Tailored chemical oxidation techniques for the abatement of bio-toxic organic wastewater pollutants: An experimental study.

Dissertation presented by

Magdalena Anna Paradowska

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Memoria presentada por

Magdalena Anna Paradowska

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Miembros tribunal de tesis
Presidente Dr. Francesc Castells i Piqué
Secretario Dr. Laureano Jiménez Esteller
Vocales
Dr. Agustí Fortuny Sanroma
Dra. M. Teresa Coll Ausio
Dra. Maria José Martín Sanchez
Suplentes
Dr. Azael Fabregat i Llangostera
Dr. Dieter Boer

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El Dr. Frank Stüber, Professor Titular del Departament d'Enginyeria Química de l'Escola Tècnica Superior d'Enginyeria Química, de la Universitat Rovira i Virgili de Tarragona,

Faig constar que el present treball, amb el títol

TAILORED CHEMICAL OXIDATION TECHNIQUES FOR THE ABATEMENT OF BIO-TOXIC ORGANIC WASTEWATER POLLUTANTS: AN EXPERIMENTAL STUDY,

que presenta la doctoranda na MAGDALENA ANNA PARADOWSKA per optar al grau de Doctor en Enginyeria Química, ha estat dut a terme sota la meva immediata direcció, i que tots els resultats obtinguts són fruit del treball i l'anàlisi realitzat per l'esmentada doctoranda.

I per a què es faci saber i tingui els efectes que correspongui, signo aquesta certificació.

Tarragona, gener de 2004

Dr. Frank Stüber
Professor Titular d'Enginyeria Química

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Resumen

La creciente presencia de los contaminantes orgánicos recalcitrantes y no biodegradables en las aguas residuales, especialmente las provenientes de la industria química y petroquímica, ha desafiado los tratamientos de aguas residuales mediante incineración y oxidación biológica.

Hay una clara necesidad de probar y poner en marcha nuevas tecnologías alternativas que pueden tratar eficazmente las aguas residuales muy concentradas en contaminantes tóxicos y no biodegradables. Sin embargo, parece imposible disponer en un futuro cercano de un método universal capaz, no solo de destruir completamente todos los contaminantes, sino también de hacerlo a un coste competitivo.

En este trabajo, varias técnicas de oxidación químicas tales como Catalytic Wet Air Oxidation (CWAO), CWAO promovida por peróxido de hidrógeno, Wet Peroxide Oxidation (WPO) y Fenton WPO han sido probadas a fin de eliminar diversos compuestos aromáticos pertenecientes a las familias de contaminantes orgánicos más comunes.

Con este objetivo, se diseñó y construyó un sistema de reacción en continuo adaptable y capaz de operar a altas temperaturas y altas presiones. En particular, este equipo puede funcionar como un sistema de oxidación catalítica o no catalítica a temperaturas y presiones de 25 a 550ºC y de 10 a 330 bares respectivamente. En CWAO se utiliza aire y carbón activo (CA) como oxidante y catalizador de bajo coste, mientras que en Fenton WPO se alimenta soluciones de hidrógeno peróxido y sulfato de hierro (II) como oxidante y catalizador homogéneo. H_2O_2 sirve también como promotor en CWAO o como oxidante liquido en WPO debido a su conocida capacidad de producir radicales hidroxilos con un alto poder oxidante.

En un estudio preliminar, conversiones de referencia fueron obtenidas para fenol y aromáticos substituidos tales como el o-cresol, m-xileno, o-clorofenol, p-nitrofenol, anilina, nitrobenceno y sulfolano mediante CWAO sobre CA usando un TBR a 140ºC y 9 bar de oxígeno. Buenos resultados fueron obtenidos para o-

cresol, m-xileno, o-clorofenol y fenol. Fenol (como el contaminante estándar), p-nitrofenol, anilina, nitrobenceno y sulfolano fueron estudiados a continuación con más detalle ya que estos compuestos no-biodegradables resultaron ser demasiado refractarios en las condiciones de CWAO aplicadas. Adicionalmente dos muestras de efluentes industriales originarias de la producción de resinas fenólicas (TRI1 y TRI2) han sido probadas.

Cada tratamiento ha sido aplicado primero al contaminante estándar, fenol, con el objetivo de estudiar la influencia de las variables de operación importantes y de preoptimizar la conversión de orgánicos y de la reducción de DQO. Posteriormente, el rendimiento de cada tratamiento también ha sido examinado con los otros compuestos en las condiciones de preoptimización, encontradas.

Como conclusión principal se puede remarcar que CWAO sobre CA añadiendo pequeñas cantidades de H_2O_2 es indudablemente una alternativa muy económica para tratar eficazmente aguas con residuos orgánicos siempre que las circunstancias lo permiten. No es un tratamiento recomendado, por otro lado, a los compuestos extremadamente refractarios o los que polimerizan tales como el nitrobenceno, el sulfolano o la anilina, respectivamente.

Aunque no se obtuvieron siempre una conversión completa de los orgánicos y de la DQO, un incremento adecuado de la carga de CA y la dosis de H_2O_2 ofrece una manera eficiente y relativamente barata para alcanzar un rendimiento satisfactorio del proceso.

El uso de un oxidante fuerte como es H_2O_2 y temperaturas más elevadas (WPO), mejoró considerablemente el grado de mineralización de todos los compuestos estudiados. Temperaturas entre 300 y 350ºC y presiones de 100-150 bar han permitido obtener conversiones de los orgánicos casi completas y de DQO de 80 a 100%. Los factores positivos del proceso WPO consisten en el uso más eficiente del oxidante H_2O_2 dando lugar a tiempos de residencia muy cortos de minutos o incluso menos. La manera optima de alimentar es mezclar previamente el oxidante con el orgánico antes de entrar en el precalentador. Los cortos tiempos de residencia con WPO posibilitan el desarrollo de reactores de pequeño tamaño incluso para tratar grandes flujos volumétricos. El tratamiento de efluentes conteniendo sulfolano y nitrobenceno mostraron grandes inconvenientes. En caso del nitrobenceno, temperaturas excesivamente altas de 550ºC fueron necesarias para obtener una conversión del 80%. La destrucción de una solución de 5000 ppm de sulfolano a 370ºC aunque satisfactoria, ha dado como resultado pH muy ácido con valores inferiores a 1 causando corrosión incluso de un material muy estable como es el Hastelloy. Esta situación requiere el ajuste inicial y el control permanente del pH durante la reacción. Las temperaturas y presiones muy elevadas así como los problemas de corrosión encarecen el proceso de WPO, pero cuando se requiere una completa conversión de los orgánicos y de la DQO de cerca del 100%, es una solución técnicamente viable.

La adición de pequeñas cantidades de reactivo de Fenton (sulfato de hierro (II)) ha demostrado ser muy eficaz para obtener rendimientos comparables a los de WPO. Cantidades de tan solo 10-20 mg Fe^{2+}/l han permitido bajar la temperatura de oxidación del nitrobenceno de 550ºC (WPO) a 200ºC (Fenton WPO) manteniendo conversiones de DQO comparables. En caso de aplicar Fenton WPO al fenol, p-nitrofenol y anilina los resultados fueron similares. Desgraciadamente, el Fe^{2+} puede formar complejos insolubles con ciertos orgánicos como se observó en el caso del p-nitrofenol y la anilina. Durante la oxidación de estos compuestos mediante el reactivo de Fenton se observó un cambio del color de las muestras liquidas y pequeñas cantidades de precipitado lo cual probablemente afectará al rendimiento del proceso a largo plazo. Es muy recomendable realizar pruebas preliminares en las que se evalúe la compatibilidad del reactivo de Fenton con las aguas residuales especificas destinadas a tratar. Finalmente, con respecto a la reactividad de los compuestos el siguiente orden ha sido observado para todos los tratamientos, aunque en algunos casos la diferencia de la reactividad era muy pequeña: fenol < anilina < p-nitrofenol < sulfolano < nitrobenceno.

La aplicación de las diferentes técnicas de oxidación a muestras de efluentes industriales de proceso de la producción de las resinas fenólicas, ha conducido a las siguientes conclusiones: Primero, resulta mucho más difícil tratar los residuos reales que aguas residuales sintéticas, aunque las técnicas probadas han permitido obtener conversiones de fenol casi completas (TRI1: 3000 ppm, TRI2: 40 ppm). Por otra parte, solo se consiguió destrucciones de DQO entre 50 y 70% (TRI1: 6000 mg/l, TRI2: 100000 mg/l). Los efluentes reales suelen caracterizarse por una composición compleja y variada, la cual muchas veces se desconoce. En nuestro caso concreto se comprobó que la muestra TRI1 polimerizaba y únicamente la aplicación de las condiciones de WPO permitió tratar eficazmente a este efluente. Por otro lado, la muestra TRI2 con una muy alta carga orgánica, dio mejores resultados durante la CWAO que la WPO, debido al uso ineficiente de H_2O_2 cuando se alimenta en altas concentraciones. Esta situación exigió la dilución del efluente TRI2, que no se debe considerara como una solución óptima.

Finalmente, podemos afirmar que este estudio claramente ha demostrado que el tratamiento de aguas residuales debe ser flexible (varios métodos deben tomarse en cuenta) y especifico adaptándose a los efluentes industriales y el grado de destrucción requeridos. Para hacer el tratamiento de aguas residuales disponible económicamente, se recomienda siempre cuando sea posible el uso de CWAO con carbón activo como un catalizador estable y barato a temperaturas suaves. Si este método no es suficiente, la mejor alternativa será la WPO con un fuerte oxidante como H_2O_2 y la adición de pequeñas cantidades de Fe^{2+} (reactivo de Fenton). Aunque todas las técnicas estudiadas han mostrado ser muy eficientes, es difícil obtener la mineralización completa. Sin embargo, la mineralización completa puede no ser necesaria para reducir la bio-toxicidad hasta los niveles aceptables. En consecuencia, el futuro de las técnicas de oxidación química está desde luego en su uso como pretratamiento seguido por el tratamiento biológico. Por ello, los estudios de los tratamientos combinados químico-biológicos son necesarios para desarrollar completamente el potencial de las técnicas de oxidación química para los tratamientos de aguas económicos.

Abstract

The identification of highly refractory and non-biodegradable organic pollutants in wastewater, especially coming from the chemical and petrochemical industry, has challenged the conventional wastewater treatment such as incineration or biological abatement.

There is a clear need to test and set-up emerging alternative technologies that can deal with highly concentrated and/or toxic non-biodegradable organic water pollutants. However, it seems impossible in the close future to dispose of one universal method able to destroy not only completely all of the detected pollutants, but also at an acceptable cost.

Thus, several chemical oxidation techniques such as Catalytic Wet Air Oxidation (CWAO), hydrogen peroxide promoted CWAO, Wet Peroxide Oxidation (WPO) and Fenton WPO have been tested to remove different aromatic organics belonging to commonly encountered pollutant families.

For this purpose, an adaptable high temperature and high pressure continuous reactor system was designed and constructed, this equipment can be run either for catalytic or noncatalytic oxidation at temperatures and pressures ranging from 25 to 550°C and 10-350 bar, respectively. Air oxidant and inexpensive activated carbon (AC) catalyst were used in CWAO, while iron sulphate and H_2O_2 were employed in WPO and homogeneous catalysed Fenton WPO. H_2O_2 is either used as a promoter in CWAO or oxidant (WPO) as it is known to be an excellent source of highly oxidative hydroxyl radicals.

In a preliminary study, reference conversion were obtained in an existing Trickle Bed Reactor using AC at 140°C and 9 bar O_2 for phenol and substituted aromatics such as o-cresol, m-xylene, o-chlorophenol, p-nitrophenol, aniline, nitrobenzene and sulfolane. Based on the results obtained, phenol (as the standard pollutant), p-nitrophenol, aniline, nitrobenzene and sulfolane were studied more in detail, because these non-biodegradable compounds were found to be very refractory to CWAO at the given operating conditions. In

addition, two samples of industrial effluents (TRI1 and TRI2) coming from the phenolic resin production were tested to assess the treatment performance in case of effluents of complex composition.

In a first step, each treatment was applied to the standard pollutant phenol in order to study the influence of important operating variables on the process performance in terms of organic conversion and COD reduction. Thus, the performance with the other compounds was examined in pre-optimised conditions. As a general results, it can be pointed out that CWAO using AC and H_2O_2 promoter is undoubtedly the most economic way to efficiently abate organic wastewater, except for extremely refractory or polymerising compounds such as nitrobenzene, sulfolane or aniline, respectively. Although in our runs, complete conversions of organics and COD destruction were not achieved, an increase in the AC catalyst load and a convenient H_2O_2 dosage are an efficient and cheap way to yield satisfactory process performance.

The use of a strong oxidant H_2O_2, and higher temperatures and pressures as in WPO significantly improves the grade of mineralisation of all compounds tested, although on cost of higher inversion and operating costs. Temperatures up to 300-350°C and pressures from 100-150 bar yielded almost complete conversion of organics and COD destruction between 80-100%. Positive factors of WPO consist in the efficient use of H_2O_2 oxidant and very small residence times in the range of a few minutes or even less. Only 100% of stoichiometric H_2O_2 quantity is sufficient when properly fed to the reactor and small residence times result in small size reactors even for high volumetric flow rates to be treated. However, sulfolane and nitrobenzene WPO exhibited once again severe drawbacks. In the case of nitrobenzene, extremely high temperatures of 550°C were required to achieve conversions about 80%. The destruction of sulfolane, although very satisfactory, resulted in acid pH values <1, and thereby in corrosion of even highly stable material such as Hastelloy making necessary the control of pH during the reaction.

To improve WPO, the addition of small quantities of Fenton reagent (iron (II) sulphate) was shown to be a very efficient means. For nitrobenzene only 10 to

20 mg Fe^{2+}/l allowed to reduce the reaction temperature from 550ºC (pure WPO) to 200ºC (Fenton WPO) while maintaining similar conversion and COD reduction. Similar results were obtained fro Fenton WPO of phenol, p-nitrophenol and aniline. Unfortunately, Fe^{2+} is able to form insoluble complex with many organic compounds ad such behaviour was observed for p-nitrophenol and aniline. Precipitation and colour change occurred during the oxidation with Fenton reagent and certainly will affect the long-term process performance. Preliminary tests are strongly recommended to assess the compatibility of Fenton reagent with the specific wastewater to be treated. Finally, with respect to compound reactivity, the following order was observed for all treatments, although in some cases the differences in the reactivity were very small: phenol < aniline < p-nitrophenol < sulfolane <nitrobenzene.

When applying the different oxidation techniques to industrial process waters from phenolic resins production, the following conclusions can be drawn. First, it becomes evident that treating real wastes is much more difficult than synthetic wastewater. Although, the techniques tested permitted to obtain nearly complete phenol conversion (TRI1: 3000 ppm, TRI2: 40 ppm), the COD destruction never reached more than 50 to 70% (TRI1: 6000 mg/l, TRI2: 100000 mg/l). Real effluents are generally characterised by a complex and varying composition that often may not be known, what can explain such observation. In our specific case, sample TRI1 had "not expected" polymerisation properties and only WPO was able to satisfactory deal with this effluent. On the other hand, sample TRI2 with a very high organic load gave better results with CWAO than with WPO due to inefficient use of high concentrated H_2O_2 oxidant, requiring undesired high dilution rates.

Thus, we can finally state that this study has clearly demonstrated that wastewater treatment has to be flexible (several methods has to be taken into account) and case specific for industrial effluents. On order to make wastewater treatment economically available, CWAO using stable and cheap active carbon catalyst at mild temperature is recommended whenever possible. If CWAO fails, WPO using strong H_2O_2 oxidant and the addition of small quantity of Fe^{2+}

(Fenton Reagent) is a good alternative. Although, all the techniques tested have shown to be efficient, it is very difficult to obtain complete mineralisation. However, complete mineralisation may not be necessary to reduce bio-toxicity to acceptable levels. Thus, the future of chemical oxidation techniques lies certainly in its use as pre-treatment followed by biological abatement and studies of combined chemical-biological treatment are required to fully develop the potential of chemical oxidation techniques in economic wastewater treatment.

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Nomenclature

Latin characters

C	Concentration of compound (ppm or g/l)
d	diameter (mm)
D_e	Effective diffusion coefficient (cm^2/s)
E_A	Activation energy (J/mol)
F	Flow rate (ml/min or ml/s)
k_0	Frequency factor (case dependent units)
L	Length (m)
P	Pressure (bar)
r	Oxidation rate (ppm/min)
Re	Reynolds number (dimensionless)
T	Temperature (ºC)
u	Velocity (m/s)
W	Weight (g)
X	Conversion (%)
X_{COD}	COD conversion (%)

Greek characters:

Δ	Change
ϕ	Thiele modulus
μ	Viscosity (cp)
ρ	Density (g/cm^3)
τ	Residence time (s or h)

Subscripts

0	Initial
AC	Activated carbon
L	Liquid
O_2	Oxygen
org	Organic
p	Particle
Ph	Phenol

Abbreviations

AC	Active Carbon
AOP	Advanced Oxidation Process
BOD	Biochemical Oxygen Demand

COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
CWAO	Catalytic Wet Air Oxidation
DOC	Dissolved Organic Carbon
EEA	European Environmental Agency
EPA	Environmental Protection Agency (US)
G	Graphite
GC	Gas Chromatograph
HP	High Pressure
HPLC	High Performance Liquid Chromatography
HT	High Temperature
LHSV	Liquid Hourly Space Velocity
NB	Nitrobenzene
NP	Nitrophenol
PCBs	Polychlorinated Biphenyls
PET	Poly(ethylene) Terephthalate
PFR	Plug Flow Reactor
PBR	Packed Bed Reactor
PhOH	Phenol
PVA	Poly(Vinyl) Alcohol
RE	Removal Efficiency
SCF	Supercritical Fluids
SCW	Supercritical Water
SCWO	Supercritical Water Oxidation
SUL	Sulpholane
TBR	Trickle Bed Reactor
TG	Thermogravimetry
TOC	Total Organic Carbon
VOC	Volatile Organic Compound
WAO	Wet Air Oxidation
WO	Wet Oxidation
WPO	Wet Peroxide Oxidation

Symbols

•	Radical

Chapter 1

Introduction

1.1. Overview

At the beginning of the 20th century, a few cities and industries began to recognise that the discharge of municipal and industrial sewage directly into the natural watercourses caused to the people health problems and this led in the late 1930s to the development and construction of the first sewage treatment facilities. During the 1950s and 1960s, the U.S. government further encouraged the prevention of pollution by providing funds for the construction of municipal waste treatment plants, water pollution research and technical training and assistance in this field. In Western Europe once established the European Community, this organ actively influenced environmental initiatives of its member states through the establishment of an environmental legislation frame (Hardman et al., 1993). In the 1980s the importance of greening all aspects of industry and its sustainability were defined. New processes and improved techniques were developed to treat sewage, analyse wastewater, and evaluate the impact of pollution on the environment. In spite of these efforts, expanding population as well as industrial and economic growth caused the pollution to increase (Microsoft Encarta Encyclopedia, 1993-1996). Thus, the adequate treatment and/or safe disposal of hazardous gaseous, liquid and solid wastes have become major issues towards the establishment of future sustainable technological progress.

This environmental concern is nowadays expressed by more and more stringent regulations imposing lower pollutant (organic and inorganic) discharge limits and replacement of toxic substances/solvents or whole manufacturing processes. One consequence is that, before discharging into the environment, industrial and municipal wastes normally must undergo various physical, biological, chemical or combined treatments to reduce their potential toxicity.

In this context, the European Union is aiming for a significant cut in the amount of rubbish generated, through new waste prevention initiatives, better use of resources, and encouraging a shift to more sustainable consumption patterns (Cosmi et al., 2000). The European Union's actual approach to waste management is based on three principles, with the following priority:

1. Waste prevention;
2. Recycling and reuse;
3. Improving final disposal and monitoring.

So, for many industry sectors, pollution prevention, waste minimization and reuse are being increasingly utilized concepts. As a matter of fact, international companies like Dow Chemicals, PPG Industries, Dupont Chemicals, Delta - Omega Technologies, Parker Amchen, etc., are substituting dangerous and toxic substances used in production processes by more environmentally friendly materials. These industries are now realising that a cleaner, greener and safer company can also contribute to cost saving, positive recognition and customer satisfaction (Allen & Butner, 2002).

1.2. Waste management

The waste management is a very broad area, and therefore we will only focus on wastewater treatment in this work, in concrete on the removal of organic non-biodegradable pollutants, because they usually are toxic, frequently encountered in today's industrial effluents, and can not be efficiently treated by the conventional methods. However, to give a more complete picture of the situation, the principle types of pollution are briefly mentioned.

In general, pollution can be caused by solid, gaseous and liquid wastes, and adequate treatment methods for pollutants abatement are selected based on the composition, quantity, and form of the waste material. Some typical threshold values for the release of these wastes to the environment are shown in table 1.1.

They basically consist in the determination of biochemical oxygen demand (BOD), chemical oxygen demand (COD) for liquid wastes, total organic carbon (TOC) for solid wastes, volatile organic compounds (VOCs), particulates etc. for gaseous wastes. For example, COD and BOD measurements indicate the amount of organic matter present in a liquid waste stream that requires stabilisation or oxidation (Chakraborty & Linninger, 2002).

Table 1.1: Threshold values for Solid, Liquid, and Gaseous Wastes discharge in the USA (Chakraborty and Linninger, 2002).

waste state	parameters	threshold value
liquid	BOD	90 mg/L
	COD	180 mg/L
	organics concentration	150 mg/L
gaseous	particulates	150 μg/m^3
	VOC	20 mg/L
	heavy metals	1.5 μg/m^3
	NO_x, SO_x	0.15 mg/L
	other acid (or basic) gases	
solid	TOC	5 wt %
	toxics	10 mg/L
	water	1 wt %

Solid waste or rubbish is the most visible form of pollution (Fehr, 2002). Most of what is thrown away is either burnt in incinerators, or dumped into landfill sites (67%), although both of these methods create secondary environmental damage. Land filling not only takes up more and more valuable land space, it also causes potential secondary air, water and soil pollution, discharging carbon dioxide (CO_2) and methane (CH_4) into the atmosphere as well as chemicals and pesticides into the earth and groundwater. On the other hand, burning waste in incinerators releases toxic chemicals and ashes with harmful metals contents into the air (Woodard, 2001).

Industries, fuel based vehicles and the burning of fossil fuels to produce electricity are among the main responsibles for air pollution. The substances that are generally recognised to be of major concern as air pollutants from human activity include: particulates, sulphur dioxide, nitrogen dioxide, carbon monoxide, lead, ozone and chlorofluorocarbons (Woodard, 2001).

Air pollution is controlled in two ways: (i) by reducing the quantity of pollutants produced in the first place and (ii) with end-of-the-pipe devices that capture pollutants already created. Common examples of end-of-the-pipe devices include catalytic converters in automobiles and various kinds of filters and scrubbers in industrial plants (http://www.eco-web.com).

1.2.1. Industrial and municipal wastewater

With respect to liquid wastes, the most important sources of water pollution are urban and industrial residue that is thrown voluntarily or involuntarily.

By urban wastewaters we mean those ones containing metabolic waste, from domestic activities and scour from the urban structures (roofs, streets, etc). The three components (metabolic waste, non metabolic domestic waste, and urban scouring water) generally flow into common sewerage, consisting of an underground sewer system removing effluents away from the urban centres delivering them into a surface water body.

Huge amounts of water are used and contaminated in the whole industrial processing, from the production of raw materials, through the preparation of intermediate, to the packaging of the finished product. Since it has been more convenient, while permitted by environmental legislation, throwing away the processing waste and remnants than recycling and reusing them, a large and complex variety of organic and inorganic material has been discharged with the industrial waste. Nowadays, over half of the waste volume is generated by paper factories, oil refineries, and chemical industries, while the remaining comes from all the other industrial activities. For example, in Poland in 1998 the quantity of wastewater registered in the public statistical system as discharged into surface waters from point pollution sources was 9.8 billion m^3, including 2.8 billion m^3 of wastewater requiring treatment. Direct discharges from industrial plants accounted for 83.2% of total wastewater, i.e., 8.2 billion m^3, and sewage systems represented 16.8%, i.e., 1.7 billion m^3 (Central Statistical Office of Poland).

Within these aqueous residues the major water pollutants are of chemical, biological, or physical nature capable to degrade water quality. Wastewater contaminants can be roughly classed into eight categories depending on their nature and origin as described in table 1.2.

Table 1.2: Wastewater contaminants categories (Nathanson, 1986).

Waste Category	Description
Petroleum Products	Oil and chemicals used for fuel, lubrication, plastics, etc.
Pesticides and Herbicides	Chemicals used to kill unwanted animals and plants
Heavy Metals	Copper, lead, mercury, and selenium from industries, automobile exhaust, mines, and evens natural soil
Hazardous Wastes	Chemical wastes: toxic (poisonous), reactive (capable of producing explosive or toxic gases), corrosive (capable of corroding steel), or ignitable (flammable)
Excess Organic Matter	Fertilisers and other nutrients to promote plant growth
Sediment	Soil particles present in large enough amounts
Infectious Organisms	Disease-causing organisms - considered pollutants when found in drinking water
Thermal Pollution	Even small temperature changes in a body of water can drive away the fish and other species that were originally present, and attract other species in place of them

As illustrated in this table there is a big variety of water pollutant from diverse sources. Physically, wastewater is usually characterised by a grey colour, musty odour, a solids content of about 0.1%, and 99.9% water content. The solids can be suspended (about 30%) as well as dissolved (about 70%). Chemically, wastewater is composed of organic and inorganic compounds as well as various dissolved gases. Organic components may consist of carbohydrates, proteins, fats and greases, surfactants, oils, pesticides, phenols, etc. Inorganic components may consist of heavy metals, nitrogen, phosphorus, pH, sulphur, chlorides, alkalinity, etc. Gases commonly dissolved in wastewater are hydrogen sulphide, methane, ammonia, oxygen, carbon dioxide and nitrogen. The first three gases result from the decomposition of organic matter present in the wastewater. Biologically, wastewater may contain many pathogenic organisms, which generally originate from human beings (www.ns.ec.gc.ca/epb/issues/wstewtr.html).

As mentioned before, wastewater typically can be divided in two categories: urban and industrial. In the urban residues the main waste load is organic, but mostly not toxic and relatively biodegradable. Usually, this kind of wastewater is treated in the conventional wastewater treatment plant. The industrial wastewaters have a very complex and toxic composition depending on the industry that generates them. Even similar industries produce wastewater of highly varying composition, when different production processes are used. Thus, the wastewater composition is very important, when choosing the appropriate treatment method. For example, the residual toxic substance levels of effluents in municipalities, whose wastewater consists mainly of industrial waste, could be harmful to the environment and adequate no conventional treatment methods have to be applied.

In the context of waste composition, the Environmental Protection Agency (EPA) has identified approximately 275 priority pollutants to be regulated by categorical discharge standards. Priority pollutants, both organic and inorganic, were selected on the basis of their carcinogenicity, mutagenicity or high acute toxicity (Metcalf and Eddy, 1991).

We will focus in this work on nonbiodegradable and/or toxic organic compounds belonging to the waste categories 1 and 4 of table 1.2, because wastewater pollutants with such organic load are increasingly encountered in industrial and domestic effluents. The necessity of abatement of toxic non-biodegradable organics is mainly determined by two important factors: their toxicity potential and as mentioned above, their annual release. Table 1.3

presents the ranking of some toxic organic compounds of interest in the priority pollutant list of EPA from the year 2001. The quantity annually released to the environment is shown in table 1.4 for the USA in the year 2000 (www.epa.gov/tri).

Table 1.3: Extract from EPA list of Priority Pollutants, 2001 (www.epa.gov/).

Compound	Hazard Ranking*
xylenes	56
phenol	162
p-cresol	169
o-cresol	194
o-chlorophenol	247
p-nitrophenol	256

* 1 means the most harmful

Table 1.4: Annual release of toxic phenol-like pollutants in the United States for the year 2000 (www.epa.gov/tri).

Compound	Emission (ton/year)	Overall Ranking
Phenol	22	35
2,4-Dinitrophenol	11	50
Catechol	8.3	59
Aniline	5.8	70
Hydroquinone	1.9	95
Quinone	0.64	115
Pentachlorophenol	0.55	120
Chlorophenols	0.046	203
2-Nitrophenol	0.026	213
4-Nitrophenol	0.007	239

As can be seen in these tables, the important pollutant families that are aromatic hydrocarbons (phenols, cresols, xylenes) and substituted hydrocarbons (chlorophenols, nitrophenols, etc.). The importance of these pollutants is clear, as they accomplish both factors we mentioned before, high toxicity and high annual release.

1.2.2. Common organic wastewater pollutants

Nowadays, there exists strong environmental concern on a large number of organic pollutants coming from a wide range of sources, which may enter in wastewater (see table 1.2-1.4). Paxéus (1996), for example, identified over 137 organic compounds in the influent of the municipal wastewater plants in Stockholm. Many of these pollutants are totally artificial organic compounds, being products of an increasingly inventive chemical industry. The potential (long term) and actual (short term) impact of each of these xenobiotic compounds, however, is extremely difficult to predict or assess.

From table 1.2 and specific literature (http://jan.ucc.nau.edu/), the following classifications of organic water pollutants can be established:

-TCE (trichloro ethylene), Chloroform, Carbon Tetrachloride;
-Herbicides, Pesticides;
-and Oil and Grease, PAHs (Poly aromatic hydrocarbons), Hydrocarbons.

In this work, we will focus on non-biodegradable organic water pollutants, namely on aromatic hydrocarbons. Due to the large variety of such existing organic pollutants, we intent to establish groups of hydrocarbons of interest and give a short description of each group properties. In table 1.5, the typical use and potential toxicity of these compounds are summarized.

In general, aromatic hydrocarbons are molecules based on the benzene ring structure. They are important components in petrol (gasoline) and usually contain carcinogenic molecules like benzene, toluene, ethylbenzene and xylene (ortho-, meta- and para). Some of them have non-organic substituents like N, Cl, S, P, so they form important subgroups, termed substituted aromatic hydrocarbons (Bingham et al., 1979).

Table 1.5: Use and hazard ranking information for chemicals (Sax & Lewis, 1992).

Group	Material	Toxicity Ranking	Use
Aromatic Hydrocarbons	**Xylenes**	3 May contain benzene, a carcinogen	Aviation gasoline, protective coatings, solvent for alkyd resins, rubber cements, synthesis of organic chemicals
Phenols	**Phenol**	3 Questionable carcinogen	Making pharmaceuticals, chemicals, plastics, resins, rubber, refining oils, fertilizer, coke, paint removers, asbestos, perfumes, disinfectants, bactericide, fungicide
	Cresols	Toxic	Making disinfectants, perfumes, preserving agents or herbicide
Chlorinated Hydrocarbons	**Chlorophenols**	Questionable carcinogen, corrosive	Making dyes, making other chemicals
Nitroaromatic Hydrocarbons	**Nitrophenols**	3	Making fungicide, pesticide, dyes and other chemicals
	Nitrobenzene	3 Also called oil of mirbane, poison, reproductive effects	Making shoe polish, dyes, explosives, floor and metal polish, other chemicals and paints
	Aniline	3 Suspected carcinogen, mutagen, allergen	Dyes, coloured pencils, lithographic and other printing inks, perfumes, pharmaceuticals, nylon fibers, resins, industrial solvents, rubber processing
Sulphur Compounds	**Sulpholane**	Toxic	Natural gas processing, making electronics and plastics

where: 3 – severe toxicity, materials that can cause injury of sufficient severity to threaten life. Data for total annual release in the USA in 2001, source: EPA.

We can distinguish several important families:

Phenols (e.g. phenol, cresols, catechol) are the most common organic pollutants in wastewaters. Phenols refer to the class of aromatic compounds having a hydroxyl group, as well as any additional organic substituent groups on a six-carbon benzene ring. Major sources of phenolic effluents include petroleum refineries, coke ovens, synfuels production facilities, wood preserving plants, and manufacturers of plastics, resins, dyes, pesticides, pharmaceuticals and a host of other chemicals. Because even at very low concentrations phenols can impart disagreeable tastes and odours to drinking water, taint fish flesh, and is harmful to the microorganisms of a biological plant, stringent limits (100 ppm) have been imposed on the discharge of phenols into municipal sewage treatment plants (Beszedits & Silbert, 1990). Phenols also occupy a prominent position on the US EPA priority pollutants list (see table 1.3).

Chlorinated Hydrocarbons (e.g. Chlorophenols, Polychlorinated Biphenyls [PCBs]) have been commonly used as solvents and degreasing agents in the past and make up a significant fraction of hazardous waste. Some of these are carcinogenic and, consequently, their fate and mobility in the environment must be understood and controlled (Callahan & Green, 1995).

Nitroaromatic hydrocarbons (e.g. nitrobenzene, nitrophenols, aniline, and nitroaniline) are anthropogenic and are released into the environment in large quantities as they are widely used for manufacturing pesticides, explosives, dyes, pharmaceuticals and plastics. The presence of substantial concentrations of toxic nitroaromatic compounds such as nitrobenzene, nitroaniline and nitrophenol in industrial effluents is inhibitory to several anaerobic biodegradative reactions, which may result in treatment process failure (http://www.eng.nus.edu.sg/Eresnews).

Nitrobenzene is an aromatic ring compound that is the major chemical intermediate required in the production of aniline (more than 98% of U.S. nitrobenzene production is used for aniline production). Additionally, nitrobenzene is used in the production of some pesticides, rubber-related chemicals, and pharmaceuticals (including acetaminophen).

Nitrophenols are pollutants, which are commonly found in industrial wastewater. They are toxic to plants, fish and many other organisms. Nitrophenols are listed by the United States Environmental Protection Agency as priority pollutants. Unfortunately, they are accumulating in the environment at a worrisome rate.

Aniline is used in rubber accelerators and antioxidants, dyes and photographic chemicals, as isocyanates for urethane foams, in pharmaceuticals, explosives, petroleum refining; and in production of diphenylamine, phenolics, herbicides and fungicides (Sax & Lewis, 1992). Aniline is highly toxic to aquatic life.

Organosulphur compounds (e.g. sulpholane, thiophene, benzothiazole) are especially noted for their poignant odours. Organosulphur compounds have an inhibitory effect on microbial activity and influences the anaerobic biodegradation activities. They are used for applications including: polymer production, agricultural products, adhesives, pharmaceuticals, fuel additives, lubricant additives or aromatic extraction (Loundry & Suflita, 1997).

Sulpholane is an organic chemical used for a wide variety of industrial purposes. The primary industries that employ sulfolane include natural gas processing, plastics, and electronics. Sulfolane has traditionally been used in the extraction of aromatics from hydrocarbon mixtures and in sour gas sweetening (i.e. removal of acid gases from a natural gas stream). Its biodegradation is insignificant (Komex International, 2001).

1.2.3. Overview

Despite many efforts of industry and the establishment of more and more stringent environmental protection legislation, it seems that nowadays the environment is increasingly polluted by gaseous, liquid or solid substances. Among them, liquid organic wastes are of particular interest for this study. The major sources of water pollution are of municipal and industrial origin. The characteristics of industrial wastewaters can differ considerably both within and among industries. Thus, the impact of wastewater effluents discharge depends strongly on their content of specific organic and inorganic components. Our attention is especially focused on the organic toxic constituents of wastewaters as both their quantity and number present in effluents increase. Main organic aromatic pollutants families are: phenols, chlorinated hydrocarbons, nitroaromatic hydrocarbons and organosulphur compounds. The wastewaters containing these compounds need a special treatment, because the conventional biological treatment methods are not longer suitable for these pollutants basically due to their refractoriness and biotoxicity.

1.3. Wastewater treatment technology

There is no doubt that water pollution, especially by a large number of different organic chemical species, is a continuing and even growing problem that arises from human activities. No unique solution seems possible for destroying all these types due to the heterogeneous composition of real wastes as well as the diversity of the pollutants chemical properties. Some waste treatment methods merely transfer the toxic component from one phase to another. While this may serve to concentrate the waste in a more readily disposable form, it does not alter the chemistry of the pollutant. Other processes use chemical reactions to transform the waste into less toxic by-products or harmless end products such as CO_2 and water.

It is clear that the selection of the correct process or the combination of treatments is a difficult task that should be generally made depending on the treated wastewater characteristics (concentration and grade of refractoriness of contaminants, the flow rate) and the destination of the effluent (grade of mineralisation required).

However, it must be said that comprehensive wastewater treatment development, involves various aspects, such as analytical chemistry, kinetics, mass and heat transfer, reactor design and process optimisation and they cannot be all addressed in this survey. Further research is certainly necessary in these fields to bring the new treatment methods to their full potential. The present study thus rather emphasises on testing recently developed chemical wastewater treatments methods with the objective to experimentally investigate the destruction efficiency of these techniques for the removal of toxic organics, typically encountered in industrial and domestic wastewaters.

1.3.1. Classification of wastewater treatment

In general, the numerous unit operations and processes to remove wastewater contaminants are grouped together to provide various levels of treatment. They are presented in table 1.6 categorised in three main types: physical, biological and chemical treatments. Historically, primary methods are referred to physical or physical-chemical unit operations; secondary referred to biological operations; and advanced or tertiary referred to chemical or to combinations of all three.

Dependently on the contaminants that should be removed from wastewater different treatment method have to be chosen, as summarised in tables 1.6 (in general) and 1.7 (for toxic compounds). These tables also give a brief idea of advantages and drawbacks of the available treatments.

Flocculation, sedimentation, flotation, filtration, extraction and adsorption on activated carbon are typical physical or physicochemical operations. Coagulation and flocculation are used to remove particles of all types from water. Air flotation is mostly applied to remove free oil and solids from the bulk waste stream. Filtration is employed, when the volume waste stream contains high concentration of solid or other phase-separable material. Adsorption is the process of removing soluble contaminants by attachment to solid. In the extraction the constituents are transferred from one liquid to the solvent phase, which is selected such that it can be reused.

Table 1.6: Advantages and disadvantages of physical, biological and chemical treatments (Belhateche, 1995).

Treatment	**Physical, Physico-chemical**	**Biological**	**Chemical**
Types of pollutants:	Typically industrial wastewater. Organics and some inorganics, metals.	Industrial and domestic wastewater. Low concentration organics, some inorganics.	Typically industrial wastewater. Organics, inorganics, metals.
Methods	Filtration, Adsorption, Air flotation, Extraction, Flocculation, Sedimentation	Anaerobic, Aerobic, Activated sludge	Thermal oxidation (combustion), Chemical oxidation, Ion exchange, Chemical precipitation
Advantages:	Low capital costs, Relatively safe, Easy to operate	Low maintenance, Relatively safe, Removal of dissolved contaminants, Easy to operate	High degree of treatment, No secondary waste, Removal of dissolved contaminants
Drawbacks:	Volatile emissions, High energy cost, Difficult maintenance	Volatile emissions, Waste sludge disposal, Susceptible to toxins	High capital and operating costs, Difficult to operate

Biological treatment usually refers to the use of microorganisms (bacteria) in engineered reactor systems for effecting the removal of certain constituent, such as organic compounds, trace elements and nutrients. In aerobic system, oxygen is provided and used by the bacteria to biochemically oxidise organic matter to carbon dioxide and water. In an anaerobic system, oxygen is excluded and the microorganisms utilise compounds other than molecular oxygen for the completion of metabolic processes (Guo & Al-Dahhan, 2003).

Table 1.7: Processes used for the removal of toxic compounds (Metcalf & Eddy, 1991).

Process	**Removal application**
Activated carbon adsorption	Natural and synthetic organic compounds including VOCs, pesticides, PCBs, heavy metals
Activated sludge powdered activated carbon	Heavy metals, ammonia, selected refractory priority pollutants
Air stripping	Volatile organic compounds (VOCs) and ammonia
Chemical coagulation, sedimentation and filtration	Heavy metals and PCBs
Chemical oxidation	Ammonia, refractory and toxic halogenated aliphatic and aromatic compounds
Conventional biological treatment	Municipal wastewaters

Chemical treatment processes manipulate the chemical properties of the contaminants to facilitate removal of pollutant from the bulk wastewater or to decompose the compound within the waste stream. Chemical precipitation is used for removal of phosphorus and enhancement of suspended solids removal. Disinfection is a selective destruction of disease-causing organisms. Chemical oxidation/reduction is applied basically for treatment of hazardous organic wastes, but also inorganics.

All above-mentioned treatments can be used separately or combined with other processes to enhance the treatment efficiency of the process. For example, a flocculation stage may be often followed by a secondary biological process.

Concerning the remediation of organic pollutants, dependently on their concentration in the wastewater, adequate conventional treatments can be chosen. As example of physical treatment, extraction can be used to recycle expensive organics present in high concentration in wastewater. When the concentration of organics is very low and organics are biodegradable, the biological treatment would be the appropriate technique. Among chemical methods, incineration can be best used for wastewater with high nonhalogenated/chlorinated organic content and chemical oxidation for moderate to high organic matter load.

1.3.2. Performance of conventional organic wastewater treatments

Te choice of correct system must be carried out considering several factors, both technical (treatment efficiency, plant simplicity, flexibility, etc.) and economical (investment and operating costs; including reagent and energy consumption, maintenance). Specific experimental tests are required, in order to assess actual efficiency and proper treatment conditions. Figure 1.1 presents the example of a schema for selection of treatment method dependently on organic matter content and flow rate.

Generally, in the case of high organic pollutant concentrations (COD > 100000 mgO_2/l) and higher flow rates classic incineration is most widely used for liquid (and solid) waste destruction (Santoleri, 1988) (see figure 1.1). For wastes with only low to moderate concentration of organic material, the process is not self sustainable and auxiliary fuel has to be added. Due to the high temperature required, incineration needs an extremely high energetic input, high temperature resistant materials (Wigston, 1995) and also may generate extremely toxic by-products, like furans and dioxins in the presence of wastes containing chlorinated compounds (Belhateche, 1995). The implant of air pollution control devices is even raising the cost of this process. Another alternative is separation and reuse of organics, but it requires additional energy costs for the facilities construction and operation.

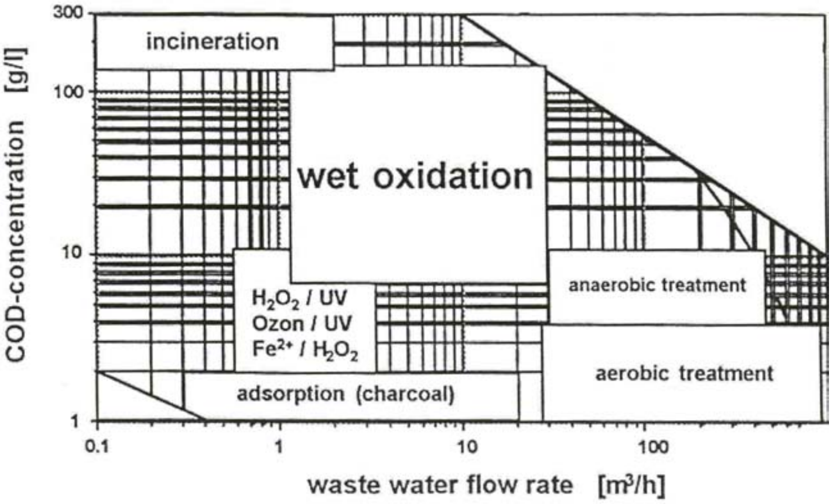


Figure 1.1: Wastewater treatment map in function of organic matter content and flow rate (Watercom).

For low to mediate concentration of dissolved organics (500 < COD < 50000 mgO_2/l), there are several ways to treat liquid waste streams. One option is the adsorption on activated carbon (see fig. 1.1) (Matatov & Sheintuch, 1998), but the saturated carbon is a hazardous waste, requiring either regeneration or transportation to a hazardous waste landfill (Voice, 1998). An apparent low cost option offers the biological oxidation (see fig. 1.1), but the organic pollutant has to be biodegradable, dilute and of low toxicity and the process generates a huge amount of sludges (Irvine & Wilderer, 1998). This high sludge generation requires physical treatments for sludge volume reduction, and the subsequent landfilled leading to a potential secondary pollution source (Bertanza et al., 2001).

Summarising, the actual state performance of conventional methods is clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested.

1.3.3. Emerging wastewater treatments

To overcome the inconveniences of conventional treatment methods such as biological treatment, physical adsorption on activated carbon or incineration, various chemical oxidation techniques have emerged in the last decades, in particular for the treatment of industrial wastewaters. The use of conventional wastewater treatment processes, especially in the case of moderate to higher organic loads, has become increasingly challenged with the identification of more and more organic and non-biodegradable contaminants.

On the other hand, the emerging wastewater treatments methods are increasingly gaining popularity since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. A simple classification of the emerging chemical technologies is given in table 1.8.

Table 1.8: Emerging chemical wastewater treatment technology.

WET AIR OXIDATION (WAO)	**200-350°C** **70-230 bar** **Air or O_2**	**Thermal oxidation processes**
CATALYTIC WET AIR OXIDATION (CWAO)	**<200°C** **<50 bar** **Air or O_2 and catalyst**	
SUPERCRITICAL WATER OXIDATION (SCWO)	**>374°C** **>221 bar** **Air, O_2 or H_2O_2 (and catalyst)**	
WET PEROXIDE OXIDATION (WPO)	**>100°C** **>1 bar** **H_2O_2**	**Wet Peroxide Oxidation Processes**
Fenton WPO	**~25 °C** **~1 bar** **H_2O_2 + Fe^{2+}**	
ADVANCED OXIDATION PROCESSES (AOPs)	**OH^- radical as intermediate (electrodes, UV light, ultrasound pulses or O_3)**	**AOPs**
COMBINED TREATMENTS	**O_3+UV** **Biological+AOPs** **Adsorption on activated carbon + CWAO**	**Combined treatments**

Thermal Wet Oxidation processes such as "already classical" Wet Air Oxidation, Catalytic Wet Air Oxidation and Supercritical Water Oxidation, use normally high temperature and pressure, air or oxygen as oxidant and frequently catalysts. Wet Peroxide Oxidation processes (WPO) benefits of H_2O_2 as a liquid oxidant source and also can employ homogeneous or heterogeneous catalysts (Fe^{2+}, Cu^{2+}). Advanced oxidation processes (ozonation, photocatalysis and electrochemical oxidation) utilise electron beams, UV light or ultrasound pulses to obtain high oxidation rate through the generation of free OH radicals (mainly hydroxyl radicals). Finally, there exist combined treatments, like AOPs with biological, ozonation with photocatalysis or adsorption on activated carbon with CWAO etc.

Depending on the reaction conditions two objectives can be achieved: (i) complete mineralisation of organics to CO_2 and H_2O or (ii) only an increase of the effluent biodegradability by orientating the conversion of toxic organic matter to the formation of biodegradable by-products such as carboxylic acids (Oliviero et al., 2003a).

The emerging treatment technologies have been already demonstrated to successfully remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes. In addition, advances in the manufacturing industry and the growing market associated with treatment processes should result in substantial improvements of the adaptability and costs for the future implementation of these processes at industrial scale (Oliviero et al., 2003a).

1.3.4. Overview

A variety of techniques is now available for the abatement of domestic and industrial wastewaters. The selection of the proper treatment both to achieve the desired degree of remediation and to be cost effective is in the most cases a challenging and complex task.

The conventional processes mostly applied for treatment of wastewater with organic load are adsorption on activated carbon, biological treatment or incineration. However, the first two are only viable for very low concentration of toxic and/or non-biodegradable organics, whereas incineration is very expensive in addition to process inherent problems of toxic gases release. Due to increasing amounts and complex composition of real organic effluents, other methods are being studied as an alternative to biological and classical physico-chemical processes. It seems that thermal oxidation processes, WPO and advanced oxidation technologies will probably constitute the best option in the near future, as they can treat wastes with high COD content that are either too diluted for incineration or too concentrated for biological treatment.

However, these promising techniques except for WAO are frequently tested with phenol as a reference toxic organic pollutant. Thus, investigation on other representative toxic organic contaminants as well as real wastewaters are certainly necessary to fully develop the potential of these improved techniques.

In the following chapters 1.4-1.6 a literature review of these emergent techniques is presented to discuss in detail the available information in terms of process performance for the abatement of toxic organic wastewater pollutants.

1.4. Thermal Wet Oxidation

Thermal Wet Oxidation is defined as the liquid oxidation of soluble or suspended oxidisable components in an aqueous environment using oxygen (or air) as the oxidising agent at elevated temperatures and pressures. When air is used as the source of oxygen, the process is referred to as 'classical' wet air oxidation (WAO). In this chapter we will review three different types of thermal wet oxidation: Wet Air Oxidation, Catalytic Wet Air Oxidation and Supercritical Water Oxidation.

1.4.1. Wet Air Oxidation

1.4.1.1. Development and Industrial Application of Wet Air Oxidation

The history of WAO started about 50 years ago, when Zimmermann observed that he could burn pulpmill liquors using air at high pressure leading to the combustion of organic compounds dissolved or suspended in liquid water, at relatively low temperatures, as long as oxygen was present (Zimmermann & Diddams, 1960).

Since then, this process (Zimpro) had been mainly used for sewage sludge treatment, but by the early 1970s, it was applied to regenerate spent powdered active carbon from wastewater treatment processes. During 1980s the process was rediscovered and gained popularity as means of detoxifying liquids prohibited from land disposal. Currently, more than 200 full-scale WAO plants are in operation for the treatment of a variety of effluent streams (Mishra et al., 1995), as presented in table 1.9 for the Zimpro oxidation installations.

Table 1.9: Zimpro Wet Air Oxidation Installations (Dietrich et al., 1985).

No. Plants	Type Wastes
109	Municipal Sludge
29	Night Soil
12	Carbon Regeneration
7	Acrylonitrile
6	Metallurgical Coking
6	Petrochemical
3	Paper Filler
2	Industrial Activated Sludge
2	Pulping Liquor
2	Hazardous Waste
1	Paper Mill Sludge
1	Explosives
1	Monosodium Glutamate
1	Polysulfide Rubber
1	Textile Sludge
1	Chrome Tannery Waste
1	Petroleum Refining
1	Misc. Industrial Sludges
Total: 186	

The most widely spread variant is the non-catalytic Zimpro process, which uses a co-current bubble column reactor, operating at temperatures between 150ºC - 325ºC and pressures of 20-210 bar. A simplified flow diagram of the process is given in Fig. 1.2. The main components in the flow diagram are separate gas and liquid feed lines, a heat exchanger unit, a gas-liquid separator and a catalytic converter to destroy any volatile organics remaining in the gas phase.

Other WAO noncatalytic commercial processes such as VerTech (vertical sub-surface reactor), Wetox (horizontal autoclave reactor), Kenox (the recirculation reactor) and OXYJET (the combination of jet-mixers and tubular reactors) are described by Luck (1999) and Kolaczkowski et al. (1999) and the interested reader may refer to these articles for more information.

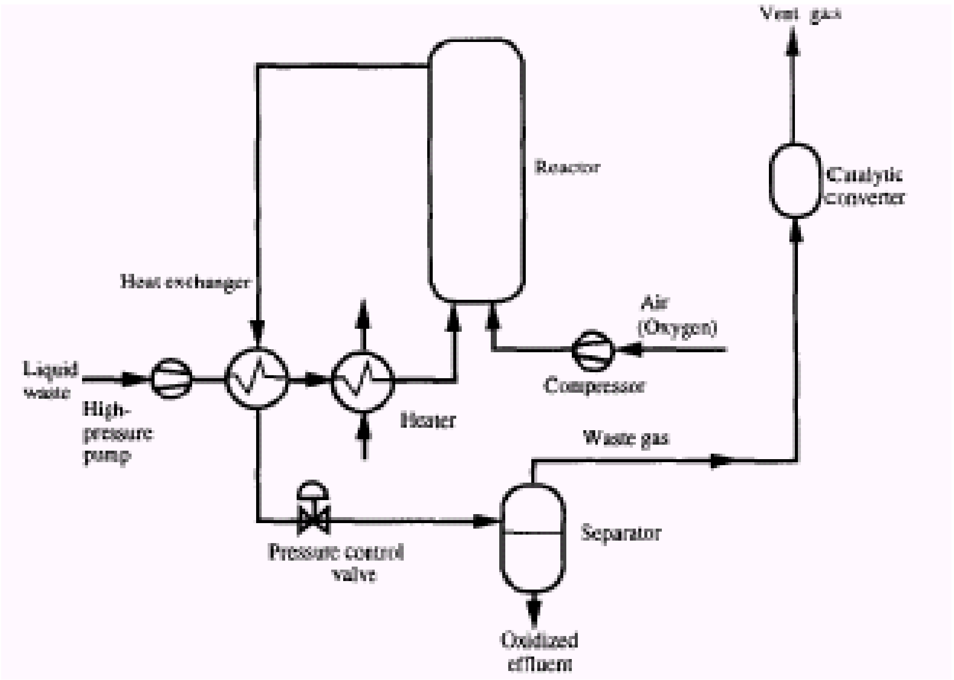


Figure 1.2: Simplified Zimpro process flow diagram.

1.4.1.2. Process fundamentals of Wet Air Oxidation

Wet Air Oxidation (WAO) is an aqueous phase oxidation process occurring, when a dissolved organic is mixed thoroughly with a gaseous source of oxygen at temperatures of 150 to 325°C and at pressures of 20 to 200 bar (Copa & Gitchel, 1998). The liquid phase is maintained by high pressure, which also increases oxygen concentration and thus, the oxidation rate. Water as an innocuous medium for oxidation has advantages of high density that allows using relatively small reactors, keeping salts dissolved in the solution, and due to quite constant heat capacity avoids pinch points caused by otherwise possible large changes in fluid densities.

The process can be controlled by two steps; (i) transfer of oxygen to the liquid phase; and (ii) reaction between dissolved oxygen and organic. The grade of oxidation principally depends on temperature, partial pressure, residence time and refractoriness of the substrate (Mishra et al., 1995; Levec, 1997; Kolaczkowski et al., 1999; Luck, 1999, Mantzavinos et al., 1999; Lei & Wang, 2000).

Usually air (Willms et al., 1987) or oxygen (Baillod et al., 1985) is used as oxidants. According to Mishra et al. (1995) one can reduce the capital investment, when using oxygen instead of air, however the cost of oxygen is higher and has to be compared with savings in initial capital investment.

WAO technologies are particularly suitable for the treatment of wastewater containing a high proportion of organic substances (including chiefly toxic and biologically difficult to decompose compounds), but also such inorganic compounds as hydrazine and sulphides. Industrial scale WAO can achieve easily up to 90-95% of conversion (Debellefontaine & Foussard, 2000), which in most cases, however, is not enough to meet actual effluent discharge regulation. Thus, most of WAO units are followed by biological treatment (Rivas et al., 2001a).

1.4.1.3. Survey of recent WAO studies

WAO has been already studied for the destruction of many synthetic and real wastewaters. As reported in the literature, wet air oxidation was investigated for treatment of phenol (Baillod et al., 1985; Willms et al., 1987) and substituted phenols (Joglekar et al., 1991), carboxylic acids (Shende & Mahajani, 1997; Shende & Levec, 1997, 2000), acrylonitrile, pentachlorophenol, o-chlorophenol (Randall & Knopp, 1980), wastewater from textile industry (Lei et al., 2000), polymers (Krisner et al., 2000), organic matter of radioactive waste (Bachir et al., 1998), biomass (McGinnis et al., 1983), paper mill black liquors, dye waste and biological sludges (Foussard et al., 1989). Respective reaction conditions and oxidising agent used in these studies are given in table 1.10.

WAO process was studied for many real wastewaters and is industrially applied, also for toxic nonbiodegradable organic pollutants. As can be seen in the table, curiously all of these studies were done in batch reactors, even if on industrial scale continuous reactors are commonly used. Mostly pure oxygen was applied as oxidant. Even if there are not many studies on pure compounds containing nitrogen, it can also be noticed that the compounds containing nitrogen are more difficult to destroy by WAO.

Table 1.10: WAO of organic pollutants and industrial effluents.

Substrate	Reaction conditions	Oxidant	Reactor type	Removal (%)	Reference
Phenol and substituted phenols	150-180ºC, 3-15 bar	O_2	Batch	>90% COD	Joglekar et al., 1991
Phenol and m-xylene	200-275ºC, 69-138 bar (total)	Air	Batch	ns	Willms et al., 1987
Phenol, o-chlorophenol, p-nitrophenol, etc.	150-320ºC	Air	Batch	RE>99%	Randall & Knopp, 1980
p-Nitrophenol	150-180ºC, 3-9 bar (total)	O_2	Batch	ns	González et al., 2002
Azo dyes	130-190ºC, 10 bar	O_2	Batch	70% TOC	Raffainer & von Rohr, 2001
Dyes	200ºC, 33 bar	O_2	Batch	37% COD 30% TOC	Chen et al., 1999
Carboxylic acids	180-280ºC, 10-55 bar	O_2	Batch	78% TOC	Shende & Levec, 1999, 2000
Formic and acetic acids	225-245ºC, 6.9-10 bar	O_2	Batch	30% COD	Shende and Mahajani, 1994
Polyvinyl alcohol	150-270ºC, 19.2 bar	O_2	Batch	80% TOC	Lei and Wang, 2000
Synthetic and natural polymers	270ºC, 0-20 bar	Air	Batch	70-80%TOC	Krisner at al., 2000
Polymer containing wastewater	100-240ºC, 30 bar	O_2	Batch	ns	Mantzavinos et al., 1999
Polyester	300ºC	O_2	Batch	92% TOC	Dinsdale et al., 1999
Desizing wastewater	150-290ºC, 3.75-22.5 bar	O_2	Batch	>90% COD >80% TOC	Lei & Wang, 2000
Paper mill black liquors, biological sludge, dyes	277-317ºC, 9-10.4 bar	O_2/Air	Batch	RE: 10-99%	Foussard et al., 1989
Biomass	171-227ºC, 17-34 bar	O_2	Batch	ns	McGinnis et al., 1983
Radioactive wastes	260-320ºC, 30 bar	50%N_2/ 50%O_2	Batch	<90% TOC	Bachir et al., 1998
Nuclear fuel chelating compounds	240-300ºC, 30-45 bar	50%N_2/ 50%O_2	Batch	80% TOC	Bachir et al., 2001

ns-not specified; RE-removal efficiency; pressure given is the oxygen partial pressure, except where total pressure specified.

The highest TOC or COD conversion obtained in WAO process was about 90%, but for most cases it was much lower. Thus, WAO process is not severe enough and should be improved to obtain higher conversion.

1.4.1.4. Kinetic Mechanism of WAO

WAO of organic pollutants is generally described by a free-radical chain reaction mechanism (Li et al., 1991; Bachir et al., 2001; Robert et al., 2002). Typically in the free radical process, the induction period to generate minimum radical concentration is of great significance (Duffy et al., 2000). During the induction period of phenol WAO, there is practically no change observed in phenol concentration. Once the critical concentration of free radical is reached, fast reaction takes place (propagation step), when almost all phenol is oxidised (Joglekar et al., 1991). Mishra et al. (1995) found that the induction period length depends on the catalyst concentration, oxygen concentration, temperature, and type of organic, in agreement with observations of other authors (Joglekar et al., 1991; Willms et al., 1987; Rivas et al., 1998; Wu et al., 2003). Sadana and Katzer (1974a) reported that also pH influences the induction period extent that is shorter for pH values of about 4, and is increasing with increase in pH.

The steady state (propagation step) is then followed by the third step (termination step) characterised by a slow oxidation rate.

These reaction steps taking place during WAO are generally described by the system of reaction equations illustrated below (Rivas et al, 1999):

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R^{\cdot}} + \mathrm{HO_2^{\cdot}} \tag{1}$$
$$\mathrm{R^{\cdot}} + \mathrm{O_2} \rightleftharpoons \mathrm{ROO^{\cdot}} \tag{2}$$
$$\mathrm{RH} + \mathrm{ROO^{\cdot}} \rightarrow \mathrm{R^{\cdot}} + \mathrm{ROOH} \tag{3}$$
$$\mathrm{ROOH} \rightarrow \mathrm{RO^{\cdot}} + \mathrm{OH^{\cdot}} \tag{4}$$
$$\mathrm{RH} + \mathrm{OH^{\cdot}} \rightarrow \mathrm{R^{\cdot}} + \mathrm{H_2O} \tag{5}$$
$$\mathrm{RH} + \mathrm{HO_2^{\cdot}} \rightarrow \mathrm{R^{\cdot}} + \mathrm{H_2O_2} \tag{6}$$

The first step is the chain initiation, in which free radicals ($R\cdot$, $OH\cdot$, $HO_2\cdot$) are produced by the bimolecular reaction of dissolved oxygen with the organic compound (reaction (1)). This reaction is found to be very slow at low temperatures. When the free radical R· is formed, it can readily react with molecular oxygen to give peroxoradical (ROO·) (reaction (2)). The peroxo compound formed in reaction (2) is able to react with parent compound (RH), yielding a hydroperoxide (ROOH) and another free radical (R·) (reaction (3)). Reactions (2) and (3) constitute the chain propagation of the cycle. The hydroperoxide ROOH formed in reaction (3) can further decompose to reactive radicals, which provide additional free radicals R·. This sequence is presented by reactions (4) and (5). In the mechanism, the organic parent compound (RH) can react thus with molecular oxygen (1) and the organic hydroperoxyl (ROO·) (3), hydroxyl (OH·) (5) and hydroperoxyl (HO_2·) (6) radicals (Vogel et al., 1999; Rivas et al, 1999).

As the hydroperoxides are quite unstable, they also decompose to form lower molecular weight intermediates (Li et al., 1991). This is the termination step, which includes formation of more stable compounds with reduced hydrocarbon chains by radical species.

1.4.1.5. Reactivity of organic compounds in WAO

The free radical chain reaction mechanism adopted for WAO suggests that aromatic hydrocarbons show different chemical reactivity due to the presence of different ring substituents that may alter the rate of the induction, propagation and termination step.

Joglekar et al. (1991) found that wet air oxidation of phenol and substituted phenols (chlorophenols, cresols, methoxyphenols, xylenes) follows three different trends depending on the substituent group:

(i) slow induction period followed by fast reaction (phenol, chlorophenol, m-xylene),

(ii) no induction period (methoxyphenol),

(iii) initial fast reaction period followed by a slow reaction (alkylphenols, i.e. cresols).

For example, phenol and chlorophenols display the first trend. In the case of methoxy phenols the induction period is not observed, probably because the methoxy group prefers the formation of aryloxy radical. The third trend is accomplished by cresols, where the oxidation of alkyl group is certainly faster than of the aromatic ring, thereby accelerating significantly the formation of free radicals.

Thus, different trends stand also for a different reactivity of the aromatic compounds and figure 1.3 shows the order starting with the highest reactivity that Joglekar et al. (1991) established from their WAO experiments. The trends and reactivities can be theoretically explained by the concept of electrophilic substitution during the induction step.

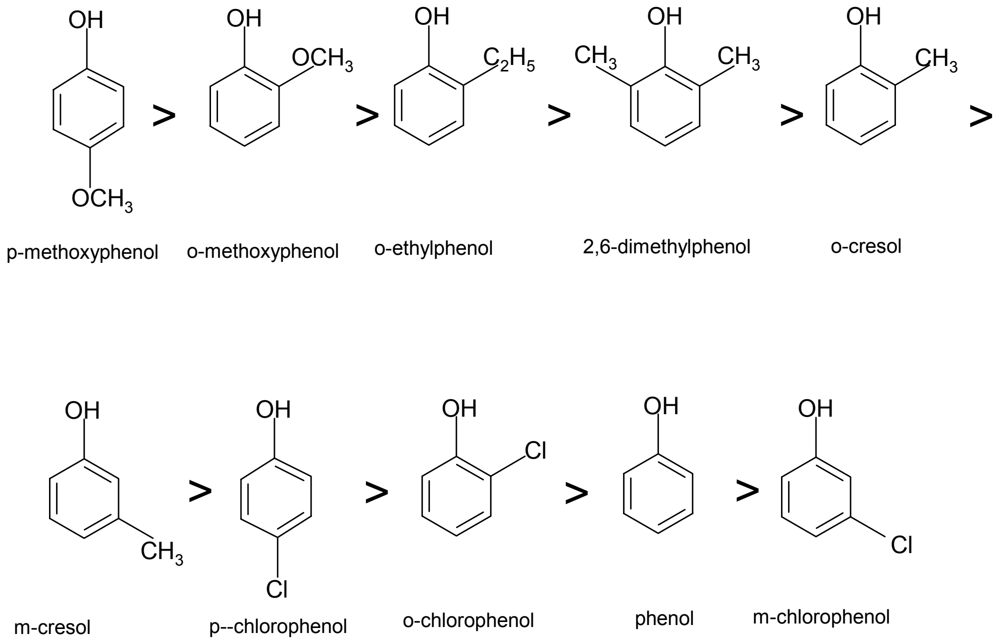


Figure 1.3: Reactivity of different substituted phenol during WAO (Joglekar et al., 1991).

As the methoxy group is an electron donor, it enlarges the electron density of the ring enhancing the oxidation potential. Alkyl group has lower electron donating capacity and chloro group the lowest. This is directly reflected in the oxidation rates (see figure 1.3).

The effect of the nature of substituent and its location on the activation of the aromatic ring is presented in table 1.11. Alkyl and methoxy groups in o/p position of hydroxyl group stabilise the oxyradical (see table 1.11). However, the ortho substituent has certain impedance to become stable, so it is no surprise that p-methoxyphenol has higher oxidation rate than o-methoxyphenol. Among the alkyl phenols, m-cresol exhibits the slowest reaction rate as meta position is known not to stabilise oxyradical. The same substituent position effect is observed in case of chlorophenols. Also chlorophenols in general display the lowest reactivity as they are poor electron donors, hence it gives poor stability to oxyradical (see table 1.11). This is also the reason why chlorophenols exhibit slow induction period.

Table 1.11: Effect of ring substituent on electrophilic aromatic substitution (Morrison & Boyd, 1992).

Ortho-Para Directors	*Meta Directors*
Strongly Activating	***Moderately Deactivating***
$-NH_2$,$-NHR$,$-NR_2$	$-CN$, $-SO_3H$
$-OH$,$-O^-$	$-CO_2H$, $-CO_2R$
	$-CHO$, $-COR$
Moderately Activating	***Strongly Deactivating***
$-NHCOCH_3$,$-NHCOR$	$-NO_2$
$-OCH_3$,$-OR$	$-NR_3$
Weakly Activating	$-CF_3$, $-CCl_3$
$-CH_3$,$-C_2H_5$,$-R$	
$-C_6H_5$	
Weakly Deactivating	
-F,-Cl , -Br, -I	

The knowledge of the reactivity and the effect of substituent and its location on the oxidation rate can be very useful to predict the reactivity of similar compounds.

1.4.1.6. Reaction products and pathways

From table 1.10 it is seen that WAO unfortunately is not able of achieving complete oxidation of many organics. These treatment limitations result from the production of either very low concentrated, but highly biotoxic intermediates or large quantities of thermally more resistant soluble by-products, such as acetic acid. Acetic acid may account for as much as 30-80% of the soluble COD in the treated effluent, depending on the degree of oxidation achieved.

Intermediates formation is thus of great importance in WAO and has been reviewed by Devlin and Harris (1984) for the oxidation of aqueous phenol with dissolved oxygen. The authors conclude that, at elevated temperatures, oxygen is capable of three different oxidation reactions with the organic: (i) it can substitute an oxygen atom into an aromatic ring to form a dihydric phenol or quinone; (ii) it is capable to attack carbon to carbon double bonds to form carbonyl compounds; and (iii) in oxidising alcohols and carbonyl groups to form carboxylic acids.

The authors found that the ring compounds (dihydric phenols and quinones) were formed under conditions near the stoichiometric ratio of phenol and oxygen, increasing in quantity when ratio phenol/oxygen increased. The unsaturated acids, namely maleic and acrylic and saturated ones, namely formic, acetic and oxalic appear independently of phenol to oxygen ratio used. Malonic, propionic and succinic acids were identified only in case of deficit oxygen. Malonic acid undergoes decarboxylation to produce acetic acid and carbon dioxide. The persistence of acetic acid was also found in the study of Vaidya and Mahajani (2002) and Bachir et al. (2001), when mass transfer limitations existed. The formation of acetic acid increases with time and contributes considerably in the global degradation yield. Vogel et al. (1999) detected alike intermediates, such as dihydric phenols and organic acids, but also dimers, during wet air oxidation of phenol promoted by ferrous ions. The complete reaction pathway of phenol Wet Air Oxidation proposed by Devlin and Harris is given in figure 1.4.

The end products detected during the oxidation of substituted phenols are similar to those of phenol and include polymeric material (tars), pyrocatechol, hydroquinone, and carboxylic acids (Kirso et al., 1972).

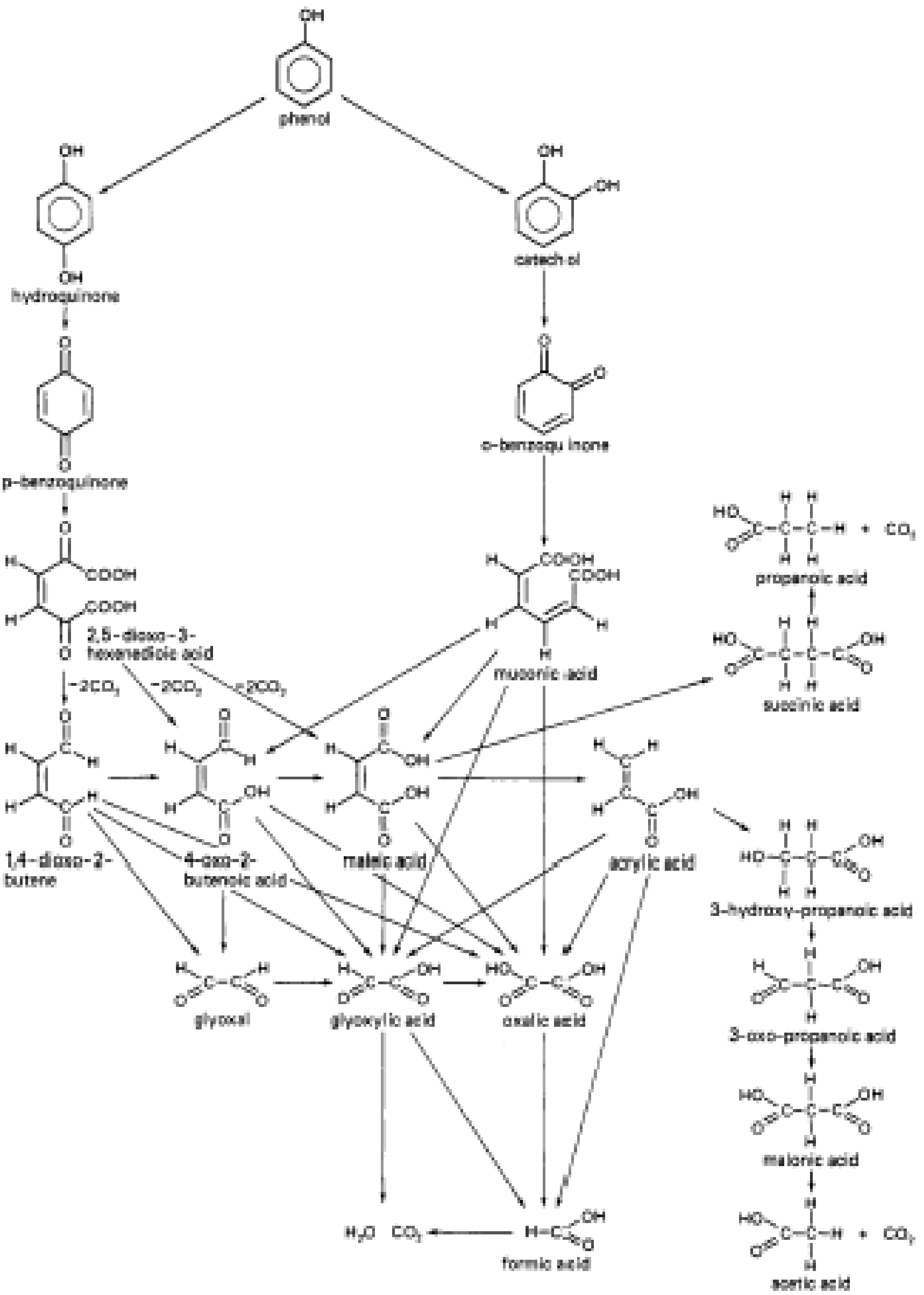


Figure 1.4: Reaction pathway for phenol oxidation by molecular oxygen (Devlin & Harris, 1984).

There exists only little information in the literature of complete oxidation pathways of compounds other than phenol and of real wastes. Thus, more studies are definitely required in this direction to establish the reaction that occurs during WAO of organic compounds.

The importance of the free radicals in the mechanism has encouraged the search for catalysts and promoters, which could overcome the thermal limitation of the radical formation reaction (Joglekar et al., 1991).

1.4.2. Catalytic Wet Air Oxidation

1.4.2.1. Development and Industrial Application of Catalytic Wet Air Oxidation

In order to reduce the severity of WAO operating conditions, catalytic wet air processes have been developed (CWAO). The use of catalyst is sought to enhance overall reaction rate and destroy intermediates refractory to noncatalytic oxidation. Milder conditions of temperature and pressure may lower equipment and operation costs, however there are some pollutants enough recalcitrant to be treated by CWAO, and rapid catalyst deactivation is still a mayor problem to overcome (Hamoudi et al., 1999; Matatov & Sheintuch, 1998).

Recently, the commercial processes of Catalytic Wet Air Oxidation were reviewed by Kolaczkowski et al. (1999). Some industrially available heterogeneous technologies are the Osaka Gas process (mixture of precious and base metals on titania or titania–zirconia carriers, conditions of 250ºC and 70 bar, treats a coal gasifier effluents, wastewater from coke ovens, concentrated cyanide and sewage sludge), the Kurita process (supported platinum catalyst, for treatment of ammonia, at temperature above 100ºC, uses nitrite as oxidant), and the Nippon Shokubai Kagaku process (several heterogeneous catalysts in both pellet and honeycomb form, treats such pollutants as acetic acid and ammonia, phenol, formaldehyde, at 220ºC and 40 bar); and with homogeneous catalyst, for instance, the Ciba–Geigy process (copper salt catalyst, for treatment of industrial wastewater, at temperature of 300ºC) or LOPROX process (low pressure oxidation, combination of Fe^{2+} ions and quinones to generate hydrogen peroxide, for treatment of industrial wastes, at conditions below 200ºC and 5-20 bar). Nippon Shokubai Kagaku process is able to oxidise 99% of phenol, formaldehyde or acetic acid (5-50% in the absence of catalyst). During

Osaka Gas process phenol, ammonia and cyanide are decomposed to levels below the detection limits (ammonia is not removed without catalyst). The Ciba-Geigy plants achieve oxidation efficiencies of 95-99% of chemical and pharmaceutical wastes. During LOPROX process about 85-90% of the organic matter is eliminated, with 60-65% oxidised directly to CO_2.

1.4.2.2. Process aspects of Catalytic Wet Air Oxidation

The reaction mechanism of CWAO is thought to be similar to the mechanism of WAO, and the function of the catalyst is essentially that of promoting the formation of free radicals. Thus, CWAO permits to work at lower temperature and pressure (< 50 bar and < 200ºC) (Duprez et al., 1996; Fortuny et al., 1995, 1998, 1999a, b; Pintar et al., 1992a, b; Luck, 1996; Lei et al., 1997; Gallezot et al., 1996).

Among the compounds studied in laboratory, CWAO of phenol was most widely conducted (Fortuny et al., 1995, 1998, 1999a, b; Duprez et al., 1996; Pintar and Levec, 1994a; Akyurtlu et al., 1998; Sadana and Katzer, 1974a, b; Qin et al., 2001). Also substituted phenols (Duprez et al., 1996; Tukac & Hanika, 1998; Pifer et al., 1999; Qin et al., 2001) and other compounds have attracted attention such as carboxylic acids (Imamura et al., 1986; Gomes et al., 2000; Lee & Kim, 2000; Beziat et al., 1999), aniline (Oliviero et al., 2003b), ammonia (Huang et al., 2001) and other nitrogenous compounds (Deiber et al., 1997), and industrial effluents (Pintar et al., 2001; Harf et al., 1999; Akolekar et al., 2002; Donlagic & Levec, 1997, 1998).

Different operating variables influence the process performance of CWAO. Initial pH was found to have a strong effect on phenol, p-chlorophenol, p-nitrophenol oxidation showing maximum at 11 (Pintar & Levec, 1994a). This conclusion disagrees with the findings of other authors (Sadana & Katzer, 1974a, Rivas et al., 1999). However, Rivas et al. (1999) observed that the most favourable conditions for phenol oxidation correspond to the use of very alkaline solutions (pH=13), or when no acid or base is added to the phenol solution (pH=4±5). Additionally, Sadana and Katzer observed that the initial oxidation rate is affected by pH having maximum at pH of 4 (Sadana and Katzer, 1974a).

Temperature has a positive effect increasing the rate and extent of oxidation (Rivas et al., 1999; Akolekar et al., 2002). In addition, an increase in temperature and the oxygen partial pressure decreases the induction period (Akyurtlu et al., 1998). Also, increase in system pressure results in the higher oxygen concentration in the liquid phase. However, temperature has stronger effect on TOC removal than pressure (Fortuny et al., 1999b).

Concerning the choice of reactors in research work, typically slurry or fixed bed, working in batch or continuous systems are used. Formation of polymers was reported for CWAO of phenol, when using batch slurry reactor (Pintar & Levec, 1992; Stüber et al., 2001; Hamoudi et al., 1999), batch-recycle (Pintar & Levec, 1994a) and rotating basket reactor (Ohta et al., 1980), but not when using fixed bed reactor (Stüber et al., 2001). However initial oxidation rates turned out to be much faster and fewer intermediates were found in slurry reactor, if compared to trickle bed reactor operation (Stüber et al., 2001). On the other hand, the continuous reactor presents possible advantage over batch and semi-batch reactors, such as elimination of the induction time and interference coming from the polymerisation, preventing fouling of catalyst (Fortuny et al., 1995; Pintar & Levec, 1994b).

As a summary, the operating conditions, oxidant and reactor type, as well as catalyst used and removal efficiency in the studies of these compounds are given in table 1.12.

1.4.2.3. Type of CWAO catalysts

One parameter of CWAO is the performance of the selected catalyst type.

It is a well-known fact that metal oxides are usually less active catalysts than noble metals (Pirkanniemi & Sillanpaa, 2002). Nevertheless, metal oxides are more suitable for most of the applications, since they are more resistant to poisoning.

Table 1.12: CWAO of organic pollutants and industrial effluents.

Substrate	Reaction conditions	Oxidant; Catalyst	Reactor	Removal %	Reference
Phenol	120-160ºC, 6-12 bar (O_2)	Air; Cu	TBR	<90% COD	Fortuny et al., 1999b
Phenol, acetic acid	170-200ºC, 20 bar O_2	O_2; Ru, Pt, Rh	Batch	<97% COD	Duprez et al., 1996
Phenol	150-210ºC, 30 bar (total)	O_2, CuO, Zn, Co oxides	TBR	>95% TOC	Pintar& Levec, 1994a
Phenol	90-150ºC, 1-20 bar	O_2; CuO+ZnO, CuO+Al_2O_3	Batch	100% X	Akyurtlu et al., 1998
Phenol	120-180ºC, 0.1-8 bar (O_2)	O_2; Pt/G	Slurry CSTR	100% X	Masende et al., 2003
Phenol	35-65ºC, 2.3-5.1 bar O_2	O_2, Pt-Ru	PBR	90% X	Atwater et al., 1997
Phenol	80-130ºC, 2-25 bar O_2	O_2, MnO_2/CeO_2	Batch	98% TOC	Hamoudi et al., 1999
Phenol, chlorophenol, nitrophenol	103ºC, 6 bar (total)	O_2, CuO, Zn, Co oxides	TBR	ns	Pintar& Levec, 1994b
Nitrophenol	130ºC, 7 bar O_2	O_2, Pd/C	Batch	>80% X	Pifer et al., 1999
Substituted phenols	110-160ºC, 20-50 bar (total)	O_2, AC	TBR	45% X	Tukac& Hanika, 1998
p-Chlorophenol	180ºC, 26 bar (total)	O_2; Pt, Pd, Ru	Slurry	<98% TOC	Qin et al., 2001
Carboxylic acids	200ºC, 6.9 bar (O_2)	Air; Pt/C	Batch	96% COD	Gomes et al., 2000
Carboxylic acids	180ºC, 1-11 bar (total)	Air, Pt/Al_2O_3	Batch	100% X	Lee& Kim, 2000
Carboxylic acids	150-200ºC, 50 bar (total)	Air; Ru/TiO2	TBR	100% TOC	Beziat et al., 1999
Ammonia	110-130ºC, 2.8-9 bar (O_2)	O_2; Pt/SDB	TBR	100% X	Huang et al., 2001
Aniline	160-230ºC, 20 bar O_2	O_2, Ru/CeO_2	Batch	100% X	Oliviero et al., 2003b
Ethylbenzene	310-390ºC, 0-1 bar (O_2)	O_2, AC	PBR	50% X	Pereira et al., 2000
Chlorobenzene	200-550ºC, 1 bar (total)	O_2, MnOx/TiO2	PBR	100% X	Liu et al., 2001
Kraft bleach plant effluents	190ºC, 8 bar (O_2)	Air, Ru/TiO2	TBR	<90% TOC	Pintar et al., 2001
Paper industry wastewater	140-190ºC, 5 bar O_2	O_2, Cu/Mn, Cu/Pd, Mn/Pd	Batch	TOC>84%	Akolekar et al., 2002
Sewage sludge	180-220ºC, 5-24 bar O_2	85%O_2/15%N_2, Fe^{2+}	Bubble column	70% TOC	Harf et al., 1999

X-substrate conversion,
SDB-porous resin, catalyst support,
G-graphite,
AC-activated carbon,
TBR-trickle bed reactor,
PBR- packed bed reactor,
(total)-total reaction pressure,
ns- not specified.

Supported noble metal catalysts

Various noble metals (Ru, Pt, Rh, Ir, and Pd) and some metal oxides (Cu, Mn, Co, Cr, V, Ti, Bi, and Zn) have traditionally been used as heterogeneous catalysts in CWAO. Several studies have ranked catalysts according to their reactivity. Imamura et al. (1988) ranked noble metal and metal oxide catalysts according to the total organic carbon (TOC) conversion achieved in 1 h, during the oxidation of polyethylene glycol at 200 °C and pH 5.4. They found the following order: Ru = Rh = Pt > Ir > Pd > MnO.

While the oxidation of *p*-chlorophenol catalysed by noble metals supported on alumina (Al_2O_3) or titania (TiO_2) at 150 °C and under 3 bar of oxygen pressure showed the following order of activity (Okitsu et al., 1995):

Pt >> Pd > Ru > Rd > Ag.

This is in agreement with Qin et al. (2001), who found the activity in total organic carbon (TOC) reduction of most common noble metals in catalytic wet oxidation of chlorophenols is in following order: Pt > Pd > Ru, whether the support is activated carbon or alumina.

Supported metal oxides

Metal oxides can be classified according their physico-chemical properties. One of these properties is the stability of metal oxide. Metals with unstable high oxidation state oxides, such as Pt, Pd, Ru, Au, and Ag do not perform stable bulk oxides at moderate temperatures. Most of the commonly used metal oxide catalysts (Ti, V, Cr, Mn, Zn, and Al) have stable high oxidation state oxides. Fe, Co, Ni, and Pb belong to group with intermediate stability of high oxidation state oxides (Pirkanniemi & Sillanpaa, 2002).

According to Kochetkova et al. (1992), the catalytic activity during phenol oxidation showed the following typical order:

$CuO > CoO > Cr_2O_3 > NiO > MnO_2 > Fe_2O_3 > YO_2 > Cd_2O_3 > ZnO > TiO_2 > Bi_2O_3$.

Mixtures of metal oxides frequently exhibit greater activity than the single oxide. Cobalt, copper, or nickel oxide in combination with the following oxides of iron (III), platinum, palladium, or ruthenium are reported as effective oxidation catalysts above 100°C (Levec & Pintar, 1995). In addition, combining two or more metal oxide catalysts may improve non-selectivity and catalytic activity.

Metal oxides usually are applied in form of fine particles or even powders. This form of catalyst gives maximum specific area, but the dispersion of particles can create unsteady state. To keep the stable state and in the same time not to loose active phase some porous support can be use. Also the residence time can be shortened, because the organic to be oxidised can adsorb on the support increasing the concentration of organic in the surface. Commonly, alumina or zeolites are used as a support, but surface area of aluminium oxide is limited and the pore size of zeolites cannot be suitable for large organic compounds. Recently activated carbon as support is of interest, as it has large surface area and broad range of pore size. Hu et al. (1999) investigated copper/activated carbon catalyst for wet air oxidation of dyeing and printing wastewater. They observed that catalyst supported by activated carbon is better than one supported on alumina in terms of COD and TOC (total organic carbon) removals.

Catalyst deactivation

Catalyst deactivation can occur due to either the poisoning of the catalytic agents, and the reduction of the catalyst surface (sintering), or the elution of the catalyst in the acid reaction media (Matatov & Sheintuch, 1998). Catalyst deactivation may also arise from strong chemisorption on the catalytic sites of heavy carbonaceous deposits (Hamoudi et al., 1999). The use of noble metals for water phase oxidation applications appears to be limited by their high sensitivity to poisoning. One of the important sources of solid catalyst deactivation in liquid-phase oxidation processes is connected with the exposure to hot acidic water, which promotes the solubility of some metal oxides. The dissolution of the metal in the hot acidic reaction medium prevents the use of catalysts, which themselves are soluble in hot acidic water or can be transformed to a soluble state during reaction in the presence of oxygen. For example, copper ions were shown to be leached out from a CuO/Al_2O_3 during phenol oxidation (Sadana and Katzer, 1974; Pintar and Levec, 1994).

Activated carbon catalyst for CWAO

A promising new catalyst can be activated carbon (AC) that shows good properties as adsorbent for both organics and oxygen, because of its porous structure and high surface area (Singh et al., 1996; Hu et al., 1999). The chemical stability of activated carbon in highly acidic and basic media is also of high importance. Furthermore, activated carbon is easy to prepare from any renewable organic resources. As a matter of fact, AC was already shown to perform as a true catalyst for different reactions (Coughlin, 1969) and, as mentioned before, as a support for other oxidation catalysts (Aksoylu et al., 2001; Birbara et al., 1995). However, if only CWAO processes are considered, AC has been referenced very few times as support for active metals (Duprez et al., 1996, Gallezot et al., 1996, Alvarez et al., 2002a, b; Hu et al., 1999; Atwater et al., 1997) or direct catalytic matter (Fortuny et al., 1996, 1998, 1999a, b; Besson et al., 2000; Qin et al., 2001, Nunoura et al., 2002; Gonzalez et al., 2002). AC is gaining popularity, because of its good performance that could be related to its high adsorption capacity and ability to generate oxygenated free radicals promote the oxidation reaction (Stüber et al., 2001). Catalytic wet air oxidation using AC can be an alternative and cost effective way of wastewater treatment. However, activated carbon can also catalyse the polymerisation reactions in the presence of oxygen via oxidative coupling. The phenol conversion is known to occur via complex pathways that could firstly lead to formation of polymeric compounds that could be adsorbed in part on the activated carbon and finally conduct to limit carbon active surface (Stüber et al., 2001; Pintar & Levec, 1992). Additionally, these polymers are particularly difficult to desorb from the activated carbon (Grant & King, 1990; Cooney & Xi, 1994).

Tukac and Hanika, (1998) and Tukac et al. (2001, 2003) have investigated phenol oxidation over activated carbon in trickle bed reactor. The authors found AC less active that metal oxides catalyst, but more stable, environmentally accepted and cost effective. Also Qin et al. (2001) successfully oxidised p-chlorophenol using activated carbon (100% conversion and 68.3% TOC reduction at T=180°C and P=26 bar).

In the last decade, our group investigated the performance of activated carbon catalyst for the Wet Air Oxidation of phenol (Fortuny et al., 1998, 1999a, 1999b; Eftaxias et al., 2001, 2002; Eftaxias, 2002).

Fortuny et al. (Fortuny et al., 1998) compared phenol conversion, when using activated carbon and copper catalyst (Cu0803). In ten days runs, Cu0803 was found to loose its activity due to the leaching of the copper phase. On the other hand, AC also exhibited a continuous drop in phenol conversion, finally reaching about 48% (30% with Cu0803). However, the loss of AC efficiency could be ascribed to its consumption during the experiment, thus the absolute activity of AC remained stable during the long term run. The authors have found that the oxidations of phenol and of carbon are the competitive reactions.

Grant & King (1990) studied adsorption of substituted phenols on activated carbon. The authors observed the order of irreversible adsorption as: p-methoxyphenol > 2,4-dimethylphenol = p-chlorophenol> phenol > aniline > p-nitrophenol = p-hydroxybenzaldehyde. Additionally, the influence of pH and an excess of oxygen on the type of adsorption were investigated. Reversible uptake is observed for lower pH, while irreversible one for higher pH. Consistently, oxidative coupling of phenolic compounds is more facile in alkaline than in acidic media. Total and irreversible uptakes were higher, when more oxygen was available. Adsorption conditions discouraging irreversibility include lower temperature, short residence times, rapid cycling, and use of smaller bed volumes, pH well below the pK_a for the phenolic solute, a low content of oxygen or other oxidizing species.

Polaert et al. (Polaert et al., 2002) described two-step adsorption-oxidation process on activated carbon. The adsorption of pollutant from wastewater and oxidation it in the next step permits to combine two features of activated carbon, a very good adsorbent and active oxidation catalyst.

1.4.2.4. Promotion of CWAO by hydrogen peroxide

Attending to the radical nature of wet air oxidation processes, the use of hydrogen peroxide as a free radical promoter has been shown to enhance the rate of phenol oxidation and eliminate the induction period. The use of hydrogen peroxide in wet air oxidation systems offers the advantages of reduced residence times and lower capital costs (Rivas et al., 1999).

Pintar and Levec (1994b) observed no influence of H_2O_2 on the chloro- and nitrophenol oxidation during CWAO in the absence of oxygen. However, in the presence of oxygen, hydrogen peroxide had slightly promoting effect on the oxidation of these phenols. Also, the authors observed the disappearance of induction period, when a small amount of H_2O_2 (0.1 wt%) was added to the reaction solution (Pintar & Levec, 1992b).

Also, Imamura (1999) tested the addition of hydrogen peroxide during the oxidation of phenol and acetic acid. The author found that even very limited contact with steel caused hydrogen peroxide to decompose completely at 120°C within 5 min. The effect of the addition of H_2O_2 (1000 ppm) on the oxidation of phenol (1750 ppm) was neither very pronounced at 130 and 150ºC, when phenol is quite stable, nor at temperatures of 180 and 200°C, when phenol shows enough reactivity and can be readily decomposed without hydrogen peroxide, and the addition of H_2O_2 has almost no effect. Therefore, H_2O_2 only exhibits its effect at the temperature of moderate phenol reactivity.

Debellefontaine et al. (1996) reported that the promoting effect of hydrogen peroxide is clear as the initiating period is shortened and the TOC removal efficiency increased (from 76 to 90%) on the addition of 10% of the stoichiometric demand of H_2O_2. They also observed that the promoting effect is more marked at 160 than above 220ºC, where a rapid decomposition occurs. The doses above 15% do not give significant increase in efficiency and doses as small as 0.2% already have a considerable effect.

Lin and Wu (1996) have oxidised phenol, m-chlorophenol, m-cresol and p-ethylphenol with addition of hydrogen peroxide as promoting agent. The authors found that COD reduction over 90% can be achieved in 30 min when 3g H_2O_2/1000 ppm COD is added at 150°C and 5 bar.

1.4.2.5. Kinetic mechanism of CWAO

As reported by Sadana and Katzer (1974a, b), likewise during noncatalytic WAO, the initial rate of oxidation exhibits an induction period, which is followed by steady state regime. The free radical initiation preceded by the propagation step was also found by Akyurtlu et al. (Akyurtlu et al., 1998). A marked dependence of the induction period length on the initial addition of a free radical inhibitor concentration essentially indicates the involvement of free radicals in the CWAO reaction. Another evidence of free-radicals participation is the dependence of rate on pH. Typically free radical reactions in aqueous media are pH dependent and they typically show a maximum with pH (Sadana and Katzer, 1974a). Also, it was observed that the induction period depends on the temperature and is inversely proportional to the partial pressure of oxygen (Sadana & Katzer, 1974b).

1.4.2.6. Reactivity of organic compounds

Pintar and Levec (1994b) noticed during CWAO of some substituted phenols, that phenols with electron withdrawing substituents are more resistant to oxidation than phenols with electron-donating substituents. This can be explained by the fact that withdrawing electron density from the aromatic ring causes decrease in its reactivity. The authors found that the reactivity order, for the oxidation with a catalyst containing copper, zinc and cobalt oxides, was as follows: phenol > p-chlorophenol > p-nitrophenol.

For the oxidative coupling reactions catalysed by activated carbon the reactivity for substituted phenols found in the work of Cooney and Xi (1994) is accelerated according to:

methoxyphenols > cresols > chlorophenols > phenol > hydroxybenzoic acids > hydroxybenzaldehydes > nitrophenols. The order is identical with denoting whether the substituent group repels or attracts electrons, thus creating higher or lower electron density on aromatic ring, respectively. This order is in agreement with order observed by Joglekar et al. (1991) for noncatalytic Wet Air Oxidation. Also the location of substituent effect was studied and Cooney and Xi (1994) concluded that it was in order ortho > para > meta. The observed substituent group effect is given in figure 1.4.

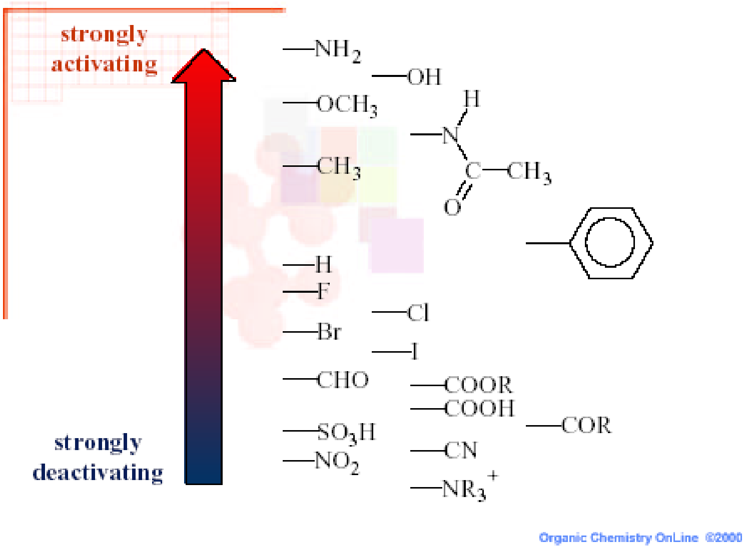


Figure 1.4: Substituent effect on the reactivity of aromatic rings.

1.4.2.7. Reaction intermediates

As the mechanism of CWAO is believed to be similar to noncatalytic process also similar pathways and intermediate distribution should be observed.

Álvarez et al. (Alvarez et al., 2002a,b) have found acetic acid and p-benzoquinone to be the main intermediates in CWAO of phenol using copper oxide supported over activated carbon. The formation of solid particles that may be the organocupric polymers was observed in the effluent resulting from the reaction of carboxylic acids with copper oxide. They could block active sites and also influence the adsorption of oxygen at the oxide sites.

Fortuny et al. (1999b) oxidised phenol with a commercial copper catalyst. They found acids (formic and acetic) and diacids (oxalic) to be the main intermediates, responsible for almost 90% of all intermediates present in liquid phase at higher residence times. However, they also observed the presence of dihydric phenols, benzoquinones, maleic, fumaric and malonic acids. Dihydric phenols and benzoquinones were identified as first stage reaction intermediates. They are especially undesired products as their toxicity is similar or higher to that of phenol. The intermediates found are coherent with the mechanism proposed by Devlin and Harris (1984).

A similar intermediate distribution was found in the work of Duprez et al. (1996) over supported Ru, Pt and Rh catalysts and Ohta et al. (1980) over supported copper oxide. In phenol oxidation they identified hydroquinone, catechol, and maleic acid that further oxidised to acrylic and acetic acid. They observed acetic acid as only refractory product.

Sadana and Katzer (1974b) in their early study, on the other hand have not observed such organic intermediates, as catechol, hydroquinone and organic acids in appreciable quantities.

In the oxidation of p-chlorophenol over noble metal catalyst Qin et al. (2001) have not detected hydroquinone, what can be related to the fact that hydroquinone is not stable and is easily transformed to p-benzoquinone. The authors have not found carboxylic acids other than acetic acid. The most significant intermediate product formed during *p*-chlorophenol oxidation is *p*-benzoquinone. Degradation of *p*-benzoquinone leads to formation of acetic acid and CO_2.

Deiber et al. (1997) reported the removal of nitrogenous compounds from p-nitrophenol, aniline etc. using Mn/Ce composite oxides. In the oxidation of p-nitrophenol, nitrogen mainly in form of NO_2 is obtained. The C-N bond is broken and there is no other evolution of nitrogen containing group. When oxidizing aniline, after the removal of the initial substrate, the concentration of ammonia is decreasing and finally is totally converted to the molecular nitrogen. No other nitrogen containing intermediates are observed. On the other hand, Oliviero et al. (2003b) oxidised aniline over Ru/CeO_2 catalyst and classified intermediates in three groups: (i) condensation intermediates (hydrazobenzene, azobenzene, azoxybenzene), (ii) nitrogenous aromatic compounds (p-aminophenol, nitrobenzene, p-nitrophenol and nitrosobenzene), and (iii) non-nitrogenous aromatics (phenol, hydroquinone, catechol and benzoquinone). The mechanism of aniline oxidation seems to be complex and not fully understood. The reaction network of aniline CWAO found by Oliviero et al. (2003b) is presented in figure 1.5.

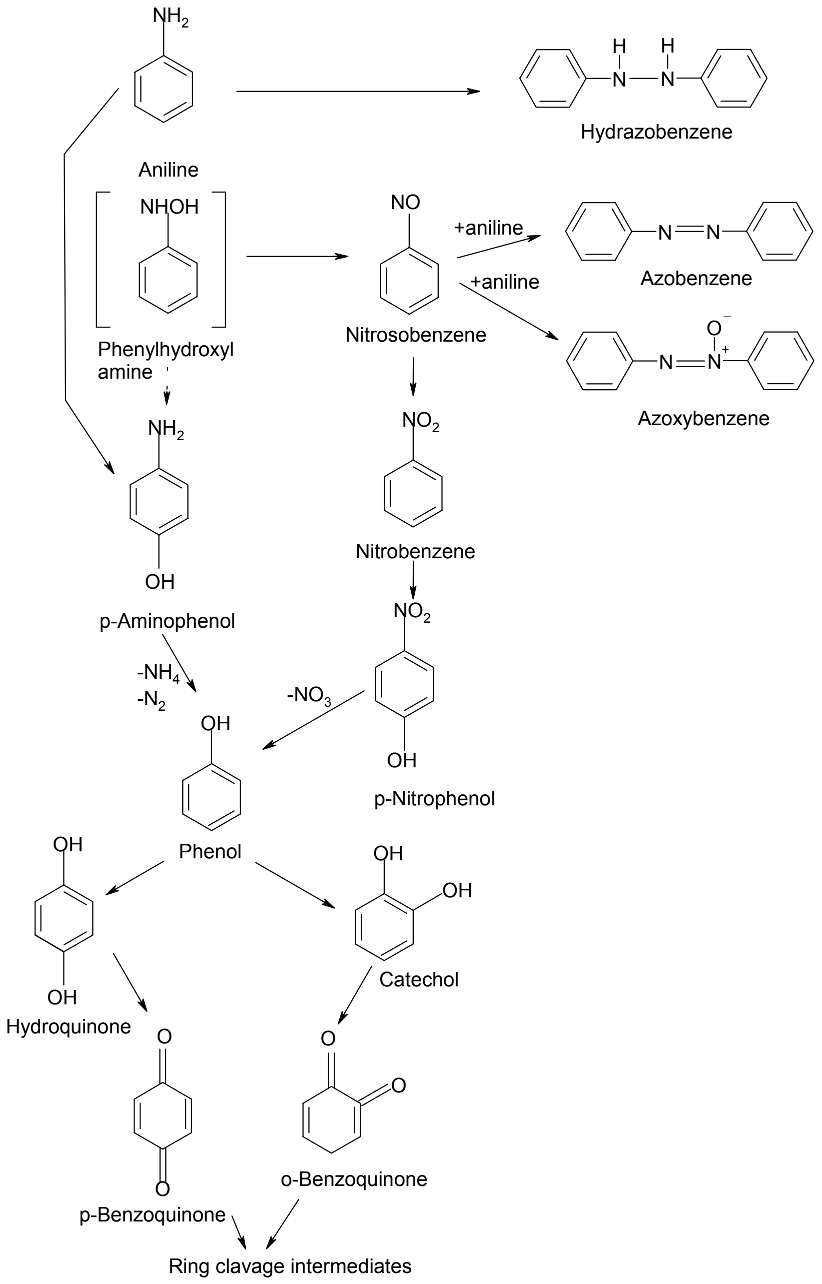


Figure 1.5: Reaction network proposed for the oxidation of aniline (Oliviero et al., 2003b).

Further developments of the CWAO technology should include high durability and low cost catalysts. Catalytic wet air oxidation would thus provide a cost-effective environmentally attractive option to manage the growing organic sludge and toxic wastewater treatment problems. Applications of catalytic abatement to real wastewater require highly active, nonselective catalysts, capable of long-life operation in hot water, without structural and/ or performance degradation.

1.4.3. Supercritical Water Oxidation (SCWO)

Supercritical fluids (SCF) are fluids brought to a temperature and pressure higher than its critical temperature and pressure. SCF have attracted attention as a media, in which to conduct chemical reactions, because their physical and chemical properties can be dramatically altered at times through only modest changes in temperature and pressure.

1.4.3.1. Development and Industrial Application of SCWO

The idea of SCWO for wastewater treatment appeared in late 1970s (Thiel et al., 1979) and the study accelerated in the 1980s. In the late 1980s, Los Alamos and Sandia National Labs began developing SCWO reactors to treat radioactive wastes with organic components. During the 1990s, the pace of SCWO research and development quickened. Meanwhile, the first commercial SCWO facility began operation in Texas in 1994, by Eco Waste Technologies (EWT, 1998; Anitescu et al., 2000) with a relatively simple feed of oxygenated and nitrogen-containing hydrocarbons. In addition, several full-scale commercial SCWO systems are either now in operation or under construction in the U.S. and Japan. These systems are treating a wide variety of wastes, ranging from wastewater sludge and industrial manufacturing wastes to hazardous wastes such as PCBs (Thiel et al., 1979; Koo et al., 1997).

1.4.3.2. Process aspects of SCWO

SCWO takes place in water above its critical point (374ºC, 221 bar) leading to unique properties of density, dielectric constant, viscosity, diffusivity, electric conductance and solvating ability (Goto et al., 1997 and 1998).

In table 1.13 the properties of SCW are compared to those of ambient water and superheated steam. In general, parameter values of SCW properties are between gas-like and liquid-like. As an example, SCW density at 450ºC and 275.6 bar is 8 times smaller than ambient water density and 30 times higher then steam density. As ambient water transforms into a supercritical fluid, about two-thirds of the hydrogen bonds are destroyed, causing a drastic drop in the dielectric constant (43 times smaller than that of ambient water). As indicated by its dielectric constant, SCW is a no polar solvent, capable of dissolving most organic compounds and gases, while solubility of inorganic salts almost drops to zero.

Table 1.13: Properties of ambient water, steam and supercritical water (Ding et al., 1996).

Fluid	Ambient water	Supercritical water	Superheated steam
Typical Conditions			
Temperature (ºC)	25	450	450
Pressure (MPa)	0.1	27.56	1.38
Properties and Parameters			
Dielectric constant	78	1.8	1.0
Hydrocarbon solubility (mg/dm^3)	variable[a]	∞	variable[b]
Oxygen solubility (mg/dm^3)	8	∞	∞
Density, ρ (g/cm^3)	0.998	0.128	0.00419
Viscosity, μ (cp)	0.890	0.0298	$2.65 \cdot 10^{-5}$
Particle Reynolds number [c]	18.5	553	622
Effective diffusion coeff., D_e (cm^2/s)	$7.74 \cdot 10^{-6}$	$7.67 \cdot 10^{-4}$	$1.79 \cdot 10^{-3}$
Thiele modulus, ϕ	2.82	0.0284	0.0122

[a] depending on the affinity of its functional group to water
[b] depending on the boiling points of hydrocarbons
[c] $Re_P=ud_P\rho/\mu$; u=10.2 m/s and d_P=0.386 mm

There are several advantages in conducting the oxidation reactions above, rather than below, the critical point. Higher temperatures promote faster reaction rates, although the temperatures used are still considerably lower than those used for incineration. This means that no pollutant gases like NO_x and SO_x are formed (Fromonteil et al., 2000). Another advantage is complete miscibility of most organic compounds and oxygen with supercritical water (Connolly, 1966; Japas & Franck, 1985; Modell, 1980), eliminating the relatively slow external mass transfer process that occurs in multiphase systems. Thus, essentially complete conversion of organic carbon to carbon oxides occurs on the time scale of a few minutes or seconds, depending on the specific operating conditions and the organic to be oxidised (Anitescu et al., 2000). SCWO is able to achieve, in totally enclosed facility, destruction efficiencies for organic wastes comparable with those attained by incineration, but without harmful emissions. Proponents of SCWO claim that the process offers significant operating cost savings, when viewed as an alternative to incineration of relatively diluted organic waste streams, as incineration requires efficient dewatering and drying of sludges before burning it (Aki & Abraham, 1998).

One of the major drawbacks of SCWO arises from the cost of reactors, tubing and valves for high pressure process that has to withstand potentially corrosive environment, as well as the cost of high pressure pumps and compressors, when high waste volume flow rates have to be treated. Reactor tubes are made of metal alloys, such as high nickel alloys (Hastelloy or Inconel) that resist corrosion and high temperatures. Stainless steel 316, which has substantial chromium and nickel, is relatively corrosion and creep resistant, and can be used for milder conditions. But, even these high performance alloys may not withstand the most challenging oxidation mixtures and reactor tube liners (e.g., Ti) have to be used (Shaw & Dahmen, 2000). The chemical composition of different alloys for SCWO application is presented in work of Mitton et al. (2001).

Another disadvantage is that salts formed from neutralization of acids during SCWO have almost zero solubility in SC water, thus can depose on reactor walls causing additional corrosion problems (Modell, 1988). Furthermore, problems of temperature control can occur due to the strong exothermic nature of the oxidation reactions. Hence, this process is not recommendable for wastes with organic concentration above 20-25% (Oh et al., 1996).

A variety of model molecules have been studied, such as methanol (Anitescu et al., 1999), methanol and ammonia (Webley et al., 1991), dodecane, o-cresol (Martino et al., 1995), acetic acid (Krajnc & Levec, 1997), formic acid (Yu & Savage, 1998), phenol (Thornton & Savage, 1990, 1992a, b; Matsumura et al., 2000), aniline and nitrobenzene (Chen et al., 2001), monosubstituted phenols (Martino and Savage, 1997, 1999a, b, c), p-chlorophenol and other chlorinated hydrocarbons (Jin et al., 1992). Also, multicomponent industrial wastewaters have been treated by SCWO, including paper mill sludges, cutting oils (Cansell et al., 1998), epoxy resins (Fromonteil et al., 2000), municipal solid wastes (Mizuno et al., 2000, Jin et al., 2001), wastewater from poly(ethylene terephthalate) industry (Cocero et al., 2000b), organic materials found aboard Navy ships and pyrotechnic munitions (Crooker et al., 2000), Aroclor 1248 (a mixture of polychlorinated biphenyls) (Anitescu et al., 2000) and municipal sludge (Goto et al., 1997). The respective operating conditions and references of these studies are given in table 1.14. As can be seen in the most of studies not only the conversion of original pollutant is complete, but also COD and TOC removal is close to 100%. Mainly tubular reactors operating in continuous are used. Also it can be observed that to treat nitrogenous compounds higher temperatures that for other pollutants treatment are employed.

In general vapour and supercritical state chemical reactions, temperature and pressure are two important factors affecting the reaction rate. Increasing temperature could improve reaction rate, so could pressure. But their effects on reaction rate were different. The effect of increasing pressure on oxidation rate is minor compared to that of temperature (Qi et al., 2002; Chen et al., 2001), similarly as was observed before for CWAO (Fortuny et al., 1999b). Cocero et al. (2000b) also found that the effect of pressure on TOC removal efficiency is almost negligible, in agreement with Gloyna and Li (1994).

Table 1.14: SCWO of organic pollutants and industrial effluents.

Substrate	Reaction conditions	Oxidant	Reactor	Removal efficiency	Reference
Phenol	400-500ºC, 250 bar	H_2O_2	PFR	83% X 40% TOC	Portela et al., 2001
Phenol	400ºC, 250 bar	49-187% H_2O_2	Continuous PBR	75% X	Nunoura et al., 2002
Phenol	300-420ºC, 190-280 bar	O_2	Continuous PFR	100% X	Thornton & Savage, 1990
Phenol, acetic acid, methanol	430-585ºC, 276 bar	H_2O_2	Tubular	<99.99% X	Rice & Steeper, 1998
Phenol, aniline, nitrobenzene	525-700ºC, 200-280 bar	O_2	Continuous PFR	>90% COD	Chen et al., 2001
p-Chlorophenol	310-400ºC, 75-240 bar	O_2	Continuous	ns	Yang & Eckert, 1988
p-Chlorophenol	450ºC	H_2O_2	Batch	>99.99% X	Gloyna et al., 1994
o-Cresol	350-500ºC, 203-304 bar	O_2	PFR	99.5% X	Martino et al., 1995
Monosubstituted phenols	460ºC, 253 bar	O_2	PFR	ns	Martino& Savage, 1999a, b, c
Methanol	400-500, 253 bar	H_2O_2	PFR	100% X	Anitescu et al., 1999
Nitrobenzene	500ºC, 240 bar	Air	Continuous	>99% X	Bleyl et al., 1997
Aniline, acetonitrile, pyridine, ammonia	530-830ºC, 250 bar	Air	Tubular	99.97% TOC	Cocero et al., 2000a
Aniline	400-500ºC, 250-320 bar	H_2O_2	Continuous	100% TOC	Qi et al., 2002
Pyridine	426-525ºC, 276 bar	O_2	PFR	95% X	Crain et al., 1993
Olive oil mill wastewater	380-500ºC, 250 bar	H_2O_2	PFR	99.99% COD	Rivas et al., 2001c
Aroclor 1248 (PCBs mixture)	450-550ºC, 253 bar	H_2O_2	PFR	99.95% X	Anitescu& Tavlarides, 2000
Epoxy resin	200-410ºC, 240 bar	O_2/Ar	Batch	90% TOC	Fromonteil et al., 2000
PET	550-750ºC, 250 bar	Air	Tubular	99.9% TOC	Cocero et al., 2000b
PCBs	200-450ºC, 300 bar	H_2O_2	Flow and batch	<99.99% X	Hatakeda et al., 1999
Municipal solid waste	400-550ºC, 280 bar	H_2O_2	Batch	ns	Mizuno et al., 2000
Sludge	280-455ºC, 280 bar	Air	Continuous	72-97% COD	Shanableh & Shimizu, 2000
Cutting oils	490ºC, 300 bar	H_2O_2	Tubular	98.5% COD	Cansell et al., 1998

PFR-plug flow reactor,
PCBs-polychlorinated biphenyls,
X-conversion of original compound,
PET-polyethylene terephthalate,
ns-not specified.

Initial pH effect is important, when using hydrogen peroxide as the oxidant, because OH ions in alkaline solutions can capture OH radicals produced by the destruction of hydrogen peroxide and reduce the oxidation rate (Qi et al., 2002). Adding more quantity of hydrogen peroxide results in improving the oxidation performance. Qi et al. (2002) observed that the increase of hydrogen peroxide quantity added up to 110 % o stoichiometric demand increase aniline destruction efficiency, but above this amount there was only a little effect.

1.4.3.3. Kinetic mechanism of SCWO

As reported in literature (Li et al., 1991), the oxidation reaction may start by activation of either the dioxygen or the hydrocarbon molecule. The oxidation reaction in SCW generally follows the free radical mechanism that dominates gas phase oxidation and WAO. The free radical reaction mechanism (as mentioned before for WAO and CWAO) often involves an induction period, the generation of a radical pool, and a fast free-radical reaction period. The induction time and free radical concentration depend on the oxidizing agent, temperature, catalyst and reactant.

When following the free-radical reaction pathway, the hydroxyl radical ($^{\bullet}OH$) is first produced from the initiation reaction of water:

$$H_2O \rightarrow H^{\bullet} + {}^{\bullet}OH$$

If the hydroxyl radical concentration is high, the balancing hydrogen radicals are consumed by oxygen to form peroxy radicals.

$$H^{\bullet} + O_2 \rightarrow {}^{\bullet}HO_2$$

Catechol, hydroquinone, benzoquinone and dimers are formed through the following free radical reactions involving the initiation or the propagation steps:

hydrogen abstraction: $RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$

peroxy formation: $R^{\bullet} + O_2 \rightarrow R\text{-}OO^{\bullet}$

homolytic hydroxylation: $R^{\bullet} + {}^{\bullet}OH \rightarrow R\text{-}OH$

condensation (termination): $R^{\bullet} + {}^{\bullet}R \rightarrow R\text{-}R$,

where $R^{\bullet}$ is the aromatic radical and R-R is the condensation product (Ding et al., 1996).

Further substitution and oxygen attacks result in the complete destabilization of the benzene ring and lead to a ring-opening reaction. The final result is the formation of relatively stable low molecular weight products (acids, alcohols, carbon monoxide, and carbon dioxide).

1.4.3.4. End products and intermediates

Li et al. (1991, 1993) have proposed generalised reaction networks for the oxidation of organic compounds in near-critical and SC water. Their premise is that complex mixtures oxidise via two parallel reaction paths. One is the direct oxidation to stable end products such as carbon dioxide and nitrogen, and the second is the initial oxidation to low molecular weight intermediates, which are then slowly oxidised to end products. Acetic acid and ammonia have been advanced as key slowly oxidising intermediates.

SCWO of phenol

Thornton and Savage (1990) identified 16 different products from noncatalytic phenol oxidation. These products included carboxylic acids, dihydroxybenzenes, and phenol dimers. It was observed that the dimer selectivity tends to decrease with increasing phenol conversion, while the selectivity to gases tends to increase with increasing phenol conversion. The decreasing selectivity of by-products such as dimers suggests that they undergo secondary reactions (Martino et al., 1995).

SCWO of nitrophenols

Phenol was observed to be the only product in liquid phase consistently present in sufficiently high yields to quantify (Martino and Savage, 1999b). SCWO of nitrophenols produce CO_2 as the major gaseous product. There are two major parallel paths. One leads to phenol and the other to ring-opening products and ultimately CO and CO_2 (Martino and Savage, 1999b).

SCWO of Cresols

The major intermediate products of o-cresol oxidation are o hydroxybenzaldehyde and phenol. At cresol conversions less than 50% the yield of the hydroxybenzaldehyde always exceeds the yield of the phenol. This behaviour demonstrates that oxidation of the -CH_3 substituent in cresols is favoured over elimination of the substituent.

The network for SCWO of o-cresols shows three parallel paths. One leads to a hydroxybenzaldehyde via oxidation of the methyl substituent, another leads to ring-opening products and the formation of CO and CO_2, and the last leads to phenol via demethylation (Martino and Savage, 1997). The hydroxybenzaldehyde reacts through two parallel paths, which lead to phenol and to ring-opening products. Phenol also reacts via two parallel paths, but these lead to phenol dimers and ring-opening products. The dimers are eventually converted to ring-opening products, and the ring-opening products are ultimately converted to CO_2.

SCWO of o-chlorophenol

During SCWO of o-chlorophenol many liquid-phase products are formed with low individual yields. The most abundant products at short reaction times are the dichlorophenoxyphenols and dichlorobiphenols. The yields of these products decrease with increasing reaction time.

Very little of the chlorine in the reaction products were associated with organic compounds. Most of it appeared as Cl^- in the cooled and depressurised reactor effluent. The Cl^- presumably arose from the dissociation of HCl (Li et al., 1993).

1.4.3.5. Reactivity

The oxidation of substituted phenols in supercritical water seems to proceed more rapidly than the oxidation of phenol itself (Martino and Savage, 1999b). It was observed that one might be able to correlate the oxidation kinetics with some reactivity index that depends upon the identity of the substituent and its position on the aromatic ring. Different reactivity of distinct substituted phenols can be supported by different reaction end products. The most reactive isomers are always the ortho isomers, then para isomers and the meta isomers being the less reactive. For a given substituent location, nitrophenols react more rapidly that other substituted phenols as chlorophenols, cresols, methoxyphenols (Martino and Savage, 1999a,c). This disagrees with findings of Joglekar et al. (1991) for WAO and Cooney and Xi (1994) for oxidative coupling with activated carbon that found cresols more reactive than chlorophenols, more reactive on the other hand than nitrophenols. The order of destruction rate for SCWO was found by Chen et al. (2001) as phenol> aniline>nitrobenzene.

1.4.3.6. Catalytic SCWO process

Even if SCWO is effective in the destruction of the original organic compound, incomplete conversion may be achieved. Some of the by-products such as dibenzofuran, 2- and 4-phenoxyphenol, dibenzo-p-dioxin and 2,2′-biphenol identified from supercritical water oxidation of organic compounds represent species that are more hazardous than the starting organic component (Matsumura et al., 2000). In order to minimize the formation of these partial oxidation products and to promote complete conversion, it is feasible to either increase the reaction temperature or add a catalyst. The use of catalyst, which may promote the desired reaction pathway, represents a logical course of investigation (Ding et al., 1996).

A successful catalytic process depends on the optimized combination of catalyst (components, manufacturing process, and morphology), reactants, reaction environment, process parameters and reactor configuration. Because of the harsh environment created by the SCWO process, the demand on material is of major importance. Catalyst must be durable as compared to catalyst used in typical gaseous phase operations. Nevertheless, the selection of catalysts used in SCWO studies is based on previous catalytic wet air oxidation research.

The oxidation of more complex aromatic compounds in SCWO results sometimes in the formation of a variety of partial oxidation and dimerization products. The high selectivity to CO_2, which is obtained in the catalytic SCWO environment, indicates that these partial oxidation and dimerization products are either destroyed or nor formed (Ding et al., 1996).

Table 1.15 there are presents catalysts used in supercritical water oxidation process. From this table, it can be deduced that heterogeneous oxidation catalysts are usually made of metal oxides (such as CuO, TiO_2, MnO_2) or metals dispersed on metal oxide supports (such as Pt/γ-Al_2O_3, MnO_2/CeO_2, MnO_2/γ-Al_2O_3).

Table 1.15: Catalysts used in supercritical water oxidation (Ding et al., 1996).

Compound Category	Catalysts	Reference
Alcohols	CuO/ZnO	Krajnc & Levec, 1994
Acetic acid	CuO/ZnO, TiO_2; MnO_2, $KMnO_4$	Frisch et al., 1994; Chang et al., 1993 Krajnc & Levec, 1994
Ammonia	Inconel beads, MnO_2,	Webley at al., 1991; Ding et al., 1998
Benzene	V_2O_5, MnO_2, Cr_2O_3	Ding et al., 1995
Benzoic acid, butanol	CuO/ZnO	Krajnc & Levec, 1994
Chlorophenol	Cu^{2+}, Mn^{2+} Pt, Pd, Ru (supported), CuO/ZSM	Yang end Eckert, 1988; Qin et al., 2001; Lin & Wang, 1999
Dichlorobenzene	V_2O_5, MnO_2, Cr_2O_3	Jin et al., 1990; Ding, 1995
2,4-Dichlorophenol	Pt (supported), TiO_2	Frisch et al., 1994
MEK	Pt (supported), TiO_2	Frisch et al., 1994
Phenol	V_2O_5, MnO_2, Cr_2O_3, CuO/ZnO	Ding et al., 1995; Krajnc & Levec, 1994
2-Propanol	CuO/ZnO	Krajnc & Levec, 1994
Pyridine	Pt (supported), TiO_2	Aki & Abraham, 1999; Frisch et al., 1994
Quinoline	$ZnCl_2$	Li & Houser, 1992

A useful catalyst is normally characterized by a balance of its activity (high surface area), selectivity and stability. In many instances, substances of high catalytic activity have been discovered only to be discarded, because their activity could neither be maintained nor regenerated effectively. In SCW, maintaining catalyst activity is even more critical because interactions between the catalyst and water may be extensive and irreversible.

For example, deactivation of Pt/ZrO_2 and Pt/TiO_2 has occurred in a short time (Frisch et al., 1994), partially due to crystalline growth of platinum particles.

Inconsistent activity has been noted in the use of TiO_2, which was likely caused by changes in oxidation states and/or pore structure of catalyst (Frisch et al., 1995). Softening and swelling of Ni/Al_2O_3 has been reported in SCW due to physical strength of the catalyst (Elliott et al., 1993). Since these phenomena may prevent or limit catalysts used in the SCWO process, it is necessary to understand the interaction between SCW and catalytic materials (Ding et al., 1996).

The SCWO environment promotes the solid-state transformation of many conventional catalysts. Generally, it appears that solid-state transformations of a catalyst are primarily responsible for catalyst deactivation in laboratory studies. In these studies, high-purity reactants and oxidants are used to avoid catalyst poisoning. As compared to typical gas-phase oxidation conditions, the extent of various solid-state transformations in SCW is higher (Ding et al., 1996). Oxidation catalysts such as ion-exchanged zeolites, supported active metals, and transition metal oxides have been studied extensively. Supported active metal catalysts and zeolites do not appear to be suitable in SCWO environment (Ding et al., 1995).

One of the potential advantages of catalytic reaction in SCW is the prevention of coke formation on catalyst. As compared to gas-phase oxidation, catalytic reactions in supercritical fluids often form much less coke on the catalyst surface. The coke precursor, if it is formed on the catalyst surface, can be carried out by SCW because of the high miscibility of organic compounds with SCW.

1.4.3.7. Future of SCWO

SCWO is challenged by treatment of organic materials containing large concentrations of heteroatoms. The processing chemistry of these materials causes the production of corrosive acids. Neutralization of these acids forms salts that may be corrosive and may foul or plug the reactor. Corrosion is most serious problem in heat-up and cool-down sections of reactor. Corrosion and salt formation should be solved in the near future.

1.4.4. Overview

Along with the increase of industrial development, more and more toxic organic pollutants appear in wastewater (municipal and industrial). The conventional treatment methods are challenged with stricter discharge limits of such toxic non-biodegradable organics and economic balance. Thus, emerging technologies with a higher destruction potential are increasingly gaining popularity. For instance, the thermal oxidation methods are capable to remove various non-biodegradable pollutants within a wide range of organic content. Thermal Wet Oxidation techniques can convert toxic refractory compounds to carbon dioxide and carboxylic acids. The use of catalyst permits to employ milder conditions than for conventional WAO, thereby reducing process cost. For extremely refractory compounds more severe conditions of temperature and pressure (SCWO) can be applied. A general comparison of the typical conditions of thermal oxidation and its process performance is given in table 1.16.

Table 1.16: Performance of different types of wet oxidation (Levec, 1997).

Operating Conditions	**WAO**	**CWAO**	**SCWO**
Temperature, °C	200-325	130-250	370-570
Pressure, bar	20-210	20-50	220-270
Residence time, min	10-90	10-60	1-10
Conversion	80-99	90-98	99-99.999
Products	CO_2, H_2O, N_2, salts, organic acids	CO_2, H_2O, N_2, salts	CO_2, H_2O, N_2, salts
Estimated operating cost*, DM/m^3	30-60 (Zimpro)	20 (Nippon Shokubai)	60-250 (EWT)

* vary with wastewater type.

1.5. Wet Peroxide Oxidation

Oxidative treatment with hydrogen peroxide has emerged as a viable alternative for wastewater treatment with organic load. Hydrogen peroxide (H_2O_2) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Numerous applications of H_2O_2 are known in the removal of pollutants from wastewater, such as sulphites, hypochlorites, nitrites, organic compounds and chlorine (Neyens et al., 2003).

1.5.1. H_2O_2 oxidant

Among different oxidizing agents, hydrogen peroxide seems to have a lot of advantages (Fochtman, 1988), as H_2O_2 is:

- *Powerful* - H_2O_2 is one of the most powerful oxidizers known - stronger than chlorine, chlorine dioxide, and potassium permanganate (see table 1.17). And through catalysis, H_2O_2 can be converted into hydroxyl radicals ($\cdot$ OH) with reactivity second only to fluorine.
- *Safe* - H_2O_2 has none of the problems of gaseous release or chemical residues that are associated with other chemical oxidants. And since hydrogen peroxide is totally miscible with water, the issue of safety is one of concentration.
- *Versatile* - The fact that H_2O_2 is used for seemingly converse applications proves its versatility. It can treat both easy-to-oxidize pollutants (iron and sulphides) and difficult to oxidize pollutants (solvents, gasolines and pesticides).
- *Selective* - The reason why H_2O_2 can be used for such diverse applications is the different ways in which its power can be directed - termed selectivity. By simply adjusting the conditions of the reaction (e.g., pH, temperature, dose, reaction time, and/or catalyst addition), H_2O_2 can often be made to oxidize one pollutant over another, or even to favour different oxidation products from the same pollutant.
- *Widely Used* - Since it was first commercialised in the 1800's, H_2O_2 production has now grown to over a billion pounds per year. Its use for pollution control parallels those of the movement itself - municipal wastewater applications in the 1970's; industrial waste/wastewater applications in the 1980's; and more recently, air applications in the 1990's.

Table 1.17: Various oxidants and its oxidation potentials.

Oxidant	Oxidation Potential, V
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Hydrogen peroxide forms OH radicals that destroy the pollutants in a chain reaction. In comparison with ozone, H_2O_2 is currently more affordable, because low capacity utilization rates have resulted in a price decrease. Further, the use of hydrogen 'autoxidation' method entails lower capital expenses. Lastly, the controversy surrounding the supposed environmental dangers of ozone has stimulated interest in the application of H_2O_2 technology.

1.5.2. Fenton promoted WPO

Almost 110 years ago Fenton (1894) reported that ferrous ions strongly promote the oxidation of maleic acid by hydrogen peroxide. Forty years later, Haber and Weiss (1934) discovered that the hydroxyl radical is the actual oxidant in such systems. Fenton catalyst (Fe^{2+}/Fe^{3+} system) causes the dissociation of hydrogen peroxide and the formation of highly reactive hydroxyl radicals that attack and destroy the organic compounds. Fenton's reagent based wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water.

1.5.2.1. Process aspects of Fenton promoted WPO

Fenton reaction has been often used to treat industrial wastewater. Many common contaminants including phenols (Solvay, 2001), chlorinated compounds (Huang et al., 1993), methanol, butanol (Yoon et al., 2001), MTBE (Ray et al., 2002) can be oxidised in a matter of hours using an appropriate treatment stoichiometry consisting of catalyst and hydrogen peroxide. Also effluents from industries, such as: explosives (Liou et al., 2003), olive mill wastewater (Beltran-Heredia et al., 2001; Rivas et al., 2001b), bleach plant effluent (Bham & Chambers, 1997), desizing water (Lin & Lo, 1997) were treated by Fenton's reagent. The operating conditions, reactor type and removal efficiency of recent studies of Fenton Oxidation are given in table 1.18. As can be seen in all of these studies batch reactors were used and in majority ambient temperature and pressures were applied. Also pH was very close to 3 in all cases.

Table 1.18: Fenton oxidation of organic pollutants and industrial effluents.

Compound	Reaction Conditions	H_2O_2/Fe^{2+} Ratio	pH	Reactor	Removal Efficiency	Reference
Phenols	20-24ºC		3-4	Batch	ns	Solvay, 2001
Chlorophenols	Ambient T, P, 8 min	0.67mM:1mM	3	Batch	100% X	Huang et al., 1993
Methanol, t-Butanol	Ambient T,P	5mM:1-10mM	3	Batch	ns	Yoon et al., 2001
Methyl tertiary-butyl ether	Ambient T,P	0.1-100:1	3-7	Batch	ns	Ray et al., 2002
Explosives (nitroaromatics)	Ambient T,P, 25 min	0.29M:0.09-2.88M	2.8	Batch	99% X	Liou et al, 2003
Sewage sludge	Ambient T,P, 60-90 min	1:0.334 w/w	3	Batch	ns	Neyens et al., 2003
Olive mill wastewater	10-40ºC, 500 min	1:10- 1-20 w/w	ns	Batch	99.8 X 33% COD	Beltran-Heredia et al., 2001
Olive mill wastewater	20-50ºC	1-0.2M:0.01-0.1M	2.5-3	Batch	85-90% COD	Rivas et al., 2001b
Bleach plant effluent	60ºC, 2.5 h	125mM:2.5mM	4	Batch	92% X	Bham & Chambers, 1997
Desizing water	20-50ºC, 20-120 min	1:0.037-0.147 w/w	2-5	Batch	82% COD	Lin & Lo, 1997
Landfill leachate	Ambient T,P 2 h	1:0.083 w/w	3	Batch	60% COD	Lopez et al., 2004
Natural organic matter, humidic acid	Ambient T,P, 30 min	1:5-20	2-8	Batch	90% DOC, 100% X_{HA}	Murray & Parsons, 2004

DOC- dissolved organic carbon.

Factors that influence Fenton's processes are pH, contaminant character and concentration, concentration Fe^{2+}, hydrogen peroxide quantity required for complete oxidation and temperature (Kakarla et al., 2002). We shortly describe the influence of some parameters on Fenton's oxidation performance.

The Fenton's reagent has been often used at room temperature, but rarely at higher temperatures (Koubek, 1975; Debellefontaine et al., 1992). Nevertheless, it is possible to achieve faster destruction of phenol at higher temperatures (e.g. 100°C) than at the room temperature (Rivas et al., 2001b; Bham & Chambers, 1997; Lin & Lo, 1997).

A pH range of 2 to 4 has been described as optimum for free radicals generation (Watts et al., 1999; Solvay, 2001; Neyens & Baeyens, 2003; Neyens et al., 2003). However, most research into the Fenton reaction has been confined to low concentration conditions. Bham and Chambers (1997) observed reduction in AOX (adsorbable organic halide) during degradation of bleach plant effluents at pH range of 3-5. They found optimum pH value of 4. It is inconsistent with findings of other investigators that have found the optimum pH below 3 for the treatment of chlorinated aromatics (Sedalk & Andren, 1991).

The optimum value of pH found by Catrinescu et al. (2003) was around 3, which corresponds to maximum concentration of the active Fe^{2+} species and the lowest rate of H_2O_2 decomposition depending on ferrous species.

In the range of pH 2-7 it was observed that independently on the initial pH the final COD values were basically the same, but when initial pH increased from 2 to 7, the induction period was experienced and its length was increasing, when starting pH was closer to the neutrality (Rivas et al., 2001b).

The explication of why acidic pH values are optimum for Fenton's process can be given by Walling (1975), who simplified the overall Fenton chemistry by accounting for the water dissociation:

$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$

This equation suggests that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals.

The ferrous ions generated in the redox reactions react with hydroxide ions to form ferric hydroxo complexes. Within pH 3 and 7 these complexes account for the coagulation capability of Fenton's reagent. Dissolved suspended solids are captured and precipitated.

Fenton's reagent is known to have different treatment functions, depending on $H_2O_2/FeSO_4$ ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to have the effect of chemical coagulation. When the two amounts are reversed, the treatment tends to have the effect of chemical oxidation (H_2O_2 >> Fe2+) (Neyens & Baeyens, 2003).

Many times the quantity of hydrogen peroxide used is bigger than the stoichiometric quantity, because the consumption of H_2O_2 is not equal of formation rate of hydroxyl radicals, because a part of hydrogen peroxide decomposes to water and oxygen via non-radical pathways (Kwan & Voelker, 2003). Even if the increase in H_2O_2 improves significantly the conversion of COD, but there is a maximal excess of hydrogen peroxide, above which the process performance does not improve anymore (Rivas et al., 2001b).

The use of high ferrous ion is believed to be appropriate for producing large quantities of OH· within a short period of time (Yoon et al., 2001). Precisely the increase in the iron concentration seems to increase the oxidation rate (Solvay, 2001) and COD reduction (Rivas et al., 2001b).

High Fe/hydrogen peroxide rate

Yoon et al. (2001) observed that ferrous ions disappeared very rapidly in the absence of organic, but not in its presence. On the other hand hydrogen peroxide is consumed within the seconds independently on the presence or absence of organic. This is because as far as hydrogen peroxide decomposes to OH radicals, they mainly react with ferrous ion and not with hydrogen peroxide. This is due to the fact that the reaction between OH radicals and ferrous ions is ten times faster than between OH radicals and hydrogen peroxide. While the presence of organic affects behaviour of ferrous ions, because both competes for OH radicals.

Medium Fe/hydrogen peroxide rate

Regardless of the presence of organic, hydrogen peroxide converts rapidly all ferrous to ferric ion. In the absence of organic the reduction of ferric ion is very slow and is rate-determining step. However, the presence of organic has an effect on hydrogen behaviour in two different ways. First, there is no more hydrogen peroxide decomposition after its initial decrease, because the inert radical is produced from the reaction of OH radical and organic. This reaction overcomes the one between OH radical and hydrogen peroxide. Second, the presence of organic can make difficult OH radicals to react with ferrous ions. So ferrous ions react with hydrogen peroxide increasing its consumption at initial stage.

Low Fe/hydrogen peroxide rate

At low Fe/H_2O_2 ferrous ion disappears rapidly, when the Fenton reaction starts, the same as in the case of medium Fe/H_2O_2 rate. However, in comparison with medium rate much larger amounts of hydrogen peroxide remain after initial consumption by ferrous ion. In the absence of organic slow decomposition of hydrogen peroxide by ferric system occurs after fast initial depletion of hydrogen peroxide. However, in the presence of organic the decomposition of hydrogen peroxide by ferric system is almost stopped.

In the industrial applications of Fenton oxidation usually the ratio of Fe^{2+}/H_2O_2 is higher. The initial ferrous ion and hydrogen peroxide are consumed in a few seconds. The use of high concentration of ferrous ion produces the sufficient quantity of OH radicals in the short period of time. However, such a high Fe^{2+} concentration can cause three problems. First, with high rate of ferrous ion to hydrogen peroxide can decrease the efficiency of OH radicals for degradation of organics as ferrous ion itself can be OH radicals scavenger. Second, very rapid production of organic radical may cause depletion of dissolved oxygen and in that way decrease the mineralisation grade. Third, such a quantity of iron will result in big amount of iron sludge (Yoon et al., 2001).

Optimum ratio of H_2O_2 and Fe^{2+} was determined as 50:1, when the highest BPE dechlorination was achieved at the same Fe^{2+} concentration. It was possible to achieve 92% AOX reduction in half an hour at the temperature as low as 60°C (Bham and Chambers, 1997).

Various iron complex compounds with both reactant and reaction products can be considered during the Fenton's oxidation. These organic ligands can be responsible for the inhibition of the catalyst active form. These ligands can block the peroxide reaction by occupying the metal binding sites, preventing either substrate oxidation or peroxide decomposition (Murphy et al., 1989). The oxidation rate depends on the substrate nature, although for mono-substituted phenols, all oxidation curves have a particular pattern with an initial induction period. A certain relation between this induction period and ability to form complexes with Fe(III) exists. Oxidation of a phenolic substance with a low induction period suggests a high stability constant of the complex: Fe(III)-R-Ph-OH. Induction period is greatly dependent on pH. The Fenton's reaction has a limited interest, because the oxidation of organic acids acts very slowly. Complexation of catalyst by organic substances can either improve or inhibit the catalytic activity of the metal.

1.5.2.2. Reaction mechanism of Fenton Oxidation

The mechanism of attack of hydroxyl radicals on aromatic compounds is analogous to electrophilic substitution, similarly as in Wet Air Oxidation (Anbar et al., 1966). This is in agreement with the assumption that in most cases of electrophilic attacks on aromatic compounds the rate-determining step involves the addition of the electrophilic reactant to the aromatic ring. The hydroxyl radical has a high electron affinity and, consequently, some electrophilic character in its reaction with aromatic compounds (Anbar et al., 1966). It can either add to an aromatic nucleus to form cyclohexadienyl-type radical or abstract a hydrogen atom from it. The formation of cyclohexadienyl-type intermediates both in electrophilic and nucleophilic aromatic substitutions has been described as initial step for these reactions (Fendler & Gasowski, 1968).

Attack of electrophilic hydroxyl radicals by Fenton's reagent effects ortho- and para-hydroxylation of phenols affording catechols and hydroquinones. Secondary processes, including quinone formation, are also observed, because the Fe^{3+} ions produced in reaction form complexes with the phenols and the ferrous-ferric system enters into oxidation-reduction processes with the products.

According to Debellefontaine et al. (1997) there is competition between two reactions: (i) the main reaction of $OH\cdot$ with organic compounds to form oxidation products, such as carboxylic acids, and finally, carbon dioxide; and (ii) the side reaction where two OH radicals react to form inert products like water and oxygen. High oxidation efficiency can be obtained, when the organic species can catch all the radicals in the moment that they are formed. This can be achieved, when there are less hydroxyl radicals than organic species in the reaction mixture.

1.5.2.3. Reactivity of aromatic compunds

A Solvay study (2001) reported differences in the activity between phenols in Fenton WPO due to the effect of the substituent whether it is a strong ring activator like the methyl group or a strong ring deactivator like chlorine. The dependency on substituent type and location was also observed by Liou et al. (2003). NO_2 group with electron-withdrawing ability (deactivates the ring) can reduce the reactivity of aromatic. On the other hand OH and CH_3 groups have electron-releasing abilities, leading to increase the reactivity of aromatics (nitroaromatics). Ortho-substituted phenols produced about half of the amount of acid that produced para and meta substituted isomer. So the reactivity of phenols toward oxidation is the same as in the case of wet oxidation methods.

As described by Mitnik et al. (1991) in the oxidation of monosubstituted phenols, three different periods can be observed: (i) an induction period; (ii) an active reaction period; and (iii) a retardation period, which depends on character of phenol. It was assumed that the presence of these periods is related to the existence of various complexes that are formed by iron compounds with both reactant and reaction products. The formation of metal complexes with organic ligands that have capacity to participate in proton exchange is responsible for the existence of the induction period and strongly depends on pH. With big drop in pH (from 4.05 to 1.50) the rapid increase in the induction period was observed. Also it was observed that with adding small quantity of pyrocatechol to the reaction mixture, the induction period is completely eliminated. Probably it influences catalyst activity. The induction period stops, when the first small quantity of pyrocatechol is formed. Retardation period is described as loss in activity of catalyst due to the oxidation products.

1.5.2.4. Future trends

New processes termed advanced oxidation processes that are based on Fenton Reaction are being under developement.

For example, photo Fenton utilises the positive effect of the UV-light on the degradation rate of pollutants. This is due to the photoreduction of Fe^{3+} to Fe^{2+}, being the main species that can catalyse H_2O_2 to produce hydroxyl radicals (Liou et al., 2003; Andreozzi et al., 1999). Photocatalysis appears very promising, especially in the regions where strong sunlight is available as a cheap energy source (Fallmann et al., 1999).

Furthermore, modified Fenton's processes that use chelated-iron catalysts and stabilised hydrogen peroxide have been developed with the goal of promoting effective in-situ filed application under native pH conditions (i.e., pH 5-7) (Kakarla et al., 2002).

In the next chapter 1.6, these new AOPs are briefly discussed.

1.5.3. Wet Peroxide Oxidation

Considering the limitations of Fenton's reaction at ambient temperature, an oxidative treatment method was developed that brought together the advantages of strong oxidiser and higher temperature (in comparison to Fenton). For example, Debellefontaine et al. (1992) developed the WPO process at laboratory scale that permits the treatment of wastewater with COD value lesser than 20000 mgO_2/l. The reaction was carried out in acidic medium with Fenton's reagent as catalyst (Fe^{2+}/H_2O_2) and quite high temperature (100 to 150°C).

1.5.3.1. Process aspects of Wet Peroxide Oxidation

The difference between Wet Air Oxidation and Wet Peroxide Oxidation is that the first one uses a gaseous oxidant and is two step process (transfer plus oxidation) and the second one uses a liquid oxidant (hydrogen peroxide), which eliminates gas-liquid mass transfer problems. The process is similar to Fenton Reaction, but higher temperatures are employed to enhance TOC reduction. The advantage of WPO process as compared with Fenton's catalysed peroxide reactions is also the lack of sludge (Kardasz et al., 1999). Although, hydrogen peroxide is a relatively costly reactant, the operating costs of WPO processes are overcome by the lower fixed costs as compared with ozonation, WAO and SCWO (Debellefontaine et al., 1996).

Wet Peroxide Oxidation can be used to treat great variety of toxic organic compounds. Various pollutants were tested by this method to see the feasibility of industrial wastes treatment. In fact, most of pollutant oxidations gave good results, when treated by WPO, however a few compounds like perchlorocarbons are refractory and in addition aliphatic hydrocarbons and carboxylic acids appear to be difficult to oxidize. Typical conditions of WPO are given in table 1.19 and the different compounds treated by this method are presented in table 1.20.

Table 1.19: Typical WPO conditions (Kardasz et al., 1999) (* is stoichiometric H_2O_2 quantity coefficient).

Parameters	Working range
Temperature (°C)	100-150
$H_2O_2^*$	1.1-1.5
Reaction time (mn)	15-60
pH	2.5-4
Catalyst (mg/l)	10-100

As can be seen in table 1.20, typically batch reactors are used, as well as low temperatures and atmospheric pressures. Usually, either homogeneous or heterogeneous catalyst is used in this process. Also, the excess of hydrogen peroxide related to stoichiometric demand is frequently applied.

Table 1.20: Process data of some recent WPO studies.

Substrate	Reaction Conditions	% of SD of H_2O_2	Reactor Type	Catalyst	Removal Efficiency	Reference
Phenol	100ºC, 10 bar, pH=5.6	100	Batch	Fe-zeolites	100% X 66% TOC	Ovejero et al., 2001a
Phenol	70ºC, 1 bar, pH=5	150	Batch	Fe-zeolites, Cu, Mn	99% X 70% TOC	Fajerwerg & Debellefontaine, 1996
Phenol	18-70ºC, P-ns, pH=3.7	700-2800	CSTR	Al-Fe Pillared clays	100% X 80% TOC	Guélou et al., 2003
Phenol	25-90ºC, 1 bar, pH=3-6	25-600	Semi-Batch	Al-Fe Pillared clays	100% X 93% TOC	Guo & Al-Dahhan, 2003
Phenol	30-70ºC, P- ns, pH=2.5-7	ns	Batch	Al- Fe Pillared beidellite	88% COD	Catrinescu et al., 2003
Phenol	25-70ºC, 1 bar, pH=3.5-4	100	Batch	Al-Fe Pillared clays	100% X 78% TOC	Barrault et al., 2000
Phenolic compounds	100-140ºC, 3-5 bar, pH=2.5-4	110-150	Batch	Fe homog.	10-95% TOC	Debellefontaine et al., 1996
Acetic acid	90ºC, 1 bar	150-260	Batch	Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ce^{3+}/NaY zeolites	63% TOC	Larachi et al., 1998
Formic, acetic and propionic acids	25-70ºC, P-ns, pH=2.8-5.2	150	Batch	Fe^{3+}	X_F=60% X_A=20% X_P=80%	Centi et al., 2000
Polyvinyl alcohol	70-150ºC, P-ns, pH=2.5-4.5	10-150	Batch	Fe^{2+}	80% TOC	Lei & Wang, 2000
1,1-dimethylhydrazine	25-50ºC, 1bar, pH=7-11	ns	Batch	Cu, Fe	ns	Pestunova et al., 2002
PCBs	125-275ºC, 20 bar, pH=2.6-7.5	ns	Semi-batch	-	99% X	Duffy et al, 2000
Dyes	110-150ºC, 10 bar, pH=3.5-8.8	50-150	Batch	Cu/AC	88% TOC	Chen et al., 1999
Petrochemical wastewater	100-140ºC, 3-5 bar, pH=2.5-4.0	110-150	ns	Fe homog.	ns	Lei & Wang, 2000

ns-not specified,
SD- Stoichiometric Demand,
PCBs-polychlorinated biphenyls.

The main problem of WPO is the inefficient use of H_2O_2. Obviously, the best results are obtained when all the radicals are trapped by the organic species. That is why H_2O_2 concentration should be kept at low values above the organic concentration. This can be resolved by step by step addition of H_2O_2 throughout the run in both batch reactor and continuous reactor (Debellefontaine et al., 1996).

1.5.3.2. Effect of operating parameters

As WPO follows the same mechanism as Fenton's (Debellefontaine et al., 1996), it should be affected by temperature, pH and H_2O_2 dosage.

Increase in temperature has been observed to increase the rate and extent of oxidation, and also reduce the induction period length (Rivas et al., 1999; Debellefontaine et al., 1996). Catrinescu et al. (2003) noted that the effect of temperature is more pronounced at shorter reaction times. This behaviour suggests that the temperature strongly affects the degradation of phenol and of cyclic intermediates produced along the reaction, and thus the resulting toxicity. When all these compounds are eliminated, the oxidation of remaining aliphatic compounds (mainly carboxylic acids) slows down, and the overall process velocity is reduced. Chen et al. (1999) reported that increasing the reaction temperature has two opposing effects. It can increase the oxidation rate in accordance with the Arhenius equation, but too high temperature will result in the destruction of H_2O_2 to produce O_2 and H_2O, an undesirable side reaction. This behaviour was also observed by Lei & Wang (2000). Also, oxidation rate of PCBs increases with increasing temperature up to an optimal temperature of 225°C, and then above 225°C, the rates decrease significantly (Duffy et al., 2000).

The most favourable pH conditions for phenols WPO are very alkaline solutions (pH=13) or when no acid or base added (pH=4-5). But, when using hydrogen peroxide, the efficacy is lower for alkaline pH, because for high pH hydrogen peroxide decomposes to oxygen and water. Additionally, ionic form of H_2O_2 presents higher scavenging power of hydroxyl radicals than its non-dissociated form (Rivas et al., 1999). Moreover, when using homogeneous Fe catalyst pH is optimum around 3, but when using heterogeneous catalyst it is possible to work at pH around 5. At short reaction times the initial pH strongly affects the oxidation rates, but as the reaction goes on there is drop in pH due to the formation of carboxylic acids and then the reaction rates accelerates (Catrinescu et al., 2003; Centi et al., 2000).

Also Guo and Al-Dahhan (2003) observed that the initial rate of oxidation is markedly affected by pH, whereas the steady-state is a much weaker function of the pH.

A higher initial rate of phenol removal results from a higher H_2O_2 concentration. Guo & Al-Dahhan (2003) reported that, for 100% of the stoichiometric amount of H_2O_2, 93% of the original carbon was mineralised. Further increase in H_2O_2 did not improve organic carbon removal. The breakdown reaction leads to the formation of high-molecular-weight intermediates and then further degradation into low molecular weight acids that are refractory to mineralisation. Also Chen et al. (1999) observed that TOC reached a plateau at 100% H_2O_2 dosage and a further increase of H_2O_2 did not lead to more TOC removal. These results suggest that the oxidation process happened in more than one step. The first step involves the breakdown the large dye molecules, but does not mineralise them. The next step is the degradation of the smaller molecules into carbon dioxide and water. At the end of the reaction, there are residual organics (mainly organic acids) that are very difficult to be oxidized further.

1.5.3.3. Process performance for aromatic compounds

Homogenous catalysts

The oxidation of phenolic compounds and industrial wastes using Fenton like catalyst (Fe^{2+}) in a batch system was investigated by Debellefontaine et al., (1996). The temperature as low as 70ºC resulted in phenol elimination, but also in carboxylic acids accumulation and poor TOC removal, while temperature increase to 140ºC led to almost complete TOC removal. In chlorophenol oxidation, this compound is completely transformed; free chlorine is obtained in stoichiometric amount. With nitrogen compounds GC/MS analysis of the oxidised mixture could not detect any residual organic nitrogen.

In the treatment of different organic compounds in the conditions of Fe^{2+} (30 mg/l), treatment time of 1h, 120% of H_2O_2 dosage, the order of TOC removal for the compounds of interest is (from the highest to lowest): nitrobenzene (83%) > phenol (75%) > o- and m-chlorophenol (73%) > aniline (6%).

Polyvinyl alcohol (PVA) containing wastewater was treated by WPO in study of Lei and Wang (2000). The highest TOC removal of 75.6% was obtained at the highest temperature (140°C), the highest H_2O_2 dosage (150%), the lowest pH (2.5) and Fe^{2+} concentration of 60 mg/L.

Lin et al. (1996) reported that the use of hydrogen peroxide oxidant permits drastic decrease in temperature and pressure as required by the ordinary WAO process. The authors achieved over 90% COD reduction in 30 minutes, when 3 g of H_2O_2/1000 mg/l of COD is employed at operating 150°C and 5 bar during wet air oxidation of phenolic compounds with hydrogen peroxide used as a homogeneous oxidant.

<u>Heterogeneous catalysts</u>

In the catalytic process until now basically homogeneous catalysts Fenton-like were used, i.e. ions of iron, copper, chrome, molybdenum, wolfram, vanadium. However use of metallic salts as catalyst induces an additional pollution. That is why the use of heterogeneous catalysts may be a good alternative.

In work of Falcon et al. (1995) salts of Fe, Cu and Mn and low temperature (100°C) were employed. The purpose of low temperature was to minimize useless decomposition of hydrogen peroxide. Laboratory work demonstrated the efficiency of a new catalytic system of three metal salts: Fe^{2+}, Cu^{2+} and Mn^{2+}. When using a mixture of these three catalysts the removal efficiency can reach 91%, while it does not exceed 22% when using a metal alone.

Also Al-Fe pillared clay catalyst exhibit high activity for phenol WPO. Applying this catalyst, Barrault et al. (2000) achieved rapid conversion of phenol mainly to CO_2 using. The study has shown that in mild conditions about 80% of phenol was transformed into CO_2 at 70ºC in 2 hours under atmospheric pressure.

Recently, interesting works have been published dealing with use of zeolites for the oxidative treatment of phenolic aqueous solutions (Centi et al., 2000; Fajerwerg et al., 1996 and 1997, Ovejero et al., 2001a and 2001b).

One of the factors of influence in the catalytic processes is pH. In the work of Fajerwerg at al. (1996) it was observed that pH of 5 is an optimum value that permits the complete elimination of phenol and significant TOC removal, using hydrogen peroxide and Fe-ZSM-5 catalyst. At lower pH (about 3.5) significant TOC removal can be achieved, but the catalyst loses activity.

The comparison of homogenous and heterogeneous WPO processes is presented in the work of Centi et al. (2000). The authors investigated the oxidation of formic, acetic and propionic acid by hydrogen peroxide with iron containing zeolites as catalysts. The rate of reaction for homogeneous catalyst is higher (by a factor of about 3-5), however much more residence time is necessary to reach the same level of conversion as in heterogeneous catalyst case (3 h instead of 1 h). This insinuates the different rate of propionic acid conversion. In the sense of activity of solid catalyst it was found that, although it is not influenced by iron leaching, slight leaching of iron was present, what can lead to deactivation with prolonged use. However, major drawback of solid catalyst is its higher rate of hydrogen peroxide decomposition to water and oxygen. On the other hand, a weakness of homogeneous catalyst use is its narrow pH range and necessity to recover the catalyst in the end of process.

Also WPO was compared to WAO of phenol using Fe and Cu containing zeolitic catalyst under mild conditions (100ºC, 10 bar and 100% of stoichiometric amount of H_2O_2) (Ovejero et al., 2001b). It was observed that the catalytic generation of hydroxyl radicals by iron ions depends only on the hydrogen peroxide amount. The results showed that Fe and Cu species do not promote free radical formation from oxygen, and that the global TOC conversion is related to the catalyst activity to promote the formation of free radicals in the presence of hydrogen peroxide.

Also Chen et al. (1999) reported that for treating the five types of high concentration reactive dye, wet air oxidation, catalytic wet air oxidation, and promoted wet oxidation were not satisfactory. Wet peroxide oxidation, however, was found to be an efficient process in terms of the removal of total organic carbon and colour.

1.5.4. Overview

The oxidation with Fenton's Reagent (that is an adequate mixture of H_2O_2/Fe^{2+}) is increasingly being used for wastewaters treatments that contain nonbiodegradable matters. Also, WPO and Fenton WPO can be used for organic pollutant destruction, reducing toxicity, improving biodegradability. The success of all the process relies on the formation of highly oxidative free hydroxyl radicals and its efficient use for the oxidation of the organic pollutants.

However, even if there is high conversion of phenolic compounds during Fenton WPO, COD reduction is not too high. Additionally, in comparison with WPO, Fenton Oxidation has a limitation of narrow pH range applicability and the problem of removing ferrous catalyst in the end of the process. WPO process has many advantages such as ease of processibility, workability within high range of temperatures and pressures. If hydrogen peroxide is efficiently used the stoichiometric quantity can be sufficient to obtain destruction efficiency close to complete. In order to avoid side-decomposition, H_2O_2 can be continuously fed into the reactor. In both Fenton WPO and WPO processes the pressure applied is a minimum necessary justo to avoid the evaporation of the reaction mixture. This results in lower operating costs as compared to thermal oxidation processes.

1.6. Advanced and Combined Oxidation Processes

Advanced Oxidation Processes (AOP's) are loosely defined as processes that generate highly reactive oxygen radicals. Advanced is called, because the reactions are just highly accelerated oxidation reactions that occur, when pollutants enter the environment. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwaters, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluents (Yue, 1997; Andreozzi et al., 1999).

Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. The processes offer several advantages over biological or physical processes, including:

- process operability;
- unattended operation;
- the absence of secondary wastes;
- the ability to handle fluctuating flow rates and compositions (Pérez et al., 2002).

Advanced chemical wet oxidation is based on the strong oxidation power of chemicals like ozone (Novak, 1988), hydrogen peroxide etc., sometimes in combination with UV (Vogna et al., 2004). The purpose is to oxidise and to detoxify the contaminants in the wastewater in order to render it biodegradable or suitable for further treatment. Electrochemical oxidation has as an aim to oxidise organics and form precipites from inorganics present in wastewaters without the addition of chemicals, but by the electrochemical action of Al- en Fe-electrodes, which form oxygen at the cathode and go into solution under formation of Fe- en Al-flocculation agents. Through the combined action organics are oxidised, heavy metals are precipitated as hydroxides and flotated through the gas formation. Photochemical Oxidation utilises ultraviolet light (UV) in combination with hydrogen peroxide, ozone, or inorganic catalysts and results in generation of free radical oxidants that can degrade various organic chemicals (Weavers et al., 1997; Hua et al., 1997; Li et al., 1999; Alnaizy &

Akgerman, 2000; Kiwi et al., 2000; Zhang et al., 2003). This process can be effective; however, energy and capital costs can be high and has problems with turbidity (Kearney & Mazzocchi, 1988).

Esplugas et al., (2002) compared different advanced oxidation processes such as ozonation, O_3/H_2O_2 system, UV, UV/O_3, UV/H_2O_2, O_3/UV/H_2O_2, Fenton's reagent, photocatalysis in terms of cost and efficiency for phenol degradation. With regard to phenol degradation Fenton's reagent showed the fastest rate, 40 times higher than UV process and photocatalysis and 5 times higher than ozonation. Also Sevimili and Kinaci (2002) compared the efficiency of ozonation and Fenton process for the decolourisation of textile wastewater and they found Fenton process to be more effective for COD removal.

Aniline was treated by electrochemical oxidation. Due to many steps involved, aniline undergoes a polymerisation reaction to form a fairly stable polymer, polyaniline. It is also reported to produce various intermediates species, such as p-aminodiphenyl amine, benzidine, p-benzoquinone and maleic acid (Chung & Park, 2000).

The effectiveness of the wastewater contaminants abatement can be enhanced by the combination of different treatment methods (Abderrazik et al., 2002; Bertanza et al., 2001).

In a combined biological-chemical-biological treatment, the first biological step removes biodegradable organics; the chemical process increases the biodegradability of residual organics for the second biological step (Bertanza et al, 2001).

For olive mill wastewater it was proposed to apply oxidation with Fenton's reagent and ozone for reducing the phenolic content and improve biodegradability. In a second stage, biological degradation with aerobic microorganisms of the pretreated wastewater was used (Beltrán-Heredia et al, 2001). Also San Sebastián et al. (2003) proposed Fenton's reaction as pre-oxidation of pharmaceutical wastewater and biological treatment as a second step.

The combination of ozonation and photocatalysis with TiO_2 gives high yields of aniline degradation in aqueous solutions. Particularly, an ozonation pretreatment followed by photocatalysis significantly increases the yield of TOC removal in comparison to either ozonation or photocatalysis acting separately (Sanchez et al., 1998).

Ledakowicz and Solecka (2000) have studied AOPs as the pretreatment of biological treatment. The authors compared various AOPs employed together with biological treatment of the textile wastewater and found the combination of $O_3/H_2O_2/UV$ as the best system in terms of reduction of COD.

The efficiency of the process can be enhanced by combination of oxidant. Li et al., (1999) studied peroxone oxidation of nitrobenzene utilising ozone and hydrogen peroxide as combined oxidants. The decomposition of ozone and interactions between ozone and hydrogen peroxide all are important indicating the formation of hydroxyl radicals in these reactions resulting in linear increase in the oxidation rate with the concentration of hydrogen peroxide. Zwiener and Frimmel (2000) and Li et al. (1999) also used both ozone and hydrogen peroxide to oxidise pharmaceuticals. Ozone alone was not capable to degrade some of drugs. The addition of hydrogen peroxide increased significantly the quantity of hydroxyl radicals and in that way improved the performance of the oxidation. Also FMC Corporation (FMC) was looking for optimal combination H_2O_2/UV, H_2O_2/O_3, $H_2O_2/O_3/UV$ for TOC removal from petroleum production wastewater. The combination of ozone, hydrogen peroxide with UV light turned out to be the most effective.

Major research efforts should be devoted in the future to fill some specific gap which exists for these techniques in the areas such as identification of reaction intermediates, development of rate expressions based on established reaction mechanisms, identification of scale-up parameters and criteria for cost effectiveness and maximum destruction efficiency.

1.7. Summary

For the treatment of wastewaters that are non-toxic in general, biological process is the most suitable from the economical point of view. However, when wastewater contains bio-toxic and/or recalcitrant organics biological processes alone are not always able to reach effluent standards for the discharge into municipal sewers and chemical or combined chemical-biological oxidation is more appropiate.

As far as chemical oxidation processes are concerned, depending on the conditions applied and the method of active oxygen species generation, the processes may be classified into two main types: advanced oxidation and thermal wet oxidation. The chemical oxidation techniques allow to reduce pollutants concentration and yield more oxidised compounds, which are in most cases more easily biodegradable than former ones.

Wet air oxidation process is efficient, but high temperatures and pressures have to be employed. Catalytic wet air oxidation was developed in order to achieve milder reaction conditions at improved destruction efficiency. However, many compounds proved too refractory to be destroyed by CWAO. Also the SCWO process was developed offering advantages of extremely high oxidation rates at very short residence time. Due to the harsh environment of supercritical water conditions corrosion and salt deposition on the reactor walls are mayor inconvenients in SCWO process. Techniques based on hydroxyl radicals formation, e.g. Fenton processes, are more cost effective method, since they only require low temperature in presence of a homogenous Fe^{2+} catalyst. This process is effective in abatement of phenolic compounds, however does not achieve high COD reduction and has an additional drawback of catalyst separation after reaction. WPO appears to be a promising technology. It applies temperatures higher than those of Fenton, but significantly lower than those of SCWO achieving high COD destruction in this way. Additionally, if optimum conditions are chosen the addition of stoichiometric quantity is sufficient for the complete mineralization of organic compounds. Among the chemical emerging oxidation process thermal oxidation processes, wet peroxide oxidation and advanced oxidation processes are of our interest as they yield high removal efficiency.

1.8. Objectives

It becomes evident from the related field literature that the correct choice of wastewater treatment depends on many factors such as the contaminants nature and toxicity, effluent composition and total organic load, final effluent destination, global process economics, etc. An issue of increasing global environmental concern is the appearance of many new bio-refractory organic pollutants in today's wastewater from petrochemical, chemical and pharmaceutical processes. In many cases, conventional biological or thermal treatments are not longer applicable to safely and efficiently remove this type of pollutants. On the other hand, the use of more recently developed oxidation techniques for bio-toxic compounds other than phenol has received only little attention up today.

The main objective of the present work is to assess experimentally the potential of diverse chemical oxidation techniques for the abatement of organic pollutants. This should allow establishing case dependant recommendations for a appropiate wastewater treatment. Four different methods, i.e. CWAO, peroxide promoted CWAO, WPO and Fenton promoted WPO have been selected according to their increasing oxidation power. As model pollutants, frequently encountered organic compounds, i.e. phenolic aromatics (phenol, o-cresol, m-xylene), halogenated phenols (o-chlorophenol), nitrogenated aromatics (nitrophenol, aniline, nitrobenzene) and sulphur containing aromatics (sulfolane) have been selected for the experimental study. Phenol was used as a model compound for preliminary studies, because of its high bio-toxicity and occurrence in industrial effluents. In addition, phenol is considered to be an intermediate product in the oxidation pathway of higher-molecular-weight aromatic hydrocarbons. The aim is to establish adequate operating conditions for each method that allow achieving a desired removal efficiency and thereby, selecting a specific treatment tailored both to the pollutant's toxicity and the final effluent's destination.

The following specific objectives can be formulated in order to meet with the main objective of the work:

- Literature survey on wastewater to create a data based guide for the experimental work.
- Design, construction and operation of an adaptable wet oxidation equipment, able to work in conditions of high temperature (up to 550°C) and high pressure (up to 400 bar).
- Experimental assessment of reference removal efficiency for the selected pollutants through continuous CWAO over active carbon catalyst, using an existing laboratory Trickle Bed Reactor.
- Experimental assessment of operating conditions and removal efficiency in terms of pollutant conversion and COD destruction for CWAO refractory pollutants using hydrogen peroxide oxidant (promoted CWAO, WPO, Fenton promoted WPO).
- Comparative end stream treatment of two real effluents from phenolic resins production applying the oxidation techniques studied.

Chapter 2

Experimental

This chapter describes in detail the experimental equipments, procedures and analysis methods used to conduct the oxidation experiments in this study. It is worth to mention that for the runs with H_2O_2 oxidant, an adaptable high temperature and high pressure experimental set-up, including a tubular reactor made of Hastelloy, was designed and constructed. In a preliminary study CWAO of organic pollutants over activated carbon were carried out in an existing small scale Trickle Bed Reactor to obtain reference conversions for comparison of performance of the different oxidation techniques tested.

2.1. Apparatus

2.1.1. High Temperature – High Pressure Equipment

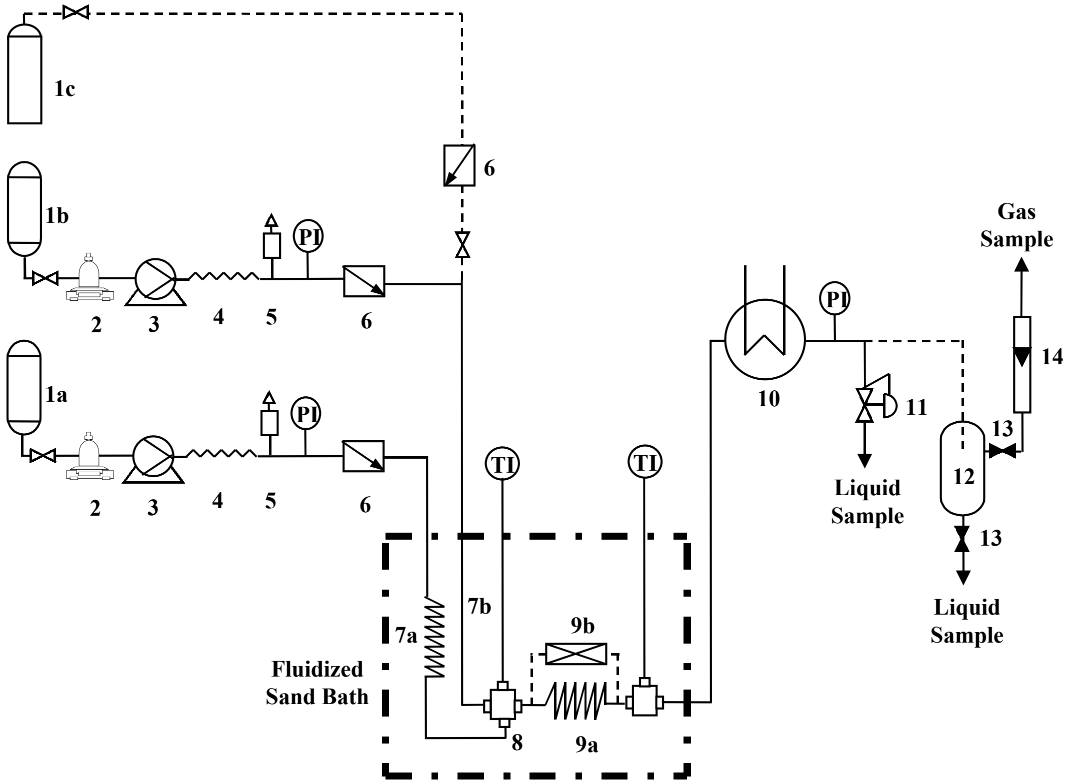
Figure 2.1 schematically shows the constructed experimental apparatus that is suitable for continuous operation at temperatures and pressures up to 550ºC and 400 bar, respectively. The equipment consists of 3 main sections: the pumping block, the reactor system placed in the sand bath (Techne) and the decompression-cooling zone.

A two head high-pressure metering pump (3) (Eldex, USA), with a nominal flow range between 4 and 600 ml/h, is used to feed in separate lines the organic solution and the oxidant - aqueous H_2O_2 solution. The feed lines contain flow dampers (4) (Hidracar U002A46E1-AI), security valves (5) (NUPRO SS-4R3A), manometers (WIKA EN-837-1) and check valves (6) (HiP 15-41AF1). The flow dampers are used to absorb the pulsations that are generated during the operation of the pump. The security valves are installed to relieve pressure in the case of pressure exceeding a given limit of 250-400 bar. Additionally, the check valves prevent high pressure to return to the pumps. When entering the sandbath, the organic and oxidant solutions first pass through two different preheaters of 0.010 in i.d., 0.9 m long (stainless steel tubing) and 0.06 in i.d., 2.6 m long (Hastelloy C-276), respectively. Hastelloy C-276 tubing had to be selected as the material of construction throughout the high temperature and high pressure sections of the system because of its favourable anti-corrosion characteristics. Before entering into the reactor tubing (9a) (0.06 in i.d., 4 m long), the organic feed is mixed with the oxidant in a Hastelloy C-276 mixing block (8) designed to combine the two flows at a 90° angle of incidence. The thermocouple placed in the mixing block is inserted deeply in the mixing cross: (i) to enhance mixing of reactants because of higher stream velocities (Phenix et al., 2002); and (ii) to correctly measure the stream temperature. The temperature is measured at the inlet and outlet of the reactor by thermocouples (type K, Inconel). The reactor and the preheating coils are immersed in a temperature-controlled, fluidised sand bath (Techne, model IFB-101). The cooling-depressurisation subsystem consists of a heat exchanger (10) and a back-pressure regulator (11) (Tescom, model 26-1721-24). The pressure in the reactor is manually adjusted by means of a back-pressure regulator.

The original standard equipment configuration was modified during the experimental runs:

1) to perform most of the Wet Peroxide Oxidation experiments, organic and oxidant solutions were premixed to have only one Hastelloy feed line, but with different preheaters lengths (0.06 in i.d.), and a tubular reactor of 3 m long (0.06 in i.d.). This was to study and to optimise the effect of reactant feeding on phenol conversions.
2) for the experiments with Fenton's Reagent, the two feed lines were joined just before entering the sand bath resulting in a new total reactor length of 8.2 m.
3) to perform the H_2O_2 promoted catalytic wet air oxidation runs, an additional air line was attached. The air oxidant is delivered from a high

pressure cylinder (1c) equipped with a pressure regulator to adjust and maintain the operating pressure constant. The lines of liquid and gas feed are joined before entering the sand bath after passing through the corresponding check valves. The gas-liquid mixture exits the catalytic fixed-bed reactor (9b), flows through the heat exchanger (10) and then enters a gas-liquid separator (12) by-passing the back pressure regulator. The liquid part of the effluent is collected in the bottom of the separator, while the effluent gas leaves the separator upwards. The gas flow rate is adjusted and measured by a downstream metering valve (13) and rotameter (14). Moreover, the reactor tubing was replaced by a packed bed reactor (9b) made of Hastelloy C-276 (0.25 in i.d., 10 cm long). Two sintered disk made of stainless steel were put in the inlet and outlet of the reactor to retain the catalyst bed of normally 0.7 g of granulated AC.



1-Feed tanks; a) organic, b) oxidant, c) high pressure air; 2-Balances; 3-High pressure pump; 4- Flow dumpers; 5-Security valves; 6-Check valves; 7a-Organic preheater; 7b-Oxidant preheater; 8-Mixing block; 9a-Tubular reactor, 9b-Fixed bed reactor; 10-Heat exchanger; 11-Back pressure regulator; 12-Gas-liquid separator; 13-Micrometering valves; 14-Gas rotameter.

Figure 2.1: High pressure and temperature equipment.

2.1.2. Trickle Bed Reactor (CWAO experiments)

Figure 2.2 presents the existing set-up for continuous oxidation including a catalytic packed bed reactor (5) operating in the trickle flow regime (Fortuny, 1996). The fixed bed reactor consists of a SS-316 tubular reactor, 20 cm long and 1.1 cm i.d., placed in a temperature controlled oven (4) (±1°C). The liquid feed is stored in a 5 L stirred glass tank (1), which is connected to a high-pressure measuring pump (2) (Eldex) that can dispense flow rates between 10 and 300 ml/h. The air oxidant comes from a high pressure cylinder equipped with a pressure regulator to maintain the operating pressure constant. A flowmeter (8) coupled with a high precision valve is used to measure and control the gas flow rate. The liquid and gas streams are mixed and then passed through a 1 m long heating coil placed in the oven to reach the reaction temperature. The mixture then enters the reactor and flows along the activated carbon bed, which is retained between two sintered metal disks. The exited solution goes to a liquid-gas separation and sampling system, to regularly withdraw liquid samples for HPLC analysis.

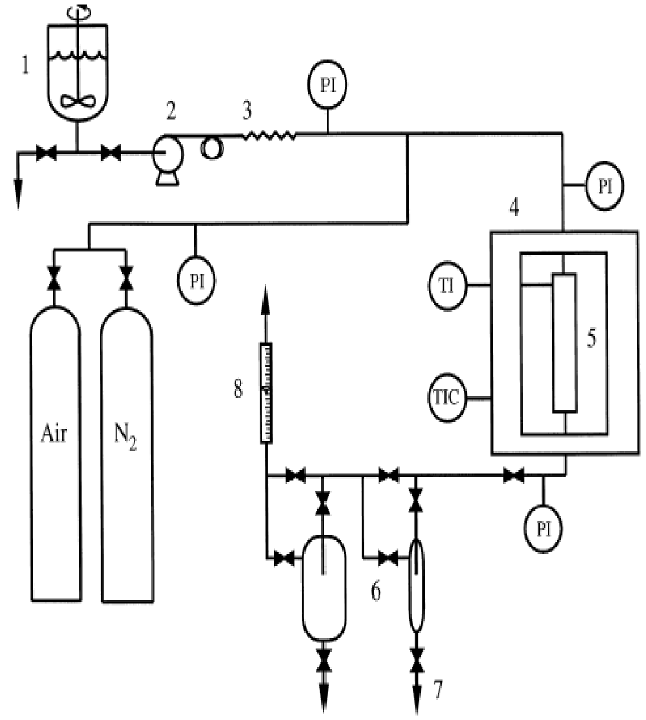


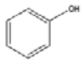
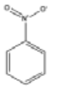
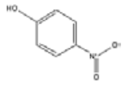
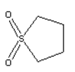
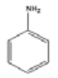
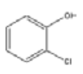
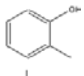
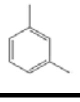
Figure 2.2: Experimental set-up for the catalytic wet oxidation: 1-Feed vessel; 2-High-pressure pump; 3-Flow dumper; 4-Oven; 5-Trickle bed reactor; 6-Gas-liquid separators; 7-Sampler; 8-Gas flowmeter.

2.2. Materials

2.2.1. Organic pollutants and oxidants

Phenol of nominal purity (98.5%) was purchased from Riser, p-nitrophenol (purity of 98%), nitrobenzene (purity of 99%), aniline (purity of 99.5%), sulfolane (purity of 99%), o-chlorophenol (purity of 99%), o-cresol (purity of 99%), m-xylene (purity of 99%) from Aldrich and hydrogen peroxide from Merck as a 30%wt/v aqueous solution. Some technical information of the model compounds are given in the table 2.1. The gaseous oxidant was compressed high purity synthetic air (Carburos Metalicos).

Table 2.1: Model compounds studied

Model Compounds	*Molecular Weight*	*Molecular Formula*		*Vapour pressure*	*Solubility in water g/l at 20ºC*	*Purity (%)*
Phenol	94.11	C_6H_6O		1 mmHg at 12.1 °C	90	98.5
Nitrobenzene	123.11	$C_6H_5NO_2$		1 mmHg at 44.4 °C	1.9	99.0
p-Nitrophenol	139.11	$C_6H_5NO_3$		0.6mmHg at 120 °C	16	98.0
Sulfolane	120.17	$C_4H_8O_2S$		0.0062mmHg at 27.6 °C	Soluble	99.0
Aniline	93.13	C_6H_7N		0.6mmHg at 20 °C	34	99.5
o-Chlorophenol	128.56	C_6H_5ClO		1.7mmHg at 20 °C	285	99.0
o-Cresol	108.14	C_7H_8O		0.25mmHg at 25 °C	20	99.0
m-Xylene	106.17	C_8H_{10}		6.0mmHg at 20 °C	0.2	99.0

2.2.2. Wastewater effluents

In addition, two real wastewater samples (TRI1 and TRI2) were studied (TRATAMIENTOS Y RECUPERACIONES INDUSTRIALES, S.A.). These effluent samples are taken from process waters of phenolic resins production and their known characteristics are given in the table 2.2. Both wastewaters samples are slightly yellow liquids and impart strong repellent odour. They probably also contain some surfactants, as during the filtration strong foam formation occurred and show different pH value of 5.7 (TRI2) and 7.4 (TRI1).

Table 2.2: Industrial wastewaters characteristics.

Sample	TRI1	TRI2
Water content, %	99.0	95.1
pH	7.6±0.2	5.6±0.2
[Phenol], ppm	1800	36.5
TOC, ppm	1850	32240
COD, mgO_2/l	5600	97000

Both real wastewaters contain several organic compounds as can be seen in figure 2.3 that shows respective HPLC chromatograms of the samples. However, the main component of TRI1 is phenol as suggested by figure 2.3a and the corresponding COD value from table 2.2. On the other hand, TRI2 contains phenol only in very low concentration (table 2.2). As illustrated in figure 2.3b, there are more compounds present, thus TRI2 is a very recalcitrant mixture having an enormous COD value of almost 100 000 mgO_2/l.

If one compares in more detail HPLC chromatograms of samples TRI1 and TRI2, it is seen that TRI1 has only a few, while TRI2 many peaks within the first 4 minutes corresponding to the range of retention time of organic acids. Also, TRI2 peaks of the supposed acids are much bigger than those of TRI1. This may explain the low pH-value of 5.7, although almost no phenol is present. On contrary, the peak with a retention time of 8 minutes is huge for TRI2 and very small in TRI1 case. Finally, at more or less 9 minutes, there is a peak in TRI1 sample, which is not observed in TRI2.

In general, the pH value of TRI1 of 7.4 seems to indicate that there is some basic compound present in this sample. Phenol solution of 2-5 g/l normally shows pH value below 6.

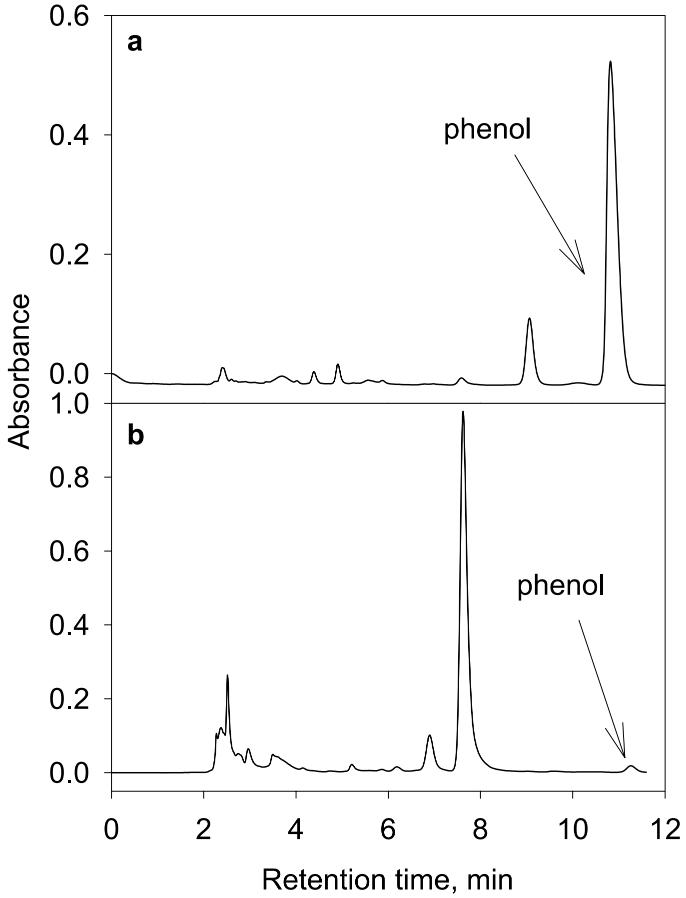


Figure 2.3: HPLC chromatograms of real wastewater feed samples: a) TRI1 and b) TRI2.

2.2.3. Catalysts

Activated Carbon (AC) was supplied by Merck (Ref. 2514) in form of 2.5mm pellets. This AC is manufactured from wood and possesses a low ash content of 3.75%. The nitrogen B.E.T. method (Micromeritics ASAP 2000) gives a specific surface area of 990 m^2/g, a pore volume of 0.55 cm^3/g and an average pore diameter of 1.4 nm. Prior to use as catalytic material, the AC pellets were crushed and sieved to have 25-50 (0.7-0.3 mm) mesh particle size. This fraction was washed to remove all the fine materials, dried at 105ºC overnight and then cooled and stored under inert atmosphere.

For Fenton catalysis, ferrous sulphate ($FeSO_4$) was purchased from Panreac. Its purity is of 99%, and solubility in water at 20ºC is 400 g/l.

2.2.4. COD reagents

Silver sulphate solution of 10 g/l in sulphuric acid (Ref. 283098) and potassium dichromate of 0.04 mol/ with 80 g/l of mercury (II) sulphate (Ref. 184385) were purchased from Panreac to determine the chemical oxygen demand of the withdrawn liquid samples.

2.3. Experimental procedures

In the following, we describe in detail the experimental procedures of the diverse oxidation techniques used. The respective operating conditions of the experiments are summarized in table 2.3.

Table 2.3: Laboratory operating conditions for different treatment methods.

Treatment	CWAO	Promoted CWAO	WPO	Fenton WPO
Reactor				
L (m)	0.20	0.10	3.0	8.2
I.D. (mm)	10.54	6.12	1.47	1.47
W_{cat} (g)	7	0.7	-	0.01-0.04
d_p (mm)	0.7-03	-	-	ns
Flow rates				
O_2 (ml/s) in air	0.48	0.48	-	-
H_2O_2 (ml/h)	-	3-300	3-300	3-300
Organic (ml/h)	10-160	6-600	6-600	6-600
P (bar)	50	16-25	20-350	10-30
T (ºC)	140	160-170	270-550	25-200
τ (h)	0.12	0.012-0.167	$8.3\cdot10^{-4}$-0.153	0.0083-0.064
Concentration (ppm):				
phenol	5000	5000	5000	5000
p-nitrophenol	5000	5000	5000	5000
aniline	5000	5000	5000	5000
nitrobenzene	2000		2000	2000
sulfolane	5000		5000	
o-chlorophenol	5000			
m-xylene	200			
o-cresol	5000			
Wastewater COD (mgO_2/l):				
TRI1	5600	5600	5600	5600
TRI2	97000	97000	97000	97000

ns-not specified.

2.3.1. Catalytic Wet Air Oxidation experiments

To obtain the reference conversion values of the selected organic pollutants, fifty hours experiments were conducted for each of the model compounds studied (Sahin, 2001). Feed concentrations, for comparison with previous studies of phenol oxidation, were taken as 5 g/l for all the model compounds, except nitrobenzene and m-xylene, 2 and 0.2 g/l, respectively due to their low solubility in water. The experimental conditions were: 140ºC, 9 bar of oxygen partial pressure, constant air flowrate of 2.4 ml/s and liquid weight hourly space velocity of 8.2 h^{-1}. The liquid flowrate was fixed according to the weight of the catalytic bed. Outlet liquid samples were periodically taken and then analysed for organic conversion. Activated carbon was collected at the end of each experiment and dried at 400^0C under inert nitrogen atmosphere in order to remove eventually absorbed products and to calculate the weight loss of each activated carbon samples used.

2.3.2. H_2O_2 promoted Catalytic Wet Air Oxidation experiments

The H_2O_2 promoted CWAO experiments were conducted in the modified high pressure and high temperature equipment. Feed concentration of the studied model compounds (phenol, p-nitrophenol, aniline) was the same as in the CWAO runs. For the industrial wastes, filtered feed samples were used without any other pretreatment, except for diluting occasionally the sample of TRI2 up to 3 times. In all runs the temperature was 170ºC, the total pressure was 25 bar (3.4 bar O_2) and the residence time was in the range of 0.01-0.167 h to obtain convenient conversion values. Different quantities of hydrogen peroxide (10-40% of stoichiometric demand) were added to the liquid organic feed solution to study the effect of H_2O_2 promotion. Usually, the air flowrate was held constant as 2.4 ml/s to ensure oxygen excess. The typical catalytic bed weight was of 0.62 to 0.71 g. Outlet liquid samples were periodically taken and analysed for conversion and COD reduction. The activated carbon samples were collected at the end of each experiment and dried at 120ºC overnight in the oven to remove humidity and physically adsorbed compounds before determining its eventual weight change occurred during the experimental runs.

2.3.3. Wet Peroxide Oxidation experiments

Feed concentration of the model compounds was kept the same as for CWAO and promoted CWAO. The reaction temperatures and pressures were fixed in the range of 300 to 500ºC and 150 to 350 bar, respectively. The residence time was varied from 2.9 to 240 s. The quantity of hydrogen peroxide used in the oxidation experiments varied from 7 to 100% of stoichiometric demand for phenol, and 50 or 100% for the rest of compounds studied. This was to obtain complete mineralisation of initial quantity, calculated by assuming that the density of the reaction mixture was the same as that of water.

In a normal oxidation series, the equipment is pressurized with distilled water and leak tests are done, both at room temperature and reaction temperature. The sandbath is heated up with electrical resistances and pure distilled water is pumped through the apparatus until the desired temperature and pressure are reached. This is done both to avoid the contact of oxidant and reactor tubing (hydrogen peroxide is a very powerful oxidant) and to economise organic and hydrogen peroxide solution consumption. In the following step, the distilled water feed is replaced by organic solution and oxidant feeds, and streams are either feed together in one line or combined in a mixing tee just before entering into the reactor. Pressure and temperature readings are taken before the reactor inlet and at the reactor outlet indicating that reactor operates essentially isobarically, but not always isothermally. At 300ºC difference between inlet and outlet reactor temperature was 1ºC at low flow rate and about 10ºC at highest flowrate, while at 400ºC this difference was 6ºC and about 14ºC, respectively.

In a normal experimental series, after adjusting all the operating parameters (T, P, flowrate) the steady state of the system is considered to be reached, when the measured conversion for a given residence time is constant in consecutively taken samples. Then, we change liquid flow rate to obtain the correspondent concentration-residence time profiles. After every flow rate modification, the system reaches a new steady state and samples are analysed every 10 minutes to know, when the concentration of organic is constant, and thus the new steady state is achieved.

In the decompression-cooling section the reactor effluent is rapidly cooled down in the heat exchanger to terminate the reaction. Then, the stream pressure is dropped to ambient pressure by the back-pressure regulator. The liquid product is collected in the graduated cylinder to determine its flow rate and to compare it with the inlet flow rate measured by precision balance. Generally, the liquid samples are analysed immediately by HPLC, or if not possible, stored in the refrigerator and analysed later.

2.3.4. Fenton Wet Peroxide Oxidation experiments

Feed concentration of phenol, p-nitrophenol, aniline and nitrobenzene was kept the same as for WPO. Also, the industrial real wastewater samples were prepared as in the previous experiments. The Fenton promoted WPO experiments were conducted in a longer continuous tubular reactor as mentioned before. After preparation of organic solution in water, ferric salts ($FeSO_4$) of different concentration (10-40 mg/l) were added to the solution to test its effect on organic conversion. Also, the temperatures and pressures were varied in the experiments from 25 to 200°C and from 1 to 30 bar, respectively to study their influence. The residence time was established in the range of 10 to 225 s, and initial pH was maintained between 3-5. In all experiments, 100% of stoichiometric quantity of H_2O_2 was used.

Before starting any experiments, the organic pollutant solution was brought in contact with Fenton's Reagent (H_2O_2 and $FeSO_4$) (in the same proportion as later used in the experiment) to observe any colour change and precipitation of the mixture due to the complex formation at room temperature.

2.3.5. Process calculations

The conversion of organic compounds (X_{org}) and COD conversion (X_{COD}) were calculated as:

$$X_{org} = \frac{C_{org,in} - C_{org,fin}}{C_{org,in}} \cdot 100\% \qquad \text{(Eq. 1)}$$

$$X_{COD} = \frac{COD_{in} - COD_{fin}}{COD_{in}} \cdot 100\%, \qquad \text{(Eq. 2)}$$

where $C_{org,in}$ is the initial organic concentration, $C_{org,fin}$ the final organic concentration, COD_{in} the initial COD concentration and COD_{fin} the final COD concentration, respectively.

The residence time (τ) was calculated for the catalytic process using AC was calculated as:

$$\tau = \frac{W}{\dot{M}_L}, \qquad \text{(Eq. 3),}$$

where W stands for the weight of the catalyst loaded and $\dot{M}_L$ for the liquid mass flow rate, and for Wet Peroxide Oxidation and Fenton Oxidation:

$$\tau = \frac{V_R}{F_R}, \qquad \text{(Eq. 4)}$$

where V_R denotes the reactor volume and F_R volumetric flow in the reaction conditions.

An example for the calculation of the stoichiometric quantity of hydrogen peroxide is presented, assuming complete mineralisation of a 5g/l phenol solution. Taking into account that 5 g/l of phenol corresponds to 0.053 mol/l and according to the equation of the reaction:

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 6\ CO_2 + 17\ H_2O, \qquad \text{(Eq. 5)}$$

the molar quantity of hydrogen peroxide needed is 14 times more than that of phenol, which is 0.75 mol of hydrogen peroxide (M= 34.01 g/mol) in one litre of solution or 25.3 g/l. If the mother solution of hydrogen peroxide is of 30% of weight in volume, in each litre there are 300 g of hydrogen peroxide.

Following a simple calculation, we obtain the required stoichiometric quantity of the 30%wt/v H_2O_2 solution:

$$x = \frac{25.3g \cdot 1l}{300g} = 0.084l = 84ml \qquad \text{(Eq. 6)}$$

84 ml/l of 30% hydrogen peroxide solution corresponds to 100% of stoichiometric quantity of hydrogen peroxide for the complete mineralisation of phenol. So to work with 100% of stoichiometric hydrogen peroxide quantity, we mix 5 g of phenol and 84 ml of hydrogen peroxide in one litre solution.

2.4. Analytical procedures

2.4.1. High Performance Liquid Chromatography analysis

Liquid samples were analysed by means of a HPLC (Beckman System Gold). The determination of the organic concentrations was done using a C18 reverse phase column (Tracer Extrasil ODS-2, 5μm 25 x 0.4 cm). A mixture of 35%/65% vol. of methanol and water (slightly acidified) was used as a mobile phase, except for nitrobenzene and aniline where the mixture composition was 50%/50% of methanol and water; and 70%/30% of acetonitrile and water, respectively. For all compounds the flow rate of the mobile phase was 1 ml/min. The detection of the compounds was performed using UV absorbance at a wavelength of 254 nm, except for aniline, where the wavelength was switched to 280 nm.

In some cases to identify intermediate compounds, a mobile phase of variable composition was programmed at a 1 ml/min flow rate starting from 100% deionised water and ending at a 40%/60% mixture of methanol and deionised water. The detection of low molecular weight carboxylic acids was performed with the UV absorbance method at a wavelength of 210 nm, while at the end of the sample analysis the wavelength was switched to 254 nm to correctly detect phenol.

Single compounds were quantitatively identified by injecting standard samples of the expected partial oxidation products. However, not all of these compounds could be identified in the reaction sample solutions. In the table 2.4 the retention times of some pure compounds injected are given.

Table 2.4: HPLC retention time of phenol and possible partial oxidation products.

Compound	Retention time (min)
Oxalic acid	1.4
Formic acid	2
Fumaric acid	2.3
Acetic acid	2.6
Hydroquinone	3.9
p-Benzoquinone	7.4
Phenol	16

An example of such a standard solution, including the most important intermediate compounds is given in Fig. 2.4a. The correspondence between standard solution peaks and those of a sample obtained from WPO of phenol at 300ºC, 150 bar, 18.4 s and 50% H_2O_2 is shown in Fig. 2.4b. As said before, in the sample solution several significant peaks remain unidentified, however they only account for 0-20% of the total detected intermediates peak area. Calibration curves were established for each intermediate detected using standard solutions that cover the composition range of the detected intermediates. Standard solutions were not only tested before starting the experiment, but also periodically between samples, to correct deviations in retention time and/or peak area, which can be caused by small changes in flow rates, column performance and temperature.

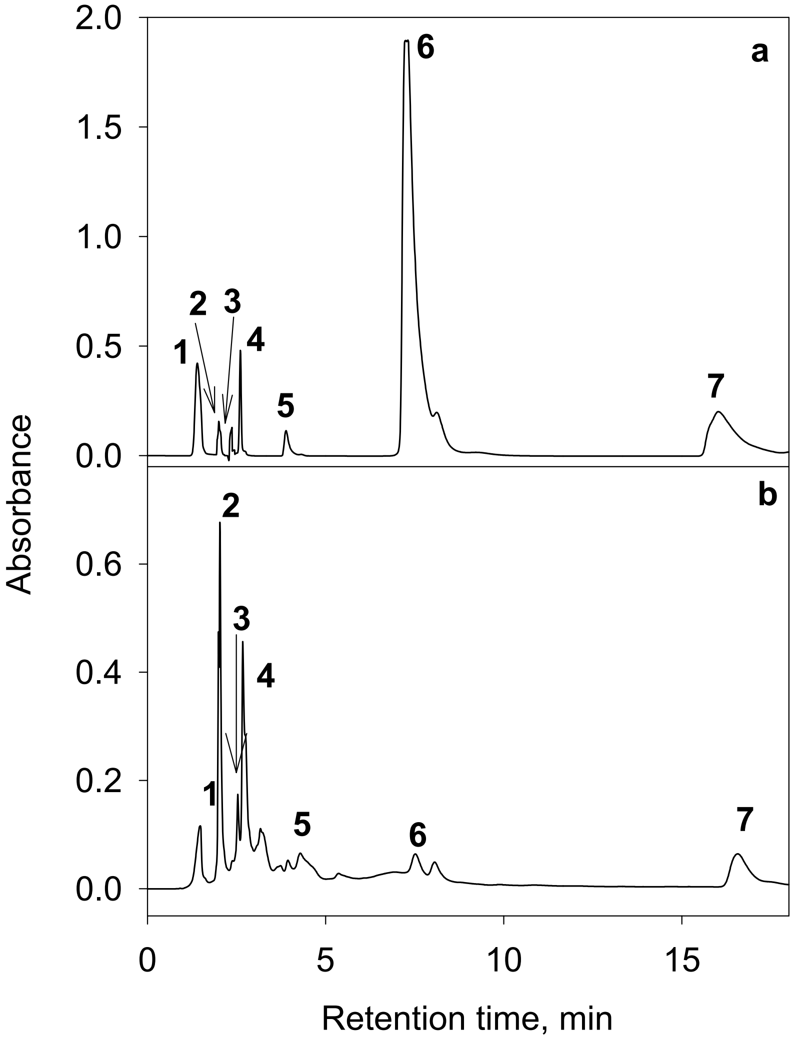


Figure 2.4: Example of HPLC chromatograms of (a) standard solution, and (b) sample solution from phenol WPO experiment at 300ºC, 150 bar, 18.4 s, 50% H_2O_2. (1) Oxalic acid, (2) Formic acid, (3) Fumaric acid, (4) Acetic acid, (5) Hydroquinone, (6) p-Benzoquinone, (7) Phenol.

2.4.2. Gas Chromatography analysis

2.4.2.1. Analysis of organic compounds in liquid phase

Occasionally analysis of the compounds was done in gas chromatograph due to technical problems of the HPLC. The analysis is carried out with a Hewlett Packard 6890N gas chromatograph equipped with a CHEMSTATION-software interface. The primary data evaluation is done by the CHEMSTATION-software. The carrier gas used for GC analysis was helium (99.999% pure). The liquid samples were analysed using a flame ionisation detector (FID) and a

HP-5 capillary column (5% Phenyl Methyl Siloxane, 30 m* 0,32 mm ID * 0,25 μm film thickness) or a HP- Innowax (polyethylene glycol, 30 m* 0,25 mm ID * 0,25 μm film thickness). A liquid volume of 1 μl was manually injected applying a convenient split to obtain reproducible results.

For separation and analysis of phenol and nitrobenzene, the HP-5 column and a FID temperature of 320ºC were used and the pulsed split option was chosen at a split ratio of 25:1. The oven temperature was held at 40°C for 1 min, then it was raised at 5°C/min to 75°C, next at 70°C/min to 160°C and finally at 10°C/min to 180°C.

Aniline concentration was determined with HP-Innowax column (splitless) with FID at 300ºC. Temperature program was applied for the oven starting from 70ºC (during 1min) to 180ºC at a rate of 8ºC/min.

Sulfolane concentration was also determined by gas chromatography. The analysis was done with a HP-5 column and a temperature program was applied for the oven starting from 140ºC (1min.) to 180ºC (10ºC/min). A FID at 250ºC was used to analyse the samples.

2.4.2.2. Analysis of effluent gas

In some experiments with real wastewaters, the effluent gases from the reactor outlet were also analysed. For this purpose, a Porapack Q 50/80 (Teknokroma) column was used together with a Thermal Conductivity Detector (TCD) at 200ºC and an automatic injection valve having a loop volume of 0.125ml. The temperature programme starts with 38ºC (during 2 min) and is then raised at a rate of 20ºC/min up to 110ºC.

The calibration of gases was done using a standard mixture of gases from a high pressure bottle with known volumetric proportion of gases (23.5% N_2, 1.1% CH_4, 12.7% CO, 12.2% CO_2, 50.5% H_2). The identification of retention time of oxygen, nitrogen (air) and hydrogen was determined by injecting separately pure sample gases to the GC, while the CO, CH_4 and CO_2 retention times were taken from the literature (Agilent catalogue). In table 2.5, the approximate retention times for calibrated gases are given. The quantitative calibration was then performed by injecting the standard mixture of gases at different pressures (1.5-3.5 bar) into the loop. The quantity of mole of each gas at a given pressure was then calculated from the ideal gas law.

Table 2.5: GC retention time of some gaseous oxidation products

Gas name	Retention time (min)
H_2	1.8
N_2/O_2	2.1
CO	2.3
CH_4	3.2
CO_2	4.9

A GC chromatograms example of the standard gases mixture, including the most important gaseous products (CO and CO_2) is given in figure 2.5a. It must be said that the peaks of N_2 and O_2 could not be separated (peak 2 in the figure 2.5a) with the column and conditions used. The correspondence between standard mixture peaks and those of a gaseous reactor effluent obtained from the Fenton oxidation of TRI2 (diluted 3 times, 200ºC, 20 bar, 37.4 s and 100% of H_2O_2) is also shown in Fig. 2.5b.

The established calibration curves can be found in appendix A.

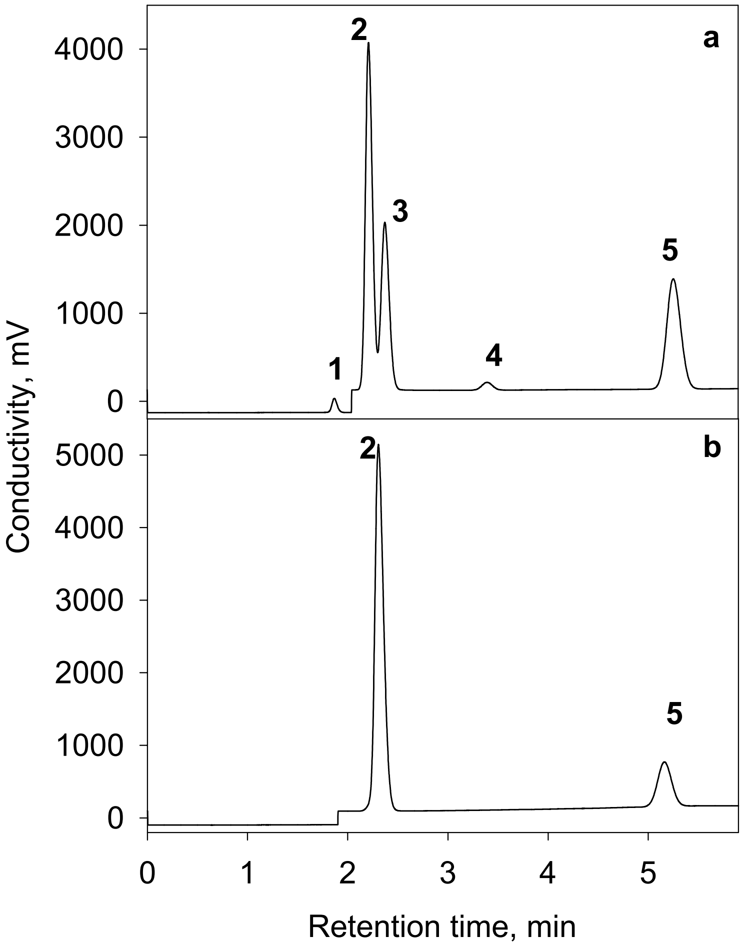


Figure 2.5: Example of GC chromatograms of (a) standard mixture, and (b) reactor gaseous effluent from Fenton oxidation of TRI2, diluted 3 times at 200°C, 20 bar, 37.4 s and 100% of H_2O_2. (1) H_2, (2) N_2/O_2, (3) CO, (4) CH_4, (5) CO_2.

2.4.3. COD and pH measurement

Chemical oxygen demand (COD) was determined by the procedure stipulated in Standard Methods 5220 D: closed reflux, colorimetric method (Clesceri et al., 1989), according to which the organic substances are oxidised (digested) by potassium dichromate $K_2Cr_2O_7$ in the presence of acid (H_2SO_4) at 160°C for two hours in a sealed tube in a thermoreactor ECO8 (Velp Scientifica). Silver sulphate is added in excess as a catalyst. The colour change from orange $Cr_2O_2^{-2}$ to green coloured Cr^{3+} due to reduction can be detected in a spectrophotometer (Optic Ivymen System) set at 580 nm. The relation between absorbance and COD concentration is established by calibration with standard solutions of potassium hydrogen phthalate, in the range of COD values between 200 and 1200 mg/l, as shown in the figure 2.5. As the real sample COD values were generally up to 10 times higher, prior to digestion all samples were accordingly diluted.

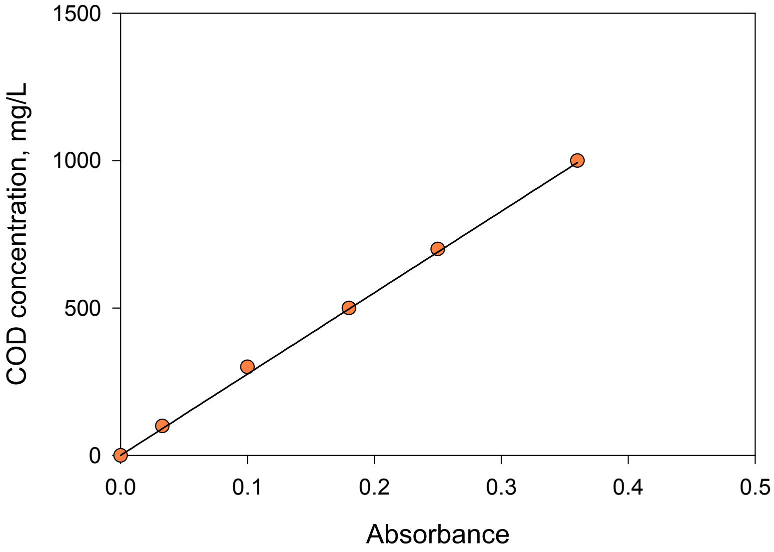


Figure 2.6: Calibration curve for COD determination obtained with standard solutions potassium hydrogen phthalate at room temperature.

COD reflects the total quantity of oxidisable components whether it is carbon and hydrogen from hydrocarbons, nitrogen, or sulphur and phosphorus. The principle of the COD analysis is the consumption of an oxidizer given to the sample and being consumed by the pollutants. Potassium dichromate method was used with silver sulphate. Addition of silver as catalyst is recommended in the case to oxidize recalcitrant compounds like aliphatic or aromatic hydrocarbons.

In addition, the pH of each liquid sample was measured using a pH-meter (CyberScan, model pH/ION510), to follow up its evolution during the oxidation treatments.

Chapter 3

Oxidation of organic model pollutants

This chapter discusses the results obtained with CWAO, hydrogen peroxide promoted CWAO, WPO and Fenton WPO for the abatement of the selected organic model compounds. The main purpose of the numerous experiments was to test whether it is possible to completely mineralise the organics or to partially reduce the toxicity of waste to acceptable values for a following biological treatment.

First, reference conversions achieved with CWAO over active carbon (AC) are presented for comparison of process performance of the different treatments studied. Then, the use of hydrogen peroxide in wet oxidation is investigated since H_2O_2 is known to increase the organic conversion at even smaller residence times (Rivas et al., 1999). Furthermore, the addition of small amounts of ferrous sulphate (Fenton's catalyst) was tested to promote the decomposition of hydrogen peroxide to active hydroxyl radicals improving thereby the performance of WAO (Debellefontaine et al., 1996).

The effect of different operating variables (pH, catalyst and hydrogen peroxide concentration, temperature, pressure, residence time) was experimentally checked to allow selecting best conditions for each process, according to the highest percentage of degraded phenol or COD obtained. During the experiments, liquid and sporadically gas samples were taken to follow the evolution of COD, organic concentration and total intermediates area as well as medium pH.

If not specified, the lines in the figures represent trends of experimental points and do not correspond to model prediction.

3.1. Catalytic Wet Air Oxidation over Activated Carbon

3.1.1. Reference conversion of organic pollutants

In previous experiments, our group has studied the destruction of several organic compounds by continuous catalytic wet air oxidation over activated carbon in a small-scale trickle bed reactor (Sahin, 2001). The 50 h oxidation tests were carried out at 140ºC, 9 bar of oxygen partial pressure and residence time of 0.12 h, using 7 g of activated carbon loaded. The following compounds were tested: phenol, p-nitrophenol, o-chlorophenol, o-cresol, m-xylene, aniline and sulfolane. As an example for the general trends observed during the 50 h runs, the conversion of o-chlorophenol, o-cresol, p-nitrophenol and sulfolane is presented in figure 3.1. The residual conversions (X) and the consumption of activated carbon (ΔW) for all model compounds found at the end of the 50 h experiments are given in table 3.1. A negative sign (in ΔW) means an increase of carbon weight compared to the carbon initially loaded. With respect to conversion, the results allow distinguishing two groups:

1) one of high reactivity including phenol, m-xylene, o-chlorophenol, o-cresol,
2) one of low reactivity including aniline, p-nitrophenol, sulfolane and nitrobenzene.

For phenol, o-chlorophenol, o-cresol and m-xylene a high removal efficiency of 70, 74, 76 and 99%, respectively, was obtained after an initial 10 h lasting adsorption period of 100% of apparent conversion (table 3.1 and figure 3.1).

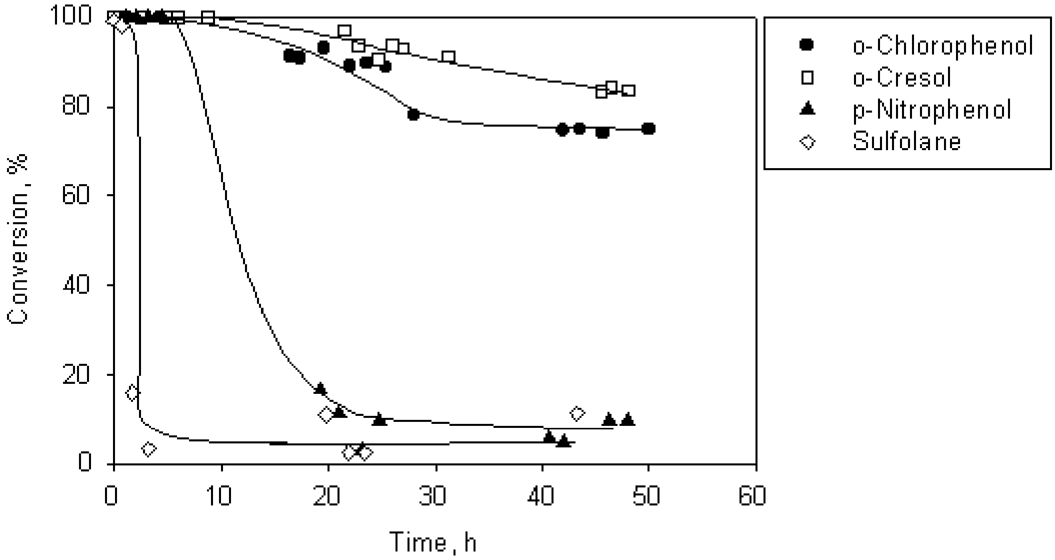


Figure 3.1: Temporal CWAO conversion of sulfolane, p-nitrophenol, o-cresol and o-chlorophenol over active carbon, T=140°C, P_{O2}=2bar, W_{AC}=7g, τ=0.12h (Sahin, 2001).

Table 3.1: Residual CWAO conversion of diverse organic compounds tested and activated carbon weight change: T=140°C, P_{O2}=9bar, C_0=5000 ppm, W_{AC}=7g, τ=0.12h (Sahin, 2001).

Model Compound	**X (50h) (%)**	**Δ W (50h) (%)**	**Observation**
M-Xylene*	99.8	35	C_0=200ppm
O-Cresol	76	-26	-
O-Chlorophenol	74	**	low pH - corrosion
Phenol	70	10	-
Aniline	8	-33	no NO_2^- detected
P-Nitrophenol	9	0	no NO_2^- detected
Sulfolane	2	**	-
Nitrobenzene	-	10	C_0=2000 ppm no NO_2^- detected

* *A total time of 96 hours is spent for the saturation of the catalytic bed*

** *The carbon consumption was not determined due to technical problems during experiment.*

The wide range of organic conversion observed can be explained by the aromatic reactivity depending both on the type and the location of the aromatic ring substituents. Joglekar et al. (1991) have reported that the noncatalytic liquid phase oxidation of substituted phenols by molecular oxygen is essentially an electrophilic substitution. Among the substituted phenols, they found an decreasing order of reactivity from o-cresol, o-chlorophenol to phenol. The same sequence was observed in our case, although the conversion differences are relatively small (see table 3.1). O-cresol shows lower reactivity than m-xylene, but higher than o-chlorophenol and phenol. The presence of a CH_3 group in ortho position makes the molecule more reactive than the presence of a Cl group in the same position or no additional group. The conversion observed for m-xylene cannot be directly compared to other compounds conversion due to the low initial m-xylene concentration being 25 times smaller than that of the other compounds. However, the conversion of m-xylene is expected to be the highest, because of the presence of an additional methyl group that is strongly activating in the meta position (see table 1.11). Joglekar et al. (1991) have also observed that substituted phenols show different reaction steps during non catalytic wet oxidation. Alkyl phenols (like o-cresol, m-xylene) exhibit initial fast reaction period followed by a slow reaction, while phenol and chlorophenols demonstrate initial slow induction period followed by a fast reaction.

On the other hand, the aniline, p-nitrophenol, sulfolane, apparent initial 100% conversion due to adsorption drops rapidly down to low final conversion value of 8, 9, 2 %, respectively. In case of nitrobenzene there was no reaction at all. The zero activity of nitrobenzene can be attributed to the nitro group that is a very strongly deactivating group. The rather mild pressure and temperature conditions prove to be insufficient to oxidize the nitrobenzene molecule. P-nitrophenol also contains a nitro group, but has in addition a hydroxyl group that is strongly activating in para position, leading to some reactivity compared to nitrobenzene. Aniline conversion (8%) is similar to that of p-nitrophenol (9%) due to NH_2 group that is rather activating, but on the other hand, aniline does not have OH group to make it more active. We did not find literature information to explain the conversion obtained for sulfolane (2%) by the electrophilic substitution mechanism. Sulpholane has a ring containing one heteroatom (sulphur) and not benzyl ring as the other compounds studied.

It has to be mentioned that the destruction rate of organic molecules in catalytic oxidation may depend on more factors such as the type and nature of catalyst (homogeneous or heterogeneous). In the case of AC catalyst, a strong adsorbent, additional factors can play a role: strong organic adsorption on activated carbon, possible catalytic surface interactions between organic adsorbate and AC, loss of the activated carbon during the oxidation, etc...

With respect to the loss of AC, Fortuny et al. (1998) observed that the consumption of AC during CWAO is greater in the absence of organic compound (phenol). A weight loss of 10% of active carbon after 50 hours at 140ºC and 9 bar of O_2 was observed, when feeding pure water and air, while in the presence of phenol the consumption of the catalyst is significantly smaller. Thus, the organic protects to some extent the AC surface from being oxidised. In the present study AC consumption of 35 and 10% was observed for m-xylene and nitrobenzene after the 50 h oxidation experiment. M-xylene at low initial concentration of 200 ppm was incapable to cover and protect all the surface of AC, therefore activated carbon was strongly oxidised. For nitrobenzene, AC consumption may indicate small adsorption capacity on AC as confirmed by the short initial adsorption zone of only two hours.

Furthermore, in the experiments of Fortuny et al. (1998) with phenol, an initial 20-30% increase in the carbon weight was found in the adsorption zone that was ascribed to the formation and strong adsorption of phenol condensation products. It can be concluded that in CWAO over AC polymer formation (oxidative coupling), phenol oxidation and carbon oxidation simultaneously occur competing for tha available oxygen dissolved in the liquid phase. Aniline is also known to polymerise easily (Oliviero et al., 2003b), so substantial polymers formation and adsorption can be the reason of the 33% increase in AC weight during aniline oxidation. Similarly, polymer formation must be also very important in the case of o-cresol, increasing the catalyst weight by about 26%. Finally, during p-nitrophenol oxidation, the AC combustion, the oxidation of the carbonaceous deposit and its formation through oxidative coupling may reach a pseudodynamic equilibrium, as there is neither consumption nor increase of active carbon weight after 50 h of oxidation in the TBR.

Conclusions

Summarizing, the reactivity of phenol and substituted phenols in CWAO may be explained on the basis of an electrophilic reaction mechanism. Our CWAO results over AC are more or less in agreement with trends from literature, the conversion of phenolic derivatives depending both on the nature and position of the aromatic ring substituents. This offers the possibility to predict the reactivity of other similar compound in CWAO from the type and location of substituents, although, other factors can have a significant influence on final oxidation results, such as organic-catalyst interaction, adsorption of organic on the catalyst, simultaneous catalyst consumption etc…, when using activated carbon as catalyst.

CWAO over activated carbon performs excellent destruction efficiency of phenols at mild conditions (Fortuny et al., 1998, 1999; Tukac and Hanika, 1998; Deiber et al., 1997; Duprez et al., 1996). It was also found in the present work that CWAO of o-chlorophenol, o-cresol and m-xylene gave promising results using activated carbon as catalyst. The search for the optimal operating conditions of phenol, o-chlorophenol and o-cresol oxidation is under study in our laboratory. Further m-xylene experiments were discarded as this compound is highly insoluble and likely not to be encountered in aqueous waste streams. In case of phenol, for example, it was observed that its conversion depends positively on temperature and the partial pressure of oxygen, as exemplarily shown in figure 3.2 for the case of 4 different pressures. It is worth to mention that lower oxygen pressure reduced substantially the consumption of activated carbon, while higher temperature inevitably leads to an enhanced AC combustion. Thus, an optimum has to be found for temperature and pressure conditions to assure both acceptable conversion and AC weight loss.

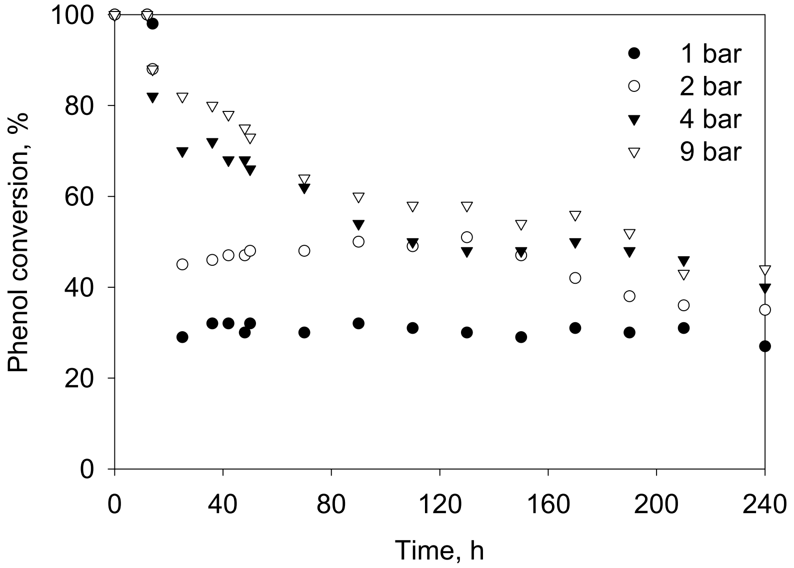


Figure 3.2: Conversion of phenol during CWAO using activated carbon in a trickle bed reactor, for different partial oxygen of phenol, T=140°C, C_0=5000 ppm, W_{AC}=7g (Fortuny et al., 1999).

Organic compounds including aniline, nitrobenzene, p-nitrophenol and sulfolane could not be efficiently destroyed at typical CWAO conditions using AC. More severe abatement techniques have to be tested to improve the degradation of these pollutants. Thus, the potential of H_2O_2 oxidant, either in promoted CWAO, WPO or Fenton WPO was assessed for the destruction of these organic pollutants (plus phenol as a reference pollutant). The obtained experimental results will be presented and discussed in the following chapters, including a comparison of H_2O_2 treatment and CWAO performance.

3.1.2. Hydrogen peroxide promoted CWAO

3.1.2.1. Preliminary experiments

In preliminary runs, phenol oxidation was undertaken to test the operation of the constructed high pressure and temperature equipment, when using the catalytic reactor tube with a load of 0.71 g of activated carbon. Low AC weight was selected in order to reduce the large times (20-25 h) required for adsorption and steady state achievement in the existing TBR. However, the 10 times smaller catalyst load, maintaining the same range of residence time will indubitably lead to very small conversions at 140ºC. Thus, new reaction conditions that will give a convenient conversion range were chosen on the basis of conversion prediction from our in house developed kinetic model for the catalytic oxidation of phenol over activated carbon (Eftaxias, 2002). Taking into account the catalyst weight that fits in the reactor (0.71 g) and the available flow rates of the high pressure pumps, the temperatures and pressures that would permit sufficient phenol conversion were determined from the model as 160-170ºC and 2-4 bar of partial pressure of oxygen (16-25 bar of total pressure). To check the model prediction, one experiment was done at 170ºC and 3.4 bar of oxygen. The results obtained are presented in figure 3.3 showing both the experimental and predicted conversion as a function of residence time.

As can be seen in figure 3.3, the predicted and experimental conversions for 170ºC and 3.4 bar of O_2 coincide very well and the conversion covers a reasonable range for further studies dedicated to assess the effect of H_2O_2 promotion.

Thus, the following experiments were all done at a constant temperature (170ºC), pressure (3.4 bar O_2) and air flow rate (2.4 ml/s). In a typical series of experiment the liquid flow rate was gradually changed, when the conversion became stable to obtain X-τ profiles as shown e.g. in figure 3.3. In figure 3.4 the evolution of conversion is given for three changes of flow rates. First of all, it can be pointed out that the time required for adsorption and steady state establishment was greatly reduced as was desired. This allows increasing progressively the residence time to raise organic conversion. Then, after changing a flow rate, a period of 50-100 min in between was sufficient to ensure stable conversion. In this way it was possible to assess X-τ profiles in experiments of reasonable run times (5-7 h).

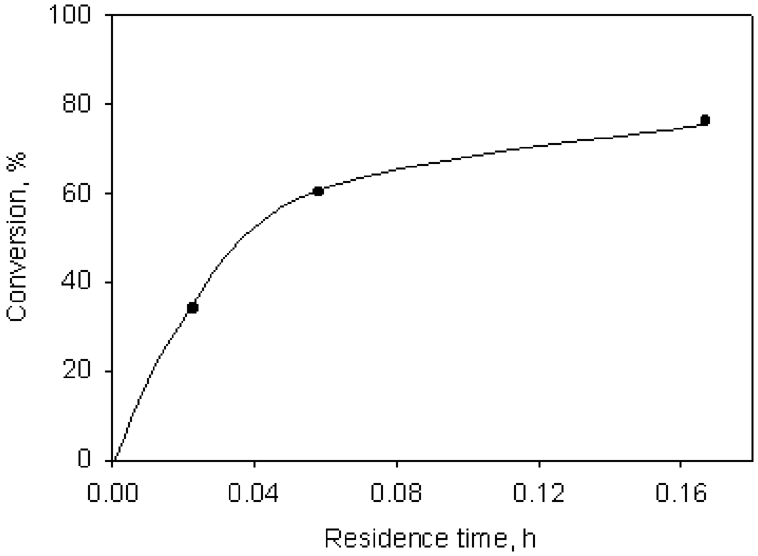


Figure 3.3: Experimental (points) and predicted (line) conversion of phenol during CWAO, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar, W_{AC}=0.71 g.

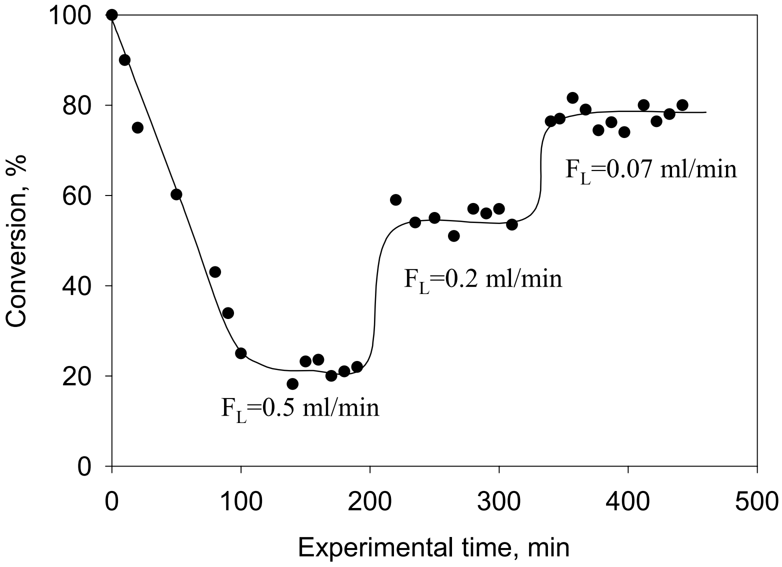


Figure 3.4: CWAO conversion of phenol over activated carbon, T=170° C, P_{O2}=3.4 bar, C_0=5000 ppm, W_{AC}=0.71g, at different liquid flow rates.

The short experimental times proved to be very useful to avoid significant AC oxidation due to the higher temperature and pressure employed in these experimental series.

The reproducibility of experiments as well as the stability of catalyst were examined by repeating an experimental series using the same AC bed and operating conditions. The results of this test are presented in figure 3.5. The fresh catalyst shows an expected initial adsorption period during the first 40 min, until AC saturation is complete. Then, the phenol conversion starts to drop down reaching a pseudo steady state of adsorption and oxidation reaction, the conversion of phenol being stable beyond 180 min.

The reused catalyst, as seen in figure 3.5, is left saturated from the previous experiments with phenol and reaction products, so the adsorption zone in the repeated run is completely eliminated. However, final conversion for fresh and reused catalyst is essentially the same, the difference in conversions observed corresponding to a proportional difference in residence times.

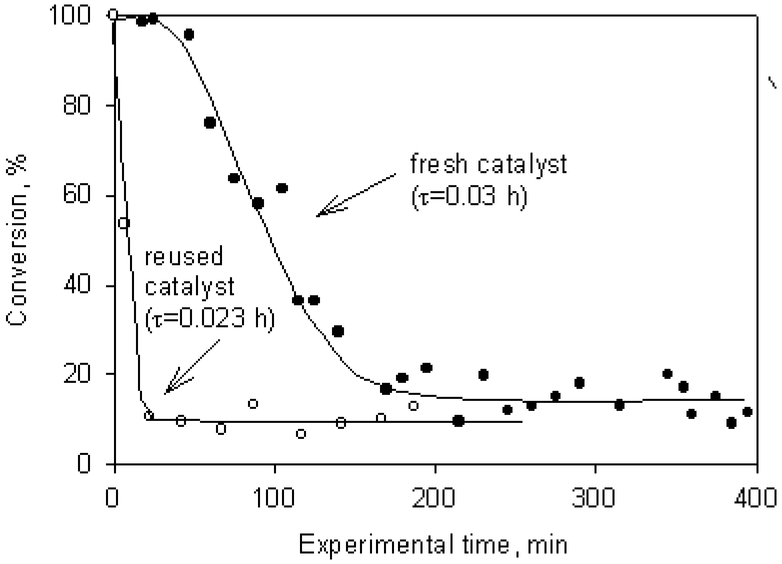


Figure 3.5: Conversion of phenol during two CWAO tests using the same activated carbon, T=170°C, P_{O2}=3.4 bar, C_0=5000 ppm, W_{AC}=0.71g.

The evolution of conversion obtained in the repeated run confirms both the reproducibility of reaction and the stability of AC catalyst over two days of use. Normally, an AC sample was replaced after a maximum of 3-5 days (corresponding to 3-5 experimental series), thereby avoiding significant deviation of experimental results.

In additional experiments, the initial phenol concentration was varied between 1000-5000 ppm to obtain the order of reaction with respect to phenol. The kinetic model of phenol CWAO developed by Eftaxias (2000) assumed first order behaviour, but this needed experimental confirmation. The experiments were carried out at the highest flow rate to keep the conversion in the linear initial X-τ zone (X < 30%), as can be seen in figure 3.3. The conversion values allowed determining the initial reaction rate for different initial phenol concentration and the results are illustrated in figure 3.6. All experimental data points of reaction rate lie on a straight line confirming that the oxidation reaction is effectively of first order with respect to the phenol concentration.

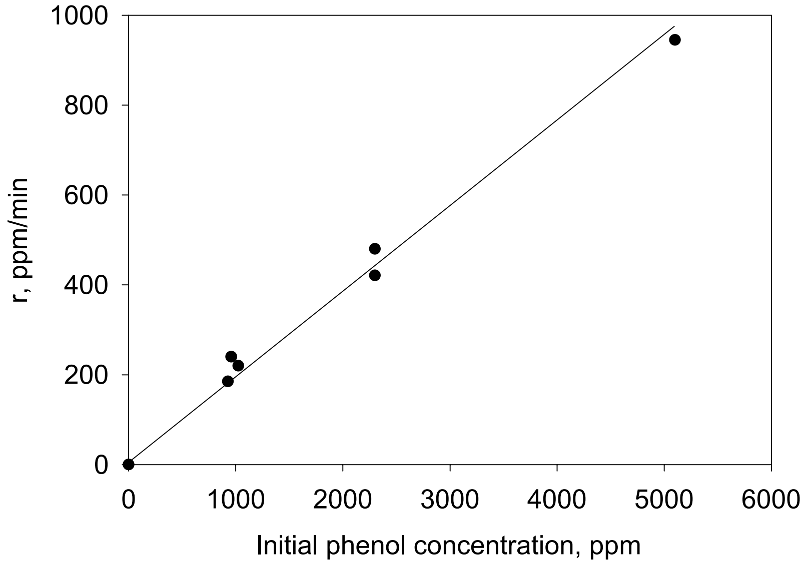


Figure 3.6: CWAO phenol destruction rate as a function of initial phenol concentration, τ=0.023h, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar and W_{AC}=0.71 g.

3.1.2.2. Phenol oxidation

Under standard conditions of reaction (170°C, 3.4 bar O_2), hydrogen peroxide was added in small stoichiometric proportion to the phenol feed to test the promoting effect of H_2O_2 on phenol CWAO. Premixing solutions of phenol and H_2O_2 oxidant have the advantage to take benefit of H_2O_2 decomposition during the short heating period initiating the oxidation reaction in the preheating zone. The results in figure 3.7 present the phenol conversion obtained, when adding 0, 10, 20 and 30% of the stoichiometric quantity of hydrogen peroxide required for complete phenol mineralisation. It is seen that the addition of H_2O_2 has a strong positive effect on phenol conversion. For low residence times of 0.012 and 0.023 h, the addition of 30% H_2O_2 results in 2 to 2.5 times higher phenol conversion. At higher residence time, the phenol conversion increase becomes quite proportional to the quantity of hydrogen peroxide added. For example at τ=0.16 h and with 30% of H_2O_2 fed, the conversion rises from about 75% to 95%. The absolute increase of conversion seems to be linear for the different H_2O_2 doses studied, although the slope decreases slightly at higher residence times (see figure 3.7).

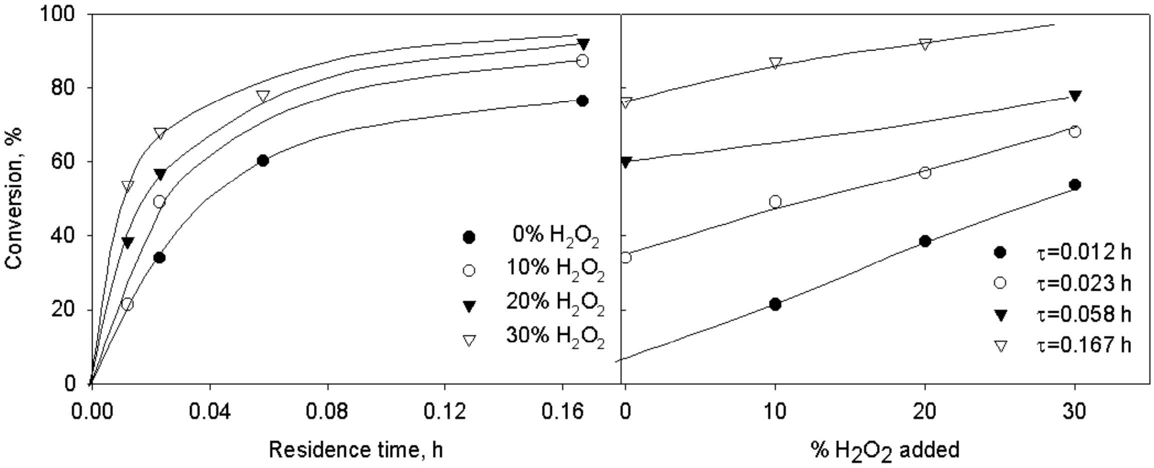


Figure 3.7: Conversion of phenol during CWAO, for different dosage of hydrogen peroxide, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar and W_{AC}=0.71 g.

As shown in figure 3.8, different behaviour was observed for COD removal, when varying the H_2O_2 dose. At a low residence time of 0.012h COD removal is about 10%, when no H_2O_2 is added, and about 50% for 30% of H_2O_2 added. At higher residence time, the increase of COD destruction becomes proportional to the added H_2O_2 dose. However, the X_{COD}-H_2O_2 profiles do not show linear trends for different residence times, as do X_{PhOH}-H_2O_2 profiles. It can be deduced that there exist a certain promotion of H_2O_2 on COD removal for all residence times studied. Another difference is that the final COD reduction rise is slightly more pronounced than that of phenol conversion and the best removal performances are: X_{PhOH}=75% and X_{COD}=60% without H_2O_2, as well as (extrapolated) X_{PhOH}=95% and X_{COD}=85% with 30% of H_2O_2.

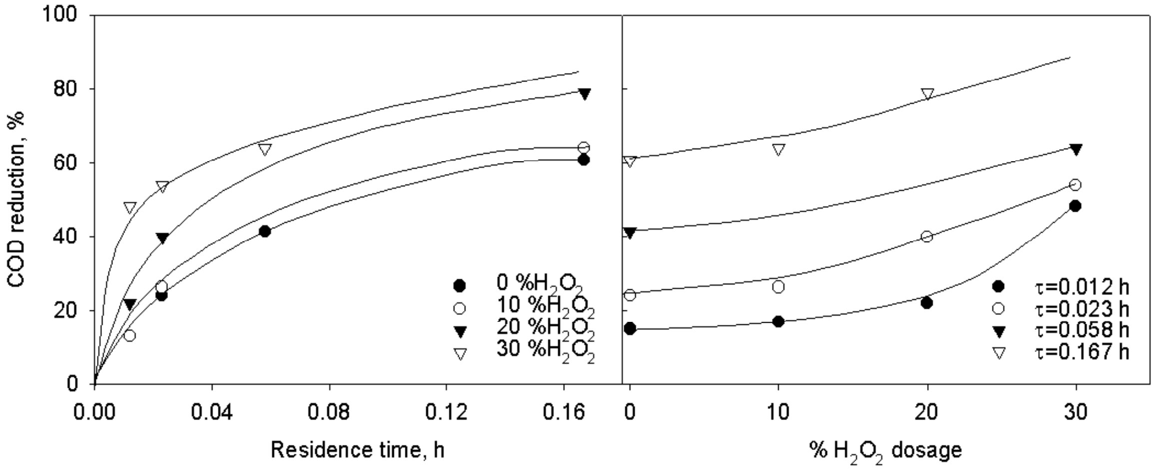


Figure 3.8: COD conversion during CWAO of phenol over activated carbon, for different dosage of hydrogen peroxide, C_0=5000 ppm, T=170°C and P_{O2}=3.4 bar, W_{AC}=0.71g.

It is interesting to note that the addition of hydrogen peroxide did not affect the pH evolution during CWAO of phenol, as illustrated in figure 3.9. In all cases, initially not adjusted pH of about 6 is decreasing rapidly to about 3.5 certainly due to the formation of short chain carboxylic acids, and then rises slightly to a plateau value of 4 indicating the persistence of some carboxylic acids at higher residence time, most probably acetic acid. This suggests that the CWAO of phenol promoted with hydrogen peroxide cascades through pathways similar to CWAO with oxygen alone, but at considerably higher COD removal value.

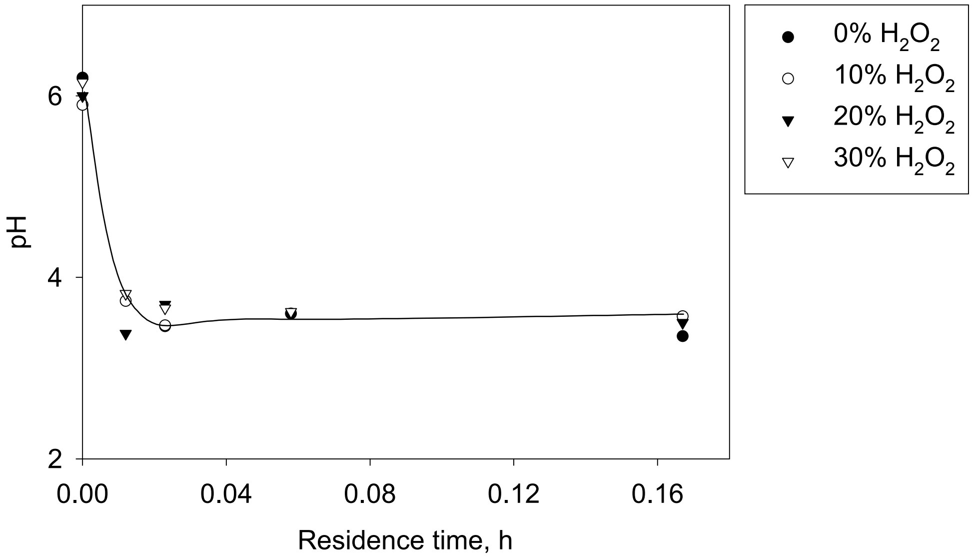


Figure 3.9: Evolution pH during CWAO of phenol using activated carbon, for different dosage of hydrogen peroxide, C_0=5000 ppm, T=170ºC, P_{O2}=3.4 bar and W_{AC}=0.71g.

3.1.2.3. p-Nitrophenol Oxidation

P-nitrophenol oxidation was carried out at standard conditions adding hydrogen peroxide quantities of 0, 20 and 40%. Figure 3.10 shows that the addition of hydrogen peroxide also considerably improved the CWAO removal efficiency of p-nitrophenol. The increase is strong at low residence times, but quickly reaches a plateau, while for phenol oxidation the rise in conversion was steadily as expected for a first order of reaction in phenol concentration. As seen in figure 3.10, the increase in conversion with the amount of H_2O_2 added does not follow an exactly linear behaviour indicating some promoting effect of H_2O_2. The improvement in conversion is stronger marked, when the hydrogen peroxide dosage is increased from 20 to 40%, than from 0 to 20%. For example, at a residence time of 0.06 h, the p-nitrophenol conversion without hydrogen peroxide is about 35%, with 20% of H_2O_2 about 50%, and with 40% of H_2O_2 about 80%.

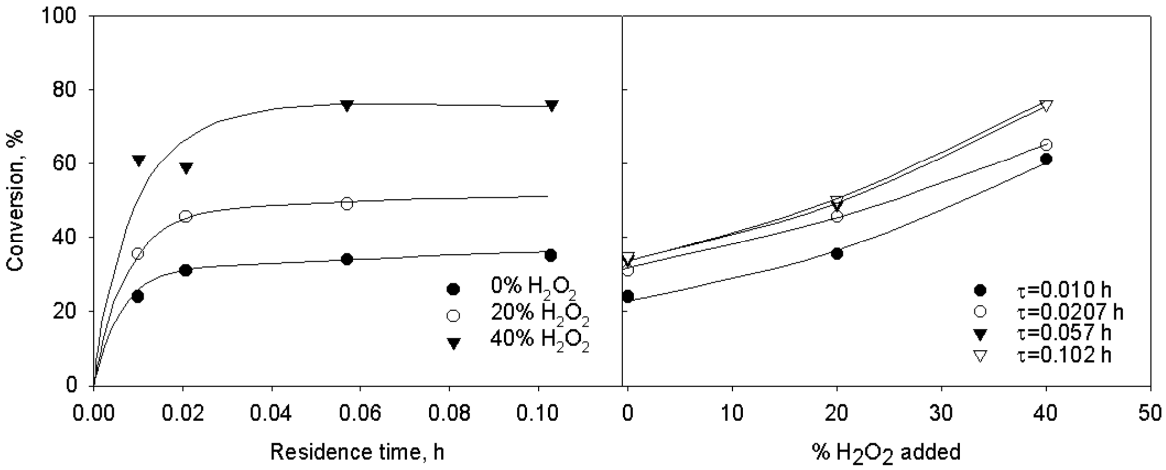


Figure 3.10: Conversion of p-nitrophenol during CWAO using activated carbon, for different dosage of hydrogen peroxide, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar and W_{AC}=0.68 g.

Hydrogen peroxide also enhances COD removal during CWAO of p-nitrophenol. Figure 3.11 indicates the same trends as observed for p-nitrophenol conversion. For example, at 0.0207 h of residence time, the COD reduction is 25, 38 and 60% for 0, 20 or 40% of hydrogen peroxide stoichiometric demand, respectively. The COD reductions reach very quickly their plateau value for all three H_2O_2 doses applied. Thus, the best performance was achieved at residence time between 0.06 and 0.10 h and 40% of H_2O_2 giving a p-nitrophenol conversion and COD removal of about 78 and 74%, respectively.

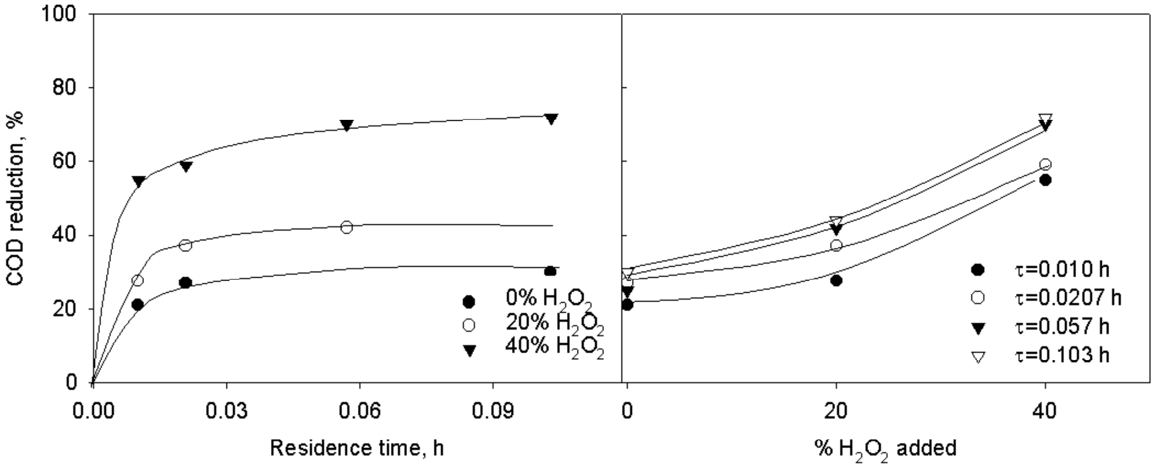


Figure 3.11: COD conversion of p-nitrophenol during H_2O_2 promoted CWAO, C_0=5000 ppm, T=170ºC, P_{O2}=3.4 bar and W_{AC}=0.68 g.

pH evolution during H_2O_2 promoted CWAO of p-nitrophenol is presented in figure 3.12. Two different trends appear depending whether hydrogen peroxide is added or not. When no hydrogen peroxide is added, the solution pH stays more or less at its initial value of 5 during the experiment. Only low conversions of p-nitrophenol are reached and the residual concentration of formed carboxylic acids is very low as conversion and COD values are quite close. For 20 or 40% of H_2O_2 added pH decreases to reach a minimum of about 3.3 and then increases slightly to a plateau at about 3.8. This is certainly because the addition of hydrogen peroxide initially promotes p-nitrophenol destruction towards carboxylic acids, that are subsequently destroyed, at higher residence times.

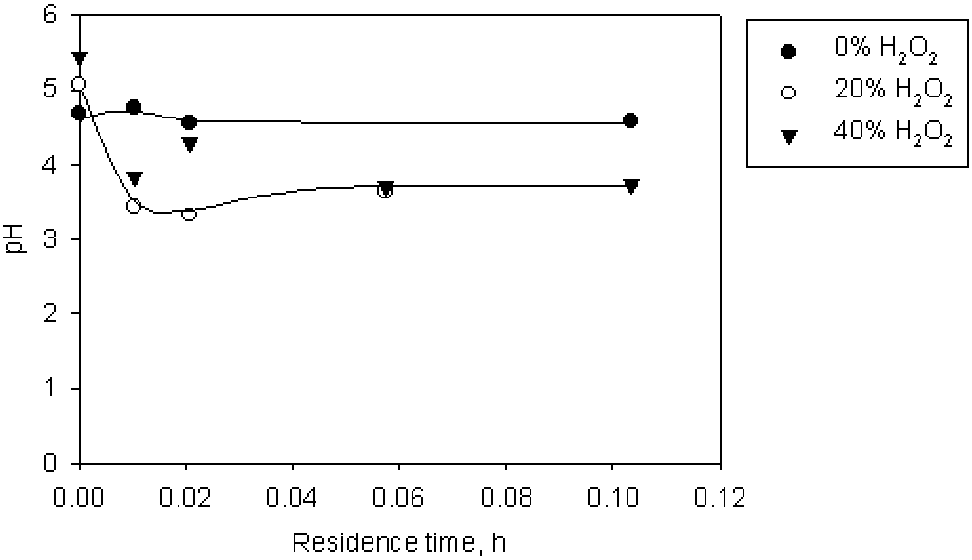


Figure 3.12: pH evolution during H_2O_2 promoted CWAO of p-nitrophenol over activated carbon, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar and W_{AC}=0.68 g.

3.1.2.4. Aniline Oxidation

Standard CWAO of aniline showed different behaviour, when compared to the oxidation of phenol and nitrophenol. Aniline is a weak base, and the pH of a 5g/l solution of aniline without adjusting was 8 (for phenol and p-nitrophenol it was about 5-6). Aniline removal efficiency and COD reduction are given in figure 3.13. At pH value of 8, only about 40% of aniline conversion was obtained (COD value were not measured in these experiments). Attempting to improve conversion of aniline, the initial pH was adjusted to 4 (with sulphuric acid) in order to increase aniline reactivity. From literature it was found that aniline is much more reactive at pH of 4 than at other pH value (Oliviero et al., 2003a). Adjusting the solution pH to 4, conversion increased to about 60% at residence time of 0.06 h. At the same time a COD reduction of about 50% was reached. This would mean that most aniline was mineralised.

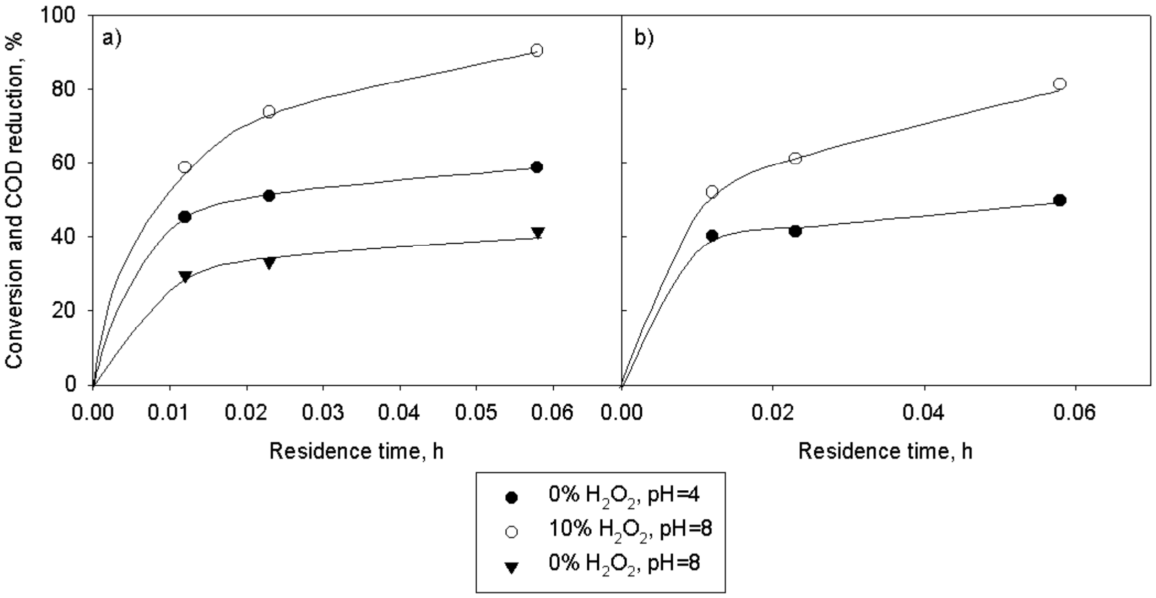


Figure 3.13: Aniline conversion (a) and COD reduction (b) during CWAO using activated carbon, and different dosage of hydrogen peroxide at pH, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar, W_{AC}=0.71 g.

Subsequently, the experiments for not adjusted pH=8 and 10% of H_2O_2 were done. In this case, the result was an aniline conversion of 90% with 80% of COD removal, so it would be expected to obtain complete conversion for pH of 4 as aniline is much more reactive at this pH (Oliviero et al., 2003a). However, at initial pH of 4, after 1.5 hour complete plugging of the catalytic reactor tube occurred, this plug being very difficult to remove from the reactor tube after reaction. It was necessary to leave the reactor tube for various hours in an oven at 400°C to partially burn off the AC. Interestingly, even after this heat treatment of the catalyst, the recovered carbon showed a greater weight than that of the initial loading.

The evolution of pH during the experiments with aniline can be seen in figure 3.14. In the absence of hydrogen peroxide pH of 8 its value drops down to about 7 and then increases to ca. 7.5. In the case of adjusted pH of 4 there is a slow and constant increase in pH value to about 5. When 10% of hydrogen peroxide was added and pH was not adjusted (pH=8) there is first decrease to about 6.8 and then pH increases to about 7.5. A decrease in pH value at lower residence time should correspond to the production and build-up of carboxylic acids, that are subsequently partially oxidised at higher residence time.

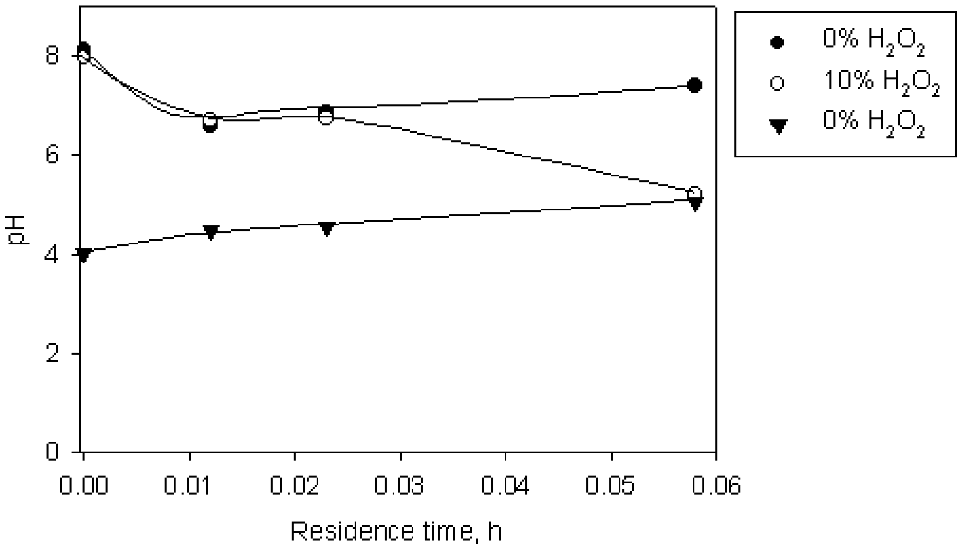


Figure 3.14: pH evolution during CWAO of aniline using activated carbon, for different dosage of hydrogen peroxide, C_0=5000 ppm, T=170ºC, P_{O2}=3.4 bar, W_{AC}=0.71 g.

Typical pH for the aniline oxidation found in the literature was 3-6 (Oliviero et al., 2003b). However, this does not seem to be applicable to CWAO or at least CWAO using activated carbon due to the observed reactor plugging at lower pH. The mechanism of aniline oxidation is still not well understood. Oliviero et al. (2003b) in a review of aniline oxidation found that aniline is a refractory compound towards oxidation and requires the use of both strong oxidising agents (ozone, hydrogen peroxide) and long times of reaction (usually more than 2 h).

3.1.2.5. Reactivity order of organic pollutants

To establish the CWAO reactivity order of the studied pollutants, the conversion and COD reduction of phenol, p-nitrophenol and aniline were plotted in figure 3.15 in the absence of hydrogen peroxide.

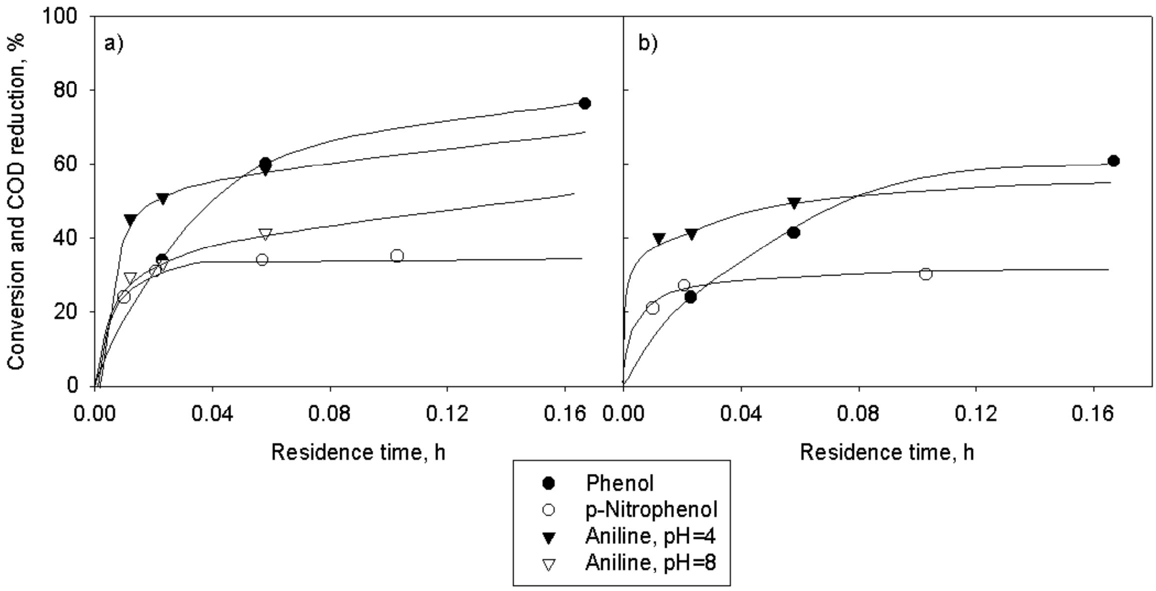


Figure 3.15: Conversion (a) and COD reduction (b) of phenol, aniline and p-nitrophenol during CWAO over activated carbon, C_0=5000 ppm, T=170ºC, P_{O2}=3.4 bar, W_{AC}=0.68-0.71g.

The observed order of reactivity at 170ºC and 3.4 bar of O_2 is as follows: phenol ≈ aniline (pH=4) > aniline (pH=8) ≈ p-nitrophenol. At 140ºC and 9 bar of O_2, the previous CWAO experiments showed: phenol > p-nitrophenol ≈ aniline (pH=8), the conversion of aniline and p-nitrophenol being, 8 and 9%, respectively. At 170ºC and 3.4 O_2, the conversion of phenol remained similar to that at 140ºC, while the aniline and p-nitrophenol conversions were greatly enhanced at 170ºC, to about 45 (pH=8, extrapolated) and 35%, respectively. In the case of aniline and p-nitrophenol, it becomes obvious that temperature has remarkable influence on CWAO conversion compared to phenol CWAO.

The trends for final COD reduction were the same as for organic conversion, i.e. phenol ≈ aniline (pH=4) > p-nitrophenol. An interesting result, as illustrated in figure 3.15, is that phenol conversion is increasing much more slowly than does the conversion of aniline and p-nitrophenol at short residence times. Residence times < 0.02 h or < 0.04 h gave phenol conversion and COD reduction smaller than for aniline or p-nitrophenol.

The destruction efficiency, when 10% of hydrogen peroxide added was also compared, in figure 3.16.

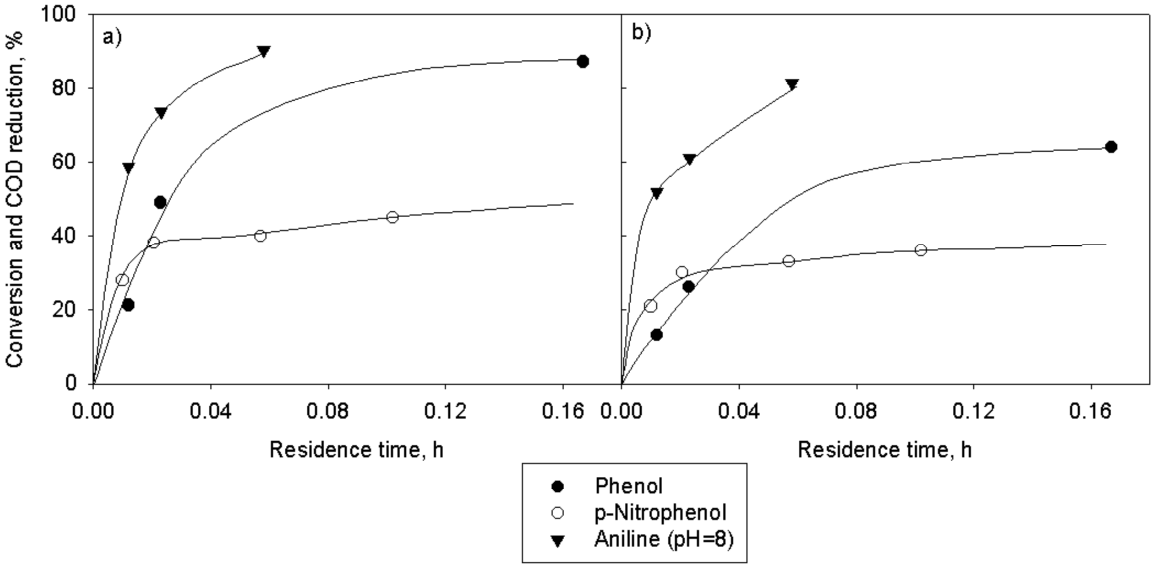


Figure 3.16: Conversion (a) and COD reduction (b) during 10% H_2O_2 promoted CWAO of phenol, p-nitrophenol (interpolated) and aniline, over activated carbon, C_0=5000 ppm, T=170°C, P_{O2}=3.4 bar, W_{AC}=0.68-0.71 g.

The same trends as for unpromoted CWAO are found for phenol and p-nitrophenol oxidation promoted by H_2O_2. The order of reactivity, however, changes for aniline at pH=8 reaching a surprisingly higher conversion and COD reduction, than phenol and p-nitrophenol. Conversion and COD are close for aniline and p-nitrophenol, but differ noticeably for phenol. P-nitrophenol seems to be mainly converted into gases, and not many intermediates remain in the liquid phase. The same trend can be seen (in figure 3.10 and 3.11) for higher doses of hydrogen peroxide for p-nitrophenol. CWAO of phenol produces more intermediates, confirming lower selectivity towards CO_2 formation, even at higher H_2O_2 doses added.

Aniline at initial pH of 8 should reach almost complete conversion, when more than 10% of H_2O_2 is added. Even if part of aniline is oxidised to gases, however a part in form of polymers remains at the activated carbon.

The best results obtained with CWAO and hydrogen promoted CWAO at standard conditions are summarised in table 3.2. Promising results were performed in case of phenol and p-nitrophenol, the performance of CWAO for both compounds being significantly improved by the promoting effect of hydrogen peroxide. Although highest conversion and COD reduction is achieved, aniline is thought to polymerise during CWAO over activated carbon. Plugging of the reactor rapidly occurred. In this situation CWAO is not functional for the effective abatement of aniline and more severe techniques are required.

Table 3.2: Best abatement of model pollutants obtained with CWAO or H_2O_2 promoted CWAO; T=170ºC, P_{O_2}=3.4bar, LHSV= 9.1 h^{-1}, $C_{org,0}$=5 g/l, F_{air}=2.4 ml/s, W_{AC}=0.7 g.

Pollutants	**CWAO**		**H_2O_2-CWAO**	
	X	**COD**	**X**	**COD***
Phenol	76	60	92 (20)	75 (20)
p-Nitrophenol	35	30	76 (40)	70 (40)
Aniline (pH=8)	42	-	92 (10)	80 (10)

* % of stoichiometric quantity in ().

3.1.2.6. AC consumption and thermogravimetry analysis

The possible loss of AC catalyst is an important factor to account for in the CWAO process. After the experimental series done for each pollutant, spent AC samples were recovered, dried at 120ºC for 12 h and then weighted. The observed weight changes are illustrated in table 3.3, together with the consumption data measured at 140°C and 9 bar of O_2.

Table 3.3: Weight change of AC samples during CWAO; T=170°C, P_{O2}=3.4bar, LHSV= 9.1 h^{-1}, $C_{org,0}$=5 g/l, F_{air}=2.4 ml/s, $W_{AC,0}$=0.68-0.71g.

Model Pollutants	Used for (h)	ΔW (%)	ΔW-TBR* (%)
Phenol	52	27	10
P-Nitrophenol	49	5	0
Aniline	30	-16	-33

* after continuous use of 50 h at 140°C and 9 bar of O_2.

It should to be mentioned that in the case of experiments at 170°C, where the intial weight of activated carbon was more or less 0.7 g the catalyst loss during taking it out from the reactor is important. For phenol and p-nitrophenol there is much more catalyst weight loss after expermients at 170°C and 3.4 bar of O_2 than after experiments at 140°C and 9 bar of O_2. Partially it results from accidental AC loss, , as mentioned above, when removing it from the reactor. But basically it is due to the combustion, that seems to be influenced more by temperature than presure. In the case of aniline, the real catalyst weight gain is probably bigger, but some quantity of activated carbon was lost during taking out from the reactor and some part when putting it in the oven at 400°C. As can be seen in figure 3.17, AC spent with aniline starts to loose weight at 400°C.

In addition, thermogravimetry analysis (TGA) was done for all recovered activated carbon samples to determine their desorption characteristics with respect to those of a fresh AC sample. Figure 3.17 presents the total weight loss of the four samples (fresh and after oxidation), when heated up to 900°C in an inert atmosphere of helium. The weight loss during TGA may allow speculating on changes in AC surface groups and the eventual presence of some strongly chemically adsorbed reaction products (polymer precursors, polymers).

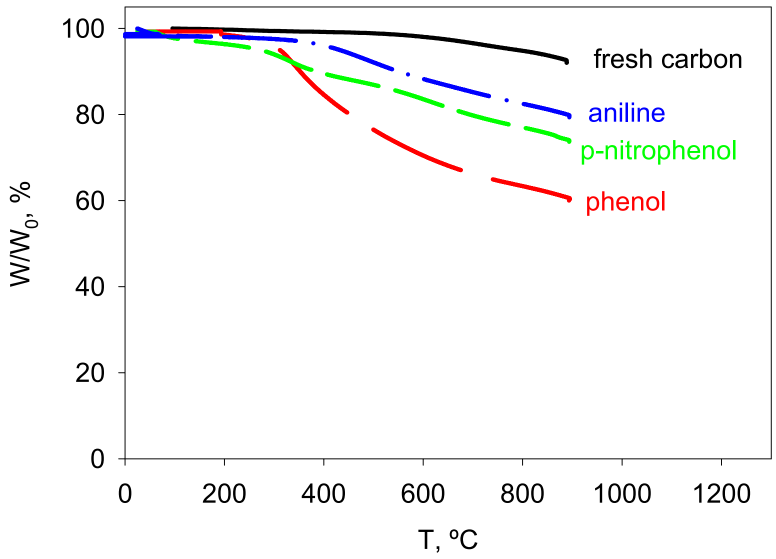


Figure 3.17: Weight change of activated carbon during thermogravimetry for fresh carbon, carbon from phenol, p-nitrophenol and aniline CWAO.

As can be seen in figure 3.17, fresh activated carbon shows only little weight loss , because it has only functional groups typical for commercial not modified carbon. Conversely, the activated carbon samples from CWAO experiments of aniline, p-nitrophenol and phenol suffer remarkable weight loss during TGA, the biggest resulting from the AC used in phenol CWAO.

Two factors are thought to be important in the AC weight change during CWAO. First, AC is lost by combustion, whereas second the formation and deposit of polymers via oxidative coupling will increase AC weight. But not only the quantity of substances adsorbed is of importance, but also their nature. Figure 3.18 shows the derivative of the weight lost in time. Peaks are generally ascribed to destruction of functional groups or some carbonaceous deposit on the surface.

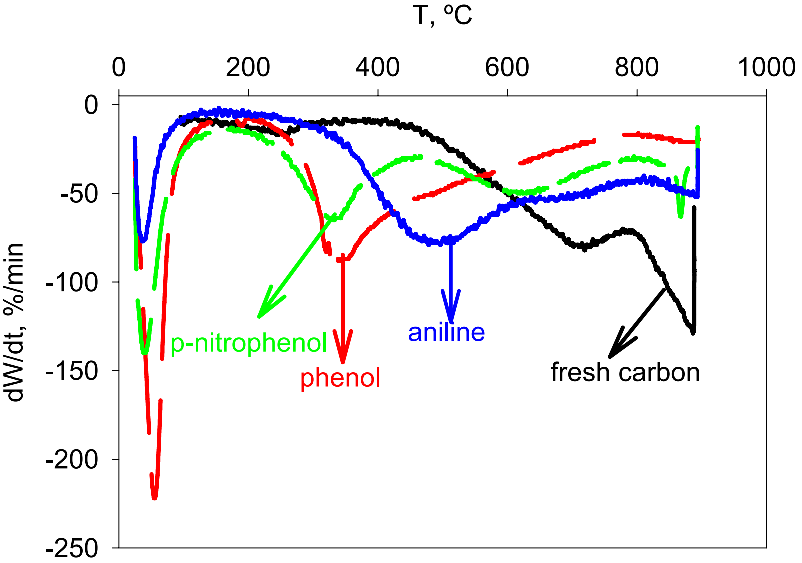


Figure 3.18: Derivative of activated carbon weight change during thermogravimetry for fresh carbon, carbon from phenol, p-nitrophenol and aniline CWAO (with and without of H_2O_2).

Depending on the activation of ACs, the groups mostly present on the surface of fresh carbon can be carboxyl, carbonyl, phenol, quinone and lactone groups (Figueiredo et al., 1999). Estimation of the surface groups desorbed from the spent and fresh AC samples can be done using reported literature information. The peaks that appear at 100°C represent the humidity removal. The curve of the fresh carbon exhibits three peaks. A first small one is seen at about 250°C representing low amounts of carboxylic groups. The second one at about 700°C can be attributed to phenol and carbonyl group. This peak can be also ascribed to some lactone groups being released at ca 450°C, i.e. the temperature at which this peak starts. The biggest (incomplete) peak at over 900°C relates to very stable quinone groups. For AC used in phenol and p-nitrophenol oxidation a new peak appears at 350°C approximately, that could indicate the formation of a considerable amount of lactone or lactol groups during the CWAO. P-nitrophenol AC has another small peak at about 900°C that is probably residual quinone groups, while for phenol AC the quinone groups completely disappeared. In contrary, aniline AC exhibits a new peak that starts at 400°C and has a minimum at about 500ºC, and it is difficult to find what group could be. So these peaks, absent in the fresh carbon curve, probably represent the polymers formed during the reaction and remaining on the AC surface, as at this temperature the polymers are being destructed.

3.1.2.7. Conclusions

It has been shown that several organic pollutants (phenol, o-chlorophenol, o-cresol, m-xylene) can be quite easily removed by means of catalytic wet air oxidation over activated carbon at mild conditions of 140ºC, 9 bar O_2 with conversions superior to 70%. These results confirm the potential of AC as a very cheap and versatile catalyst for CWAO processes. However, other pollutants such as aniline, p-nitrophenol, nitrobenzene or sulfolane give rather poor destruction, when treated with CWAO over AC. To improve CWAO performance the effect of hydrogen peroxide on CWAO of aniline, p-nitrophenol and phenol as a reference pollutant has been tested.

For aniline and p-nitrophenol, surprisingly an increase in temperature from 140 to 170°C, even with a decrease in oxygen pressure, improved significantly conversion and COD reduction. The destruction efficiencies of phenol, p-nitrophenol and aniline as well as COD removal were further enhanced with the addition of hydrogen peroxide. The promoting effect of H_2O_2 was found for p-nitrophenol and for COD destruction of phenol. For aniline and phenol with 10 and 30% of stoichiometric H_2O_2 quantities added, respectively, conversions reached over 90%. However, in case of aniline, which is more reactive at acidic pH, plugging in the catalytic reactor tube rapidly occurred for pH of 4 and when 10% of H_2O_2 was added. Thus, H_2O_2 promoted CWAO is not feasible for aniline abatement, because the high aniline and COD conversions are partially due to the polymerisation and adsorption.

The weight change of catalyst was measured and the thermogravimetry analysis was done to obtain additional information on catalyst stability during CWAO. The carbon from phenol oxidation shows the biggest weight loss. An increase in temperature from 140 to 170°C resulted in (for both phenol and p-nitrophenol oxidation) higher AC weight loss. The AC sample from aniline CWAO, on the other hand, showed increase in weight. At the same time, TGA analysis has shown that peaks that appeared in this analysis are different than the peaks from phenol and p-nitrophenol AC samples. Aniline polymerisation and strong adsorption on AC during CWAO is thought to be responsible for high aniline and COD reduction, and rapid reactor plugging after time on streams of 1.5 h.

Hydrogen peroxide promoted CWAO can be thus recommended as an economic and effective (due to a cheap catalyst) method for treating phenol and p-nitrophenol. In case of aniline, formation of polymers and its irreversible adsorption on the carbon surface can lead to unacceptable plugging in the reactor. To avoid activated carbon loss during CWAO, temperature has to be decreased. The resulting lower activities may be compensated by increasing adequately the AC catalyst load. Finally, TGA analysis clearly demonstrated important surface changes of AC during CWAO, and this can strongly influence the CWAO performance.

3.2. Wet Peroxide Oxidation of refractory organic wastewater pollutants

In this chapter we present the experimental results obtained from continuous wet oxidation of refractory organic pollutants using hydrogen peroxide as liquid oxidant. This method is claimed to be more efficient than conventional WAO, since hydrogen peroxide decomposes to OH radicals that are very oxidative species. We first studied the abatement of phenol (reference pollutant), as well as p-nitrophenol, nitrobenzene, aniline and sulpholane that were found to be refractory to CWAO using AC catalyst. The experiments were carried out in the constructed high pressure – high temperature equipment. Phenol WPO was studied in order to find the effect of operating parameters (temperature, pressure, residence time, H_2O_2 dosage) on process performance. The optimal conditions found for phenol WPO were then applied to the destruction of the refractory compounds.

3.2.1. Preliminary tests (reproducibility and hydrolysis)

The reproducibility of phenol WPO and HPLC analysis was studied by repeating a WPO experiment two times and each sample analysis three times. The conversions and analysis errors obtained for experiment at 300ºC and 150 bar are presented in figure 3.19.

The bars present the experimental error interval of HPLC analysis in each conversion point. As can be seen the error is more marked for the experiment 1, although the points at highest residence time are practically free of error. The analytical error in conversions for experiment 1 has an acceptable value of ±4%. The conversion of phenol obtained in both experiments is very similar, the difference being less than 5%. This is certainly due to the fact that it is impossible to reproduce exactly the same operating conditions. We conclude that our experiments are sufficiently reproducible with an acceptable analysis error.

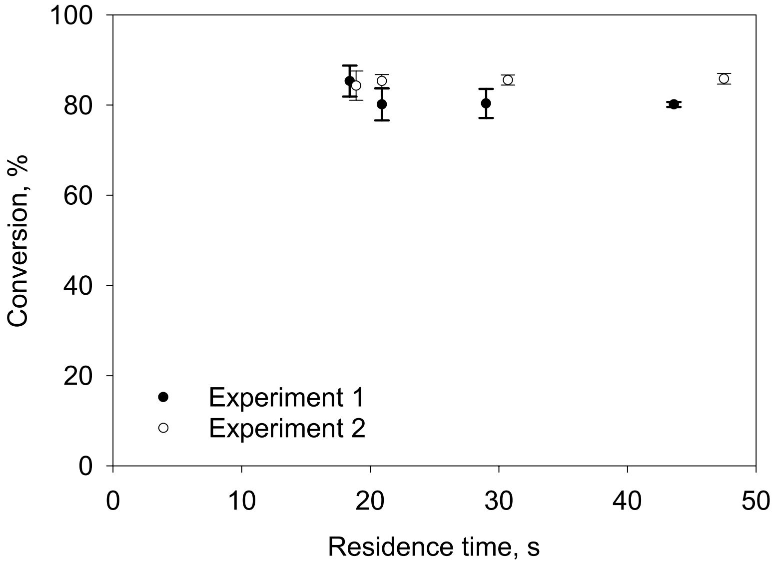


Figure 3.19: Phenol conversion of two experiments done in the same conditions, $C_{Ph,0}$=5000 ppm, T= 300°C, P=150 bar, 50% H_2O_2.

For temperatures of 300 and 400°C and pressures of 150 to 350 bar, blank experiments without H_2O_2 were done to quantify the influence of thermal decomposition on phenol conversion. Figure 3.20 shows that, at the given operating conditions, decomposition of phenol due to hydrolysis was negligible, with a maximum of 1.5% at 400°C and 250 bar. This confirms as well that the equipment metallic parts (tubing walls) do not catalyse phenol thermal decomposition.

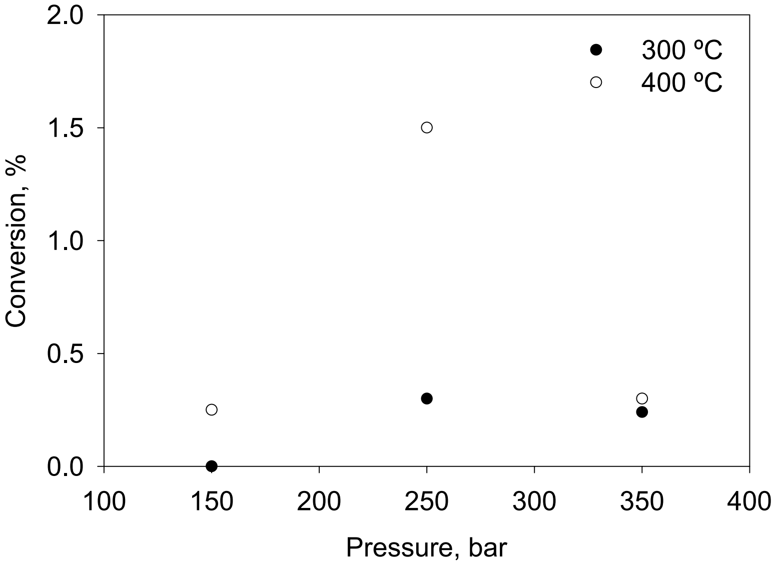


Figure 3.20: Hydrolysis of phenol at sub- and supercritical conditions, τ=46 s, $C_{Ph,0}$=5000 ppm.

It is interesting to notice, that the highest conversion from hydrolysis of phenol was found close to the critical point of water. The explanation of this observation can be related to the variation of the water dissociation constant with pressure and temperature. The constant has a value of 10^{-14} at ambient conditions, then increases to 10^{-12} at the critical point and in supercritical water decreases again to values in the range of 10^{-14} to 10^{-20}. Due to its increase near the critical point, the equilibrium of water dissociation is moved towards the formation of ions. At the critical point water becomes more polar and can promote hydrolysis. No intermediates were found in detectable quantities, so it is reasonable to neglect the contribution of hydrolysis in the overall disappearance rate of phenol oxidation for operating conditions far from the critical point of water.

3.2.2. Influence of operating variables in phenol WPO

Numerous experiments were conducted with phenol to study the influence of operation variables on WPO performance and to pre-optimise WPO reaction conditions. Parameters of interest were H_2O_2 feeding, residence time, hydrogen peroxide concentration, temperature and pressure. These pre-optimised conditions were then tested to assess the WPO performance of the organic pollutants aforementioned.

3.2.2.1. Effect of H_2O_2 - feeding

Three ways of feeding H_2O_2 to the reactor were tested:

1) the oxidant solution was separately passed firstly through a preheater coil of 2.6 m,
2) the oxidant solution was separately passed through a 3 times shorter preheater of 0.9 m,
3) H_2O_2 and phenol solutions were pre-mixed and fed together to the preheater of 2.6 m.

Literature data (Rivas et al, 1999) indicates that a mayor problem of WPO is the inefficient use of hydrogen peroxide in form of $OH^{\cdot}$ radicals, i.e. the formation of molecular O_2, less reactive in the oxidation process.

The results obtained for 300°C, 150 bar, 50% of stoichiometric H_2O_2 demand and 5 g/l phenol solution are given in figure 3.21. The results clearly demonstrate the effect that has preheater length and premixing on phenol conversion. The two different H_2O_2 preheater lengths for H_2O_2 and phenol being fed separately performed similar final phenol conversion and COD removal in the range of 60 and 40%, respectively, at residence time of about 60 s. At smaller residence times however, the conversion for the short preheater was considerably higher than for the long preheater. Higher hydrogen peroxide decomposition to water and oxygen can be expected to occur in case of the long preheater. Less $OH^{\cdot}$ radicals are available for oxidation in the reaction zone and the initial rate is small. In the short preheater at smaller residence time hydrogen peroxide decomposition to oxygen cannot develop. The presence of more hydroxyl radicals results increasing noticeably the initial rate of phenol oxidation.

As deduced from figure 3.21, pre-mixing of organic and oxidant solutions gave much higher phenol conversion and COD removal of 90 and 60%, respectively, in a 2 times shorter residence time of 30 s and use only one feed line. It can be assumed that the reaction started as soon as the mixture entered the heated fluidised sand bath. The preheater coil must be considered as a (non isothermal) part of the reactor resulting in a total reactor length of 6.6 m (V=0.012 l). When phenol and hydrogen peroxide solutions are fed together, the hydroxyl radicals formed from hydrogen peroxide decomposition can immediately react with phenol explaining the high destruction rate observed at small residence time. At a residence time of about 30-40 s all of the available H_2O_2 oxidant is consumed by the reaction as confirmed by stable ~ 50-60% COD reduction. This is not the case for feeding H_2O_2 and phenol solution in different lines to the reactor tube.

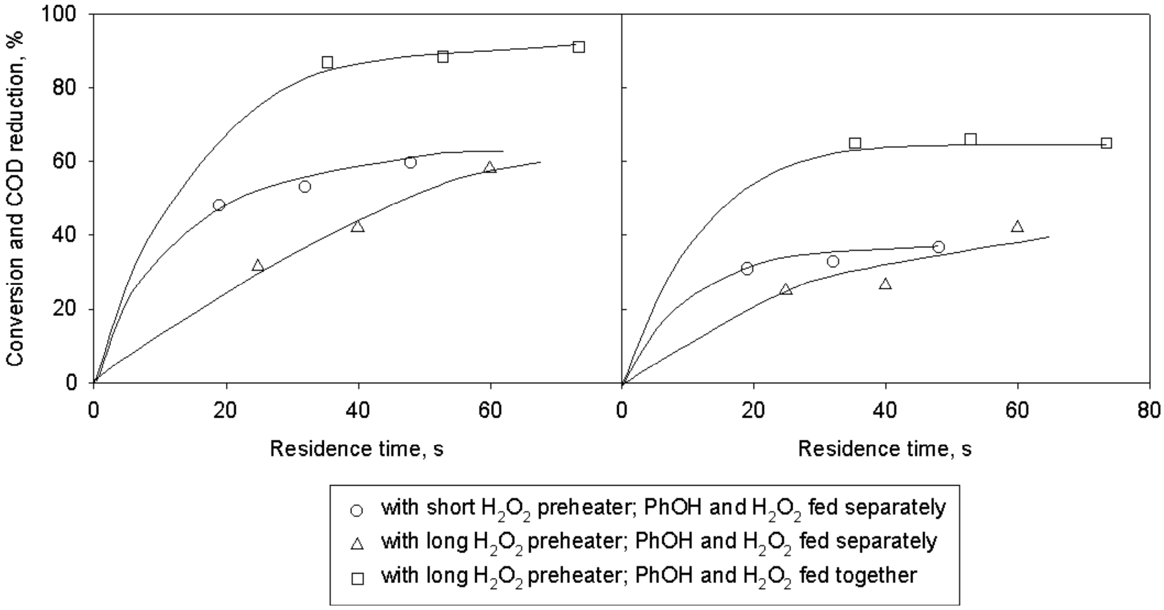


Figure 3.21: Phenol conversion (a) and COD reduction (b) versus residence time for different reactant feeding, T=300°C, P=150bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=50%.

Concluding, the most appropriate hydrogen peroxide feeding, i.e. premixed with phenol, offers a very efficient use of forming OH-radicals. High initial rates and high conversion are obtained already in short residence times of about 20-30s. When the thermal decomposition of hydrogen peroxide is favoured in the absence of phenol (separate feed lines for phenol and oxidant), lower initial rates resulted. Excessive residence times would then be needed to reach comparably high conversion and COD removal (see figure 3.21). In the following experiments, phenol and H_2O_2 solutions were thus premixed and fed.

3.2.2.2. Effect of residence time

An increase in residence time evidently results in higher phenol conversion and COD removal, as illustrated in figure 3.21. However, the residence time seems to affect phenol conversion and COD removal only during small residence times, then the conversions stabilise. Explanation is that most of the available oxidant is rapidly consumed in form of OH radicals at small residence time. The reaction rate of phenol and COD destruction then slows down because either all oxidant is consumed or only available in form of less reactive molecular oxygen dissolved in the liquid phase.

3.2.2.3. Effect of H_2O_2 concentration

Figure 3.22 presents the experimental phenol conversion and intermediates peak area as a function of the inlet H_2O_2 concentration at standard conditions. From the figure, it can be deduced that the initial quantity of hydrogen peroxide added has a significant positive influence on the phenol and intermediates conversion. The destruction of phenol strongly increased with higher H_2O_2 concentration, reaching almost complete conversion (>99%) at 100% of the stoichiometric demand of hydrogen peroxide at 300°C. The intermediate peaks area also shows a strong dependence on H_2O_2 concentration. An increase at small hydrogen peroxide concentration is observed, reaching a maximum at approximately 25% of stoichiometric demand of peroxide and then decreases almost to zero with 100% of stoichiometric H_2O_2 demand. Stoichiometric quantity of H_2O_2 at 300°C, proves to be sufficient to achieve almost complete phenol and intermediate conversion. This is impossible when using a gaseous oxygen source, requiring a great excess of O_2 and higher temperature to reach complete conversion of phenol (Lee & Gloyna, 1990).

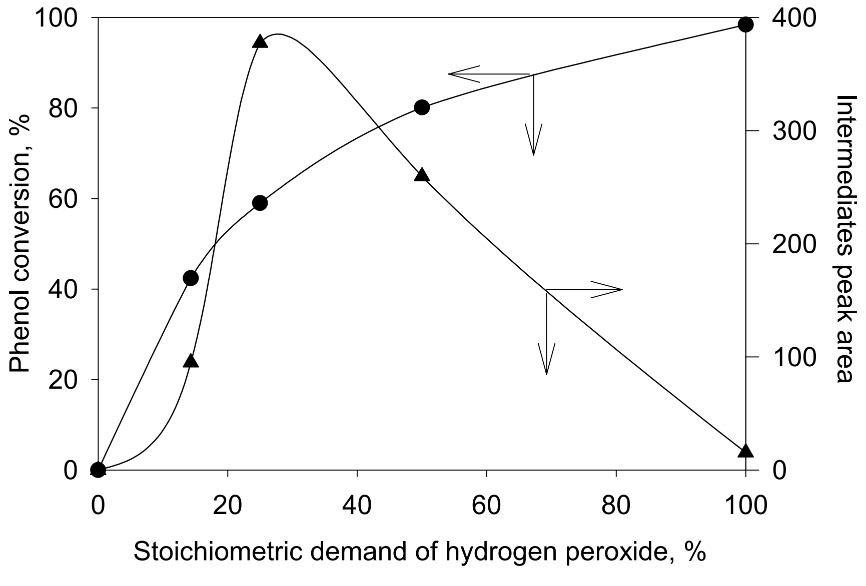


Figure 3.22: Phenol conversion (circles) and change in total area of intermediates (triangles) as a function of stoichiometric demand of hydrogen peroxide; T=300°C, P=150bar, $C_{PhOH,0}$=5g/l, τ=46s.

3.2.2.4. Effect of temperature

As expected, temperature has a considerably favourable effect on phenol oxidation (see figure 3.23). The maximum conversions obtained at 50% of stoichiometric H_2O_2 demand are similar (ca 80%) for 300 and 400°C, but the enhancement of temperature results in about four times shorter residence time at 400°C.

At 300°C and 150 bar reaction takes place in the liquid phase, but raising the temperature to 400°C leads to phase change. At 400°C due to the density change, concentrations are much smaller, and so are the reaction rates. With these smaller concentrations in the gas phase, even if residence times are 5-10 times smaller than in the liquid phase, they are sufficient to reach the maximum conversion of about 80%.

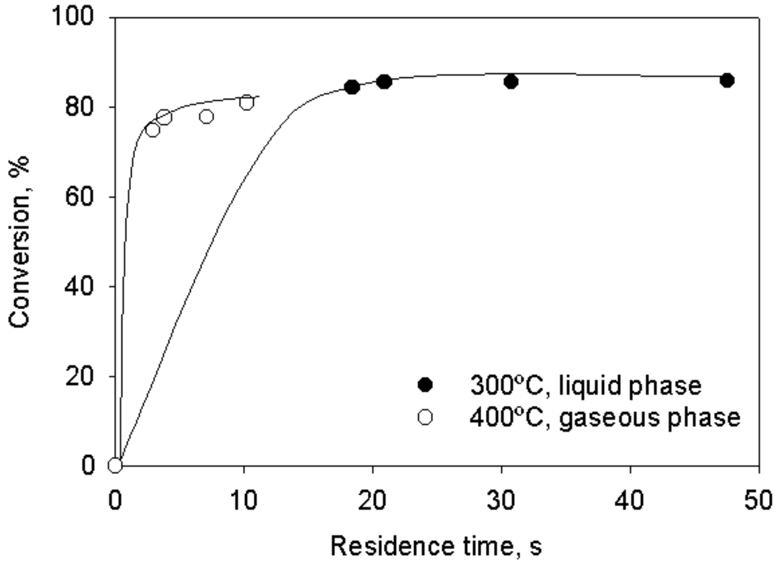


Figure 3.23: Phenol conversion as a function of residence time for two different temperatures, P=150bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=50%.

3.2.2.5. Effect of pressure

The pressure effect on conversion was verified through experiments at standard conditions, varying pressure in the range from 20 to 150 bar at constant flow rate (figure 3.24a).

The results show that, as expected from literature data (Modell, 1985; Martino & Savage, 1999a; Bird et al., 1982), the change in pressure far from the critical point of water does not affect the conversion as far as the reaction is conducted in the liquid phase (density change is very small) with a liquid oxidant.

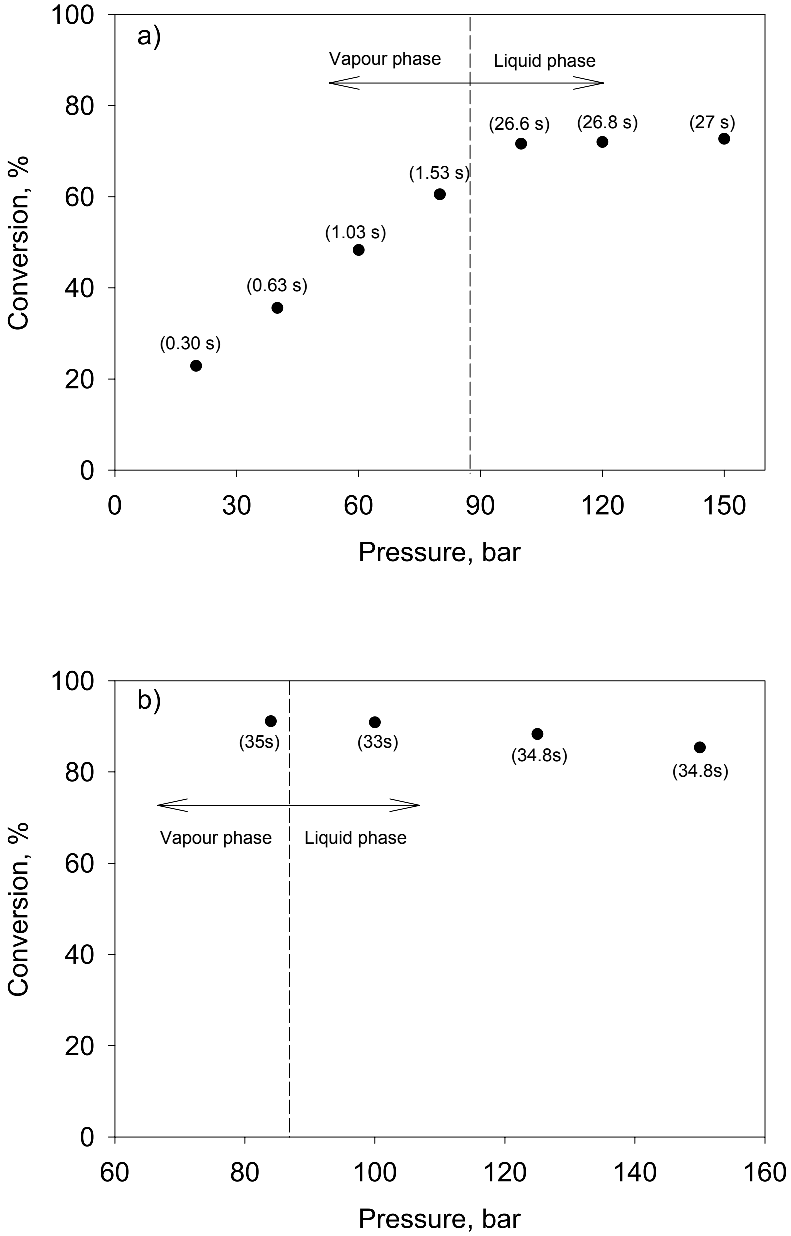


Figure 3.24: Phenol conversion as a function of pressure at a) constant liquid flow rate of 0.600l/h and b) constant residence time of about 34s, T=300°C, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=50%, residence time indicated in brackets.

When the reaction changes from liquid to vapour phase, the density drops drastically. With the fall of density the residence times decreases about an order of magnitude, explaining the observed linear reduction in phenol conversion (see figure 3.24a). To ensure that the conversion decrease was only due to the residence time decrease, also experiments varying pressure at constant residence time were done. In these conditions, when the reaction medium changes from liquid to vapour phase, the phenol conversion was found to be very similar, as presented in figure 3.24b.

Summarising, the change in pressure (20-150 bar) affects the organic conversion only by change in density and residence time. When using hydrogen peroxide, one can work in the liquid phase as close as possible to the vapour pressure of water at the given temperature to reduce the equipment cost. However, this is only valid far from the critical point of water, because close to the critical point the properties of water change significantly.

3.2.3. Intermediates distribution in phenol Wet Peroxide Oxidation

The analysis of intermediates is important to discuss the quality of the treated effluent. The formation of intermediates during phenol WAO is known (Devlin & Harris, 1984) and it is of interest to compare WAO and WPO intermediate distributions. Intermediates distribution of phenol WPO was assessed at 50% H_2O_2 and 300 and 400ºC. Our aim was not to obtain exact experimental data for a kinetic analysis and kinetic parameter identification, but rather to discuss qualitatively the distribution of main intermediates.

It was possible to identify the main liquid intermediate products from oxidation of phenol using HPLC analysis. As can be seen in figure 3.25, the sum of all identified intermediates peak areas were compared to the total area of intermediates indicating an identification of 80% at 300ºC and almost 100% at 400ºC. The identified intermediates were acetic acid, formic acid, oxalic acid, hydroquinone and p-benzoquinone. Their variation with residence time is illustrated in figure 3.26 at the given operating conditions. All the experimental points from this figure are also listed and can be found in Appendix B.

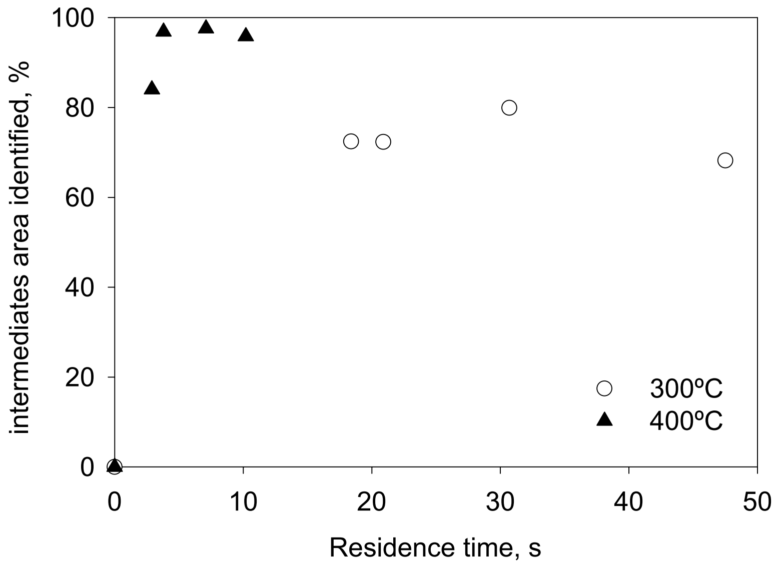


Figure 3.25: Intermediates area identified during phenol oxidation, P=150bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=50%.

In related studies on WAO most of the initial intermediates directly formed from phenol are rapidly oxidised to end products (CO_2) or to low molecular carboxylic acids (Portela et al., 2001). The end products formed during the Wet Air Oxidation identified by the authors include polymeric material (tars), pyrocatechol, hydroquinone, and carboxylic acids. Under conditions of oxygen excess, intermediate ring compounds, i.e. dihydric phenols and quinones were not observed (Devlin & Harris, 1984). When phenol is in excess (deficit of oxygen) hydroquinone yield was found smaller than that of p-benzoquinone. The same trend was observed in our study. During catalytic WAO over CuO/Al_2O_3, benzoquinones, and small amounts of hydroquinone and catechol were observed (Fortuny et al., 1999, Sadana and Katzer, 1974b). P-benzoquinone was detected also in studies of catalytic and noncatalytic SCWO of phenol (Krajnc & Levec, 1997; Thornton & Savage, 1992).

The WPO of phenol should occur in several steps, hydroxylation intermediates like catechol and benzoquinone being firstly formed. These products undergo further oxidation to muconic and then to oxalic acid (Fajerwerg & Debellefontaine, 1996; Debellefontaine et al., 1996).

In figure 3.26 we can observe that p-benzoquinone was found in the smallest quantity in comparison with the other identified intermediates. In addition, it disappears completely at higher residence times. Hydroquinone yield is higher than that of p-benzoquinone, however the difference is only noticeable at 300ºC. It may be concluded that the overall formation of hydroquinone and p-benzoquinone has a different temperature sensibility probably due to a more enhanced reaction rates of p-benzoquinone towards the formation of carboxylic acids at higher temperatures.

Interestingly, HPLC analysis confirms the formation of formic acid in significant concentrations (figure 3.26c), reaching about 50 mmol/l at 300 and 400ºC, 150 bar and 50% of stoichiometric H_2O_2 demand. This result suggests that there exists a preferential pathway toward formic acid in WPO. In CWAO of phenol over activated carbon, formic and acetic acid were found in big quantities, when O_2 was present in excess (Eftaxias, 2002). Thornton and Savage (1992b) have observed the same trend in Supercritical Water Oxidation. They found that the formic acid was the most abundant intermediate product detected at operation conditions of 380ºC, 280 bar, but 250% excess of oxygen. The work of Fortuny (1996) on WAO of phenol over CuO catalyst shows a similar intermediates distribution as in the SCWO of phenol, however in the former case the most abundant intermediate is rather oxalic acid than formic acid. An important difference to CWAO is that acetic acid is destroyed during WPO (300°C, 150 bar, 50% H_2O_2). However at deficit H_2O_2, oxalic acid is found more refractory to WPO, although only formed in small concentrations (see figure 3.26 b,c).

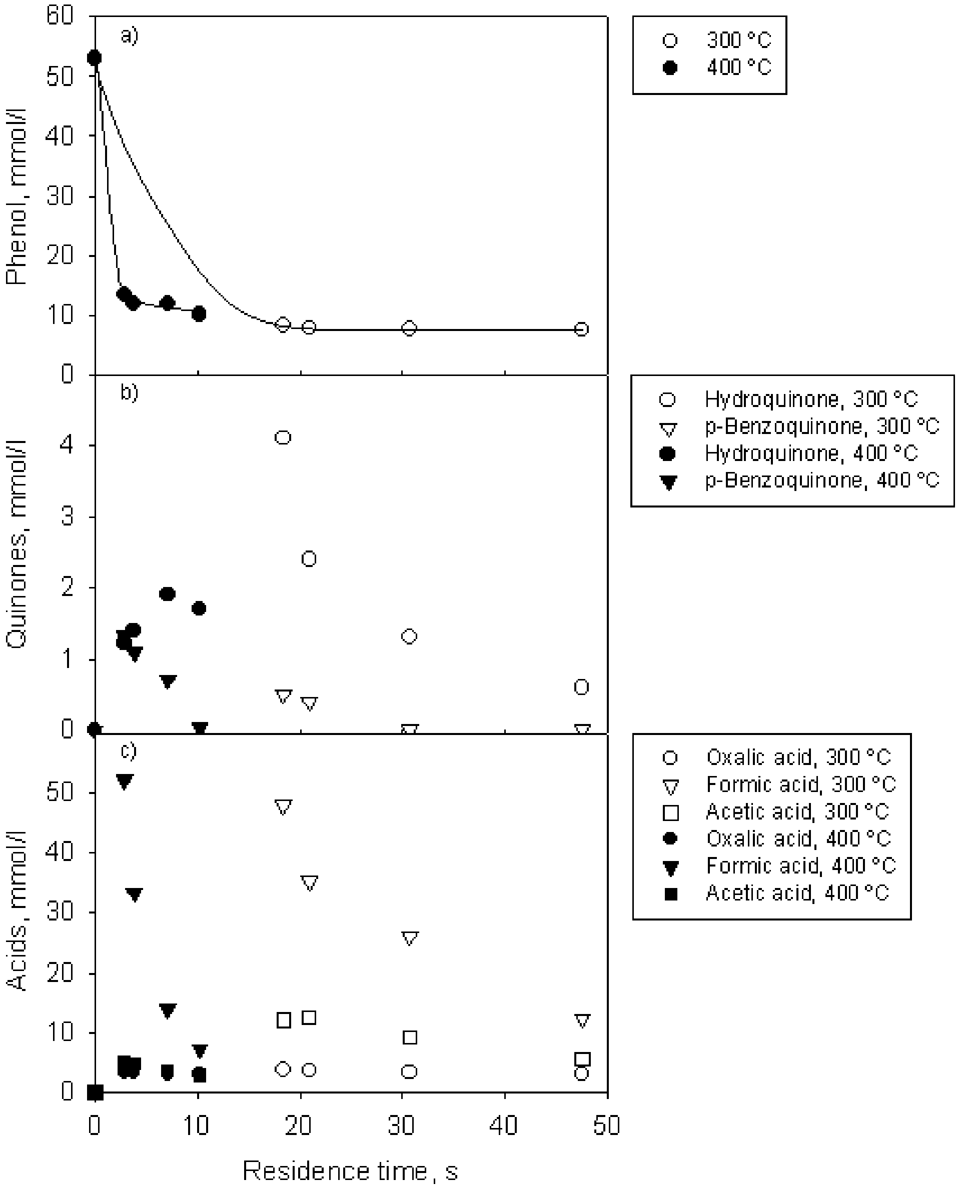


Figure 3.26: Evolution of concentration of phenol (a) and oxidation intermediates (b, c); P=150 bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=50%.

From the intermediate distribution identified by HPLC analysis and comparison with literature data on phenol oxidation in WAO, CWAO and SCWO, a simplified reaction pathway for phenol WPO has been proposed as illustrated in figure 3.27. Hydroquinones are first formed, followed by its transformation to benzoquinones. The aromatic ring is then opened to produce saturated and unsaturated organic acids. Finally, the low chain carboxylic acids are decomposed to carbon dioxide and water.

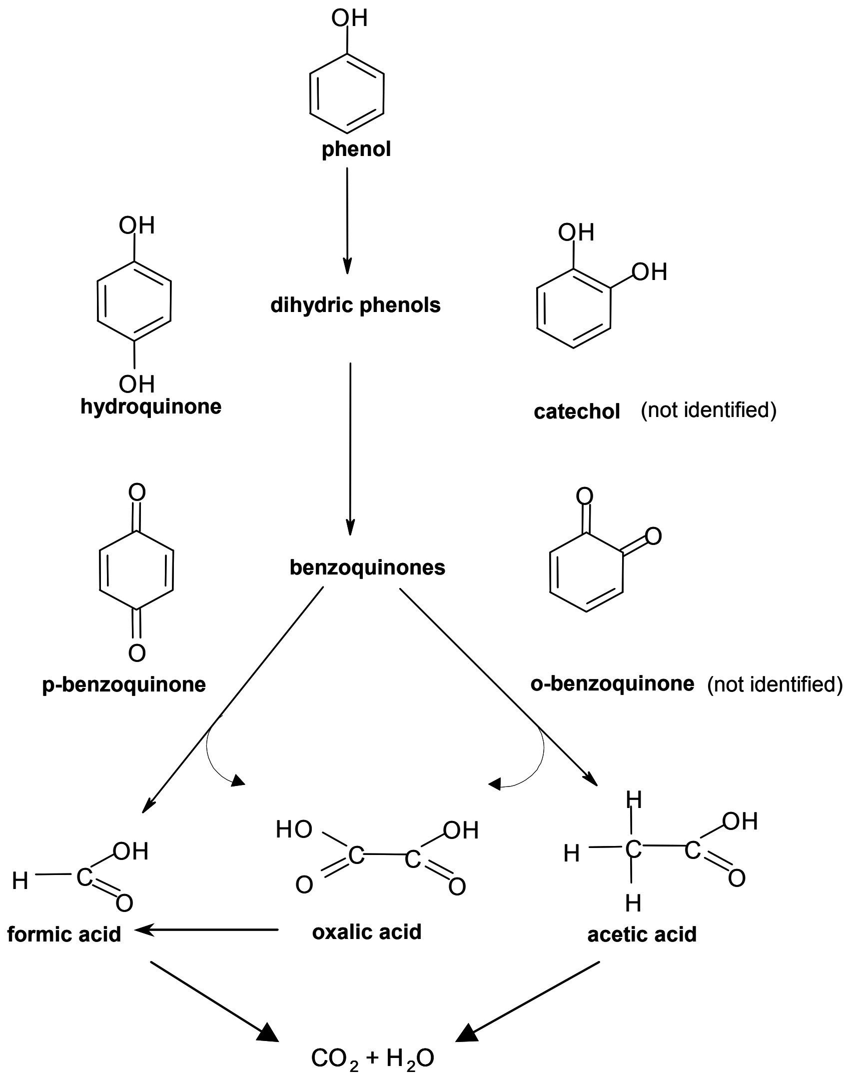


Figure 3.27: Simplified reaction network for phenol Wet Peroxide Oxidation deduced from the identified intermediates.

CO_2 formation

Using the quantified concentration of liquid products from phenol oxidation, the organic carbon balance in the liquid phase was performed to estimate CO_2 yield. In the calculation, it was assumed that gas product was essentially CO_2. The calculation of the CO_2 formation and the concentration of the identified intermediates can be found in the Appendix B.

The yield of carbon dioxide reaches about 70% that is not possible, because the only 55% of stoichiometric hydrogen peroxide was added in these experiments. The error is partially due to the intermediates that were not identified by the HPLC analysis. However, it is also possible that the gaseous product is not only

CO_2, but also CO might be formed due to oxygen deficit, as reported by Gopalan & Savage (1995) that have observed that CO constituted from 11 to 35 % of the total gas yield from supercritical oxidation of phenol.

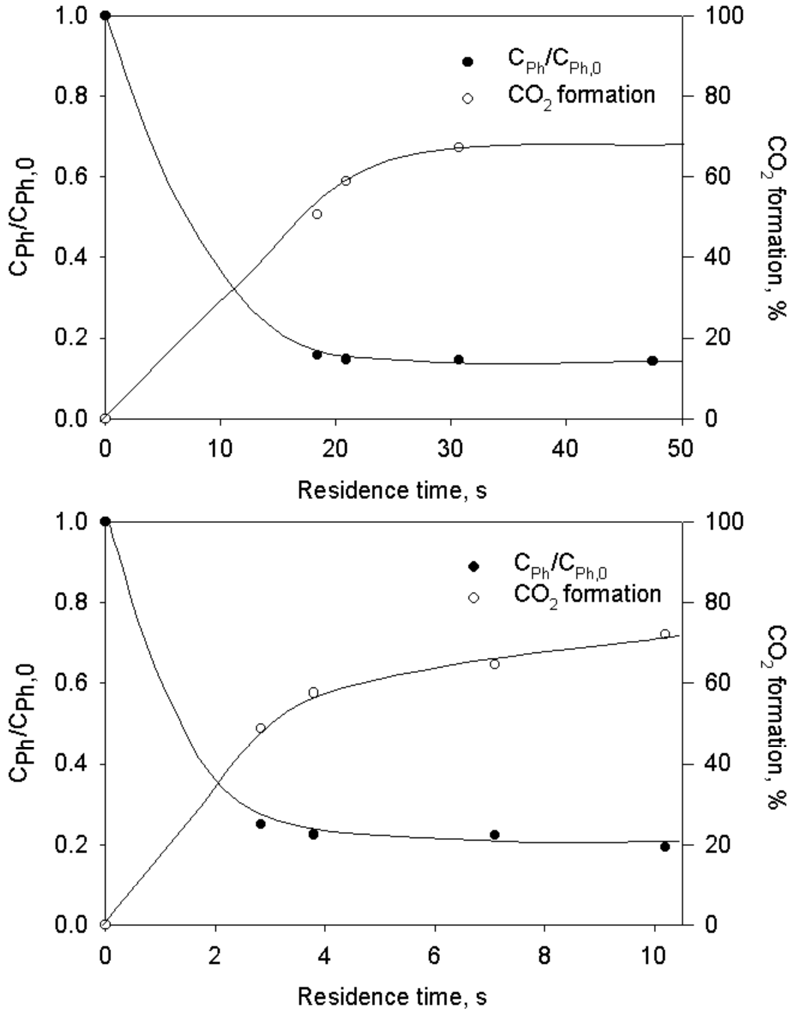


Figure 3.28: Phenol consumption and CO_2 formation calculated from HPLC analysis at a) 300°C and b) 400°C, $C_{Ph,0}$=5 g/l, C_{H2O2}=55%, P=150 bar.

3.2.4. Wet Peroxide Oxidation of refractory pollutants (p-nitrophenol, nitrobenzene, aniline, sulfolane)

Phenol WPO permitted to preselect convenient operating conditions, for the study of aniline, nitrobenzene, p-nitrophenol and sulfolane. The experiments were generally performed at 150 bar and 300ºC, but different temperatures up to 550ºC were also applied dependently on the refractoriness of the compound studied.

Our goal was to obtain high destruction efficiency of these compounds. If the preselected conditions from WPO of phenol did not yield the expected conversion and COD range, temperature, as the most influent parameter, was increased to improve the process efficiency. In phenol WPO, total pressure was found to have only a small effect, and feeding higher hydrogen peroxide quantity than stoichiometric one is also not recommended, enhancing mostly the H_2O_2 decomposition to water and oxygen. Figures 3.29 to 3.37 present the results of p-nitrophenol, nitrobenzene, aniline and sulfolane destruction and COD removal obtained during Wet Peroxide Oxidation.

A general observation is that at the selected WPO conditions, all refractory compounds show greatly enhanced conversion and COD destruction compared to CWAO using AC. The same trend of conversion and COD reduction for residence time – sharp increase at low τ, followed by a plateau - is confirmed for all compounds studied. However, there exist substantial differences in performance among these compounds with respect to WPO of phenol. These findings will be discussed in detail on the following pages.

3.2.4.1. p-Nitrophenol

In terms of conversion and COD reduction, p-nitrophenol WPO leads to similar results of almost complete conversion and ~ 90% COD reduction at 100% H_2O_2, 300ºC and residence times (20s) comparable to those of phenol. Furthermore, the positive influence of increasing temperature can be clearly appreciated through figures 3.29 to 3.31, conversion (fig. 3.29) and COD reduction (fig. 3.31) reaching high values in much shorter residence time. Conversely to phenol

WPO with 50% of hydrogen peroxide, higher temperature (400°C) results also in higher conversion and 3 times less maximum of intermediates peak area (fig. 3.30). This result may indicate a different temperature dependence of reaction intermediates during p-nitrophenol WPO. For 100% of stoichiometric H_2O_2, almost complete conversion is obtained at all temperatures, and COD reduction yields 76, 81 and 84%, at 300, 330 and 400°C, respectively. Either very refractory intermediates are accumulated or the inefficient use of H_2O_2 oxidant at higher residence time does not allow achieving 100% of mineralisation with stoichiometric H_2O_2 doses added.

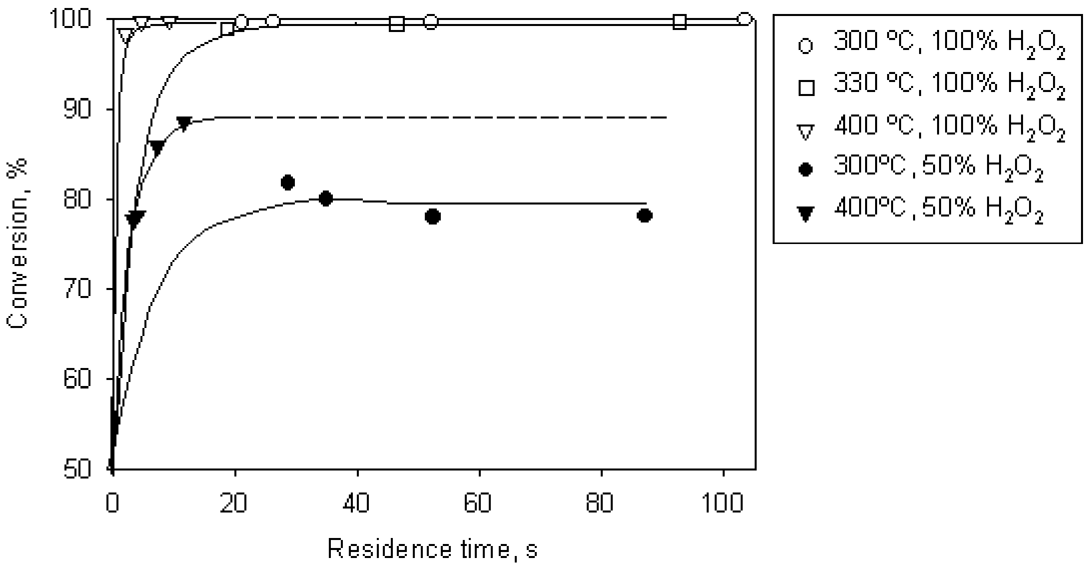


Figure 3.29: Nitrophenol conversion versus residence time at different temperatures and H_2O_2 initial concentrations, P=150bar, $C_{NP,0}$=5g/l.

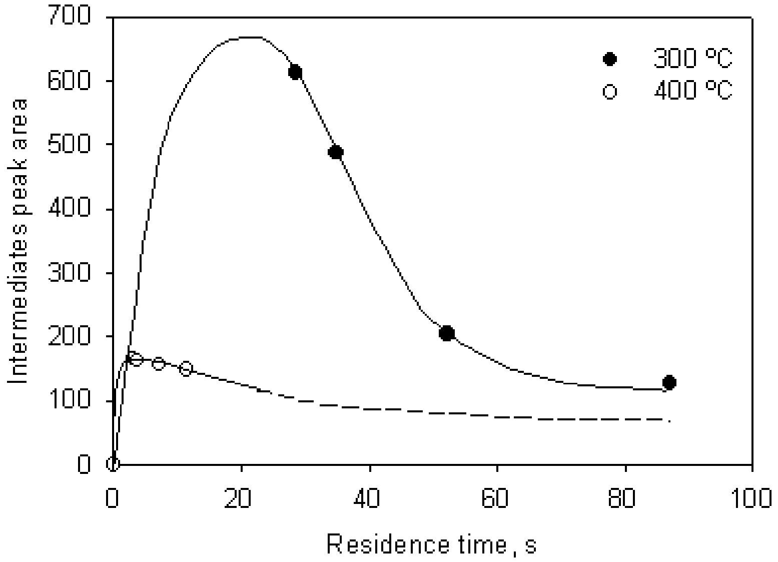


Figure 3.30: Intermediates peak area from p-nitrophenol oxidation versus residence time, P=150bar, $C_{NP,0}$=5g/l, $C_{H2O2,0}$=50%.

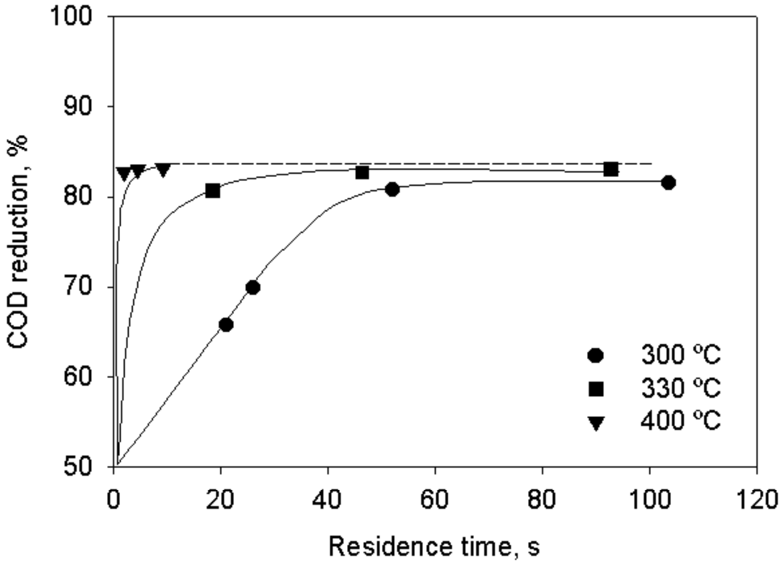


Figure 3.31: COD conversion during nitrophenol WPO as a function of residence time, P=150bar, $C_{NP,0}$=5g/l, $C_{H2O2,0}$=100%.

Variation of pH during oxidation of nitrophenol is presented in figure 3.32. At 300 and 330°C, pH rapidly falls from 4.3 to 2-3 for small residence time, because p-nitrophenol is disappearing and organic acids are rapidly formed. Then, pH slowly starts to rise to its initial value of about 4.5, because concentration of organic acids diminishes due to their reaction towards carbon dioxide and water. On the other hand, at 400ºC, pH increases straight from the beginning to about 5 indicating that at this temperature, the intermediates are formed and destroyed very quickly. Continuous increase in pH values at 300 and 330°C, however, suggests that at high residence time, the same pH value is achieved. This observation is in agreement with the evolution of COD removal that becomes also very similar for all temperatures at higher residence times (see figure 3.31).

The colour of samples at smaller residence time was brownish and with little foam. At increasing residence time, the samples became clearer, rather yellowish and a strong foaming was observed due to the formation of gas products. The persistence of some colour in the liquid samples, even for highest COD removal supports the accumulation of some intermediates refractory to WPO conditions.

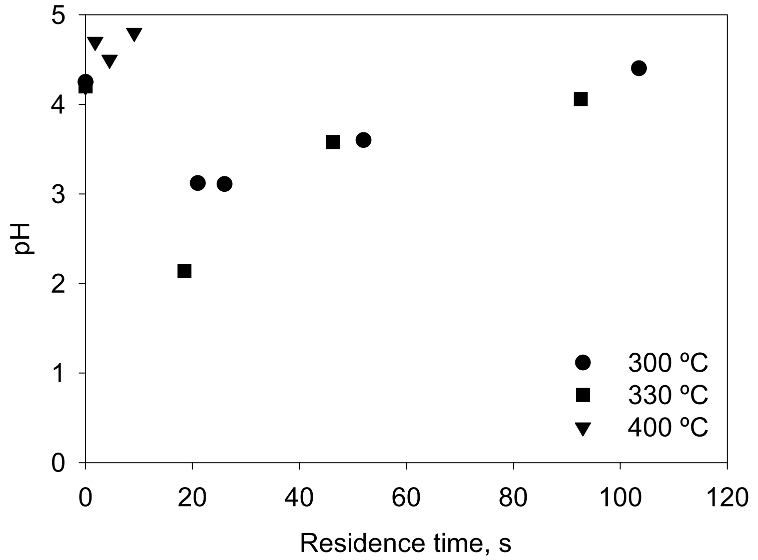


Figure 3.32: pH variation during WPO of nitrophenol, P=150bar, $C_{NP,0}$=5g/l, $C_{H2O2,0}$=100%.

3.2.4.2. Aniline

WPO of aniline shows almost complete conversion at 300°C and 150 bar, although COD destruction is found to be substantially smaller in the range of only 60% (see figure 3.33 and 3.34). Temperature was raised to 370°C to perform higher destruction efficiency. As expected, the increase in temperature from 300 to 370°C resulted in equally complete aniline conversion at reduced residence times, as illustrated in figure 3.33. Further, COD conversion enhanced from 60 to about 80% at lower residence times, when temperature increased to 370°C as in the case of phenol and p-nitrophenol WPO. COD destruction is much more sensitive to temperature than observed in the case of p-nitrophenol and phenol WPO.

But, the residence times needed to reach maximum conversion and COD destruction are for all three temperatures about 5 times larger than in the case of phenol and p-nitrophenol. Thus, it must be claimed that aniline is more refractory to WPO than phenol and p-nitrophenol.

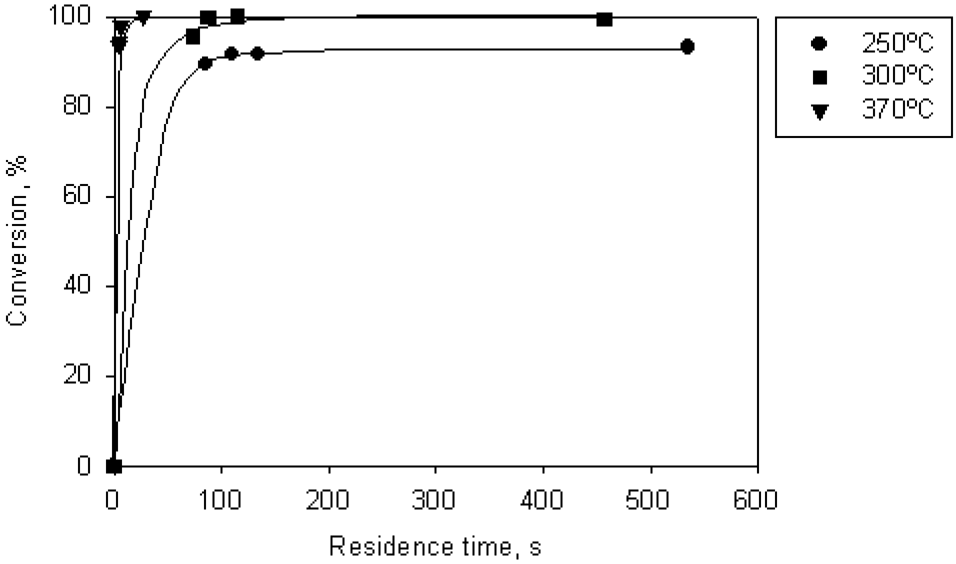


Figure 3.33: Aniline conversion versus residence time at different temperatures, P=150bar, $C_{AN,0}$=5g/l, $C_{H2O2,0}$=100%.

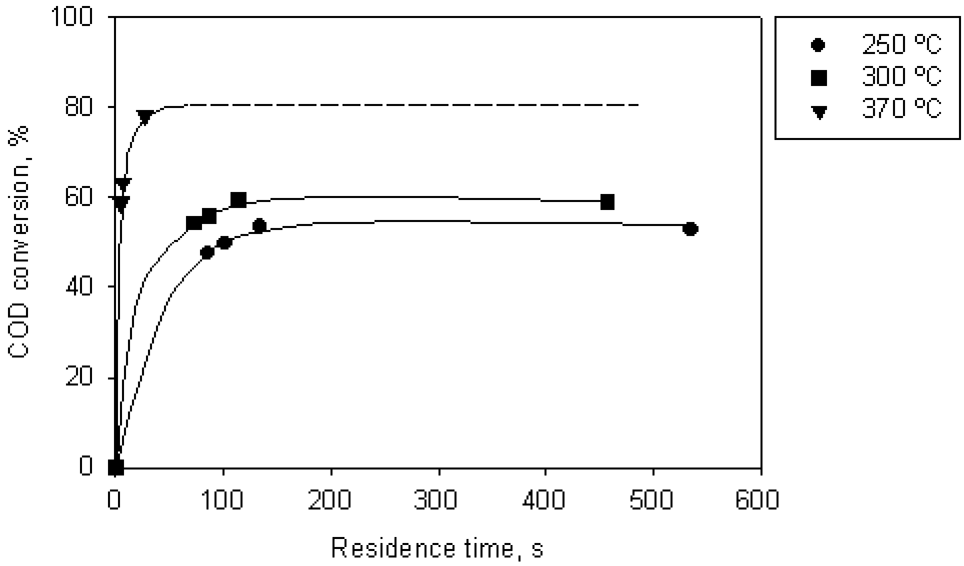


Figure 3.34: COD conversion versus residence time at different temperatures in aniline WPO, P=150bar, $C_{AN,0}$=5g/l, $C_{H2O2,0}$=100%.

3.2.4.3. Sulpholane

The feed solution of sulpholane (5g/l) gives starting pH value of 6.15. During the reaction, the sulpholane solution occurred to be very corrosive, due to the formation of sulphuric acid during WPO. Experiment at 370°C and 150 bar showed that the effluent from the reactor exit occasionally had a clear green colour and pH values below 1. Effectuated mass spectrometer analysis of liquid sample found liquid concentrations of 240 ppm of Ni and 70 ppm of Cr, indicating a severe corrosion problem of the Hastelloy reactor tubing. Low pH due to sulphuric acid formation is a serious process inconvenient and corrosion of reactor (low pH) must be prevented by adjusting pH. WPO test with adjusted pH should be carried out to find out whether similar destruction efficiency can be obtained for adjusted pH.

With respect to destruction efficiency, good results of about 90% sulpholane conversion and 80% COD reduction were obtained at 370°C, for 100% of H_2O_2 as presented in figure 3.35. A plateau is rapidly reached within 20 s, and close values of conversion and COD reduction suggest that almost all the intermediates from sulpholane oxidation were converted to gaseous products.

Sulpholane was found to be more refractory than phenol, p-nitrophenol and aniline, however the destruction of intermediates, measured by the comparison of the conversion of sulpholane and COD, seems better than for p-nitrophenol and aniline.

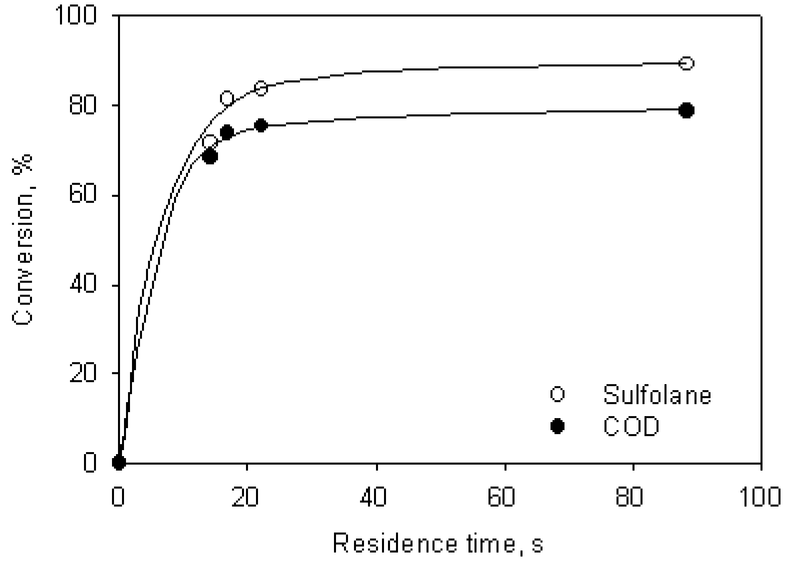


Figure 3.35: Sulfolane and COD conversion as a function of residence time, T=370°C, P=150bar, $C_{SUL,0}$=5g/l, $C_{H2O2,0}$=100%, pH_0=6.15.

3.2.4.4. Nitrobenzene

Literature data (Chen et al., 2001) indicate that nitrobenzene is a very recalcitrant compound. At conditions of standard WPO (150 bar, and 370°C), conversion and COD reduction are greatly enhanced compared to CWAO, although they are still far from being satisfactory (see figure 3.36 and 3.37). Temperature had to be strongly incremented up to 550°C to obtain better performance in nitrobenzene WPO (figure 3. 36 and 3.37). In figure 3.36 it can be seen that at 370°C the conversion reached is less than 30%, at 500°C it increased to about 55%, and at highest sand bath temperature of 550°C it reached 80%.

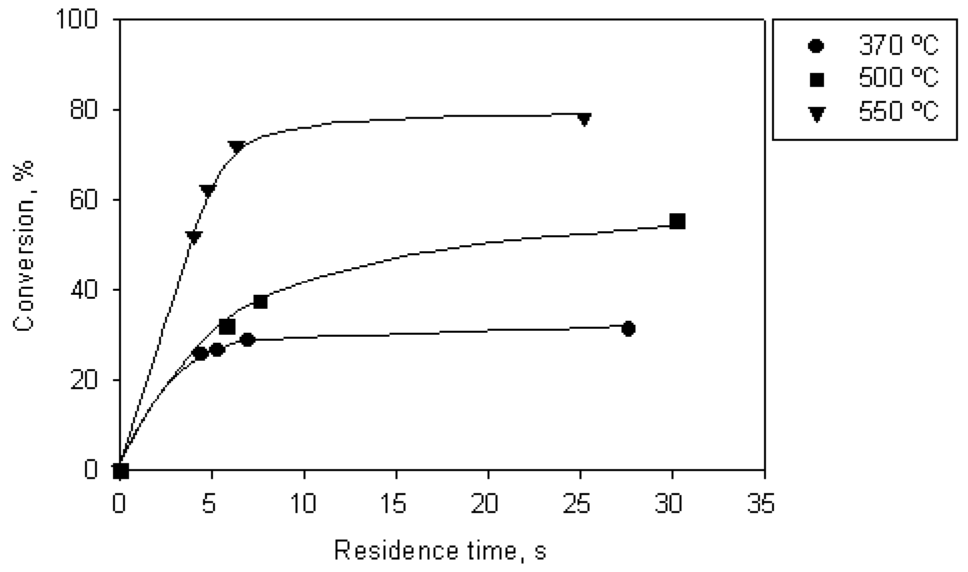


Figure 3.36: Nitrobenzene conversion versus residence time in WPO at different temperatures, P=150bar, $C_{NB,0}$=2g/l, $C_{H2O2,0}$=100%.

Similar behaviour was observed for COD destruction, shown in figure 3.37. At 370°C, COD reduction is only about 20%, at 500°C it increases to about 45% and at 550°C it reaches a plateau of about 65%.

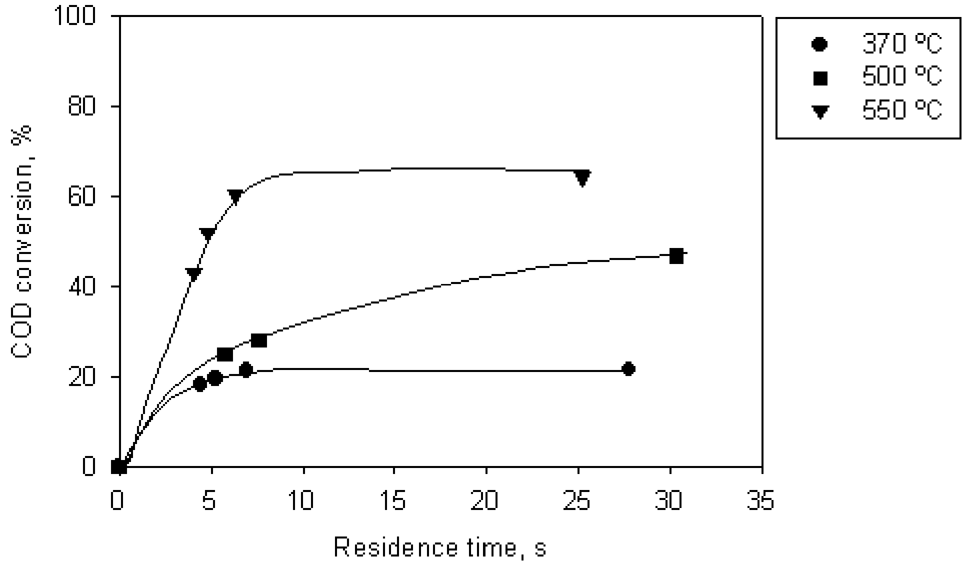


Figure 3.37: COD conversion versus residence time in WPO of nitrobenzene at different temperatures, P=150bar, $C_{NB,0}$=2g/l, $C_{H2O2,0}$=100%.

It is interesting to note that, the residence time needed to reach a stable nitrobenzene or COD conversion seems to be about 10 s, for 370 and 550ºC, while for 500ºC neither nitrobenzene nor COD conversion reaches plateau even at 30 s. Our results of nitrobenzene WPO confirms that nitrobenzene is a very refractory compound and needs for its destruction very high temperature (and pressure) even in the presence of strong H_2O_2 oxidant.

3.2.5. Overview

Preliminary WPO experiments with the reference pollutant phenol, verified that the runs are reproducible with low analytical error and that hydrolysis plays a negligible role in phenol decomposition in the conditions of temperature and pressure selected.

The important operating parameters of phenol WPO are the hydrogen peroxide feeding manner, H_2O_2 concentration and reaction temperature. Optimal H_2O_2 feeding consists in mixing phenol and H_2O_2, prior to preheating of reactants in the sand bath. In this way, hydroxyl radicals that form during the preheating before entering the reactor, immediately can attack the organic pollutant leading to higher destruction efficiency. Temperature, H_2O_2 concentration and residence time increase greatly enhance phenol and COD conversion. The effect of residence time is more marked for short initial period, the conversion quickly reaching a plateau. In the pressure range studied, pressure affects the gaseous reaction medium by changing drastically density that, on the other hand, results in a considerable variation of the residence time. As long as the reaction takes place in the liquid phase, little influence of pressure on performance was observed. So the maximum pressure needed is just little above vapour pressure of water at the given reaction temperature, to keep the reaction media in the liquid phase.

Standard reaction conditions that ensure high phenol and COD conversion could be established and were applied to the WPO of the more recalcitrant pollutants. For phenol, p-nitrophenol and aniline, conversion was found to be almost complete for temperatures ranging from 300 to 370ºC. Nitrobenzene resulted to be the most refractory to oxidation, a temperature as high as 550ºC being necessary to convert 80% of nitrobenzene. Values of COD reduction in the range of 65-83% were not too different from conversion values (except for aniline below 370ºC). The original organics and liquid intermediates were essentially converted to gaseous products. Additionally, the residence time necessary for highest oxidation of all the compounds was very short about 20 s, except for aniline, reaching values of 80 s at 250-300ºC. During sulpholane WPO experiments, severe corrosion problems occurred due to the formation of sulphuric acid. A possible solution could be a basic pH adjustment. However, it has to be verified experimentally, whether similar performance can be obtained under such conditions.

Phenol, p-nitrophenol, nitrobenzene, aniline and sulfolane WPO experiments showed a following reactivity order: phenol > p-nitrophenol > aniline > sulpholane > nitrobenzene. The fast reaction rate of WPO is due to the strong liquid oxidant used additionally eliminating oxygen mass transfer from the gas phase to the liquid phase.

The performance of WPO is significantly better than that of CWAO, for p-nitrophenol, aniline, sulpholane and nitrobenzene. During CWAO over AC 9, 8, 2 and 0, respectively, to WPO conversion of these compounds of ~100, ~100, 90 and 80%, respectively are performed. Additionally, our results showed that the residence time can be shorten from ~440 s for CWAO to ~50 s (for WPO). WPO is a good alternative to treat refractory organic pollutants that cannot be efficiently destroyed by CWAO.

3.3. Fenton promoted Wet Peroxide Oxidation of refractory pollutants

The performance of WPO can be increased by addition of small amounts of ferric catalyst termed Fenton catalyst. Fenton WPO is a well known process, but mostly applied in batch reactors and at ambient or slightly higher temperature. Continuous Fenton WPO experiments were carried out, to test whether pressure and temperature of pure WPO could be reduced for the refractory pollutants, especially in the case of nitrobenzene. As for WPO, first experiments with phenol were done to assess the influence of operating variables on process performance and to preselect convenient reaction conditions that enhance phenol degradation. Important variables of the Fenton process studied are pH value, ferrous catalyst concentration, temperature, pressure and residence time. The predetermined 'best' conditions obtained for phenol were tested to perform oxidation of aniline, p-nitrophenol and nitrobenzene. All experiments were conducted in the high temperature-high pressure equipment with separate feed lines (organic + Fe^{2+} line and H_2O_2 oxidant line), which were joined before entering in the sand bath, resulting in a total reactor of 8.2 m.

3.3.1. Influence of operating variables

First, the effect of Fe^{2+} concentration on both phenol destruction and H_2O_2 decomposition was studied. Then, initial pH value of solution, reaction temperature and pressure were investigated with a given Fe^{2+} concentration.

3.3.1.1. Effect of Fe^{2+} on phenol conversion and H_2O_2 decomposition

The range of concentration of Fe^{2+} was chosen based on literature data that recommends certain ratio of H_2O_2:Fe^{2+}=50-725:1 or substrate:Fe^{2+}=4-71:1. A minimum quantity of Fe^{2+} (10-15 mg/l) to have catalytic effect is also reported in literature. Environmental release limit of 10 mg/l for Fe^{2+} in wastewater was selected as a starting value. Phenol and Fe^{2+} were premixed with hydrogen peroxide before experiments to check whether there is any colour change and/or precipitation, but there were no significant changes in the solution. The influence of quantity of ferrous salt on phenol conversion was verified during the experiments adding 0, 10, 20 or 40 mg/l of ferrous sulphate as a homogeneous catalyst. Operating conditions were set to 100°C, 10 bar and initial concentrations of phenol and H_2O_2 of 5 g/l and 100% of stoichiometric demand, respectively. The obtained results are presented in figures 3.38 and 3.39. Phenol conversion was found to strongly depend on quantity of Fe^{2+} added, as shown in fig. 3.38. For the highest $FeSO_4$ concentration of 40 mg/l added, phenol conversion at residence time of 150 s is significantly higher (~90%) than for 20 mg/l (~65%), and 10 mg/l (~30%). However, the enhancement of conversion is even more marked between pure phenol WPO and 10 mg/l of Fe^{2+}, performing only 10% without Fe^{2+} and respectable 30% with Fe^{2+} at residence time of 150 s. Due to lower temperatures of 100°C, phenol conversion is steadily rising with increasing residence time, and no plateau is reached in the studied range of residence times of 0 to 250 s as was in WPO.

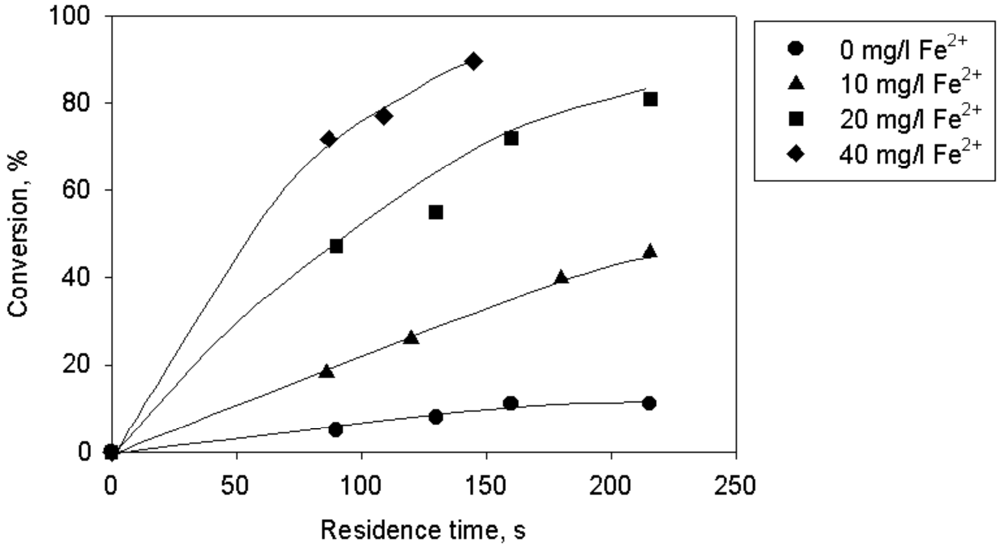


Figure 3.38: Evolution of phenol conversion during Fenton WPO for different Fe^{2+} concentrations, T=100°C, P=10bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, pH_0=4.90.

Similarly, COD reduction (fig. 3.39) is enhanced with higher quantity of iron added, but differences exist, when compared to WPO of phenol. COD reduction values are quite below phenol conversion values. An important quantity of the intermediates formed persist in the liquid phase due to formation of carboxylic acids that are quite refractory to oxidation at 100°C. Also, for 40 mg/l Fe^{2+}, COD reduction curve is reaching a plateau at about 100 s, conversely to phenol conversion. The progress of COD conversion is less rapid than that of phenol conversion suggesting that phenol is rapidly oxidised to ring opening products (carboxylic acids), that are much more refractory. It is important to remark that phenol oxidation proceeds via free radical mechanism, with free radicals being formed by Fe^{2+}. While, carboxylic acids oxidation implies also redox mechanism, but goes not only via free radical mechanism.

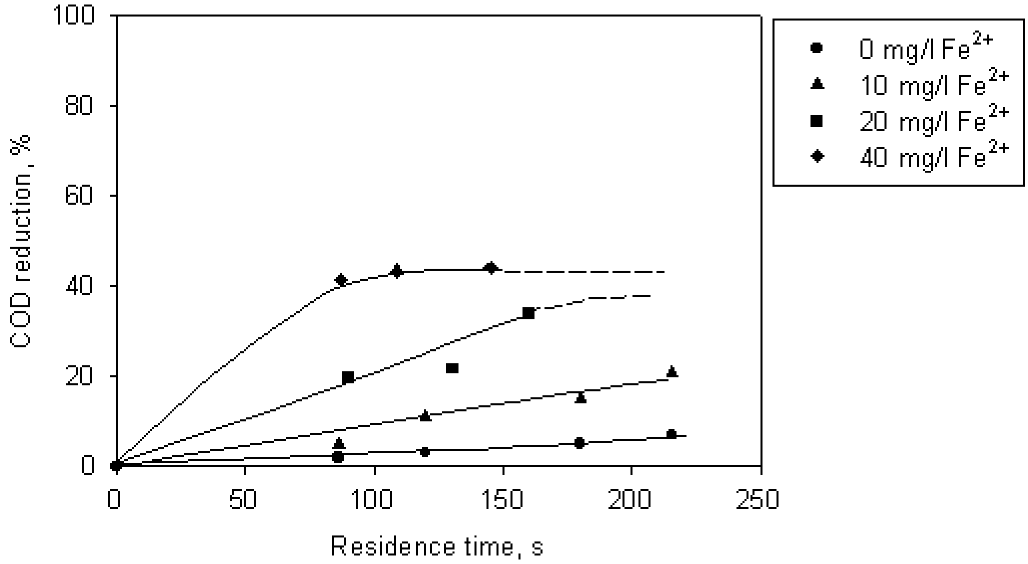


Figure 3.39: Evolution of COD conversion during Fenton WPO of phenol for different concentrations of Fe^{2+}, T=100°C, P=10bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, pH_0=4.90.

The pH evolution supports the rapid destruction of phenol and the subsequent formation and slow destruction of carboxylic acids. pH trends, shown in figure 3.40, are quite similar for all cases. A sharp decrease at small residence time is produced by phenol destruction and acids formation, then pH stabilises after a residence time of 90 s at values of 2.5 for 20 or 40 mg/l of Fe^{2+}, 3 for 10 mg/l and about 3.7 without Fe^{2+}. The difference in pH evidently means that more stable carboxylic acids are formed from the oxidation of phenol.

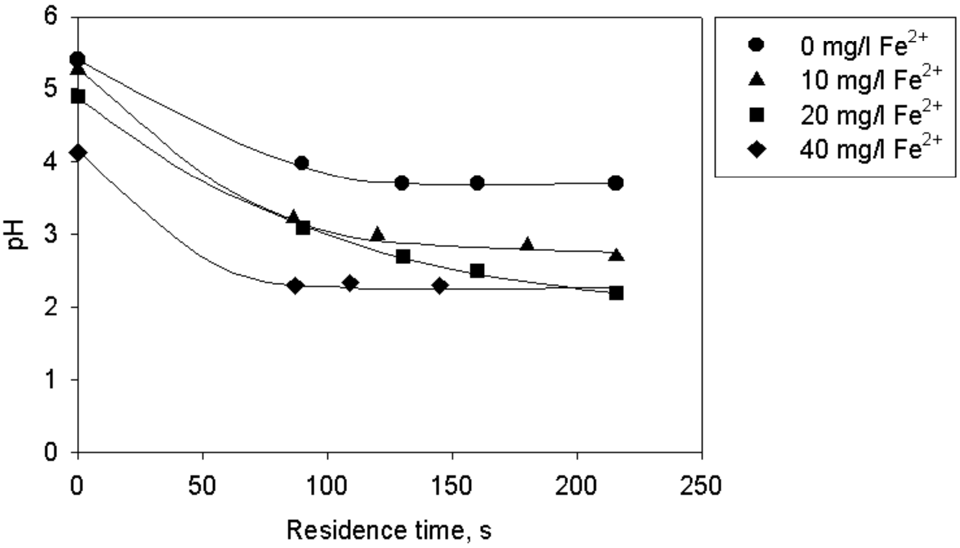


Figure 3.40: pH evolution during Fenton WPO of phenol for different concentrations of Fe^{2+}, T=100°C, P=10bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, pH_0=4.90.

The observed trends in phenol oxidation with different Fe^{2+} concentrations can be closely related to the decomposition of H_2O_2 in presence of Fe^{2+} ions. Figure 3.41 present (a) thermal and (b) thermal Fe^{2+} catalysed decomposition of hydrogen peroxide. From this figure, it can be seen that for all temperatures studied (50-200°C), H_2O_2 decomposition is greatly enhanced in presence of iron (Fe^{2+} catalyst). For example, at residence time of 100 s for 50, 100, 150 and 200°C no catalysed H_2O_2 decomposition reaches 0, 25, 57 and 95%, respectively, while it is 3, 50, 95 and 100% for Fe^{2+} catalysed decomposition. As a consequence the phenol conversion and COD reduction can be significantly increased in Fenton WPO at lower temperature (~100-200°C). Increase of temperature should substantially increase process performance as hydrogen peroxide decomposition becomes complete in both cases (thermal and Fe^{2+} catalysed) (see figure 3.41).

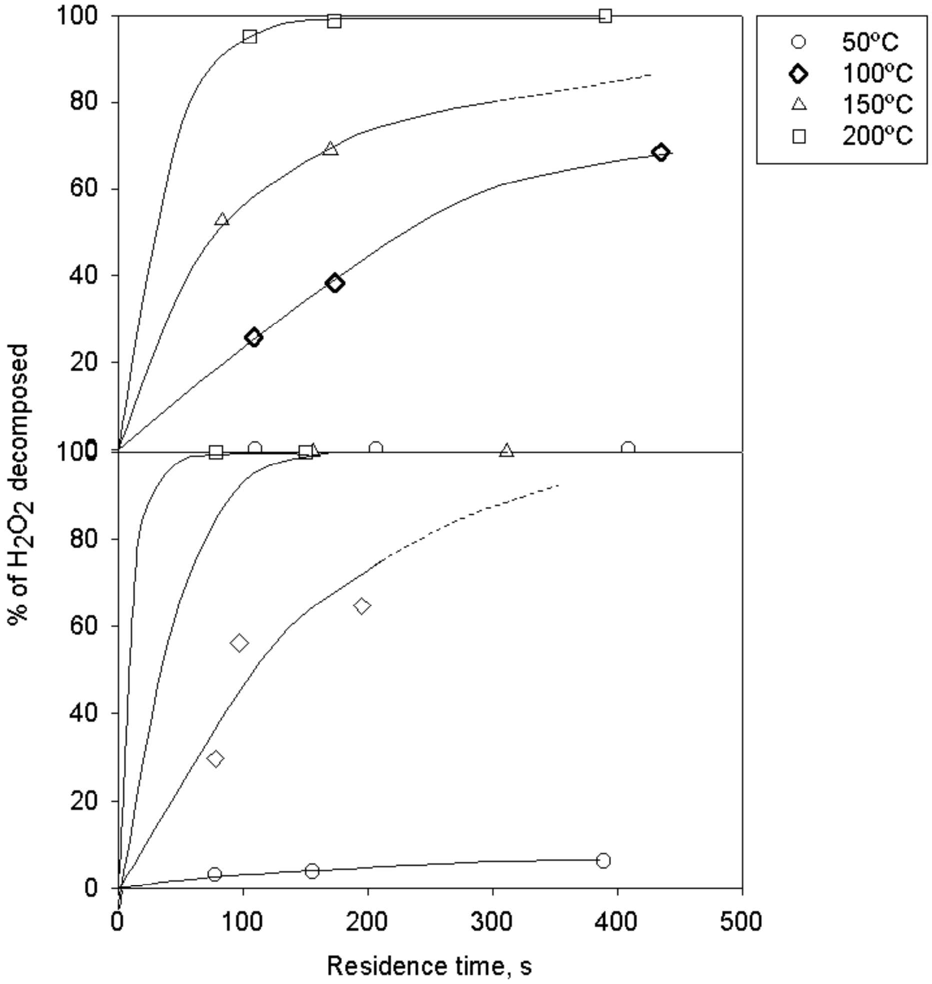


Figure 3.41: Thermal hydrogen peroxide decomposition at different temperatures; a) without Fe^{2+} catalyst, b) with 20 mg/l of Fe^{2+} catalyst; P=20bar, $C_{H2O2,0}$=0.74.mol/l.

3.3.1.2. Effect of initial pH

During wet peroxide oxidation processes, the pH value of wastewater has a significant impact on the stability of hydrogen peroxide oxidant (Rivas et al., 1999).

As reported by Rivas et al. (1999) alkaline pH promotes hydrogen peroxide decomposition to oxygen and water, diminishing the amount of oxidant available for H_2O_2 decomposition to hydroxyl radicals. In addition, the ionic form of hydrogen peroxide present in the alkaline solution exhibits a higher scavenging power of hydroxyl radicals.

The promoting effect of acidic pH on hydrogen peroxide decomposition to hydroxyl radicals was observed by Neyens and Bayens (2003). This was already suggested by Walling (1975) that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals.

Phenol conversion in CWAO is known to depend on initial pH. Sadana and Katzer (1974a) found a maximum oxidation rate for phenol at pH of about 4, and Debellefontaine et al. (1996) reported optimal pH value in the range of 2.5 to 4. In the degradation of many aromatic pollutants, it is generally observed that the efficiency of Fenton systems decreases with increasing pH (Solvay, 2001). It was suggested that $^{\bullet}OH$ radicals are formed only at low pH of 3-5. Upon decreasing or increasing the initial pH of the solution below 3 or above 6, the rate of hydrogen peroxide decomposition to water and oxygen increased due to partial transformation of iron to other species catalysing this reaction. For example, at pH values higher than about 5.5 the precipitation of iron-hydroxide starts to occur and this leads to an enhanced rate of hydrogen peroxide decomposition (Neyens & Baeyens, 2003). Thus only a narrow range of pH values is useful for Fenton WPO (Centi et al 2000; Bham & Chambers, 1997).

Phenol oxidation experiments were conducted for pH values in the range of 3.2 to 4.9, at 100°C, 10 bar, initial concentrations of phenol, ferrous sulphate and hydrogen peroxide of 5 g/l, 20 mg/l and 100% of stoichiometric demand, respectively. Initial pH for 3.20 and 4.13 was adjusted with sulphuric acid, while experiments with pH_0 of 4.90 were done without pH adjusting. The results obtained are shown in figures 3.42 to 3.44. At shorter residence time, the lower is the initial pH the higher are both the phenol conversion and COD removal. At higher residence time, final phenol conversion levels off and is quite similar for all initial pH values. The faster oxidation rate for lower initial pH could be due to a more rapid decomposition of hydrogen peroxide to hydroxyl radicals at lower pH.

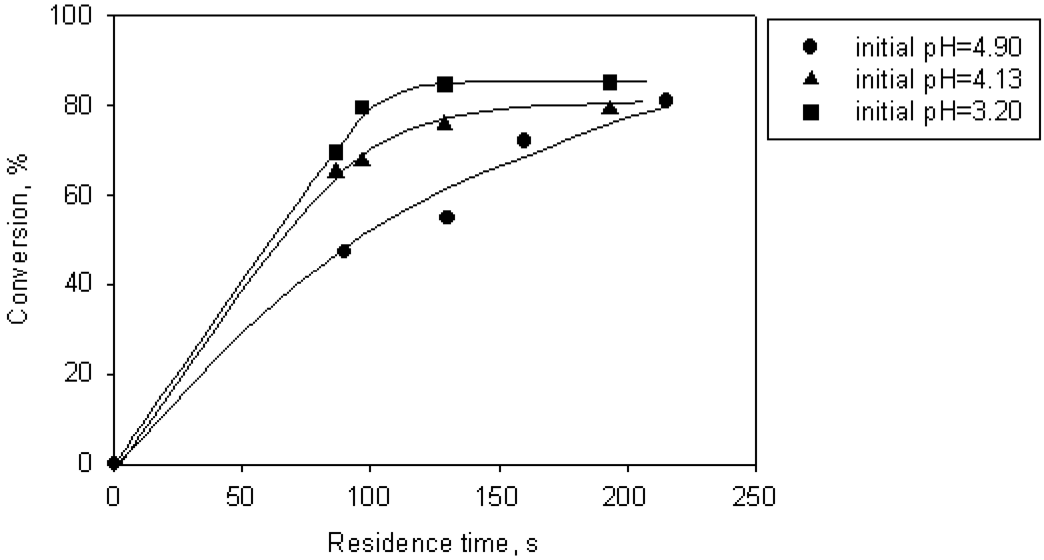


Figure 3.42: Variation of phenol conversion during Fenton WPO at different initial pH, T=100°C, P=10 bar, $C_{PhOH,0}$=5g/l,$C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l.

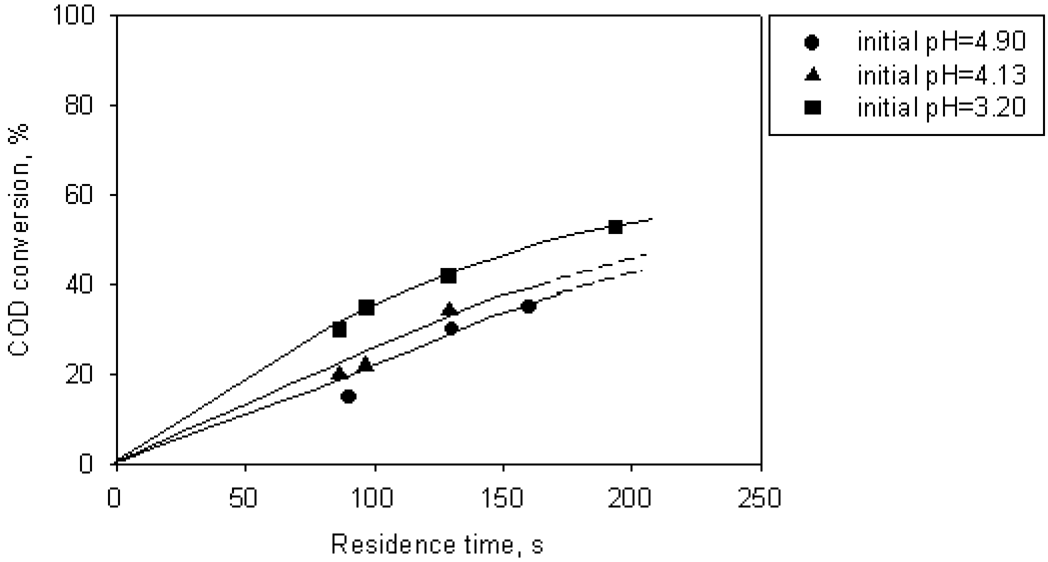


Figure 3.43: COD conversion during Fenton WPO of phenol at different initial pH, T=100°C, P=10 bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l.

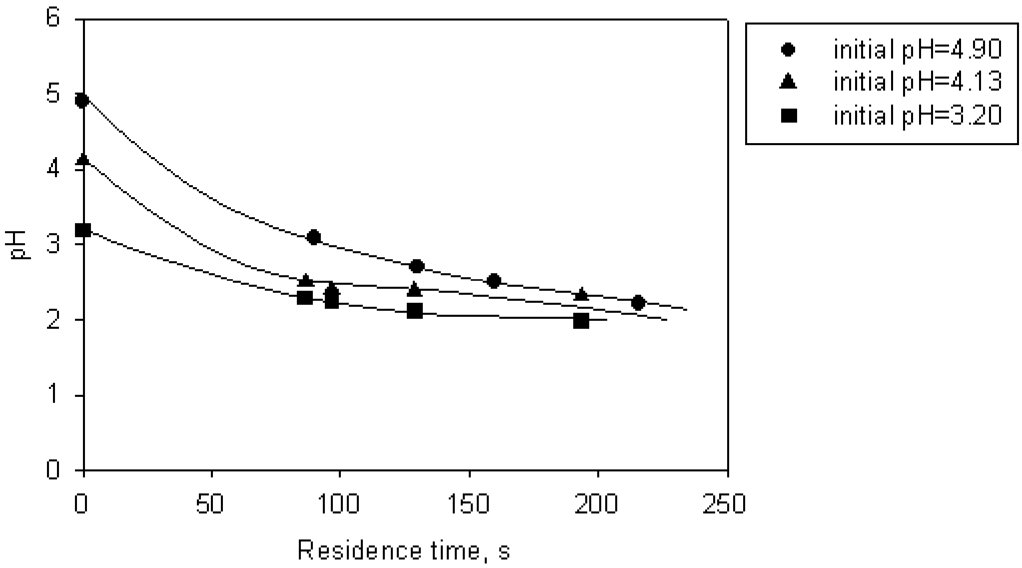


Figure 3.44: pH evolution during Fenton WPO of phenol at different initial pH, T=100°C, P=10 bar, $C_{PhOH,0}$=5g/l, $[H_2O_2]_0$=100%, $[Fe^{2+}]_0$=20mg/l.

Low pH adjusted to about 3 was found to enhance phenol conversion at small residence time, then levelling off to conversion at higher residence time, similar to those achieved for not adjusted initial pH. During Fenton WPO, pH can drop down to values as low as 2 (see figure 3.44). The acceleration performed at adjusted pH of 3 is partially set off by severe corrosive conditions that can affect the choice and stability of reactor material. Although, temperatures are lower compared to WPO conditions what should help to reduce the severity of corrosion.

3.3.1.3. Temperature effect

In order to reach higher process performance, temperature increase is very effective, as H_2O_2 decomposition becomes complete above 150°C and residence times below 100 s (see figure 3.41b). The effect of temperature was examined over a range of 25 to 200°C, at 10 bar (20 bar at 200°C), 5 g/l of phenol, 20 mg/l of ferrous sulphate and 100% of hydrogen peroxide inlet concentrations. The results of conversion and intermediates peak area obtained are given in figures

3.45 and 3.46, respectively. At 25 °C, no phenol destruction was detected. Increasing the temperature, figures 3.45 and 3.46 confirm a strong increase of phenol conversion as well as intermediates peak area. At temperatures of 50 to 200°C conversion improves from about 10% to almost 100% for a residence time of 100 s.

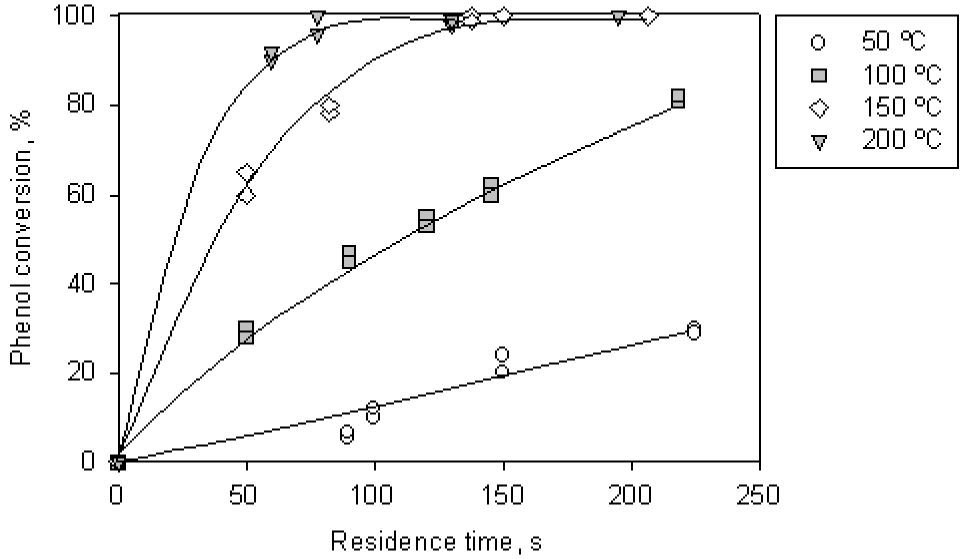


Figure 3.45: Phenol conversion during Fenton WPO at different temperatures, P=10-20 bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=4.90.

As far as intermediates peak area is concerned, its continuous growth at lower temperatures indicate the enhanced formation of intermediates from phenol oxidation (see figure 3.45). At 150°C, the area steeply increases to reach a maximum at about 60 s of residence time and then starts to decrease at higher residence time. The rates of intermediate destruction start to dominate over the rates of formation. At 200°C finally the area of intermediates is always very close to 0 for all residence times applied (fig. 3.46). Intermediates formed are immediately destroyed and do not have the time to accumulate in the liquid phase. At this temperature phenol can be completely mineralised to CO_2 and H_2O within 80 to 100 s of residence times.

Additionally, the samples colour is changing with increase in both temperature and residence time from brown to almost transparent. And the foam formation is more intense at higher temperature and residence time due to a stronger formation of CO_2.

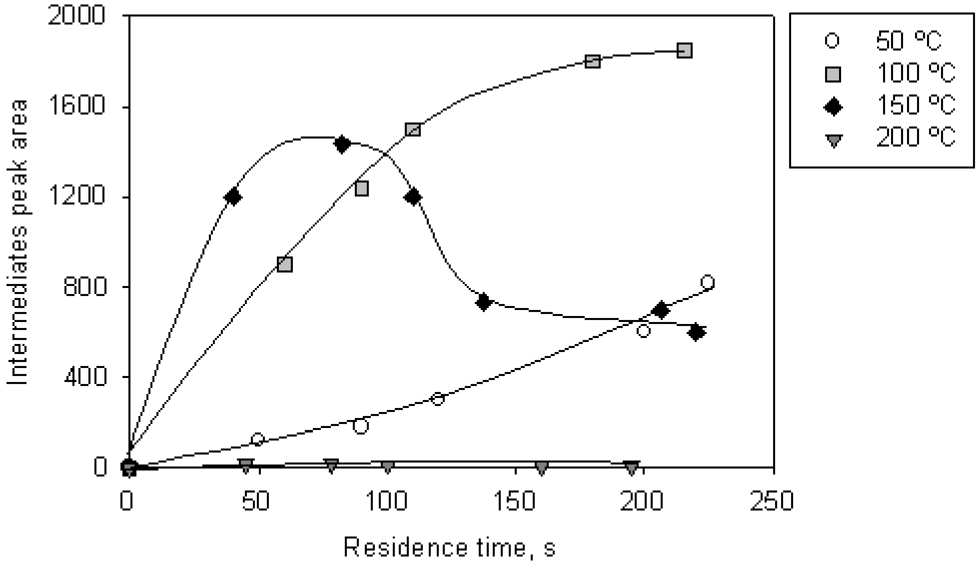


Figure 3.46: Area of intermediates peak during Fenton WPO at different temperatures, P=10-20 bar, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=4.90.

3.3.1.4. Pressure effect

Finally, to study the effect of pressure, experiments at 10, 20 and 30 bar and 100°C, phenol concentration of 5 g/l, ferrous sulphate of 20 mg/l and hydrogen peroxide of 100% of stoichiometric demand were performed. The results are shown in figure 3.47. A starting pressure of 10 bar was selected to maintain the reaction medium in the liquid phase and particularly to ensure the correct functioning of the of back-pressure regulator.

In figure 3.47 it can be noted that in the range of 10-30 bar, pressure change affects slightly positively the phenol conversion. At a residence time of 220 s conversions reaches 80% for 10 bar and about 85-87% for 20 and 30 bar. This small process improvement with pressure increase is probably due to increased solubility of unreacted oxygen formed from H_2O_2 decomposition. The optimal working pressure should be that corresponding to the vapour pressure of water at the given reaction temperature.

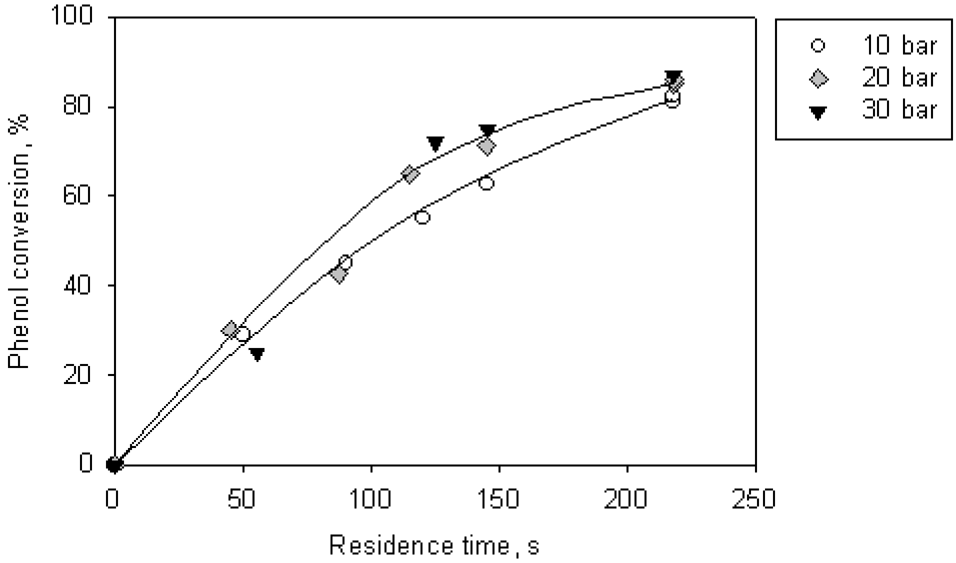


Figure 3.47: Variation of phenol conversion during Fenton WPO for different pressures, T=100°C, $C_{PhOH,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=4.90.

3.3.2. Fenton Wet Peroxide Oxidation of refractory pollutants

Previous results obtained with Fenton WPO of phenol allowed establishing convenient operating conditions to perform experiments with p-nitrophenol, aniline and nitrobenzene, in particular a temperature of 200ºC and 20 mg/l of $FeSO_4$ to ensure complete H_2O_2 decomposition. The initial pH value was adjusted to 3 wit sulphuric acid. Experiments were conducted in the same high pressure – high temperature equipment. Prior to each experiment, organic pollutant, Fe^{2+}at 20 mg/l and H_2O_2 were premixed as done for phenol to detect any colour change and complexation reaction.

3.3.2.1. p-Nitrophenol

The results for Fenton WPO at 200ºC, 20 bar, 5 g/l of p-nitrophenol, 20 mg/l of ferrous sulphate and 100% of hydrogen peroxide initial concentrations are plotted in figure 3.48.

A residence time about 90 s is required to reach the p-nitrophenol and COD conversion plateau and the intermediates peak area reached a maximum. The p-nitrophenol conversion was almost complete and COD reduction was about 85%. Unlike the phenol Fenton WPO, the intermediates peak area values were not close to zero and showed a maximum with residence time. At higher residence time, the area goes down although p-nitrophenol and COD conversions remain stable, indicating the presence of small amounts of stable intermediates.

The colour of the effluent confirmed this situation. Liquid samples withdrawn showed a brown-yellow colour, and a repellent odour different from that of p-nitrophenol was noted at higher residence time.

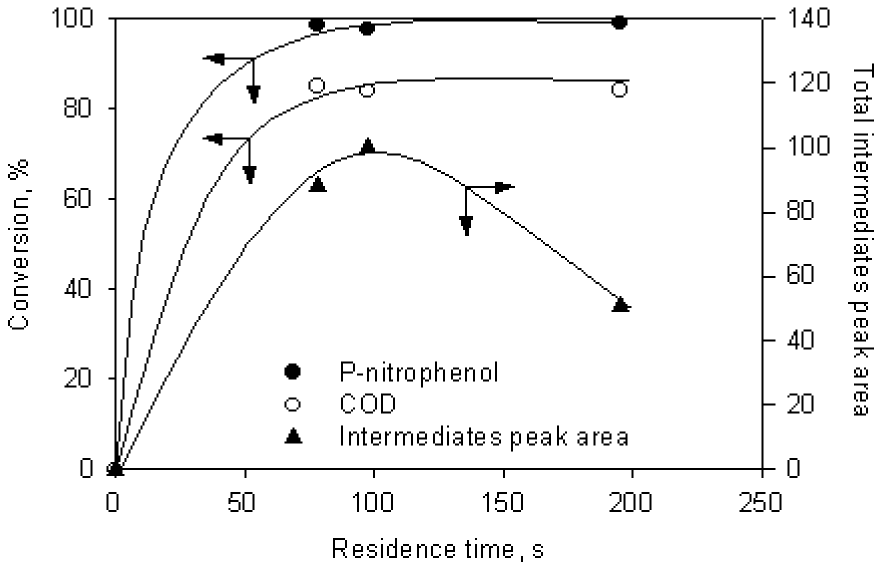


Figure 3.48: P-nitrophenol and COD conversion and area of intermediates peak during Fenton WPO at T=200°C, P=20 bar, $C_{NP,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=3.

3.3.2.2. Aniline

The conversion of aniline at 200°C, 20 bar, 5 g/l of aniline, 20 mg/l of ferrous sulphate, 100% of hydrogen peroxide initial concentrations and initial pH adjusted to 3 was complete and COD reduction was over 90%, as presented in figure 3.49.

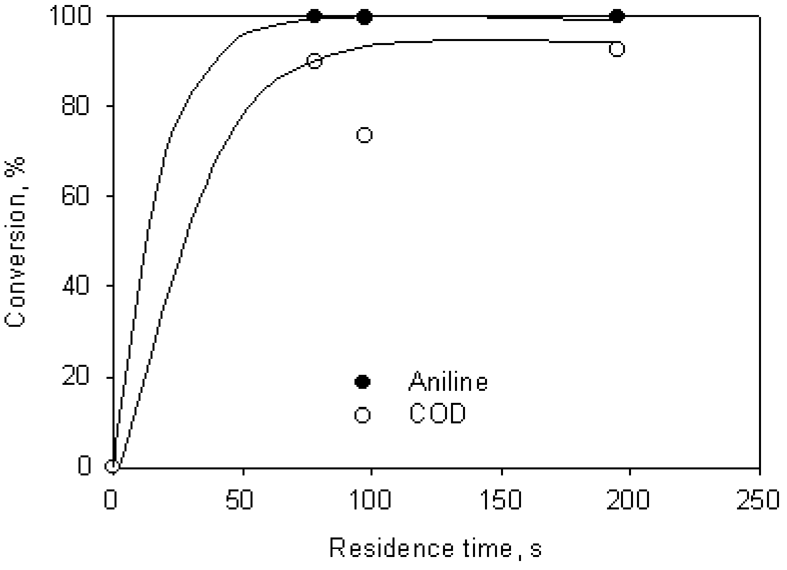


Figure 3.49: Aniline and COD conversion during Fenton WPO at T=200°C, P=20bar, $C_{AN,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=3 (adjusted).

The pH of solution has a more or less constant value of 3 during the experiment and intermediates seem to reach a maximum, but absolute values are very small (figure 3.50). The pH being constant, no acid accumulation should take place in the liquid phase. So it suggests that most of aniline is converted to CO_2 and water. This result is positive, because corrosion at least is not enhanced during the reaction by decreasing pH of solution.

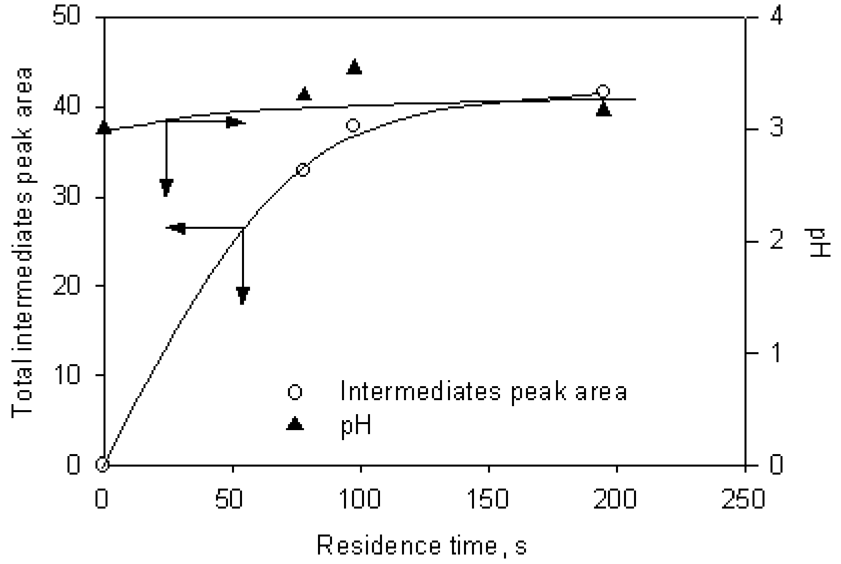


Figure 3.50: Intermediates peak area and pH during Fenton WPO of aniline at T=200°C, P=20bar, $C_{AN,0}$=5g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=3 (adjusted).

However, during the experiment reactor plugging occurred after a few hours of operation. Probably, aniline formed insoluble complexes with $FeSO_4$ that precipitated and led to reactor plugging. Evidence of precipitation was inferred from the mixing tests at 25°C, as the colour changed and solution turned turbid. Similar, the effluent odour was repellent with a yellow oily colour.

3.3.2.3. Nitrobenzene

The results for Fenton WPO at 200°C, 20 bar, 2 g/l of nitrobenzene, 20 mg/l of ferrous sulphate and 100% of hydrogen peroxide initial concentrations and initial pH adjusted to 4 are presented in figure 3.51. The conversion obtained was about 70%. This is an excellent result, taking into account that without ferrous ions 550°C was needed to obtain 80% of conversion. Additionally, the 65% of COD conversion observed is very close to the nitrobenzene conversion. Almost all nitrobenzene was converted to gas in only about 80 s of residence time. The pH of solution, as for aniline, shows a quite constant value of about 4. Again the reactor effluent colour was brownish having the odour of almonds of nitrobenzene.

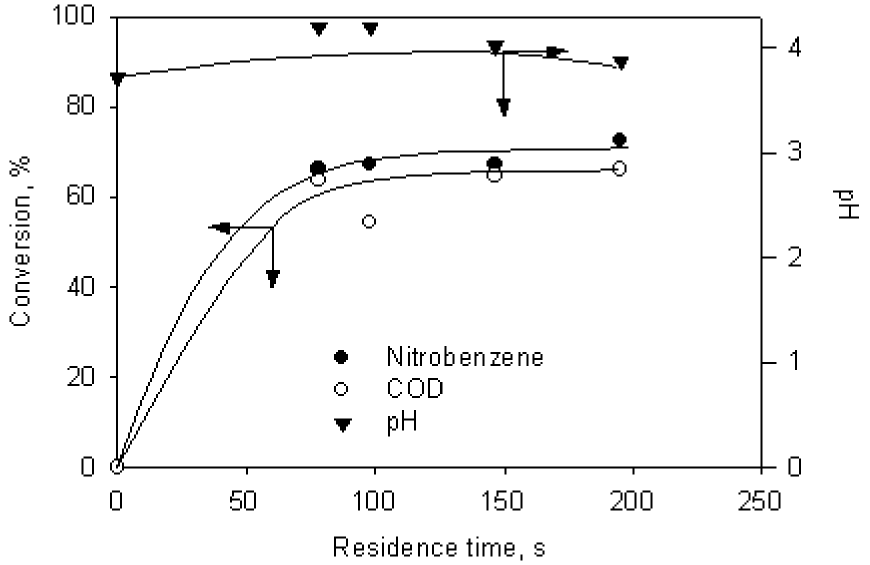


Figure 3.51: Nitrobenzene and COD conversion and pH evolution during Fenton WPO at T=200°C, $C_{NB,0}$=2g/l, $C_{H2O2,0}$=100%, $C_{Fe2+,0}$=20mg/l, pH_0=4.

3.3.3. Overview

Experiments confirmed that hydrogen peroxide decomposition is significantly catalysed by ferrous ions. Reaction temperature and initial ferrous sulphate concentration have a strong influence on Fenton WPO of phenol. Increase in temperature and Fe^{2+} concentration enhances both phenol and COD destruction. Pressure change had only a negligible effect on phenol oxidation. Adjusting pH in the range of 3.20-4.90 resulted in similar phenol conversion and COD destruction at high residence time, but the rate of reaction at low residence time was found to be considerably faster at smaller pH.

All the compounds studied gave almost complete conversion (except for nitrobenzene ≈ 70%) and close COD conversion values indicating an advanced degree of mineralisation of the initial reactant. The order of reactivity for Fenton WPO was phenol=aniline > p-nitrophenol > nitrobenzene. Rapid reactor plugging could not be avoided during aniline oxidation invalidating the apparent good results obtained for Fenton promoted WPO of aniline. Another striking result is the performed nitrobenzene conversion of 70% at 200ºC and 20 bar in presence of 20 mg/l ferrous sulphate. WPO alone required a temperature of 550ºC and 150 bar to obtain 80% of conversion. A strong reduction of temperature and pressure is achieved and Fenton promoted WPO appears to be very attractive for the abatement of nitrobenzene containing effluents.

3.4. Conclusions

Mild CWAO over activated carbon proved to exhibit good destruction efficiencies for organic pollutants including phenol, m-xylene, o-chlorophenol and o-cresol. Very poor pollutant degradation was observed for nitrogen and sulphur containing molecules such as p-nitrophenol, aniline, nitrobenzene and sulpholane. Compounds refractory to CWAO over AC and phenol, as a reference compound, were thus subjected to diverse oxidation techniques, using H_2O_2 oxidant such as H_2O_2 promoted CWAO over AC, WPO and Fenton WPO.

Numerous experiments showed that the removal of the organic pollutants depends on the operating conditions and nature of the organic compound. The best results obtained and the operating conditions used are summarised in table 3.4.

Phenol gave good results with all methods studied. If the ultimate treatment objective aims not at the complete phenol mineralisation, H_2O_2 promoted

CWAO is recommended over Fenton WPO as reaction conditions are slightly milder and no additional step of catalyst removal is required.

Refractory p-nitrophenol showed almost complete conversion and comparable COD removal with WPO and Fenton WPO treatment. Fenton WPO could be chosen for p-nitrophenol to reduce WPO temperature and pressure including a posterior step of catalyst removal.

Aniline oxidation resulted in rapid reactor plugging during catalytic oxidation methods tested (H_2O_2 promoted CWAO and Fenton). Thus, WPO of aniline is the most appropriate technique. At temperature of 370°C and residence time of only 30 s, the conversion of aniline is complete and COD removal is close to 80%.

WPO of nitrobenzene gave only satisfactory conversion at temperatures as high as 550°C. The use of small amounts of homogeneous Fenton catalyst (20 mg/l) resulted in comparable compound and COD destruction at significantly lower temperature of 200°C. Lower operation and investment costs associated with mild conditions make Fenton WPO an attractive method for effective nitrobenzene removal.

Very refractory sulfolane oxidation was only studied by WPO performing high conversion and high COD reduction. The release of sulphuric acid, however, generated pH values < 1 and corrosion of highly resistant Hastelloy material.

The diverse techniques studies performed satisfactory results, and there exists at least one method for effective abatement of each pollutant. Further research should be focussed to find optimal conditions for each treatment depending on the refractoriness of the organic pollutants. Corrosion of material and possible solution has to be addressed, particularly for chlorine and sulphur containing compounds.

Long term tests of continuous operation as well as kinetic and reactor modelling are required to assess the potential of the diverse oxidation technique for its successful application and scale-up to pilot plant or industrial throughput.

Table 3.4: Operating conditions and best pollutants abatement obtained with the methods studied in this work.

MODEL COMPOUND ($C_{ORG,0}$)	**WPO**[1]					**FENTON WPO**[2]					**CWAO**				**H_2O_2 PROMOTED CWAO**					
	X (%)	X_{COD} (%)	T (ºC)	P (bar)	τ (s)	X (%)	X_{COD} (%)	T (ºC)	P (bar)	τ (s)	X (%)	T (ºC)	P (bar)	τ (s)	X (%)	X_{COD} (%)	H_2O_2 (%)	T (ºC)	P (bar)	τ (s)
Phenol (5 g/l)	~100	-	300	150	46	>99	-	150	20	130	43	140	48.5	440	92	75	20	170	25	60
p-Nitrophenol (5 g/l)	~100	85	300	150	30	>99	80	200	20	100	9	140	48.5	440	76	70	40	170	25	180
Aniline (5 g/l)[3]	~100	80	370	150	30	>99	90	200	20	100	8	140	48.5	440	92	80	10	170	25	215
Sulfolane (5 g/l)[4]	90	78	370	150	25	-	-	-	-	-	2	140	48.5	440	-	-	-	-	-	-
Nitrobenzene (2 g/l)	80	65	550	150	7	70	65	200	20	100	0	140	48.5	440	-	-	-	-	-	-

1. 100% of stoichiometric H_2O_2 quantity is used,
2. $[Fe^{2+}]$=20 mg/l and 100% of stoichiometric H_2O_2,
3. reactor plugging observed for Fenton WPO and H_2O_2 promoted CWAO,
4. corrosion problems detected (pH<1 due to the formation of H_2SO_4).

Chapter 4

Oxidation of real wastewater

Treatments techniques that proved to give good results for synthetic single component effluents should subsequently be tested on more complex industrial process wastewater. To this purpose, two industrial wastewater samples (TRI1 and TRI2) were provided by a local wastes treatment plant (TRATAMIENTOS Y RECUPERACIONES INDUSTRIALES, S.A.). The two samples come from the phenolic resins production. Sample TRI1 is characterised by about 1800 ppm of phenol and 5600 mgO_2/l of COD, while sample TRI2 contains only 36.5 ppm of phenol, but 97000 mgO_2/l of COD load. More details of the samples composition can be found in table 2.2 in chapter 2.

The goal was to test the four oxidation techniques (CWAO, H_2O_2 promoted CWAO, WPO and Fenton WPO) on these industrial samples under the same 'best' conditions as for pure pollutants. The results obtained allow then comparing the respective process performance of the different techniques when applied to synthetic or industrial effluents.

Before discussing the results, it should be mentioned that some problems occurred to correctly measure COD values. These problems were most probably due to the colorimeter failure. Continuous reactor operation was also affected by the slow formation of O_2 bubbles from H_2O_2 decomposition in the pump feed line. This played a minor role for low H_2O_2 concentrations. When treating the TRI2 sample with a high COD value of about 100 000 mgO_2/l (H_2O_2 concentration of 6.06 mol/l), pump cavitation occurred frequently and feed line had to be vented off. In an industrial application, this problem may easily be avoided by protecting the feed deposit (made of glass) and lines (made of transparent Teflon) from light contact and eventual cooling of the feed deposit and in particular the build-in of an automatic vent-off system in the feed line.

4.1. Unpromoted and H_2O_2 promoted Catalytic Wet Air Oxidation

First, the results of unpromoted CWAO and H_2O_2 promoted CWAO are presented. All runs were conducted in the high pressure-high temperature equipment using the catalytic reactor tube with an activated carbon load of about 0.7 g.

4.1.1. Catalytic Wet Air Oxidation of TRI1

CWAO experiments of TRI1 were carried out at standard conditions of 170ºC, 25 bar of total pressure (3.4 bar of O_2), 0.68 g of activated carbon and 0.011h of residence time. Typically for the CWAO process, phenol conversion, as presented in figure 4.1, was apparently complete during the first 50 min of experiment until saturation of the AC catalytic bed. Then, conversion was decreasing gradually, but at the same time the pressure measured at the reactor inlet started to increase (see figure 4.2) confirming reactor plugging. The experiment was stopped at 50 bar upstream pressure to open the catalytic reactor tube. A solid plug being difficult to remove was found at the reactor inlet.

After drying the catalyst (12 h at 120ºC), the weight of the activated carbon was found to be very close to the initial load (0.66 g as compared to 0.68 g of initial carbon weight), although a significant portion of the catalyst was lost during the removal procedure. The remaining granulates of the carbon were found to be a little bigger and more greyish after the experiment. These results support the formation of a solid plug inside the catalytic reactor tube. A possible explanation may be the presence of polymerisation and irreversible adsorption of condensation products formed on the activated carbon. Formation of such condensation products was already observed, but this never led to complete reactor plugging. The origin of the effluent (resin production) and its abnormal pH values of 8 indicate the presence of other compounds (see also figure 4.3) that are sought to strongly promote polymerisation reactions.

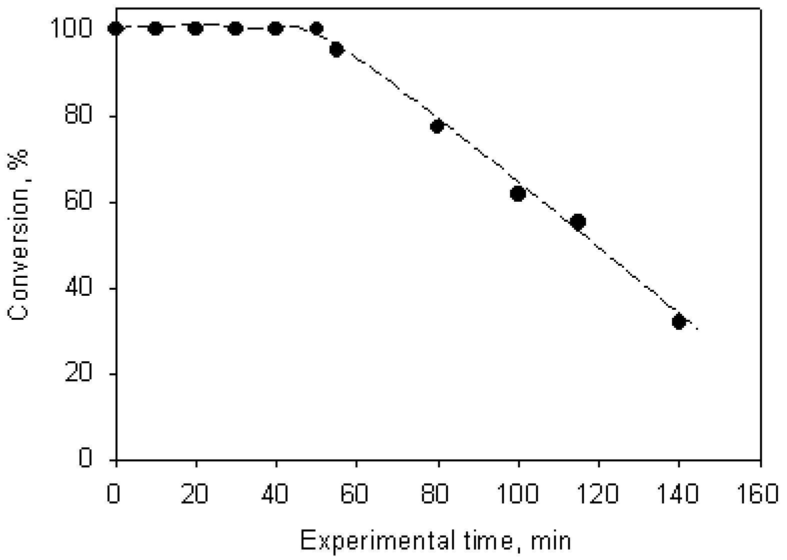


Figure 4.1: Phenol conversion versus experimental time during CWAO of TRI1, T=170°C, P=25bar, $C_{PhOh,0}$=1800 ppm, W_{AC}=0.68g, τ=0.011h and F_{air}=2.4 ml/s.

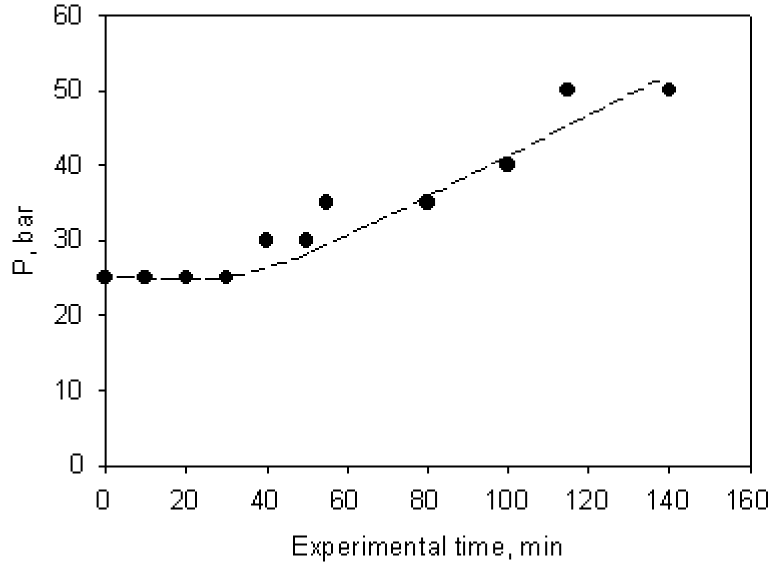


Figure 4.2: Reactor inlet pressure with experimental time during CWAO of TRI1, T=170°C, P=25bar, W_{AC}=0.68g, τ= 0.011h, F_{air}=2.4ml/s.

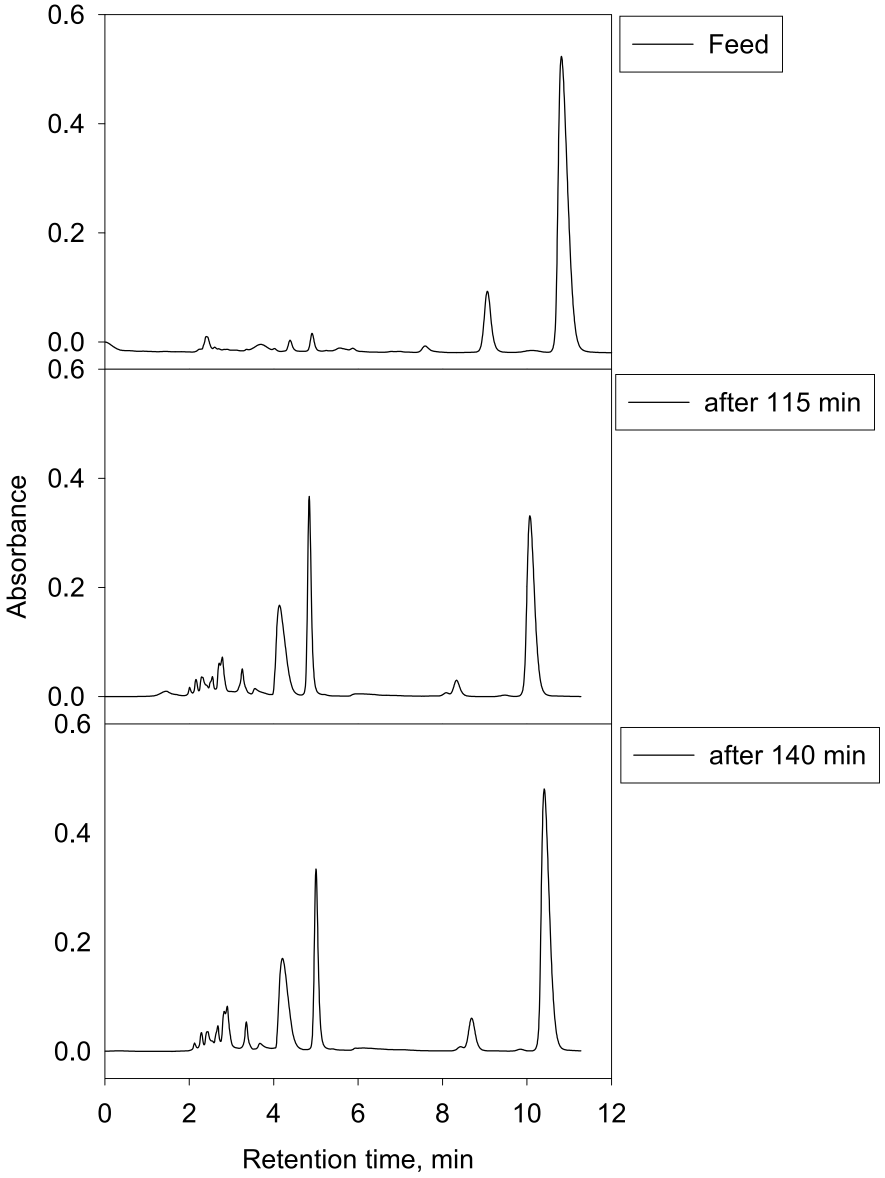


Figure 4.3: HPLC chromatograms versus experimental time for CWAO of TRI1, T=170°C, P=25bar, W_{AC}=0.68g, τ= 0.011h, F_{air}=2.4ml/s, $C_{PhOh,0}$=1800 ppm and $C_{COD,0}$=5600 mgO_2/l.

The results demonstrate that the sample TRI1 cannot be treated by CWAO over AC due to reactor plugging. Experiments of H_2O_2 promoted CWAO of TRI1 were directly discarded. Reactor plugging occurred very rapidly and it would be interesting to identify the responsible compounds of TRI1 sample that provoked this situation.

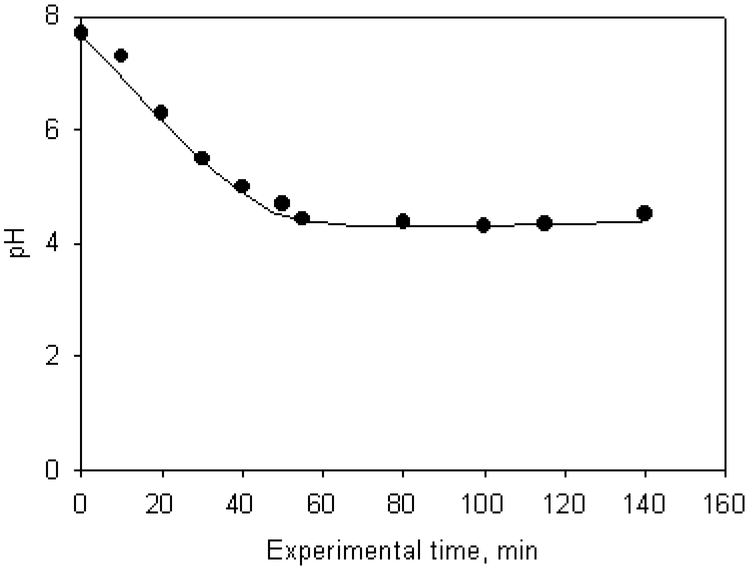


Figure 4.4: pH evolution during CWAO of TRI1; T=170°C, P=25bar, W_{AC}=0.68g, τ=0.011h, F_{air}=2.4ml/s and $C_{COD,0}$=5600 mgO_2/l.

4.1.2. Catalytic Wet Air Oxidation and H_2O_2 promoted CWAO of TRI2

Surprisingly, the TRI2 phenolic effluent, could be treated using pure CWAO and CWAO with 10 and 25% of stoichiometric quantity of hydrogen peroxide added (calculated on the basis of feed sample COD). The operating conditions fixed were T=170°C, P_{O2}=3.4bar, W_{AC}=0.68g, F_{air}=2.4ml/s, for a feed solution that contains 36.5 ppm of phenol and 97000 mgO_2/l of COD. No occurrence of reactor plugging was observed during CWAO of TRI2 over activated carbon. As can be seen in figure 4.5, phenol conversion rapidly stabilises to about 60% after the typical saturation period and conversion drop while reaching steady state of reaction and adsorption.

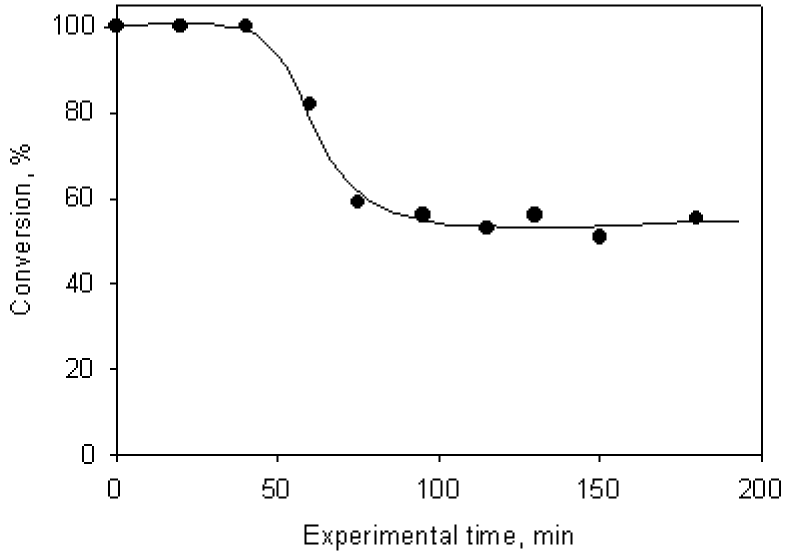


Figure 4.5: Phenol conversion reaching steady state during CWAO of TRI2, T=170°C, P=25 bar, W_{AC}=0.68g, F_{air}=2.4ml/s, $C_{COD,0}$=97000 mgO_2/l, τ=0.012h.

In the experiments, the residence time was varied from 0 to 0.04 h to obtain X-τ and X_{COD}-τ profiles (see figure 4.6). Only a small increase in phenol conversion was achieved with the addition of hydrogen peroxide. The maximum phenol conversion (figure 4.6) reached 85%, with 25% of H_2O_2 added. This is probably due to 1) very low remaining concentration of phenol, thus very low reaction rate and 2) strong competition of intermediates for H_2O_2 oxidant.

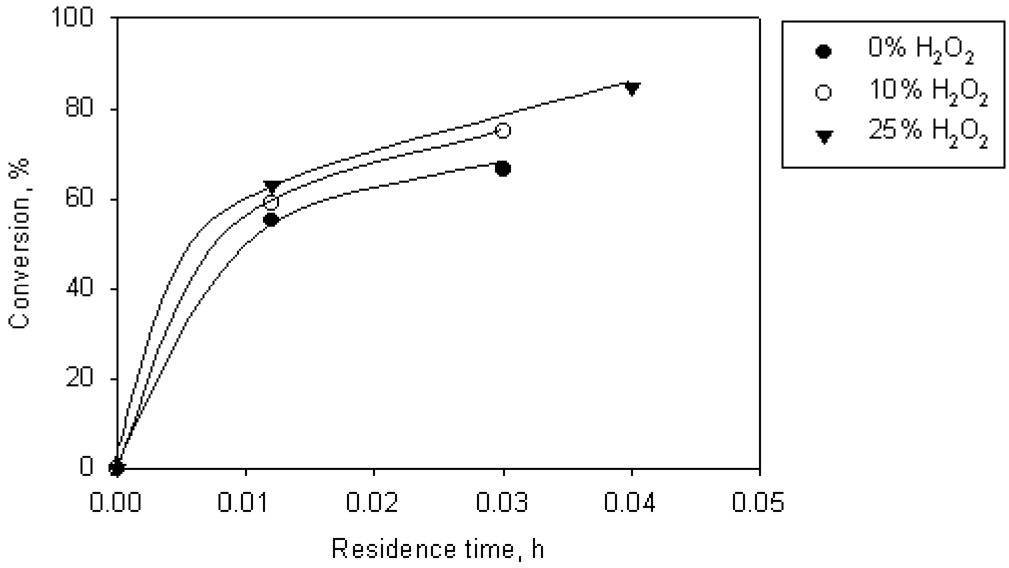


Figure 4.6: Phenol conversion versus residence time during H_2O_2 promoted CWAO of TRI2, T=170°C, P=25 bar, W_{AC}=0.68g, F_{air}=2.4ml/s, $C_{PhOH,0}$=36.5 ppm.

The measured COD reduction is shown in figure 4.7 for different H_2O_2 dosage. It can be seen that COD conversion is relatively low about 30-40% without H_2O_2, but increases to 50% and 60% for 10% and 25% of H_2O_2 added, respectively. Practically all of the H_2O_2 added was thus available for oxidation of organics. It could be concluded that activated carbon also plays the role of concentrating reactants, both organics and H_2O_2 on its surface, thereby yielding a very efficient use of the H_2O_2 oxidant, as long as fed in quantities below the stoichiometric one.

The trends of COD destruction are also reflected in the evolution of pH during the oxidation, illustrated in figure 4.8. As seen pH drops rapidly from its inlet value for low residence time to reach a plateau. The decrease must be related to the formation of carboxylic acids. The formation is enhanced by adding H_2O_2 oxidant, as figure 4.8 shows a plateau pH value of 5, 4 and 3 for 0%, 10% and 25% H_2O_2 added, respectively. The constant pH values observed for higher residence times could then be interpreted as a situation of more or less equal formation and destruction rates of carboxylic acids to explain also the increasing COD destruction found for higher residence time.

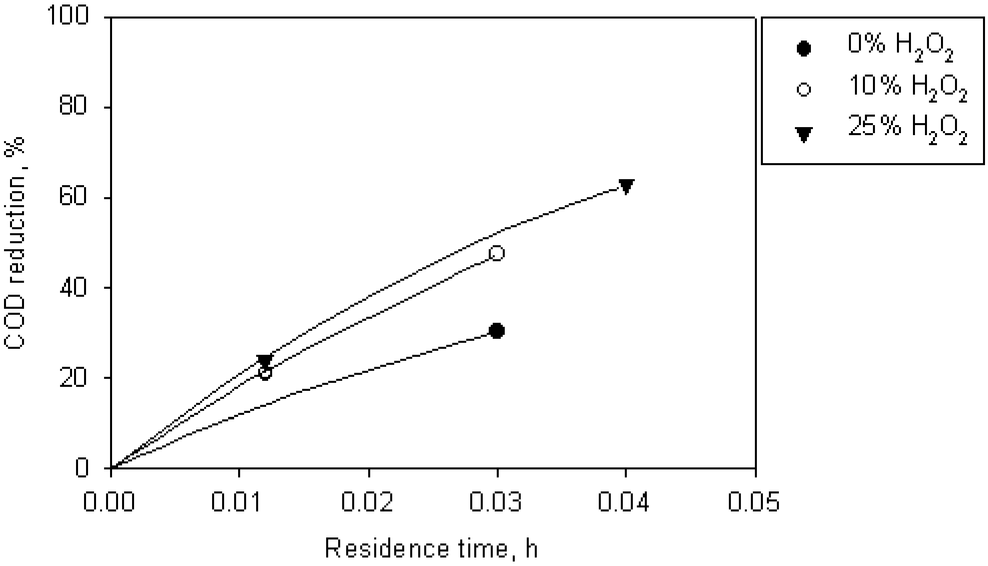


Figure 4.7: COD conversion versus residence time during H_2O_2 promoted CWAO of TRI2, T=170°C, P=25 bar, W_{AC}=0.68g, F_{air}=2.4ml/s, $C_{COD,0}$=97000 mgO_2/l.

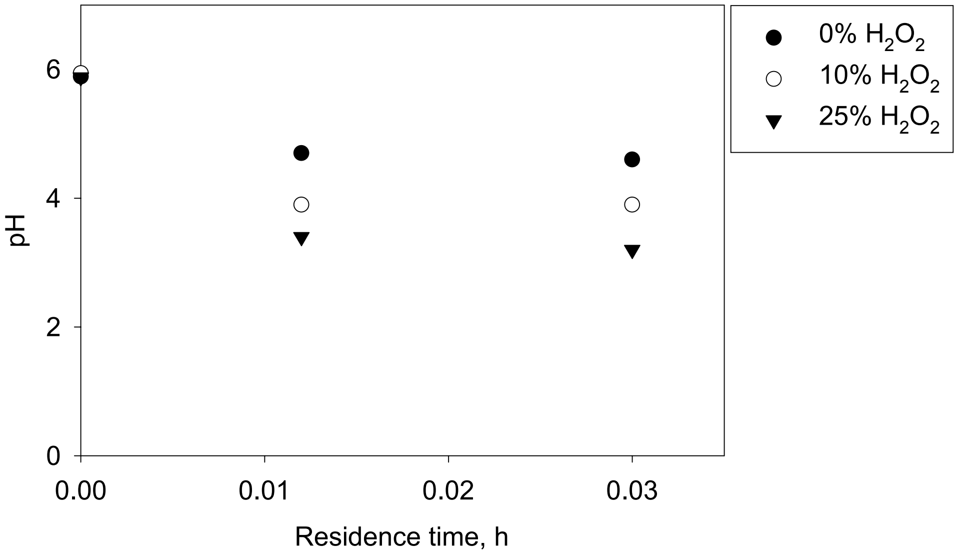


Figure 4.8: Evolution of pH during H_2O_2 promoted CWAO of TRI2, T=170°C, P=25 bar, W_{AC}=0.68g, F_{air}=2.4ml/s, $C_{COD,0}$=97000 mgO_2/l.

HPLC analyses are shown in figure 4.9 for different residence times. The distribution of peaks may explain the initial drop of pH due to appearance of peaks that should correspond to of carboxylic acids (see τ=0.012h in figure 4.9).

However, the constant pH and the remaining 40% of COD, for higher residence time, is not evidenced, as no peaks appeared during 12 minutes of HPLC analysis. Some very small peaks persisting at higher residence times may correspond to very high concentration (as peak area and concentration are not directly proportional), although this is not very likely. Or, in the HPLC conditions applied, not all compounds in the feed or reaction samples may be detected. The duration of analysis was not the problem as some analyses were run for about 60 min in order to prove that there are any compounds detectable at higher retention times.

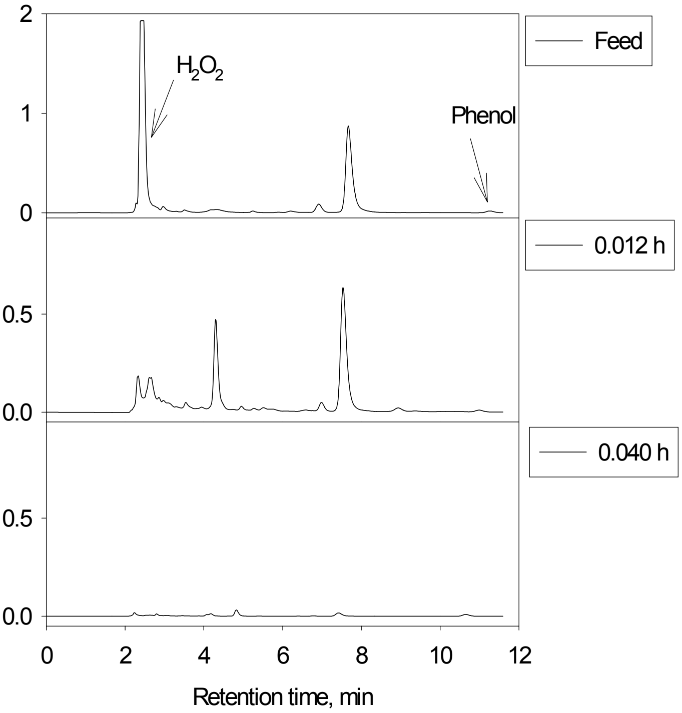


Figure 4.9: HPLC chromatograms for different residence times during CWAO of TRI2, T=170ºC, P=25 bar, W_{AC}=0.68g, F_{air}=2.4ml/s, $C_{COD,0}$=97000 mgO$_2$/l with 25% of H_2O_2.

The activated carbon was also dried and weighted after the experiments with TRI2. Surprisingly, the majority of carbon was consumed during CWAO of TRI2, the loss being about 80% of the initial load. The consumption of AC should occur at a constant rate (probably higher at 25% H_2O_2) and the relatively small increase of phenol and COD conversion between 10 and 25% of H_2O_2 may be caused by an advanced AC loss. However, it is worth to note that there was still a high destruction of phenol and COD with a strongly reduced AC load of only 20%. Some activated carbon loss cannot be avoided during catalyst drying and removing. The high consumption of AC must be also related to the use higher temperature and higher pressure as well as the presence of H_2O_2. Moreover, the low phenol concentration of TRI2 enhances carbon consumption as phenol adsorbed on AC was found to act as a protection layer against AC combustion. This could indicate that the rest of organic compounds present in TRI2 sample do not act (adsorb or protect) in the same manner, thereby compensating the phenol protection function.

The results show that CWAO alone is not sufficient for TRI2 treatment, but the addition of relatively small H_2O_2 doses is very effective. An increase of the AC weight and adequate addition of H_2O_2 should allow applying lower temperature (≈140°C) and oxygen pressure (≈2 bar). Such conditions are required to greatly reduce the activated carbon consumption, thereby achieving a stable process activity over a long period.

4.1.3. Overview

The TRI1 sample cannot be treated 'as received' by CWAO, because of a rapid plug formation in the reactor during the oxidation. It was observed that phenol conversion did not stabilise, while reactor pressure increased slowly to unacceptably high values. The TRI1 sample mainly contains phenol, but some substances that enhance polymerisation of phenol must be present. Oxidative coupling, known to be catalysed by AC cannot explain alone the rapid plug formation.

Reactor plugging was not observed during CWAO of TRI2. The removal efficiency of CWAO at the standard conditions of 170°C and 3.4 bar of O_2 was rather unsatisfactory. One should have in mind that the TRI2 sample is extremely refractory having high COD of 97000 mgO_2/l. The addition of 25% of hydrogen peroxide yielded promising COD reductions of 60% at a residence time of 0.04 h. It seems that H_2O_2 in the presence of AC catalyst is completely used for oxidation, as long as added in small quantities. The colour of treated samples was yellowish and its repellent odour persisted. At 40% of remaining COD, the HPLC chromatograms of the liquid samples showed that there was almost complete destruction of intermediates. These opposite results arise the questions whether there may exist by-products not detected in the HPLC conditions applied or that the COD analysis was not precise due to the technical problems with the colorimeter. A surprising result is the considerable 80% consumption of activated carbon during CWAO of TRI2. This high consumption can be explained by some AC loss during removal and by the higher temperature and pressure used. In addition, the small phenol content of TRI2 sample produced low surface coverage of phenol that can act as a protecting layer against AC combustion. More experiments are necessary to study and explain the residual high activity shown, when the AC load is reduced by a factor 5.

4.2. Wet Peroxide Oxidation and Fenton Wet Peroxide Oxidation

The previous experiments with the industrial effluents have indicated that CWAO over activated carbon is only suitable for the TRI2 sample. The use of H_2O_2 was shown to be very effective in enhancing the process performance. Thus, the two samples TRI1 and TRI2 were also treated with WPO and Fenton promoted WPO. The obtained results with these two advanced treatment techniques are discussed in the following chapters.

4.2.1. Wet Peroxide Oxidation of sample TRI1

WPO experiments of TRI1 were done at standard conditions of 300°C, 100 bar, and with 50, 100 and 150% of stoichiometric hydrogen peroxide demand. In all experiments, organic solution (COD of 5600 mgO_2/l) was premixed with hydrogen peroxide oxidant. Figure 4.10 presents the so obtained phenol conversion as a function of residence time during WPO of TRI1. The measured conversion - residence time profiles show the typical sharp increase at low residence time, before the conversion reaches its plateau value of about 50-60%, and almost 100% with 50 and 100 or 150% of hydrogen peroxide, respectively.

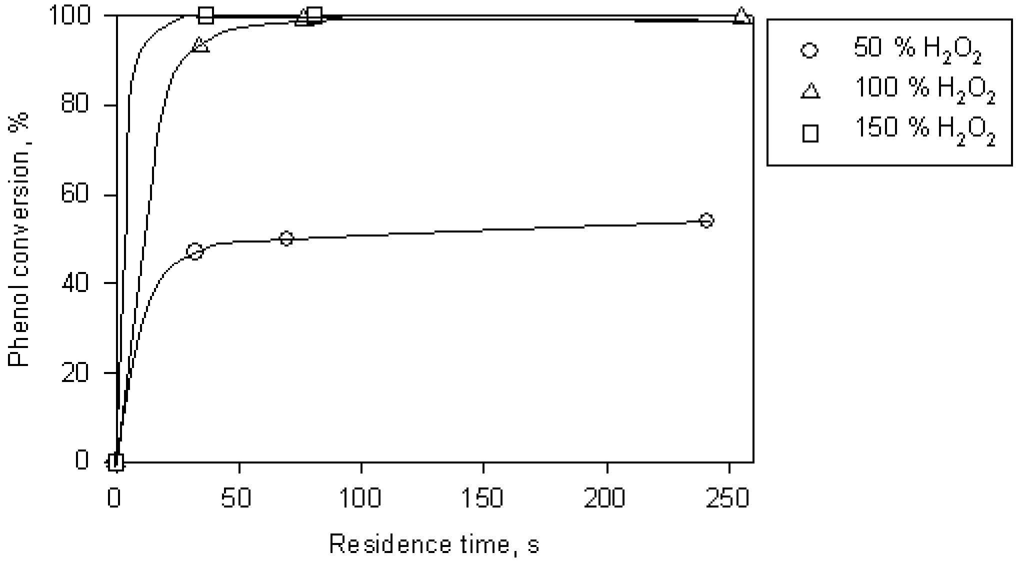


Figure 4.10: Evolution of phenol conversion for different H_2O_2 dosage during WPO of TRI1 at T=300°C, P=100bar, $C_{PhOH,0}$=1800ppm.

With 150% of hydrogen peroxide dosage, the time needed to obtain almost complete conversion was about two times shorter (40 s) than that with 100% of H_2O_2 (80 s). For comparison CWAO of model pollutants required an order of magnitude higher residence time in the range of 400 to 500 s.

Figure 4.11 illustrates that COD reduction was only 30% with 50% of H_2O_2 and increased to about 70%, with 100 or even 150% of stoichiometric hydrogen peroxide demand added. The formation of very refractory compounds at higher residence times may explain this trend, as oxidation rate at high phenol conversion would greatly slow down. Decomposition of hydrogen peroxide may also proceed at higher rate for H_2O_2 excess, enhancing the formation of much less active O_2. As it can be seen in figure 4.12, numerous intermediates are formed at low residence time, but are also almost completely destroyed at higher residence time. It is not believed that the remaining trace peaks in the low chain carboxylic acid retention time range account for the residual 30% of COD. Formation of not detectable by products may occur, but we think that the technical dysfunction of colorimeter caused unprecise COD measurements.

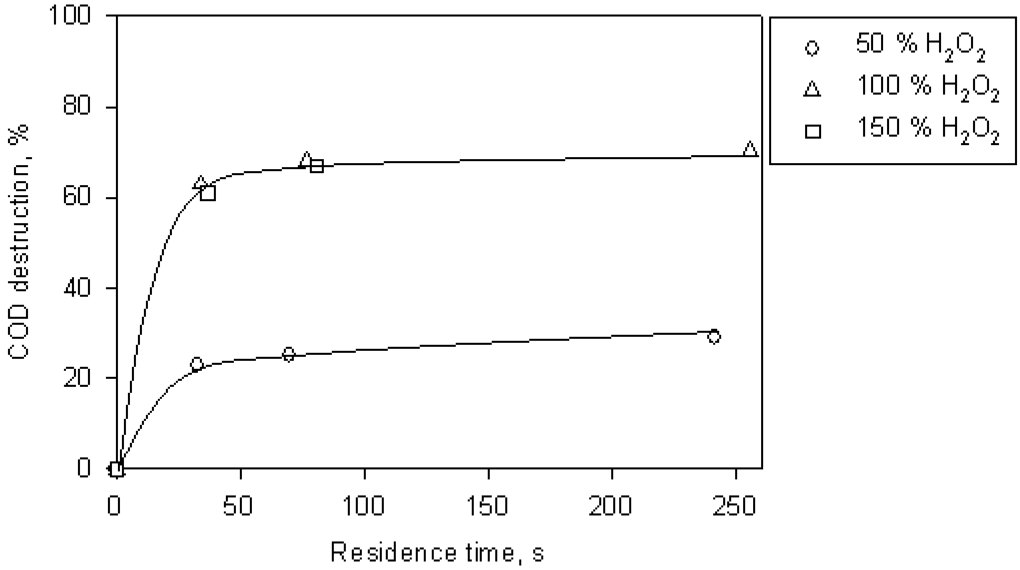


Figure 4.11: COD conversion for different H_2O_2 dosage during WPO of TRI1, T=300°C, P=100bar, $C_{COD,0}$=5600 mgO_2/l.

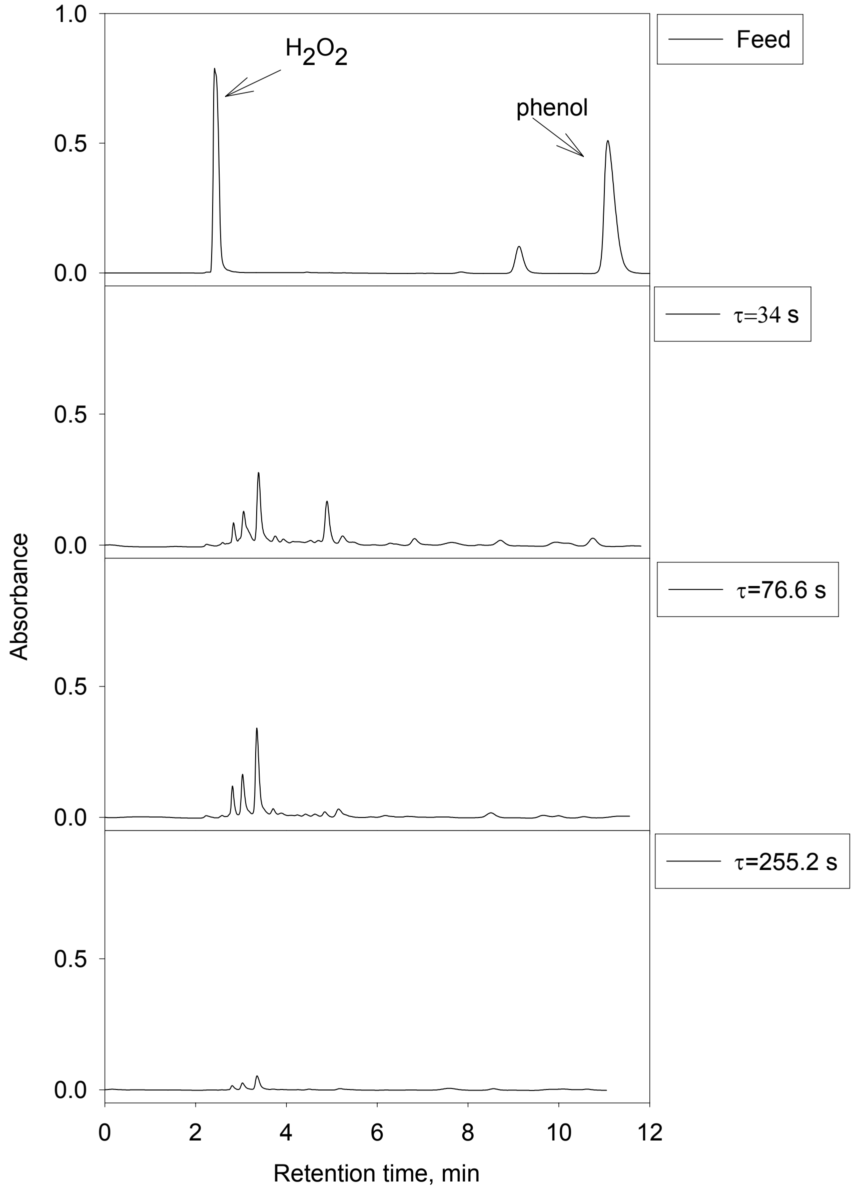


Figure 4.12: HPLC chromatograms for different residence times during WPO of TRI1; T=300ºC, P=100bar, $C_{COD,0}$=5600 mgO_2/l and 100% H_2O_2.

The pH evolution, presented in figure 4.13, gives some support to this hypothesis. We can observe that for 50% of H_2O_2 stoichiometric demand there is pronounced drop from pH=8 to a constant pH value of 3 at low residence time. Rapid formation of acids stands for the decrease in pH that remains constant due to the deficit of H_2O_2 oxidant. For 100 and 150% of H_2O_2 pH first decreases to similar values (~3), but then increase to reach a final plateau value of about 4. The final increase at higher residence times in pH value can be ascribed to the destruction of acids (H_2O_2 is still available), what is also indicated by the disappearance of acid peaks in the HPLC chromatograms (see figure 4.12).

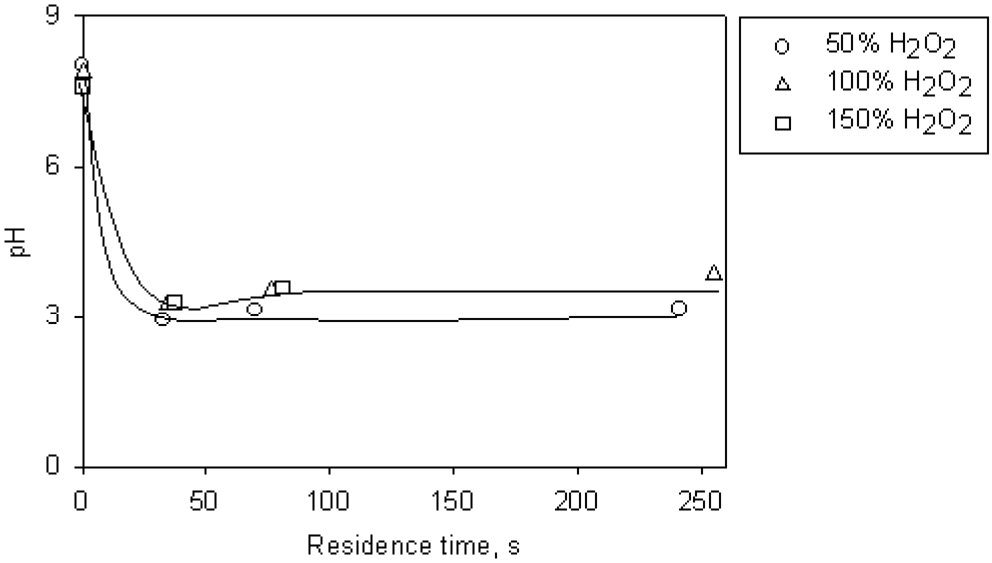


Figure 4.13: pH evolution during WPO of TRI1 at T=300°C, P=100bar, $C_{COD,0}$=5600 mgO_2/l at different H_2O_2 dosage.

In case of WPO of the sample TRI1, some GC analysis of gas effluent was done. Figure 4.14 illustrates the formation of carbon dioxide for 50 and 100% H_2O_2. The concentration of CO_2 produced increases almost twice from about 0.030 to 0.050 mol/l, when increasing hydrogen peroxide dosage from 50 to 100%. This is in agreement with higher COD reduction observed, when adding 100 instead of 50% of hydrogen peroxide.

CO and O_2 were also detected in significant quantities, but proper separation of peaks was not achieved with the column used.

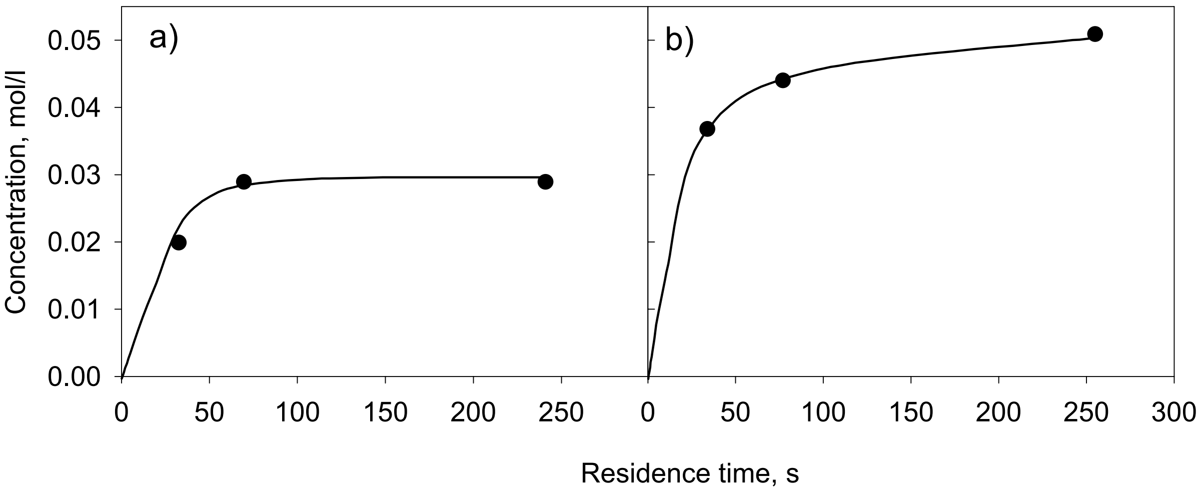


Figure 4.14: CO_2 formation during WPO of TRI1; T=300°C, P=100 bar, $C_{COD,0}$=5600ppm; a) at 50% H_2O_2, b) at 100% H_2O_2.

The results show that for 50% of H_2O_2 stoichiometric demand both phenol conversion and COD reduction are very low. Increasing H_2O_2 to 100% of stoichiometric demand results in complete phenol conversion and COD reduction of 70%. This is in accordance with HPLC and GC analysis that show very small quantity of intermediates remaining in the liquid phase and increasing concentration of CO_2 with 100% H_2O_2 demand. Further increase of H_2O_2 quantity to 150% of stoichiometric demand shows no improvement in process performance. The addition of a homogeneous catalyst could enhance the process yield instead of adding more hydrogen peroxide.

4.2.2. Fenton promoted Wet Peroxide Oxidation of sample TRI1

Additional Fenton WPO experiments with sample TRI1 were programmed in an attempt to enhance pure WPO efficiency. Standard conditions applied were 200°C, 20 bar, 20 mg/l Fe^{2+}, 100% H_2O_2 and the initial pH value was fixed at 3. The sample TRI1 was premixed with H_2O_2 and Fe^{2+} amounts corresponding to reaction conditions to check for precipitation or colour change of the sample. No colour change and precipitation was observed at ambient temperature. The results obtained with Fenton catalyst are presented in figure 4.15. It can be seen that phenol conversion and COD reduction are almost 100% and about 60 %, respectively, for residence time of about 30 s. Thus, values of phenol and COD conversion are similar to those obtained in WPO without Fe^{2+} catalyst addition, but they were achieved in residence time two times shorter, and at significantly lower temperature and pressure. Adjusted pH decreases from initial 3.05 to about 2.60 and remains constant, when phenol and COD conversion values stabilise.

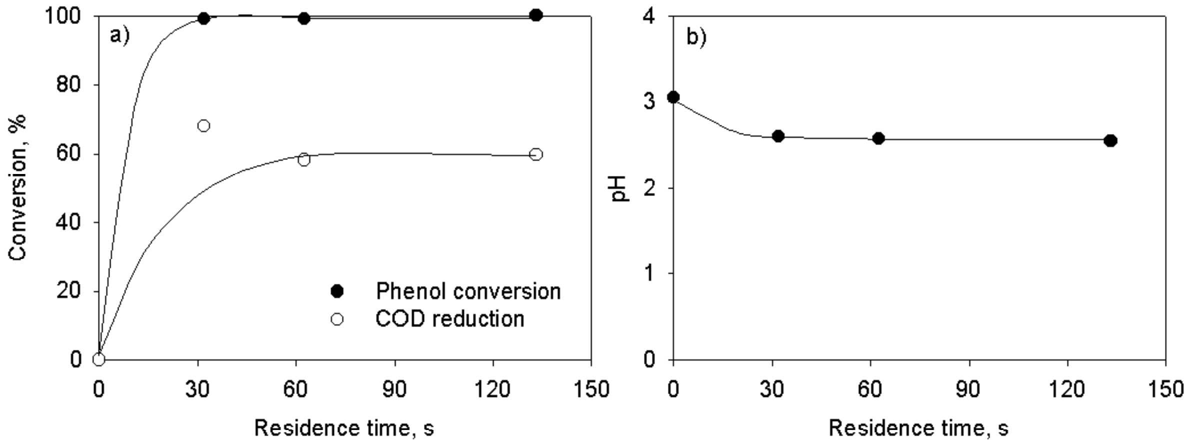


Figure 4.15: Phenol and COD conversion (a) and pH evolution (b) during Fenton WPO of TRI1 at T=200°C, P=20bar, 20mg/l Fe^{2+}, 100% H_2O_2, $C_{PhOh,0}$=1800 ppm and $C_{COD,0}$=5600 mgO2/l.

Figure 4.16 shows HPLC chromatograms of reaction samples at different residence times. From this figure, it can be seen that during the Fenton WPO of

TRI1 practically all intermediates that are formed at low residence time fall within the acid retention time range. These organic acids seems not to be destroyed at higher residence time, thus being refractory at the employed reaction temperature. This trend is supported by the evolution of pH with residence time, decreasing to value of 2.6 and then remaining constant for higher residence time (see fig. 4.15b).

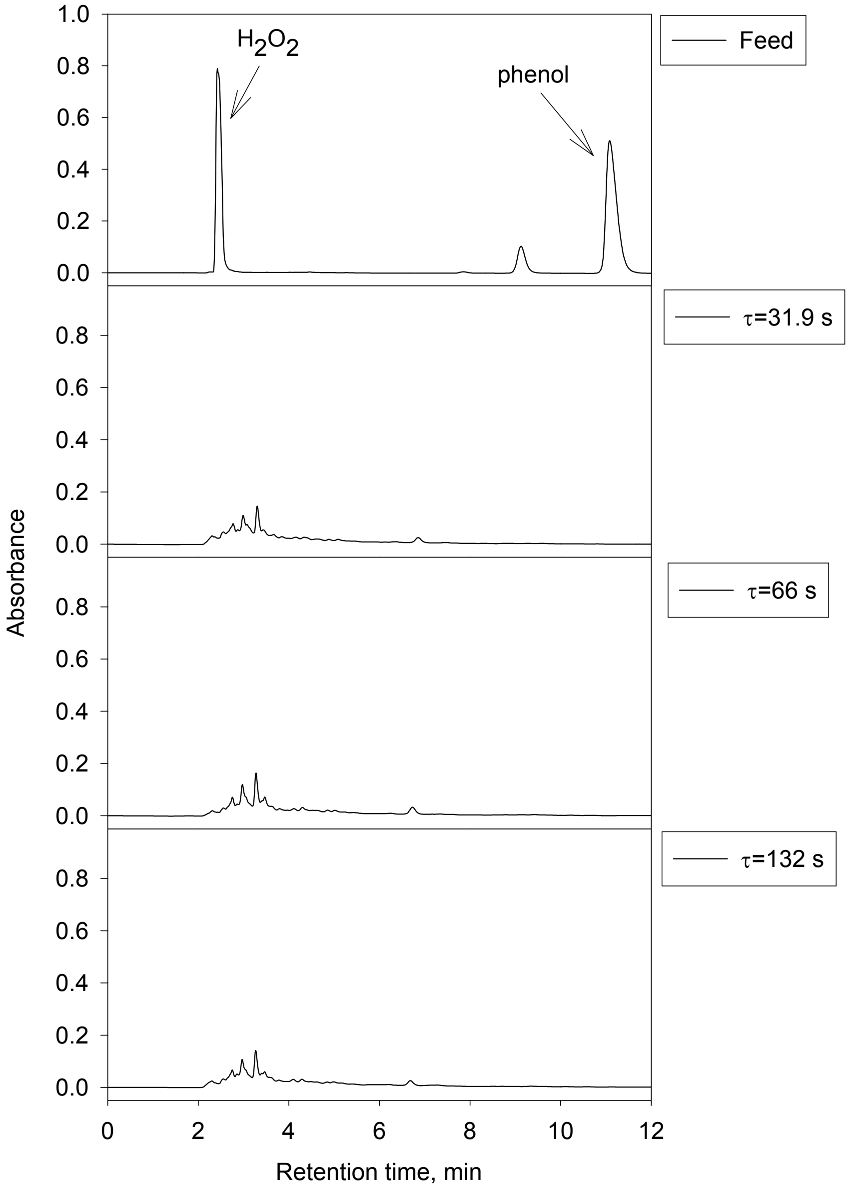


Figure 4.16: HPLC chromatograms during Fenton WPO of TRI1; T=200°C, P=20 bar, 20mg/l Fe^{2+}, 100% H_2O_2, $C_{COD,0}$=5600 mgO_2/l.

Although COD reduction values of sample TRI1 are similar for both WPO and Fenton WPO, a different distribution of reaction products can be observed in HPLC chromatograms. For WPO, almost all intermediates disappear, while for Fenton WPO peaks in the range of residence time of 2 to 4 are persisting even at higher residence time. Thus, the contribution of the remaining acid intermediates to the COD value is not very significant, or the COD values measured are not precise due to the technical problems with the COD colorimeter.

4.2.3. Wet Peroxide Oxidation of sample TRI2

The treatment of TRI2 sample with H_2O_2 promoted CWAO yielded promising results. We further checked the performance of WPO and Fenton WPO for the abatement of sample TRI2, that represents effluent of very high COD load (100 gO_2/l). WPO experiments of TRI2 were carried out at 300ºC, 100 bar, and 100% of stoichiometric H_2O_2 quantity. Sample TRI2 tested without dilution led to pump cavitation in the inlet line. The high initial COD load of sample TRI2 required high feed H_2O_2 concentration thereby enhancing the formation of O_2 bubbles in the suction line during WPO experiments making it difficult to correctly operate the equipment. The sample TRI2 was also diluted three times to allow for correct operation of the equipment.

In figure 4.17, phenol conversion during WPO of TRI2 is presented for both cases. It can be seen that for the diluted solution complete conversion of phenol is reached at already 40 s, while undiluted feed only yielded 90% of conversion after 150 s. It seems that phenol conversion is enhanced by dilution due to a more efficient use of H_2O_2 oxidant at lower concentration. The same trend is observed for COD reduction as presented in figure 4.18. COD reduction measured for concentrated feed was only about 55% meaning that almost half of the H_2O_2 oxidant amount was lost due to its decomposition to H_2O and O_2. When diluting three times the inlet COD load from about 100000 mgO_2/l to 30000 mgO_2/l, COD reduction increased to about 70%, and operation of the equipment became more stable avoiding pump cavitation. Additional increase of COD reduction to 80% was then obtained by incrementing temperature and pressure to 340ºC and 150 bar, respectively.

The WPO efficiency is comparable to the results obtained in H_2O_2 promoted CWAO (at 25% of H_2O_2) for undiluted TRI2 sample. The dilution of TRI2 considerably improves WPO performance, but on cost of a substantially higher reactor volume.

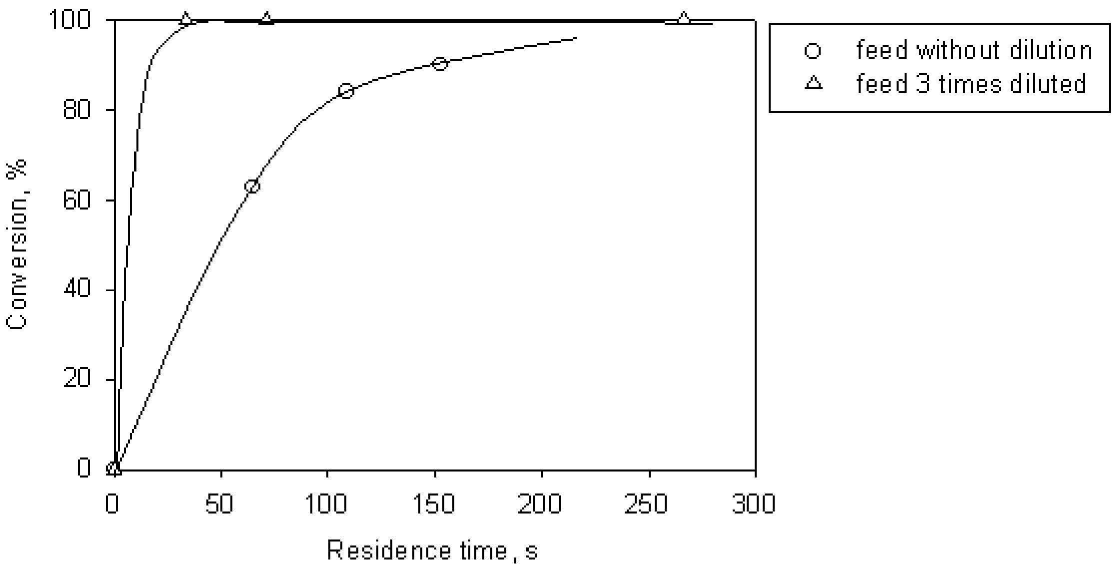


Figure 4.17: Phenol conversion for feed with and without dilution during WPO of TRI2; T=300ºC, P=100 bar, 100%H_2O_2, $C_{PhOH,0}$=36.5ppm .

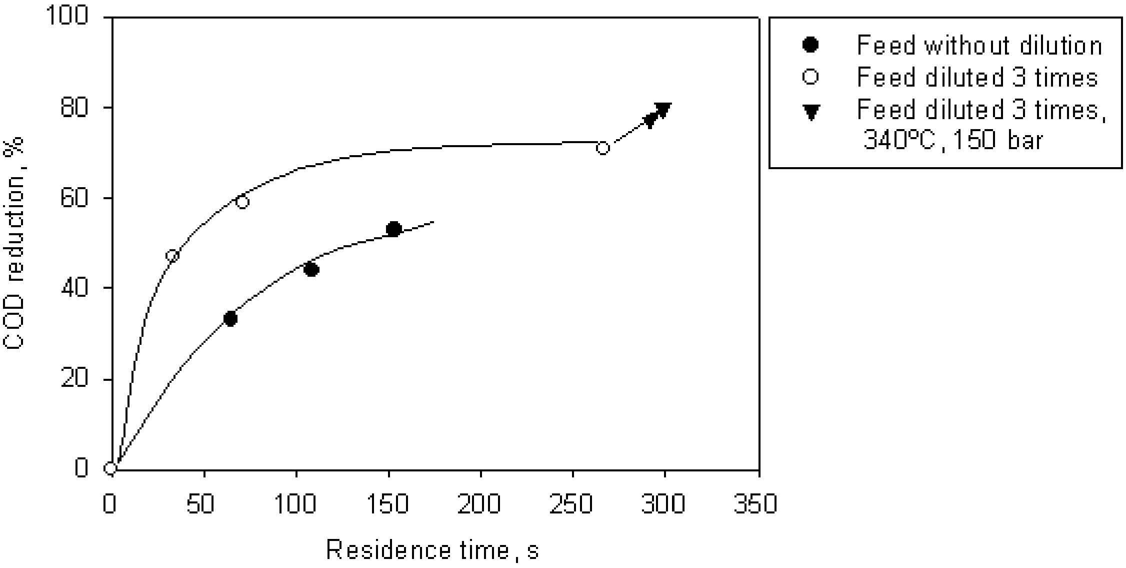


Figure 4.18: COD conversion for feed with and without dilution during WPO of TRI2; T=300ºC, P=100 bar, 100% H_2O_2, $C_{COD,0}$=97000 mgO_2/l.

pH evolution during WPO of sample TRI2 is indicated in figure 4.19. The pH of undiluted TRI2 is decreasing faster due to a higher absolute production of carboxylic acids. At higher residence time, pH starts to increase indicating the destruction of these organic acids. The decrease in pH values for diluted TRI2 sample is smaller and almost remains constant due to the dilution effect.

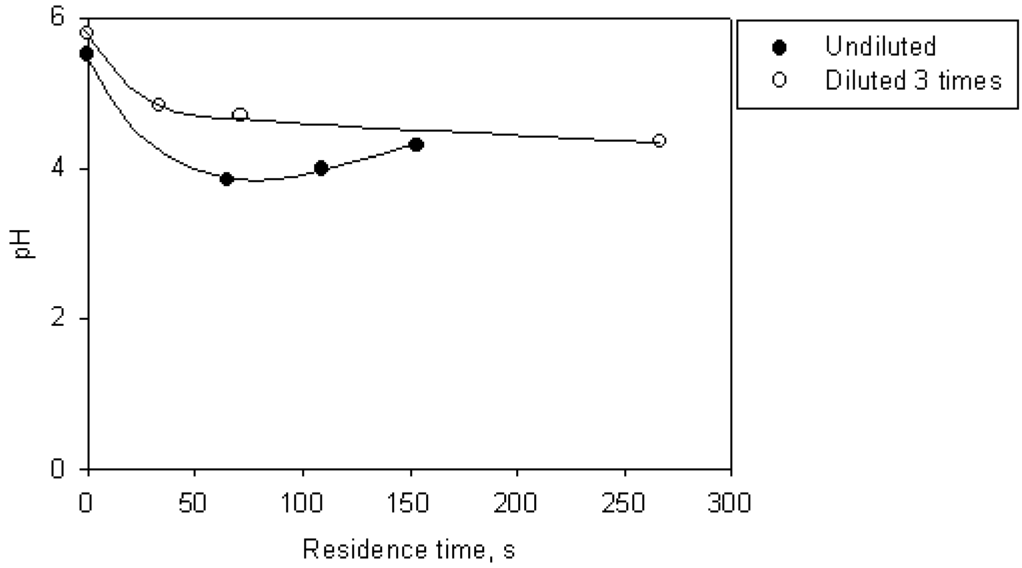


Figure 4.19: pH evolution for TRI2 sample with and without dilution during WPO of TRI2; T=300°C, P=100 bar, 100% H_2O_2, $C_{COD,0}$=97000 mgO_2/l.

Figure 4.20 presents HPLC chromatograms for diluted TRI2 sample. Fewer intermediates are formed during WPO than CWAO, but there appears a persistent peak at a retention time of 6 min. It could be a very refractory compound responsible for a great part of remaining COD, however, it is not detected in HPLC chromatograms from H_2O_2 promoted CWAO (see figure 4.9).

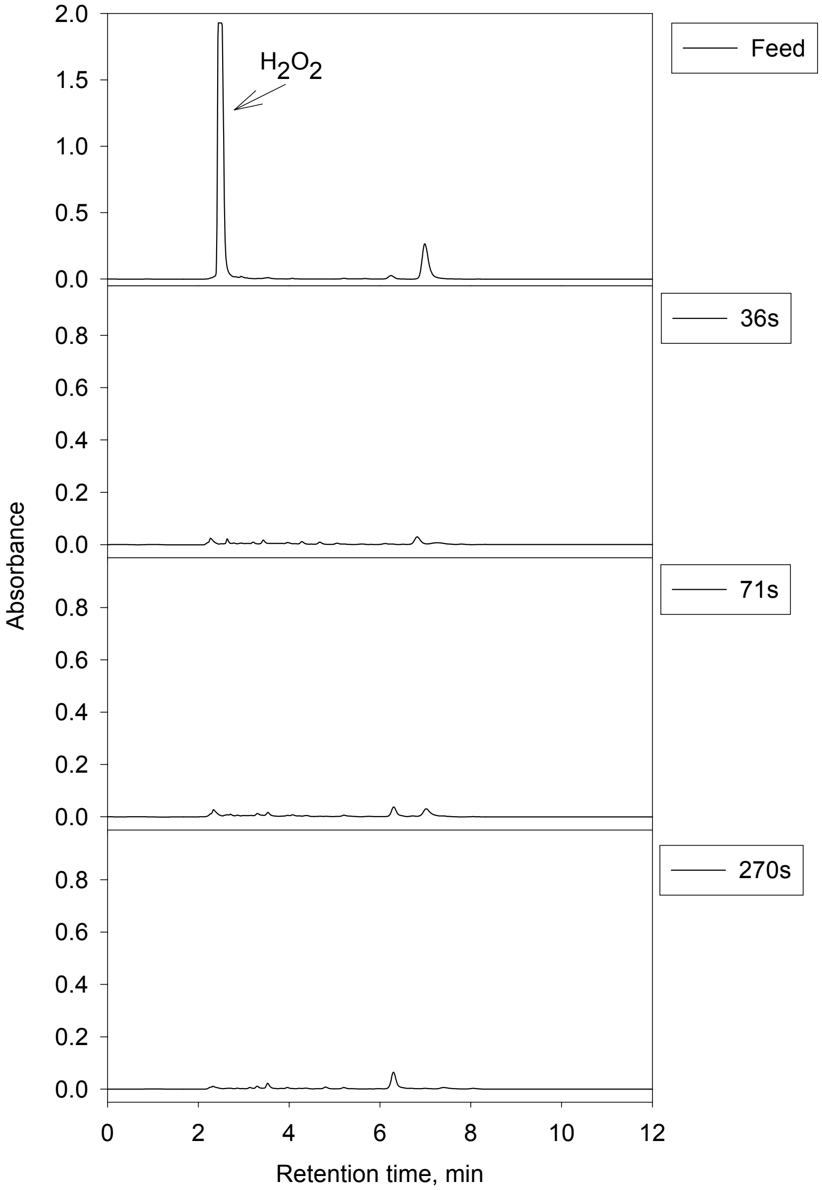


Figure 4.20: HPLC chromatograms for feed diluted 3 times during WPO of TRI2; T=300°C, P=100 bar, 100% H_2O_2, $C_{COD,0}$=32000 mg/l.

4.2.4. Fenton Wet Peroxide Oxidation of TRI2

The WPO performance for TRI2 sample treatment may be improved by the addition of small quantities of Fe^{2+} catalyst. Prior to the experiments all reagents: sample TRI2, Fe^{2+} catalyst and hydrogen peroxide were premixed to check for any possible precipitation reactions in the reactor. Effectively, complexation reaction with colour change to dark brown was observed for pH of 4-5, but not for pH of 3. The operating conditions were set to 200°C, 20 bar, 20 mg/l of Fe^{2+}, 100% H_2O_2, feed diluted 3 times and initial pH adjusted to 2.90.

The obtained phenol conversion, COD reduction and pH evolution are presented in figure 4.21. Similarly as in WPO, phenol conversion is complete, but COD reduction only reaches about 40-50% that is less than for WPO and CWAO promoted by 25% of H_2O_2 demand. Initial decrease in pH is probably due to the formation of carboxylic acids, and its increase should be cause by the acids destruction. Then, at higher residence time pH stabilises similarly as phenol conversion and COD reduction.

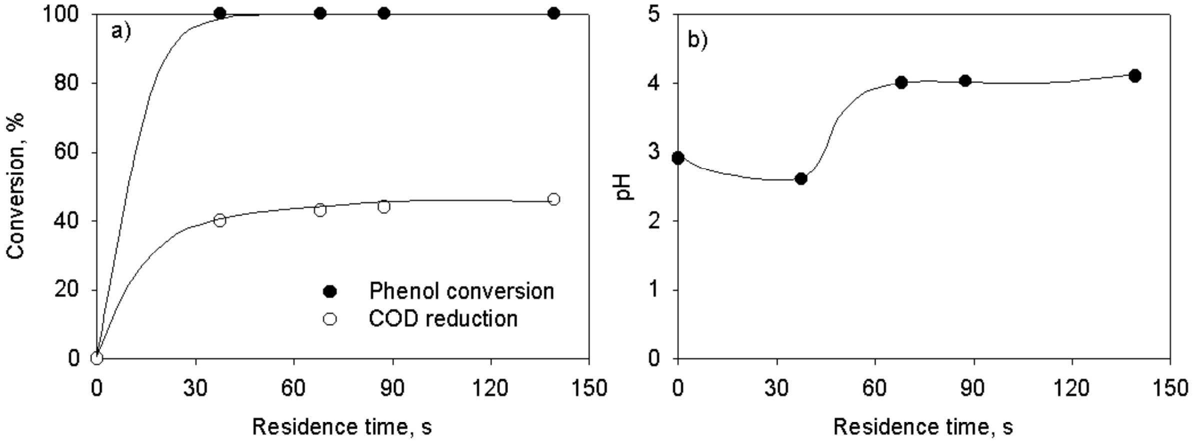


Figure 4.21: Phenol and COD conversion (a) and pH evolution (b) for Fenton WPO of TRI2; T=300°C, P=100 bar, 100% H_2O_2, $C_{PhOH,0}$=36.5 ppm, $C_{COD,0}$=32000 mgO_2/l.

In the HPLC chromatograms at different residence time (figure 4.22) there can be seen trends similar to WPO, i.e. destruction of almost all intermediates, with a persistent peak at retention time 6-7 min. At low residence time, there is formation of acids within the retention times of 2-4 minutes causing the observed decrease of pH value (figure 4.21).

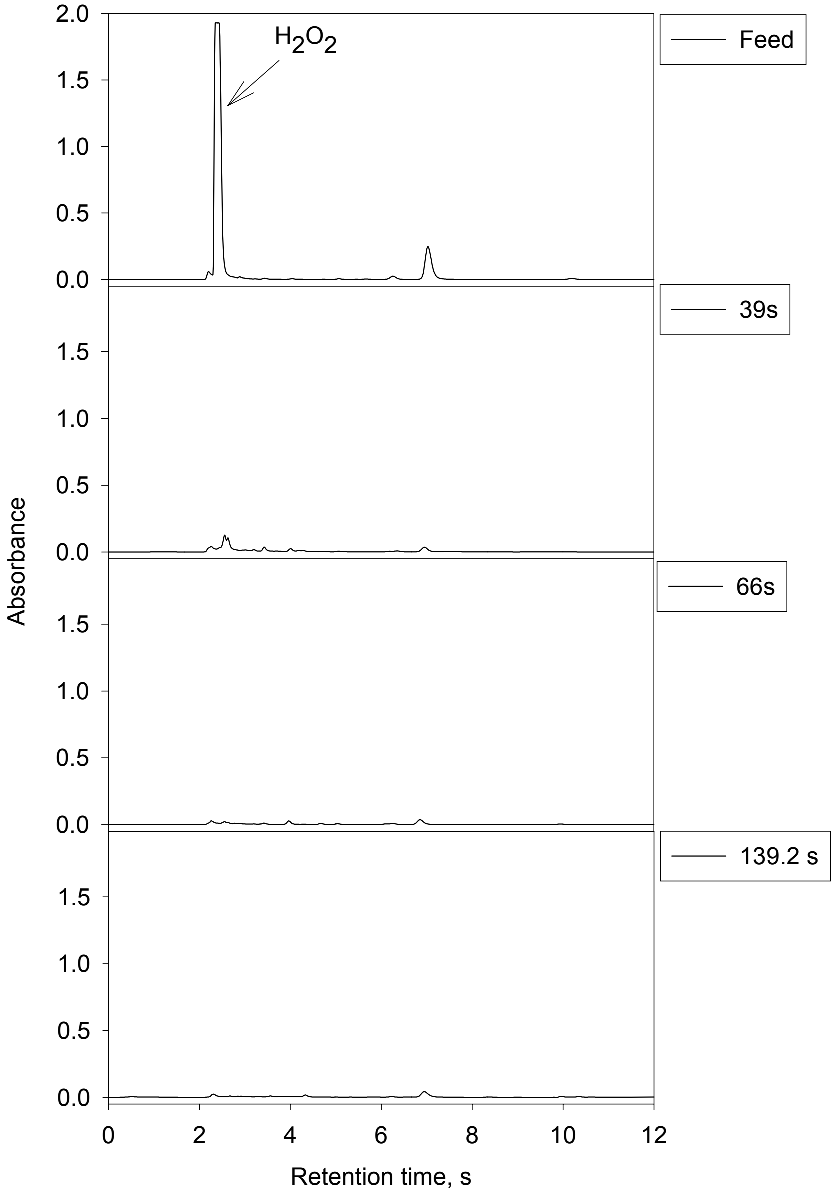


Figure 4.22: HPLC chromatograms for Fenton WPO of TRI2; T=300°C, P=100 bar, 100% H_2O_2, $C_{PhOH,0}$=36.5 ppm, $C_{COD,0}$=32000 mg/l.

4.2.5. Overview

The results obtained for WPO and Fenton promoted WPO of the industrial effluents TRI1 and TRI2, highlight the following findings. Phenol is completely destroyed in WPO and Fenton promoted WPO of TRI1 and TRI2 samples at similar residence time of about 30-50s. COD reduction of TRI1 sample gave similar results with WPO and Fenton promoted WPO at 100% of H_2O_2 demand, however Fenton promoted WPO requires significantly milder temperature and pressure. HPLC analysis of the samples indicates the formation of several intermediates. Peaks at retention time corresponding to carboxylic acid are more resistant and persist even at higher residence time, thus being probably the responsible for the remaining COD. That is also supported by the pH evolution showing a constant low value of 2-3.

Sample TRI2 had to be diluted prior to reaction. The high initial COD load requires high concentrations of hydrogen peroxide that causes pump cavitation due to H_2O_2 decomposition to water and oxygen bubbles.

COD reduction of TRI2 sample is lower for Fenton promoted WPO (40-50%) than that for WPO (60%), when diluted feed is tested. In HPLC chromatograms a few intermediates are detected, however there is a peak at retention time of 6-7 min that persists at even higher residence times.

4.3. Summary

H_2O_2 promoted CWAO was the less successful method to treat industrial effluents samples TRI1 and TRI2. TRI1 oxidation over AC resulted in reactor plugging and 25% H_2O_2 promoted CWAO over AC of TRI2 allowed reaching only 80% of phenol and 60% of COD conversion.

In WPO of both industrial wastewaters samples phenol destruction was complete, and COD reduction of TRI1 and TRI2 were 70 and 80%, respectively. TRI2 sample has to be diluted to be efficiently treated due to its enormous inlet COD charge. This dilution leads to bigger volumes of effluent to treat.

Fenton promoted WPO performed complete phenol removal for TRI1 and TRI2 (diluted), and COD reduction of 60 and 50%, respectively. Thus results obtained with WPO and Fenton WPO are very similar for TRI1 sample, the conditions being however milder for Fenton WPO.

During treatment of sample TRI1 by all the techniques studied there was a strong formation of intermediates in the range of carboxylic acids range. These acids were very refractory and could not be destroyed completely even at higher residence times.

During the oxidation of TRI2 sample not many intermediates were observed independently on a technique applied. However, a persistent peak at retention time of 6-7 minutes was observed in all cases, and was not destroyed even at higher residence times.

The following observations were made:

- The promoting effect of hydrogen peroxide during CWAO is clearly shown. The COD removal efficiency is increased. It can be concluded that this method is efficient for reducing the capital cost of CWAO without increasing the running cost too much.
- Stoichiometric or slightly higher quantity of hydrogen peroxide added during WPO is sufficient for the highest destruction efficiency. The

addition of over stoichiometric quantity does not improve significantly phenol nor COD removal.

- The results indicate, over the range of variables tested, that Fenton's reagent leads only to a moderate decrease in COD, but an enhanced destruction of phenolic compounds is achieved. Fenton WPO offers a convenient means to produce OH radicals, although two major drawbacks limit the industrial application of this technology: (i) the tight range of pH (2-4) required for Fenton WPO and (ii) the eventual recovering of catalyst after the treatment.

The best experimental results are summarised in table 4.1.

Table 4.1: Best treatment results obtained for TR1 and TRI2 samples;
TRI1: $C_{PhOH,0}$=1800 ppm, $C_{COD,0}$=5600mgO_2/l, pH_0=7.8,
TRI2: $C_{PhOH,0}$=36.5 ppm, $C_{COD,0}$=97000 mgO_2/l, pH_0=5.7.

	TRI1			**TRI2**		
	X_{PhOH}, %	X_{COD}, %	**pH**	X_{PhOH}, %	X_{COD}, %	**pH**
H_2O_2-CWAO	**-**	**-**	**-**	**80**	**60**	**3.5-5**
WPO	**100**	**70**	**4.0**	**100**	**80**	**4.3**
Fenton WPO	**100**	**60**	**2.7**	**100**	**50**	**4.2**

For TRI1 the best results were obtained in WPO, however the results for Fenton WPO are quite similar and with milder conditions, thus lower cost.

For TRI2 also WPO presents the best process performance, however taking into account COD reduction, lack of cavitation problems due to lower hydrogen peroxide concentration, milder condition, lower cost (energy, oxidant, etc.) and low activated carbon cost, CWAO with 25% of H_2O_2 demand appear as the most recommended method for TRI2 abatement.

Chapter 5

Conclusions and outlook

5.1. Conclusions

In the first part of this work, the destruction efficiency of diverse oxidation techniques (CWAO, peroxide promoted CWAO, WPO and Fenton promoted WPO) was assessed for the treatment of several toxic organic compounds including phenol, o-cresol, m-xylene, o-chlorophenol, nitrophenol, aniline, nitrobenzene and sulfolane. The target of this study was to check the feasibility of application of each method depending on the nature of pollutant. Then the operating conditions were pre-optimised for each method through studying closely the parameters that have influence on the process performance. Numerous experiments were conducted in two different continuous reactor systems, including noncatalytic and homogeneously or heterogeneously catalysed oxidation. The temperature and pressure were varied from 25 to 550°C and 10 to 350 bar, respectively, using air and/or H_2O_2 oxidant.

The most important conclusions that arise from the results can be summarised as follows for diverse methods studied.

<u>For CWAO:</u>

- The compounds treated by CWAO can be divided in two groups, the ones easily oxidised such as phenol, o-chlorophenol, o-cresol, m-xylene, and the compounds refractory to CWAO like p-nitrophenol, aniline, sulpholane and nitrobenzene.
- To improve CWAO performance, the effect of hydrogen peroxide on CWAO of aniline, p-nitrophenol and phenol as a reference pollutant has been tested.

The destruction efficiencies of phenol, p-nitrophenol and aniline as well as COD removal were enhanced with the addition of hydrogen peroxide.

- Activated carbon also catalyses oxidative coupling reactions that can lead to polymers formation. An example is H_2O_2 promoted CWAO of aniline, when reactor plugging occurs due to the formation and strong adsorption of polymers on the activated carbon surface.

For WPO:

- The most important operating parameters of phenol WPO are the hydrogen peroxide feeding manner, H_2O_2 concentration and reaction temperature.
- Optimal H_2O_2 feeding consists in mixing phenol and H_2O_2, prior to preheating of reactants.
- Temperature, H_2O_2 concentration and residence time increase greatly enhance phenol and COD conversion.
- The WPO operating pressure needed is just a pressure slightly above vapour pressure of water at the given reaction temperature, to keep the reaction media in the liquid phase.
- WPO of phenol, p-nitrophenol and aniline, gave almost complete conversion for temperatures ranging from 300 to 370ºC. Nitrobenzene resulted to be the most refractory to oxidation, a temperature as high as 550ºC being necessary to convert 80% of nitrobenzene.
- Additionally, the residence time necessary for highest oxidation of all the compounds was very short about 20 s, except for aniline, reaching values of 80 s at 250-300ºC.
- During sulpholane WPO experiments, severe corrosion problems occurred due to the formation of sulphuric acid.

For Fenton WPO:

- Fenton process is an old and known method, but its continuous operation is quite innovative, and proved to be feasible at temperatures higher than ambient to enhance the process yield (200ºC).

- Hydrogen peroxide decomposition is significantly catalysed by ferrous ions. Reaction temperature and initial ferrous sulphate concentration have a strong influence on Fenton WPO of phenol.
- The careful attention should be put on insoluble complexes that can be formed between ferrous salt and the organic compound causing plugging in the reactor.
- Pressure change, studied in the range of 10 to 30 bar, had only a negligible effect on phenol oxidation. Adjusting pH in the range of 3.20-4.90 resulted in similar phenol conversion and COD destruction at high residence time, but the rate of reaction at low residence time was found to be considerably faster at smaller pH.
- All the compounds tested gave almost complete conversion (except for nitrobenzene ≈ 70%) and close COD conversion values, indicating an advanced degree of mineralisation of the organic pollutant.
- Rapid reactor plugging could not be avoided during aniline oxidation invalidating the apparent good results obtained for Fenton WPO.
- A striking result is the obtained nitrobenzene conversion of 70% at 200°C and 20 bar in presence of only 20 mg/l ferrous sulphate, clearly outperforming WPO that required a temperature as high as 550°C to achieve 80% of conversion.

As far as the reactivity order is considered, the following trends were observed:

1) for unpromoted CWAO: m-xylene > o-cresol > o-chlorophenol > phenol ≈ aniline (pH=4) > aniline (pH=8) ≈ p-nitrophenol,
2) for H_2O_2 promoted CWAO: aniline (pH=8) > phenol > p-nitrophenol,
3) for unpromoted WPO: phenol > p-nitrophenol > aniline > sulpholane > nitrobenzene,
4) for Fenton promoted WPO: phenol=aniline > p-nitrophenol > nitrobenzene.

As can be seen the reactivity of diverse compounds may change for different methods. However, it appears that methyl and chlorine substituted phenols are more reactive, phenol and sulphur and nitrogen containing aromatics being less reactive, in particular nitrobenzene and sulpholane.

Based on the experimental findings, a 'best' specific treatment can be proposed depending on the nature of the refractory compounds.

- For phenol, cresol, o-chlorophenol, m-xylene: CWAO or H_2O_2 promoted CWAO is recommended, with 20-30% of H_2O_2 demand, providing milder conditions to reduce AC consumption;
- For p-nitrophenol and nitrobenzene: Fenton WPO at 200°C, 20 bar, 20 mg/l of Fe^{2+} and 100 s of residence time is particularly attractive;
- For aniline: application of CWAO and Fenton WPO resulted in reactor plugging. High destruction efficiency can be only obtained under conditions of WPO, at 370°C, 100 bar, 30 s, and 100% of stoichiometric demand of H_2O_2;
- For sulfolane: WPO at 370°C gives high yield, however the severe corrosion due to sulphuric acid release has to be addressed as a mayor problem of operation.

The second part of this work was dedicated to study two industrial effluents from the phenolic resins production with the diverse techniques, tested before.

The selected methods were proven feasible to treat these industrial wastewaters. Due to the complex and often unknown composition of the effluents some abatement techniques can fail to treat them effectively. For example, the treatment of phenolic effluent TRI1 sample with CWAO over activated carbon resulted in complete reactor plugging for a few hours of operation.

The inlet COD concentration being usually very high for industrial wastewaters, led to another problem of efficient use of H_2O_2 in WPO. The destruction efficiencies obtained for abatement of industrial effluents are generally lower than those achieved for single component, synthetic pollutants.

For the abatement of the two industrial wastewater, it can be concluded that:

- CWAO alone is not effective for treating phenolic effluents treated. However, H_2O_2 promoting effect was observed for CWAO of TRI2, being small for phenol and more pronounced for COD reduction.
- WPO of TRI1 and TRI2 gave very promising results of 100% phenol conversion and 60% and 70% COD conversion, respectively. Sample TRI2 cannot be efficiently treated without dilution due to its very high inlet COD load. The dilution of the sample is not convenient, because results in bigger volume of the effluent to treat.
- Fenton promoted WPO of TRI1 and TRI2 allowed achieving complete phenol conversion and 60% and 50% of COD reduction, respectively. The advantage of this method is much lower temperature and pressure than this applied in unpromoted WPO. Drawback of Fenton WPO lays, on the other hand, in the catalyst removal required after the reaction.

5.2. Outlook

Clearly, the process efficiency of diverse oxidation techniques depends on the model pollutant nature and/or the composition in case of complex industrial effluent. It would be, thus, of great interest to conduct comprehensive comparative studies involving diverse emerging oxidation techniques and organic pollutants. Further research should be focussed on finding optimal conditions for the respective treatment depending on the refractoriness of the organic pollutants. For example, the more profound study of the efficient use of hydrogen peroxide in order to economise these processes would be very practical. Corrosion of material and possible solution has to be addressed, particularly for chlorine and sulphur containing compounds.

Also detailed kinetic and reactor modelling are required to assess the potential of the diverse oxidation technique for its successful application and scale-up to pilot plant or industrial throughput. Such studies may also improve the precision of economical balances that are important criteria for the industrial application of any process.

Chapter 6

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Appendix A

The calibration curves of CO and CO_2 identified by GC are given in figures B1 and B2.

The calibration of gases was done using a standard mixture of gases from a high pressure bottle with known volumetric proportion of gases (23.5% N_2, 1.1% CH_4, 12.7% CO, 12.2% CO_2, 50.5% H_2). The identification of retention time of oxygen, nitrogen (air) and hydrogen was determined by injecting separately pure sample gases to the GC, while the CO, CH_4 and CO_2 retention times were taken from the literature (Agilent catalogue). The quantitative calibration was then performed by injecting the standard mixture of gases at different pressures (1.5-3.5 bar) into the loop. The quantity of mole of each gas at a given pressure was calculated from the ideal gas law following:

$n = \frac{PV}{RT}$ in mole,

where:

P-is varying,

$V=1.25 \cdot 10^{-7} m^3$ (loop volume),

T=333 K (loop temperature),

R=8.314 J/(mol·K) (universal gas constant).

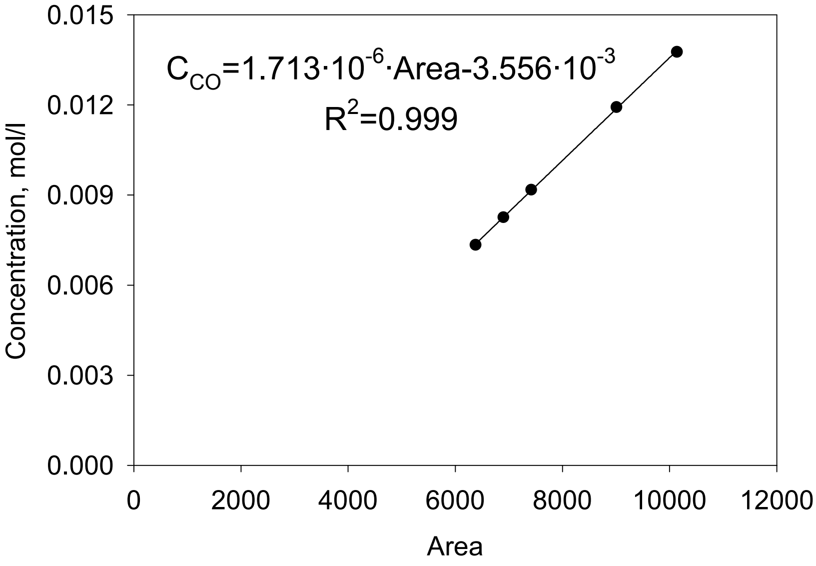

Figure B.1: Calibration curve of CO.

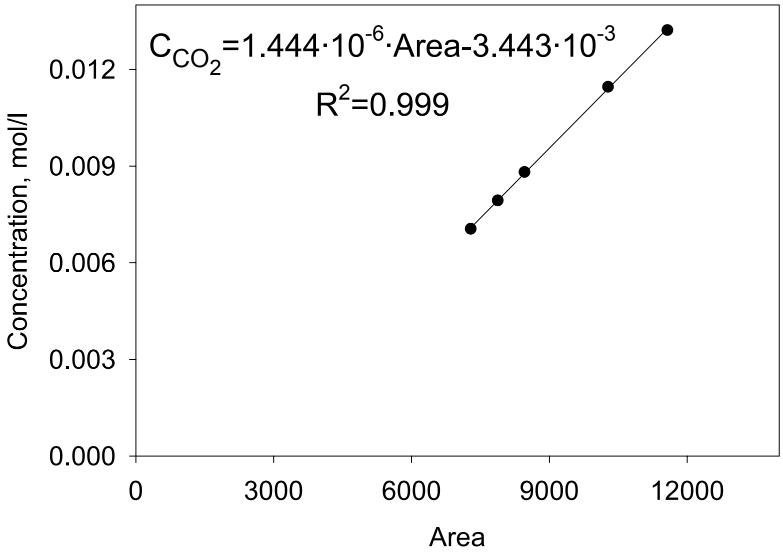

Figure B.2: Calibration curve of CO_2.

Appendix B

The carbon balance for WPO of phenol was calculated in the following manner. The reaction can be presented as:

$$\mathrm{PhOH} + 14\mathrm{H_2O_2} \rightarrow \mathrm{intermediates_{liq}} + \mathrm{H_2O} + \mathrm{CO_2}$$

Assuming that CO_2 is the only gaseous reaction, CO not being formed, the formation of CO_2 can be given by a following equation:

$$\mathrm{CO_2}\,(\%) = \frac{6 \cdot C_{\mathrm{PhOH},0} - (2 \cdot C_{\mathrm{oxal},0} + C_{\mathrm{form},\tau} + 2 \cdot C_{\mathrm{acet},\tau} + 6 \cdot C_{\mathrm{hdqn},\tau} + 6 \cdot C_{\mathrm{bnqn},\tau} + 6 \cdot C_{\mathrm{PhOH},\tau})}{6 \cdot C_{\mathrm{PhOH},0}}$$

The total amount of CO_2 formed is equal to the quantity of carbon in the initial phenol feed less the carbon present in the identified liquid intermediates and the residual phenol after a given residence time (τ).

The concentration in mmol/l of phenol (initial and residual) and intermediates identified in liquid phase as well as CO_2 formed is given in the table A1.1.

Table A.1: Intermediate distribution during WPO of phenol, $C_{PhOH,0}$=52.8-53.5mmol/l, P=150 bar, $C_{H2O2,0}$=50%.

T °C	τ s	C_{oxalic} mmol/l	C_{formic} mmol/l	C_{acetic} mmol/l	$C_{hydroquinone}$ mmol/l	$C_{benzoquinone}$ mmol/l	$C_{PhOH,\tau}$ mmol/l	CO_2 %
300	18.4	3.73	47.96	11.96	4.08	0.53	8.29	50.5
300	20.9	3.51	35.33	12.51	2.36	0.4	7.74	58.83
300	30.7	3.2	26.12	9.08	1.27	0.012	7.63	67.1
300	47.5	3	12.3	5.56	0.06	0.002	7.48	76.41
400	2.9	3.02	52.23	4.9	1.25	1.3	13.52	48.71
400	3.8	3.01	33.38	4.7	1.43	1.1	12.02	57.56
400	7.1	2.95	13.93	3.5	1.88	0.7	11.97	64.41
400	10.2	2.93	7.06	2.8	1.66	0	10.26	71.91

* calculated CO_2 formation.