressure. As it was experimentally observed, a higher pressure results in a higher flux, however, the increase in the pressure is higher that the related increase of the flux and consequently, an increase of the pressure results in a decrease in the ratio flux/pressure.

As an example, the results of the flux and permeability obtained when ultrafiltrating fulvic acid solutions with the 5 kDa membrane at different transmembrane pressures are shown in figures 4.3.2-1 and 2. According to this, it would appear that an increase of the driven force might provoke a higher efficiency of the whole process since more permeate is obtained per unit of time. However the influence that an increase of the pressure can have in the retention obtained at the end of the filtration can not be despised.

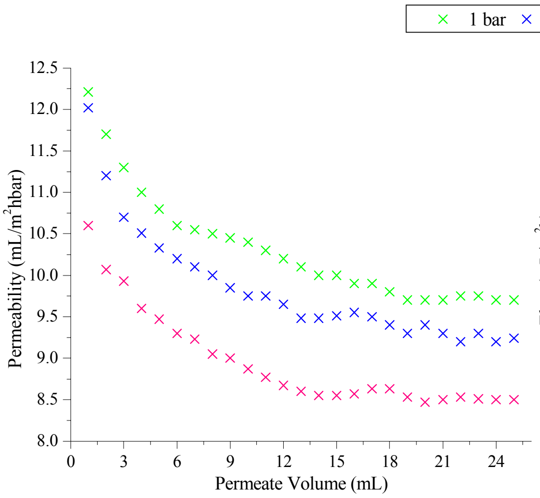


Figure 4.3.2-1 Permeability vs. volume of permeate. Initial solutions containing 10 mg/L of fulvic acid.

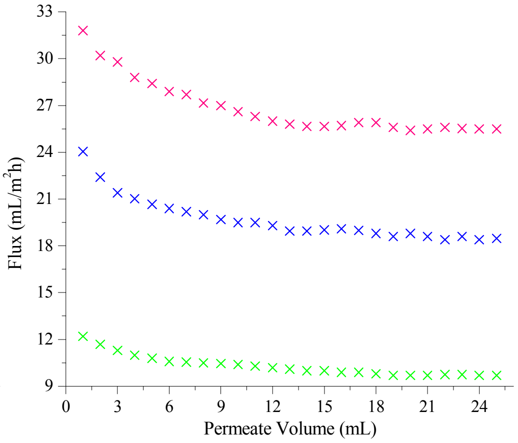


Figure 4.3.2-2 Flux vs. volume of permeate. Initial solutions containing 10 mg/L of fulvic acid.

Table 4.3.2-1 shows the influence of the applied pressure on the retention achieved at the end of the ultrafiltration experiments of the solutions containing the dextran and the two different NOM. In all the cases it can be observed that the highest retention was attained when working at the lowest pressure. This is due to two different phenomena. In the first place an increase in the pressure provokes a higher amount of solution crossing the membrane. Since the solution contains water and the molecules, a higher pressure results in a higher amount of molecules in the permeate at the end of the filtration. On the other hand, high fluxes favour the concentration polarization on the membrane surface. As a result of this phenomenon, the concentration difference between both sides of the membrane increases, therefore, the diffusion driven force increases and more particles cross the membrane.

Table 4.3.2-1 Retention values attained at the end of UF experiments of solutions containing NOM and dextran at different transmembrane pressures.

	1 bar	1.5 bar	2 bar	2.5 bar	3 bar
NOM 1R101N (10 mg/mL)	0.65		0.57		0.45
NOM 1R108N (10 mg/L)	0.62		0.44		0.27
Dextran (3 mg/mL)	0.48	0.36	0.29	0.28	0.25

4.3.3 INFLUENCE OF THE PH OF THE FEED SOLUTION

The pH conditions under which UF proceeds has been reported to be a determining aspect under certain operating parameters. To study whether pH has an influence or not during the course of the UF of solutions containing polymers some tests have been effectuated. Experiments with solutions containing polymers at different pHs, maintaining the applied pressure at 1 bar and working with the 30 and 5 kDa membrane were performed. Detailed information of the operating conditions of these experiments is given in table 4.3.3-1.

Before starting the discussion of the obtained results of this investigation, it is important to mention the possible influence that the pH of the solution can have in the performance of UF units. Two important aspects must be taken into account. On one side there is the influence of the pH on the surface charge and on the other side the influence of the pH on the charge and structural properties of the substances contained in the solution to be filtrated. Regarding the surface charge of the membranes used in this investigation, it was found out that the higher the pH of the solution, the more negatively charged the membrane becomes. If the particles contained in the solution are positively charged, then, the obstruction of the membrane pores will be more likely to happen as a result of the higher attraction between positive and negative charges. On the other hand, certain molecules have different structures depending on the pH which may difficult or facilitate its pass through the membrane, being this the case of humic acids, previously explained.

Table 4.3.3-1 Operating parameters (feed, membrane, pH and buffer solution) employed in each one of the experiments made to determine the influence of the pH of the initial solution in the UF.

Feed	Membrane	pH	Buffer solution
10 mg/L NOM 1R101N	5 kDa	3	Hydrogenphtalate of potassium + HCl
		7	$KH_2PO_4 + Na_2HPO_4$
10 mg/L NOM 1R108N		3	Hydrogenphtalate of potassium + HCl
		7	$KH_2PO_4 + Na_2HPO_4$
10 mg/L Humic Acid		3	Hydrogenphtalate of potassium + HCl
		7	$KH_2PO_4 + Na_2HPO_4$
10 mg/L Fulvic Acid		3	Hydrogenphtalate of potassium + HCl
		7	$KH_2PO_4 + Na_2HPO_4$
3 mg/mL Dextran	30 kDa	4.7	$KH_2PO_4 + Na_2HPO_4$
		6	
		8	
		9.8	$Na_2CO_3 + NaHCO_3$

In figure 4.3.3-1, the flux obtained throughout the UF of solutions containing dextran at different pH conditions is depicted. From this plot it can be concluded, that the flux was lower at a pH close to 5 than at the rest of the pH studied. This fact can be easily understood by considering the deprotonation of dextran and the charge of the membrane. On one side, the higher the pH, the more deprotonated the dextran; consequently the negatively charged specie is the predominant in the solution. On the other hand, and according to the Zeta Potential measurements of the 30 kDa membrane, and increase in the pH of the solution results in an increase in the negative charge of the membrane. As a result of these two facts, at high pH, both the particles and the membrane are negatively charged, provoking the repulsion between them and making the fouling of the membrane less favourable. The flux of water through the membrane is then lower at the lowest pH conditions because the electrostatic repulsion is poor and thus, pore blocking is more likely to happen under this pH conditions.

Similar results were obtained when ultrafiltrating solutions containing the two NOM and the humic and fulvic. The pH chosen for this investigation were 3 and 7 and the membrane used was the one with a MWCO of 5 kDa due to the smaller size of the particles. It was observed that at low pH the fluxes were lower than at high pH. As it happened with the dextran solutions, at low pH the functional groups from the molecules are non-dissociated and their surface charge is weak. Consequently, electrostatic repulsion is poor, not only between the molecules but also between the molecules and the membrane surface. In figure 4.3.3-2 the normalized flux obtained over the duration of the UF of solutions containing the two different NOMs at pH 3 and 7 is shown. The normalized flux was calculated as the ratio between the flux of NOM attained at any time and the flux obtained using distilled water at the same time using the same membrane. As it was previously discussed, the fluxes were higher when operating with the higher pH solution.

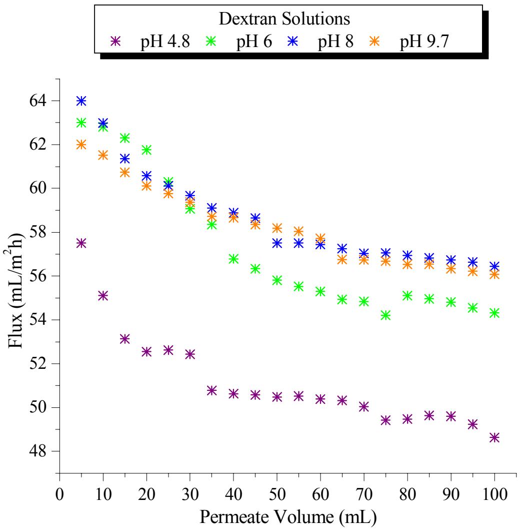


Figure 4.3.3-1 Flux vs. volume of permeate. UF of dextran solutions at different pH conditions. 30 kDa membrane.

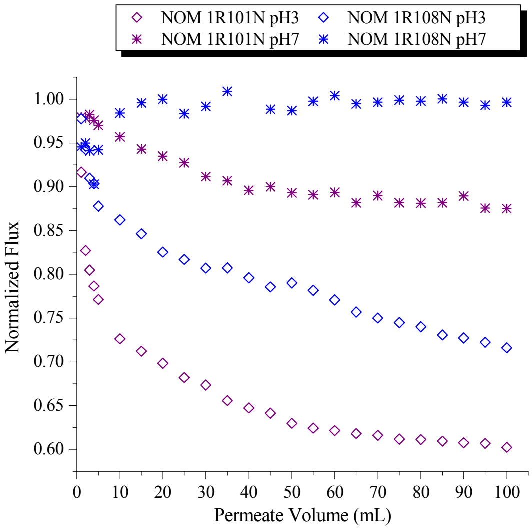


Figure 4.3.3-2 Flux vs. volume of permeate. UF of dextran solutions at different pH conditions. 30 kDa membrane.

4.3.4 INFLUENCE OF THE CALCIUM CONTAINED IN THE INITIAL SOLUTION

Divalent ions are widely thought to be responsible or precursors of fouling. For this reason, ultrafiltration experiments were carried out maintaining the operating conditions and varying only the concentration of $CaCl_2$ in the solution to be filtrated. On one side, experiments of solutions containing 10 mg/L of the two NOM and 0.3 mg/mL of alginic acid were conducted with the 5 kDa and 30 kDa membrane respectively, adding 218.2 mg/L of $CaCl_2.2H_2O$. On the other hand, experiments with initial solutions containing 3 mg/mL of dextran and different amounts of $CaCl_2.2H_2O$, i.e., 18.3, 218.2 and 765 mg/L were carried out using the 30 kDa membrane.

In Fig. 4.3.4-1, the normalized flux calculated as previously explained is depicted versus the volume of permeate collected during the course of the UF of NOM solutions with and without calcium. It can be observed that the presence of the cation results in a lower flux. This may be caused by the formation of insoluble calcium salts or colloids with the solute, or due to the characteristics of the calcium to act as a bridge between the solutes and the membrane, which results in the fouling of the membrane and consequently, in the decay of the flux. As reported by Hong and Elimelech (*Hong and Elimelech, 1997*), in the presence of calcium ions the charge of the NOM is reduced significantly, not only because of effective charge screening but also due to complex formation. The decrease in the charge of the NOM results in an increased deposition rate of the polymer on the surface of the membrane.

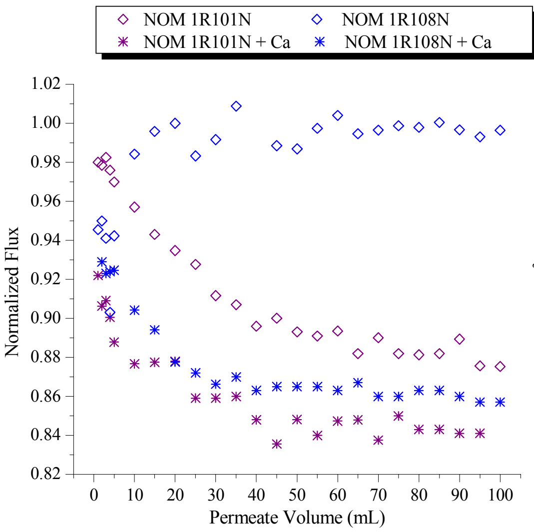


Figure 4.3.4-1 Normalized flux vs. volume of permeate. UF of NOM solutions with and without Ca^{2+}. 5 kDa membrane.

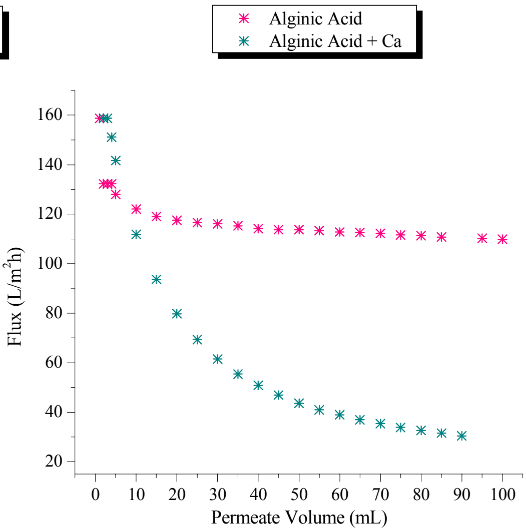


Figure 4.3.4-2 Flux vs. volume of permeate. UF of Alginic Acid solutions with and without Ca^{2+}. 5 kDa membrane.

The calcium also creates bonds between the polymer and the membrane surface. The influence of calcium on the performance of UF of solutions containing alginic acid using 30 kDa membranes was tested as well. Solutions with a concentration of 0.3 mg/L of alginic acid were prepared and $CaCl_2.2H_2O$ was added to one them, having a final concentration of 218.2 mg/L. In Fig. 4.3.4-2, the permeability vs. the permeate collected during these experiments is depicted. In this figure the fouling effect of the addition of calcium is remarkable. In fact, when ultrafiltrating the alginic acid, a reduction in the permeability from 160 to 120 $Lm^{-2}h^{-1}bar^{-1}$ was attained, while, in the presence of calcium, this the permeability decreased until 30 $Lm^{-2}h^{-1}bar^{-1}$. Exactly the same effect was observed when ultrafiltrating solutions containing dextran and different amounts of divalent cation Ca^{2+}, the higher the amount of calcium, the lower the flux throughout the membrane.

5 CONCLUSIONS AND RECOMMENDATIONS

The first conclusion reached from the experimental work of this Doctoral Thesis is that Wet Oxidation Processes are promising technologies for the treatment of solutions containing chlorophenols and wastewaters coming from the pulp and paper industry.

More specifically it has been proved that wet oxidation and wet peroxide oxidation are effective methods to treat 4-chlorophenol effluents since by both methods its complete removal together with high levels of mineralization can be accomplished. Under the operating conditions studied (solutions containing from 300 to 1000 ppm of 4-chlorophenol), complete chlorophenol removals were attained by wet peroxide oxidation even at the lowest temperature (100 ºC) and with the lowest peroxide dose (1 mL) within 40 minutes of reaction. On the other hand, wet oxidation needed higher temperatures (minimum 160 ºC) to reach the same goals.

As for the influence of the operating conditions during the **wet peroxide oxidation** of solutions containing 4-chlorophenol, it has to emphasized that an increase in the temperature of the reaction involved an increase in the mineralization at the end of the reaction and a fastest monochlorophenol removal. The wet peroxide oxidation reactions with initial solutions of 300 ppm and 5 mL of H_2O_2 showed an increasing tendency of the Total Organic Carbon (TOC) removal 85 %, 93 % and 95 % when increasing the temperature 100, 130 and 160 ºC respectively. The 4-chlorophenol was removed within the first 25 minutes when working at 160 ºC and during the first 35 and 44 minutes when working at 130 and 100 ºC respectively. On the other hand, an increase in the concentration of parachlorophenol in the initial solution resulted in a decrease of the TOC removal reached at the end of the reaction. This is because when working with solutions containing higher concentrations of chlorophenols, higher amount of Low Molecular Weight Acids are generated. These compounds are known by their properties refractory to oxidation. As for the influence of the dosage of hydrogen peroxide, it can be affirmed that higher amounts involved higher mineralization at the end of the reaction, meaning that the hydrogen peroxide was not in excess with respect to the organic matter under these conditions.

When comparing the results of the wet peroxide oxidation when treating 4-chlorophenol and 2,4-dichlorophenol, it was found out that both compounds were degraded at a similar rate, however differences were found regarding the TOC removal. It was thus concluded that the intermediate organic compounds generated during the wet peroxide oxidation of 2,4-dichlorophenol are more refractory to oxidation than the ones generated from the degradation of 4-chlorophenol.

Regarding the influence of the temperature and the partial pressure of oxygen in the **wet oxidation** of solutions containing 4-chlorophenol, it is concluded that an increase of the temperature in the range 150-190 ºC results in a faster reaction rate. In fact, it was observed that 150 ºC was not enough for the reaction to occur. The influence of the partial pressure of oxygen was also studied at two temperatures 160 and 190 ºC. It was found that an increase in the partial pressure of oxygen involved an increase in the reaction rate in the range 5 to 10 bar, however, from 10 bar on an increase in the partial pressure did not show any improvement in the reaction rate because the oxygen was already in excess respect to the organic load. Concerning the influence of the initial concentration of monochlorophenol, it has been proved that lower concentrations achieved higher TOC and 4-chlorophenol removal levels. Another conclusion reached from the wet oxidation reactions of solution containing 4-chlorophenol is that the reaction can be divided into two different parts. In the first one "Induction Period", the radicals were formed and thus a slight TOC and/or 4-chlorophenol removals were observed. In the second part, the oxidation took part and a faster TOC and 4-chlorophenol removals occurred.

Concerning the results of the chlorine study from the wet oxidation of solutions containing 4-chlorophenol, it can be concluded that in the course of the reactions, intermediates containing chlorine atoms are not formed. On the other hand, the study of the biodegradability during these processes showed that wet oxidation enhances the biodegradability of the solution to be treated. More specifically, during de course of the wet oxidation at 190 ºC and

10 bar pressure of solutions containing 500 ppm of 4-chlorophenol, the Biochemical Oxygen Demand (DBO) increased from an initial value of 20 mg O_2 L^{-1} until 245 mg O_2 L^{-1} after one hour of reaction.

Hydroquinone and quinone, despite low molecular weight acids, have been found to be the most important intermediates of the wet oxidation of 4-chlorophenol. The high feasibility of the suggested kinetic model suggests that the three compounds (4-chlorophenol, hydroquinone and quinone) follow a pseudo-first kinetic order reaction rate, after an initial induction period, in which the radicals are thought to be formed. According to this, from the modeling of the kinetics, not only the concentration of the compounds throughout the reactions can be calculated but also the length of the induction period at each time. The duration of the induction period was then found to be inversely proportional to the temperature: 23.4 min at 160 ºC, 10.1 min at 175 ºC and 5.02 min at 190 ºC.

Regarding the results from the experiments with multi-component wastewater, the first conclusion to mention is that wet oxidation is an appropriate process to treat wastewaters from pulp and paper mills. More specifically, organic load removals an increase in the level of biodegradability were attained after oxidizing nanofiltration concentrate thermo-mechanical pulp (TMP) process water and evaporation concentrate debarking water.

A study of the most suitable temperature to carry out the wet oxidation of TMP process wastewater was done. In the range of temperatures 120-150 ºC no high organic load removals were observed. However, when analyzing the tendency of the Lipophilic Wood Extractives content, it was found that their concentration diminished remarkably at this range of temperatures, especially at the highest (150 ºC). On the other hand, when the reaction was carried out in the range of temperatures from 160 to 200 ºC, higher Chemical Oxygen Demand (COD) removal and higher increases in the biodegradability were observed. It seems important to mention that when carrying out the WO at 200 ºC, a COD removal of 70 % and levels of 97 % of BOD/COD were achieved.

Concerning the study of the pressure, the most remarkable conclusion to mention is that the higher the operating pressure, the higher the organic load removal. So, the best results were observed when working at the highest pressure and temperature.

Two kinetic models suggested in the literature have been evaluated in order to be able to predict the evolution of the wet oxidation reactions of TMP process water. It can be concluded that both models seemed to predict the experimental values with a certain degree of precision. When calculating the error associated to each model, it was found out that the model of Verenich and Kallas presented higher errors. However, it should be emphasized that the kinetic model of Verenich and Kallas presents an advantage over the model of Li et al. since it allows the prediction, not only of the COD but also of the BOD throughout the reaction.

Concerning the wet oxidation of the debarking wastewater (previously concentrated by evaporation), it has to be concluded that the operating conditions evaluated were not sufficient to achieve high levels of organic load removal. More specifically, in the range of temperatures tested (from 170 to 200 ºC) the COD removals achieved at the end of the reaction were between 20 and 30 %, depending on the temperature. On the other hand, ratios of BOD/COD lower than 0.4 were observed in all the experiments. These results suggest that stronger operating conditions or the use of a catalyst might be needed in order to degrade this type of wastewater by means of wet oxidation reactions.

From the Ultrafiltration experiments it can be concluded that the studied operating parameters: initial concentration in the feed, pH of the solution, presence of Calcium cation and transmembrane pressure applied were found to be determining factors under the operating conditions evaluated. However, possible synergistic effects of these parameters as well as the suitability of the process for a certain type of wastewater can only be proved when operating in real life conditions.

As for the **recommendations**, in the first place, the scaling-up of these processes (wet oxidation and wet peroxide oxidation) is strongly recommended together with a change in the operating mode from batch to continuous mode. Under these conditions, not only the efficiency of the processes in terms of organic load or pollutants degradation could be investigated, but also the real economical aspects of the process. In this sense, the recovery of energy by means of temperature and pressure could provide useful information about the advantages of wet oxidation processes versus other wastewater treatments.

Secondly, once this study about the scaling-up would have been done, a research focused on the feasibility of a biological post-treatment should be carried out, since it has been already proved that the wet oxidation processes enhance the biodegradability of the water to be treated.

Another recommendation regarding the wet peroxide oxidation is related to the way the hydrogen peroxide is supplied into the system. Higher hydrogen peroxide doses generate higher concentrations of hydroxyl radicals in the medium. It is well known that high concentrations of hydroxyl radicals in the system favor the following reaction: $2\ OH^{\cdot} \rightarrow H_2O_2$, consequently is it interesting to have the maximum possible concentration of radicals avoiding this auto-scavenging effect. One possible solution consists of feeding the hydrogen peroxide meanwhile it is consumed. Working under these conditions, over-concentrations of radicals would be minimized as well as loss of hydrogen peroxide.

A final recommendation is the use of a catalyst to increase the reaction rate of the process. However, special attention should be paid when selecting it due to the possible leaching of the catalyst into the solution. In addition, a fixed bed reactor is suggested in order to avoid the use of a post-treatment after the oxidation to separate the catalyst.

6 NOTATION

A	Pre-exponential factor (s^{-1} or L $mol^{-1}s^{-1}$) depending on the order of the reaction
Cat	Catalyst
Da	Dalton (1.650 10^{-24} g)
dp	Particles diameter
e	Electron
E	Enhancement factor
Ea	Activation Energy (kJ mol^{-1})
[Fe]	Iron content (g kg^{-1})
$[Fe^{2+}]_o$	Initial concentration of ion Fe^{2+} (mmol L^{-1} or mol L^{-1})
$[4\text{-}CP]_o$	Initial concentration of 4-CP (mmol L^{-1} or mol L^{-1})
h	Planck Constant: 6.6262 10^{-34} J.s
h^+	“hole” regarding electron/hole pairs
Ha	Hatta Number
$[H_2O_2]_o$	Initial concentration of hydrogen peroxide (mmol L^{-1} or mol L^{-1})
K	Rate constant (s^{-1}, L $mol^{-1}s^{-1}$) depending on the order of the reaction
k_La	Liquid phase volumetric mass transfer coefficient (s^{-1})
P	Pressure (Pa, MPa, bar)
Po_2	Partial Pressure of oxygen (Pa, MPa, bar)
r	Global Oxidation Rate (mol m^{-3} s^{-1})
r_{chem}	Chemical Reaction Rate (mol m^{-3} s^{-1})
r_{mt}	Mass Transfer Rate (mol m^{-3} s^{-1})
R	Gas Constant 8.314 J K^{-1} mol^{-1}

RH	Organic Compound
S	Solid / Catalyst surface
T	Temperature (º C)
t	Time (s or min)
$t_{1/2}$	Half-life time (s or min)

Greek letters

ν	Frequency of the light (Hz)
ν_o	Molecular Volume ($cm^3\ mol^{-1}$)
λ	Wavelength of the light (nm)
μ	Dynamic viscosity (m Pa s)

Subscripts

Ads	Adsorbed
Chem.	Chemical
L	Liquid
O	Oxygen
o	Initial
org	pollutant

Superscripts

s	Saturated
m	Reaction order with respect to organic substance
n	Reaction order with respect to oxygen

Acronyms

4-CP	4-chlorophenol
AO	Aesthetic Objective
AOPs	Advanced Oxidation Processes
BOD	Biochemical Oxygen Demand
BW	Body Weight
CESARS	Chemical Evaluation Search and Retrieval System
CPs	Chlorophenols
COD	Chemical Oxygen Demand

DCS	Dissolved Colloid Substances
DO	Dissolved Oxygen
EHP	Environmental Health Program
ELKM	Extended Lumped Kinetic Model
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
GLKM	General Lumped Kinetic Model
HPLC	High Pressure Liquid Chromatograph
IC	Ion Chromatograph
LD_{50}	Lethal Dose for the 50 % of the population
LWEs	Lipophilic Wood Extractive Compounds
MAC	Maximum Acceptable Concentration
MCP	Monochlorophenol
MF	Microfiltration
MWCO	Molecular Weight Cut Off
NOM	Natural Organic Matter
NF	Nanofiltration
PACT	Powdered Activated Carbon Treatment
PCP	Pentachlorophenol
RO	Reverse Osmosis
SCWO	Supercritical Water Oxidation
TCP	Trichlorophenols
TOC	Total Organic Carbon
TOD	Total Oxygen Demand
TTCP	Tetrachlorophenols
UF	Ultrafiltration
UN	United Nations
UV	Ultraviolet Light
VUV	Visible Ultraviolet Light
WAO	Wet Air Oxidation
WHO	World Health Organization
WO	Wet Oxidation
WPO	Wet Peroxide Oxidation

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APPENDIX I WET OXIDATION OF SINGLE-COMPOUND SOLUTIONS

Table 4.1.1-1 Results of the heating period to 200 ºC (without oxidizing agent) of a 300 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	6.49	197	322.5	312.6
100	100	10	5.98	174.5	396.6	335.3
125	125	20	6.1	181.2	359.6	348.7
150	150	40	5.78	184.2	322.5	338
175	175	110	6.2	192.7	396.6	344.3
200	200	210	6.39	188.1	359.6	325

Table 4.1.1-2 Results of the heating period to 200 ºC (without oxidizing agent) of a 400 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	5.61	233.6	693.1	422.9
100	100	10	5.4	217.9	582	404.2
125	125	20	5.52	237.5	717.9	413.2
150	150	50	5.66	226.3	582	394.3
175	175	110	5.19	217.8	755	404.1
200	200	210	5.7	211.5	705.5	402.7

Table 4.1.1-3 Results of the heating period to 200 ºC (without oxidizing agent) of a 500 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	5.89	273.3	903.2	493.3
100	100	10	5.94	270.3	767.3	486.3
125	125	20	5.91	268.3	853.8	485.3
150	150	50	5.95	273.8	829.1	488.9
175	175	110	5.93	264.5	767.3	474.4
200	200	210	5.94	264.3	730.2	466

Table 4.1.1-4 Results of the heating period to 200 ºC (without oxidizing agent) of a 600 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	6.15	326.7	878.5	585.7
100	100	10	6.34	332.1	841.4	582.6
125	125	20	6.33	316.1	890.8	595
150	150	50	6.04	328.4	905.8	582.3
175	175	120	6.02	329.3	915.5	574.7
200	200	200	6.24	326.4	878.8	571.2

Table 4.1.1-5 Results of the heating period to 200 ºC (without oxidizing agent) of a 700 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	5.77	429.2	730.2	771.6
100	100	10	4.04	433.4	582	752
125	125	20	3.8	429.6	717.9	773.9
150	150	50	6.2	427.9	767.3	761.1
175	175	120	3.8	423.1	631.4	751
200	200	210	3.89	428.9	804.3	739.6

Table 4.1.1-6 Results of the heating period to 200 ºC (without oxidizing agent) of a 800 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	6.09	466.4	754.9	861.2
100	100	10	6.3	473.1	890.8	859.4
125	125	20	6.27	482.3	767.3	843.7
150	150	50	6.15	484.8	680.8	811.1
175	175	120	6.66	480.8	705.5	861.5
200	200	210	6.44	486.6	754.9	859.9

Table 4.1.1-7 Results of the heating period to 200 ºC (without oxidizing agent) of a 900 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	5.05	544.3	1200	962.8
100	100	10	3.91	547.1	1175	954
125	125	20	4.11	540.5	1286	956
150	150	50	5.54	541.9	1200	946.4
175	175	110	4.59	539.2	1360	956.9
200	200	210	5.61	547.8	1447	955.5

Table 4.1.1-8 Results of the heating period to 200 ºC (without oxidizing agent) of a 1000 ppm 4-CP solution.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	COD (mg O_2/L)	4-CP (ppm)
20	20	-	7.25	605.3	1459	1058
100	100	10	6.94	610.9	1397	1055
125	125	20	8.01	600.2	1336	1050
150	150	50	7.42	600.2	1360	1051
175	175	110	7.93	592	1373	1036
200	200	210	8.17	601.6	1323	1038

Table 4.1.1-9 Comparison between TOC and TOC related to 4-CP in the course of the preheating period. (TOC values are expressed in all the cases in ppm).

	$[4\text{-CP}]_o$= 300 ppm		$[4\text{-CP}]_o$= 400 ppm		$[4\text{-CP}]_o$= 500 ppm		$[4\text{-CP}]_o$= 600 ppm	
T (ºC)	TOC exp*	TOC theor**	TOC exp	TOC theor	TOC exp	TOC theor	TOC exp	TOC theor
20	197	175.2	233.6	237.0	273.3	276.4	326.7	328.2
100	174.5	187.9	217.9	226.5	270.3	272.5	332.1	326.4
125	181.2	195.4	237.5	231.5	268.3	271.9	316.1	333.4
150	184.2	189.4	226.3	220.9	273.8	273.9	328.4	326.3
175	192.7	192.9	217.8	226.4	264.5	265.8	329.3	322.0
200	188.1	182.1	211.5	225.6	264.3	261.1	326.4	320.0

exp* are the values of the TOC measured directly from the solution
theor** are the values of the TOC calculated from the concentration of 4-CP

Table 4.1.1-10 Comparison between TOC and TOC related to 4-CP in the course of the preheating period. (TOC values are expressed in all the cases in ppm).

	$[4\text{-CP}]_o$= 300 ppm		**$[4\text{-CP}]_o$= 400 ppm**		**$[4\text{-CP}]_o$= 500 ppm**		**$[4\text{-CP}]_o$= 600 ppm**	
T (ºC)	**TOC exp***	**TOC theor****	**TOC exp**	**TOC theor**	**TOC exp**	**TOC theor**	**TOC exp**	**TOC theor**
20	429.2	432.3	466.4	482.5	544.3	539.5	605.3	592.8
100	433.4	421.4	473.1	481.5	547.1	534.5	610.9	591.2
125	429.6	433.6	482.3	472.7	540.5	535.7	600.2	588.2
150	427.9	426.5	484.8	454.5	541.9	530.3	600.2	588.9
175	423.1	420.8	480.8	482.7	539.2	536.2	592	580.7
200	428.9	414.4	486.6	481.8	547.8	535.4	601.6	581.7

Table 4.1-11 WO reaction. Conditions: 500 ppm of 4-CP, 10 bar of Po$_2$, 160 ºC and 500 rpm.

Sample	**T (ºC)**	**P (psi)**	**pH**	**4-CP (ppm)**	**TOC (ppm)**
Original	Room	-	5.7	502.0	277.1
0	80	160	5.02	502.0	280.1
5	230	161	4.55	490.1	278.2
15	224	159	3.75	485.9	275.6
30	205	160	3.28	450.7	269.5
45	198	160	2.98	360.0	250.4
60	185	161	2.86	267.9	240.1
75	188	160	2.69	150.3	200.7
90	186	160	2.57	100.3	160.9
Last	Room	-	2.6	106.1	158.3

Table 4.1.1-12 WO reaction. Conditions: 500 ppm of 4-CP, 10 bar of Po$_2$, 160 ºC and 750 rpm.

Sample	**T (ºC)**	**P (psi)**	**pH**	**4-CP (ppm)**	**TOC (ppm)**
Original	Room	-	6.07	502.0	277.1
0	77	160	4.87	502.0	277.1
5	217	160	4.65	484.1	276.1
15	213	161	3.89	470.9	272.7
30	208	161	3.19	417.7	266.5
45	202	161	2.88	309.2	245.3
60	196	161	2.7	193.7	220.1
75	188	160	2.53	100.5	187.5
90	186	161	2.44	33.1	147.3
Last	Room	-	2.35	23.6	156.1

Table 4.1.1-13 WO reaction. Conditions: 500 ppm of 4-CP, 10 bar of Po_2, 160 ºC and 900 rpm.

Sample	T (ºC)	P (psi)	pH	4-CP (ppm)	TOC (ppm)
Original	Room	-	5.98	504.6	277.1
0	70	160	4.81	504.6	279.9
5	219	158	4.7	480.6	277.5
15	215	161	3.95	470.9	271.3
30	210	161	3.07	425.6	267.9
45	204	160	2.79	314.7	243.3
60	200	160	2.65	207.3	222.1
75	184	159	2.43	95.5	185.2
90	179	160	2.44	35.8	148.6
Last	Room	-	2.42	23.6	150.3

Table 4.1.2-1 Wet Peroxide Oxidation. Conditions: 300 ppm 4-CP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.08	181.3	334.8
0	13.48	100	15	3.65	172.5	141.5
15	28.48	100	15	2.71	131.5	57.12
30	43.48	100	20	2.51	96.89	0
45	58.48	100	50	2.58	84.79	0
60	73.48	100	80	2.57	77.09	0
75	88.48	100	80	2.47	65.55	0
90	103.48	100	80	2.44	56.57	0
Last	123.48	20	-	2.45	57.2	0

Table 4.1.2-2 Wet Peroxide Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	3.7	250.2	522.9
0	13.6	100	15	3.25	250.4	399.1
15	28.6	100	15	2.29	194.2	123.1
30	43.6	100	20	2.06	130.2	35.08
45	58.6	100	20	2.08	84.49	0
60	73.6	100	40	2.12	53.63	0
75	88.6	100	60	2.24	51.37	0
90	103.6	100	50	2.4	51.49	0
Last	123.6	20	-	2.3	51.35	0

Table 4.1.2-3 Wet Peroxide Oxidation. Conditions: 750 ppm 4-CP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.54	395.2	686.3
0	12.35	100	15	2.69	352.4	68.32
15	27.35	100	15	2.27	323.6	5.54
30	42.35	100	15	1.93	234.1	0
45	57.35	100	20	2.04	161.3	0
60	72.35	100	20	2.22	118.6	0
75	87.35	100	20	2.19	77.29	0
90	102.35	100	25	2.45	85.69	0
Last	122.35	20	-	2.4	83.29	0

Table 4.1.2-4 Wet Peroxide Oxidation. Conditions: 1000 ppm 4-CP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	3.58	550.3	873.5
0	13.7	100	15	2.13	472.1	118.3
15	28.7	100	20	1.91	316.8	24.54
30	43.7	100	25	1.92	219.2	0
45	58.7	100	40	2.02	145.0	0
60	73.7	100	60	2.06	125.4	0
75	88.7	100	50	2.05	135.8	0
90	103.7	100	50	2.11	132.7	0
Last	123.7	20	-	2.1	133.4	0

Table 4.1.2-5 Wet Peroxide Oxidation. Conditions: 500 ppm DCP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	4.95	291	435.9
0	14	100	15	2.36	212.7	198.3
15	29	100	20	2.16	173.2	45.63
30	44	100	25	2.01	140.2	0
45	59	100	40	1.97	108.1	0
60	74	100	60	1.96	86.75	0
75	89	100	50	1.98	57.67	0
90	104	100	50	2.08	53.39	0
Last	134	20	-	2.12	70.55	0

Table 4.1.2-6 Wet Peroxide Oxidation. Conditions: 1000 ppm DCP, 750 rpm, 5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	4.41	531	1175
0	14	100	15	2.62	422.1	626.8
15	29	100	20	2.03	324.5	126
30	44	100	25	1.96	249.3	62.98
45	59	100	40	1.94	191.1	0
60	74	100	60	1.94	162.3	0
75	89	100	50	1.98	125.8	0
90	104	100	50	2	111.2	0
Last	134	20	-	2.03	150.3	0

Table 4.1.2-7 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2, 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.17	171.4	259.8
0	12.9	100	15	3.3	163.8	103.3
15	27.9	100	15	2.46	110.0	26.7
30	42.9	100	15	2.39	82.79	0
45	57.9	100	20	2.4	66.63	0
60	72.9	100	20	2.42	53.04	0
75	87.9	100	20	2.47	42.59	0
90	102.9	100	25	2.48	28.64	0
Last	122.9	20		2.47	30.9	0

Table 4.1.2-8 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.1	250.0	296.9
0	13.15	100	15	2.86	231.2	132.9
15	28.15	100	15	2.32	166.9	23.73
30	43.15	100	15	2.25	127.8	0
45	58.15	100	15	2.26	108.0	0
60	73.15	100	15	2.26	90.19	0
75	88.15	100	15	2.28	75.39	0
90	103.15	100	15	2.31	69.37	0
Last	123.15	20	-	2.29	68.98	0

Table 4.1.2-9 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.98	399.3	593.0
0	12.1	100	15	3.27	385.0	585.6
15	27.1	100	15	2.16	301.2	86.14
30	42.1	100	15	2	213.8	0
45	57.1	100	15	1.97	168.0	0
60	72.1	100	20	1.99	140.0	0
75	87.1	100	20	2.03	113.3	0
90	102.1	100	25	2.06	90.99	0
Last	122.1	20	-	2.05	89.76	0

Table 4.2.1-10 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.73	532.0	941.5
0	12.7	100	15	3.05	510.9	727.0
15	27.7	100	20	1.96	351.1	112.0
30	42.7	100	20	1.93	236.5	0
45	57.7	100	25	1.9	189.1	0
60	72.7	100	25	1.94	163.6	0
75	87.7	100	30	1.98	143.0	0
90	102.7	100	25	1.99	159.4	0
Last	122.7	20	-	1.99	160.2	0

Table 4.1.2-11 Wet Peroxide Oxidation. 500 ppm DCP, 750 rpm, 2.5 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	5.11	238.4	424.5
0	14	100	15	3.65	205.3	332.2
15	29	100	20	2.79	198.6	279.8
30	44	100	20	2.23	179.1	99.1
45	59	100	25	2.04	154.6	9.13
60	74	100	25	2.01	142.3	0
75	89	100	30	2.03	109.5	0
90	104	100	25	2.08	97.54	0
Last	134	20	-	2.11	104.9	0

Table 4.1.2-12 Wet Peroxide Oxidation. 1000 ppm DCP, 750 rpm, 2.5 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	5.09	517.5	1107
0	14	100	15	2.65	476.8	697.2
15	29	100	20	2.02	363.3	225.6
30	44	100	20	1.91	269.8	20.4
45	59	100	25	1.88	238.1	21.56
60	74	100	25	1.88	210.2	22.89
75	89	100	30	1.89	184.7	19.71
90	104	100	25	1.92	157.8	18.94
Last	134	20	-	1.97	202	19.42

Table 4.2.1-13 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.67	153.2	292.6
0	12.1	100	15	3.85	153.2	233.4
15	27.1	100	15	2.4	102.4	26.93
30	42.1	100	15	2.49	75.19	0
45	57.1	100	15	2.7	63.08	0
60	72.1	100	15	2.47	60.49	0
75	87.1	100	15	2.45	57.21	0
90	102.1	100	15	2.47	51.73	0
Last	122.1	20	-	2.47	52.00	0

Table 4.2.1-14 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.24	248.9	481.5
0	12.4	100	15	3.96	245.4	379.5
15	27.4	100	15	2.31	192.2	58.67
30	42.4	100	15	2.23	129.5	0
45	57.4	100	15	2.21	105.5	0
60	72.4	100	15	2.23	89.79	0
75	87.4	100	15	2.18	85.29	0
90	102.4	100	15	2.23	75.89	0
Last	122.4	20	-	2.29	74.12	0

Table 4.2.1-15 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.89	418.1	707.1
0	12.6	100	15	2.51	412.6	260.3
15	27.6	100	15	2.01	278.0	36.93
30	42.6	100	15	1.93	250.7	5.06
45	57.6	100	15	1.96	245.0	6.06
60	72.6	100	15	1.99	237.8	3.05
75	87.6	100	15	1.96	228.7	6.09
90	102.6	100	15	2.01	231.5	0
Last	122.6	20	-	1.98	230.5	0

Table 4.1.2-16 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.72	530.0	946.7
0	12.03	100	15	2.73	527.1	461.7
15	27.03	100	15	2.06	409.9	117.5
30	42.03	100	15	2.01	394.1	25.27
45	57.03	100	15	1.98	387.9	24.89
60	72.03	100	15	1.99	385.8	24.64
75	87.03	100	15	1.98	383.8	25.09
90	102.03	100	15	1.98	371.9	24.64
Last	122.03	20	-	1.98	372.1	24.75

Table 4.1.2-17 Wet Peroxide Oxidation. 1000 ppm DCP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	5.32	463.5	1014
0	14	100	15	3.3	437.4	960.6
15	29	100	15	2.02	351.2	251.3
30	44	100	15	1.9	345	267.9
45	59	100	15	1.89	346.2	247.8
60	74	100	15	1.88	342.9	262.3
75	89	100	15	1.87	341.8	263.4
90	104	100	15	1.84	348.7	259.8
Last	139	20	-	1.98	356.9	263.1

Table 4.1.2-18 Wet Peroxide Oxidation. 500 ppm DCP, 750 rpm, 1 mL H_2O_2 and 100 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	2,4-DCP (ppm)
Original	0	20	-	4.56	253.3	495.3
0	17	100	15	4.21	223	347.2
15	32	100	15	3.17	193.8	52.47
30	47	100	15	2.21	172.2	10.26
45	62	100	15	2.1	156.9	6.94
60	77	100	15	2.12	145.1	0
75	92	100	15	2	131.5	0
90	107	100	15	2.05	113.8	0
Last	152	20	-	2.12	131.3	0

Table 4.1.2-19 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.45	204.1	289.8
0	19.3	130	25	2.83	162.7	88.46
15	34.3	130	55	2.54	85.29	9.71
30	49.3	130	110	2.57	24.93	0.0
45	64.3	130	100	2.68	17.87	0.0
60	79.3	130	95	2.67	17.10	0.0
75	94.3	130	90	2.65	17.91	0.0
90	109.3	130	90	2.66	18.17	0.0
Last	129.3	20	-	2.69	17.90	0.0

Table 4.1.2-20 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	3.63	280.0	499.7
0	20.3	130	30	2.51	216.2	64.56
15	35.3	130	90	2.3	86.59	0.0
30	50.3	130	110	2.34	39.12	0.0
45	65.3	130	100	2.32	29.79	0.0
60	80.3	130	95	2.51	41.82	0.0
75	95.3	130	90	2.65	39.84	0.0
90	110.3	130	85	2.5	38.99	0.0
Last	130.3	20	-	2.52	39.01	0.0

Table 4.1.2-21 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.1	443.2	686.3
0	19.4	130	35	2.19	286.9	68.32
15	34.4	130	120	2.12	81.89	5.54
30	49.4	130	110	2.14	62.48	0.0
45	64.4	130	100	2.22	62.81	0.0
60	79.4	130	95	2.19	63.35	0.0
75	94.4	130	90	2.19	57.90	0.0
90	109.4	130	85	2.16	54.72	0.0
Last	129.4	20	-	2.17	55.25	0.0

Table 4.1.2-22 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.89	618.7	947.0
0	19.6	130	40	1.99	362.0	21.17
15	34.6	130	110	1.98	115.6	0.00
30	49.6	130	105	2.03	103.1	0.0
45	64.6	130	100	2.02	95.9	0.0
60	79.6	130	90	2.17	97.5	0.0
75	94.6	130	85	2.12	97.0	0.0
90	109.6	130	80	2.08	95.1	0.0
Last	129.6	20	-	2.09	96.1	0.0

Table 4.1.2-23 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 130 ºC .

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.06	181.4	267.1
0	17.8	130	25	2.89	155.7	59.44
15	32.8	130	70	2.67	63.66	0.00
30	47.8	130	65	2.65	22.67	0.0
45	62.8	130	60	2.71	22.30	0.0
60	77.8	130	55	2.69	22.07	0.0
75	92.8	130	50	2.71	20.42	0.0
90	107.8	130	50	2.72	21.83	0.0
Last	127.8	20	-	2.69	21.50	0.0

Table 4.1.2-24 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.05	285.7	483.8
0	19.5	130	30	2.31	179.0	31.42
15	34.5	130	65	2.37	62.36	0.0
30	49.5	130	60	2.32	45.91	0.0
45	64.5	130	60	2.39	46.41	0.0
60	79.5	130	50	2.36	45.41	0.0
75	94.5	130	50	2.71	46.72	0.0
90	109.5	130	50	2.39	44.08	0.0
Last	129.5	20	-	2.40	45.03	0.0

Table 4.1.2-25 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.34	462.1	721.0
0	18.7	130	30	2.13	248.1	26.86
15	33.7	130	60	2.14	85.79	0.00
30	48.7	130	60	2.16	72.49	0.0
45	63.7	130	55	2.21	71.14	0.0
60	78.7	130	55	2.36	70.47	0.0
75	93.7	130	40	2.44	71.99	0.0
90	108.7	130	40	2.25	66.45	0.0
Last	128.7	20	-	2.28	65.98	0.0

Table 4.1.2-26 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 130 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.29	542.7	953.3
0	17.1	130	30	1.95	344.1	44.38
15	32.1	130	60	1.92	128.8	0.00
30	47.1	130	55	2.02	108.4	0.0
45	62.1	130	55	2.04	105.9	0.0
60	77.1	130	50	1.98	104.8	0.0
75	92.1	130	45	2.06	111.6	0.0
90	107.1	130	40	2.04	108.8	0.0
Last	127.1	20	-	2.03	109.0	0.0

Table 4.1.2-27 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 160 ºC.

Sample	**Time (min)**	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**
Original	0	20	-	5.25	160.0	284.4
0	26.3	160	165	2.75	22.9	0.00
15	41.3	160	155	2.65	10.50	0.00
30	56.3	160	145	2.80	10.80	0.0
45	71.3	160	135	2.73	10.96	0.0
60	86.3	160	130	2.78	10.01	0.0
75	101.3	160	130	2.81	9.56	0.0
90	116.3	160	130	2.81	7.82	0.0
Last	136.3	20	-	2.80	8.02	0.0

Table 4.1.2-28 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 160 ºC.

Sample	**Time (min)**	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**
Original	0	20	-	4.52	296.3	501.3
0	25.8	160	150	2.42	53.6	0.00
15	40.8	160	145	2.52	42.80	0.0
30	55.8	160	140	2.45	39.33	0.0
45	70.8	160	135	2.46	37.04	0.0
60	85.8	160	140	2.51	36.68	0.0
75	100.8	160	135	2.42	38.67	0.0
90	115.8	160	130	2.39	34.82	0.0
Last	135.8	20	-	2.40	33.99	0.0

Table 4.1.2-29 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 160 ºC.

Sample	**Time (min)**	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**
Original	0	20	-	4.84	325.2	695.3
0	25.6	160	150	2.3	38.8	0.00
15	40.6	160	150	2.41	38.83	0.00
30	55.6	160	135	2.36	29.65	0.0
45	70.6	160	135	2.24	27.05	0.0
60	85.6	160	135	2.21	22.44	0.0
75	100.6	160	135	2.25	9.21	0.0
90	115.6	160	130	2.25	19.09	0.0
Last	135.6	20	-	2.26	18.75	0.0

Table 4.1.2-30 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 5 mL H_2O_2 and 160 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.78	593.0	956.8
0	24.7	160	150	2.17	94.2	0.0
15	39.7	160	145	2.18	84.6	0.0
30	54.7	160	140	2.24	85.1	0.0
45	69.7	160	130	2.26	83.8	0.0
60	84.7	160	130	2.25	84.0	0.0
75	99.7	160	130	2.28	80.8	0.0
90	114.7	160	145	2.24	78.6	0.0
Last	134.7	20	-	2.25	79.0	0.0

Table 4.1.2-31 Wet Peroxide Oxidation. 300 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 160 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	6.02	181.8	283.1
0	28	160	105	2.56	27.3	0.00
15	43	160	100	2.52	15.85	0.00
30	58	160	95	2.60	15.96	0.0
45	73	160	95	2.59	15.26	0.0
60	88	160	100	2.50	15.71	0.0
75	103	160	105	2.47	16.28	0.0
90	118	160	105	2.38	13.20	0.0
Last	138	20	-	2.38	13.21	0.0

Table 4.1.2-32 Wet Peroxide Oxidation. 500 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 160 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	4.52	296.3	503.9
0	25.8	160	150	2.42	53.6	0.00
15	40.8	160	145	2.52	42.80	0.0
30	55.8	160	140	2.45	39.33	0.0
45	70.8	160	135	2.46	37.04	0.0
60	85.8	160	140	2.51	36.68	0.0
75	100.8	160	135	2.42	38.67	0.0
90	115.8	160	130	2.39	34.82	0.0
Last	135.8	20	-	2.40	33.99	0.0

Table 4.1.2-33 Wet Peroxide Oxidation. 750 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 160 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.39	235.7	728.1
0	29.9	160	90	2.35	28.4	0.00
15	44.9	160	100	2.35	27.15	0.00
30	59.9	160	95	2.33	20.38	0.0
45	74.9	160	90	2.26	22.38	0.0
60	89.9	160	90	2.28	21.47	0.0
75	104.9	160	95	2.32	19.64	0.0
90	119.9	160	100	2.37	21.47	0.0
Last	139.9	20	-	2.36	21.05	0.0

Table 4.1.2-34 Wet Peroxide Oxidation. 1000 ppm 4-CP, 750 rpm, 2.5 mL H_2O_2 and 160 ºC.

Sample	Time (min)	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)
Original	0	20	-	5.69	637.7	987.4
0	27.6	160	90	2.17	144.4	5.6
15	42.6	160	90	2.21	122.2	0.0
30	57.6	160	85	2.27	118.7	0.0
45	72.6	160	85	2.2	118.6	0.0
60	87.6	160	90	2.31	117.7	0.0
75	102.6	160	100	2.24	118.5	0.0
90	117.6	160	100	2.23	118.3	0.0
Last	137.6	20	-	2.25	119.0	0.0

Table 4.1.3-1 Wet Oxidation. Conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and 150 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20	-	4.44	480.1	890.5	11
0	150	54(199)	4.4	514.4	945.1	7.8
5	150	197	4.26	523	959.2	8.5
15	150	188	4.11	523.7	959	4.7
30	150	181	3.98	525.5	962.1	5.5
45	150	174	3.74	519.8	941.5	6.3
60	150	168	3.61	522.9	947.6	10.7
75	150	164	3.47	524.4	939.0	9.1
90	150	161	3.34	518.7	935.0	11
Last	20	-	3.26	528.2	946.3	11.6

Table 4.1.3-2 Wet Oxidation. Conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and 160 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20	-	5.2	489.3	938.7	8.65
0	160	54(199)	4.96	515.8	980.1	4
5	160	197	4.11	520.1	975.8	4.2
15	160	188	3.42	507.1	930.4	13.2
30	160	181	2.96	492.5	831.9	28.95
45	160	174	2.65	470.9	670.5	63.95
60	160	168	2.47	436.4	498.8	118
75	160	164	2.35	392.1	326.7	167
90	160	161	2.31	347.2	229.2	203.7
Last	20	-	2.2	345.4	220.9	205.3

Table 4.1.3-3 Wet Oxidation. Conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and 175 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20	-	4.82	521	908.1	3
0	175	109(254)	3.8	514.5	947.6	5.05
5	175	247	3.9	512.3	930.5	5.1
15	175	239	3.41	504.5	898.4	13.3
30	175	229	2.81	475.6	737.6	55.05
45	175	222	2.53	416.9	476.8	126.6
60	175	212	2.39	344.3	269.7	183.2
75	175	208	2.36	272.2	136.0	229.2
90	175	203	2.38	192.9	46.59	262.1
Last	20	-	2.26	241.1	46.39	257.2

Table 4.1.3-4 Wet Oxidation. Conditions: 1000 ppm 4-CP, 750 rpm, 10 bar Po_2 and 190 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20			539.5	951.6	2.3
0	190	167	3.86	539.5	951.6	2.3
5	190	294	3.45	535.3	927.2	31.5
15	190	286	2.71	479.9	688.1	70.8
30	190	276	2.42	375	363.7	162.6
45	190	269	2.36	270.4	169.1	233
60	190	264	2.36	193.9	74.40	250
75	190	259	2.35	172.2	40.83	254.4
90	190	256	2.31	161.4	31.63	264.6
Last	20		2.26	178.2	27.22	261

Table 4.1.3-5 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and 150 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		6.56	276.5	501	4
0	150	56	4.67	276	501	4
5	150	200	4.58	275.9	492.3	4
15	150	193	4.51	278.1	493.6	3.85
30	150	187	4.31	276.5	490.3	4
45	150	182	3.99	277	487.6	5.65
60	150	175	3.74	275	477.8	9.15
75	150	170	3.5	274.7	467.2	9.1
90	150	166	3.34	271.7	457.9	11.8
Last	20		3.27	274.3	437.3	12

Table 4.1.3-6 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and 160 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		6.07	277.1	502.0	4
0	160	77	4.87	277.1	502.0	4
5	160	217	4.65	276.1	484.1	3.65
15	160	213	3.89	272.7	470.9	3.95
30	160	208	3.19	266.5	417.7	14.75
45	160	202	2.88	245.3	309.2	51
60	160	196	2.7	220.1	193.7	81
75	160	188	2.53	187.5	100.5	104.9
90	160	186	2.44	147.3	33.10	137.2
Last	20		2.35	156.1	23.58	157.2

Table 4.1.3-7 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and 175 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		5.74	267.7	498.8	4
0	175	116	4.68	266.8	504.9	4
5	175	258	4.31	268.3	479.2	4
15	175	249	3.7	268.9	442.1	17
30	175	241	2.95	258.6	302.6	57
45	175	234	2.7	234.3	178.2	94
60	175	228	2.59	188.8	78.2	111
75	175	222	2.51	138.8	43.2	120.3
90	175	219	2.49	96.9	11.49	132.3
Last	20		2.43	101.9	5.065	132.3

Table 4.1.3-8 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 10 bar Po_2 and 190 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		6.06	267.8	508.2	5.19
0	190	171	4.65	267	508.2	2.7
5	190	315	3.32	256.3	415.8	20.52
15	190	302	2.66	189.3	170.4	102.7
30	190	294	2.55	108.9	28.42	136.7
45	190	288	2.54	85.13	9.51	135.7
60	190	282	2.53	80.06	5.12	141.2
75	190	278	2.55	73.88	3.9	137.9
90	190	274	2.55	69.24	2.49	137.9
Last	20		2.46	78.13	2.05	5.19

Table 4.1.3-9 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 5 bar Po_2 and 160 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		6.2	269.1	487.8	4
0	160	78(160)	4.57	269.1	487.8	3.525
5	160	158	4.53	268.2	474.6	6
15	160	150	4.32	271.5	477.3	2.15
30	160	145	3.97	269.3	473.6	3
45	160	139	3.74	271.2	468.4	4.8
60	160	136	3.55	293.2	450.3	6.5
75	160	133	3.38	264.3	441.8	9.4
90	160	130	3.23	260.3	428.6	14.4
Last	20		3.24	264.8	431.9	14.25

Table 4.1.3-10 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 7.5 bar Po_2 and 160 ºC.

Sample	T (ºC)	P (psi)	pH	TOC (ppm)	4-CP (ppm)	Cl^- (ppm)
Original	20		6.02	254.4	464.5	3.65
0	160	80(200)	5	254.3	462.3	1.4
5	160	197	4.65	253.1	458.8	1.05
15	160	192	4.01	253.5	452.9	1.7
30	160	189	3.6	250.8	442.7	2.95
45	160	185	3.25	242.6	432.5	6.25
60	160	182	3.01	231.7	329.7	38.3
75	160	179	2.82	216.8	254.3	53.2
90	160	177	2.67	196.7	168.8	83.4
Last	20		2.54	179.7	108.4	29

Table 4.1.3-11 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 15 bar Po_2 and 160 ºC.

Sample	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**	**Cl^- (ppm)**
Original	20		5.99	279.8	492.6	5.94
0	160	79(296.5)	4.57	279.5	492.6	4
5	160	290	4.22	280.7	479.9	2.55
15	160	279	3.84	279.6	473.2	4.25
30	160	268	3.37	274.2	440.7	9.75
45	160	260	2.95	261.3	350.0	38
60	160	252	2.64	230.1	204.2	78
75	160	254	2.49	186.9	76.55	115
90	160	248	2.41	134.7	14.44	137
Last	20		2.37	141.2	12.56	152.9

Table 4.1.3-12 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 5 bar Po_2 and 190 ºC.

Sample	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**	**Cl^- (ppm)**
Original	20		4.1	268	507.9	4
0	190	164(239)	4.65	267	508.2	4.1
5	190	236	3.7	264.6	471.4	2.1
15	190	230	3.28	264.1	457.6	4.55
30	190	225	2.96	254.9	418.7	13.8
45	190	220	2.83	238.7	362.6	31.7
60	190	216	2.74	219.4	299.5	50.65
75	190	213	2.71	200.5	250.6	67.75
90	190	209	2.72	189.8	232.9	76.85
Last	20			191.5	234.5	4.1

Table 4.1.3-13 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 7.5 bar Po_2 and 190 ºC.

Sample	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**	**Cl^- (ppm)**
Original	20		4.58	267.3	500.3	0.55
0	190	166(278)	4.58	267.3	500.3	2.15
5	190	276	3.89	262.1	471.9	5.3
15	190	268	3.52	268.7	455.7	6.95
30	190	260	3.22	253	414.7	18.85
45	190	254	2.95	232.6	338.5	36.3
60	190	248	2.73	201.2	239.8	72.2
75	190	243	2.58	163.2	129.0	107.8
90	190	240	2.58	120.4	62.27	133.3
Last	20		2.55	133.9	72.42	129.5

Table 4.1.3-14 Wet Oxidation. Conditions: 500 ppm 4-CP, 750 rpm, 15 bar Po_2 and 190 ºC.

Sample	**T (ºC)**	**P (psi)**	**pH**	**TOC (ppm)**	**4-CP (ppm)**	**Cl^- (ppm)**
Original	20		6.12	268.5	499.2	4
0	190	167(386)	4.88	262.6	481.3	3.95
5	190	376	3.59	260.7	433.6	8.55
15	190	359	2.7	198.5	180.3	79.8
30	190	348	2.54	101.4	26.34	124
45	190	340	2.52	84.35	5.846	135
60	190	335	2.51	77.9	3.17	145
75	190	335	2.52	74.22	3.595	129
90	190	330	2.53	70.5	1.1	137
Last	20		2.47		6.965	156.4

APPENDIX II WET OXIDATION OF MULTI-COMPOUND SOLUTIONS

Table 4.2.1-1 Wet Oxidation of TMP concentrated wastewater at 120 ºC and 10 bar of Po_2.

Sample	**COD (mg O_2/L)**	**COD $_{soluble}$ (mg O_2/L)**	**TOC $_{soluble}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	7875	4048	1177	2825	200	234	6.3
0 min	7775	4506	1356	3025	161	277	5.3
10 min	7875	4410	1266	2487	179	279	5.2
30 min	7975	4372	1310	2675	56	319	5.0
60 min.	7950	4151	1294	2450	63	277	4.8
90 min.	7850	3857	1283	2275	97	267	4.6
120 min.	7800	3705	1181	2625	161	253	4.4
Residue	7525	4315	1134	2038	167	250	4.3

Table 4.2.1-2 Wet Oxidation of TMP concentrated wastewater at 130 ºC and 10 bar of Po_2.

Sample	**COD (mg O_2/L)**	**COD $_{soluble}$ (mg O_2/L)**	**TOC $_{soluble}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	8090	4834	1471	3419	130	230	6.8
0 min.	9072	5239	1426	3159	104	300	5.6
10 min.	8542	5375	1486	2600	104	227	5.3
30 min.	8542	5239	1414	2184	78	234	5
60 min.	8496	5239	1446	2080	91	216	4.8
90 min.	8406	5330	1424		182	209	4.4
120 min.	8451	5330	1409	1937	260	208	4.2
Residue	7955	4247	1224	2145	260	160	4.1

Table 4.2.1-3 Wet Oxidation of TMP concentrated wastewater at 140 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{soluble}$ (mg O_2/L)	TOC $_{soluble}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	8165	4951	1375	2145	26	126	6.6
0 min.	8567	5442	1431	1755	26	163	5.1
10 min.	8611	5487	1433	1846	26	124	4.9
30 min.	8924	5487	1448	1651	26	1274	4.6
60 min.	8790	5531	1481	1846	104	118	4.2
90 min.	8879	5308	1478	1820	156	114	4
120 min.	8745	5264	1483	1859	205	113	3.8
Residue	7987	4192	1253	1768	364	87	3.7

Table 4.2.1-4 Wet Oxidation of TMP concentrated wastewater at 150 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{soluble}$ (mg O_2/L)	TOC $_{soluble}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	8343	5263	1379	858	0	215	6.5
0 min.	8299	5531	1474	585	0	300	5.1
10 min.	8120	5397	1481	1066	0	262	4.9
30 min.	8299	5397	1526	806	0	241	4.5
60 min.		5576	1507	832	26	242	4.0
90 min.	8433	4906	1386	780	143	234	3.9
120 min.	8165	4817	1365	1066	650	215	3.7
Residue	7183	4683	1438	1144	676	262	3.7

Table 4.2.1-5 Wet Oxidation of TMP concentrated wastewater at 160 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{soluble}$ (mg O_2/L)	TOC $_{soluble}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	8606	4996	1400	10010	23	310	6.3
0 min.	8632	5040	1539	1924	176	281	4.7
10 min.	8502	5085	1558	1976	368	277	4.3
30 min.	8502	4907	1579	2236	606	260	3.8
60 min.	8372	4460	1540	1989	1004	248	3.4
90 min.	8294	4103	1511	2483	1192	243	3.2
120 min.	7176	3657	1407	1924	1664	210	3.1
Residue	5876	3612	1309	1664	1863	205	3.1

Table 4.2.1-6 Wet Oxidation of TMP concentrated wastewater at 170 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{soluble}$ (mg O_2/L)	TOC $_{soluble}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	8339	5058	1918	2444		319	6.3
0 min.	8923	5238	2042	2587	319	281	4.6
10 min.	8833	4968	2058	2652	704	267	4
30 min.	8698	4384	1964	2808	1155	238	3.5
60 min.	7934	4024	1938	2964	1727	217	3.2
90 min.	6676	3844	1868	3328	2013	200	3.1
120 min.	5148	3709	1788	3185	1958	172	3.1
Residue	4951	3925	1015	3185		176	3.1

Table 4.2.1-7 Wet Oxidation of TMP concentrated wastewater at 180 ºC and 10 bar of Po$_2$.

Sample	**COD (mg O_2/L)**	**COD $_{\text{soluble}}$ (mg O_2/L)**	**TOC $_{\text{soluble}}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	8199	1402	3122	825	227	6.6	6.4
0 min.	7760	1552	2830	816	319	4.9	3.9
10 min.	7360	1522	3000	1010	266	3.6	3.7
30 min.	6280	1380	3060	1355	231	3.1	3.5
60 min.	4480	1070	3180	1810	132	3.2	3.3
90 min.	3280	804	2770	1975	99	3.2	3.2
120 min.	3100	751	2720	2000	77	3.2	3.1
Residue	3060	582	2720	2163	74	5.9	3.2

Table 4.2.1-8 Wet Oxidation of TMP concentrated wastewater at 190 ºC and 10 bar of Po$_2$.

Sample	**COD (mg O_2/L)**	**COD $_{\text{soluble}}$ (mg O_2/L)**	**TOC $_{\text{soluble}}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	7851	4071	1598	1131	54	300	6.6
0 min.	7131	3935	1606	1768	610	281	3.8
10 min.	6906	3620	1601	1924	884	277	3.3
30 min.	5646	3170	1573	2340	1430	257	3.1
60 min.	3440	2495	1281	2340	1637	140	3.1
90 min.	3215	2360	1073	2280	1610	91	3.2
120 min.	2682	1955	935	1976	1644	72	3.2
Residue	2682	1955	930	2158	1648	67	3.2

Table 4.2.1-9 Wet Oxidation of TMP concentrated wastewater at 200 ºC and 10 bar of Po$_2$.

Sample	**COD (mg O_2/L)**	**COD $_{\text{soluble}}$ (mg O_2/L)**	**TOC $_{\text{soluble}}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	7993	4353	1670	1384	825	248	7.4
0 min.	8413	4213	1784	1985	816	310	5
10 min.	5940	4470	1894	2329	1010	288	3.6
30 min.	3863	3046	1517	2747	1355	139	3.6
60 min.	2906	2230	1189	2599	1810	64	3.6
90 min.	2673	2113	1068	2309	1975	41	3.7
120 min.	2463	1996	982	2403	2000	36	3.7
Residue	2463	2159	1007	2403		38	3.8

Table 4.2.1-10 Wet Oxidation of TMP concentrated wastewater at 170 ºC and 5 bar of Po$_2$.

Sample	**COD (mg O_2/L)**	**COD $_{\text{soluble}}$ (mg O_2/L)**	**TOC $_{\text{soluble}}$ (mg C/L)**	**BOD (mg O_2/L)**	**IABOD (mg O_2/L)**	**Lignin (mg/L)**	**pH**
Original	7880	5060	1930	117	0	322	6.7
0 min.	7740	5240	1950	1440	144	317	4.5
10 min.	7610	4970	2150	1530	237	307	4.1
30 min.	7480	4380	2030	1720	495	302	3.6
60 min.	6990	4020	1950	1980	775	286	3.2
90 min.	6550	3840	1890	2210	1070	270	3.1
120 min.	6230	3710	1880	2290	1110	242	3.1
Residue	5920	5060	1370		798		6.7

Table 4.2.1-11 Wet Oxidation of TMP concentrated wastewater at 170 ºC and 7.5 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{\text{soluble}}$ (mg O_2/L)	TOC $_{\text{soluble}}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	6370	4150	1810	2000	768	348	6.4
0 min.	7080	4700	1920	2260	946	296	4.6
10 min.	7080	4420	1830	2570	1130	262	3.7
30 min.	6810	3930	1700	2520	1240	262	3.5
60 min.	6370	3790	1690	2830	1590	253	3.1
90 min.	5920	3610	1680	3070	1670	246	3
120 min.	5380	3560	1650	2940	1780	219	3
Residue	5380	4150	1580	2780	1780	222	3

Table 4.2.1-12 Wet Oxidation of TMP concentrated wastewater at 170 ºC and 15 bar of Po_2.

Sample	COD (mg O_2/L)	COD $_{\text{soluble}}$ (mg O_2/L)	TOC $_{\text{soluble}}$ (mg C/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)	Lignin (mg/L)	pH
Original	6400	4830	1710	2410	456	343	6.2
0 min.	6670	5350	1720	1990	745	355	4.5
10 min.	6580	4750	1700	2240	1030	324	3.8
30 min.	4680	4380	1670	2770	1460	305	3.2
60 min.	4410	3930	1650	3040	1790	296	2.9
90 min.	3410	3650	1630	2990	1990	248	2.9
120 min.	3140	3380	1590	2680	2020	205	2.9
Residue	3140	4830	1490	2810		231	2.9

Table 4.2.1-13 Fatty Acids concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	120 ºC	130 ºC	140 ºC	150 ºC
Original	40.4	39.2	25.4	30.0
0	38.6	36	21.9	18.6
10	35.7	32.5	22.9	18.7
30	31.4	29	20.1	18.6
60	29.7	28.5	20.5	16.1
90	28.4	25	13.6	10.9
120	27.2	19.9	8.2	8.9

Table 4.2.1-14 Resin Acids concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	120 ºC	130 ºC	140 ºC	150 ºC
Original	53.9	52.6	61.3	60.8
0	50.9	50.1	48.4	47.6
10	46.7	47.4	45.5	37.9
30	40.4	40.2	41.4	32.0
60	31.8	39.5	36.4	16.2
90	28.4	35.6	25.1	9.3
120	19.7	30.5	15.1	7.8

Table 4.2.1-15 Lignans concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	**120 ºC**	**130 ºC**	**140 ºC**	**150 ºC**
Original	101.8	120.6	125.8	126.2
0	109.6	116.4	124	126.5
10	107.6	116.6	101.3	96.5
30	84.6	85.4	80.2	60.5
60	59.1	71.6	47.5	29.6
90	35.3	47.3	27.9	12.5
120	28.9	39.4	11.5	7.8

Table 4.2.1-16 Steroids concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	**120 ºC**	**130 ºC**	**140 ºC**	**150 ºC**
Original	8.6	9.2	9.0	11.8
0	4.7	9.1	9.3	10.2
10	2.2	8.6	9.4	9.4
30	1.8	8.5	8.7	7.0
60	1.7	8.2	6.3	1.8
90	1.2	6.3	4.8	1.1
120	1.1	4.5	2	0.9

Table 4.2.1-17 Steryl Esters concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	**120 ºC**	**130 ºC**	**140 ºC**	**150 ºC**
Original	81.5	84.1	72.8	77.2
0	79.4	78.8	69.9	74.8
10	72.1	76.7	68.2	68.2
30	65.2	72.1	65.0	38.9
60	57.5	65.5	43.2	17.7
90	47.2	55.3	22.6	6.8
120	40.2	46.4	13.2	4.6

Table 4.2.1-18 Triglycerids concentration (mg/L) at different temperatures.Wet Oxidation of TMP concentrated wastewater at 10 bar of Po_2.

Sample	**120 ºC**	**130 ºC**	**140 ºC**	**150 ºC**
Original	108.9	138	102.9	108.4
0	133.7	131.3	111.4	112.9
10	128.6	128.4	105.6	93.9
30	114.1	102.8	92.3	40.4
60	92.8	97.6	49.5	13.1
90	75.4	74.9	18.3	3.6
120	58.7	55	7.2	1.7

Table 4.2.2-1 Wet Oxidation of debarking wastewater at 170 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	Volatile Acids (mg/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)
0	38570	3050	13120	6080
10	55992	10056	16960	12800
30	51014	9746	17120	13600
60	45899	10180	16320	13760
90	44378	11234	15360	13280
120	44239	11730	14720	13760

Table 4.2.2-2 Wet Oxidation of debarking wastewater at 180 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	Volatile Acids (mg/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)
0	46037	3670	12160	8480
10	59311	7390	16000	11840
30	53780	8630	16640	13120
60	52121	8568	16640	13120
90	49770	8444	15360	13440
120	47834	8072	15040	13760

Table 4.2.2-3 Wet Oxidation of debarking wastewater at 190 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	Volatile Acids (mg/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)
0	44654	4910	13200	9333
10	52259	9250	15600	12067
30	48526	10056	13680	11520
60	48387	9994	14240	13120
90	46452	9932	15040	14240
120	45760	9870	14720	13440

Table 4.2.2-4 Wet Oxidation of debarking wastewater at 200 ºC and 10 bar of Po_2.

Sample	COD (mg O_2/L)	Volatile Acids (mg/L)	BOD (mg O_2/L)	IABOD (mg O_2/L)
0	50461	4476	12400	9867
10	55301	7886	15467	12733
30	53642	8754	15911	14489
60	52259	8630	16267	15556
90	51153	8506	15680	14400
120	47281	8196	14844	14044

APPENDIX III ULTRAFILTRATION

Table 4.3.1-1 Flux (mL/m^2 h) throughout UF experiments of solutions containing Dextran.

Permeate Volume (mL)	**20 kDa membrane**					**30 kDa membrane**				
	1 mg/mL	3 mg/mL	5 mg/mL	8 mg/mL	10 mg/mL	1 mg/mL	3 mg/mL	5 mg/mL	8 mg/mL	10 mg/mL
5	64.0		25.8	30.29	33.07	73.5	99.2	45.6	45.61	36.40
10	61.0	52.6	28.9	29.72	32.13	72.8	71.5	44.3	45.35	34.21
15	60.4		29.5	29.25	31.91	71.7	64.0	49.6	43.13	31.91
20	60.1	45.3	30.0	29.02	31.49	71.8	63.0	47.9	40.70	32.13
25	59.6		30.4	28.75	31.29	71.1	61.6	47.9	40.32	30.66
30	59.4	43.8	30.6	28.68	31.12	71.1	60.0	47.4	39.09	31.00
35	59.0		30.2	28.69	31.00	71.0	59.0	47.9	39.34	31.17
40	58.8	44.5	30.4	28.52	30.76	71.0	57.8	47.4	39.63	30.15
45	58.7		30.5	28.07	30.57	70.9	57.0	47.6	38.65	30.37
50	57.8		30.7	28.00	30.43	70.7	56.2	47.1	38.94	30.22
55	57.7		30.8	28.01	29.75	70.6	55.7	47.1	38.35	29.83
60	57.7	43.3	30.9	27.70	29.67	70.9	55.2	46.0	37.76	29.95
65	57.6		31.0	27.70	29.61	70.8	54.9	46.0	37.93	30.13
70	57.6	42.8	31.1	27.68	29.58	70.1	54.3	45.8	37.33	29.60
75	57.6		31.1	27.48	29.35	70.0	54.0	45.9	37.48	29.67
80	57.6	42.4	31.1	27.46	29.28	69.5	53.8	45.7	37.61	29.51
85	57.2		31.1	27.45	29.20	69.5	53.6	45.6	37.14	29.20
90	57.1	42.2	30.9	27.30	29.14	69.5	53.4	45.5	37.28	29.27
95	57.1		31.0	27.29	29.05	69.5	53.3	45.4	37.32	28.95
100	57.0	42.3	31.0	27.23	28.87	69.5	53.2	45.4	36.81	28.70

Table 4.3.1-2 Flux (mL/m^2 h) throughout UF experiments of solutions containing Alginic Acid and Ca^{+2}.

Permeate Volume (mL)	**30 kDa membrane - Alginic Acid**			
	3 mg/mL	0.3 mg/mL	0.3 mg/mL 218 mg/L $CaCl_2.2H_2O$	0.3 mg/mL 765 mg/L $CaCl_2.2H_2O$
1	79.36	158.7	264.52	264.5
2	56.68	132.3	158.71	198.4
3	51.75	132.3	158.71	198.4
4	48.10	132.3	151.16	198.4
5	47.24	128.0	141.71	208.8
10	42.90	122.1	111.77	180.4
15	41.33	119.0	93.73	177.7
20	40.28	117.6	79.76	168.8
25	38.98	116.7	69.37	164.0
30	38.40	116.1	61.52	158.7
35	38.10	115.2	55.44	156.0
40	37.65	114.2	50.87	153.3
45	37.32	113.7	46.93	150.0
50	36.91	113.7	43.65	147.0
55		113.4	41.02	144.5
60	36.43	112.8	38.93	142.6
65	36.17	112.6	37.00	140.2
70	35.88	112.2	35.36	137.5
75	35.70	111.7	33.89	135.0
80	35.45	111.4	32.64	133.4
85	35.24	110.8	31.54	131.5
90	35.03		30.50	129.6
95	34.84	110.2		127.8
100	34.71	109.9		126.2

Table 4.3.1-3 Flux (mL/m^2 h) throughout UF experiments of solutions containing Cellulose.

Permeate Volume (mL)	30 kDa membrane - Cellulose			
	1 mg/mL	3 mg/mL	5 mg/mL	10 mg/mL
5	345.0	330.6	330.6	360.7
10	292.0	273.6	283.4	293.96
15	258.7	264.5	258.7	264.5
20	255.9	255.9	255.9	247.9
25	253.6	251.1	247.9	247.9
30	247.9	250.6	250.6	242.9
35		247.9	247.9	241.5
40	247.9	247.9	247.9	236.8
45	244.5	244.5	244.5	238.0
50	244.9	246.4	244.9	237.5
55	243.8	243.8	242.4	237.2
60	244.1	242.9	242.9	236.8
65	243.3	242.1	241.0	235.5
70	244.7	242.5	242.5	236.3
75	244.6	242.0	242.3	236.1
80	244.1	241.3	242.3	236.0
85	240.9	240.8	240.9	235.8
90	245.4	241.2	241.2	235.7
95	244.7	240.0		235.5
100	244.9	240.4	240.4	234.7

Table 4.3.1-4 Flux (mL/m^2 h) throughout UF experiments of solutions containing Dextran at different pressure conditions.

Permeate Volume (mL)	30 kDa membrane - 3 mg/mL Dextran				
	1 bar	1.5 bar	2 bar	2.5 bar	3 bar
5	99.2	113.37	86.3	84.42	92.28
10	71.5	95.61	89.2	104.42	111.77
15	64.0	88.83	91.6	112.30	112.30
20	63.0	81.81	92.3	104.42	107.97
25	61.6	80.32	86.6	101.74	103.33
30	60.0	75.34	85.9	99.20	99.20
35	59.0	75.48	84.9	96.11	96.44
40	57.8	77.42	82.0	93.36	92.01
45	57.0	74.87	81.2	93.98	89.95
50	56.2	74.17	79.2	88.77	88.57
55	55.7	72.50	79.2	86.43	84.75
60	55.2	71.92	77.4	73.48	83.83
65	54.9	71.64	77.2	84.56	82.66
70	54.3	70.32	76.9	83.91	81.93
75	54.0	70.10	75.9	81.76	81.20
80	53.8	69.01	75.2	81.08	80.36
85	53.6	69.04	74.9	79.08	79.17
90	53.4	68.87	74.0	78.66	78.31
95	53.3	68.16	73.7	78.29	76.77
100	53.2	68.18	72.9	77.05	76.45

Table 4.3.1-5 Flux (mL/m^2 h) throughout UF experiments of solutions containing Humic and Fulvic acids at different pressure conditions.

Permeate Volume (mL)	**5 kDa membrane**					
	Humic Acids (10 mg/L)			**Fulvic Acids (10 mg/L)**		
	1 bar	2 bar	3 bar	1 bar	2 bar	3 bar
1	11.84	23.34	29.39	12.21	24.04	31.80
2	11.34	16.71	29.95	11.70	22.40	30.21
3	10.92	17.51	28.68	11.30	21.40	29.79
4	10.72	17.63	28.60	11.00	21.02	28.80
5	10.61	17.71	28.34	10.80	20.66	28.41
6	9.19	15.56	24.17	10.60	20.40	27.90
7	9.23	15.87	24.47	10.55	20.20	27.70
8	9.31	16.15	24.99	10.50	20.00	27.15
9	9.41	16.34	25.33	10.45	19.70	27.00
10	9.38	15.38	25.27	10.40	19.50	26.60
11	9.45	15.59	25.45	10.30	19.50	26.30
12	9.48	15.92	25.67	10.20	19.30	26.00
13	9.49	16.12	25.86	10.10	18.96	25.80
14	9.55		26.02	10.00	18.96	25.65
15	9.55		26.16	10.00	19.02	25.65
16	9.41	17.66	26.34	9.90	19.10	25.71
17	8.90	17.75	26.35	9.90	19.00	25.90
18	8.97	17.79	26.40	9.80	18.80	25.90
19	9.47	18.78	27.87	9.70	18.60	25.60
20	9.48	18.83	27.89	9.70	18.80	25.40
21	9.52	18.85	27.82	9.70	18.60	25.50
22	9.53	18.85	27.80	9.75	18.40	25.60
23	9.53	18.53	27.82	9.75	18.60	25.53
24	9.54	18.49	27.80	9.70	18.40	25.50
25	9.57	18.49	27.75	9.70	18.48	25.50

Table 4.3.1-6 Flux (mL/m^2 h) throughout UF experiments of solutions containing NOM 1R101N and 1R108N at different pressure conditions.

Permeate Volume (mL)	5 kDa membrane					
	NOM 1R101N (10 mg/L)			NOM 1R108N (10 mg/L)		
	1 bar	2 bar	3 bar	1 bar	2 bar	3 bar
1	15.87	22.67	27.00	8.92	22.04	36.07
2	11.84	16.36	21.30	8.40	17.83	26.45
3	11.28	15.07	19.30	8.15	17.25	23.81
4	10.76	14.49	18.00	8.04	16.80	22.67
5	9.70	12.60	17.33	7.87	16.60	21.80
6	8.80	11.34	16.60	6.86	14.34	18.31
7	8.80	11.52	16.60	6.82	14.58	18.33
8	8.80	11.76	16.45	7.04	10.72	18.56
9	8.60	12.19	17.01	7.21	11.09	19.10
10	8.80	12.23	17.14	7.35	11.34	19.08
11	8.80	12.40	17.42	7.40	11.53	19.14
12	8.60	12.56	17.57	7.45	11.28	19.32
13	8.60	12.67	16.80	7.47	11.02	19.39
14	8.80	12.83	17.15	7.56	11.24	19.59
15	8.16	12.97	17.23	7.65	11.40	19.61
16	8.25	13.06	17.39	7.70	11.55	19.72
17	8.28	12.64	17.50	7.77	11.64	18.69
18	7.92	12.65	17.63	7.82	11.71	18.75
19	8.36	13.36	18.61	8.25	12.36	19.79
20	8.47	13.51	18.76	7.92	12.51	19.94
21	8.52	13.50	18.77	7.99	11.97	19.91
22	8.52	13.53	18.34	8.01	11.98	19.93
23	8.60	13.56	18.40	8.07	12.03	20.01
24	8.63	13.60	18.44	8.10	11.84	19.88
25	8.71	13.68	18.58	8.20	11.75	19.36

Table 4.3.1-7 Flux (mL/m^2 h) throughout UF experiments of solutions containing Dextran at different pH conditions.

Permeate Volume (mL)	Dextran (3 mg/mL)							
	30 kDa membrane				20 kDa membrane			
	pH 4.8	pH 6	pH 8	pH 9.7	pH 4.98	pH 6.03	pH 8.3	pH 10.07
5	57.51	101.74	64.00	62.00	35.75	44.58	36.07	37.08
10	55.11	70.85	62.98	61.52	37.08	42.44	35.11	36.40
15	53.14	62.98	61.36	60.73	37.79	41.48	34.21	36.18
20	52.55	61.76	60.58	60.12	38.24	41.44	34.58	35.75
25	52.62	60.30	60.12	59.76	38.30	41.25	35.05	35.62
30	52.44	59.07	59.67	59.37	38.46	41.12	34.65	35.69
35	50.78	58.35	59.10	58.72	38.58	41.15	34.72	35.61
40	50.63	56.78	58.89	58.67	37.88	41.01	34.88	35.51
45	50.58	56.33	58.64	58.35	37.83	40.12	34.34	35.53
50	50.48	55.81	57.51	58.18	37.97	40.12	34.44	35.46
55	50.52	55.53	57.51	58.04	37.63	40.08	34.50	35.51
60	50.39	55.30	57.44	57.71	37.20	40.11	34.55	35.40
65	50.32	54.93	57.25	56.75	37.82	40.05	34.55	35.31
70	50.04	54.84	57.03	56.74	37.48	39.65	34.63	35.31
75	49.43	54.21	57.06	56.68	37.57	39.68	34.64	35.26
80	49.48	55.11	56.94	56.53	37.63	39.63	34.63	35.21
85	49.63	54.97	56.83	56.54	37.43	39.56	34.49	34.75
90	49.60	54.81	56.73	56.33	37.43	39.29	34.50	34.75
95	49.24	54.55	56.64	56.22	37.47	39.31	34.47	34.98
100	48.63	54.32	56.44	56.08	37.29	39.27	34.40	35.18

Table 4.3.1-8 Flux (mL/m^2 h) throughout UF experiments of solutions containing NOM 1R101N, NOM 1R108N, Humic and Fulvic acids at different pH conditions.

Permeate Volume (mL)	5 kDa membrane (10 mg/L)							
	pH 3				pH 7			
	NOM 1R101N	NOM 1R108N	HA	FA	NOM 1R101N	NOM 1R108N	HA	FA
1	16.53	17.63	22.04	14.70	9.02	14.43	11.84	12.21
2	14.43	15.26	16.88	12.12	8.53	12.12	11.34	10.17
3	13.68	14.34	15.87	11.67	8.32	11.56	10.92	10.00
4	13.28	13.92	15.26	11.34	8.31	11.84	10.72	9.71
5	12.97	13.45	14.97	11.02	8.05	12.06	10.61	9.68
10	12.34	13.01	13.64	10.71	7.97	12.48	9.19	8.18
15	11.98	12.72	12.91	10.44	7.89	12.53	9.23	8.25
20	11.68	12.38	12.37	10.24	7.84	12.52	9.31	8.34
25	11.45	12.23	12.03	10.08	7.80	12.25	9.41	8.29
30	11.28	12.09	11.76	9.97	7.77	12.33	9.38	8.22
35	10.98	11.82	11.51	9.67	7.64	12.25	9.45	8.27
40	10.83	11.49	11.34	9.62	7.64	12.04	9.48	8.10
45	10.74	11.41	11.16	9.55	7.63	12.08	9.49	8.12
50	10.53	11.33	11.01	9.49	7.62	12.05	9.55	8.22
55	10.45	11.23	10.86	9.42	7.61	12.11	9.55	8.31
60	10.38	11.11	10.74	9.27	7.54	12.11	9.41	8.39
65	10.32	10.95	10.62	9.22	7.55	12.00	8.90	8.43
70	10.27	10.87	10.52	9.18	7.55	12.05	8.97	8.46
75	10.14	10.80	10.41	9.14	7.56	12.03	9.47	8.93
80	10.12	10.74	10.31	9.10	7.56	12.02	9.48	8.97
85	10.09	10.62	10.21	9.00	7.56	11.98	9.52	9.01
90	10.07	10.58	10.12	8.98	7.57	11.99	9.53	9.03
95	10.03	10.53	10.00	8.96	7.53	11.95	9.53	9.05
100	9.95	10.47	9.93	8.94	7.54	11.95	9.54	9.05

Table 4.3.1-9 Flux (mL/m^2 h) throughout UF experiments of solutions containing Dextran and NOM 1R101N and NOM 1R108N with different amounts of Ca^{2+}.

Permeate Volume (mL)	**5 kDa membrane 218 mg/L $CaCl_2 2H_2O$**		**30 kDa membrane Dextran 3 mg/mL**		
	NOM 1R101N	NOM 1R108N	18.3 mg/L $CaCl_2 2H_2O$	218.2 mg/L $CaCl_2 2H_2O$	765 mg/L $CaCl_2 2H_2O$
1	8.26	11.17	48.99	52.90	60.12
2	8.26	9.39	48.99	53.62	58.35
3	8.01	9.15	49.39	51.75	58.64
4	7.89	9.04	49.29	50.71	57.30
5	7.81	8.79	49.11	50.23	57.01
10	7.76	8.73	48.79	49.81	56.55
15	7.75	8.69	48.73	49.60	56.22
20	7.74	8.59	48.76	49.37	55.98
25	7.73	8.60	48.52	49.05	55.62
30	7.72	8.45	49.17	48.45	55.34
35	7.72	8.60	48.33	48.33	55.32
40	7.68	8.57	48.34	48.14	55.11
45	7.66	8.59	48.16	47.94	54.87
50	7.66	8.59	48.05	47.76	54.62
55	7.64	8.581	48.11	47.69	54.50
60	7.65	8.50	47.91	47.95	54.31
65	7.65	8.50	47.67	47.81	54.22
70	7.65	8.50	47.61	47.42	54.11
75	7.65	8.49	47.50	47.30	53.73
80	7.65	8.49	47.38	47.24	53.66
85	7.65	8.48	48.99	52.90	60.12
90	7.67	8.47	48.99	53.62	58.35
95	7.68	8.43	49.39	51.75	58.64
100		8.41	49.29	50.71	57.30

SUMMARY IN SPANISH

Hoy en día los problemas relacionados con el agua pueden diferenciarse dependiendo del lugar geográfico evaluado. Por una parte, las regiones en vías de desarrollo, focalizados en Asia, América Latina y África, padecen la falta de agua en condiciones higiénicas y de calidad mínimas para su consumo. En la otra cara de la moneda se encuentras las regiones civilizadas (o desarrolladas) comúnmente llamadas "el primer mundo", donde la problemática del agua reside en su consumo excesivo junto con el vertido desmesurado de grandes cantidades de agua contaminada, además de la poca cultura de reutilización de los recursos hidráulicos. Analizando la situación un poco más en profundidad parece incluso irónico que mientras millones de personas no tienen agua potable para su propio consumo y mueren debido a enfermedades derivadas de la mala calidad del agua, el mundo civilizado no sabe cuidar el agua de la que dispone, consumiendo más de lo necesario y contaminando sus propios recursos de de agua potable.

Con el propósito de controlar y en cierto modo mejorar la situación en los países industrializados, en los últimos años los tratamientos de aguas residuales se han ido implantando con más y más fuerza. Esta implantación se puede analizar como el resultado de tres aspectos fundamentales:

1- Legislación más estricta. En este sentido, los límites de vertidos impuestos por la legislación ha provocado que empresas que antes vertían libremente hayan dejado de hacerlo.

2- Escasez del agua, cada vez más acusada debido al inminente y progresivo cambio climático. La política de la reutilización del agua, previo acondicionamiento con tratamientos adecuados, está adquiriendo más y más importancia debido al cambio de las condiciones meteorológicas, que ha provocado por ejemplo épocas de sequía más duraderas en ciertas regiones.

3- Creciente preocupación medioambiental. Los tratamientos de las aguas residuales están consiguiendo una mayor aceptación del público en general dado la mayor preocupación de los diferentes colectivos sociales por el medioambiente.

En esta Tesis Doctoral diversos tipos de aguas contaminadas han sido tratados mediante una tecnología emergente dentro del campo de los tratamientos de aguas: La Oxidación Húmeda.

1 FUNDAMENTO TEÓRICO

Dentro de los tratamientos de aguas podemos distinguir un conjunto de técnicas poco convencionales hasta ahora llamadas “Procesos de Oxidación Avanzada”. Estos procesos están basados en una generación inicial de radicales hidroxilos ($OH^{\cdot}$), que, una vez formados actúan como principales agentes oxidantes del sistema, destruyendo parcial o totalmente la materia orgánica e inorgánica (oxidable) del medio a tratar. Los Procesos de Oxidación Avanzada incluyen diferentes tecnologías, que se diferencian principalmente, en el camino seguido a la hora de generar los radicales. Algunas de estas tecnologías se describen brevemente a continuación:

1.1 Ozonización

Las propiedades desinfectantes del ozono se conocen desde principios del siglo XX, sin embargo, sus utilidades dentro del campo de los tratamientos de agua no fueron desarrolladas hasta las dos últimas décadas del mismo siglo.

La ozonización se basa en la descomposición en radicales hidroxilos que el ozono sufre en condiciones básicas de pH. Una vez generado, y tal y como sucede en el resto de Procesos de Oxidación Avanzada, el radical hidroxilo reacciona no selectivamente con la materia orgánica. Una de las mayores características de la ozonización es su gran dependencia del pH. Mientras que a pH básico el ozono se descompone en radicales, a pH ácido esta reacción no tiene lugar y por tanto, el agente oxidante del sistema pasa a ser el ozono (en vez del radical hidroxilo). La diferencia entonces entre ambas condiciones de pH reside en que el radical oxida no selectivamente, mientras que el ozono ataca únicamente a determinados grupos funcionales, dado su menor poder oxidante. A pH medio ambos procesos conviven y la materia es oxidada mediante los radicales y el ozono molecular.

El rendimiento de la ozonización puede ser mejorado mediante el uso de radiación ultravioleta externa o mediante el uso de catalizadores, siendo el peróxido de hidrógeno un ejemplo de ellos.

1.2 Proceso Fenton

Sin duda, el proceso Fenton constituye una de las más conocidas aplicaciones del peroxido de hidrógeno dentro del campo de los tratamientos de aguas. La reactividad del sistema (metal/peroxido) fue observada por su inventor Fenton en 1894, pero no fue hasta el 1930 cuando su utilización fue reconocida, una vez desarrollado un mecanismo basado en radicales hidroxilos.

Esta tecnología se basa en la transferencia de un electrón entre el peróxido de hidrógeno y un metal que actúa de catalizador homogéneo. Con diferencia, el hierro es el metal más comúnmente empleado. A pesar de su probada efectividad, el proceso Fenton presenta una desventaja, que consiste en el consumo sin recuperación del catalizador, hecho que influye negativamente en la economía del sistema. Con tal de mejorar este aspecto, otro tipo de catalizadores heterogéneos sobre soportes han sido estudiados, dando lugar a los procesos llamados “Fenton-like”. Otra posibilidad para mejorar la efectividad del sistema consiste en irradiarlo con luz ultravioleta o visible.

1.3 Fotocatálisis

La Fotocatálisis en un Proceso de Oxidación Avanzado basado en la generación de radicales y el posterior tratamiento de corrientes contaminadas mediante el uso de semiconductores. Éstos son materiales de bajo coste que permiten el tratamiento y la mineralización de compuestos altamente resistentes a la oxidación. Este proceso se encuentra todavía en su etapa de desarrollo y por este motivo su utilización no está muy extendida.

Este proceso se basa en la excitación de un electrón desde la banda de valencia hasta la banda de conducción mediante la radiación de luz. La degradación de los contaminantes o de la materia orgánica en general contenida en el sistema a tratar se da gracias al electrón excitado y al hueco generado en la banda de valencia, que mediante diferentes mecanismos generan radicales hidroxilo.

1.4 Ultrasonido

Esta tecnología se basa en la formación de cavitaciones que tienen lugar cuando un medio acuoso se expone a ultrasonidos por encima de un determinado umbral. La cavitación por su parte consiste en la formación y crecimiento de microburbujas y de su violento colapso durante el ciclo compressor de las ondas. Como resultado de este colapso de burbujas, la temperatura y la presión dentro de éstas puede alcanzar e incluso superar temperaturas y presiones de 3000 K y 1000 bar respectivamente. Bajo estas condiciones, cualquier tipo de enlace químico padece ruptura, por lo que, la materia orgánica o los contaminantes contenidos en una corriente acuosa se transformarían en dióxido de carbono y agua.

La elevada efectividad de esta técnica se debe a la conjunción de dos factores. Por una parte, la materia contenida en el medio acuoso puede padecer pirólisis dadas las elevadas condiciones de presión y temperatura. Por otra parte, los radicales hidroxilos, generados a partir de la pirólisis de moléculas de vapor de agua, también contribuyen a la purificación del medio acuoso.

1.5 Procesos de oxidación húmeda

Al igual que el resto de los Procesos de Oxidación Avanzada, los procesos de Oxidación Húmeda están basados en la generación de radicales hidroxilo que posteriormente actúan como agentes oxidantes del sistema. Sin embargo, y a diferencia del resto de los Procesos de Oxidación Avanzada, los Procesos de Oxidación Húmeda se llevan a cabo a elevadas condiciones de presión y temperatura. Los Procesos de Oxidación Húmeda encuentran su campo de aplicación en aquellas corrientes acuosas que presentan una concentración demasiado elevada para ser tratadas biológicamente y demasiado disuelta para ser tratada por incineración.

La primera patente de Procesos de Oxidación Húmeda data del año 1950 (*Zimmerman, 1950*) y aunque inicialmente esta tecnología fue concebida como una manera alternativa de obtener vainilla, actualmente sus aplicaciones residen en el campo de los tratamientos de aguas residuales. En la actualidad existen más de 200 plantas que operan con Oxidación Húmeda para el tratamiento de diferentes tipos de aguas residuales concentradas, entre los que destacan aguas procedentes de la producción de etileno, de plantas de refinado de crudo o de la industria papelera.

Una de las ventajas que presentan los Procesos de Oxidación Húmeda, cuando operan en continuo, es la posibilidad de recuperación de energía, hecho que condiciona el abaratamiento de los costes de operación. Por una parte, las elevadas condiciones de presión y temperatura hacen que la corriente de salida pueda utilizarse para acondicionar la corriente de entrada mediante por ejemplo, intercambiadores de calor. Por otro lado, la naturaleza exotérmica de la reacción hace que en determinadas ocasiones, cuando la corriente de entrada está suficientemente concentrada, el aporte de energía necesario para llevar a cabo el proceso sea mínimo. Otra de las ventajas que presentan estas tecnologías es que durante el proceso no se generan compuestos dañinos para la salud o para el medio ambiente. Este hecho se debe a que durante las reacciones los compuestos orgánicos son oxidados a dióxido de carbono o a otros compuestos inocuos, el nitrógeno se convierte en amoniaco, nitratos o nitrógeno elemental y los compuestos halogenados y sulfuros se transforman en haluros y sulfatos.

Esta tecnología está basada en la formación de los radicales a partir de una fuente de oxígeno (normalmente aire u oxígeno), que en condiciones elevadas de presión y temperatura genera radicales hidroxilo. Dentro de los Procesos de Oxidación Húmeda se pueden distinguir diferentes tecnologías dependiendo, de entre otros aspectos, del agente oxidante utilizado, las condiciones de operación y la utilización o no de catalizador. Estas tecnologías son: oxidación húmeda supercrítica, oxidación húmeda (subcrítica), oxidación húmeda con peróxido y los respectivos procesos con catalizador (oxidación húmeda catalítica supercrítica, oxidación húmeda catalítica, etc…).

- ✓ Oxidación húmeda supercrítica: utiliza aire u oxígeno puro como fuente de oxígeno y opera en condiciones de presión y temperatura superiores al punto crítico del agua (374 ºC y 22.1 MPa).

- ✓ Oxidación húmeda (oxidación húmeda subcrítica). Al igual que en el caso anterior el agente oxidante es aire u oxígeno puro. Sin embargo las condiciones de operación son menos drásticas que en el caso anterior y oscilan entre 125 y 300 ºC de temperatura y entre 0.5 y 20 MPa de presión.

- ✓ Oxidación húmeda con peróxido. Tal y como su nombre indica, se emplea peróxido de hidrógeno para llevar a cabo la oxidación. Ésta es una tecnología muy reciente y pocos pero interesantes resultados han sido publicados en esta disciplina. Las condiciones de operación son difíciles de delimitar, dado el poco trabajo realizado en este campo. Una de las ventajas que presenta esta tecnología es que se eliminan los problemas de transferencia de materia que podía presentar el oxígeno en los dos procesos anteriores.

En el siguiente esquema de reacciones se muestran los procesos de iniciación, propagación y terminación de los radicales, así como la paralela degradación de los compuestos orgánicos, de acuerdo con la información publicada por *Li et al.* en 1991.

a) Reacciones de Iniciación. Dos reacciones parecen ser las responsables de la generación inicial de radicales:

- Según el primer mecanismo, las moléculas de oxígeno reaccionan con los enlaces carbono-hidrógeno más débiles. Como resultado de este primer ataque se forman radicales hidroxilo ($HO_2^{\cdot}$) y radicales orgánicos ($R^{\cdot}$) tal y como se muestra en la reacción R-1. Además, los radicales hidroxilo formados pueden continuar reaccionando con más enlaces del tipo carbono-hidrógeno dando lugar a la formación de más radicales orgánicos y de peróxido de hidrógeno (reacción R-2).

$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$ Reacción R-1

$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O_2$ Reacción R-2

- De acuerdo con el segundo camino de generación de radicales, el peróxido de hidrógeno (obtenido en la reacción R-2) se descompone dando lugar a radicales hidroxilo ($HO^{\cdot}$) (reacción R-3). Dicha descomposición tiene lugar en la superficie del reactor o en otra especie heterogénea u homogénea, indicada por la letra M en la reacción R-3. Otro aspecto a considerar, es que en este rango de temperaturas y presiones la descomposición del peróxido en agua y oxígeno también puede darse (reacción R-4).

$H_2O_2 + M \rightarrow 2\ HO^{\bullet}$ Reacción R-3

$H_2O_2 \rightarrow H_2O + \frac{1}{2}\ O_2$ Reacción R-4

b) Reacciones de Propagación. En este punto del mecanismo, los radicales hidroxilo reaccionan con los compuestos orgánicos, más específicamente abstraen un hidrógeno de la molécula orgánica, generando radicales orgánicos ($R^{\cdot}$) y moléculas de agua.

$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$ Reacción R-5

El radical orgánico generado reacciona entonces con el oxígeno disuelto formado radicales peroxo ($ROO^{\cdot}$) tal y como se muestra en la reacción R-6. Este radical peroxo rápidamente abstrae un átomo de hidrógeno de una de las moléculas orgánicas dando lugar a un hidroperoxo inestable (HOOR) y a otro radical orgánico ($R^{\cdot}$) de acuerdo con la reacción R-7.

$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ Reacción R-▯

$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$ Reacción R-7

c) Reacciones de Terminación. Las reacciones de propagación concluyen cuando el hidroperoxo reacciona con un compuesto orgánico dando lugar alcoholes (reacción R-8) que posteriormente degeneran en cetonas y ácidos de bajo peso molecular (reacción R-9).

$ROOH \rightarrow 2ROH$ (alcohol) Reacción R-8

ROOH → Cetonas → Ácidos Reacción R-9

Estas reacciones tienen lugar hasta que ácidos del tipo acético o fórmico se generan. Estos ácidos tienen un tiempo de existencia superior al de otros compuestos dadas sus propiedades refractarias a la oxidación. En otras palabras, es más difícil oxidar estos ácidos que otros intermedios o que los compuestos iniciales. Eventualmente, la mineralización de estos ácidos ocurre, de acuerdo con la reacción R-10.

Ácidos de bajo peso molecular → $CO_2 + H_2O$ Reacción R-10

En cuanto a la ingeniería de la reacción, hay que tener en cuenta que la oxidación húmeda es un proceso trifásico en el caso de utilizar oxígeno como agente oxidante, que hoy por hoy es la práctica más común. Debido a la presencia de las tres fases y dado que la transferencia del oxígeno desde la fase gaseosa a la fase líquida es el requisito previo a la oxidación, es importante mantener una buena agitación en el sistema, evitando así problemas de transferencia de materia. Normalmente estos problemas son eludidos o solucionados y la reacción química representa la etapa limitante del proceso.

1.6 Aguas tratadas

En esta Tesis Doctoral se han utilizado Procesos de Oxidación Avanzada, concretamente la oxidación húmeda y la oxidación húmeda con peróxido, para degradar aguas procedentes de la industria papelera y aguas sintéticas que contienen clorofenoles. Se estudiaron dos tipos diferentes de aguas de la industria papelera que previamente se habían concentrado por diferentes técnicas.

1- Agua procedente del proceso de descortezado concentrada mediante evaporación.

Este tipo de aguas están altamente contaminadas por ácidos grasos y resínicos, taninos, ligninos así como por sus derivados. La presencia de estos compuestos en el agua provoca una coloración marronosa oscura de gran impacto visual. Además, los taninos son compuestos fenólicos polares altamente tóxicos que contribuyen con hasta el 50 % de la Demanda Química de Oxígeno de este agua. Una industria papelera en Finlandia fue la suministradora de estas aguas, que fueron tratadas previamente por evaporación para obtener un grado de concentración mayor.

2- Aguas procedentes de la fabricación termo-mecánica de pasta de papel concentrada por nanofiltración.

El proceso termo-mecánico de fabricación de pasta de papel comúnmente abreviado por TMP, es un proceso mediante el cual se convierte la madera en pasta de papel utilizando medios mecánicos y térmicos. Un conjunto de muelas cilíndricas o discos de metal giratorios (parte mecánica) ejercen fricción sobre la madera en un entorno de vapor de agua (parte térmica) que ayuda a ablandar la lignina y permite de este modo una más fácil separación de las fibras de celulosa. El concentrado de este agua se obtuvo mediante nanofiltración.

Por otra parte y tal y como se ha indicado anteriormente, en esta Tesis Doctoral también se han estudiado aguas sintéticas que contenían clorofenoles (CPs). Estos compuestos están incluidos dentro de la lista de contaminantes tóxicos prioritarios de la US EPA y por la Directiva Europea 2455/2001/EC, debida a su elevada toxicidad y baja biodegradabilidad. Los clorofenoles son productos químicos derivados del fenol que contienen de uno a cinco átomos de carbono. Fueron descubiertos en 1836 cuando Laurent cloró alquitrán. Existen 19 clorofenoles que se forman al sustituir de uno a cinco átomos de hidrógeno (no del grupo alcohol) por átomos de cloro. Se incluyen tres monoclorofenoles, seis diclorofenoles, seis triclorofenoles, tres tetraclorofenoles y un pentaclorofenol.

En cuanto a las concentraciones máximas permitidas en el medio acuático, la primera edición de "Guidelines for Drinking-water Quality" (normativa para la calidad del agua potable) publicado en 1984 por la Organización Mundial de la Salud, indicaba una concentración máxima de clorofenoles de 1 μg/L. Años más tarde, en 1998, la Comisión Europea sugería la misma concentración en la Directiva 98/83/CE.

Dado que en este trabajo se estudia en profundidad el 4-clorofenol, información adicional sobre sus orígenes y usos se ofrece a continuación. Este compuesto se obtiene industrialmente por cloración directa del fenol y se introduce en el medio ambiente como resultado de vertidos de fábricas donde se produce o de industrias donde se utilice como intermedio en la producción de otros clorofenoles, de herbicidas o a partir de la degradación de otros productos químicos. También puede encontrarse en el medio acuático como resultado de la cloración de substancias húmicas o ácidos carboxílicos naturales durante la etapa de desinfección de algunas plantas de tratamientos de aguas residuales o estaciones depuradoras.

Fuentes indirectas de entrada del 4-clorofenol al medio ambiente incluyen vertidos de la industria papelera, donde se forma por ejemplo como subproducto del proceso de blanqueo, como resultado de la desinfección del alcantarillado, de la cloración de residuos industriales y de la descomposición de herbicidas como el 2,4-D, por parte de microorganismos. Por ultimo, cenizas procedentes de plantas incineradoras, estaciones generadoras de energía, chimeneas e incendios forestales también contribuyen a su expansión por el medio ambiente.

En general, los Clorofenoles se utilizan en la agricultura, la industria farmacéutica, como biocidas y tintes. Debido a sus características biocidas, los clorofenoles se emplean muy frecuentemente para evitar el crecimiento de microorganismos durante la fabricación de algunos productos industriales como pinturas, almidón, aceites, tejidos, colas, gomas, productos proteínicos, champús, etc… Dentro de éstas, las principales aplicaciones del 4-clorofenol son: extracción de sulfuro y nitrógeno del carbón, intermedio en la síntesis de tintes y drogas, desnaturalizante de alcoholes, disolvente en el refinado del crudo, producción del herbicida 2,4-D, de los germicidas 4-CP-o-cresol y 2,4-CP.

Como consecuencia de su amplio campo de aplicación y de sus numerosos orígenes, el 4-clorofenol puede encontrarse en aguas superficiales o subterráneas así como en aguas residuales y suelos, incluso en la cadena trófica de lugares con bajos niveles de contaminación.

2 OBJETIVOS

El objetivo principal de esta Tesis Doctoral reside en el estudio de la eficacia de los Procesos de Oxidación Húmeda a la hora de degradar diferentes tipos de aguas contaminadas. Por un lado se ha evaluado su eficiencia frente a compuestos fenólicos clorados, como el 4-clorofenol y el 2,4-diclorofenol. Por otra parte, se ha investigado el tratamiento mediante estas técnicas de aguas residuales de la industria papelera, que son consideradas como vías indirectas de entrada de clorofenoles en el medio.

En cuanto a los clorofenoles, especial atención se ha dado al estudio de la eliminación del 4-clorofenol mediante oxidación húmeda y oxidación húmeda con peróxido, siendo este trabajo uno de los pioneros en utilizar la oxidación húmeda con peróxido. Este compuesto aromático se eligió como modelo a investigar dadas sus propiedades tóxicas y su amplia presencia en el medio. Una vez quedó demostrado que el 4-clorofenol no era refractario a la oxidación por estas técnicas, se investigó la influencia de los parámetros de operación en el resultado del proceso. De este modo, en ambas técnicas, oxidación húmeda y oxidación húmeda con peróxido se estudiaron la influencia de la concentración inicial del contaminante, la temperatura a la que se lleva a cabo la reacción y la dosis de agente oxidante (oxígeno en el caso de oxidación húmeda y peróxido en el caso de oxidación húmeda con peróxido).

Otra parte importante de esta investigación consistió en la determinación y cuantificación de los intermedios de reacción de la oxidación húmeda del 4-clorofenol. Una vez realizada esta parte, se procedió al estudio de la cinética de la reacción. Se asumió un camino de reacción y después de aplicar un programa de simulación se obtuvo un modelo cinético basado en ecuaciones relativamente simples que permiten calcular la concentración de 4-clorofenol, así como la de los intermedios, en cualquier momento de la reacción. Cabe destacar que los resultados de los análisis del ión cloruro presentes en el medio supusieron una inestimable herramienta a la hora de determinar qué reacciones tenían lugar en el reactor.

Otro objetivo de este trabajo de investigación consistió en el estudio de la biodegradabilidad a lo largo de las reacciones. Éste es un tema muy importante dentro de los tratamientos de aguas residuales debido a la posible y favorable combinación de un Proceso de Oxidación Avanzada con un post-tratamiento biológico. El objetivo en estos casos consiste en tratar una corriente tóxica y no biodegradable mediante oxidación y una vez la biodegradabilidad alcanza niveles aceptables se para la oxidación y se prosigue la mineralización con un tratamiento biológico. De esta manera se favorece la economía del proceso.

El estudio sobre el tratamiento de las aguas residuales procedentes de la industria papelera mediante procesos de oxidación húmeda, constituye otro objetivo de esta Tesis. Se trabajó con dos aguas diferentes que previamente habían sido concentradas, una por evaporación y la otra por nanofiltración, con el fin de mejorar la economía del proceso. Con ambas aguas (una procedente del descorchado de la madera y otra del proceso termo-mecánico de obtención de pasta de papel) se ha estudiado la influencia de las variables de operación durante la oxidación húmeda. Más concretamente se ha investigado el efecto de las variaciones de temperatura y presión parcial de oxígeno durante la oxidación húmeda. Especial peso se le dio al estudio de la evolución de los compuestos lipofílicos, ya que su presencia en las aguas recirculadas dentro de una misma fábrica papelera resulta especialmente perjudicial para la calidad final del papel. Además, dentro de este mismo capítulo se han aplicado dos modelos cinéticos encontrados en la literatura para predecir el comportamiento de soluciones concentradas durante la oxidación húmeda.

Dado que la economía de los procesos de oxidación húmeda depende en parte de cuánto concentrada esté la solución a tratar, un capítulo adicional sobre una técnica emergente, la Tecnología de Membranas ha sido incluído en esta Tesis. Más concretamente, los parámetros que se piensa pueden afectar el correcto funcionamiento de estos procesos han sido investigados.

3 RESULTADOS EXPERIMENTALES Y CONCLUSIONES

En este capítulo se incluyen la discusión de los principales resultados experimentales así como las conclusiones de este trabajo de investigación. En una primera parte se explicarán los resultados obtenidos de la oxidación húmeda con peróxido y de la oxidación húmeda de aguas procedentes de la industria papelera y de soluciones sintéticas de clorofenol. En la parte final de este capítulo se incluyen también los resultados de los experimentos llevados a cabo para estudiar la influencia de ciertos parámetros en la ultrafiltración.

3.1 Degradación del 4-clorofenol mediante oxidación húmeda con peróxido

Este tipo de procesos han sido utilizados para la degradación de soluciones que contienen 4-clorofenol. La influencia de diferentes parámetros de operación como temperatura, dosis de peróxido de hidrógeno y concentración de clorofenol en la solución inicial, han sido estudiados durante el proceso de oxidación. Con este fin, reacciones variando cada uno de estos parámetros han sido llevadas a cabo. La temperatura de operación se fijó en 100, 130 y 160 ºC, mientras que la dosis de peróxido se estudió en el rango de 1 a 5 mL. Por último, la concentración de clorofenol en la solución a tratar fue 300, 500, 750 y 1000 ppm. Con el objetivo de seguir la evolución de las reacciones diferentes muestras fueron tomadas y analizadas en el transcurso de los experimentos. Más concretamente, se analizaron el Carbono Orgánico Total (COT), el pH y la concentración de clorofenol, siendo determinada ésta última mediante cromatografía de líquidos.

La primera conclusión alcanzada a partir de esta serie de reacciones es que la oxidación húmeda es un proceso efectivo a la hora de eliminar el clorofenol de una solución contaminada ya que elevados niveles de mineralización y de destrucción del compuesto se pueden obtener en condiciones no muy severas de trabajo. Trabajando a la temperatura más baja estudiada (100 ºC) y con la menor dosis de agente oxidante (1 mL), se logró degradación total del 4-clorofenol para cualquiera de las concentraciones iniciales (desde 300 a 1000 ppm) después de 40 minutos de reacción.

En cuanto a la influencia de las condiciones de operación en el proceso de oxidación húmeda con peróxido de soluciones de 4-clorofenol, cabe destacar que un aumento de la temperatura resulta en un aumento en los niveles de mineralización alcanzados al final de la reacción así como en una más rápida desaparición del compuesto a tratar. De hecho, las reacciones de oxidación húmeda con peróxido de las soluciones con 300 ppm de clorofenol mostraron una degradación del carbono orgánico total del 85 % operando a 100 ºC. Cuando la temperatura de operación se incrementó hasta 130 y 160 ºC, el carbono orgánico degradado al final de la reacción fue del 93 y 95 % respectivamente. El carbono orgánico total degradado se calcula como el cociente entre la diferencia del contenido en carbono inicial y a un determinado tiempo dividido por el carbono inicial y multiplicado por cien, para expresar el resultado en tanto por ciento. La forma análoga del 4-clorofenol se utiliza para expresar su degradación respecto al contenido inicial. La cantidad de 4-clorofenol degradado en estas reacciones fue del 100 % y la diferencia entre las tres temperaturas reside en el tiempo necesario para alcanzar la completa degradación. Así mismo, cuando la reacción de oxidación con peróxido se lleva a cabo a 160 ºC, el compuesto desaparece durante los primeros 25 minutos de reacción independientemente de la concentración inicial. Al trabajar a temperaturas inferiores el tiempo necesario es mayor, concretamente, a 130 ºC se necesitan 35 minutos y a 100 ºC 44 minutos para obtener una concentración nula del 4-clorofenol en el medio.

Por otra parte, la variación en la concentración inicial de clorofenol resultó en variaciones en cuanto a la degradación del carbono orgánico total. En este sentido, las reacciones con mayores concentraciones presentaron una menor degradación de la carga orgánica. Este hecho se atribuye a que cuanto más concentrada está la solución inicial, mayores cantidades de ácidos de bajo peso molecular se generan. Estos ácidos resultan más difíciles de oxidar que el compuesto original y por tanto, cuanto mayor es su concentración, menor es la degradación total del carbono orgánico.

En cuanto a la influencia de la dosis de peróxido utilizado en las reacciones de oxidación húmeda con peróxido, se puede afirmar de acuerdo con los resultados que mayores dosis implican mayor degradación del clorofenol así como mayor eliminación de la carga orgánica. Este hecho implica que bajo las condiciones de operación estudiadas, el agente oxidante no se encuentra en exceso respecto a la carga orgánica inicial.

Experimentos de oxidación húmeda con peróxido fueron llevados a cabo con otro compuesto de la misma familia, en particular con 2,4-diclorofenol con tal de poder establecer comparaciones entre ambos compuestos. Los resultados experimentales sugerían que ambas substancias se degradan a una velocidad similar mediante esta tecnología, sin embargo, diferencias en cuanto a la degradación de la carga orgánica total fueron observados. Los experimentos llevados a cabo con el diclorofenol obtuvieron una menor degradación de la carga orgánica total. Este hecho indica que los intermedios de reacción formados durante la degradación del diclorofenol son más refractarios a la oxidación que los formados a partir de la eliminación del monoclorofenol.

3.2 Degradación del 4-clorofenol mediante oxidación húmeda

Para el estudio sobre la degradación del 4-clorofenol mediante oxidación húmeda, con oxígeno como agente oxidante, se llevaron a cabo diversas reacciones variando la concentración inicial de clorofenol, la temperatura de reacción así como la presión parcial de oxígeno suministrada al sistema. La concentración inicial de clorofenol se fijó en 500 y 1000 ppm. Las temperaturas de reacción estudiadas fueron 150, 160, 175 y 190 ºC. Por último, las presiones parciales evaluadas fueron de 5, 7.5, 10 y 15 bares. El estudio sobre la influencia de cada uno de estos parámetros en la evolución de la oxidación húmeda, fue llevado a cabo variando cada uno de ellos y manteniendo el resto constantes dentro de una misma serie de experimentos.

De las muestras tomadas durante estos experimentos se analizó el pH, el COT, la concentración de iones cloruros, la concentración de clorofenol e intermedios (mediante cromatografía de líquidos) y la demanda bioquímica de oxígeno.

La influencia de la temperatura fue estudiada llevando a cabo reacciones a diferentes temperaturas manteniendo la presión de oxígeno a 10 bares. Se realizaron dos series de experimentos, a 500 y a 1000 ppm de concentración inicial. De estos experimentos se extrae la conclusión de que temperaturas superiores a 150 ºC son necesarias para degradar el 4-clorofenol en estas condiciones de operación. A partir de 160 ºC un aumento en la temperatura resultó en un aumento en la degradación del clorofenol y de la carga orgánica total.

En cuanto a la dosis de agente oxidante, o en otras palabras, la presión parcial de oxígeno utilizada, se llevaron a cabo experimentos a cuatro presiones diferentes, manteniendo la concentración inicial de contaminante en 500 ppm y utilizando dos temperaturas, 160 y 190 ºC. Se observó que un aumento de la presión de oxígeno en el rango de 5 a 10 bares provocaba un aumento en cuanto al rendimiento de la reacción, es decir, mayor degradación del clorofenol y del carbono orgánico total. Sin embargo, al aumentar la presión aplicada de 10 a 15 bares no se observaron mejoras notables. Este hecho sugería que a partir de 10 bares el oxígeno se encuentra en exceso con respecto al contenido orgánico de la solución.

Otra conclusión importante extraída de los experimentos de oxidación húmeda de soluciones que contienen 4-clorofenol, es que las reacciones presentan dos etapas diferenciadas. En la primera, denominada periodo de inducción, los radicales se forman y por tanto la degradación del compuesto es muy lenta y casi inapreciable. En la segunda etapa, u oxidación, los radicales atacan la materia orgánica y por tanto, la eliminación del 4-clorofenol es más notable.

En cuanto a los análisis de la concentración del ión cloruro a lo largo de las reacciones, se observó que durante la oxidación ningún intermedio que contuviera cloro se formaba. Esta conclusión se alcanzó tras comparar la concentración de cloruros en solución con la concentración de cloruros procedentes de la degradación del 4-clorofenol. Ambas concentraciones resultaron similares, indicando que los cloruros generados a partir de la degradación del monoclorofenol no formaban intermedios clorados durante el proceso.

Otro aspecto importante a mencionar sobre la oxidación húmeda del 4-clorofenol es la biodegradabilidad. En el transcurso de los experimentos se observó que la biodegradabilidad del as muestras aumentaba, favoreciéndose por tanto, la posibilidad de acoplar un tratamiento biológico después de la oxidación. Concretamente, la oxidación húmeda a 190 ºC y 10 bares de presión, de soluciones de 500 ppm de clorofenol presentó un aumento en la biodegradabilidad de la solución de 20 a 245 mg O_2 L^{-1} desde el momento inicial hasta los 60 minutos de experimento. La combinación de procesos de oxidación avanzada con tratamientos biológicos es una práctica económicamente viable, sin embargo, especial atención debe dedicarse a la toxicidad de la solución. Es necesario estudiar y reconocer el momento justo de la oxidación en el que la solución presenta un nivel de biodegradabilidad aceptable para poder continuar con la mineralización mediante un tratamiento biológico.

Por último, con los datos experimentales de esta sección se sugirió un modelo cinético. Los principales intermedios detectados fueron hidroquinona y quinona, además de ácidos de bajo peso molecular. El modelo suponía que los tres compuestos (clorofenol y los dos intermedios) siguen una cinética de pseudo-primer orden y que además, el reactor se comporta como un reactor ideal de mezcla perfecta. Según el mecanismo de reacción propuesto, el clorofenol se degrada durante el transcurso de la reacción generando hidroquinona, que a su vez se descompone en quinona. La quinona, una vez formada se descompone en ácidos de bajo peso molecular. Las constantes cinéticas de las reacciones fueron encontradas matemáticamente mediante un método de optimización de mínimos cuadrados, comparando las concentraciones experimentales de cada uno de los compuestos con las calculadas a partir del modelo cinético y de los valores de las constantes. Mediante esta modelización también se calcularon los periodos de inducción correspondientes a cada temperatura de reacción, que son 23,4 minutos a 160 ºC, 10,1 minutos a 175 ºC y 5,02 minutos a 190 ºC. De estos resultados se deduce que el tiempo necesario para que los radicales se generen y empiecen a atacar la materia orgánica es inversamente proporcional a la temperatura de reacción.

3.3 Degradación de aguas residuales de la industria papelera mediante oxidación húmeda

Después de realizar el estudio sobre la degradación de dos tipos de aguas residuales de la industria papelera mediante oxidación húmeda, se puede llegar a la conclusión que está tecnología es adecuada para tratar este tipo de aguas ya que en ambos casos se obtuvieron ciertos niveles de degradación de la materia orgánica junto con aumentos en la biodegradabilidad de las muestras. A continuación se explican por separado los resultados y conclusiones relacionados con cada una de estas dos aguas residuales.

i- Oxidación húmeda de aguas de proceso de la obtención de pasta de papel obtenida termo-mecánicamente

El estudio de la oxidación húmeda de este tipo de aguas se llevó a cabo desde diferentes puntos de vista. Por una parte se estudió la influencia de la temperatura, realizando experimentos en el rango desde 120 hasta 200 ºC manteniendo la presión constante en 10 bares. En segundo lugar se analizó la influencia de la presión parcial de oxígeno entre 5 y 15 bares a dos temperaturas diferentes, 160 y 190 ºC. Las muestras tomadas durante los experimentos se analizaron en cuanto a pH, carbono orgánico total, demanda química de oxígeno, demanda bioquímica de oxígeno y contenido en compuestos lipofílicos de la madera.

En cuanto a la influencia de la temperatura, los resultados experimentales mostraron que a partir de 150 ºC, un aumento de la temperatura resulta en un aumento en la eliminación de la carga orgánica. Sin embargo, por debajo de esta temperatura, la degradación es insuficiente, alcanzando una reducción del carbono orgánico total no superior al 10 %. En cambio, cuando la temperatura de reacción fue fijada en 200 ºC, reducciones de la demanda química de oxígeno del 70 % y biodegradabilidades del 0,97 fueron alcanzadas.

Tal y como se ha mencionado anteriormente, el contenido en compuestos lipofílicos de la madera fue analizado. Resulta de especial interés que pesar de que las reacciones llevadas a cabo por debajo de 160 ºC no mostraron grandes niveles de degradación de la materia orgánica sí que adquirieron cierto grado de degradación de los compuestos lipofílicos. En particular, a 150 ºC se midieron las siguientes concentraciones al final de la reacción: 70 % de reducción en la concentración de ácidos grasos, 90 % en la de ácidos resínicos y en la de lignanos y destrucción total de triglicéridos.

En cuanto al estudio sobre la influencia de la presión parcial de oxígeno durante la oxidación de este tipo de aguas residuales, se puede afirmar que, en ninguna de las condiciones de operación en las que se trabajó el oxígeno se encontraba en exceso con respecto a la carga orgánica de la solución. Se llegó a esta conclusión dado que un aumento en la presión parcial de oxígeno resultó en un aumento en la degradación en todos los casos estudiados.

Dos modelos cinéticos para la predicción de la evolución de la oxidación húmeda de soluciones concentradas han sido aplicados a los resultados experimentales de este apartado. La modelización para encontrar los valores de las constantes cinéticas incluidas en cada uno de los modelos se llevó a cabo mediante un proceso de optimización por mínimos cuadrados. Con las constantes cinéticas y las ecuaciones propuestas por los modelos, se calcularon los parámetros de las reacciones y se compararon con los valores obtenidos experimentalmente. De esta comparativa se lleva a la conclusión de que ambos modelos pueden predecir la evolución de las reacciones pero con cierto nivel de error. Sin embargo, se ha resaltar que uno de los modelos predice no únicamente la evolución de la degradación de la carga orgánica, sino también la evolución de la biodegradabilidad. Esto supone una ventaja cuando se piensa en combinar la oxidación húmeda con un proceso biológico.

ii- Oxidación húmeda de aguas de descortezado concentrada por evaporación

Las reacciones de oxidación húmeda de aguas residuales procedentes de la etapa de descortezado de una industria papelera se llevaron a cabo en un rango de temperaturas de 170 a 200 ºC, manteniendo en todos los experimentos la presión de oxígeno constante en 10 bares. Los resultados de estas reacciones de oxidación muestran que la temperatura no es suficiente para obtener niveles altos de degradación de la materia orgánica. Concretamente, en este rango de temperaturas se obtuvieron reducciones de la demanda química de oxígeno de entre el 20 y el 30 %. Además biodegradabilidades inferiores al 40 % se observaron en todos las reacciones. De acuerdo con estos resultados sería conveniente realizar los experimentos en condiciones de presión y temperaturas más elevadas o quizás, recurrir al uso de algún catalizador.

La diferencia en los resultados de la oxidación húmeda obtenidos con los dos tipos de aguas es debida probablemente a las diferentes propiedades de las soluciones a tratar. En particular, parece interesante destacar la demanda química de oxígeno presente en cada solución. Por una parte, las aguas procedentes de los procesos de fabricación de la pasta de papel contenía inicialmente una DQO de entre 8 y 9 g L^{-1}, mientras que el agua procedente del descortezado contenía una carga mucho mayor, entre 47 y 60 g L^{-1}.

3.4 Ultrafiltración

Esta serie de experimentos se llevó a cabo para estudiar la influencia de ciertos parámetros de operación que se piensa son responsables del deterioro del funcionamiento de las membranas. Este deterioro de las membranas aparece reflejado en una menor retención y una disminución del flujo de permeado y es una consecuencia de dos fenómenos principalmente: la polarización inversa y el ensuciamiento de la membrana.

Para llevar a cabo esta investigación se trabajó con diferentes disoluciones que contenían dextran, celulosa, ácido alguínico, ácido húmico, ácido fúlvico y materia orgánica natural. Los experimentos de ultrafiltración se realizaron utilizando membranas con diferente tamaño de poro, 5, 20 y 30 kDa. Variando las condiciones de operación se pretendió determinar la influencia de la concentración en la solución a filtrar, el efecto del pH de la solución y de la presencia de cationes divalentes así como de la presión aplicada.

En cuanto a la influencia de la concentración en la solución inicial, se llegó a la conclusión de que un aumento en este parámetro conlleva una disminución del flujo a largo plazo. Este hecho se explica teniendo en cuenta que cuanto más concentrada está la solución, mayor probabilidad de que la membrana sufra polarización inversa y ensuciamiento.

El siguiente parámetro estudiado fue la influencia de la presión aplicada en la cámara del alimento. Los resultados obtenidos mostraban que a mayores presiones, mayores caudales de agua atravesaban la membrana. Este hecho se puede entender fácilmente ya que el flujo que atraviesa la membrana es, por definición proporcional a la diferencia de presiones. En otras palabras, la presión aplicada es la fuerza impulsora del proceso, y por tanto, a mayor presión mayor flujo. Sin embargo, la utilización de altas presiones conlleva una menor retención de partículas en la membrana. De hecho, cuando los caudales de agua que atraviesan la membrana son elevados tienden a arrastrar consigo más partículas. Esta inercia de las partículas resulta en una menor eficacia en cuanto a capacidad de separación de la membrana y calidad del permeado obtenido. Como conclusión, a la hora de variar las condiciones de presión es necesario establecer los criterios de operación en cuanto a calidad o cantidad del permeado.

En cuanto a la influencia del pH de la solución a filtrar, diferentes experimentos fueron llevados a cabo añadiendo disoluciones tamponadas al alimento con tal de asegurar unas determinadas condiciones de pH durante la ultrafiltración. Del resultado de los experimentos se concluye que los medios alcalinos resultan más favorables dentro de las condiciones de operación estudiadas ya que permiten mayores caudales de agua a través de la membrana. Este resultado se puede explicar teniendo en cuenta las características tanto de los solutos como de la membrana. Por una parte a pH básico los solutos se encuentran desprotonados y cargados negativamente. Por otra parte, de acuerdo con los resultados de los análisis del potencial zeta de las membranas, cuanto más básico es el medio, la membrana se encuentra más negativamente cargada. Por tanto, en medio alcalino, ambos están cargados negativamente y tienen lugar repulsiones electrostáticas entre la membrana y los solutos. Estas repulsiones provocan que las acumulaciones del soluto en la superficie de la membrana sean poco frecuentes, del mismo modo que la polarización inversa y el ensuciamiento de la membrana.

La influencia de la presencia del catión divalente Ca^{2+} en la solución a tratar se estudió mediante la realización de experimentos con diferentes concentraciones de $CaCl_2$ en el alimento. De estos experimentos se concluye que cuanto mayor es la concentración del catión en la disolución mayor disminución del flujo se observa. Este hecho se atribuye a las propiedades del catión que favorece las interacciones entre el soluto y la superficie de la membrana provocando su ensuciamiento.

4 RECOMENDACIONES

La primera recomendación que se sugiere en vista a los resultados obtenidos de esta Tesis Doctoral es el escalado de los procesos estudiados junto con el cambio de modo de operación de discontinuo a continuo. Bajo estas nuevas condiciones, se podrían estudiar no únicamente el efecto de los parámetros de operación en la degradación de los compuestos sino también, los aspectos económicos y de recuperación de energía. En este sentido, la recuperación de energía en forma de presión o de temperatura puede facilitar información sobre las ventajas del uso de la oxidación húmeda frente a otros tratamientos del agua.

En segundo lugar y una vez se haya llevado a cabo el escalado del proceso, sería conveniente investigar la posibilidad y las ventajas que supondrían la incorporación de un post-tratamiento biológico para complementar la mineralización.

Otra recomendación relacionada con la oxidación húmeda con peróxido reside en la optimización de la dosificación del agente oxidante en el transcurso de la reacción. Grandes dosis de peróxido de hidrógeno en el medio generan grandes cantidades de radical hidroxilo que pueden resultar en su desactivación mediante la siguiente reacción: $2\ OH^{\cdot} \rightarrow H_2O_2$. Por tanto, resulta conveniente tener la máxima cantidad posible de hidroxilos que no provoque una desactivación masiva. Una posible solución para este problema sería alimentar el peróxido mientras se va consumiendo, es decir, dosificarlo a diferentes tiempos de reacción. De esta manera, la cantidad de agente oxidante suministrada al medio sería la misma, pero la desactivación del radical se vería menos favorecida ya que se evitarían grandes concentraciones de peróxido.

Una recomendación final consistiría en el uso de catalizadores con tal de aumentar la velocidad de reacción del proceso. Sin embargo, especial atención debe prestarse a la hora de elegir el catalizador. En este sentido no sería conveniente utilizar un catalizador que pudiera disolverse en alguna medida ya que se estaría contaminando aún más el medio acuoso. También se recomienda el uso de un reactor catalítico de lecho fijo, ya que así se evitaría la necesidad de tener que instalar una etapa posterior para separar el catalizador.