UNIVERSITAT ROVIRA I VIRGILI
PEROXIDE PROMOTED CATALYTIC WET AIR OXIDATION OF PHENOLIC AQUEOUS SOLUTIONS USING
ACTIVATED CARBON AS CATALYST
Alícia Rubalcaba Mauri
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Dissertation presented by

Alícia Rubalcaba Mauri

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Memòria presentada per:

Alícia Rubalcaba Mauri

per optar al grau de Doctora en Enginyeria Química

Tesi dirigida pel Dr. Azael Fabregat Llangostera

Membres del tribunal de tesi

President Dr. Javier Lafuente, Universitat Autònoma de Barcelona
Secretari Dr. Josep Font , Universitat Rovira i Virgili
Vocals Dra. María José Martín, Universitat de Girona
Dr. Fernando Martínez, Universidad Rey Juan Carlos
Dra. Rosa M. Quinta-Ferreira, Universidade de Coimbra

Suplents Dr. Julián Carrera, Universitat Autònoma de Barcelona
Dr. Agustí Fortuny, Universitat Politècnica de Catalunya

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El Dr. Azael Fabregat Llangostera, Catedràtic 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:

Peroxide Promoted Catalytic Wet Air Oxidation
of Phenolic Aqueous Solutions using Activated Carbon as Catalyst

que presenta la doctoranda ALÍCIA RUBALCABA MAURI

per optar al grau de Doctora 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, 2007

Dr. Azael Fabregat Llangostera
Catedràtic d'Enginyeria Química

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A mons pares, Reyes i Alícia,
a ma germana, Esther,
i a tothom que m'estimo.

To my parents, Reyes i Alícia,
to my sister, Esther,
and to everyone I love.

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Foreword

The accepted wisdom regarding the research process is that the first step consists of turning an idea into a research question. The sequence which then must follow is a thorough literature review, a proper design of the methodology and tools that will be applied, the collection of data, analysis of that data and interpretation to get to a discussion of the results obtained. However, I think that the first step must be initiative and motivation. One must first of all ask the question “why do I want to dedicate time to clarifying aspects of a scientific topic?” Once this question is answered and a personal objective is fixed, it is time to begin with the research process.

My personal objective was to give myself some more time to grow and discover which were my best abilities and skills whilst building on my educational training, not just in a theoretical way, as during my undergraduate studies. When I finished my Environmental Sciences degree, I knew that I could enjoy working on practical solutions to the world’s environmental problems and that some more technical knowledge would be very useful. Doing research and becoming a doctor in a Chemical Engineering department, in a research group focussed on reaction processes for waste water and sludge treatment seemed to me an excellent opportunity to achieve my personal objective. By this point I have fulfilled most of my expectations and have learnt a few other things I did not expect, so I think I am ready to go into the next stage of my personal research process.

I wish to express my sincere gratitude to all members of the Chemical Engineering Department at *Universitat Rovira i Virgili* and the Chemical Reaction Engineering and Process Intensification Group. I especially wish to thank my supervisor Dr. Azael Fabregat and Drs. Josep Font and Agustí Fortuny for their constant help throughout the production of this thesis.

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I must attribute a large part of my achievements to the research stay I did at *Universidad Rey Juan Carlos*, in the *Grupo de Ingeneriería Química y Ambiental*, under the supervision of Dr. Fernando Martínez and Dr. Juan A. Melero. I must also thank Dr. Angel Botas, Dr.-to-be Isabel Pariente and the rest of the group. It is essential to go and see other ways of thinking and of working and being part of this research group was a very fruitful and personally constructive experience.

I would also like to acknowledge the kindness of Dr. J. Lafuente, Dr. J. Font, Dr. M.J. Martín, Dr. F. Martínez and Dr. R.M. Quinta-Ferreira for accepting to participate in the examining committee of this PhD. thesis, as well as Dr. A. Fortuny and Dr. J. Carrera who are the substitute members of the committee.

I will forever be indebted to Dr. María Eugenia Suárez-Ojeda for all the time she has dedicated to this project. I have learned by watching her and she has given me all the necessary tools to grow as a scientist.

My best wishes to María Eugenia, Carmelo, Luizildo, Esther, Xavier, Isabel, Ana, Rita and Santi who I met at University but with whom I share many other things apart from work. I would not have enjoyed producing this thesis nearly as much without you being around for the last five years. I am sure we will continue to share experiences, even though our paths will take us in different directions, sometimes more than a thousand kilometres apart.

This research would not have been possible without the economic support provided to me by the *Universitat Rovira i Virgili* and *Ministerio de Educación y Ciencia* through the PhD grants I was awarded and also through the project REN2002/03565/TECNO from the *Ministerio de Ciencia y Tecnología* and project REMOVALS (FP6-018525) from the European Union.

Alícia Rubalcaba Mauri
Tarragona, June 2007

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Resum

La creixent complexitat dels efluents residuals així com la manifesta oposició pública cap a determinades tècniques convencionals per a la gestió de residus, com és la incineració, ha accelerat el desenvolupament de tractaments econòmics i respectuosos amb el medi ambient. Hi ha pocs dubtes sobre que els processos de degradació biològica continuïn sent els més utilitzats pel tractament d'aigües residuals. Malgrat això, quan els processos biològics s'apliquen al tractament d'efluents industrials, no sempre arriben a nivells de depuració satisfactoris, ja que moltes substàncies orgàniques produïdes per les indústries químiques són inhibidores, tòxiques o resistents a l'oxidació biològica. L'Oxidació Humida Catalítica (CWAO, de l'anglès *Catalytic Wet Air Oxidation*) és una de les tecnologies més prometedores per al tractament d'aigües que continguin una alta càrrega orgànica o amb presència de contaminants biotòxics. A més a més, el procés CWAO ha demostrat recentment la seva eficàcia com a pretractament químic, produint efluents que poden ser tractats posteriorment mitjançant un sistema biològic. Una opció per suavitzar les condicions d'operació de la CWAO o per al tractament de contaminants resistents a aquest procés és afegir petites quantitats d'un oxidant més potent que l'aire, com ara el peròxid d'hidrogen. Aquest procés s'anomena Oxidació Humida Catalítica Promoguda amb Peròxid d'Hidrogen (PP-CWAO, de l'anglès *Peroxide Promoted Catalytic Wet Air Oxidation*). Per a l'estudi d'aquest procés recentment desenvolupat, l'activitat i l'estabilitat del carbó actiu (AC) s'han provat a la PP-CWAO de solucions aquoses de fenol. Aquest compost s'ha elegit com a model degut a que els residus fenòlics són uns dels contaminants més habituals als efluents de les indústries químiques, que a més es caracteritzen per una elevada toxicitat i una escassa biodegradabilitat. A aquesta tesi, les solucions fenòliques s'han tractat en un reactor de llit fix de goteig a condicions de pressió i temperatura mitjanes (<15 bar, <150 ºC), amb aire com a principal agent oxidant i peròxid d'hidrogen com a promotor de la oxidació. En primer lloc, s'ha estudiat l'efecte sinèrgic o promotor de l'H_2O_2 per a facilitar la reacció d'oxidació del fenol sobre AC. A continuació, el procés PP-CWAO s'ha aplicat al tractament d'altres compostos fenòlics a unes condicions d'operació seleccionades. Finalment, s'han preparat uns catalitzadors de ferro suportat sobre AC i s'han aplicat a la oxidació de fenol. Els resultats d'aquest estudi s'han avaluat en funció de la reducció

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de la càrrega orgànica i l'augment de la biodegradabilitat de les solucions tractades. Es pot concloure que el procés PP-CWAO podria ser inclòs entre els pretractaments químics aplicables a aigües residuals tòxiques o concentrades, que, un cop optimitzat, produiria efluents innocus per un posterior tractament biològic.

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Resumen

La creciente complejidad de los efluentes residuales así como la oposición pública hacia algunas técnicas convencionales para la gestión de residuos, como es la incineración, está forzando el desarrollo de tratamientos de residuos económicos y respetuosos con el medio ambiente. Existen pocas dudas sobre que los procesos de degradación biológica sigan siendo los más extendidos para el tratamiento de aguas residuales. Sin embargo, cuando los procesos biológicos se aplican al tratamiento de efluentes industriales, no siempre dan lugar a resultados satisfactorios, ya que muchas substancias orgánicas producidas por las industrias químicas son inhibidoras, tóxicas o resistentes a la oxidación biológica. La Oxidación Húmeda Catalítica (CWAO, del inglés *Catalytic Wet Air Oxidation*) es una de las tecnologías más prometedoras para el tratamiento de aguas con alta carga orgánica y/o que contengan contaminantes biotóxicos. Además, el proceso CWAO recientemente ha demostrado ser efectivo como pretratamiento químico, dando lugar a efluentes que pudieran ser tratados con un posterior tratamiento biológico. Una opción para suavizar las condiciones de operación en la CWAO o para el tratamiento de contaminantes resistentes a este proceso es añadir pequeñas cantidades de un oxidante más potente que el aire, como es el peróxido de hidrógeno. Este proceso se ha denominado Oxidación Húmeda Catalítica Promovida con Peróxido de Hidrógeno (PP-CWAO, del inglés *Peroxide Promoted Catalytic Wet Air Oxidation*). Para el estudio de este recientemente desarrollado proceso, la actividad catalítica y la estabilidad del carbón activo (AC) se ha probado en la PP-CWAO de soluciones acuosas de fenol. Este compuesto se ha elegido como compuesto modelo ya que los residuos fenólicos son unos de los contaminantes más habituales en los efluentes de la industria química, además de que se caracterizan por una elevada toxicidad y una escasa biodegradabilidad. En la presente tesis, las soluciones fenólicas se han tratado en un reactor de lecho fijo de goteo a condiciones de presión y temperatura medias (<15 bar, <150 ºC), usando aire como principal agente oxidante y peróxido de hidrógeno como promotor de la oxidación. En primer lugar se ha estudiado el efecto sinérgico o promotor del H_2O_2 para facilitar la reacción de oxidación del fenol sobre AC. A continuación, el proceso PP-CWAO se ha aplicado al tratamiento de otros compuestos fenólicos a unas condiciones de operación seleccionadas. Finalmente, se han preparado catalizadores

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de hierro soportado sobre AC y se han aplicado a la oxidación de fenol. Los resultados de este estudio se han evaluado en términos de reducción de la carga orgánica de las soluciones tratadas, así como del aumento de su biodegradabilidad. Puede concluirse que el proceso PP-CWAO podría incluirse entre los pretratamientos químicos aplicables a aguas residuales tóxicas o concentradas, que, una vez optimizado, daría lugar a efluentes inocuos para un posterior tratamiento biológico.

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Summary

The increasing complexity of wastewater streams as well as the unfavourable public opinion about some conventional waste management techniques, e.g. incineration, is forcing the development of cost-competitive and environmentally acceptable waste treatments. There is little doubt that biological processes will continue to be employed as a baseline treatment processes for most wastewater. However, when biological processes are applied to treatment of industrial effluents, they do not always give satisfactory results, sine many organic substances produced by the chemical and related industries are inhibitory, toxic and/or resistant to biological oxidation. The Catalytic Wet Air Oxidation (CWAO) process is one of the most promising technologies for the remediation of concentrated and/or biotoxic water pollutants, when a stable and active catalyst can be provided. In addition, CWAO has recently proved to be effective as chemical pre-treatment that could give effluents suitable for a subsequent biological end treatment. An alternative to lower CWAO operation conditions or to treat some refractory compounds is to supply little amount of a stronger oxidant such as hydrogen peroxide in a process referred as to Peroxide Promoted Catalytic Wet Air Oxidation (PP-CWAO). To study the potentialities of this newly developed oxidation process, the catalytic activity and stability of activated carbon (AC) was tested in the PP-CWAO of phenolic aqueous solutions. Phenol was chosen as model compound because of phenolic wastes are one of the most prevalent forms of chemical pollutants, characterised by a high toxicity and a poor biodegradability. In this work, phenolic water was treated in a trickle bed reactor (TBR) at mild pressure and temperature conditions (<15 bar, <150 ºC), using air as main oxidant agent and hydrogen peroxide merely being a promoter. First, the synergistic or promoting ability of H_2O_2 to facilitate the oxidation reaction of phenol over AC was analysed. Secondly, some selected conditions were tested for the oxidation of other phenolic compounds such as o-cresol and p-nitrophenol. Finally, iron containing AC catalysts were prepared and applied to the oxidation of phenol. Results were evaluated in terms or organic load removal and biodegradability improvement. It can be concluded that this newly developed process could be included among chemical pre-treatments for toxic and concentrated wastewater that, once optimised, could lead to innocuous effluents for a subsequent biological process.

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Nomenclature and abbreviations

A	Frequency factor in Arrhenius Equation
AC	Activated carbon
AC-APS	AC-L oxidised with $NH_4S_2O_8$
AC-APS-Fe	AC-APS after iron impregnation
AC-APS-Fe-250	AC-APS-Fe calcined at 250 ºC in air
AC-APS-Fe-500	AC-APS-Fe calcined at 500 ºC in nitrogen
AC-CN	AC-L oxidised with HNO_3
AC-CN-Fe	AC-CN after iron impregnation
AC-CN-Fe-250	AC-CN-Fe calcined at 250 ºC in air
AC-CN-Fe-500	AC-CN-Fe calcined at 500 ºC in nitrogen
AC-HP	AC-L oxidised with H_2O_2/H_2SO_4
AC-HP-Fe	AC-HP after iron impregnation
AC-HP-Fe-250	AC-HP-Fe calcined at 250 ºC in air
AC-HP-Fe-500	AC-HP-Fe calcined at 500 ºC in nitrogen
AC-L	Demineralised commercial activated carbon
AC-L-Fe	AC-L after iron impregnation
AC-M	Commercial activated carbon
AC-M-Fe	AC-M after iron impregnation
AOP	Advanced Oxidation Processes
BOD	Biological Oxygen Demand
C_0	Initial concentration (mg L^{-1})
C_e	Effluent concentration (mg L^{-1})
COD	Chemical Oxygen Demand
COD_{rb}	COD readily biodegradable (%)
COD_{sb}	COD slowly biodegradable (%)
CWAO	Catalytic Wet Air Oxidation
CWPO	Catalytic Wet Peroxide Oxidation
ΔS_{BET}	BET surface changes in AC after different treatments (%)
ΔW	Catalyst mass change after reaction (%), from TGA up to 400 ºC
DAD	Diode Array Detector
DO	Dissolved Oxygen (mg L^{-1})
E_a	Activation energy (kJ mol^{-1})
FeAC	Iron containing activated carbon
FID	Flame Ionisation Detector

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GC	Gas Chromatography
GDP	Gross Domestic Product
HPLC	High Performance Liquid Chromatography
ICP-AES	Induced Coupled Plasma for Atomic Emission Spectroscopy
IEP	Isoelectric Point
IS	Inert Support (SiC)
k_{ap}	Apparent kinetic constant (mL h^{-1} g^{-1})
k_{La}	Oxygen transfer coefficient (g O_2 min^{-1})
k	First-order kinetic rate constant (s^{-1})
LFS	Liquid-Flow-Static respirometer type
LHSV	Liquid Hourly Space Velocity (h^{-1})
m, n, p	Reaction orders
m_{AC}	Initial AC weight (g)
m_{fAC}	Remaining AC weight after reaction (g)
NMR	Nuclear Magnetic Resonance
NPOC	Non-Purgeable Organic Carbon
OC	Oxygen Consumption (mg L^{-1})
OUR	Oxygen Uptake Rate (g O_2 g VSS^{-1} min^{-1})
OUR_{end}	Endogenous Oxygen Uptake Rate (g O_2 g VSS^{-1} min^{-1})
OUR_{ex}	Exogenous Oxygen Uptake Rate (g O_2 g VSS^{-1} min^{-1})
OUR_{MAX}	Maximum Oxygen Uptake Rate (g O_2 g VSS^{-1} min^{-1})
P	Pressure (bar)
P_{O2}	Oxygen partial pressure (bar)
P_{N2}	Nitrogen partial pressure (bar)
P^{v}_{H2O}	Water vapour partial pressure (bar)
PP-CWAO	Peroxide Promoted Catalytic Wet Air Oxidation
PZC	Point Zero Charge
Q_L	Liquid flow rate (mL h^{-1})
R	Gas constant (m^3 Pa mol^{-1} K^{-1})
ρ_L	Liquid density (g L^{-1})
δ	Chemical shift (ppm)
S_0	Dissolved oxygen concentration (mg L^{-1})
S_{oe}	Oxygen concentration in equilibrium (mg L^{-1})
S_{BET}	BET surface area (m^2 g^{-1})
SOG	Surface Oxygen Groups
τ	Space time (h)
T	Temperature (ºC, K)
TBR	Trickle Bed Reactor
TGA	Thermogravimetric Analyses
ThCOD	Theoretical Chemical Oxygen Demand

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TOC	Total Organic Carbon
TSS	Total Suspended Solids (mg L^{-1})
TWL	Total Weight Loss (%), from TGA up to 900 ºC
UV	Ultra Violet
$V_{micropore}$	Micropore volume (cm^3)
VSS	Volatile Suspended Solids (mg L^{-1})
W_{105}	Catalyst weight after drying at 105 ºC (mg)
W_{400}	Catalyst weight after drying at 400 ºC (mg)
WAO	Wet Air Oxidation
WPO	Wet Peroxide Oxidation
WWTP	Waste Water Treatment Plant
X	Conversion (%)
X_{COD}	COD conversion (%)
X_{TOC}	TOC conversion (%)
Y_H	Heterotrophic yield coefficient

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PART I

Introduction and Methodology

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1. Introduction

1.1. Wastewater management

Human ingenuity has produced well over fourteen million chemicals substances which have never before been part of the terrestrial environment and the rate of discovery is increasing every day as illustrated on Figure 1.1 [1]. Some of these newly synthesised compounds, such as substances containing heavy metals and persistent organic pollutants, have been known to be dangerous for many years already, while fears have been raised about many others recently. [2]. The world-wide chemicals industry produced 400 million tons of chemicals in 1995. Europe is the largest chemicals-producing region in the world, accounting for 38 % of the total; Western Europe alone accounts for 33 % [3]. Chemicals production and use provide 2 % of Europe's gross domestic product (GDP) and 7 % of its employment. Chemicals production grew roughly in line with GDP until 1993 when it began to grow faster. Thus, the "chemicals intensity" (i.e. the volume of chemicals per unit of GDP) of Europe's economy is now considerably higher than it was years ago [3].

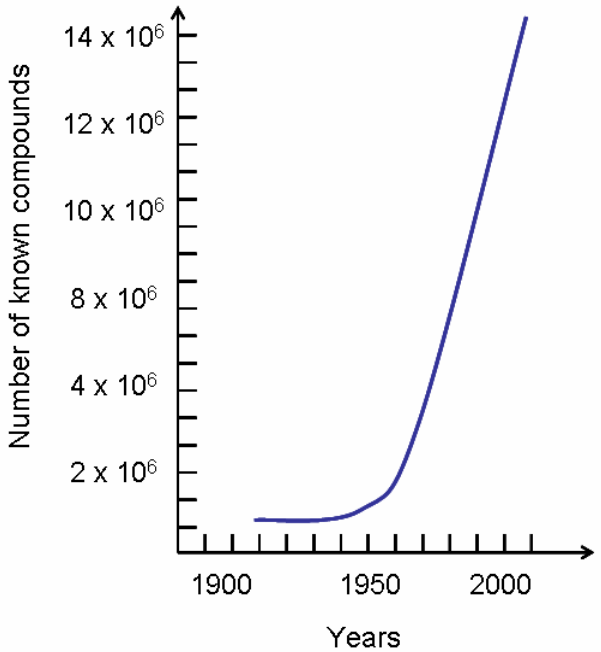

Figure 1.1. Rapid growth of chemical knowledge [1].

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The number of existing chemicals on the market is large, but the exact number is unknown. Over 100000 were registered in the European Inventory of Existing Commercial Chemical Substances in 1981, but the current estimate of marketed chemicals varies widely, from 20000 to as many as 70000 [3]. Several hundred new substances are marketed each year after some basic premarket toxicity testing and these are registered in the European List of Notified Chemical Substances, which presently contains about 2000 chemicals [3].

In addition to chemicals that are placed on the market, either as intermediates within a production process, or as part of final products, there is the unintentional formation of chemical by-products in many industrial processes, which can also impact on the environment. Clearly, solutions must be tailored to the properties and uses of each particular chemical and groups of chemicals, as well as to each country's unique circumstances. But action must be taken quickly. Each year that passes without effective action will result in decades of additional, unintended exposure to chemicals that are likely to be harmful to human health and the environment.

Water is a key resource for our quality of life. Access to clean water for drinking and sanitary purposes is a precondition for human health and well-being. Most people in Europe have access to drinking water of good quality. However, in some parts the quality still frequently does not meet basic biological and chemical standards.

Almost all human activities can and do impact adversely upon the water. Discharges from wastewater treatment plants and industry cause pollution by oxygen consuming substances, nutrients and hazardous substances. The adverse impacts depend very strongly upon the degree to which (if at all) such discharges are treated before reaching waterways.

In 2002, 90 % of the European Union's (25 countries) population was connected to sewage networks [4]. However, some of this wastewater is discharged either without or with only limited treatment. Regional differences in sewage treatment exist. For example, in the central European and Nordic countries more than 90 % of the population is connected to wastewater treatment plants, while the percentage in southern Europe and new Member States varies between 50 to 80 %. Over the last twenty years, marked increases have occurred both in the proportion of the population connected to wastewater treatment as well as in wastewater treatment technology.

Figure 1.2 illustrates the water stress in European countries by means of the Water Exploitation Index, which is the mean annual total abstraction of freshwater divided by the mean annual total renewable freshwater resources in each country [4].

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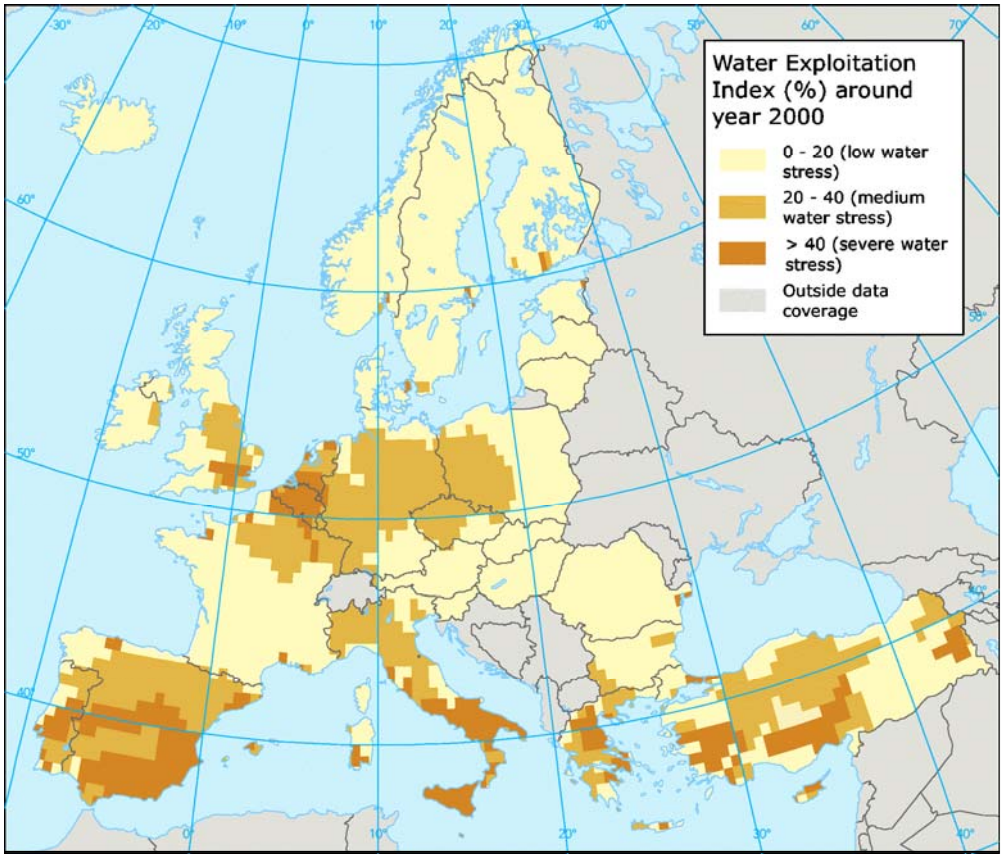

Figure 1.2. Water stress in Europe (2000) [4].

In Europe, on average about 21 % of the annually renewable freshwater resources are abstracted. In southern European countries, the pressure on water resources can be severe during summer when water abstraction to meet demands from the agricultural and tourist sectors is highest. Climate change and increasing water abstraction are expected to exert additional pressures on water resources, particularly in southern and Eastern Europe, and no differences on the map presented in Figure 1.2 are expected by year 2030 [4].

Therefore, in the world's consumer-based economy, the sustainable wastewater management is a critical issue associated to this rapid industrial and scientific development. The environmental concern is nowadays expressed by more and more governmental regulations imposing lower pollutant discharges limits. So, for many industrial sectors, pollution prevention, waste minimisation and reuse are being increasingly integrated in their environmental policies. Thus, challenges faced by chemical and related industries, due to unprecedented market demands and public environmental concern, are to imagine efficient and cost-competitive remediation processes and minimisation strategies for water pollution problems [1].

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Wastewater typically can be divided in two categories: urban and industrial. In the urban residues, the main pollutant load is organic, mostly non toxic and biodegradable. Usually, this kind of wastewater is treated in conventional wastewater treatment plants (WWTP) based on biological oxidation. On the contrary, industrial effluents usually have a very complex and toxic composition, depending on the industry that generates them, which often requires more severe remediation treatments. Examples of toxic and therefore non biodegradable organic pollutants are phenols, surfactants, chlorinated compounds, pesticides, aryl and chlorinated alkysulfonates, polyethylene and aromatic hydrocarbons, among many others [5].

Despite the banned or severely restricted use of all those chemicals since the late 1970s, their continued presence in groundwater, soil, sediment, surface water, and living tissues emphasises the concern regarding their persistence in the environment. Organic pollutants tend to accumulate in the tissues of animals and plants, often becoming more concentrated as they move up through the food chain. Many times, the symptoms of contamination may not manifest themselves until several generations after initial contact with the chemical of concern [6].

The importance of phenolic effluents, a part from their potential toxicity, is outlined by the high quantities that are eventually rejected in the environment. In addition, phenol is considered to be an intermediate product in the oxidation pathway or higher-molecular-weight aromatic hydrocarbons. Thus, it is usually taken as a model compound for wastewater treatment studies, as it is for the present research work.

Table 1.1 lists the amount of phenolic compounds released by some European countries in terms of direct emissions to water as well as the indirect emissions by transfer to an off-site wastewater treatment plant. It is noticeable that Spain releases the highest fraction of direct emissions (i.e. 44 %), which points out the deficiency of effective and cost-competitive wastewater processes in this country as well as the lack of severe environmental legislation on discharge limits for selected pollutants.

There is no doubt that water pollution is a continuing and even growing problem that arises from human activities. No unique solution seems possible for destroying all kind of water pollutants due to the heterogeneous composition of real wastes as well as the diversity of new chemical compounds that are continuously being synthesised. Some waste treatments merely transfer the toxic component from one phase to another. While this may serve to concentrate the wastes in a more readily disposable form, it does not alter the chemistry of the pollutants. Other processes use chemical reactions to transform the wastes 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 and should be generally made depending

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on the treated wastewater characteristics (e.g. concentration of target pollutants, degree of refractoriness, flow rate) and the destination of the effluent (i.e. natural media or subsequent treatment plant).

Table 1.1. European emissions of phenolic compounds to water (2004) [7].

Country	Direct emissions		Indirect emissions	
	Total (t year^{-1})	% of European emissions	Total (t year^{-1})	% of European emissions
Latvia	--	--	0.208	0.01
Slovenia	--	--	0.125	0.01
Portugal	0.1138	0.02	3.15	0.14
Finland	0.156	0.02	3.56	0.16
Austria	0.47	0.09	340.13	15.63
Denmark	0.4645	0.09	1.20	0.06
Ireland	0.692	0.13	0.049	0.00
Belgium	0.7162	0.14	2.28	0.10
Czech Republic	0.9623	0.18	611.60	28.10
Hungary	1.34	0.26	--	--
Greece	1.85	0.35	--	--
Netherlands	3.07	0.59	22.20	1.02
Slovakia	3.13	0.60	108.00	4.96
Sweden	7.82	1.50	--	--
Germany	13.45	2.58	841.97	38.68
Italy	21.75	4.17	149.82	6.88
France	35.54	6.82	10.13	0.47
Poland	38.13	7.32	18.99	0.87
United Kingdom	162.38	31.16	55.47	2.55
Spain	229.06	43.96	7.82	0.36
TOTAL	521.095	100.00	2176.702	100.00

Oxidation processes aim at the mineralisation of the contaminants to carbon dioxide, water and inorganic compounds or, at least, at their transformation into harmless products. There are four types of oxidative processes to treat wastes polluted with organic matter [8]:

- Biological treatment, which is not suitable for toxic waters or with a chemical oxygen demand (COD) >10 g L^{-1} and produces large amounts of sludge, although it is the most economical and extended process.
- Wet oxidation, well suited for COD loads ranging from 10 to 100 g L^{-1} and able to treat toxic wastes, under high temperature and pressure [9].

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- Advanced chemical oxidation processes at mild temperature and pressure conditions and using strong oxidisers (like chlorine, ozone or hydrogen peroxide), which are well suited to treat low concentrations of highly toxic or biological refractory organic pollutants.
- Incineration, which is appropriate for effluents having COD >100 g L^{-1}, although with high energetic costs, and being not environmental friendly due to the dissemination of dust to the atmosphere and related problems as the production of dioxins [9].

Figure 1.3 shows a technology map classifying several technologies available depending on their applicability depending on total organic carbon (TOC) concentration and effluent flow rate. The map outlines the areas where technologies are most effective, although boundaries should be only used as a guide [11]. As it can be seen in the map, biological treatment is the most versatile technique. Due in part to its cost effectiveness and versatility in handling a wide variety or organic pollutants, the attention traditionally received by biological oxidation processes far exceeds that of the other remediation processes. However, the presence of toxic chemicals in the waste streams makes difficult a biological treatment with a non-acclimatised culture. Then, when biological treatment is unfeasible, Wet Oxidation and Advanced Oxidation Processes (AOP) lead normally to the best yields in pollutant destruction [9,10].

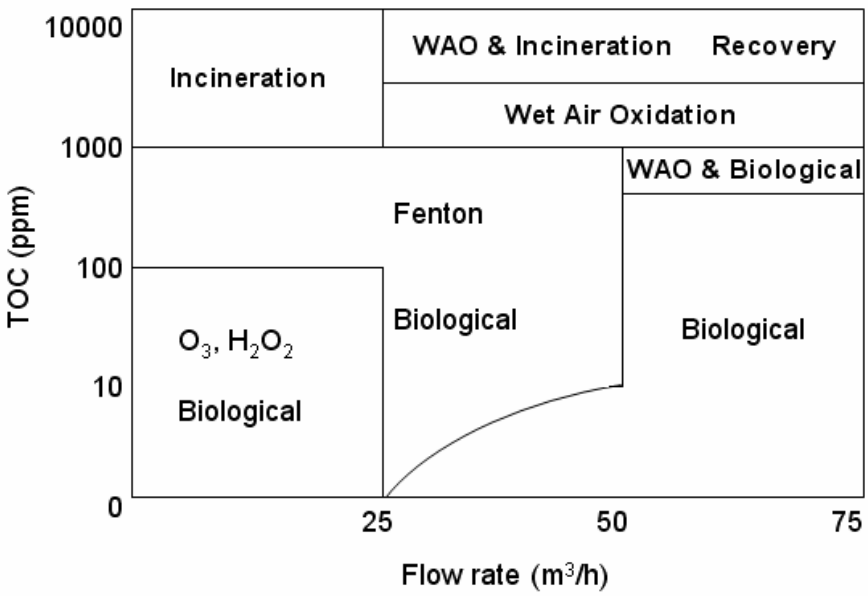

Figure 1.3.Technology map for the selection of suitable wastewater treatments [11].

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1.2. Wet Oxidation

Wet oxidation, also known as hydrothermal treatment, refers to the process of oxidising materials suspended or dissolved in liquid water with dissolved oxygen at elevated temperature. The wet oxidation technology has been successfully commercialised for 50 years. Over 200 full scale wet oxidation systems have been constructed and operated for a variety of applications ranging from elimination of hazardous wastes to the production of vanilla flavouring agent [12].

1.2.1. Wet Air Oxidation and Catalytic Wet Air Oxidation

The Wet Air Oxidation (WAO) process was originally developed by F.J. Zimmermann and its first industrial applications appeared in the late 1950s [13]. According to this method, the dissolved or suspended organic matter is oxidised in the liquid phase by some gaseous source of oxygen, which may be either pure oxygen or air. Typical operating conditions are in the range of 100-300 ºC and 0.5-20 MPa [9]. At high temperatures in aqueous solutions, the form in which oxygen participate in the chemical reaction is complex. The elevated temperatures necessary can lead to the formation of oxygen radicals, O·, which in turn can react with water and oxygen to form peroxide, H_2O_2, ozone, O_3, so that these four species (i.e. O_2, O·, H_2O_2, O_3) are all capable of participating in the organic compounds oxidation [14].

WAO is one of the few processes that do not turn pollution from one form to another, really makes it disappear. This process can achieve easily 90 to 95 % conversion [15], which usually is not enough to meet effluent discharge regulations despite biodegradability had been improved. Therefore, most WAO units are followed by a biological treatment step. Acetic and propionic acids appear to be the refractory to WAO. However, by increasing the temperature up to 310 ºC, all the compounds, including the previously mentioned acids, can be oxidised to over 90 %. Besides, organic nitrogen compounds are easily transformed into ammonia, which is also very stable in WAO conditions [16]. This in an attractive treatment for waste streams which are too diluted to incinerate and too concentrated for biological treatment. The main differences between the distinct industrial applications consist in the reaction type used and the incorporation, or not, of a catalyst.

A generalised kinetic model based on a simplified reaction scheme with acetic acid as the rate-limiting intermediate has been proposed by Li et al. (1991) [17], as presented in Figure 1.4. It is usually used to represent the kinetic data of WAO reaction with reasonably good fits [18]. Also it has been the starting point for more

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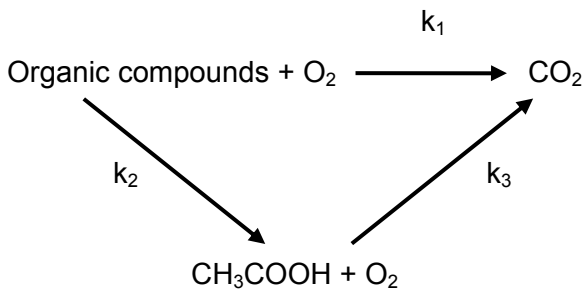
complex models accounting for other refractory reaction intermediates different from acetic acid [19].



$$\frac{[\text{Org.Comp.} + CH_3COOH]}{[\text{Org.Comp.} + CH_3COOH]_0} = \frac{k_2}{k_1 + k_2 - k_3} e^{-k_3 t} + \frac{k_1 - k_3}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t}$$

Figure 1.4. Simplified kinetic model for Wet Air Oxidation [17].

The challenging operating conditions of WAO provided a strong driving force to investigate catalysts which could allow substantial gains on temperature, pressure and residence time. Another major benefit of using catalysts in the WAO, the so called Catalytic Wet Air Oxidation (CWAO) process, is the possibility to oxidise refractory compounds, namely acetic acid and ammonia, at much lower temperatures than in the absence of catalyst. Compared to conventional WAO, CWAO offers lower energy requirement and much higher oxidation efficiencies. Commercial CWAO processes rely either on supported precious metal and/or base metal oxide catalysts or on homogeneous catalysts such as Fe or Cu. Although increasing the catalyst concentration can markedly increase the oxidation rate, an overloading of the catalyst would result in separation problems reducing the interest of such catalytic technique [20].

Up to date, the main drawback of CWAO, preventing it from a broad industrial application, consists in the catalyst deactivation, which occurs mainly due to active phase leaching or formation of carbonaceous deposits during the oxidation process. The most prominent catalysts affected by leaching of the active phase are mixed oxide catalysts [21]. Nevertheless, catalysts based on cerium oxide have recently shown a promising behaviour for the CWAO process of refractory compounds [22]. On the other hand, the carbonaceous deposits are related both to the nature of the organic pollutant and the reactor type used. The enhanced formation of such species has been confirmed by several authors in slurry reactors [23] with a characteristic high liquid to catalyst ratio that promotes the homogeneous polymerisation reactions. Comparative studies for different types of reaction systems have shown that the extent of these

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parallel side reactions in the liquid phase is significantly reduced in Trickle Bed Reactors (TBR) [24,25]. In addition, the large experience on the operation of TBRs in industrial hydrotreatment processes as well as the possibility to operate in different flow regimes (i.e. cocurrent downflow or upflow and countercurrent) makes them the first choice for the performance of CWAO reactions [26].

The pathways and mechanism of CWAO reactions have been studied in detail only for pure compounds. In the case of phenol, the existing reaction schemes available in the literature are generally based on the pioneer work of Devlin and Harris (1984) [14]. These authors in a study of the non-catalytic WAO of phenol carried out a deep analysis both to identify the most important intermediate products and to propose the reaction pathway as illustrated in Figure 1.5. More recent studies on the catalytic phenol oxidation showed similar intermediates in the presence of solid catalysts [27,28].

1.2.2. Wet Peroxide Oxidation and Catalytic Wet Peroxide Oxidation

As opposed to WAO, which uses a gaseous oxidising agent (molecular oxygen) and within a two step process (transfer plus oxidation), Wet Peroxide Oxidation (WPO) uses a liquid oxidising agent (hydrogen peroxide) which eliminates mass transfer problems. This process is adapted from Fenton's reaction but operates at a temperature of about 100-140 ºC, so higher TOC removal efficiency can be obtained (usually >25 % than with classical Fenton process). Unlike WAO, which is capital intensive, WPO needs limited capital but generates higher operating costs. The oxidation mechanism is the same as for Fenton's reaction, both based in the hydroxyl radical [8].

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. This can be favoured by step by step addition of H_2O_2 throughout the run in both batch and continuous reactor [8]. If hydrogen peroxide is efficiently used, the stoichiometric amount quantity can be sufficient to obtain nearly complete removal of pollutants [29].

In order to obtain higher pollutant removal using milder conditions, the development of the Catalytic Wet Peroxide Oxidation (CWPO) processes has received considerable interest. The comparison of homogeneous and heterogeneous CWPO processes is presented by Centi et al. (2000) [30]. Unlike homogeneous systems, heterogeneous systems can be recuperated by means of a simple separation

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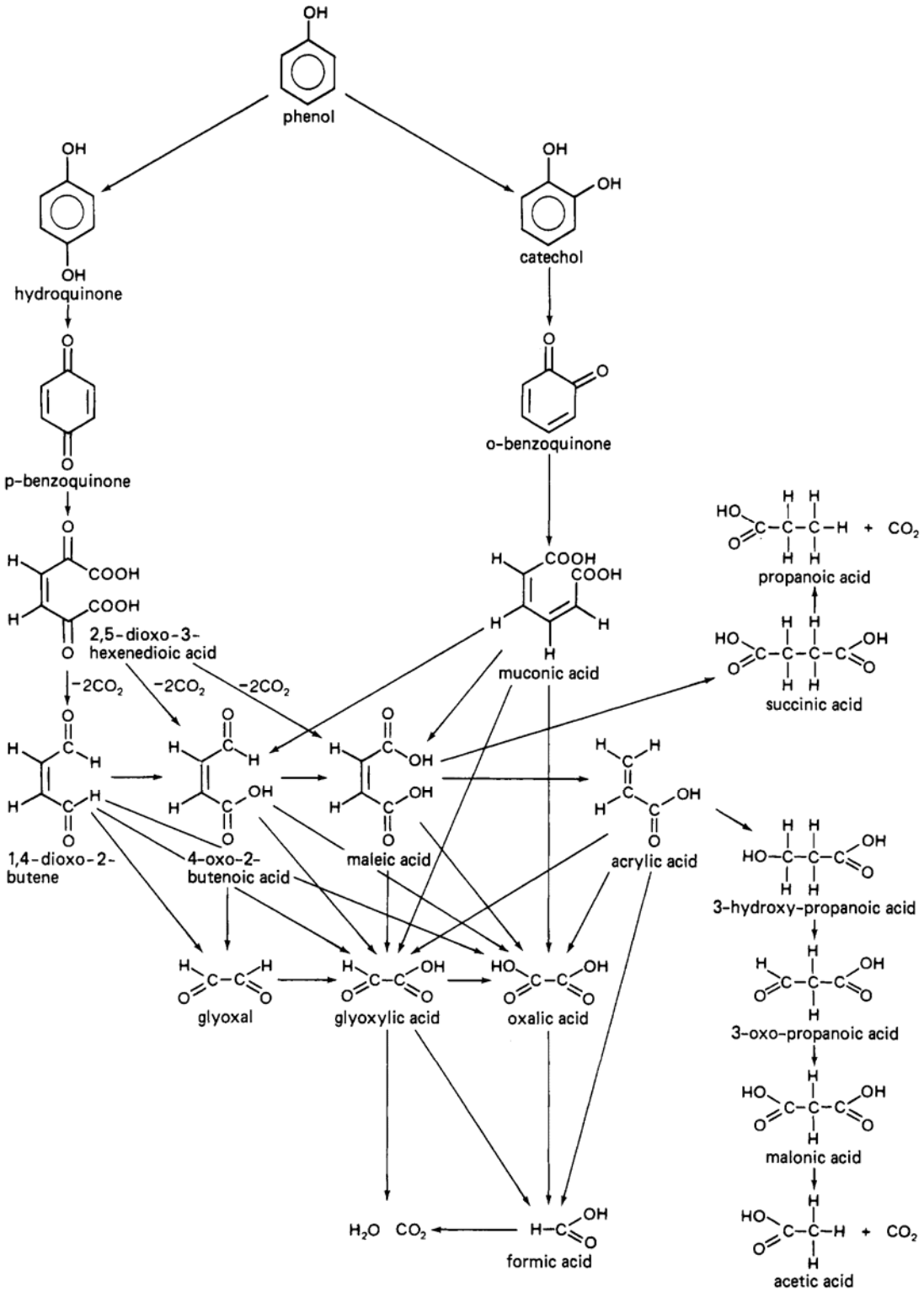

Figure 1.5. Proposed reaction pathway for phenol oxidation by molecular oxygen [14].

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operation and reused in the next run. Besides, heterogeneous catalysts have a higher reactivity and a reduced dependence on the pH of the solution. A review of the kinetics and mechanisms of the H_2O_2 decomposition by complexes of Cu(I), Cu(II), Fe(II), Fe(III), Mn(II), Mn(III), Ru(III), Ru(IV), V(V) and Ti(IV) has been recently published [31] and some specific soluble transition metal salts have shown to enhance the overall performance of WAO processes in presence of hydrogen peroxide [32-33]. Recently, novel materials such as iron containing zeolitic materials [34] or SBA-15 based nanocomposites [35] have shown a great potential for the CWPO of phenolic aqueous solutions. However, the main drawback of solid catalyst is its higher rate of hydrogen peroxide decomposition to water and oxygen.

1.3. Advanced Oxidation Processes

Advanced oxidation processes are alternatives to the incineration of wastes, which has many disadvantages. Conventional incineration is commonly thought to be a feasible alternative to landfill, but as presently practised, incineration may bring about serious problems due to releasing toxic compounds such as polychlorinated debenzodioxins and polychlorinated dibenzofurans into the environment via the incinerator off-gas emissions and/or fly ash [36].

The AOPs have proceeded along one of the two routes:

- oxidation with O_2 in temperature ranges intermediate between ambient conditions and those found in incinerators and WAO processes in the region of 1-20 MPa and 200-300 ºC; and
- the use of high energy oxidants such as ozone and H_2O_2 and/or photons that are able to generate highly reactive intermediates (•OH radicals) [36].

In 1987, Glaze et al. [37] defined AOPs as “near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification”. The hydroxyl radical (•OH) is a powerful non-selective chemical oxidant (as illustrated by Table 1.2), which acts very rapidly with most organic compounds (as illustrated by Table 1.3). The reaction rate constants of molecular ozone with different organic compounds are also given in Table 1.3. These reaction constants vary in quite a wide range from 0.01 to 10^4 M^{-1} s^{-1}. Once generated, the hydroxyl radicals aggressively attack virtually all organic compounds. Depending upon the nature of the organic species, two types of initial attack are possible: the hydroxyl radical can abstract a hydrogen atom from water, as with

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alkanes or alcohols, or it can add itself to the contaminant, as in the case of olefins or aromatic compounds [36].

Table 1.2. Relative oxidation power of some oxidising species [36].

Oxidising species	Relative oxidation power
Chlorine	1.00
Hypochlorus acid	1.10
Permanganate	1.24
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on TiO_2^+	2.35

Table 1.3. Reaction rate constants (k, M^{-1} s^{-1}) of ozone vs. hydroxyl radical [36].

Compound	O_3	·OH
Chlorinated alkenes	10^3-10^4	10^9-10^{11}
Phenols	10^3	10^9-10^{10}
N-Containing organics	10-10^2	10^8-10^{10}
Aromatics	1-10^2	18^8-10^{10}
Ketones	1	10^9-10^{10}
Alcohols	10^{-2}-1	10^8-10^9

A common reaction is the abstraction of hydrogen atom to initiate a radical chain oxidation can be summarised by Equations 1.1 to 1.5, as follows:

$$RH + \cdot OH \rightarrow H_2O + \cdot R \qquad \text{Eq. 1.1}$$

$$2 \cdot OH \rightarrow H_2O_2 \qquad \text{Eq. 1.2}$$

$$\cdot R + H_2O_2 \rightarrow ROH + \cdot OH \qquad \text{Eq. 1.3}$$

$$\cdot R + O_2 \rightarrow ROO\cdot \qquad \text{Eq. 1.4}$$

$$ROO\cdot + RH \rightarrow ROOH + \cdot R \qquad \text{Eq. 1.5}$$

The attack by the ·OH radical, in the presence of oxygen, initiates a complex cascade of oxidative reactions leading to mineralization of the organic compound. The exact routes of these reactions are still not quite clear. For example, chlorinated organic compounds are oxidised first to intermediates, such as aldehydes and carboxylic acids, and finally to CO_2, H_2O and the chloride ion. Nitrogen in organic

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compounds is usually oxidised to nitrate or to free N_2, sulphur is oxidised to sulphate [36].

As a rule or thumb, the rate of destruction of a contaminant is approximately proportional to the rate constant for the contaminant with ·OH radical. From Table 1.3 it can be seen that chlorinated alkenes are treated most efficiently because the double bond is very susceptible to hydroxyl attack. Saturated molecules (i.e., alkenes) react at a much slower rate and, therefore, are more difficult to oxidise.

Glaze et al. (1991) [38] conducted a bench scale study of the oxidation of concentrated nitrobenzene solutions using different AOPs: ozone at elevated pH, O_3/H_2O_2, H_2O_2/UV and O_3/UV. This study showed the existence of severe limitations of the application of typical AOPs for the treatment of concentrated wastewaters. In contrast to the oxidation of some micro-pollutants in fairly pure water (groundwater, process water of semiconductors, etc.), the treatment of organic compounds in water at relatively high concentrations (>1000 mg C L^{-1}) in complex matrices is energy and oxidant consuming. Therefore, taking into account that the efficiency of AOPs is compound specific, the final choice of the AOP system can be made only after preliminary laboratory tests.

Table 1.4 list a classification on AOP depending on whether UV light was used for the generation of radicals or not. The radical generation stage is the main difference among the following AOPs, since the substrate attack occurs similarly in all cases.

Table 1.4. Classification of AOP [36].

Non-photochemical processes	Photochemical processes
Ozonation	Ozonation + UV light (O_3/UV)
Ozonation + Hydrogen peroxide (O_3/H_2O_2)	Hydrogen peroxide + UV light (H_2O_2/UV)
Fenton systems (Fe^{2+}/ H_2O_2)	O_3/H_2O_2/UV
Electrochemical oxidation	Photo-Fenton (Fe^{2+}/ H_2O_2/UV)
Radiolysis and electron-beam treatments	Photocatalytic oxidation (UV/TiO_2)
Non-thermal plasma	
Ultrasounds	

1.3.1. Hydrogen peroxide

Hydrogen peroxide is a clear, colourless liquid which is completely miscible with water. Some physical constants of the main commercially available grades are recorded in Table 1.5 [39].

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Table 1.5. Physical properties of commercial H_2O_2 solutions [39].

Property	H_2O_2 strength (wt%)		
	35	50	70
Density at 20 ºC (g cm^{-3})	1.1312	1.1953	1.2886
Viscosity at 20 ºC (mPa s)	1.11	1.17	1.23
Freezing point (ºC)	-33	-52.2	-40.3
Boiling point (ºC)	107.9	113.8	125.5

The decomposition of hydrogen peroxide (Equation 1.6) is extremely important in handling and storing because the generation of gas and heat (-98.3 kJ mol^{-1}) may cause safety problems. The rate of decomposition increases with temperature and decomposition can be further accelerated by the presence of impurities, e.g. metal ions or metal oxides, or by increasing pH [39].

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad \text{Eq. 1.6}$$

H_2O_2 is a strong oxidant (standard potential 1.80 and 0.78 V at pH 0 and 14, respectively) 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 suphites, hypochlorites, nitrites, organic compounds and chlorine [40]. Oxidation by H_2O_2 alone is not effective for high concentrations of certain refractory contaminants, such as highly chlorinated aromatic compounds and inorganic compounds (e.g. cyanides), because of low rates of reaction at reasonable H_2O_2 concentrations. Transition metal salts (e.g. iron salts), ozone and UV-light can activate H_2O_2 to form hydroxyl radicals which are strong oxidants, as previously mentioned.

A great advantage or H_2O_2 compared to other common low cost oxidants comes from the active oxygen content, as reported in Table 1.6. This active oxygen content is calculated as the ratio between the weight of oxygen that can be transferred to a suitable substance and the molecular weight of the oxidant [39]. As can be seen, H_2O_2 largely exceeds all the other oxidants, with the exception of ozone which has important drawbacks such as the costly equipment required for its generation as well as its potential noxious effects. Then, from Table 1.6 it can be extracted that the price per kilo of H_2O_2 corresponds to 470 g of active oxygen, while in the case of e.g. NaBrO it drops down to 134 g.

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Table 1.6. Active oxygen content of some common oxidants [39].

Donor	% Active oxygen	Product
H_2O_2	47.0[a]	H_2O
O_3	33.3	O_2
t-BuOOH	17.8	t-BuOH
NaClO	21.6	NaCl
NaBrO	13.4	NaBr
HNO_3	25.4	NO_x
$KHSO_5$	10.5	$KHSO_4$
$NaIO_4$	7.2[b]	$NaIO_3$
PhIO	7.3	PhI

[a] calculated on 100% H_2O_2

[b] assuming only one oxygen atom is utilised

Industrially, hydrogen peroxide is used mainly as a non-selective oxidant, i.e. for paper, textile and cellulose bleaching, water purification and, particularly in Europe, in the manufacture of perborate and percarbonate used in detergents [39].

Hydrogen peroxide can be activated in the presence of transition metals with the general aim of increase its reactivity by converting H_2O_2 into a different, more active species. This is accomplished by three general methods [39]:

- By reacting H_2O_2 with metals capable to generate metal peroxy or hydroperoxy species, where the peroxo bond remains intact, resulting in an increase of either the electrophilic or the nucleophilic character of the peroxygens with respect to the initial oxidant.
- By using H_2O_2 as a monoxygen donor to produce highly reactive metal-oxo species, which is a typical behaviour of biomimetric systems based for example on Fe(II), Ru(II) and Mn(II).
- Through a radical decomposition of H_2O_2 with one-electron redox couple like Fe(II)/Fe(III) or Ti(III)/Ti(IV). These are the basis for the well known Fenton and Udenfriend systems, respectively, and a way for generating the highly reactive HO· radical. Although these systems are not very selective they do have some interesting applications such as in the wastewater treatment field.

1.3.2. Fenton process

Fenton's reagent was discovered more than 100 years ago, but its application as an oxidising process for destroying toxic organics was not applied until the late 1960s [41]. Fenton reaction wastewater treatment processes are known to be very effective in the removal of many hazardous organic pollutants from water. The main

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advantage is the complete destruction of contaminants to harmless compounds, e.g. CO_2, water and inorganic salts.

Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron initiates and catalyses the decomposition of H_2O_2, resulting in the generation of highly reactive hydroxyl radicals [42,43,44]. The generation of the radicals involves a complex reaction sequence in an aqueous solution [40]:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^-$ $k_{1.7} \approx 70\ M^{-1}\ s^{-1}$ (chain initiation) Eq. 1.7

$OH\cdot + Fe^{2+} + \rightarrow OH^- + Fe^{3+}$ $k_{1.8} = 3.2\cdot10^8\ M^{-1}\ s^{-1}$ (chain termination) Eq. 1.8

Moreover, the newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen (this reaction is referred to as a Fenton–like reaction). Ferrous ions and radicals are also formed in the reactions. The reactions are as shown in Equations 1.9-1.13.

$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{-}OOH^{2+} + H^+$ $k_{1.9} = 0.001\text{-}0.01\ M^{-1}\ s^{-1}$ Eq. 1.9

$Fe\text{-}OOH^{2+} \rightarrow HO_2\cdot + Fe^{2+}$ Eq. 1.10

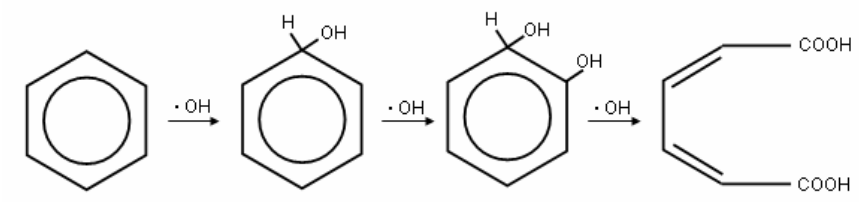
$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO_2^-$ $k_{1.11} = 1.3\cdot10^6\ M^{-1}\ s^{-1}$ Eq. 1.11

$Fe^{3+} + HO_2\cdot \rightarrow Fe^{2+} + O_2 + H^+$ $k_{1.12} = 1.2\cdot10^6\ M^{-1}\ s^{-1}$ Eq. 1.12

$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$ $k_{1.13} = 3.3\cdot10^7\ M^{-1}\ s^{-1}$ Eq. 1.13

As seen in Equation 1.13, H_2O_2 can act as an OH· scavenger as well as an initiator (Equation 1.7). Since $k_{1.13} = 3.3\cdot10^7\ M^{-1}\ s^{-1}$ while $k_{1.18} = 3.2\cdot10^8\ M^{-1}\ s^{-1}$, Equation 1.13 can be made unimportant by maintaining a high ratio of organics to H_2O_2.

Hydroxyl radicals can add to the aromatic or heterocyclic rings (as well as to the unsaturated bonds of alkenes or alkynes) [40], as illustrated by Equation 1.14.



Eq. 1.14

Hydroxyl radicals can also oxidise organics by abstraction of protons producing organic radicals (R·), which are highly reactive and can be further oxidised [40]:

$RH + OH\cdot \rightarrow H_2O + R\cdot \rightarrow$ further oxidation (chain propagation) Eq. 1.15

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The organic free radicals produced in Equation 1.15 may then be oxidised by Fe^{3+}, reduced by Fe^{2+} or dimerised according to the following reactions [40]:

$$R\cdot + Fe^{3+}\text{-oxidation} \rightarrow R^{+} + Fe^{2+} \qquad \text{Eq. 1.16}$$

$$R\cdot + Fe^{2+}\text{-reduction} \rightarrow R^{+} + Fe^{3+} \qquad \text{Eq. 1.17}$$

$$2R\cdot\text{-dimerisation} \rightarrow R - R \qquad \text{Eq. 1.18}$$

The sequence of Equations 1.7, 1.8, 1.15 and 1.16 constitute the present accepted scheme for the Fenton's reagent chain. Reaction rates with Fenton's reagent are generally limited by the rate of ·OH generation (i.e. concentration of iron catalyst) and less so by the specific wastewater being treated.

Fenton oxidation process has been successfully applied to wastewater, sludge or contaminated soil, with the effects being: organic pollutant destruction, toxicity reduction, biodegradability improvement, colour and odour removal [45]. Nevertheless, it should be noted that Fenton's chemistry is not a universal solution as there are many chemicals which are refractory towards Fenton's reagent such as acetic acid, acetone, carbon tetrachloride, methylene chloride, n-paraffins, maleic acid, malonic acid, oxalic acid, trichloroethane, etc. Moreover, it may happen that a certain compound in the waste stream is oxidised to some of the above-mentioned compound, which still acts as a pollutant and may not be allowed to be discharged, e.g. iso-propanol may be oxidised to acetone [46].

1.4. Activated Carbon

Carbon as a solid covers all natural and synthetic substances consisting mainly of atoms of the element carbon, such as single crystals or diamond and graphite, as well as the full variety of carbon and graphite materials [53]. Because of the increasing interdisciplinary importance of this group of materials in science and technology, the International Union of Pure and Applied Chemistry (IUPAC) took responsibility and recommended some terminology of "carbon as a solid" to facilitate consistency within the scientific nomenclature. The resulting definition for activated carbon is: a porous carbon material, a char, which has been subjected to reaction with gases, sometimes with the addition of chemicals, e.g. $ZnCl_2$, before during or after carbonisation in order to increase its adsorptive properties [47].

Any cheap material with a high carbon content, low in inorganics, can be used as a raw material for the production of activated carbon (AC). In early production

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procedures, preference was given to fossil materials such as wood, peat and wastes from vegetable origin, which included fruit stones and nutshells [48]. The current trend, however, is toward waste valorisation using different materials such as waste lignin [49] and sludge from biological treatment facilities [50].

The adsorbent properties of AC are essentially attributed to their large surface area, a high degree of surface reactivity and favourable pore sizes. The commercially available AC have a specific surface area of the order of 800-1500 $m^2 g^{-1}$ [48]. This surface area is contained predominantly within micropores, which have effective diameters smaller than 2 nm, but also within mesopores with diameters between 2 and 50 nm and macropores, having diameters greater than 50 nm, according to the Dubinin classification officially accepted by the IUPAC [51]. The macropores do not contribute much to the surface area but facilitates the access to micropores and mesopores, where most of the adsorption takes place. This classification is not entirely arbitrary, as it takes into account differences in the behaviour of molecules adsorbed in micropores and in mesopores. It appears that from pore widths exceeding 1.5 to 2.0 nm, the adsorbate condenses in a liquid-like state and a meniscus is formed. As a consequence, a hysteresis loop appears on desorption and its interpretation can lead to the distribution of the mesopores in the solid [48]. The limit between mesopores and macropores at 50 nm is more artificial and it corresponds to the practical limit of the method for the pore size determination based on the analysis of the hysteresis loop.

At the present time, the average structure of AC can be imagined as stacks of flat aromatic sheets cross-linked in a random manner, as shown in Figure 1.6 [54] and in agreement with Transmission Electron Microscopy direct observations.

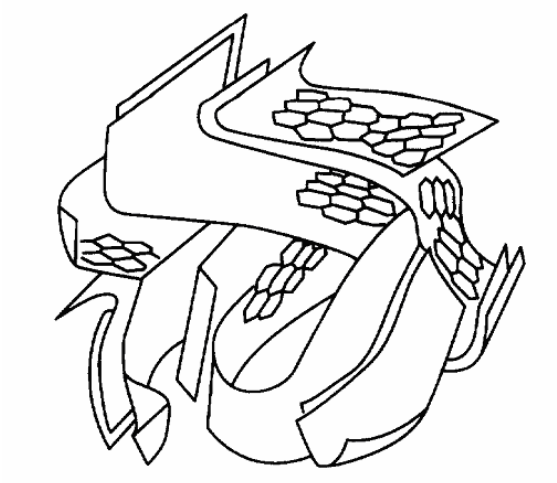

Figure 1.6. Schematic representation of the structure of AC [54].

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Besides the physical structure, AC has also a chemical structure that strongly influences the adsorption capacity. AC is associated with appreciable amounts of heteroatoms such as oxygen and hydrogen, but may also contain atoms of chlorine, nitrogen and sulphur, derived from the raw material or the activation process for the production of the carbon. These heteroatoms are chemically bonded at the edges of the aromatic sheets and form surface compounds or heterocyclic ring systems if they are incorporated within the carbon layers. Some of the surface oxygen groups found on AC are schematically represented on Figure 1.7 [53].

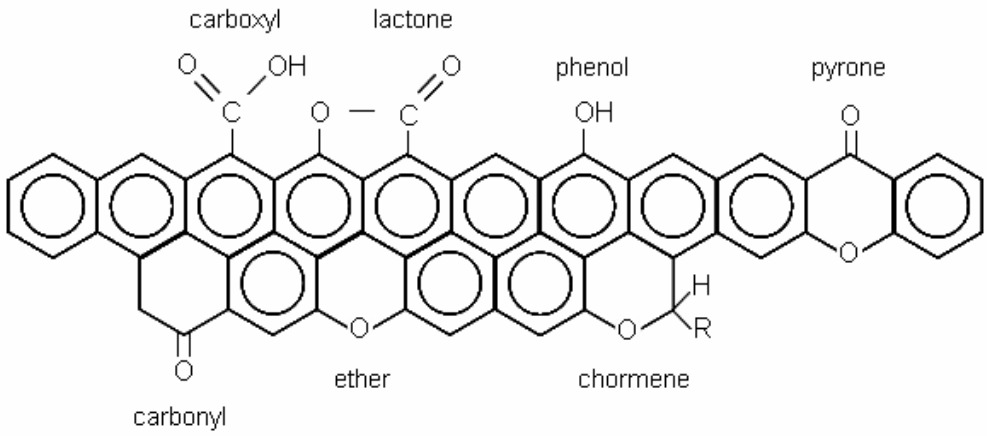

Figure 1.7. Examples of postulated oxygen functional groups existing on carbon surfaces [53].

Carbons have an acid-base character, developed as a result of surface oxidation depending on the history of its formation and the temperature at which it was oxidised. The surface oxygen structures are generally quite stable even under vacuum at temperatures below their formation temperature. However, when they are heated at higher temperatures they decompose to produce CO_2 and H_2O at lower temperatures and CO and H_2 at higher temperatures [48].

Boehm [52] differentiated the acidic group present on oxidised charcoals and carbon blacks by selective neutralisation techniques using bases of different strengths. In this method the carbon sample was agitated for at least 16 hours with 0.05 N solutions of $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa (sodium ethoxide). The strongly acidic groups neutralised by $NaHCO_3$ were postulated as carboxyl groups, whereas those neutralised by Na_2CO_3 but not by $NaHCO_3$ were believed to be lactones. The weakly acid groups neutralised by NaOH but no by Na_2CO_3 were postulated as phenols. The reaction with C_2H_5ONa was not considered a true neutralisation reaction since it did not involve exchange of H^+ by Na^+ ions. The groups reacting with C_2H_5ONa

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but not with NaOH were suggested to be carbonyls. The nature of the basic groups is less known an although structures of ether, chromene or pyrone type (see Figure 1.7) have been proposed, and which would be neutralised by HCl in the Boehm's neutralisation method, their structure is still under discussion [53].

Activated carbon is the most versatile adsorbent because of its large surface area, polymodal porous structure, high adsorption capacity and variable surface chemical composition. As a consequence, there are numerous applications in many different fields either in gas-phase or liquid phase. Liquid-phase applications require AC with larger pore size than gas-phase uses, because of the need for rapid diffusion of the liquid to the interior of the carbon particles and because of the large size of many dissolved molecules to be retained. Classically, the two main applications in liquid-phase have been water purification and sugar and sweeteners decolourisation [53].

There are three applications for AC in the treatment of wastewater. AC can be used as an adsorbent after primary and secondary biological processes, as an independent physico-chemical AC treatment of it can be added to biological aeration tanks and used as part of the secondary biological treatment. The choice of an appropriate treatment depends on the nature and contaminant loading of the wastewater, the scale of operation, specific requirements for effluent purity and the cost of carbon regeneration compared with alternative available treatments.

Growing concern over the treatment of industrial wastewater provides good opportunities for AC due to its ability to adsorb a wide variety of pollutants, including aromatic compounds, hydrocarbons, detergents, soluble dyes, chlorinated solvents, phenols and hydroxyl derivatives [53].

Removal of phenolic compounds by adsorption on AC has been extensively reviewed [48] and it has been found to be function of the surface area as well as the oxygen-containing surface structures. While the presence of an acidic group decreases adsorption of phenols, the presence of carbonyl oxygen enhances the adsorption. The choice of the carbon for the removal of phenols from aqueous solutions should favour AC having large surface areas but low acidic oxygen content, such as carbon prepared at high temperatures.

A part form their properties as adsorbents, carbon materials are well established, commercially available catalysts supports. Activated carbon is essential as support material for precious metal catalysts, which are widely used in the synthesis of high-value-added chemical products [53]. The fundamental properties that confer unique virtues to carbon as support are [54]:

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- the possibility of tailor the physical surface properties of the support (i.e., pore size distribution and surface area);
- the possibility to modify, over a very wide range, the chemical surface properties of the support; and
- the possibility to modify the nature of the (generally week) metal/support interaction.

Nevertheless, few large-volume catalytic processes currently use carbon-supported catalyst, despite the steady research in some promising areas such as glyphosate synthesis (a very efficient herbicide sold under the name of Roundup®) or the oxidation of cyclic ketone to dicarboxylic acids [55]. This situation is in part due to the lack of reliability that carbon enjoys as a support, both in industry and academia [53]. Since most manufacturers use a small fraction of their products for catalyst support applications, both the quality control methods and the batch-to-batch reproducibility of the product leave much to be desired. This leads to the undesirable situation in which under very similar reaction conditions, widely differing catalyst performance is achieved not only when different carbon supports are used, but also when one uses supports that are thought to be identical. Therefore, as already stated by Marsh et al. [53], the future growth of this industry depends on a better understanding and control of the chemistry of the carbon surface, which can then be exploited in the design of truly unique catalysts.

1.4.1. AC as catalyst in the CWAO process

As previously commented, AC has been most commonly used as adsorbent and catalyst support. Only in the last 10 years, AC without any additional active phase has shown to posses a long term catalytic activity in the oxidation of phenol [56,57], that could even surpass that of a conventional copper catalyst as shown in Figure 1.8. More recently AC has shown to be active for the oxidation of o-cresol, o-chlorophenol and aniline, while nitrophenol, sulpholane and nitrobenzene are extremely refractory to the CWAO process at the conditions tested by Suárez-Ojeda (2006) [58] (i.e. 140-160 ºC and 2-9 bar of P_{O2} in a trickle bed reactor). Parallel studies performed by Santos et al. (2006) [59] reach almost total phenol, o-cresol, p-cresol, o-nitrophenol and p-nitrophenol using AC but at more severe operation conditions (i.e. 160 ºC, 16 bar of P_{O2} in a fixed-bed reactor).

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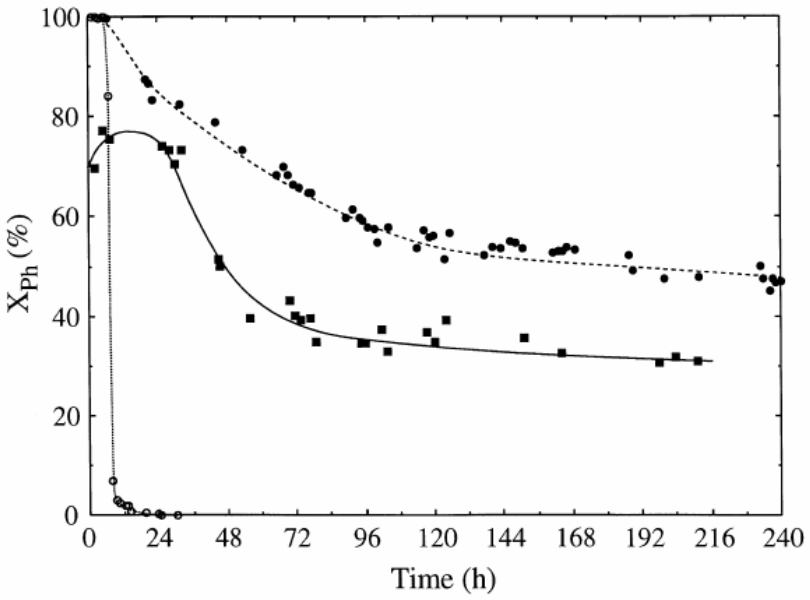

Figure 1.8. Comparison of phenol conversion profiles at 140 ºC and 4.7 MPa using AC in nitrogen (○) or air (●) and Cu0803 in air (■) [56].

Fortuny et al. (1998) [56] compared phenol conversion when using AC and a commercial copper catalyst (Cu0803) and both catalysts shown a continuous drop in phenol conversion for a 10 days run. For the case of Cu0803, the loss of activity was found to be due to leaching of the copper phase. On the other hand, the loss of AC efficiency could be attributed to its consumption during the experiment, since carbon and phenol oxidation are competitive reactions.

The key issue for the development and application of any CWAO process is the stability and deactivation of catalyst used under the given conditions. During phenol CWAO carbon textural and surface properties are likely to undergo modifications. On one hand the deposition of carbonaceous material on the carbon surface can physically block the pores giving rise to undesired catalyst fouling. On the other hand the soft attack of oxygen, if not leading to important burn-off, may continuously produce new surface oxide groups altering the original catalytic activity of the carbon [60].

The underlying mechanisms that are responsible for the catalytic activity of AC in CWAO are far from being well understood. To bring some light in this open aspect, a wide recompilation on carbon materials and CWAO of organic pollutants in wastewater has been carried out by Stüber et al. (2005) [60]. This review points out that special efforts have been made to assess the catalytic activity, stability and reactor performance rather than to elucidate the role of textural properties and surface groups

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in the oxidation reaction over AC. Nevertheless, it is now recognised that the carbon surface chemistry plays a key role on the origin of its activity. However, surface area and pore size distribution mainly control the access of reactants to the active sites of AC, thus being also of equal importance. Moreover, the last review prognostics an increasing catalytic use of AC for a wide range of commercial processes and a potential application in fine chemicals, fuel cells and environmental friendly technologies.

1.5. Combined processes

In general, a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. A potentially attractive alternative to complete oxidation through chemical means is the use of a chemical oxidation pre-treatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water [61].

As illustrated by Figure 1.9, coupling chemical pre-oxidation and biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared to the efficiency of each individual step [61,62]. It can be observed that, based on the molecular size of the pollutant, there is a breakpoint beyond which biological treatment is more attractive than chemical oxidation in terms of rate of C-C bond scission. This behaviour is though to be due to the increased difficulties of chemical oxidation processes (i.e. reduction of rate of C-C bon scission) with decreasing molecular size.

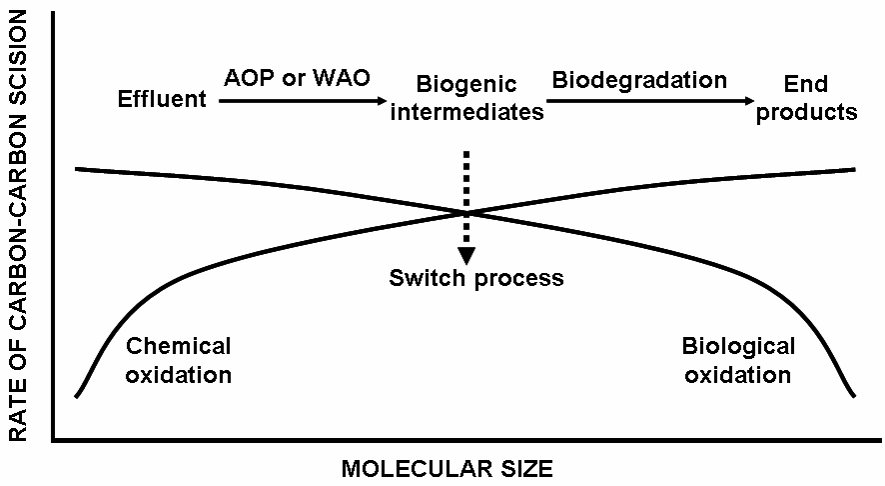

Figure 1.9. The concept of integrated chemical and biological treatment [61].

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Following this emerging concept, studies integrating WAO with biotreatment were done by Mantzavinos et al. (1999) [63], by Otal et al. (1997) [64] and by Patterson et al. (2002) [65]. These authors concluded that the overall reactor space time required during the integrated treatment is almost an order of magnitude less than that for a direct biological treatment of polyethylene glycol, p-coumaric acid and a mixture of linear alkylbenzene sulfonates, thus making the integrated process an attractive option. Besides, Donlangic and Levec (1998) [66] reported that CWAO yields products more biodegradable than WAO as a pre-treatment step. Finally, Suárez-Ojeda (2006) [58] has recently found that effluents from CWAO, using AC as catalyst for the oxidation of high strength o-cresol solutions, could be successfully combined with a conventional WWTP using non-acclimatised activated sludge in a pilot scale study. Thus, even in the case of non-toxic pollutants, process integration could be an advantageous option.

1.5.1. Biodegradability measurement

If an effluent from a chemical treatment is sent to a biological oxidation process, the characterisation of the effluent's biodegradability would be a key point to protect the biological system and assure the viability of such process combination. Some of the biodegradability determination tests that can applied to assess wastewater toxicity are: the Biochemical methane potential test, Biological Oxygen Demand (BOD) test and comparisons based on the BOD/COD ratio, Nitrification/denitrification inhibition, Respirometry, Ademosine triphospahate luminescence, Enzyme inhibition, the *Vibrio fishceri* bioassay (Microtox®) and Molecular based sensors [67,68]. However, the literature indicates that bioluminescence and respirometry based methods received much attention in recent research.

The drawbacks of using BOD for assessing the aerobic biodegradability of organics have been recognised since the early 1950s [61]. The limitations of the BOD test arise mainly form the fact that the microorganisms may not be adapted to utilise the organic compounds tested, while the rate of biodegradation also appears to vary with the pollutants concentration. On the other hand, most of the previously mentioned methods are either time consuming or not able to establish the biodegradability, toxicity or inhibitory effects of an organic compound over a non-acclimated biomass. Thus, its implementation to monitor and control a WWTP is not straightforward. What is more, for the evaluation of the potential toxicity of a compound, the preferred biological material should be activated sludge itself, since results obtained with any

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other biological material would be just an approach to reality. Therefore, although bioluminescent assays proved to have higher sensitivity to toxicants, they are less representative of effects on activated sludge compared to respirometry [69,70].

The basis of respirometric tests is that the respiration rate of activated sludge can be reduced in the presence of toxicants. The most common measure of bacterial respiration rate is the oxygen uptake rate, i. e. the amount of oxygen per unit volume and time that is consumed by the microorganisms [71]. Respirometry is a widely used technique to characterise wastewater toxicity to activated sludge and is a well-established procedure to assess the state of microbial activity and the quality of substrate and for calibrating microbial kinetic models [72]. Also, this technique can be applied to control and monitor WWTP [73] and it has just recently been applied to test biodegradability, toxicity or inhibition effects of WAO and CWAO effluents [58].

1.6. Peroxide Promoted Catalytic Wet Air Oxidation

The Peroxide Promoted CWAO (PP-CWAO) technique is a combination between WPO and WAO in which H_2O_2 is added at a low dose in order to promote radical reactions. When hydrogen peroxide is added to the WAO process, it may be assumed to decompose thermally by breaking the oxygen-oxygen bond resulting in the generation of two hydroxyl radicals. This results in the availability of free radicals at the very beginning of the process, thereby enhancing the degradation of the parent compound and eliminating the induction period [74].

The use of hydrogen peroxide in WAO systems offers the advantages of reduced residence times and lower capital costs. Its use may therefore be economically advantageous, especially when disposing of wastes from industries that already used hydrogen peroxide in the production process, such as textile industries [74].

This method was tested by Debellefontaine et al. (1996) [8] using a completely mixed batch reactor, loaded with phenol and ferrous sulphate (10 mg L^{-1}) solution at a convenient acidic pH (3.5). The total amount of hydrogen peroxide injected was usually 10 % of the amount necessary for a stoichiometric oxidation. The promoting effect of H_2O_2 on molecular oxygen at 160 ºC is shown in Figure 1.10. At that temperature, the initiating period with H_2O_2 was shorter and the final removal of TOC increased form 76 to 90 %. It can be seen that H_2O_2 promoted the oxidation reaction since the oxidation efficiency actually observed (i.e. curve 3 in Figure 1.10) was higher than that expected by adding the efficiencies of molecular oxygen and H_2O_2 if separate

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(i.e. curve 2 in Figure 1.10). The authors also found that WAO promoted with H_2O_2 gave better oxidation efficiencies at 160 ºC than conventional WAO at 220 ºC, therefore turning a high pressure process into a medium pressure one. Also, the promoting effect of peroxide was more marked at 160 ºC than at 220 ºC, where rapid thermal decomposition occurred. On the other hand, doses higher than 15 % did not significantly increase the efficiency and doses as small as 0.2 % had quite significant effect on the process performance. Finally, the work from Debellefontaine et al. (1996) [8] also shows that the oxidation intermediates identified were the same as during conventional WAO. Thus, both processes follow similar reaction pathways.

Imamura (1999) [20] found that the addition of H_2O_2 on the CWAO of phenol was neither very pronounced at 130 and 150 ºC, when phenol is quite stable, nor at temperatures of 180 and 200 ºC, when phenol shows enough reactivity and can be readily oxidised without H_2O_2. Thus, H_2O_2 addition only could exhibit its effect at moderate temperatures between 150-180 ºC.

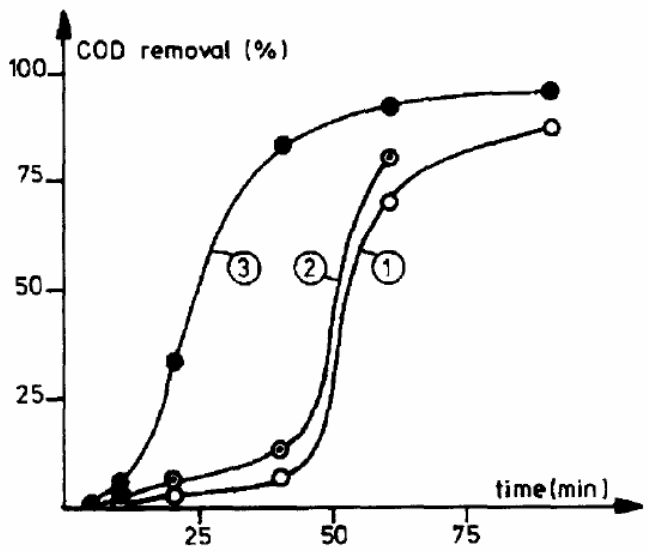

Figure 1.10. Effect of hydrogen peroxide during WAO of phenol at 160 ºC [8]:
① no peroxide; ② calculated curve from the addition of the theoretical effect of peroxide on curve 1; ③ with peroxide.

Table 1.7 summarises the most relevant contributions on CWAO processes using H_2O_2 for the oxidation of organic pollutants. It can be seen that usually the reactions were performed in batch reactors and using metal based catalysts. It was not until Paradowska (2004) [29] that the PP-CWAO process was conducted in a continuous reaction system and using AC as catalyst without any metal supported

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species. This author found that addition of 20 % of the stoichiometric H_2O_2 for complete mineralisation lead to 92 % phenol removal, while 40 % H_2O_2 was necessary to remove 76 % of p-nitrophenol and only 10 % H_2O_2 for removing 92 % of aniline at 170 ºC in a packed bed reactor (τ =0.11 h).

In this research work, the performance of the PP-CWAO process will be tested for the oxidation of phenolic aqueous solutions taking advantage of the combined effect of H_2O_2 and the classical CWAO process over a highly adsorbent and catalytic material such as activated carbon and in a trickle bed reactor configuration, as already presented in Rubalcaba et al. (2007) [77].

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Table 1.7. Review of CWAO processes using H_2O_2 for the oxidation of organic pollutants.

Substrate	Operation conditions	Catalyst	Reactor configuration	Removal efficiency	Ref.
phenol	160-200 ºC, excess O_2, pH 3.5, 0.2-20 % H_2O_2	$Fe(SO)_4$ 10 mg L^{-1}	batch	X_{COD} = 90 %	Debellefontaine et al. (1996) [8]
m-chlorophenol, m-cresol and p-ethylphenol	150 ºC, P_{O2} 0.5 bar, 3 g H_2O_2/ 1 g COD L^{-1}	--	batch	X_{COD} = 90 %	Lin and Wu (1996) [75]
dyeing wastewater (TOC_0= 4300 mg L^{-1})	200 ºC, excess O_2	Cu supported on AC	batch	X_{TOC} = 72 % 80 % colour removal	Lei et al. (1998) [76]
phenol 0.01 mol L^{-1}	328-468 K, pH 2-13, P_{O2} 0.4 MPa, H_2O_2 0.01-0.04 mol L^{-1}	Cu^{2+}, Co^{2+}, Mn^{2+} 10 mg L^{-1}	batch	X_{phenol}= 100 %	Rivas et al. (1999) [33]
phenol (1750 mg L^{-1}) acetic acid (5000 mg L^{-1})	100-200 ºC, P_{O2} 1 MPa, H_2O_2 1000 mg L^{-1}	$Cu(NO_3)_2$ for acetic acid	batch	X_{TOC} = 100 % for phenol X_{TOC} = 15 % for acetic	Imamura (1999) [20]
phenol, p-nitrophenol and aniline (5000 mg L^{-1})	170 ºC, P_{O2} 3.4 bar, H_2O_2 10-40 % stoichiometric, τ = 0.010-0.167 h	activated carbon	packed bed reactor	X_{phenol}= 92 % $X_{p\text{-}nitrophenol}$= 76 % $X_{aniline}$= 92 %	Paradowska (2004) [29]
phenol, o-cresol and p-nitrophenol (5000 mg L^{-1})	140 ºC, P_{O2} 2 bar, H_2O_2 20 % stoichiometric, τ = 0.12 h	activated carbon	trickle bed reactor	X_{phenol}= 64 % $X_{o\text{-}cresol}$= 64 % $X_{p\text{-}nitrophenol}$= 49 %	Rubalcaba et al. (2007) [77]

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2. Hypotheses and objectives

2.1. Hypotheses

The treatment and safe disposal of hazardous organic waste materials in an environmentally acceptable manner and at reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment processes for most wastewaters since they fulfil the above two requirements. Nonetheless, biological processes do not always give satisfactory results, especially when applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic and/or resistant to biological oxidation [1]. In view of these challenges, advances in chemical wastewater treatments are essential.

WAO is suitable for effluents that are either too dilute for incineration of too toxic and concentrated for biological treatment. Using a catalyst such as activated carbon in WAO process [2], lead to employ both milder temperatures and pressures to oxidise refractory contaminants in water, since on AC surface there are active sites capable to generate oxygen radicals. When CWAO is applied, the oxidised effluents are more biodegradable allowing the combination of chemical oxidation with a subsequent biological treatment [3]. At the conditions typically employed in CWAO, hydrogen peroxide is a known source of highly reactive hydroxyl radicals [4]. According to the radical nature of CWAO processes, the use of hydrogen peroxide as a free radical promoter increases the rate of oxidation, speeding up the initiation step of reaction [5].

All these evidences permit to propose the following:

- The addition of H_2O_2 to the CWAO process would promote the oxidation reactions leading to a higher organic removal than when only molecular oxygen is used.
- Active carbon would be able to decompose H_2O_2 much faster than when H_2O_2 decomposes freely. So, H_2O_2 could give the initial radical concentration that help starting the oxidation chain.
- Combination of catalytic and adsorption characteristics of AC and promotion of CWAO with H_2O_2 would give more biodegradable effluents.

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2.2. Objectives

According to the conclusions extracted from the literature review, there is a need for new technologies to enhance detoxification and biodegradability of industrial effluents. To address this emerging concept, the here named Peroxide Promoted Catalytic Wet Air Oxidation Process will be developed as the main objective of this doctoral research. In particular, the following specific tasks were formulated in order to meet with the main objective:

1. To study of the classical Fenton process (hydrogen peroxide oxidation with iron salts as catalyst) in a batch reaction system, aiming to:
    - Select suitable analytical techniques for samples containing H_2O_2.
    - Study the dependence of phenol degradation on H_2O_2, Fe^{2+} catalyst, pH and reaction temperature.

2. To study of effect of H_2O_2 in the CWAO process in a TBR using AC as catalyst, by means of:
    - Supply different amounts of H_2O_2 for the CWAO of phenol.
    - Perform control tests over an inert support to highlight the catalytic and adsorption properties of AC.
    - Perform control tests in inert atmosphere to discriminate the promoting or synergistic effect of combining O_2 and H_2O_2 in a single process.
    - Apply the PP-CWAO for the treatment of substituted phenolic compounds different from phenol.
    - Produce iron containing AC that could be applied to the PP-CWAO as a Fenton-like catalyst.
    - Characterise the biodegradability enhancement of oxidised effluents as an indicator of the viability of PP-CWAO as a chemical pre-treatment that could be combined with a classical biological treatment.

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3. Methodology

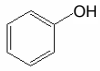
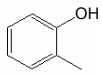
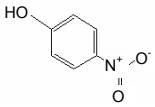
This chapter describes in detail the materials, experimental set-ups and analytical techniques used for characterising the effluents from the Fenton and PP-CWAO processes as well as the AC and the FeAC catalysts employed. These characterisation techniques were selected and adapted to deal with the complex matrix found in the outlet samples from phenolic compounds oxidation on one hand, and on the other hand to shed some light on the catalytic performance of AC.

3.1. Materials

3.1.1. Model compounds

Deionised water and analytical grade phenol, o-cresol, p-nitrophenol and 2-chlorophenol were used to prepare 5 g L^{-1} initial solutions. Some technical information about these model compounds is given in Table 3.1.

Table 3.1. Model compounds referenced in this study.

Compound	Molecular Formula and Structure	Molecular mass (g mol^{-1})	Solubility in water (g L^{-1} at 20 ºC)	Purity (%)	Supplier
phenol	C_6H_6O 	94.11	90	99.0	Panreac
o-cresol	C_7H_8O 	108.14	20	99.0	Aldrich
p-nitrophenol	$C_6H_5NO_3$ 	139.11	16	98.0	Aldrich

3.1.2. Oxidants

Hydrogen peroxide was supplied by Panreac as a 30 % w/v aqueous solution. The gaseous oxidant was high purity synthetic air (C45), 99.9995% purity, from *Carburos Metálicos*.

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3.1.3. Catalysts

For Fenton experiments, Fe^{2+} salt used as catalyst was ferrous sulphate 7-hydrate ($FeSO_4 \cdot 7H_2O$). It was obtained from Panreac at 99% purity.

Activated carbon was supplied by Merck (Reference 2518) in the form of 2.5 mm pellets. Some characteristics of this carbon are in Table 3.2. Prior to use, AC was crushed and sieved. The size fraction between 25 and 50 mesh (0.7-0.3 mm) was chosen for experiments in the trickle bed in order to minimise both pressure drop and internal mass transfer limitations [1]. This fraction was washed with deionised water to remove all fines, then dried at 105±1 ºC overnight, allowed to cool and stored under inert atmosphere until use. This AC was selected based on a previous study from Fortuny et al. (1999) [2].

Table 3.2. Physical characteristics of AC as supplied by the manufacturer.

Source	Charcoal
Ash content (%)	3.75
Surface area (m^2/g)	1140
Average pore diameter (nm)	1.4
Pore volume (cm^3/g)	0.48

3.1.3.1. Fe containing activated carbon materials (FeAC)

This section describes the preparation of different FeAC materials obtained during a research stay in the *Grupo de Ingeniería Química y Ambiental* (GIQA) from the *Universidad Rey Juan Carlos* in Móstoles (Madrid).

a) Materials:

The AC was the same as when used as direct catalyst (Merck ref. 2518). Chlorohydric acid (35%), nitric acid (37%), hydrogen peroxide (30% wv) and sulphuric acid (98%) used in AC oxidation treatments were from Sigma-Aldrich. Ammonium persulphate (ACS) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were from Acros Organics.

b) Preparation:

First of all, to prepare the FeAC catalysts, the 25-50 mesh fraction of commercial AC (AC-M) was washed with HCl 2N overnight under reflux in order to remove all traces of metals and any other impurity that may be present [3]. Then it was washed with ultrapure water until the pH of the rising waters reached a value of 6, and finally it was dried overnight at 105±1 ºC. Secondly, this demineralised AC (AC-L) was

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submitted to three different oxidation treatments following the study by Salame et al. (1999) [4]. The first treatment was carried out in nitric acid for 24h at room temperature and the second in a mixture (50:50) of hydrogen peroxide and 1M sulphuric acid for 1 h at 50 ºC. The third oxidation treatment took place in a saturated solution of ammonium persulphate in 1M sulphuric acid, for 18h at room temperature. These oxidised carbons were named after the three oxidation treatment methods as it appears in Table 3.3. All three oxidized carbons were then allowed to adsorb iron from an iron nitrate solution prepared to be 10% of Fe in weight with respect to the AC-L sample for 24h at room temperature. Finally these FeAC catalysts were calcined in two different ways to gain stability by fixing the iron species into the AC matrix and to remove the less stable oxygen surface groups [5]. The first calcination took place at 250±5 °C for 2h in air atmosphere. The second calcination was carried out under inert N_2 atmosphere at 500±5 °C for 5h. Eventually, 6 different FeAC catalysts were available (Table 3.3).

Table 3.3. Description of all carbon materials used in this study.

Carbon material	Description
AC-M	Commercial AC (25-50 mesh)
AC-L	AC-M after washing with HCl
AC-CN	AC-L oxidised with HNO_3
AC-HP	AC-L oxidised with H_2O_2/H_2SO_4
AC-APS	AC-L oxidised with $NH_4S_2O_8$
AC-M-Fe	AC-M after iron impregnation
AC-L-Fe	AC-L after iron impregnation
AC-CN-Fe	AC-CN after iron impregnation
AC-HP-Fe	AC-HP after iron impregnation
AC-APS-Fe	AC-APS after iron impregnation
AC-CN-Fe-500	AC-CN-Fe calcined at 500ºC in N_2
AC-HP-Fe-250	AC-CN-Fe calcined at 250ºC in air
AC-APS-Fe-500	AC-HP-Fe calcined at 500ºC in N_2
AC-CN-Fe-250	AC-HP-Fe calcined at 250ºC in air
AC-HP-Fe-500	AC-APS-Fe calcined at 500ºC in N_2
AC-APS-Fe-250	AC-APS-Fe calcined at 250ºC in air

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3.2. Fenton process

3.2.1. Experimental set-up

Figure 3.1 schematically shows the batch reactor used for Fenton experiments. The equipment consists of three main sections: the thermostatic bath, the reaction system and the hydrogen peroxide pumping block.

The thermostatic bath (Haake, model T3) filled with water was used as a heating system to control the operating temperature. The reaction system consists of a 250 mL jacketed glass reactor, which allowed the flow of heating water. The vessel was magnetically stirred. A thermometer placed inside allowed measuring the temperature. Hydrogen peroxide was initially added using a 25 mL burette which was changed by a Micro Pump (Bio-Chem Valve, Series 120 SP) to better control the rate of oxidant addition, fixed at 2 mL min^{-1}. Samples were periodically withdrawn using a 10 mL glass syringe.

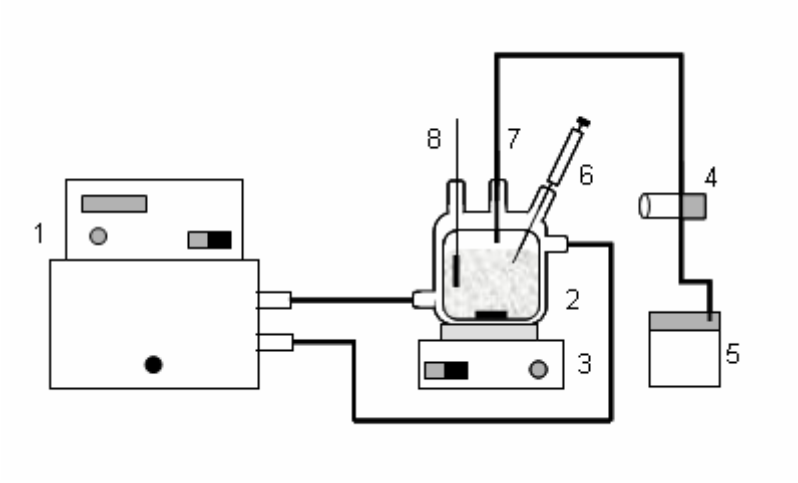

Figure 3.1. Experimental set-up for Fenton Oxidation Process: (1) thermostatic bath, (2) jacketed glass reactor, (3) magnetic stirrer, (4) Micro Pump, (5) H_2O_2 reservoir, (6) sampling port, (7) H_2O_2 injection port and (8) thermometer.

3.2.2. Experimental procedure

The reactor was filled with 150 mL of phenolic compound solution (5 g L^{-1}), then the initial pH was measured and in some cases adjusted to 2.8 with H_2SO_4. Before adding the corresponding amount of ferrous catalyst, the system was allowed to reach the operating temperature. The reaction time started when hydrogen peroxide addition began. Batch experiments were performed for 60 minutes. Samples (2 mL) were periodically withdrawn every approximately 1, 3, 5, 10, 15, 30 and 60 minutes of

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reaction and placed in the refrigerator at 4±1 ºC or basified with NaOH to stop the reaction.

Organic compounds were analysed by high performance liquid chromatography (HPLC) or occasionally by gas chromatography (GC). Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and pH were also measured to all the samples.

The operating parameters studied for phenol were:

- H_2O_2 concentration: the stoichiometric quantities for phenol complete mineralization, according to Equation 3.1, and the double of that stoichiometric quantity, were used.

$$C_6H_5OH_{(aq)} + 14\ H_2O_{2\ (aq)} \rightarrow 6\ CO_{2\ (g)} + 17\ H_2O_{(l)} \qquad \text{Eq. 3.1}$$

- Catalyst concentration: high concentrations of Fe^{2+} catalyst, expressed as 1/10 or 1/5 w/w of the amount of H_2O_2 (ranging from 450 to 1700 mg L^{-1} of Fe^{2+}), and also low concentrations, ranging from 5 to 100 mg L^{-1} of Fe^{2+}, were tested.
- pH: experiments were performed adjusting the pH of the initial solutions to pH 2.8 using H_2SO_4 and also without adjustment.
- Temperature: 30, 50 and 85 ºC were fixed as operating temperatures.

The previous parameters can be combined to give four different experimental sets at high concentrations of catalyst (A, B, C and D, in Table 3.4), which have been tested for each temperature and for the two pH giving a total number of 24 variables combination. From those results, the best combination of temperature, pH and hydrogen peroxide concentration was selected to study the effect of low concentrations of catalyst (E, F, G and H, in Table 3.4).

Table 3.4. Operating parameters for Fenton Oxidation Process.

Experimental set	H_2O_2*	Fe^{2+}	Molar ratio organic:H_2O_2:Fe^{2+}
A	100 %	1/5 w/w of H_2O_2	1:14:0.343
B	200 %	1/5 w/w of H_2O_2	1:28:0.685
C	100 %	1/10 w/w of H_2O_2	1:14:0.171
D	200 %	1/10 w/w of H_2O_2	1:28:0.343
E	100 %	100 mg L^{-1}	1:14:0.034
F	100 %	50 mg L^{-1}	1:14:0.017
G	100 %	10 mg L^{-1}	1:14:0.003
H	100 %	5 mg L^{-1}	1:14:0.002

*% of stoichiometric H_2O_2 for complete mineralisation to CO_2 and H_2O (Eq. 3.1).

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3.3. Peroxide promoted catalytic wet air oxidation

3.3.1. Experimental set-up

The original experimental set-up was designed by Fortuny (1996) [6] to study the CWAO of phenol in cocurrent downflow Trickle Bed Reactor (TBR) using copper-based catalysts. The fixed bed reactor was chosen to reduce polymerisation reactions, which take place in slurry systems as was demonstrated by Fortuny et al. 1998 [7] and Stüber et al. 2001 [1]. The original standard TBR configuration was modified as the experimental methodology was being optimised by adding a parallel pumping system to be able to feed the organic and the oxidant influents in two separated pipe lines.

Figure 3.2 shows a detailed scheme of the system used in this work. The original standard TBR configuration was modified as the experimental methodology was being optimised by adding a parallel pumping system to be able to feed the organic and the hydrogen peroxide influents in two separate pipe lines, which were joined before entering the oven. Therefore, the experimental set-up contains two 5 L stirred tanks for the liquid feed solutions (i.e. phenolic and H_2O_2 aqueous solutions), which are connected to two high precision metering pumps (Eldex, Recipro HP Series model AA-100-S-2-CE) that can deliver up to 500 mL h^{-1} at a maximum pressure of 350 bar. These pumps feed a TBR made of a titanium tube (20 cm long and 1.1 cm i.d.) filled with the catalytic material. A thermocouple is inserted axially into the reactor to measure the temperature inside the bed. The AC is retained by a sintered metal disk at the bottom of the reactor.

The reactor is placed in a temperature-controlled air convection oven (±1 ºC). The air comes from a high pressure cylinder equipped with a pressure regulator to maintain the operating pressure constant. The gas and the liquid streams are mixed and pre-heated before entering the reactor. There are two vessels to separate the outlet effluent, and a 2 mL tube for sampling. A rotameter placed at the end line allows to measure and control the air flow rate. Besides the reactor itself, all the piping system is made of stainless-steel 316.

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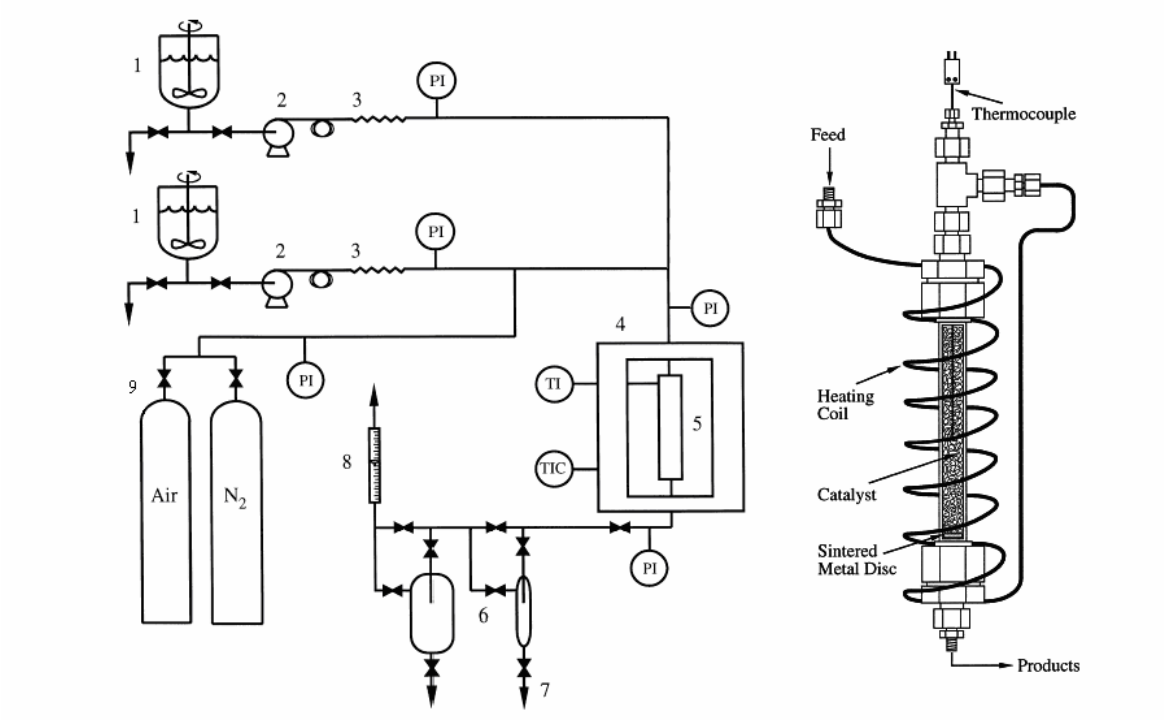

Figure 3.2. Trickle bed reactor and experimental set-up for the PP-CWAO: (1) feed vessels, (2) high pressure liquid pumps, (3) pulse dampeners, (4) oven, (5) trickle bed reactor, (6) gas liquid separation system, (7) sampler, (8) gas flow meter and (9) gas cylinders.

3.3.2. Experimental procedure

Each experiment in the TBR was conducted for 72 h since usually this was the necessary time for the system to achieve the steady state. The air flow rate was held constant at 2.4 mL s^{-1} (STP conditions) to guarantee excess oxygen. The liquid hourly space velocity (LHSV) was set to 8.2 h^{-1}, which is equivalent to a space time (τ) of 0.12 h, i.e. a liquid flow rate of 57 mL h^{-1}, according to the weight of the catalytic bed (usually 7.00 g). Phenolic compound feed concentration was 5 g L^{-1}. Three different temperatures were tested (120, 140 and 160 ºC) at an oxygen partial pressure of 2 bar, respectively giving a total working pressure of 11.5, 13.1 or 15.6 bar depending on the reaction temperature. In the above conditions, the fixed bed reactor operates in trickle flow regime [8].

The above conditions were selected in order to achieve phenol conversions in the range 40-80% according to previous results [9], so a better comparison of results can be done. Higher temperatures or lower liquid flow rates would give too high phenol conversions and, on the other hand, lower temperatures or higher liquid flow rates would yield very low phenol conversions [10].

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Some experiments were performed with nitrogen instead of air, keeping the same working pressure and hydrodynamic conditions. Also, some experiments were performed without AC, using SiC as inert support (IS) to reproduce the trickle flow regime.

A given amount of H_2O_2 corresponding to 10, 15, 20 or 30% of the stoichiometric amount needed for complete phenol mineralization (see Equation 3.1) was added directly to the feed tank. This tank was refilled with new solution every 24 h, to avoid any loss of H_2O_2 by decomposition. After the TBR configuration was modified to feed the phenolic aqueous solution and the oxidant though separated lines, it was no longer necessary to prepare new daily initial solutions.

The H_2O_2 dose for the oxidation of o-cresol and p-nitrophenol aqueous solutions was calculated according to the following equations:

$$C_7H_8O_{(aq)} + 17\ H_2O_{2\ (aq)} \rightarrow 7\ CO_{2\ (g)} + 21\ H_2O_{(l)} \qquad \text{Eq. 3.2}$$

$$C_6H_5OH_{(aq)} + 14\ H_2O_{2\ (aq)} \rightarrow 6\ CO_{2\ (g)} + 16\ H_2O_{(l)} + NO_3^- + H^+ \qquad \text{Eq. 3.3}$$

The starting-up of the experiments begins by filling the reactor with the corresponding mass of catalyst or inert support. Then the system is pressurised with N_2 to check possible leaks. After that, the oven is turned on and set to the reaction temperature, while the gas (N_2) is allowed to flow and adjusted until the required pressure is reached. In the meantime, the phenolic and H_2O_2 solutions are prepared and placed in the feed vessels. When the reactor temperature is close to the set point, the liquid flow is started and controlled through a mass flowmetre. The reaction is considered to start (i.e. time on stream= 0 h) once the liquid flow, the reaction pressure and temperature are stable. When necessary, this is the moment in which the gas flow is changed to air.

Outlet liquid samples were periodically withdrawn and stored at 4 ºC until they were analysed for organic removal, COD or TOC reduction. pH was also measured to all the samples. At the end of each run, the AC was dried at 105±1 ºC under nitrogen flow, weighted and stored under inert atmosphere until characterisation.

All the experiments were performed twice and results showed an acceptable experimental error of ±5 %.

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3.3.3. Process calculations

a) Liquid flow rate:

The operation liquid flow rate was calculated according to the fixed LHSV and the weight of the catalytic bed as follows:

$$Q_L = \frac{m_{AC}}{\rho_L} \cdot LHSV = \frac{m_{AC}}{\rho_L \cdot \tau} \quad (mL\ h^{-1}) \qquad \text{Eq. 3.4}$$

where, Q_L: liquid flow rate (mL h^{-1}) = 57.4 mL h^{-1}

m_{AC}: catalyst weight (g) = 7.00 g

ρ_L: liquid density (g mL^{-1}) ≈ 1 g mL^{-1}

LHSV: liquid hourly space velocity (h^{-1}) = 8.2 h^{-1}

τ: space time (h) = 0.12 h

b) Total pressure:

It can be considered that $P_{total} = P_{air} + P_{solution} \approx P_{O2} + P_{N2} + P_{H2O2}$. Then, knowing that the air composition is 21% O_2 and 79% N_2, and if the O_2 partial pressure is fixed at 2 bar, the partial pressure for N_2 is 7.52 bar. The water vapour pressure can be obtained from steam tables [11] for each reaction temperature studied. So, the system total pressure easily calculated is listed as summarised in Table 3.5.

Table 3.5. Total system pressure at the reaction temperatures tested.

T (ºC)	P_{O2} (bar)	P_{N2} (bar)	P^v_{H2O} (bar)	P_{total} (bar)
120			1.9854	11.5
140	2	7.52	3.6138	13.1
160			6.1806	15.7

c) Conversion:

The disappearance of organic compounds (X), COD (X_{COD}) or TOC (X_{TOC}) was calculated as:

$$X = \frac{C_e - C_0}{C_0} \cdot 100 \quad (\%) \qquad \text{Eq. 3.5}$$

where, X: conversion of the reported variable (%)

C_e: concentration in the effluent (mg L^{-1})

C_0: concentration in the influent (mg L^{-1})

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3.4. Analytical procedures

3.4.1. Effluent characterisation

3.4.1.1. Hydrogen peroxide interference and analysis

Hydrogen peroxide has three properties which may cause it to interfere with conventional analytical procedures [12]:

1. it is an oxidising agent: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2\ H_2O$ (1.776 mV)
2. it may also be a reducing agent: $H_2O_2 + 2OH^- \rightarrow O_2 + H_2O + 2e^-$ (-0.146 mV)
3. it liberates oxygen: $H_2O_2 \rightarrow O_2 + H_2O$

The best remedy to prevent possible interferences due to hydrogen peroxide special properties is to remove it prior to the analyses either by selective separation or destruction through decomposition.

Liquid samples from Fenton experiments contained unreacted peroxide that interferes in COD determination, increasing the real value of COD in the samples [12-15]. It was especially noticeable in experimental sets using low amounts of ferrous catalyst, were lower organic removals were achieved. This interference also reflected that refrigeration of samples at 4 ºC was not enough to stop the oxidation reaction. Therefore, it was necessary to look for an effective method to decompose or neutralise residual H_2O_2. The applied procedures were: decomposition of peroxide to oxygen and water by catalase enzyme [12,16], chemical neutralisation using sodium thiosulphate [12,16] and increasing the pH [12].

Hydrogen peroxide concentration was determined following the Standard Iodometric Method 4500-CI B [17].

a) <u>Enzymatic decomposition by catalase enzyme</u>:

Catalase enzyme destroys H_2O_2 with high efficiency [16]. The mechanism of removal is catalytic decomposition of H_2O_2 to oxygen and water (Equation 3.8). The amount of enzyme added depends on its activity and the time permitted before analysis. In using this procedure is important to quantify the impact of the enzyme in the analysis. This is better done by adding an identical amount of enzyme to a sample of deionised water, performing the analysis on this sample and subtracting the value from the pre-treated sample.

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad \text{Eq. 3.6}$$

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To test the capability of catalase to remove peroxide interference in the COD analysis, the corresponding amount of catalase from bovine liver (Sigma, 1870 units/mg solid) was added to the Fenton samples. As presented in Figure 3.3, catalase was unable to avoid the peroxide interference in the COD determination. It can be due to the strong acidic conditions (between 3 and 1) of the oxidised samples which would inhibit catalase activity that has its optimal pH around 7. Consequently, for removing H_2O_2 by means of an enzymatic reaction, a different form of catalase enzyme such as *Aspergillis niger* would be recommended, since it has the advantage of retaining activity over a wider range of pH [15].

b) Chemical neutralisation using sodium thiosulphate:

Sodium thiosulphate ($Na_2S_2O_3$) reacts quickly to remove residual H_2O_2 (Equation 3.7), as it does with other oxidants. However, over-addition may impact the analysis, and quantifying the effect is not as straightforward as with catalase enzyme.

$$2\ Na_2S_2O_3 + H_2O_2 \rightarrow Na_2S_4O_6 + 2\ NaOH \qquad \text{Eq. 3.7}$$

The stoichiometric dose needed for sodium thiosulphate to destroy 1 mg L^{-1} H_2O_2 is 9.29 mg L^{-1}, according to Equation 3.7. Due to the high concentration of organic compound in the initial solutions under study (5 g L^{-1}), samples from the Fenton process could have as much as 25.3 g L^{-1} of H_2O_2. Therefore, a high concentration of sodium thiosulphate is needed to neutralise all peroxide, which then required a huge number of dilutions prior to COD determination. After some tests, this method was discarded due to the difficulty in quantifying the effect of unreacted thiosulphate and its oxidised form, tetrathionate ($Na_2S_4O_6$).

c) Chemical decomposition by basification:

The rate of H_2O_2 decomposition (to oxygen and water) increases several fold as pH increases. For treated samples of wastewater containing several hundred mg L^{-1} H_2O_2, it may be eliminated raising the pH to 10-12 and allowing the sample to sit overnight [15].

On this basis, a fixed amount of NaOH was added to the samples for increasing the pH between 11 and 12. COD determination was performed after 24 h. As it can be seen in Figure 3.3, this procedure was capable to avoid peroxide interferences giving reasonable results in the COD analysis. Accordingly, this last methodology was chosen to remove residual H_2O_2 on the Fenton samples and to avoid its interference on COD determination. Increasing the pH has no effects on organic conversion. However it is

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necessary to re-acidify the samples before HPLC analysis in order to have all substances in its protonated form for its better identification, thus introducing another source of experimental error.

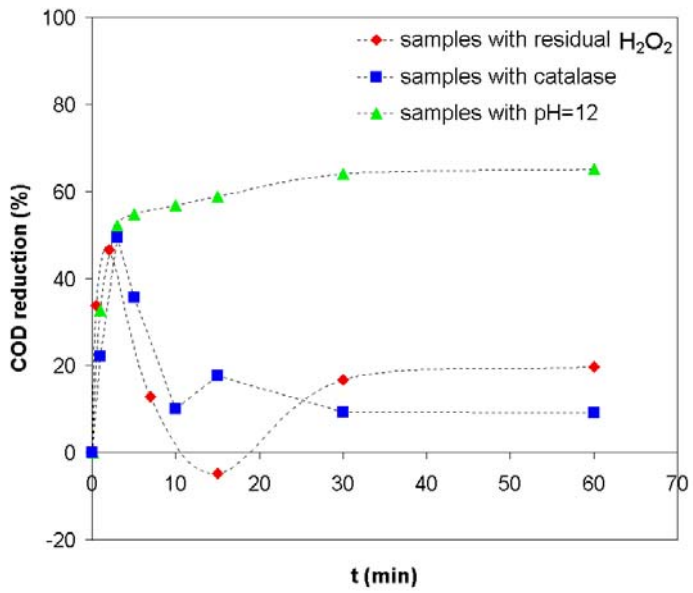

Figure 3.3. Different methods for removing H_2O_2 interference on COD determination (Molar ratio of phenol:H_2O_2:Fe^{2+} as 1:14:0.034).

In order to determine the possible remaining H_2O_2 in the PP-CWAO effluents, which could also have adverse effects on sample storing and interferences with COD determination, a control test (140 ºC, 2 bar P_{O2}) with a H_2O_2 solution (30 % of the stoichiometric amount for phenol mineralization) as inlet flow was performed. H_2O_2 conversion was close to 99% in all the samples through all the 72 h run, confirming that no residual H_2O_2 can be found in the TBR effluents. Therefore, any of the previous treatments was applied to PP-CWAO samples, which could be kept refrigerated until its analysis.

3.4.1.2. High performance liquid chromatography analyses

Liquid samples from Fenton experiments were analysed by means of an high liquid performance chromatograph (Beckman System Gold) using a C18 reverse phase column (Tracer Extrasil ODS-2, 5 µm, 25 x 0.4 cm). To properly separate phenol from the partial oxidation products, the mobile phase was a 35:65 vol. mixture of methanol (99.9 %, Sigma-Aldrich) and deionised water, slightly acidified, at a flow rate of

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1 mL min^{-1}. The detection of phenol was performed by UV absorbance at a wavelength of 254 nm.

To analyse the samples from the rest of experiments, the previous method was adapted to a new chromatograph (Agilent Technologies 1100 Series), using a C18 reverse phase column (Hypersil ODS, 5 µm, 25 x 0.4 cm from Agilent Technologies). With the aim of separating the phenolic target compound from its oxidation products, a gradient high liquid performance chromatography (HPLC) method was developed using the same column, as in a previously published method [18] (see Table 3.6). The flow rate was 0.75 mL min^{-1} and the wavelengths used in the diode array detector (DAD) were 210 and 254 nm, depending on the identified compound.

Table 3.6. Mobile phase composition for the HPLC gradient method.

Time period (min)	Gradient segment	Mobile phase composition (%)	
		Acidified ultrapure water	Methanol
0.0	0	100	0
25.0	1	50	50
32.0	2	50	50
34.0	Reset to initial	100	0

Figure 3.4 presents a typical HPLC chromatogram from a standard calibration mixture containing all phenolic compounds tested and their common reaction products, listed in Table 3.7 [19].

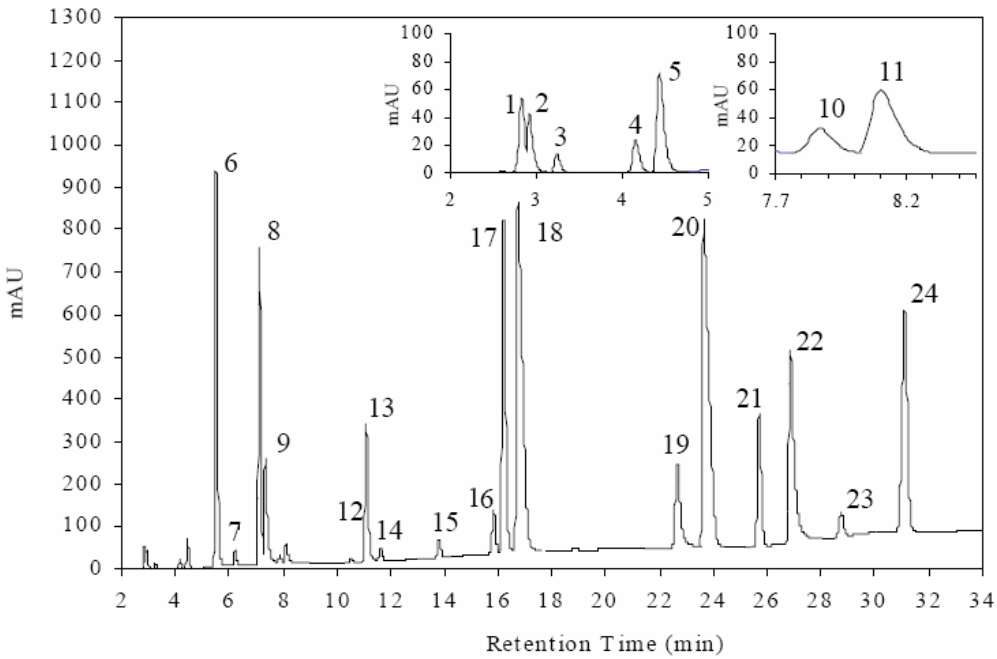

Figure 3.4. HPLC chromatogram from a standard calibration mixture [19].

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Table 3.7. List of compounds identified by HPLC analyses as it appears in Figure 3.4.

Peak number	Compound	Retention time (min)
1	Glyoxylic acid	2.826
2	Oxalic acid	2.923
3	Formic acid	3.245
4	Malonic acid	4.157
5	Acetic acid	4.433
6	Maleic acid	5.499
7	Succinic acid	6.204
8	Fumaric acid	7.111
9	Acrylic acid	7.342
10	Hydroquinone	7.884
11	Propionic acid	8.110
12	Resorcinol	10.547
13	p-Benzoquione	11.091
14	Catechol	11.640
15	trans,trans-Muconic acid	13.809
16	cis,cis-Muconic acid	15.856
17	4-Hydroxibenzoic acid	16.202
18	Phenol	16.566
19	Salicyladehide	22.688
20	o-Cresol	23.661
21	1-Indanone	25.727
22	Salicylic acid	26.894
23	1,3-Benzodioxole	28.813
24	2,2'-Biphenol	31.154

3.4.1.3. Gas chromatography analyses

Occasionally, liquid samples were analysed by GC (Agilent Technologies GC 6890) when the HPLC was not available due to technical problems. The analytical method used an HP-5 (5% phenyl-methyl-siloxane, 30 m x 0.32 mm i.d. x 0.25 µm film thickness, Agilent Technologies) capillary column with a constant temperature program for the oven at 40 ºC for 6.30 min, then the temperature raised up to 60 ºC (at 20 ºC min^{-1}) and finally a second raise from 60 ºC to 120 ºC (at 30 ºC min^{-1}). The injection volume was 0.5 µm and the injector temperature was 250 ºC. The carrier gas was helium (99.99 % pure, 13.5 ml min^{-1}) and phenol was detected using a flame ionisation detector (FID) at 300 ºC. Results from GC, using this method, are comparable to those from HPLC in terms of phenolic model compounds. Intermediate reaction products can not be measured by this method.

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3.4.1.4. Chemical Oxygen Demand

The Chemical Oxygen Demand is the amount of oxygen consumed to completely chemically oxidise the organic water constituents in inorganic end products. COD is commonly used to indirectly measure the amount of organic compounds in water, being a useful measure of its quality. Remaining COD in the liquid stream was analysed by the Closed Reflux Colorimetric Standard Method 5220D [17], which consists of digesting a sample for two hours in an acidic medium in the presence of a strong oxidant as potassium dichromate ($K_2Cr_2O_7$) and a silver sulphate catalyst. Mercury sulphate is usually added to eliminate possible interferences from chloride ions. During the test, organic compounds are oxidised and the orange coloured dichromate ($Cr_2O_7^{2+}$) is reduced to green coloured chromate (Cr^{3+}), which is then detected colorimetrically. The relation between Cr^{3+} absorbance and COD concentration is established by calibration with a standard solution of hydrogen phthalate, in the range of COD values between 25 and 500 mg L^{-1}. As the COD in samples was up to 25 times higher, all samples were accordingly diluted before digestion.

For COD analyses, Velp ECO8 thermoreactors were used as sample digesters and a Dinko 8500 UV/Vis Spectrophotometer was used for excess dichromate detection. Potassium dichromate and silver sulphate reagents were from Riedel-de Haën.

The theoretical COD for phenol and for the rest of phenolic compounds tested can be calculated using the following equations.

$$C_6H_5OH_{(aq)} + 7\ O_{2\ (g)} \rightarrow 6\ CO_{2\ (g)} + 3\ H_2O_{(l)} \qquad \text{Eq. 3.8}$$

$$2\ C_7H_8O_{(aq)} + 17\ O_{2\ (g)} \rightarrow 14\ CO_{2\ (g)} + 8\ H_2O_{(l)} \qquad \text{Eq. 3.9}$$

$$C_6H_5NO_{3(aq)} + 5\ O_{2\ (g)} \rightarrow 6\ CO_{2\ (g)} + H_2O_{(l)} + 4NH_{3(aq)} \qquad \text{Eq. 3.10}$$

Equation 3.10 does not include the oxygen demand caused by the oxidation of ammonia into nitrate, the nitrification process. Since dichromate does not oxidise ammonia into nitrate, this nitrification can be safely ignored in the standard COD test [20].

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3.4.1.5. Total Organic Carbon

The Total Organic Carbon is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality. The Non-Purgeable Organic Carbon (NPOC) Combustion Infrared Standard Method 5310B [17] was used for TOC determination, which involves purging an acidified sample with carbon-free air to remove all inorganic carbon prior to measurement. The sample is injected into a combustion chamber which is raised up to 850 °C. Here, all the carbon reacts with oxygen forming carbon dioxide, which is then flushed into a cooling chamber, and finally into the non-dispersive infrared spectrophotometer detector. TOC concentration is also established by calibration with a standard solution of hydrogen phthalate in the range of 30 to 2000 mg L^{-1}, which in some cases requires sample dilution.

For TOC analyses two different equipments were used. First, it was a Shimatzu TOC analyser belonging to *Tratamientos y Recuperaciones Industriales, S.A.* (TRISA), and lately an Analytic Jena TOC Analyser (model multi N/C 2001), recently incorporated to the CREPI laboratories.

The theoretical COD and TOC for phenol and for the rest of phenolic compounds studied can be calculated using equations 3.8 to 3.10 and they are summarised in Table 3.8.

Table 3.8. Theoretical COD and TOC values for the phenolic compounds studied.

Compound	Theoretical COD ($g\ O_2\ g\ compound^{-1}$)	Theoretical TOC ($g\ C\ g\ compound^{-1}$)
phenol	2.38	0.76
o-cresol	2.51	0.78
p-nitrophenol	1.51	0.52

3.4.1.6. Iron leaching

Effluents from PP-CWAO experiments using FeAC were analysed for determining the amount of iron leached from the catalyst. Analyses were done by means of a Perkin Elmer atomic adsorption spectrophotometer (Model 3110) using a multicomponent lamp set at 248.8 nm for Fe determination. Calibration with solutions of known Fe concentration up to 10 mg L^{-1} was used to determine the exact Fe concentration in the samples, which usually did not require any dilution or further preparation.

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3.4.1.7. Respirometric tests

Respirometry is the measurement and interpretation of the biological oxygen consumption rate under well-defined experimental conditions. Because oxygen consumption is directly associated with both biomass growth and substrate removal, respirometry is a useful technique for modelling and operating the activated sludge process [21]. As already commented in the Introduction chapter, respirometry was chosen over other conventional techniques such as Microtox® because it allows determining biodegradability, toxicity and inhibitory effects over a real sample of microorganisms from a WWTP, thus being a more realistic analysis than those using a specific strain of bacteria. Moreover, this technique is applied as an instrument-based alternative to Biological Oxygen Demand (BOD) test and therefore, is a valuable tool for biodegradability characteristics estimation.

a) Analytical set-up and procedure:

The respirometer used in this work is a LFS (liquid-flow-static) type, where dissolved oxygen concentration (S_o) is measured in the liquid phase which is static and continuously aerated [21]. The air flows through a pressure manoreductor and through a gas rotameter to ensure constant flow. The vessel (1 L) is magnetically stirred to guarantee total mixing and placed in a thermostatic bath set at 31.0±0.5 ºC. The pH, S_o and temperature are measured with probes connected to a computer for data acquisition. Figure 3.5 shows a schematic representation of the equipment used in the respirometric tests.

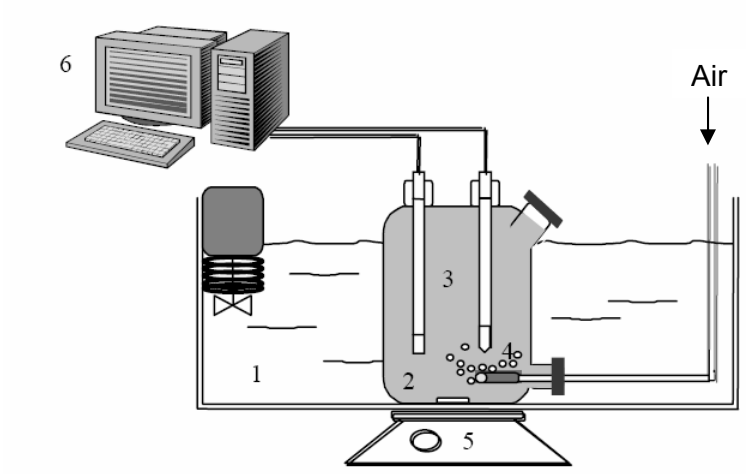

Figure 3.5. Experimental set-up for respirometry: (1) thermostatic bath, (2) activated sludge reactor, (3) pH and O_2 probes, (4) air diffuser, (5) magnetic stirrer and (6) recorder.

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The activated sludge used in this respirometric determinations came from the municipal biological WWTP in Tarragona (Catalonia, Spain), which was not adapted to metabolise phenolic compounds. After collecting the sludge, it was aerated overnight to ensure that the biomass was under endogenous conditions before each respirometric test. Determination of total suspended solids (TSS) and volatile suspended solids (VSS) was done according to the Standard Methods 2540D and 2540E, respectively [17]. The average value of biomass concentration in the respirometer was 2550±300 mgVSS L^{-1}. A 1-allyl-2-thiourea solution (20 mg L^{-1}) was added to the biomass to avoid any interference from nitrifying microorganisms.

Biodegradability characterisation was performed using an off-line respirometric procedure [22] to determine inhibition, toxicity and fraction of readily biodegradable COD (%COD_{rb}) present in the PP-CWAO effluents. This procedure follows a sequence of 4 steps summarised as follows:

1. A pulse of 20 mg_{COD} L^{-1} of a control substrate (sodium acetate) is added to the activated sludge in the respirometer vessel.
2. After the control substrate is consumed (i.e. the S_0 has recovered the equilibrium level), a pulse of the sample tested usually having also 20 mg_{COD} L^{-1} is added. The fraction of COD_{rb} in the sample can be assessed in this step (Equations 3.15 and 3.16).
3. When the S_0 equilibrium is recovered, a pulse of control substrate at the same concentration than in step 1 is added. Comparing the Oxygen Consumption (OC) profiles obtained in steps 3 and 1, the toxicity in the sample can be determined (Equation 3.13).
4. Finally, new biomass is placed in the respirometer and the control substrate (20 mg_{COD} L^{-1}) and the sample pulse (in the same concentration than in step 2) are fed together. The fraction of inhibitory COD in the sample can be assessed by comparing the Oxygen Uptake Rate (OUR) from steps 1, 2 and 4 of this procedure (Equation 3.14).

b) <u>Biodegradability parameters calculation</u>:

Figure 3.6 shows a typical respirogram obtained by Guisasola et al. (2003) [22] with the LFS respirometer. The respirogram starts with the aeration stopped in order to measure the value of endogenous OUR (OUR_{end}), which is equal to the slope value of the dissolved oxygen (DO) profile. Then, the vessel is aerated again and the DO level increases until it reaches a constant value called S_{oe} that balances the external oxygen transfer due to aeration with the OUR_{end}.

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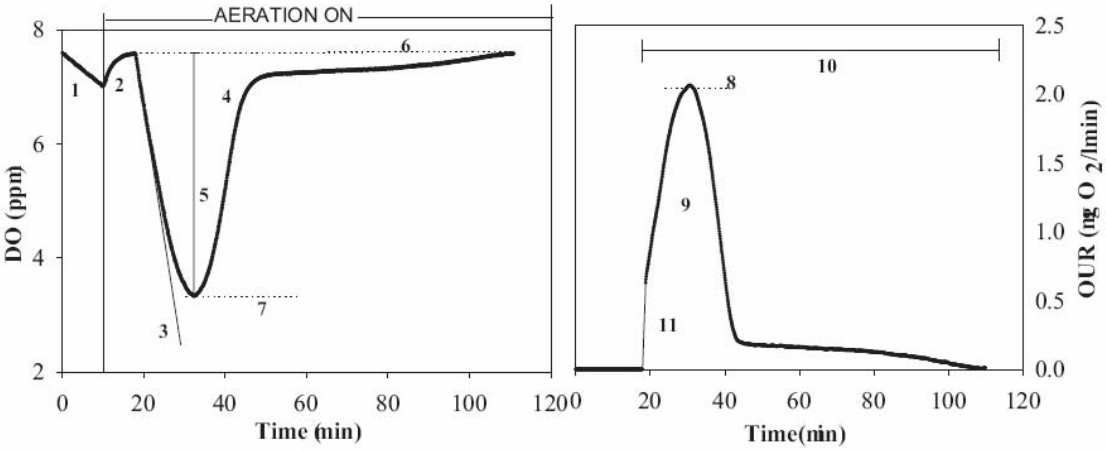

Figure 3.6. LFS respirogram (a) and the OUR profile (b) obtained with 10 mgN-NH^{4+} L^{-1} [22]: (1) OUR_{end}, (2) reaeration profile, (3) initial peak slope, (4) peak area, (5) peak height, (6) S_{oe}, (7) S_{oMIN}, (8) OUR_{MAX}, (9) oxygen consumed (OC), (10), consuming time, (11) OUR model.

The value of global oxygen transfer coefficient (k_{La}) must be estimated for OUR profile calculation. The k_{La} of the system is estimated from the reaeration profiles through a non-lineal least square regression according to Equation 3.11:

$$\frac{dS_0}{dt} = k_{La} \cdot [S_{oe} - S_0(t)] \qquad \text{Eq. 3.11}$$

When a pulse of substrate is added, because of the OUR due to the external substrate (exogenous OUR or OUR_{ex}), $S_0(t)$ decreases as follows:

$$\frac{dS_0}{dt} = k_{La} \cdot [S_{oe} - S_0(t)] - OUR_{ex} \qquad \text{Eq. 3.12}$$

Then, when the substrate is totally consumed, the DO level returns again to the S_{oe} level, since at this moment the OUR value equals the OUR_{end}. The OUR profile is obtained mathematically from the LFS respirogram by solving the oxygen balance in the liquid phase in each point of the respirogram (Equation 3.12). In addition, other indirect parameters such as the maximum OUR (OUR_{MAX}) and the total oxygen consumption (OC) can be obtained, which in combination with the direct parameters allow assessing the toxicity (Equation 3.13) and inhibition (Equation 3.14) of a given substrate sample.

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$$\%\ \text{toxicity} = \left(\frac{OC_{step1} - OC_{step3}}{OC_{step1}}\right) \cdot 100 \qquad \text{Eq. 3.13}$$

$$\%\ \text{inhibition} = \left(\frac{OUR_{MAXstep1} - \left(OUR_{MAXstep4} - OUR_{MAXstep2}\right)}{OUR_{MAXstep1}}\right) \cdot 100 \qquad \text{Eq. 3.14}$$

The biological COD removal is a process where part of the substrate is directly used for new biomass growth and the rest is oxidised for energy production. In this context, the heterotrophic yield coefficient (Y_H) represents the fraction of substrate used for production of new biomass. This coefficient can be calculated also using respirometric techniques [23]. For this work the Y_H was 0.71 $mg_{COD}\ mg_{COD}^{-1}$, as in a previous work using biomass coming form the same WWTP and calculated based on intermediate products from CWAO of phenol [19].

Once the OC is obtained from the respirometric tests, the COD_{rb} can be calculated using Equation 3.15.

$$COD_{rb} = \frac{OC_{step2}}{1 - Y_H} \qquad \text{Eq. 3.15}$$

Then, the COD_{RB} fraction of CWAO effluents is calculated according to:

$$\%\ COD_{rb} = \frac{COD_{rb}}{COD_{added\ step2}} \cdot 100 \qquad \text{Eq. 3.16}$$

c) <u>Examples for the interpretation of results obtained from respirometry</u>:

To illustrate the different biodegradability parameters measured by respirometry, some typical cases will be presented extracted from the research work by Suárez-Ojeda (2006) [19]. Figure 3.7 shows the OUR profiles of selected compounds.

The respirometric experiment with 5 mgL^{-1} of maleic acid (Figure 3.7) showed that this compound was non-readily biodegradable, since there is no oxygen consumption (OC) (i.e. the area below the OUR curve) in step 2 from the applied procedure. Besides, given that OUR and OC from steps 1, 3 and 4 were similar, with ±10 % as acceptable reproducibility, and that any toxic or inhibitory effect could be observed, maleic acid can be classified as inert reaction intermediate.

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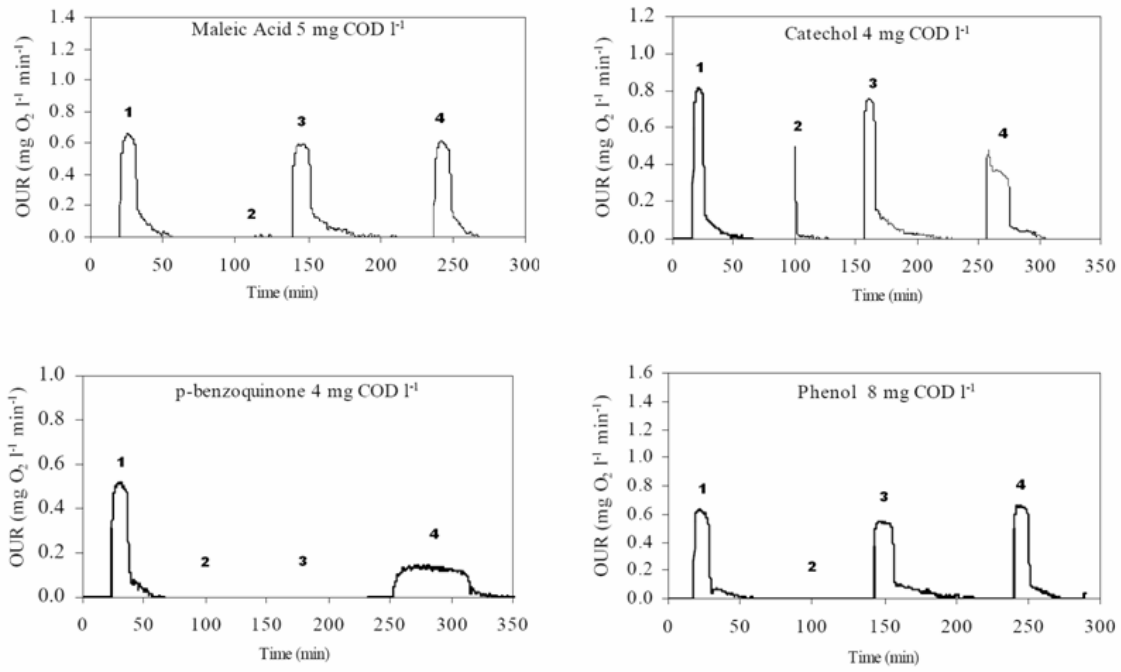

Figure 3.7. OUR profiles for maleic acid, catechol, p-benzoquinone and phenol [19] (the numbers in the figure refer to each step in the experimental procedure).

The OUR profile for catechol (Figure 3.7) shows some OC in step 2, which means that this compound is readily biodegradable, at some extent. However, the decrease in the OUR_{max} in step 4 with respect to step 1 is a sing on inhibition.

On the other hand, there is no OC in step 2 for p-benzoquinone, which means that it is not biodegradable. Moreover, the absence of OC also in step 3 and the pronounced decrease of OUR_{max} observed in step 4 points out that p-benzoquinone has a high toxic effect for non-acclimatised biomass at this concentration.

Finally for the case of phenol, respirometric tests demonstrate that this compound is not readily biodegradable since there is no OC in step 2. Nevertheless, the slightly higher OC found in step 3 compared to step 1 indicates that, at this concentration, phenol is not toxic and that probably it can be biodegraded though cometabolic pathways thanks to the presence of other readily biodegradable compounds such as acetate [24].

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3.4.2. Activated carbon characterisation

Characterisation of AC samples was systematically done by thermogravimetric analyses (TGA) in order to quantify the weight change due to chemisorption of polymeric compounds or direct AC combustion during reaction. In the iron containing AC samples, some other techniques to determine the surface oxygen groups, the BET area, the iron loading and the isoelectric point of surface charge (also known as point of zero charge) were also applied.

3.4.2.1. Thermogravimetric analyses

At the end of each experiment, the AC was recovered and dried overnight at 105 ºC under nitrogen flow. Later, each sample of used AC was subjected to Thermogravimetric Analyses (TGA, Perkin-Elmer thermobalance, model TGA7). One fraction of the sample was kept at 400ºC for 60 minutes under N_2 atmosphere to remove physisorbed compounds and subsequently weighted to measure the catalyst mass change after reaction (ΔW) as follows:

$$\Delta W = \frac{W_{400} - W_{105}}{W_{105}} \cdot 100 \qquad \text{Eq. 3.17}$$

where, W_{400} is the weight of AC after TGA at 400 ºC and W_{105} is the used AC weighted after drying at 105 ºC.

Another fraction was heated from 100 to 900 ºC under N_2 flow at a heating rate of 10 ºC min^{-1}, allowing measuring the total weight loss (TWL) for each AC, in a similar way than in Equation 3.17. From the TWL it is possible to calculate the remaining AC mass (m_{fAC}) after removing physisorbed and chemisorbed compounds by TGA, using Equation 3.18.

$$m_{fAC} = W_{105} - \frac{TWL}{100} \cdot W_{105} \qquad \text{Eq. 3.18}$$

3.4.2.2. Boehm titration

Surface oxygen groups (SOG) on AC surface were determined by Boehm titrations, following a procedure described elsewhere [24-27].

In order to selectively neutralise the acidic groups on AC surface, different samples of 1 g of AC-L were left in contact for 24 h with 0.05M solutions of NaOH,

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Na_2CO_3 or $NaHCO_3$. Afterwards, the solutions were filtered and titrated with 0.05M HCl in order to quantify the excess base that had not been neutralised. The number and type of acidic sites were calculated by considering that NaOH neutralises carboxylic, lactonic and phenolic groups, that Na_2CO_3 neutralises carboxylic and lactonic groups and that $NaHCO_3$ neutralises only carboxylic groups. Carboxylic groups were therefore quantified by direct titration of residual $NaHCO_3$. The difference between the groups neutralised by Na_2CO_3 and those neutralised by $NaHCO_3$ was assumed to be lactones, and the difference between the groups neutralised by NaOH and those neutralised Na_2CO_3 was assumed to be phenols.

Basic sites were determined by titration with 0.05M NaOH of a 1 g AC-L sample in contact with 0.05M HCl for 24h.

3.4.2.3. Nuclear Magnetic Resonance spectroscopy

Nuclear Magnetic Resonance (NMR) is a physical phenomenon based upon the quantum mechanical magnetic properties of an atom's nucleus, which occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. All nuclei that contain odd numbers of protons or neutrons have an intrinsic magnetic moment and angular momentum. The most commonly measured nuclei are hydrogen-1 (the most receptive isotope at natural abundance) and carbon-13, although nuclei from isotopes of many other elements can also be observed.

NMR spectroscopy is the use of the NMR phenomenon to obtain physical, chemical, electronic and structural information about molecules. It is a powerful and theoretically complex analytical tool that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in solution and the solid state. In NMR, the chemical shift describes the variation in the resonance frequency of a nuclear spin due to the chemical environment around the nucleus. The chemical shift (δ) is usually expressed in parts per million (ppm) by frequency [29].

^{13}C Magic Angle Spinning NMR spectra of original and oxidised AC powdered samples were recorded at 100.52 MHz using pulse decoupling acquisition with a 4 mm probe in a 400-Varian NMR equipment with a spinning frequency of 12000 kHz and a pulse delay of 12 seconds.

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3.4.2.4. Ultimate analyses

Ultimate analyses were performed to determine the hydrogen, nitrogen, sulphur carbon and oxygen content in AC and FeAC samples. This technique is based on the complete combustion at 1150 ºC of all constituents in the sample, giving rise to the elements C, H, N, S and combustion gases (i.e., N_2, CO_2, H_2O, NO_x, SO_2 and SO_3) that are reduced at 850 ºC using a copper catalyst to CO_2, H_2O, SO_2 and N_2. Then, these compounds are driven by means of a gas carrier (He) through specific columns for separation by thermal desorption. Those gases pass through a thermal conductivity detector that gives a signal proportional to the concentration of each elemental compound in the sample.

The analytical equipment used was an Elemental Analyser CHNOS, model Vario EL III from Elementar Analysesysteme GMHB.

3.4.2.5. Isoelectric Point of charge

The Isoelectric Point (IEP), of a solid placed in an electrolyte corresponds to the pH value at which the surface of the solid is electrically neutral. This IEP was determined by mass titration [30], i.e. by measurement of pH in the system to which the solid sample is added in subsequent portions. In order to cover a pH range of interest, at least two experiments should be performed; one with a low pH and the other with high initial pH. Following this method, various amounts of each carbon sample were added to solution of constant ionic strength and resulting pH values were measured after one day of equilibration. Initial pH was adjusted by addition of HNO_3 or NaOH. A constant ionic strength of 0.001 mol L^{-1} was controlled by $NaNO_3$. The pH was measured by the combined (glass-Ag/AgCl) electrode from a Crison Compact Titrator. Typical values of carbon concentration in the $NaNO_3$ solutions were 0, 2, 5, 10, 15, 20, 25 g L^{-1}. The increase in mass concentration causes a change in pH so that the value asymptotically approaches the IEP, as illustrated in Figure 3.8 for AC-L.

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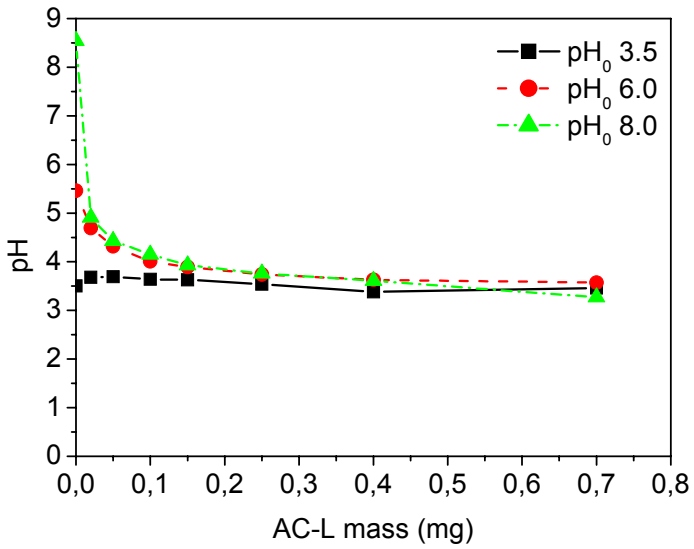

Figure 3.8. Isoelectric point determination by mass titration for AC-L.

The terms Isoelectric Point and Point of Zero Charge (PZC) are often used interchangeably, although under certain circumstances it is important to make the distinction. In the absence of positive or negative charges, the surface is best described by the PZC. If positive and negative charges are both present in equal amounts, then this is the IEP. Thus, the PZC refers to the absence of any type of surface charge, while the IEP refers to a state of net neutral surface charge [31]. Therefore, the difference between the two is quantity of charged sites at the point of net zero charge. In the case of AC, the term IEP is more suitable.

3.4.2.6. Nitrogen adsorption/desorption isotherms

Nitrogen adsorption/desorption isotherms at 77 K were performed to determine the surface area and pore volume of all AC samples prepared. Before adsorption, samples were degasified submitting them to vacuum for 5h at 250 ºC in order to remove all substances initially adsorbed on the AC surface. These analyses were carried out in a Micromeritics Tristar 3000 equipment. Specific surface area was calculated by the BET method (after Brunauer, Emmett and Teller) [32]. The total pore volume (V_T) was measured at P/P_0 = 0.975 whereas the micropore volume ($V_{micropore}$) was determined using the t-plot method [33].

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3.4.2.7. Iron content

Bulk iron content in the commercial AC and in the prepared FeAC catalysts was obtained by atomic emission spectroscopy with induced coupled plasma (ICP-AES) analysis collected in a Varian Vista AX system. Before this determination, it was necessary to calcinate and to give an acidic attack to the AC matrix in order to remove all organic matter from the samples. The calcination was done for 60 minutes at 500 ºC and following 5 hours at 750 ºC in a muffle oven. The remaining solid residue was digested with HF and HCl to get an iron solution from the ashes. This acidic solution was then solved with distilled water for its ICP-AES analysis. Iron concentration in the acidic solutions obtained was determined by interpolation to a standard calibration performed using different solutions of known iron concentration.

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PART II

Results and Discussion

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4. Fenton process

Fenton oxidation process was investigated as a screening tool to learn about the potential of H_2O_2 for the oxidation of phenolic aqueous solutions, at different operating conditions and in a batch reactor configuration. Most importantly, this process helped to develop an experimental procedure and some analytical techniques required for the later study of the PP-CWAO process.

As previously presented in the Methodology section, the operation parameters studied for the Fenton oxidation of phenol were: H_2O_2 and catalyst concentration, initial pH and temperature. First of all, the results referring to the effect of the different operation conditions using high concentrations of Fe^{2+} in phenol oxidation are discussed. Secondly, the oxidation capacity of the system using low concentrations of ferrous catalyst was tested and it helped to determine the effect of residual H_2O_2 on the analytical methods and in the sample conservation. With this information it was possible to deal with samples from other processes using hydrogen peroxide, as in the PP-CWAO.

4.1. Phenol oxidation: kinetic studies

Several series of experiments on phenol oxidation using the Fenton reagent (i.e. iron salts and hydrogen peroxide) were conducted varying the temperature (30-85 ºC), the initial concentration of H_2O_2 (100-200 % of the stoichiometric demand according to Equation 3.1), the Fe^{2+}:H_2O_2 ratio (1:5-1:10 w:w) and the initial pH (adjusted to 2.8 and without initial adjustment). Table 4.1 summarises the values of these operating variables and the results in terms of phenol conversion, COD removal. Table 4.1 also includes the pseudo-first order kinetic rate constant (k) for phenol degradation, which will be discussed later. The initial phenol concentration was 5 g L^{-1} in all cases.

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Table 4.1 Results for Fenton process using high concentration of Fe^{2+} catalyst.

Molar ratio $Ph:H_2O_2:Fe^{2+}$	$Fe^{2+}:H_2O_2$ ratio (w:w)	H_2O_2 (%)*	T (ºC)	pH_0	X_{phenol} (%)	X_{COD} (%)	k (s^{-1})
1:14:0.343	1:5	100	30	2.8	100	94	7.21
			50		100	93	2.14
			85		100	96	0.82
1:28:0.685	1:5	200	30	2.8	100	91	3.62
			50		100	95	0.33
			85		100	96	0.22
1:14:0.171	1:10	100	30	2.8	100	73	167.50
			50		100	73	4.25
			85		100	84	3.97
1:28:0.343	1:10	200	30	2.8	100	91	30.59
			50		100	89	0.50
			85		100	93	0.86
1:14:0.343	1:5	100	30	free	100	89	18.49
			50		100	97	2.53
			85		100	91	1.47
1:28:0.685	1:5	200	30	free	100	92	3.47
			50		100	91	0.59
			85		100	94	0.57
1:14:0.171	1:10	100	30	free	100	86	82.22
			50		100	92	3.80
			85		100	92	3.68
1:28:0.343	1:10	200	30	free	100	90	9.10
			50		100	92	0.50
			85		100	93	0.62

* Percentage of the stoichiometric amount for complete mineralisation.

The chemical oxidation of the Fenton process can be expressed in a simple way as:

$$\frac{d[phenol]}{dt} = -k[phenol]^m [Fe^{2+}]^n [H_2O_2]^p \qquad \text{Eq. 4.1}$$

where *k* is the reaction rate constant, *t* the time and *m*, *n* and *p* are the reaction orders with respect to phenol, Fe^{2+} and H_2O_2, respectively. Assuming a first-order reaction for the oxidation of phenol, the above equation becomes:

$$\ln\left(\frac{[phenol]}{[phenol]_0}\right) = -k[Fe^{2+}]^n [H_2O_2]^p t \qquad \text{Eq. 4.2}$$

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in which $[phenol]_0$ is the initial phenol concentration. In this case, a plot of $ln([phenol]/[phenol]_0)$ vs. time in every experiment must lead to a straight line with the slope corresponding to an observed reaction rate constant (k_{obs}).

Figure 4.1 show these plots for experiments in which the temperature and initial Fe^{2+}:H_2O_2 ratio were varied. As it can be observed, points lie in satisfactory straight lines with correlation coefficients greater than 0.9. As the reaction evolved so fast, complete phenol removal was reached in less than ten minutes. Therefore, in some cases, only two points were available to build the $ln([phenol]/[phenol]_0)$ vs. time plots.

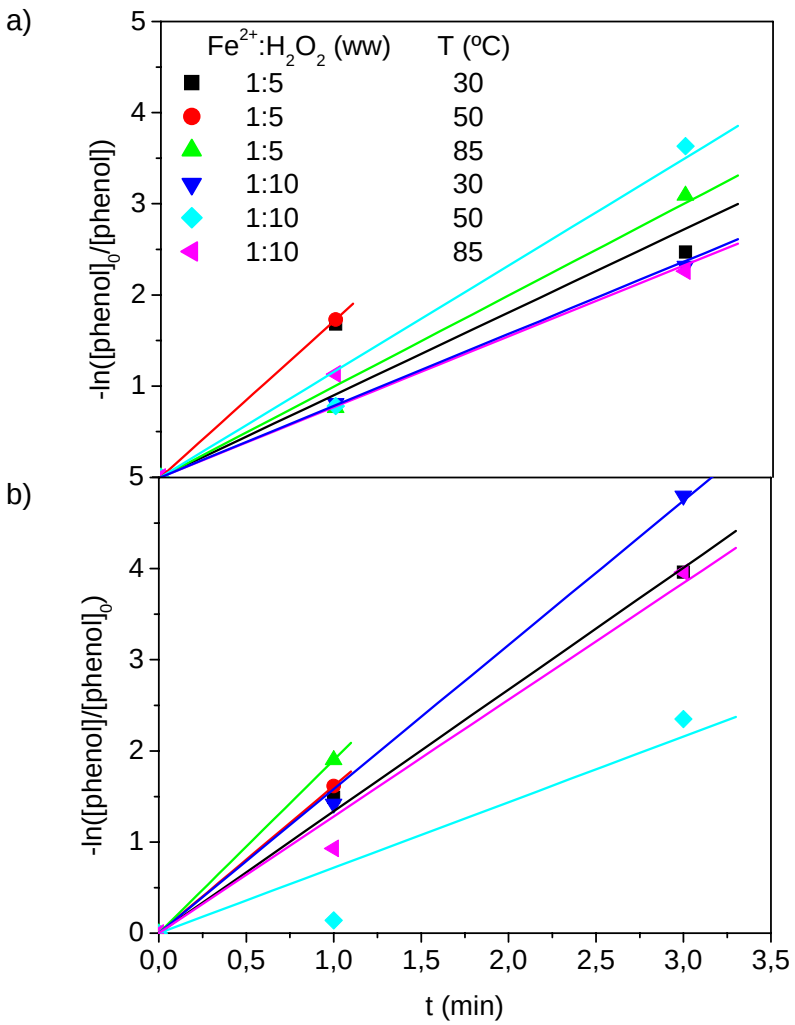

Figure 4.1. Determination of the observed reaction rate (initial pH not adjusted): a) 100% stoichiometric H_2O_2 and b) 200% stoichiometric H_2O_2.

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The observed reaction rate constants obtained in from Figure 4.1 are, in fact, a function of Fe^{2+} and H_2O_2 concentrations. Taking rate order for Fe^{2+} as 1.67 and the rate order for H_2O_2 as 0.68 [1], the first-order kinetic constant for phenol degradation can be expressed using Equation 4.3. These constants are included in Table 4.1 and will be later used in an attempt to evaluate the activation energy (E_a) of the phenol oxidation by the Fenton reagent.

$$k = \frac{k_{obs}}{[Fe^{2+}]^{1.67}[H_2O_2]^{0.68}} \qquad \text{Eq. 4.3}$$

4.1.1. Influence of initial pH

Fenton process is efficient only in the pH range 2-4 and it is usually most efficient at around pH 2.8. This is particularly due to the precipitation of ferric oxyhydroxide (FeOOH) and $Fe(OH)_3$, which have low catalytic activity, at pH > 3-4 (depending on the iron concentration) [2]. Also, the oxidation potential of HO• radical is known to decrease with an increase in the pH [3].

In this study, phenol oxidation was done adjusting the initial pH to 2.8 but also without modification, with a pH around 5.9 which corresponds to the 5 g L^{-1} phenol solution. As it can be seen in Table 4.1, phenol was completely removed whatever the reaction conditions used. Since complete elimination of phenol was achieved in less than ten minutes, results will be discussed in terms of COD removal. The difference in COD conversions between experiments performed at the same reaction conditions but varying the initial pH was ±5 % in all cases except for the molar ratio 1:14:0.171, i.e., when using the lowest initial concentrations of H_2O_2 and Fe^{2+}. This difference can be considered as acceptable experimental error. For the molar ratio 1:14:0.171, variations in COD conversion were between 10 and 26%, higher for experiments without initial pH adjustment. Therefore it seems that the initial pH adjustment is not necessary at the present conditions since even at initial pH around 5.9, some active iron species are present ant they are able to establish an effective redox system for the generation of hydroxyl radicals with H_2O_2. Moreover, the generation of organic acids from phenol degradation leads to a drop in pH, which in all cases reached values between 1 and 2.

Figure 4.2 illustrates the typical pH profile of Fenton oxidation of phenol, supporting the viability of the process without acidification of the initial solution. The first inflection is caused by the addition of $FeSO_4$ catalyst which typically contains some residual H_2SO_4. A more pronounced drop in pH occurs when the H_2O_2 is added, and continues gradually at a rate which is largely dependent on catalyst concentration [4]. In

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the present reaction conditions, the quite high amounts of Fe^{2+} used may have ensured the availability of catalyst for the generation of hydroxyl radicals and consequently, the complete elimination of phenol.

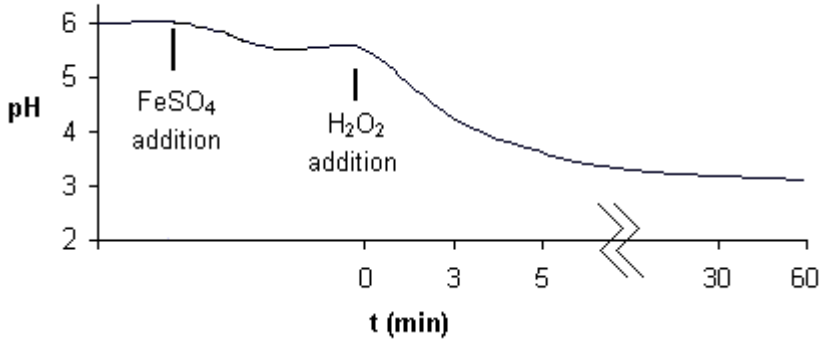

Figure 4.2. Typical pH profile of phenol Fenton oxidation [4].

The influence of initial pH is also noticeable from observation of the calculated kinetic constants. It can be seen in Table 4.1, that usually the rate constant was higher if the initial pH was not adjusted for the molar ratios 1:14:0.343 and 1:28:0.685 (i.e. for the highest Fe^{2+}:H_2O_2 ratio, 1:5 w:w). On contrary, the higher rate constants were found when initial pH was set to 2.8 for the molar ratios using the lowest Fe^{2+}:H_2O_2 ratio (1:10 w:w), 1:14:0.171 and 1:28:0.343. This fact points out that the relationship between Fe^{2+} and H_2O_2 is important for the initial reaction stages, although similar results are found for similar reaction times.

4.1.2. Influence of H_2O_2 concentration

It has been generally observed that the percentage of degradation of an organic pollutant increases with an increase in the dosage of hydrogen peroxide [5]. Results in Table 4.1 show very little improvement when using the stoichiometric or double of the stoichiometric H_2O_2 quantity. However, for a given Fe^{2+}:H_2O_2 ratio, COD removals were slightly higher at the highest stoichiometric H_2O_2 dose.

On one hand, this behaviour could be due to the enhanced thermal decomposition of hydrogen peroxide into water and oxygen when temperature is greater than 50 ºC [4]. On the other hand, if peroxide is present in very large quantities it can act as a scavenger for the generated hydroxyl radicals [6], as shown in Equation 4.4.

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad \text{Eq. 4.4}$$

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Moreover, as already discussed in the Methodology section, residual hydrogen peroxide contributes to COD and must be removed before analyses. Also, the presence of H_2O_2 is harmful to many microorganisms [5] and so it should be eliminated from the process out streams. Therefore, the loading of H_2O_2 should be adjusted in such a way that the entire amount is used for the oxidation reactions. In this case, the stoichiometric quantity of peroxide was enough to achieve the complete elimination of phenol and COD reductions from 86 to 97%, without initial pH adjustment.

With regard to the influence of H_2O_2 concentration on the process kinetics, no clear trend can be extracted from values presented in Table 4.1. Thus, it has to be concluded that H_2O_2 thermal decomposition, radical scavenging reactions and oxidation processes are all present and competing, which increases the process complexity for the range of conditions in this study.

4.1.3. Temperature influence

Not many studies are available focused on the effect of temperature on the degradations rates and usually ambient conditions can safely be used with good efficiency [5]. The rate of reaction with Fenton's reagent increases with increasing temperature, with effect more pronounced at temperatures higher than 20 ºC. However, as temperature increases above 40-50 ºC, the efficiency of H_2O_2 utilization declines, due to its accelerated decomposition into oxygen and water [4]. Nevertheless, reaction temperatures up to 100ºC have been tested in the CWPO processes [7] or the Fenton process using heterogeneous iron based catalysts [8]. Therefore, in this research three different temperatures mostly covering the conventional working range were tested to check the effects on phenol oxidation but also on H_2O_2 performance.

Unexpectedly and as it can be seen in Table 4.1, the kinetic rate constants found significantly decrease with an increase of the reaction temperature from 30 to 50 ºC. Moreover, a rise of temperature from 50 to 85 ºC produce a further decrease in the phenol reaction rate, which could be explained by thermal decomposition of H_2O_2 as previously stated. Nevertheless, after 60 minutes of reaction, irrespective of the temperature, both phenol and COD elimination are quite comparable. These results agree with most authors [4-5,9-10], which recommend between 20 and 50 ºC for Fenton oxidation, since at higher temperature the increase in the COD removal is marginal. Therefore, in the present work, the lower temperature of 30 ºC was fixed for the study of phenol reaction at lower Fe^{2+} concentrations.

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Figure 4.3 illustrates the small effect that temperature has on phenol and COD removal. As reported on Table 4.1, all reaction conditions reached 100 % phenol conversion and COD removals higher than 80 %, without initial pH adjustment.

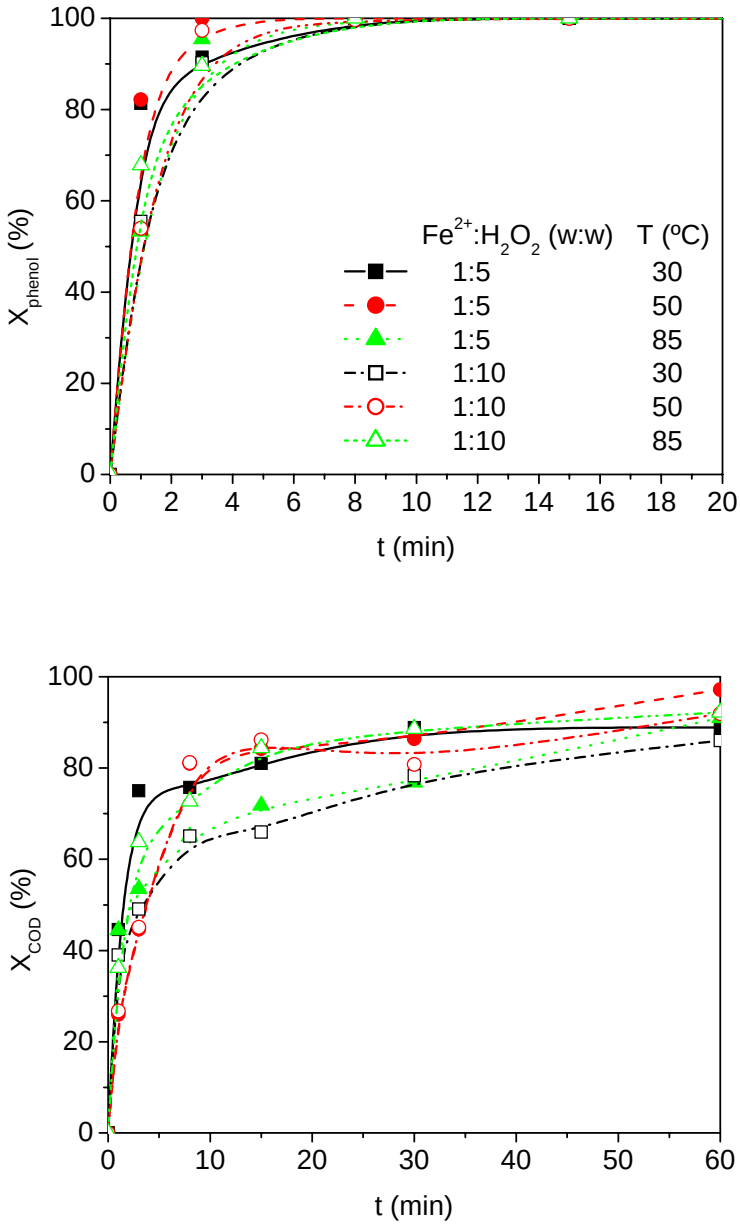

Figure 4.3. Temperature effect on a) phenol and b) COD conversion (initial pH not adjusted and 100% stoichiometric H_2O_2). Lines represent trends.

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In an attempt to determine the activation energy for the oxidation of phenol using the Arrhenius Equation (Equation 4.5), the natural logarithm of the previously calculated rate constants was plotted against the inverse of each temperature tested and it is presented in Figure 4.4. Then, the activation energy could be calculated from the slope of each series in Figure 4.4 using Equation 4.6, where *A* is the frequency factor, *R* the gas constant and *T* the temperature.

$$k = A \cdot e^{-Ea/RT} \qquad \text{(Arrhenius Equation)} \qquad \text{Eq. 4.5}$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{Eq. 4.6}$$

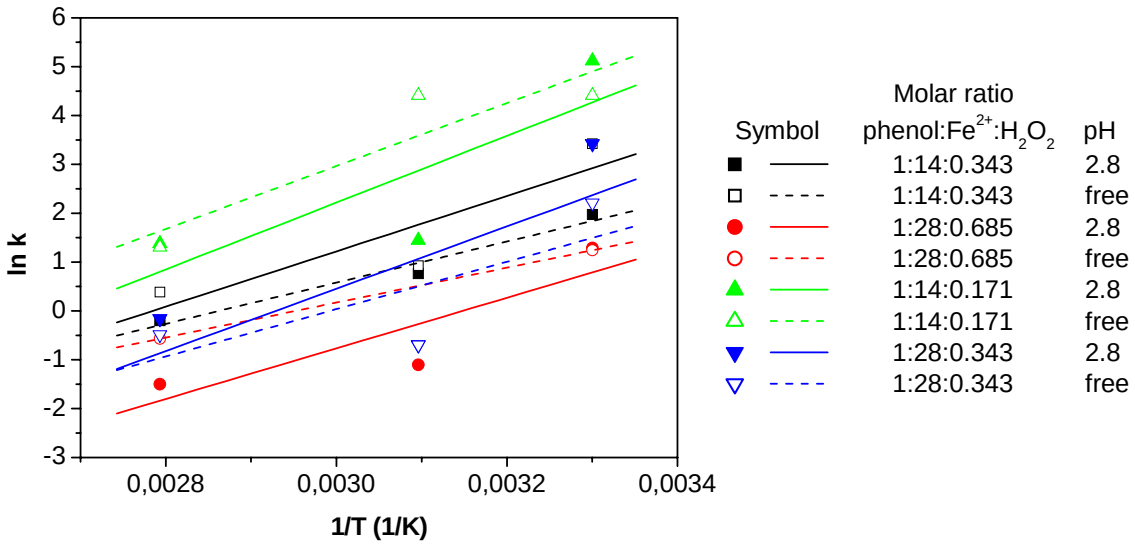

Figure 4.4. Plot of lnk vs. 1/T for the degradation of phenol using high Fe^{2+} concentration.

It can be seen in Figure 4.4 that although all series of experiments preformed could be fitted to a straight line, they followed the opposite trend expected from the Arrhenius Equation, i.e., positive slopes. This behaviour leads to negative values for E_a, meaning that the higher reaction temperature, the lower the reaction rate, which has no physical sense. So, it was not possible to obtain E_a from the experiments performed. This observation could be expected from the previous discussion on the influence of each variable studied and from the values of the kinetic constants obtained.

Thus, it has been demonstrated that hydrogen peroxide consumption by oxidation, thermal degradation and radical scavenging reactions must be considered for an accurate kinetic modelling of the Fenton reaction at the temperature range covering 30 to 85 ºC.

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4.2. Phenol oxidation at low Fe^{2+} concentration

For homogeneous Fenton processes, there is a direct correlation of phenol removal efficiency with iron concentration, up to a certain concentration, where further addition of iron becomes inefficient. Typical $Fe:H_2O_2$ ratios are 1:5/1:10 w:w, though iron concentrations of less than 25-50 mg L^{-1} can require excessive reaction times [11].

In order to determine the process performance using low concentrations of catalyst, phenol oxidation in the range of 5-100 mg L^{-1} Fe^{2+} was studied. The operating conditions chosen from the previous experiments were set at 30 ºC, pH not adjusted and stoichiometric H_2O_2 dose.

The discussion in this section will be based on phenol and TOC conversions, since interferences of H_2O_2 in COD determination were found due to the presence of unreacted peroxide in the samples. Then, the investigation of methods to quench or remove unreacted H_2O_2 from the samples was started using the following series of experiments and reliable COD analyses were not available for all tests.

Figure 4.5 presents phenol and TOC removals for experiments using 5, 10, 50 and 100 mg L^{-1} of Fe^{2+}. As expected, phenol disappearance proceeds faster as Fe^{2+} concentration increases. However, for 50 and 100 mg L^{-1} of Fe^{2+} differences are undetectable because conversion is already complete in just a few minutes.

As it can be seen, similar results were obtained for phenol conversion when using 100 or 50 mg L^{-1} of catalyst and also comparable results were found for 5 and 10 mg L^{-1} of catalyst. On the other hand, the improvement on TOC removal is clearly dependent on Fe^{2+} concentration. Therefore it can be concluded that a Fe^{2+} dosage above 50 mg L^{-1} can not increase phenol removal because it is already completed, but there is an effect on the overall TOC conversion. Given the uncertainty with regard to the precise mechanism of the Fenton reaction, the results only show how important is the concentration of ferrous ions for the production of hydroxyl radicals or hydroxyl radical-like species (such as particularly, the ferryl species FeO^{2+}) considered being the active species for the oxidation reactions to proceed [2].

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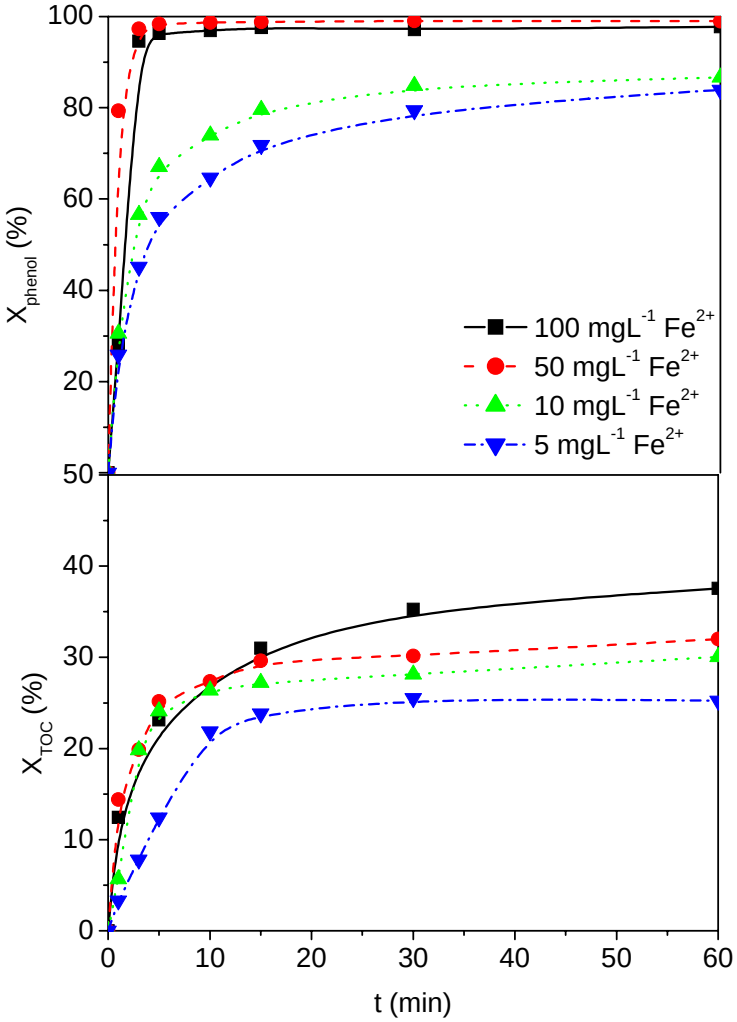

Figure 4.5. Phenol conversion and TOC reduction using low concentrations of Fe^{2+} (T=30ºC, initial pH not adjusted, 100% stoichiometric H_2O_2).

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4.3. Overview

The study of several variables in the Fenton Oxidation Process has been the starting point on the research for an oxidation process capable to use hydrogen peroxide efficiently in order to achieve good results in the elimination of phenolic compounds.

The effects of operating variables such as pH, temperature and ratio of H_2O_2 to Fe^{2+} on the treatment performance have been explored. Experimental results show that there is no need of adjusting initial pH when dealing with concentrated phenolic aqueous solutions (i.e. 5 g L^{-1}). This is due to the formation of organic acids as the reaction proceeds, which leads to a drop in pH within the 1.5-2.5 range. It has been found that neither using double of the stoichiometric dose for phenol mineralisation nor operating at temperatures higher than 30 ºC leads to significant benefits, since all reaction conditions tested reached similar results, i.e., complete phenol conversion in just 10 minutes of reaction and COD removals higher than 70 % after 60 minutes of reaction.

A kinetic model for the Fenton treatment could not be proposed since at the temperature range studied, the process is affected by hydrogen peroxide thermal decomposition and radical scavenging reactions that must be considered as well as phenol oxidation.

When phenolic solutions were treated using low concentrations of iron catalyst, a Fe^{2+} dosage above 50 mg L^{-1} already lead to complete phenol removal after 10 minutes, but TOC conversion increased with increasing Fe^{2+} concentration. This last set of experiments helped to choose the procedure to avoid interferences with the analytical methods due to residual H_2O_2 in the samples as already presented in the Methodology (see section 3.4.1.1). This information was critical to deal with oxidised samples from other processes using hydrogen peroxide, such as the Peroxide Promoted CWAO.

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5. Peroxide Promoted Catalytic Wet Air Oxidation of phenol over activated carbon

This chapter includes the results and discussion obtained from the here called Peroxide Promoted Catalytic Wet Air Oxidation process. The main purpose of the experiments performed was to find out whether it is possible to improve the mineralisation capacity of CWAO or to enhance the biodegradability of oxidised effluents to acceptable values for a subsequent biological treatment.

In the first section, the effect of adding under stoichiometric amounts of hydrogen peroxide to the classical CWAO process has been investigated for the removal of phenolic aqueous solutions in a TBR configuration, using activated carbon as catalyst and at three different reaction conditions (120, 140, 160ºC). Secondly, control tests in which an inert support was used instead of AC and in which air was replaced by N_2 were performed in order to distinguish between the effect that could be attributed to the addition of H_2O_2 and to the promoting or synergistic effect derived from its combination with O_2 and AC catalyst. Following, the AC performance is discussed based on the results from thermogravimetric analyses. Finally, the characterisation of the oxidised effluents and the possibility of its combination with a biological treatment are also commented.

Process performance was evaluated by characterising the effluent (organic load, pH, biodegradability and iron leaching when necessary), but also the weight changes on the AC used as catalyst.

The nomenclature used in this chapter is listed in the following table (Table 5.1).

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Table 5.1. Nomenclature used in the PP-CWAO experiments.

Experiment	Reactor bed filling	Atmosphere	H_2O_2 (%)*
AC-O2-00			0
AC-O2-10			10
AC-O2-15	AC	Air	15
AC-O2-20			20
AC-O2-30			30
AC-N2-10			10
AC-N2-20	AC	N_2	20
AC-N2-30			30
IS-N2-10			10
IS-N2-20	IS	N_2	20
IS-N2-30			30
IS-O2-10			10
IS-O2-20	IS	Air	20
IS-O2-30			30

* Stoichiometric amount of H_2O_2 according to Equation 3.1.

5.1. Effect of hydrogen peroxide on the CWAO

Based on previous studies from our research group, the initial temperature tested was 140 ºC [1-2]. However, to test the influence of the temperature on the PP-CWAO performance, experiments at 120 ºC and 160 ºC were also conducted and will be discussed along this section.

Figure 5.1 shows the phenol, COD and TOC conversions obtained for the experiments with AC at 140 ºC and 2 bar of P_{O2} without hydrogen peroxide (AC-O2-00) and when different stoichiometric ratios of H_2O_2 for the complete phenol mineralisation were added to the initial 5 g L^{-1} phenol solutions: 10 % (AC-O2-10), 15 % (AC-O2-15), 20 % (AC-O2-20) and 30 % (AC-O2-30).

It must be pointed out that the experiments using AC as catalyst are initially influenced by an adsorption period. Roughly, three different zones can be distinguished in all the profiles using AC. An initial adsorption-dominating period results in an apparent total conversion until the AC bed is equilibrated. Then, a sudden decrease in phenol conversion is observed when the breakthrough comes out. Finally, the AC bed reaches a pseudo-equilibrium that gives a roughly constant conversion at the steady state [3-4].

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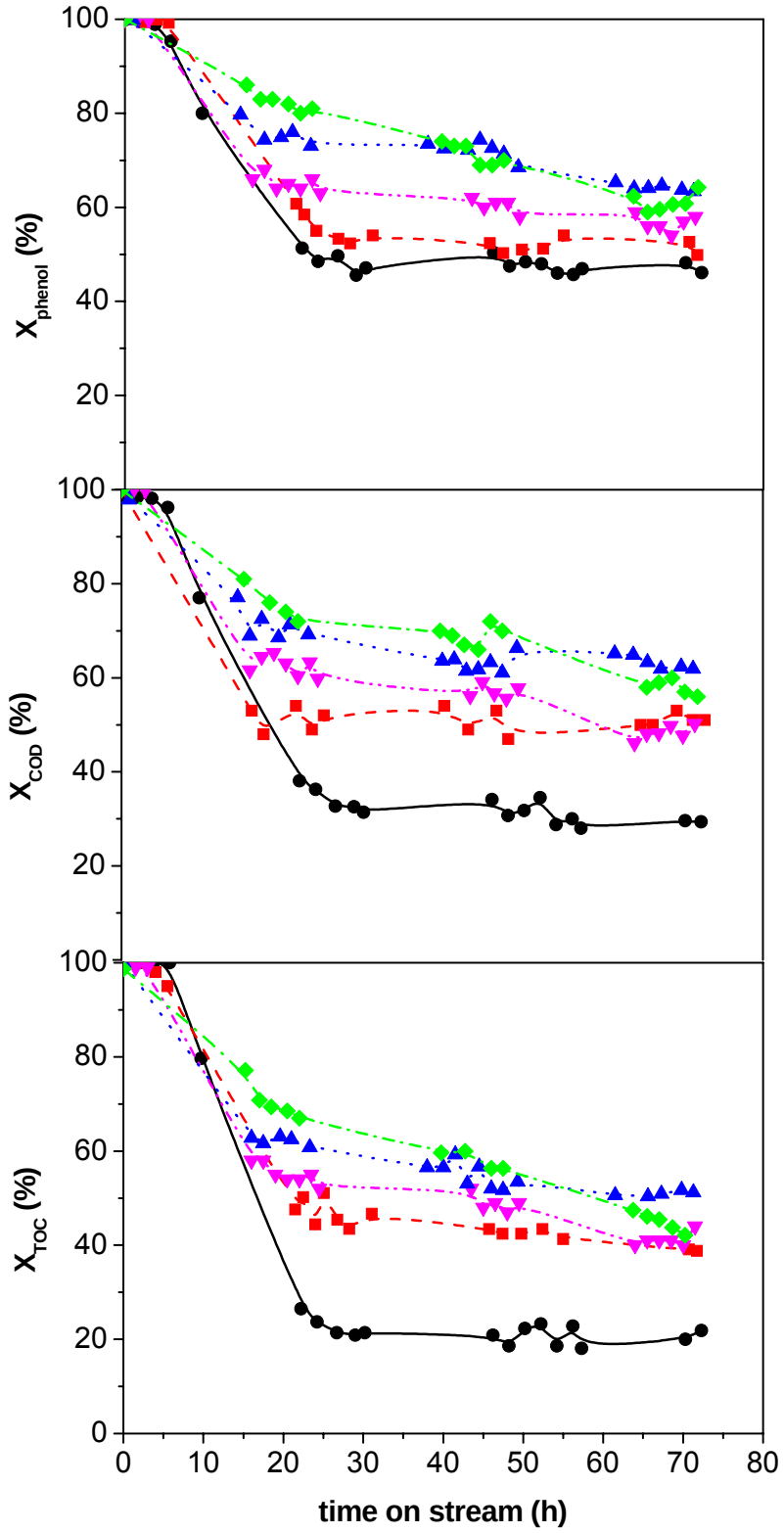

Figure 5.1. Conversion profiles for the PP-CWAO process at 140 ºC.

Symbols: (●) AC-O2-00, (■) AC-O2-10, (▼) AC-O2-15, (▲) AC-O2-20, (◆) AC-O2-30.

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The adsorption-dominating period lasts for about 8-10 h, mostly in agreement with both adsorption capacity and bed loading. The saturation time according to the flow-rate and adsorption capacity calculated from the Freundlich equation at 20 ºC is 10 h for phenol [4], as it will be discussed in Chapter 6. The difference between the experimental and theoretical saturation time could be due to the fact that the adsorption capacity decreases as temperature increases [5], and it must be noted that the adsorption isotherms were obtained at 20 ºC while the experiments were done at 140 ºC. In any case, these initial profiles do not affect the steady state conversion achieved, so it is not relevant for the further discussion of the results.

Along the experiments, intermediate compounds and polymeric chains of high dimensions are formed and can be irreversibly adsorbed on the AC, blocking the micropores and surface active sites [6-7]. In these pores and active sites AC is sought to concentrate the reactants and to generate active species from both dissolved molecular oxygen and H_2O_2 [8-9], which are responsible for phenol oxidation. These processes lead to a slow but progressive decrease of the AC performance observed in the conversion profiles, more significant when using higher amounts of peroxide, as Figure 5.1 shows. Since the AC surface is continuously changing, under some reaction conditions it is not possible to reach a true steady-state. Therefore, in the present work, the considered steady-state conversions will be those obtained from the average results between 64 and 72 h of time on stream.

The presence of H_2O_2 in the reaction gave significantly higher phenol removals, as can be seen in Figure 5.1. Besides, higher overall mineralisation was achieved, since the enhancement on COD and TOC removals was even higher than for phenol removal itself. Then, phenol removal increases from 45 % (AC-O2-00) to 64 % (AC-O2-20) after adding 20 % of H_2O_2, while COD conversion increased from 30 % to 63 % and TOC removal from 21 % to 51 %, as summarised in Table 5.2. It is noticeable that conversion enhancements are reduced when increasing the amount of H_2O_2 supplied. Thus, possibly there is some inefficient use of the oxidant at these reaction conditions. A similar behaviour was observed in the work of Debellefontaine et al. (1996) [10], who concluded that H_2O_2 doses higher than 15 % did not significantly increase the process efficiency (in a stirred batch reactor, using ferrous sulphate as catalyst, 160ºC and excess oxygen for the oxidation of phenol), while stoichiometric doses as small as 0.2 % already had a significant effect.

In the light of the results, having achieved very similar conversions whether 20 or 30 % H_2O_2 was used, it can be concluded that the critical amount of H_2O_2 for the PP-CWAO at 140 ºC is 20% of the stoichiometric demand for complete phenol mineralisation.

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Table 5.2. Steady-state conversions of PP-CWAO effluents at 140 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-O2-00	45	30	21	2.70
AC-O2-10	52	47	40	2.36
AC-O2-15	57	50	43	2.26
AC-O2-20	64	63	51	2.27
AC-O2-30	62	58	45	2.26

The pH profiles for the experiments conducted at 140 ºC are plotted in Figure 5.2. Initially, phenol solutions have a pH around 5.9 that quickly goes down when the reaction products appear as the AC bed equilibration approaches. As it will be discussed in a following section, these reaction intermediates are mostly organic acids, which account for the pH decrease up to 2.3-2.7 depending on the extent of the oxidation process. The lower pH obtained for the PP-CWAO runs agrees with the higher organic removals achieved, although no significant differences could be detected just from the measured pH.

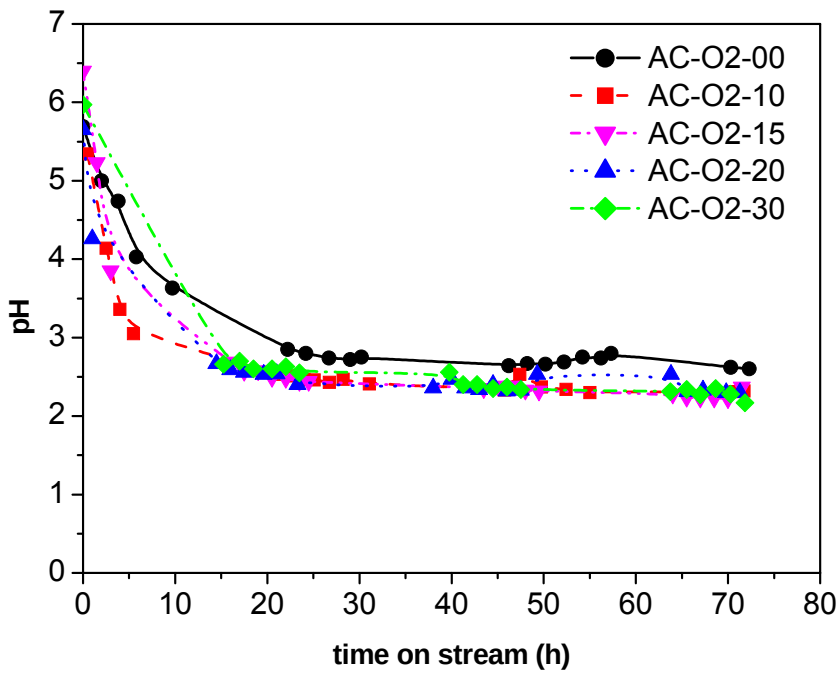

Figure 5.2. pH profiles of the PP-CWAO tests at 140 ºC.

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PP-CWAO was also tested at a 160 ºC and the obtained conversions are presented in Figure 5.3. At this temperature is rather difficult to distinguish an adsorption-dominating period since the conversion continuously decreases along the time on stream tested. Yet, pseudo steady-state results taken as the average from the last 8 h of process are summarised in Table 5.3. From this table and from observation of Figure 5.3, it is noticeable that although H_2O_2 slightly improves phenol removal, COD and TOC abatements remain invariable. Taking into account that the rate of H_2O_2 decomposition increases with temperature [11], thermal decomposition must be an important reason for the inefficient use of peroxide compared to the results obtained at 140 ºC. At these conditions and only based on conversion results, it would not be recommended the use of hydrogen peroxide as oxidation promoter. It is obvious that the low benefits obtained would not overcome the increased cost of adding H_2O_2 to CWAO and, as it will be discussed later, the AC consumption.

Table 5.3. Steady-state conversions of PP-CWAO effluents at 160 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-O2-00	78	65	62	3.22
AC-O2-10	78	70	55	2.57
AC-O2-20	85	70	66	2.67
AC-O2-30	91	72	67	2.67

It is surprising that although at 160 ºC organic removals are higher than at 140 ºC, pH values in the effluents were less acidic. Nevertheless, since phenol, COD and TOC conversion values were so close, it is expected that the effluent composition is mainly unreacted phenol. While on the contrary, at 140 ºC the presence of carboxylic acids from phenol partial oxidation gives the more acidic properties found in the oxidised effluents. Still, different compositions in terms of acidic intermediates could give very different pH, so this could be the reason for the measured pH values. An extended discussion on the effluents composition will be given in a following section.

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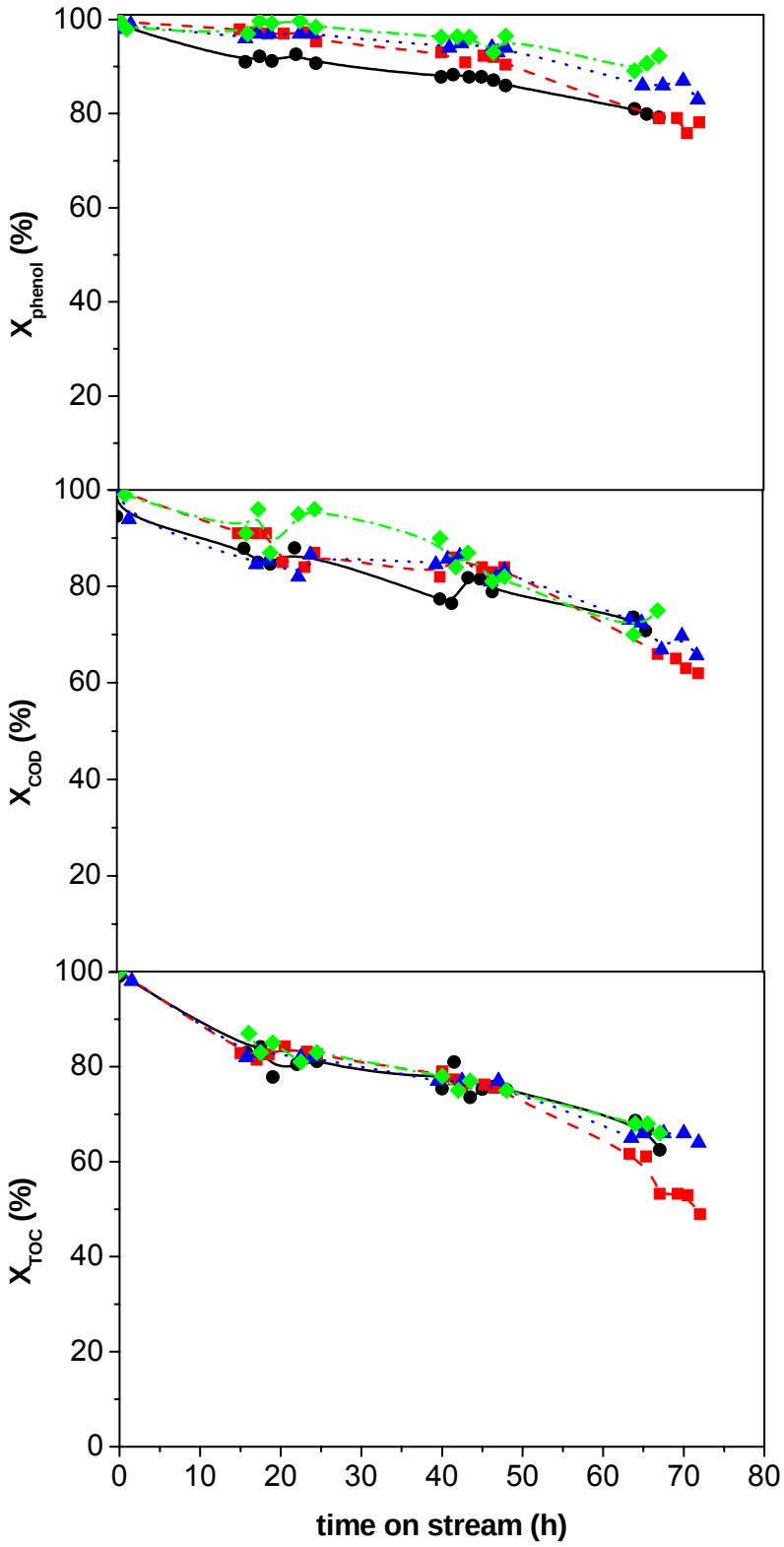

Figure 5.3. Conversion profiles for the PP-CWAO process at 160ºC.
Symbols: (●) AC-O2-00, (■) AC-O2-10, (▲) AC-O2-20, (◆) AC-O2-30.

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Conversion profiles found for experiments at 120 ºC are shown in Figure 5.4. Because experiments were still performed in the TBR over AC catalyst, the same adsorption-dominating and saturation effects observed for the process at 140 ºC are found at this reaction temperature. However, what is significantly different is that conversion profiles seem more stable and only a slow decrease is observed at the highest H_2O_2 dose (AC-O2-30). Consequently it appears that any loss of AC catalytic activity is less accentuated at these conditions.

Table 5.4 lists the steady-state results for phenol effluents treated at 120 ºC. It was possible to observe an increase of the phenol conversion from 15 % (AC-O2-00) to 51 % (AC-O2-30) after adding 30 % of H_2O_2. Besides, as also found at 140 ºC, higher overall mineralization was detected, with TOC conversions increasing from 2 % to 37 % and COD removals from 6 % to 38 %. Even though the improvement over the classical CWAO process is not proportional to the amount of H_2O_2 supplied, since conversions increase at higher oxidant doses supplied, it seems that peroxide is very efficiently used at this temperature. It has not been proved that adding higher H_2O_2 percentages would not lead to higher organic abatements. Nevertheless, AC-O2-30 is considered the optimal condition at this temperature, because adding more than one third of the stoichiometric demand for complete phenol mineralisation could not be considered just as a promoted process but a CWPO process under an oxic environment.

Table 5.4. Steady-state conversions for PP-CWAO effluents at 120 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-O2-00	15	6	2	2.90
AC-O2-10	28	25	18	2.69
AC-O2-20	43	33	19	2.10
AC-O2-30	51	38	37	2.09

pH profiles followed the same trend as in Figure 5.2, although as it can be seen in Table 5.4, lower pHs were obtained at higher conversions, i.e., when using higher doses of H_2O_2. In accordance with this lower pHs, more oxidised products are expected at these reaction conditions as it will be discussed later. The lower pH values found at 120 ºC than at 140 or 160 ºC can be attributed to the presence of carboxylic acids and other reaction products more acidic than those obtained at higher temperatures.

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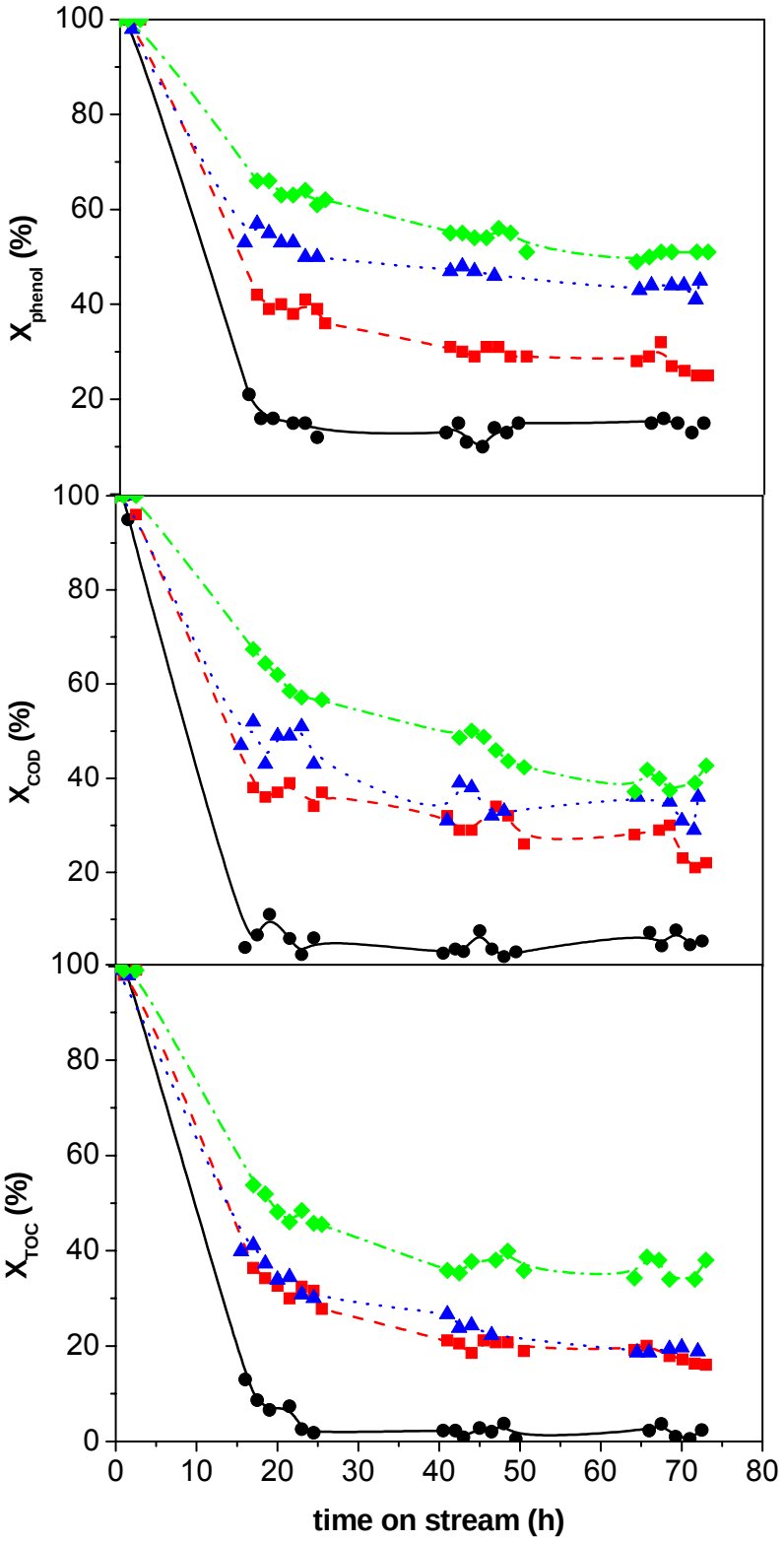

Figure 5.4. Conversion profiles for the PP-CWAO process at 120 ºC.
Symbols: (●) AC-O2-00, (■) AC-O2-10, (▲) AC-O2-20, (◆) AC-O2-30.

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5.1.1. Control tests: Air vs. N_2 atmosphere over AC or inert support

In order to find out the direct effects of adding H_2O_2 to the classical CWAO process, control tests were performed using silicon carbide (SiC) as inert support instead of AC and replacing air by N_2. In Table 5.5, phenol, COD and TOC conversions at 140 ºC are presented. Three distinct blocks can be identified: a set of experiments conducted with AC in an inert atmosphere, but also tests made over an IS in an inert atmosphere and tests using IS and air.

Table 5.5. Summary of control tests at 140 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-N2-10	11	9	5	3.21
AC-N2-20	30	17	13	2.59
AC-N2-30	36	27	22	2.34
IS-N2-10	12	10	4	3.17
IS-N2-20	27	23	6	2.78
IS-N2-30	30	26	9	2.74
IS-O2-10	25	17	10	2.83
IS-O2-20	46	29	12	2.52
IS-O2-30	56	33	15	2.37

If no oxygen is used in the reaction media, similar results for phenol removal are obtained when using either AC or IS as bed filling. Nevertheless, one can observe a higher mineralisation for the activated carbon. In fact, besides the capacity of decomposition of the O_2 molecule, AC is also capable of decomposing H_2O_2 molecules into hydroxyl radicals [8-9] and other active species. Therefore, the contact between phenol and active radicals at the carbon surface is enhanced due to the presence of H_2O_2 from the very beginning of the process as also found by Rivas et al. (1999) [12]. In addition, it is noticeable from experiments IS-10-N2, IS-20-N2 and IS-30-N2 that the degree of mineralisation achieved, i.e., TOC conversion, was smaller than the corresponding fraction of H_2O_2 supplied, therefore, a Fenton-like effect due to a possible metal contribution of the system pipes was not detected.

With an IS and O_2 atmosphere the results are significantly improved, showing that although in the absence of catalyst the combination of oxygen and hydrogen peroxide is profitable. However, it is worth mentioning that a blank test at 140 ºC, over an inert support and air at 2 bar P_{O2} gave negligible phenol conversion in the same reaction system [13].

Coming back to Table 5.2, if the performance of AC when using 10 % of the stoichiometric hydrogen peroxide demand (AC-O2-10) is compared with that conducted

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over IS (IS-O2-10 in Table 5.5), both of them in an air atmosphere at 140 ºC, phenol conversion is twice that obtained over the IS (i.e. 25 % in IS-O2-10 against 52 % in AC-O2-10). It must be noted that, when using IS it is necessary to use 20 % H_2O_2 (IS-O2-20) to reach the same phenol conversion than in presence of AC without H_2O_2 (AC-O2-00). Using 30 % H_2O_2 (IS-O2-30) does not give a significant benefit neither in COD conversion nor in TOC removal compared to IS-O2-20, which shows a non-efficient use of H_2O_2 at high doses, as also found for AC-O2-30. Then, radical scavenging effects, also identified in the Fenton process, may compete with the reaction of hydroxyl radicals and organic molecules when excess oxygen and 30 % of H_2O_2 are present in the reaction media.

In conclusion, the combination of oxygen and hydrogen peroxide improves the oxidation capacity even in the absence of catalyst. However, over AC, adding H_2O_2 significantly increases phenol mineralisation (i.e. increasing COD and TOC removals).

Even though AC is known to decompose H_2O_2 [8,14], the limited hydrogen peroxide availability could explain that phenol oxidation extent was similar for experiments using either AC or IS. Nevertheless, AC is also capable to adsorb oxygen and to activate H_2O_2 on its surface involving the formation of oxygen active species [15], which could be the reason for the improvement in terms of phenol mineralisation using simultaneously both oxidants over AC catalyst. These results are in agreement with the work of Lüking et al. (1998) [16] who examined iron powder, graphite and AC for the oxidation of 4-chlorophenol with H_2O_2. These authors concluded that, although highest reaction rates were found for the Fenton reactions induced by dissolved iron powder, AC acts as a heterogeneous catalyst for the activation of hydrogen peroxide and can be used for the oxidation of organic substances. In addition, they also suggested that the granular structure with a high specific surface area of AC could be advantageous in the case of fixed bed reactors, such as the TBR.

The hydrogen peroxide decomposition-activation mechanism is not completely understood but several electron transfer processes have been suggested to take place during the reaction. Oliveira et al. (2004) [9] proposed a competitive mechanism for the peroxide decomposition and organic oxidation in the presence of AC. In their work, reducing sites in the AC surface, i.e., basic oxygen surface groups, could promote the decomposition of hydrogen peroxide and the oxidation of organic compounds (phenol and hydroquinone). These reactions seem to take place by a radical mechanism probably initiated by an electron transfer from the reducing site in the AC to the hydrogen peroxide molecule to produce species such as $\cdot OH$ and $\cdot OH_2$. Other authors [8,14-16] mainly assume that the H_2O_2 decomposition on AC involves the exchange of a surface hydroxyl group with a hydrogen peroxide anion (Equation 5.1). The formed

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surface peroxide is regarded as having an increased oxidation potential which enables the decomposition of another H_2O_2 molecule with the release of O_2 and regeneration of the carbon surface (Equation 5.2).

$$AC\text{-}OH + H^+OOH^- \rightarrow AC\text{-}OOH + H_2O \qquad \text{Eq. 5.1}$$

$$AC\text{-}OOH + H_2O_2 \rightarrow AC\text{-}OH + H_2O + O_2 \qquad \text{Eq. 5.2}$$

Apart form the decomposition reaction in Equation 5.2, considering that AC acts as an electron transfer catalyst, H_2O_2 can also be activated on AC surface involving the formation of free radicals (Equations 5.3 and 5.4). Nevertheless, heterogeneous decomposition of hydrogen peroxide on AC may also be considered to depend on both the carbon porosity and the chemical properties of the surface, which are associated with surface and bulk diffusion of the hydrogen peroxide molecules [8].

$$AC + H_2O_2 \rightarrow AC^+ + OH^- + OH\cdot \qquad \text{Eq. 5.3}$$

$$AC^+ + H_2O_2 \rightarrow AC + HO_2\cdot + OH\cdot \qquad \text{Eq. 5.4}$$

Control tests were also performed at 160 and 120 ºC and results are summarised in Table 5.6 and 5.7. Again three distinct blocks can be distinguished for experiments over AC in nitrogen atmosphere and for tests over IS either in nitrogen or air atmosphere. At 160 ºC, conversion profiles at AC-N2-10 conditions oscillate in a range around 0 ± 10 %. As it will be discussed later, this fact points out that consumption of AC during reaction not only takes place by direct combustion. It must be also some disintegration or dissolution of AC that contributes to increase the organic load found in the effluent leading to negative conversion values. Since it is not possible to distinguish between the fraction of COD or TOC that comes from phenol oxidation and that coming from AC contribution, conversion values given should be considered observable results, lower than those corresponding to process capacity in terms of phenol removal. On this basis, although results at 160 ºC must be considered carefully, it can be said that the use of AC in N_2 atmosphere does not allow observing a significant improvement over the process using IS apart from a slightly higher mineralisation for AC-N2-30. Meanwhile, although very similar results are found for experiments using IS, slightly higher phenol removal and mineralisation are found when combining O_2 and H_2O_2 than in N_2 atmosphere.

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Table 5.6. Summary of control tests at 160 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-N2-10	--	--	--	--
AC-N2-20	17	15	12	2.94
AC-N2-30	40	36	25	2.56
IS-N2-10	12	6	4	3.24
IS-N2-20	32	18	16	2.28
IS-N2-30	60	20	17	2.40
IS-O2-10	23	13	4	2.77
IS-O2-20	47	27	19	2.54
IS-O2-30	59	34	22	2.34

Table 5.7. Summary of control tests at 120 ºC.

Experiment	X_{phenol} (%)	X_{COD} (%)	X_{TOC} (%)	pH
AC-N2-10	16	14	7	2.90
AC-N2-20	33	28	18	2.44
AC-N2-30	47	38	29	2.31
IS-N2-10	10	2	1	3.08
IS-N2-20	19	7	2	2.84
IS-N2-30	28	10	5	2.80
IS-O2-10	11	4	2	2.31
IS-O2-20	14	5	4	3.05
IS-O2-30	27	18	16	3.07

At 120 ºC, comparing experiments over AC or IS in an inert atmosphere it can be seen that higher organic removal was obtained for activated carbon. The same effect was observed at 140 ºC, which means that at this temperature AC is able to produce hydroxyl radicals from H_2O_2 and facilitate its reaction with the organic compounds. With IS and N_2 atmosphere the results are not much different from those in the presence of O_2, since being the inert support unable to decompose the O_2 molecule in active radicals, it is not possible to profit from the oxidation conditions in the IS-O2-10/20/30 tests.

Figure 5.5 summarises all control tests discussed in this section for its better comparison.

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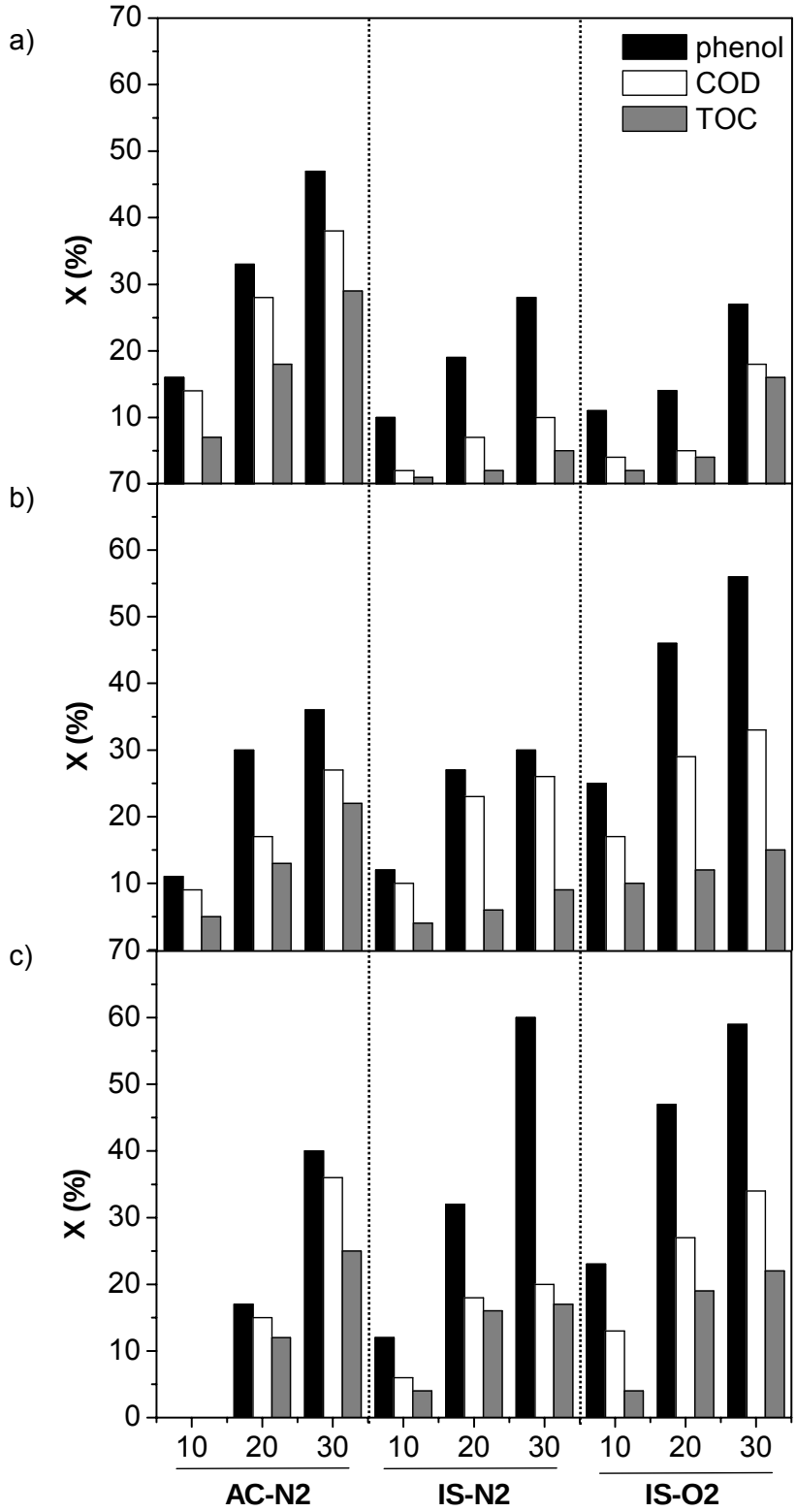

Figure 5.5. Control tests at different temperatures: a) 120 ºC, b) 140 ºC, c) 160ºC.

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5.1.2. Promoting or synergistic effect

First of all it would be very useful to define what is exactly understood by a promoting or synergistic effect. To promote is to raise, to advance or to contribute to the growth progress. Then, a promoting effect will be the one which helps increasing the starting value of a given parameter. On the other hand, a synergistic effect is that capable of producing synergy, which is the interaction of two or more agents or forces that produce a combined effect greater than the sum of their individual effects; the cooperative interaction among groups that creates an enhanced combined effect.

To study whether the oxidation capacity of combining O_2 and H_2O_2 over AC is greater than that predicted by knowing their separate effects (i.e. the sum of AC-O2-00 and AC-N2-10/20/30), experimental and predicted results for phenol, COD and TOC conversions at 140 ºC are plotted in Figure 5.6.

In general terms, it can be noticed that results form the PP-CWAO process (AC-O2-10, AC-O2-20 and AC-O2-30) in Figure 5.6 are higher than those corresponding to CWAO (AC-O2-00), which means that H_2O_2 has a promoting effect over the CWAO process (AC-O2-00) that increases its oxidation capacity. Adding 10 % of the stoichiometric demand of H_2O_2 leads to predicted values of phenol conversion slightly higher than those experimentally obtained (i.e. 52 % for AC-O2-10 against and expected 56 %). However, if COD and TOC reductions are compared, the experimental conversions found were higher than expected, e.g. 47 % for X_{COD} against a predicted 39 %, and 40 % for X_{TOC} against an expected 26 %. For experiments using 20 and 30 % H_2O_2, the same effect was obtained: lower phenol conversions than those predicted, but higher COD and TOC removals than the expected ones just from the addition of AC-O2-00 and AC-N2-20/30 experiments. In fact, the much higher TOC and COD reduction actually obtained result in a preferential use of the oxygen radicals to degrade partial oxidation products with a slight detrimental effect on the phenol conversion. This means that the beneficial effect of using small doses of a stronger oxidant in the reaction media mainly lies in the degree of phenol mineralisation. Therefore, adding H_2O_2 to the classical CWAO at 140 ºC over AC has a promoting effect for phenol removal and a synergistic effect in terms of mineralisation, i.e., over enhanced COD and TOC removals. Surprisingly, the major improvement was for 20 % H_2O_2 and not from the addition of 30 % H_2O_2. Also observed in Figure 5.1, the higher concentration of oxygen and hydroxyl radicals present in AC-O2-30 may be affected by radical scavenging phenomena [18] that prevents from an efficient use of the oxidation potential at this reaction conditions.

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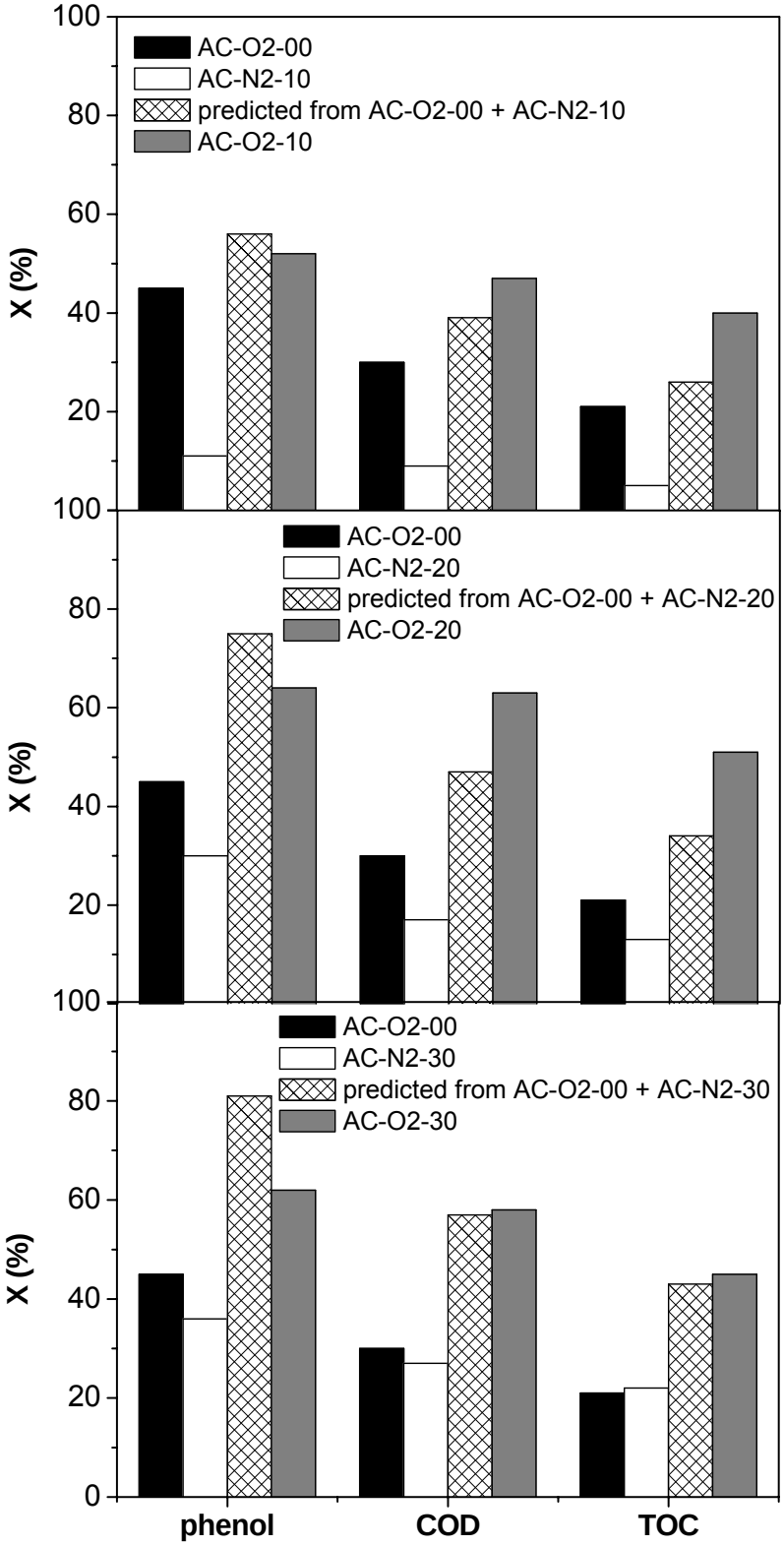

Figure 5.6. Promoting or synergistic effect of H_2O_2 on CWAO at 140 ºC.

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As can be extracted from Tables 5.3 and 5.6 for experiments at 160 ºC, supplying H_2O_2 to the classical CWAO process leads to slightly higher organic removals. However, the experimental values found were always lower than the predicted for AC-O2-20 and AC-O2-30. Since AC-N2-10 results could not be clearly extracted, predicted values for 10 % H_2O_2 can not be speculated. As commented for Figure 5.2, an enhanced thermal decomposition of peroxide can be inferred at this temperature. Thus, hydrogen peroxide would still have some promoting functions but it will not keep the synergistic capacity to improve phenol mineralisation.

For experiments at 120 ºC (data shown in Tables 5.4 and 5.7), usually the predicted values for phenol conversion were slightly lower than the experimental ones, but different trends were obtained when comparing COD and TOC removals. When using 10 % of stoichiometric H_2O_2, COD (25 %) and TOC (18 %) reductions were respectively 5 and 9 % higher than the predicted values (COD: 14+6=20 %; TOC: 7+2=9 %), which means that higher mineralisation of partially oxidised compounds was achieved and that synergistic effects able to increase the process efficiency were present. What can be inferred is that the higher occurrence of reaction intermediates in AC-O2-10 facilitates the reaction between a hydroxyl radical and a partially oxidised compound resulting in an enhanced mineralisation efficiency of the process. However, for experiments AC-O2-20 (COD: 33 %) and AC-O2-30 (COD: 38 %), the previously found synergistic processes are not so significant and for COD conversions the trend is even opposite, having worse experimental results than what could be predicted (34 % COD, for AC-O2-20 and 44 % COD, for AC-O2-30). In turn, TOC closely reached the expected reductions for experiment AC-O2-20 (TOC: 19 % versus a predicted 20 %) and gave just 6 % of improvement for AC-O2-30 (TOC: 37 % versus a predicted 31 %). The loss of H_2O_2 mineralisation capacity has to be discussed taking into account the changes that AC suffers during reaction. When the activated carbon is used in a CWAO process or PP-CWAO as an adsorbent catalyst it is necessary to take into account their specific characteristics, which involve physical adsorption of the compounds from the solution, oxidation of the organic pollutants, as well as other parallel reactions that may include oxidation/combustion of the AC itself and condensation reactions of the phenolic compounds resulting in long polymeric chains that can be irreversibly adsorbed onto the AC surface [7], as it will be discussed in the following section.

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5.2. Activated carbon performance

To evaluate the weight change and to highlight the presence of polymeric material attached to the AC surface, thermogravimetric analyses were completed at the end of each run. Figures 5.7, 5.8 and 5.9 show the thermograms for parent AC, phenol saturated AC and AC samples from oxidation experiments at the three temperatures studied. Since no identification of the evolving groups was performed, TGA discussion will follow the interpretation of Figueiredo et al. (1999) [19], in agreement with other studies on this issue [20-22]. This interpretation allows to assign surface groups depending on their desorption temperature.

As can be seen in Figures 5.7, 5.8 and 5.9, the weight change recorded for the used AC was notably higher than for the original AC, since for the latter the weight loss is only due to desorption of surface oxygen groups and some water from sample humidity. Besides, differences can be observed between the AC used in the CWAO process (AC-O2-00) and the samples from the PP-CWAO, which shows that using H_2O_2 has some influence on the formation of carbonaceous deposits on AC surface. First derivative on the thermograms highlights the temperature ranges at which higher desorption could be detected. The main peaks observed around 200 and 400 ºC in the phenol saturated AC correspond to phenol thermal desorption, since at 200 ºC physically adsorbed phenol is desorbed while at 400 ºC chemically adsorbed phenol desorbs [22].

For the AC samples after reaction, all TGA profiles show similar trends with two main desorption regions. Since the previous peaks found for phenol saturated AC are less marked in AC samples after reaction, some other compounds different from phenol should also be adsorbed. According to thermal decomposition of surface oxygenated groups on carbon surface [19], the progressive weight loss between 200 and 400 ºC can be attributed to the decomposition of carboxylic groups that evolve as CO_2. It must be noted that the used AC gives a much higher weight loss in this zone probably due to the reoxidation of the surface during its use or other adsorbed compounds present. The weight loss beyond 400 ºC is likely due to the release of various oxygen surface groups such as carbonyl, phenolic or ether-type structures that evolve as CO. In the range between 400 and 500ºC, the weight loss mainly correspond to chemically adsorbed polymers formed by oxidative coupling reactions [6,23].

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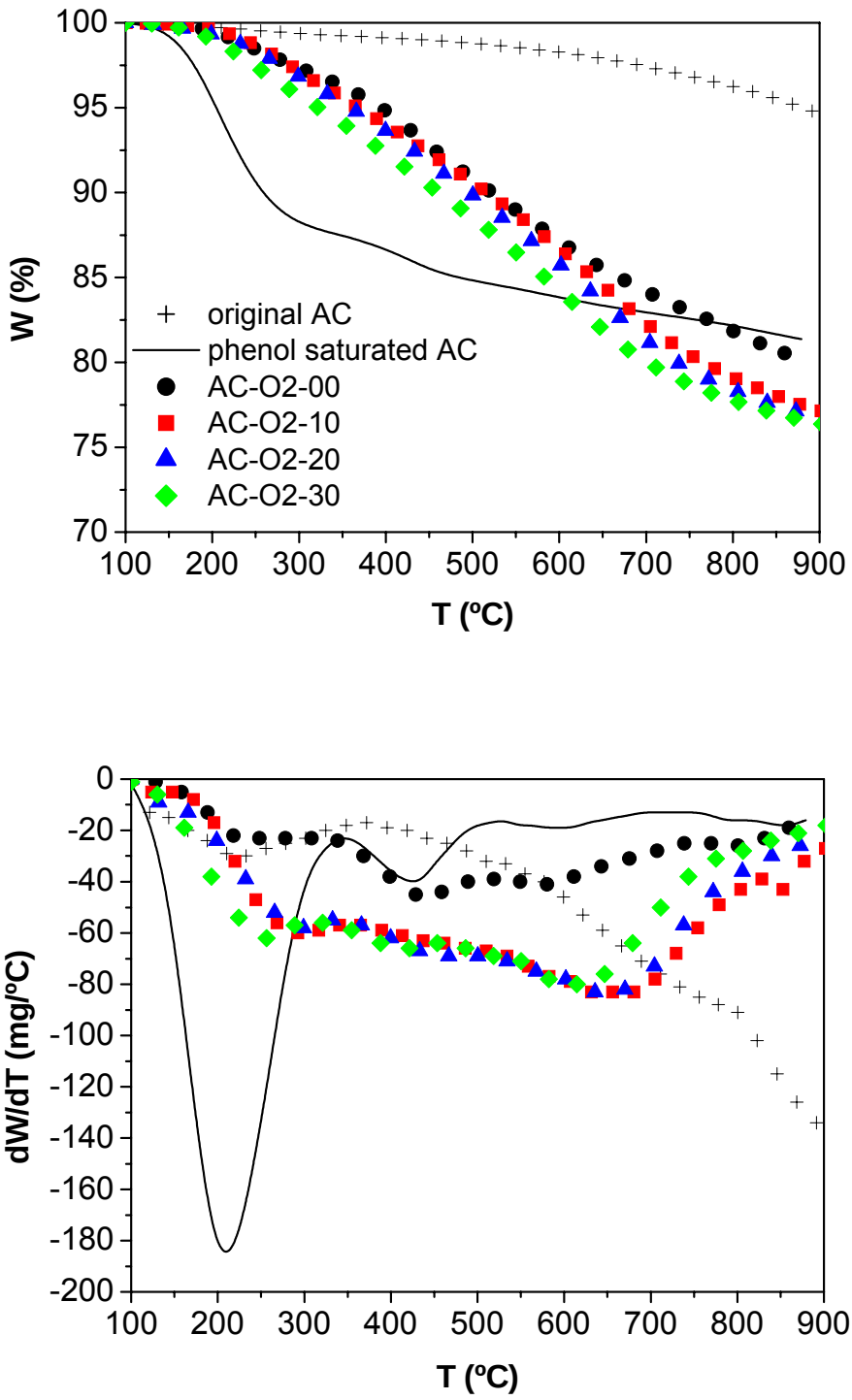

Figure 5.7. TGA data and first derivative of TGA data for reactions at 120 ºC.

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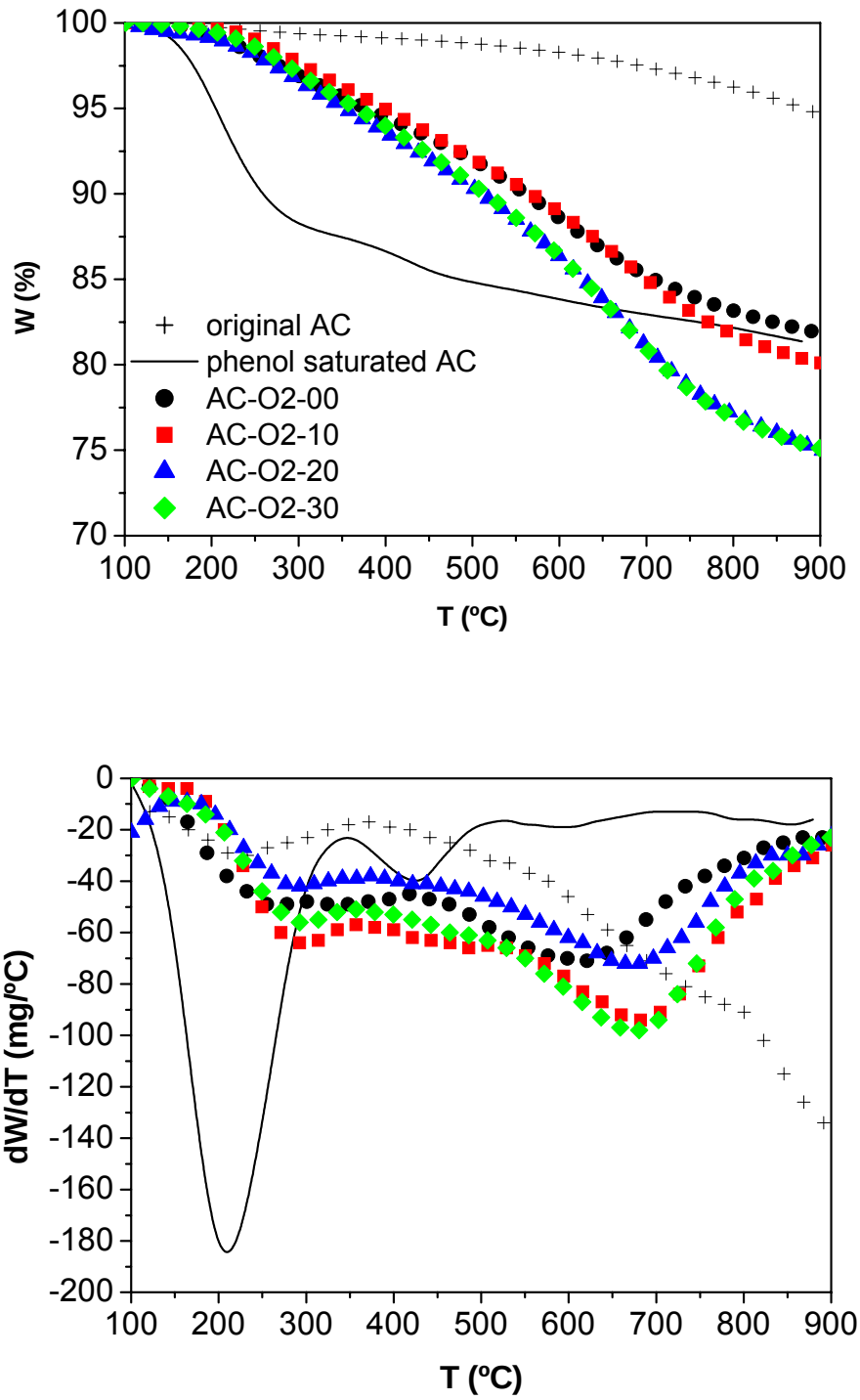

Figure 5.8. TGA data and first derivative of TGA data for reactions at 140 ºC.

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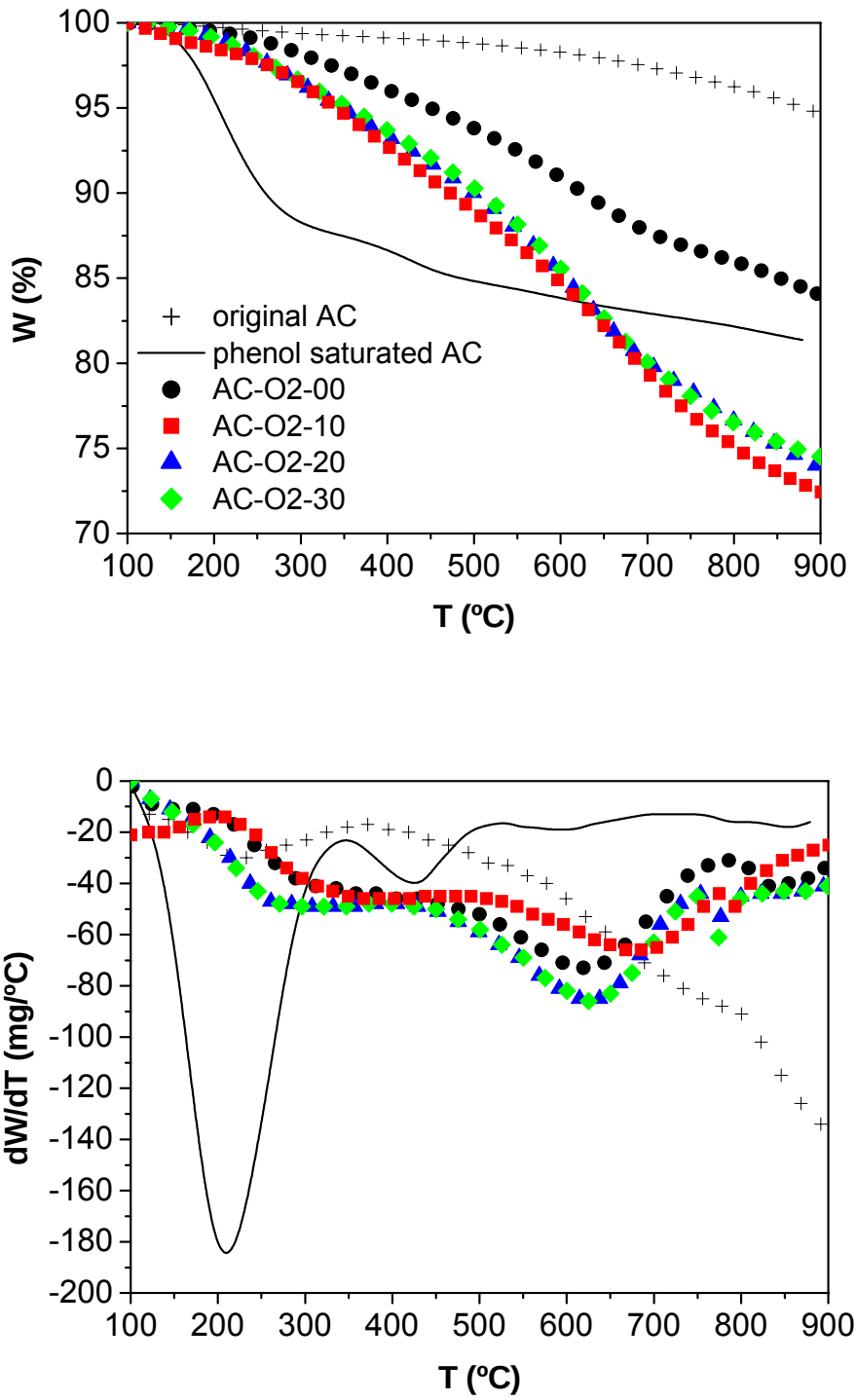

Figure 5.9. TGA data and first derivative of TGA data for reactions at 160 ºC.

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During the oxidation tests, AC simultaneously suffers from burning-off, due to its own oxidation and phenol oxidative coupling reactions that lead to carbonaceous depositions on AC surface. The AC weight change (ΔW) helps to quantify which process occurred at a higher extent, since a positive ΔW indicates that oxidative coupling prevails over combustion, whereas a negative ΔW implies the opposite effect. The ΔW (Equation 3.20) and the TWL resulting from conventional and hydrogen peroxide promoted CWAO tests are collected in Table 5.8. It also included the AC weight after reaction (m_{fAC}), once physisorbed and chemisorbed compounds have been removed during TGA analyses (see Equation 3.8). It is worth mentioning that ΔW was obtained applying over the initial AC mass the weight loss recorded for AC samples during TGA up to 400 ºC. On the other hand, the TWL is directly the weight loss determined for AC samples after TGA up to 900 ºC.

Table 5.8. Weight changes of original and AC samples after reaction.

T (ºC)	Sample	ΔW (%)	TWL (%)	m_{fAC} (g)
120ºC	AC-O2-00	37.70	18.64	8.53
	AC-O2-10	36.81	22.59	8.09
	AC-O2-20	39.64	23.31	8.24
	AC-O2-30	37.76	23.60	8.33
140ºC	AC-O2-00	3.61	12.20	7.28
	AC-O2-10	20.97	20.00	7.30
	AC-O2-20	17.63	26.40	6.68
	AC-O2-30	15.51	24.98	6.62
160ºC	AC-O2-00	7.40	16.17	7.08
	AC-O2-10	-24.25	27.55	4.15
	AC-O2-20	-28.58	26.16	4.05
	AC-O2-30	-37.89	25.50	3.67
--	original AC	--	5.36	--

As it can be observed also in Figure 5.7, the ΔW for reactions at 120 ºC is positive and very similar for all oxidation conditions. It does not follow any clear trend, which seems to indicate that at this temperature there is no relationship with the amount of H_2O_2 used in the reaction and that carbonaceous deposits prevailed over combustion. However, for the TWL, where desorption of long polymeric carbon chains are included, the differences between each experiment appear, showing a trend that correlates with the amount of H_2O_2 as well as the phenol, COD and TOC conversions obtained. Therefore, it seems that the contribution of hydrogen peroxide promotes phenol mineralisation but also phenol polymerisation and chemisorption on AC surface.

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Reactions at 140 ºC also lead to positive ΔW showing that the extent of oxidative coupling reactions was higher than the direct carbon consumption by burning-off. For experiments AC-O2-10, AC-O2-20 and AC-O2-30 ΔW was positive and up to 7, 6 and 5 times higher than that of AC-O2-00, respectively. This means that oxidative coupling processes occurred in a major extent than AC combustion. Since the total weight loss measured from TGA up to 900 ºC was higher for experiments using higher doses of H_2O_2 it seems that an important fraction of polymeric depositions was present. However, since carbon depositions could also be burned during reaction, it is not possible to assure the exact extent of oxidative coupling or burning just from TGA analyses. Nevertheless, the much higher ΔW found in samples form PP-CWAO points out that the addition of hydrogen peroxide in the system favours the formation of condensed carbonaceous species, as also reported in the study by Santiago et al. (2005) for the same reaction system and temperature, but using different activated carbons that had been submitted to oxidation pre-treatments [24]. They concluded that the deposition of polymeric compounds was influenced by a carbon pre-treatment with hydrogen peroxide being an oxidant that enhanced the formation of those species on the carbon surface. Moreover, the authors considered the 50 h phenol CWAO experiments by themselves as soft liquid phase oxidation treatments of the carbon leading to gradual changes in its surface area, progressive carbon consumption as well as continuous formation of a carbonaceous deposit on the carbon surface. The last effect can be extended to the present results if the 72 h PP-CWAO process is seen as a soft liquid phase oxidation of the AC itself. The polymeric compounds condensed on the AC could eventually block the surface active sites and be responsible of the progressive catalytic activity drop found in experiments using higher amounts of oxidant (i.e. experiments AC-O2-20 and AC-O2-30). This adverse effect highlights that there is a compromise between having higher organic removals by using H_2O_2 and facilitating the loss of AC catalytic activity by carbonaceous deposits.

On contrary, for PP-CWAO tests performed at 160 ºC, ΔW turned out to be negative. This is that the extent of AC burning-off processes overcame oxidative coupling reactions, which as previously commented, are responsible for the continuous decrease on AC catalytic activity at this temperature (see Figure 5.3). Thus, results at 160 ºC are clearly affected by AC consumption, which correspond to a continuous decrease of the space time (τ), leading to a fall in conversion as the reaction proceeds. On contrary, the ΔW for AC-O2-00 at 160 ºC was positive and in the range scale of the weight change recorded for AC-O2-00 at 140 ºC. Therefore, AC weight changes are affected by both temperature and presence of H_2O_2.

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From Table 5.8 it is noticeable that, regardless the reaction temperature, TWL values were very similar, while large differences appeared for ΔW. Since the latter values accounted for desorption of physisorbed compounds (see Figures 5.7, 5.8 and 5.9), once they are removed by heating up to 400 ºC during TGA analyses, what is left is AC and the polymeric carbonaceous compounds chemically bonded to its surface. From the ΔW obtained, apparently there is no direct relation with reaction temperature and only some differences can be observed between AC-O2-00 samples and those from the process using peroxide, as previously commented. On the other hand, after observation of TWL values, all PP-CWAO samples reached TWL around 20-28 % whereas for AC-O2-00 samples this TWL was lower and from 12 to 19 %. Thus, in the case of TWL it seems that influence of reaction temperature is not as important as that of the addition of peroxide. Yet, processes modifying AC surface can not be assessed individually.

5.3. Partial oxidation products

Characterisation of reaction products present in the outlet stream is a very important factor if the combination with a biological end treatment is pursued. The effluent composition, assessed by HPLC analyses, will give some light on the deepness on the oxidation pathway that has been achieved and together with biodegradability characterisation will allow determining the viability of process combination.

Partial oxidation products were identified and quantified by an HPLC method designed according to the phenol oxidation pathways proposed in the literature [18,25-27]. The intermediates considered were as reported in Table 3.7: glyoxilic acid, oxalic acid, formic acid, malonic acid, acetic acid, maleic acid, fumaric acid, succinic acid, acrylic acid, propionic acid, mucconic acid, 4-hydroxibenzoic acid, salicylic acid, quinone-like products, being hydroquinone, p-benzoquinone, resorcinol and catechol. The theoretical chemical oxygen demand (ThCOD) of each one of the intermediates detected was calculated and then grouped into four categories such as carboxylic acids, condensation products (4-hydroxybenzoic acid and salicylic acid), quinone-like products and unreacted phenol. These groups were used to build Figure 5.10 that gives the effluents composition in terms of fraction of COD compared to the experimental COD values obtained. As can be seen in Figure 5.10, the fraction of non-identified compounds was always less than 10 % of the remaining COD.

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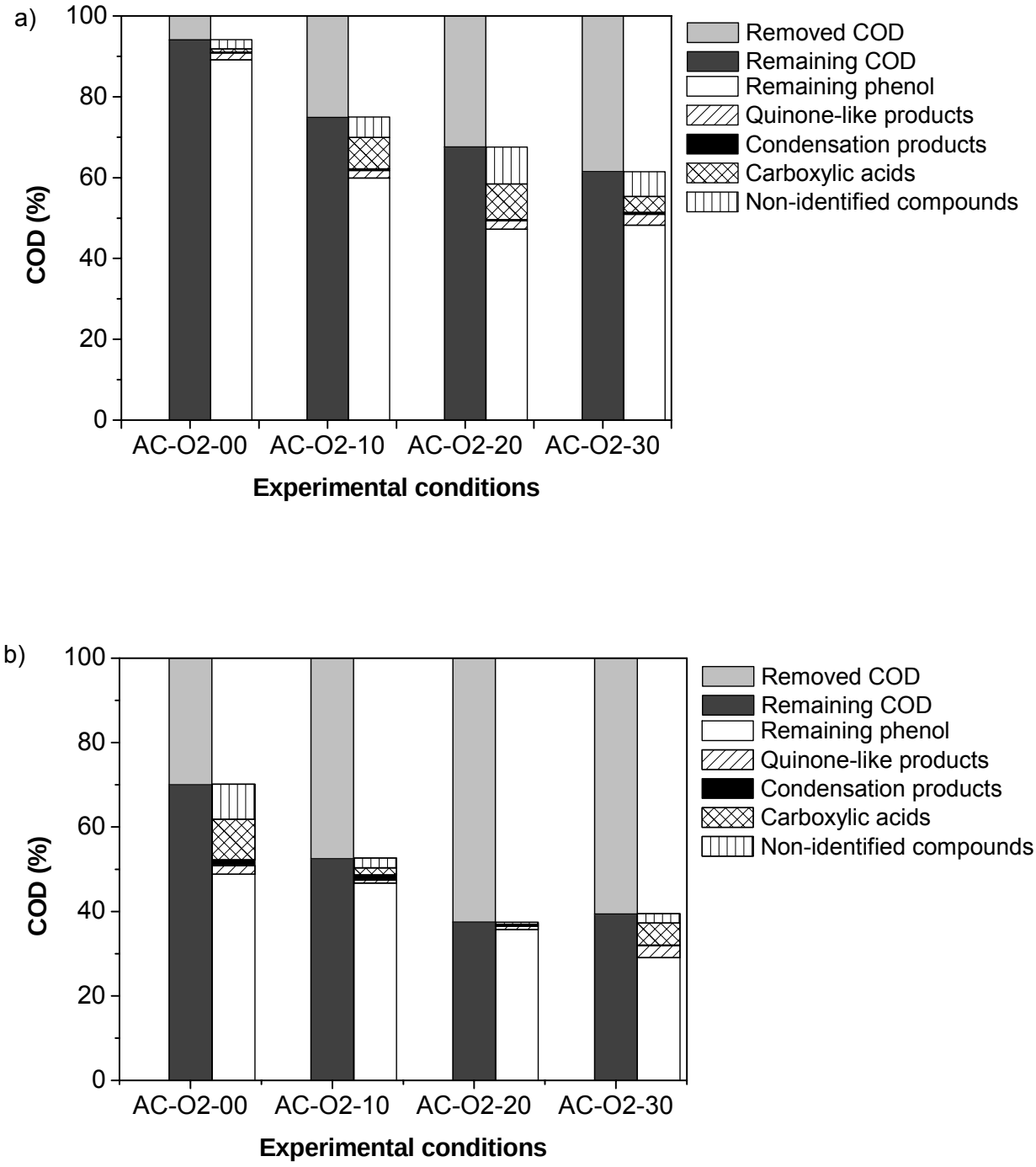

Figure 5.10. Effluent composition in terms of fraction of COD:
a) 120 ºC, b) 140 ºC and c) 160 ºC.

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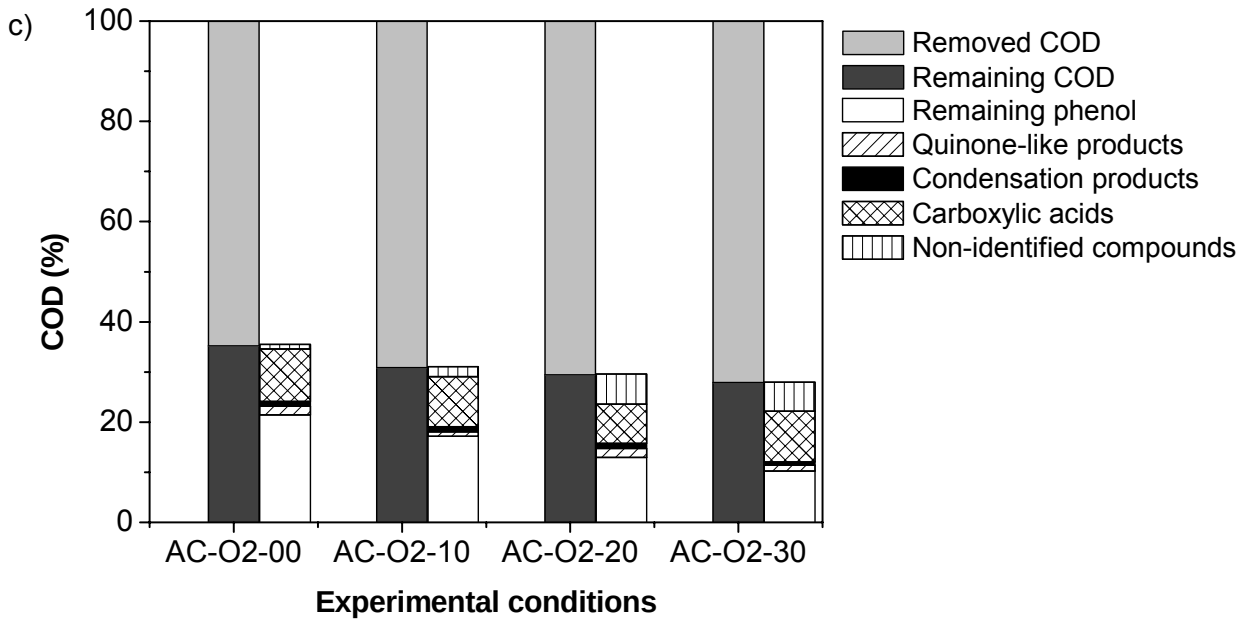

Figure 5.10 (Continued).

Observation of intermediate distribution points out that the PP-CWAO at 120 ºC not only leads to higher phenol removal, but also to higher partially oxidised intermediates in the treated effluents. However, using higher amount of H_2O_2 does not directly correlate neither with the occurrence of undesirable quinone-like products nor carboxylic acids, since regardless the H_2O_2 dose used the intermediate distribution is very similar for all cases. Besides, it was found that intermediates for AC-O2-00 were mainly oxalic, maleic and propionic acids, some hydroquinone and higher amounts of p-benzoquinone. For experiments using hydrogen peroxide, some other carboxylic acids such as formic, acetic were also found in the effluents. Meanwhile, using peroxide increased the amounts of hydroquinone and catechol, but reduced the p-benzoquinone occurrence.

At 140 ºC most of the residual COD correspond to unreacted phenol, being 70 % of all remaining COD for AC-O2-00 and up to 95 % for AC-O2-20. This fact could be expected from the very close phenol and COD conversions found for PP-CWAO experiments (Table 5.2) that indicate a high degree of mineralisation (i.e. low occurrence of partially oxidised products in the effluent). The carboxylic acids present were mainly oxalic, formic, acetic, maleic and propionic. At this temperature, the concentration of p-benzoquinone was also lower for the process using H_2O_2 and higher amounts of hydroquinone, resorcinol and catechol were produced.

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For reactions at 160 ºC, the intermediates distribution is roughly the same whether hydrogen peroxide was supplied to the reaction or not. Reaction products were mainly oxalic, formic, acetic acid and propionic, hydroquinone and p-benzoquinone, which followed the same trend found for 120 and 140 ºC reactions. This is that hydroquinone increased and p-benzoquinone concentrations decreased for the process using peroxide if compared to the non promoted CWAO process.

The identified oxidation intermediates suggest that the CWAO of phenol promoted with H_2O_2 evolves through a pathway similar to CWAO with oxygen as unique oxidant, as also observed from Debellefontaine et al. (1996) [10].

5.4. Implications for integrated treatment

Coupling chemical pre-oxidation with biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared with the efficiency of each individual stage [28]. According to Scot and Ollis (1995) [29], four wastewater contaminant types are identified which can benefit from combined processes: 1) recalcitrant compounds, 2) biodegradable wastes with small amounts of recalcitrant compounds, 3) inhibitory compounds and 4) intermediate dead-end products. Assuming that wastewater that is toxic, inhibitory or refractory to biological cultures can be chemically pretreated to produce biogenic intermediates, respirometric techniques were applied to determine which kind of wastewater came out form the PP-CWAO and if it would be possible its combination with a subsequent biological treatment based on non-acclimatised activated sludge.

As Y_H is necessary to calculate the $\%COD_{RB}$ (Equation 3.19), an average Y_H was estimated using the data obtained from several respirometric tests [30] performed with acetic and propionic acid. Those acids were chosen due to its predominant occurrence in all CWAO and PP-CWAO effluents. The obtained Y_H value was 0.71±0.02 mg COD mg^{-1} COD, which is in the range of the reported values in the literature (0.61-0.87 mg COD mg^{-1} COD) [31].

Biodegradability evaluation of oxidised effluents was done by determining the fraction of COD readily biodegradable, the toxicity and inhibition properties. Results for the three temperatures studied can be found in Table 5.9. For a better understanding of the results, it must be said that for instance a 10 % of toxicity means that the microorganisms' metabolism has been reduced a 10 % with respect to an easily biodegradable substrate, such as acetate. Similarly, a certain value of inhibition would mean that microorganisms' metabolism has been inhibited in that percentage.

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Table 5.9. Biodegradability characterisation of CWAO and PP-CWAO effluents.

T (ºC)	Sample	COD_{rb} (%)	Toxicity (%)	Inhibition (%)
120ºC	AC-O2-00	2.1	0.0	30.0
	AC-O2-10	2.9	1.4	31.8
	AC-O2-20	11.7	10.5	34.6
	AC-O2-30	6.4	16.8	38.9
140ºC	AC-O2-00	4.3	7.2	41.7
	AC-O2-10	11.1	13.8	44.8
	AC-O2-20	14.3	16.2	44.8
	AC-O2-30	12.7	4.1	48.1
160ºC	AC-O2-00	35.9	12.5	63.7
	AC-O2-10	39.7	15.3	74.6
	AC-O2-20	33.2	6.3	57.2
	AC-O2-30	28.7	0.0	39.7

It can be observed that the fraction of COD_{rb} in the effluents significantly increases when increasing the reaction temperature. However, for toxicity and inhibition different trends are found, depending on the temperature. In addition, although higher biodegradability is obtained for the PP-CWAO process if compared to the process without peroxide (AC-O2-00), it seems that there is no relation with the amount of H_2O_2 added.

For experiments at 120 ºC, the highest fraction of COD_{rb} was obtained for AC-O2-20, whereas the toxicity decreased and the inhibitory effect increased for PP-CWAO effluents with increasing dose of H_2O_2. At 140 ºC, again the highest fraction of COD_{rb} was for AC-O2-20, which also had the highest toxicity, while inhibition levels were very similar for all effluents at this temperature. For experiments at 160 ºC, COD_{rb}, toxicity and inhibition decreased with increasing doses of H_2O_2, although still the highest inhibition properties were recorded at this temperature.

This contradictory behaviour that gives more toxic effluents when phenol, TOC and COD removals improve can be understood taking into account the biodegradability characteristics of each one of the intermediate products identified in the reaction effluents. As reported by Santos et al. (2004) [32] using Microtox®, toxicity can be directly related to the amount of hydroquinone, which for instance was only 15 mg L^{-1} in AC-O2-00 but from 50 to 75 mg L^{-1} in the experiments using H_2O_2 in reactions at 120 ºC. At 140 ºC, hydroquinone concentrations were 32 mg L^{-1} for AC-O2-00, but from 178 to 304 mg L^{-1} for PP-CWAO experiments. Yet, for reactions at 160 ºC, hydroquinone concentration was 21 mg L^{-1} in AC-O2-00 and ranged between 33 to 61 mg L^{-1} in experiments using H_2O_2. The higher hydroquinone concentration found in effluents treated at 140 ºC agrees with the higher toxicity registered. Nevertheless, as

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recently found by Suárez-Ojeda et al. (2007) [30] using respirometry, although hydroquinone and p-benzoquinone were found to be the most toxic CWAO intermediates for the aerobic biological treatment, its toxic effect decreased after 125 days of operation in a pilot scale WWTP. These findings highlight the importance of using robust techniques, such as respirometry, that avoid overestimation of the toxicity effects of an *a priori* undesirable compound to the aerobic biomass in a WWTP.

Likewise, despite of the temperature or presence of H_2O_2, the inhibitory character was significantly high (i.e. 30-75 %), which can be associated to the amounts of unreacted phenol still present in the effluents [30]. This inhibitory behaviour of phenol leads to a reduction of microorganisms' effectiveness for the oxidation of biodegradable organic matter, expressed in the respirometric tests by a reduction on the rate of oxygen consumption. However, inhibition should be distinguished from toxicity, since in the former case the inhibitor only hinders the biological oxidation, while in the latter case the toxic compound irreversibly blocks the microorganisms' metabolism. Therefore, when phenol would be eventually released from the aerobic sludge system, it would recover its treatment capacity.

In this context, if the final goal of the PP-CWAO process is to produce effluents that could be discharged in a municipal WWTP, the oxidation products formed should be in the form of biodegradable compounds, increasing the amount of carboxylic acids and reducing phenol and quinone-like products concentration. What has been obtained from the PP-CWAO process is a mixture of recalcitrant, biodegradable and inhibitory compounds that, according to the previously mentioned classification of Scott and Ollis [29], could benefit from a combination with a biological treatment.

It has been reported that although phenol is toxic, 200 and 1000 mg L^{-1} could be decomposed by biological treatment in 40 h and 340 h, respectively [33]. However, the actual legislation [34] fixes 2 mg phenol L^{-1} and 1500 mg C L^{-1} (TOC) as discharge limits to biological WWTP. Therefore, with the PP-CWAO process it was not possible to obtain effluents that could be directly sent to a biological WWTP. Nevertheless, the enhanced phenol removal points out the potentialities of PP-CWAO as a chemical pre-treatment and efforts must be focussed on the optimisation of the actual working conditions, specifically the space time (τ), which has been kept constant in this study.

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5.5. Kinetic study

In order to relate the catalyst mass change during reaction with phenol conversion and to find out which is the relationship with the studied range of reaction temperature, the experimental results have been fitted to a first-order kinetic model for substrate concentration assuming an ideal plug-flow model for the TBR [13], which is a reasonable assumption taking into account the high reactor diameter to catalyst particles diameter ratio used [3]. For a first order of reaction, integration of the differential phenol mass balance in the reactor gives the following expression:

$$k_{ap} = -\frac{Q_L}{m_{fAC}} \ln\left(1 - \frac{X_{phenol}}{100}\right) \qquad \text{Eq. 5.5}$$

where k_{ap}: apparent kinetic constant (mL h^{-1} g^{-1})
Q_L: liquid flow rate (mL h^{-1}) = 57.4 mL h^{-1}
m_{fAC}: AC weight at the end of the test (g)

At the end of each oxidation experiment, the carbon material inside the reactor contains the remaining AC, physisorbed compounds (i.e. some unreacted phenol and its reaction products) and carbonaceous deposits from oxidative coupling reactions. Therefore, the catalyst weight at the end of each oxidation test considered for k_{ap} calculations is that obtained after heating the samples up to 900ºC during the TGA analyses. It is accepted that AC will suffer from different modifications depending on the reaction conditions and the oxidation extent achieved. Besides, carbonaceous polymers formed during reaction may have prevented AC from being consumed by oxidation and since it is not possible to quantify the exact amount of polymers formed, it is not possible to assure that all samples would have been affected in the same way. In addition, reoxidation of AC surface leading to the formation of new oxygen surface groups would also be different depending on the reaction conditions. Yet, once the physisorbed and chemisorbed compounds are removed, what is left is the AC material with the closest characteristics to the initial AC. Thus, the AC weight after TGA in N_2 atmosphere up to 900ºC (m_{fAC}, according to Equation 3.18) will be considered the carbon material that brings catalytic properties to the system and so, which should be used for kinetic calculations.

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The resulting calculated apparent kinetic constants, as well as activation energies (E_a) and frequency factors (A) are in Table 5.10.

Table 5.10. Kinetic parameters for CWAO and PP-CWAO at different temperatures.

Experimental conditions	k_{ap} (mL h^{-1} g^{-1})			E_a (kJ mol^{-1})	A
	120ºC	140ºC	160ºC		
AC-O2-00	1.09 ± 0.03	4.71 ± 0.06	12.28 ± 0.15	85.7 ± 0.9	$3.48 \pm 2.30 \cdot 10^9$
AC-O2-10	2.33 ± 0.04	5.77 ± 0.07	20.94 ± 0.24	77.4 ± 1.2	$4.99 \pm 2.91 \cdot 10^8$
AC-O2-20	3.92 ± 0.05	8.78 ± 0.10	26.89 ± 0.36	67.9 ± 1.0	$4.69 \pm 2.41 \cdot 10^7$
AC-O2-30	4.92 ± 0.06	8.39 ± 0.09	37.66 ± 0.67	71.4 ± 2.6	$1.55 \pm 6.35 \cdot 10^8$

To determine the activation energy (E_a) of the phenol oxidation, the first-order reaction rate constants were plotted against the inverse of the temperature (Figure 5.11), as already done in Chapter 4 (see Equation 4.5 and 4.6). Linear regression analysis of the data showed values of E_a ranging from 67.9 to 85.7 kJ mol^{-1}, with regression coefficients higher than 0.9 for all experimental conditions. The E_a values were comparable to those frequently reported in the literature for the oxidation of phenol over metal supported catalysts (85 kJ mol^{-1} for CuO/Al_2O_3 and $CuO.ZnO/Al_2O_3$ [35-36] and 65 kJ mol^{-1} for MnO_2/CeO_2 [37]) or over activated carbon (69.3 kJ mol^{-1} [38]). It is not possible to obtain a global value of E_a for the PP-CWAO of phenol at reaction conditions tested because the kinetic law (Equation 5.5) employed do not account for the concentration of oxidant present in the system, which varied according to the different percentages of H_2O_2 supplied.

From Table 5.10 it is easily noticeable that temperature has a strong influence on the process kinetics, since increasing the temperature from 120ºC to 160ºC increases the kinetic constant around 10 times. Also, the effect of H_2O_2 is noticeable but it is much less marked than that of temperature.

On the other hand, the variations in the activation energies found agree with the obtained phenol removals. Thus, the lower E_a do not correspond to the process using the highest dose of H_2O_2 but to the conditions at which the process has the highest oxidation capacity, i.e., AC-O2-20.

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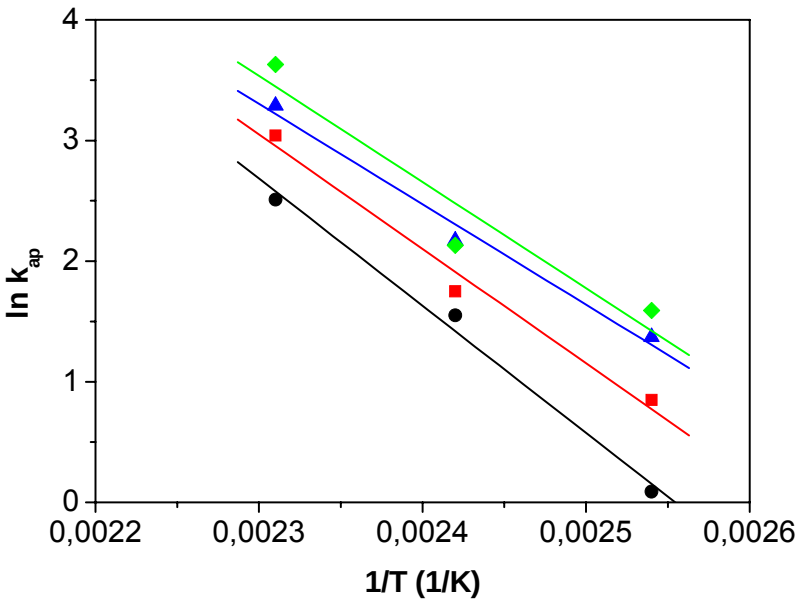

Figure 5.11. First-order kinetic model for CWAO and PP-CWAO of phenol.
Symbols: (●) AC-O2-00, (■) AC-O2-10, (▲) AC-O2-20, (◆) AC-O2-30. Lines represent trends.

5.6. Overview

Tests in a trickle bed reactor at mild total pressure (11-16 bar) and temperature (120-160 ºC) and feeding small amounts of H_2O_2 confirm that AC can be included among the catalysts able to be used in the PP-CWAO process. The role of AC is to adsorb and concentrate the pollutants on its surface, where surface functional sites are able to activate molecular oxygen and hydrogen peroxide.

Simultaneous use of oxygen and H_2O_2 as oxidants leads to higher phenol, COD and TOC conversions. Although the improvement on the oxidation efficiency was not proportional to the amount of H_2O_2 added, a synergistic effect is outlined by the deepness in phenol mineralisation. This synergistic effect was predominant when using 20 % of the stoichiometric H_2O_2 (AC-O2-20) for complete phenol mineralisation at 140 ºC, when it was possible to reach up to 16 % more COD conversion and up to 17 % more TOC removal than expected by simple addition of isolated contribution of each oxidant. These results show that there should be a preferential use of the oxygen radicals to degrade partially oxidised products rather than to oxidise phenol.

On the other hand, TGA on samples after reaction reveal that AC suffers from partial burning-off and deactivation by formation of carbonaceous deposits that are

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favoured by the presence of hydrogen peroxide, being less influenced by the reaction temperature. Nevertheless, the low cost of AC should largely offset this drawback. Thus, when thinking of an industrial application, it would be affordable to change an exhausted or consumed AC as many times as needed, although reaction temperature should be kept below 140 ºC to prevent the striking AC burning-off observed at 160 ºC.

After characterisation of partially oxidised products it seems that the CWAO of phenol promoted with H_2O_2 evolves through a pathway similar to CWAO with oxygen alone. Only a slight increase in hydroquinone and a reduction in p-benzoquinone concentrations were found for effluents from PP-CWAO.

Respirometric analyses pointed out that although higher organic conversions were accompanied by higher fractions of COD readily biodegradable in the effluents, and enhancement on toxicity and inhibition properties was also achieved. This contradictory behaviour was related to the increased amount of hydroquinone and to the predominant presence of un-reacted phenol in the oxidised effluents. Yet, previous results from CWAO coupled to a biological WWTP pointed out the potential suitability of PP-CWAO as chemical pre-treatment, since higher organic removals and biodegradability fractions were obtained with the promoted process. Therefore, longer tests on a pilot scale WWTP would be recommended to ascertain the viability of PP-CWAO effluents for a biological end treatment.

The activation energy values obtained ranged between 67.9 to 85.7 kJ mol^{-1} and were comparable to those frequently reported in the literature for the oxidation of phenol. The lower activation energy was found for the process using 20 % of the stoichiometric demand for complete phenol mineralisation, confirming that the highest oxidation capacity was obtained for the AC-O2-20 system.

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6. PP-CWAO of substituted phenols over activated carbon

The aim of section was to study the viability of the PP-CWAO process, using activated carbon as catalyst, to increase the biodegradability of phenolic aqueous solutions. Typical 72 h experiments were performed in a TBR at 140 ºC and 2 bar of oxygen partial pressure. Feed concentrations, in terms theoretical COD, were 11.8 g COD L^{-1} for phenol, 12.6 g COD L^{-1} for o-cresol and 8.0 g COD L^{-1} for p-nitrophenol, which corresponds to 5 g L^{-1} of each model compound. Air was used as main oxidant and 20% of the stoichiometric amount of H_2O_2 needed for pollutant complete mineralisation was added as oxidation promoter. The results and discussion are divided into three sections. In the first one, the performance of each process is discussed by means of the organics removal (X, X_{COD} and X_{TOC}). In the second, AC performance is examined and in the last one, the biodegradability enhancement of the effluents is presented.

As previously commented, several simultaneous reactions occur when using AC as catalyst in CWAO or PP-CWAO. There is not only the expected oxidation of the target compound and its intermediates, but also two parallel reactions of the AC are occurring to some extent: on one hand, AC oxidation/burning and, on the other hand, oxidative coupling reactions (or irreversible adsorption) of the phenolic compounds over the AC. Moreover, physical adsorption of the substrate and of the partial oxidation products is also happening at the same time. Therefore, using AC as catalyst in CWAO or PP-CWAO increases even more the already high intrinsic complexity of wet oxidation processes. Thus, only global information can be taken from the effluent and the AC characterisation, attempting to establish the contribution of each one in the biodegradability enhancement.

6.1. Model compounds removal

Figure 6.1 shows the X, X_{COD} and X_{TOC} profiles obtained from CWAO and PP-CWAO tests of phenol, o-cresol and p-nitrophenol, at 2 bar of P_{O2} and 140 ºC.

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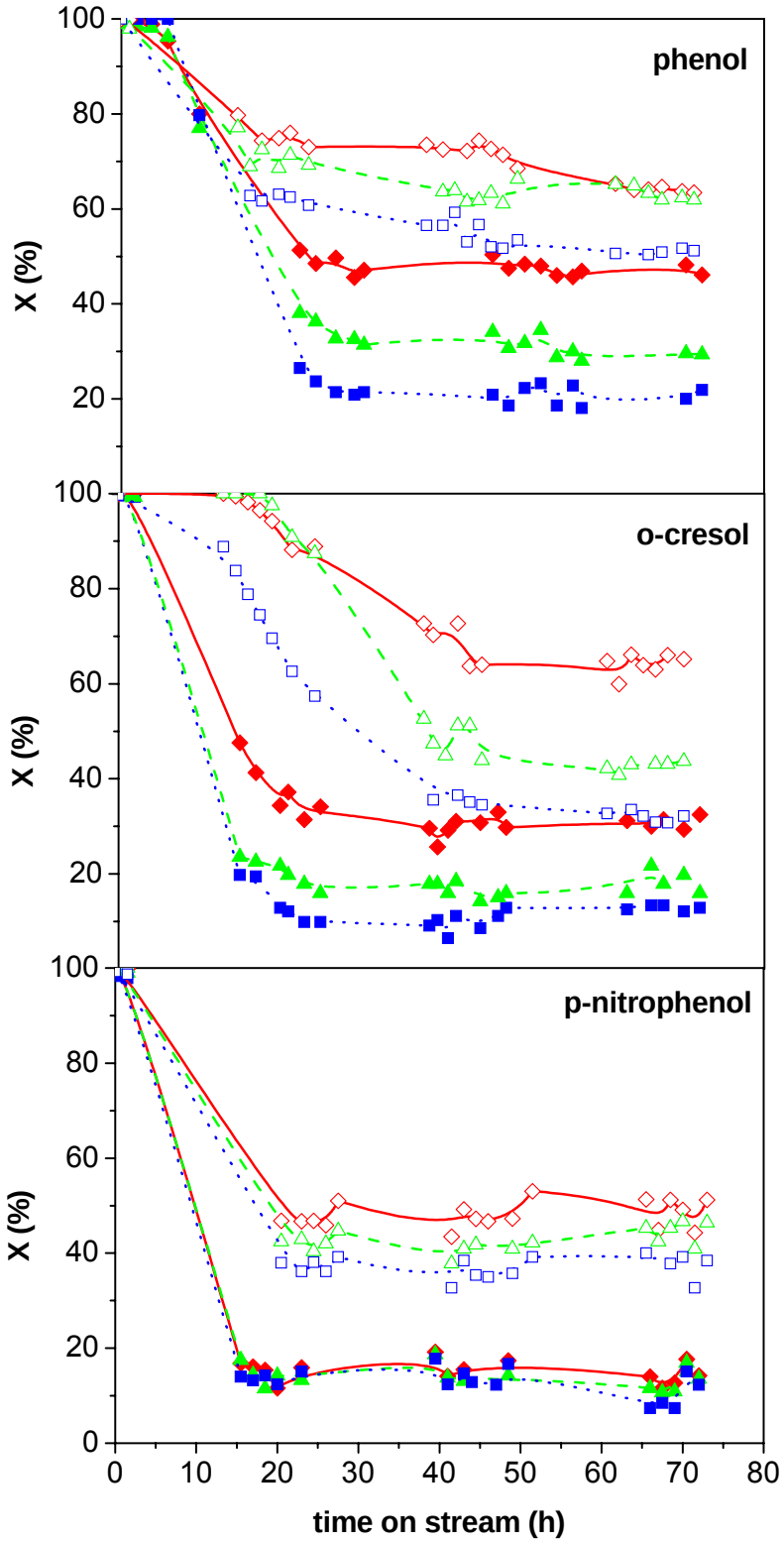

Figure 6.1. CWAO (full symbols) and PP-CWAO (open symbols) for phenol, o-cresol and p-nitrophenol. Symbols: (◇,◆) X, (△,▲) X_{COD} and (□,■) X_{TOC}.

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As previously observed [1-2], when using AC as catalyst in CWAO or PP-CWAO, three different zones can be distinguished in the conversion profiles obtained from the effluent characterisation. First, after the start-up, an adsorption-dominating period results in an apparent total conversion. Secondly, as the run proceeds, the adsorption-equilibration zone progresses and when the breakthrough exits the catalytic bed a rapid conversion fall is observed. Finally, conversion almost attains steady state.

Following phenol behaviour, the use of H_2O_2 as oxidation promoter also leads to a remarkable raise in the conversions. For example, as it summarised in Table 6.1, in the case of p-nitrophenol, X goes from just 15 % to 49 %. In addition, the beneficial effect of using a stronger oxidant in the reaction media leads to an improvement in the oxidation performance also in terms of pollutant mineralisation, i.e., higher X_{TOC}, leading to more oxidised intermediate products. As it would be discussed in the next section, this higher mineralisation should have an impact in increasing the effluents biodegradability.

Because of the presence of partially oxidised products, X_{COD} should be equal or lower than the respective X. The higher the difference between X and X_{COD}, the higher the amount of partially oxidised products in the liquid effluent. In the case of phenol oxidation, the PP-CWAO gives closer values of X and X_{COD}, that clearly indicates a higher degree of mineralisation (Table 5.11). The difference between X and X_{TOC}, which directly gives the selectivity towards carbon dioxide as X and X_{TOC} get closer, like for phenol, the higher degree of mineralisation in PP-CWAO than in CWAO. In the case of o-cresol and p-nitrophenol, although higher conversions were achieved, the opposite effect was observed when comparing X to X_{COD} and X to X_{TOC}, showing a higher occurrence of partially oxidised reaction products, as it will be discussed later.

Table 6.1. Steady-state results of phenolic compounds treated by CWAO and PP-CWAO.

Target pollutant	CWAO			PP-CWAO		
	X (%)	X_{COD} (%)	X_{TOC} (%)	X (%)	X_{COD} (%)	X_{TOC} (%)
phenol	45	30	21	64	63	51
o-cresol	33	15	14	64	43	32
p-nitrophenol	15	13	11	49	45	38

Regardless the use of H_2O_2 in the reaction and as far as X is concerned, the experimental reactivity order is phenol = o-cresol > p-nitrophenol. This reactivity order can be explained by the nucleophilic aromatic substitution mechanism [1]. In this mechanism, the substituents can be classified by their capacity to stabilise the benzonium carbanion. The substituents are strongly deactivating if they withdraw

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electrons and strongly activating if they release electrons. Hence, the hydroxyl group (-OH) is activating and the methyl and nitro groups (-CH_3 and –NO_2) are weakly or strongly deactivating groups, respectively, for the nucleophilic aromatic substitution. Therefore, these compounds are expected to be destroyed in the order phenol > o-cresol > p-nitrophenol, which closely matches the experimental results in this work and as also found by other authors for similar reaction conditions [1,3].

At the selected conditions (140 ºC, 20 % H_2O_2), control tests to find out the contribution of H_2O_2 and AC to the CWAO process were performed for o-cresol and p-nitrophenol as previously done for phenol. Results are summarised in Table 6.2. As already discussed for phenol, in the absence of oxygen, similar phenolic compounds conversion is obtained for the reactions using either AC or IS. However, a slightly higher TOC removal was reached over AC for phenol and p-nitrophenol oxidation. Control tests with IS and O_2 atmosphere lead to higher phenol and p-nitrophenol conversions, whereas o-cresol removal remained nearly invariable and TOC removal from p-nitrophenol oxidation was reduced. Therefore, the combination of O_2 and H_2O_2 improves the oxidation capacity of phenol and p-nitrophenol even in the absence of catalyst, o-cresol oxidation being less affected.

Table 6.2. Control tests for phenol, o-cresol and p-nitrophenol.

Experiment	phenol		o-cresol		p-nitrophenol	
	X (%)	X_{TOC} (%)	X (%)	X_{TOC} (%)	X (%)	X_{TOC} (%)
AC-N2-20	30	13	29	10	38	20
IS-N2-20	27	6	24	10	43	12
IS-O2-20	46	15	26	14	53	11

On the other hand, adding H_2O_2 to the CWAO not only has a promoting effect that leads to higher organic removals. It also shows a synergic effect that makes the process more efficient than what could be expected from the isolated contribution of small amounts of H_2O_2 to the CWAO over AC. This synergic effect can be observed in Figure 6.2 where X and X_{TOC} of each phenolic compound studied are compared for the conventional CWAO process (AC-O2-00) and adding 20 % H_2O_2 under N_2 atmosphere (AC-N2-20) or air (AC-O2-20). Figure 6.2 also shows the predicted conversions that could be expected in the PP-CWAO process if the effect of a small amount of H_2O_2 could just be added to the results obtained from the process using only oxygen from air as oxidant (AC-N2-20 + AC-O2-00). As it can be seen in Figure 6.2, the predicted conversions for phenol and p-nitrophenol are higher than those actually obtained in the PP-CWAO. However, if TOC reductions are considered (Figure 6.2), the promoted process gives always better results than expected, e.g. 17 % higher TOC removal than

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the predicted for phenol oxidation. The higher TOC reductions obtained show a preferential use of the oxygen radicals to degrade partial oxidation products rather than the parent phenolic compound. The explanation of this preferential use should have into account that since hydrogen peroxide is already present in the liquid stream when it enters the reactor bed, mass transfer problems related to using gaseous oxidants such as air are avoided. Therefore, the availability of oxidant to react with a phenolic molecule is higher than in the non-promoted process. Consequently, the amount of partially oxidised products appearing in the reaction media should also be higher, facilitating their oxidation by the oxygen radicals once they are formed and solved in the reaction solution.

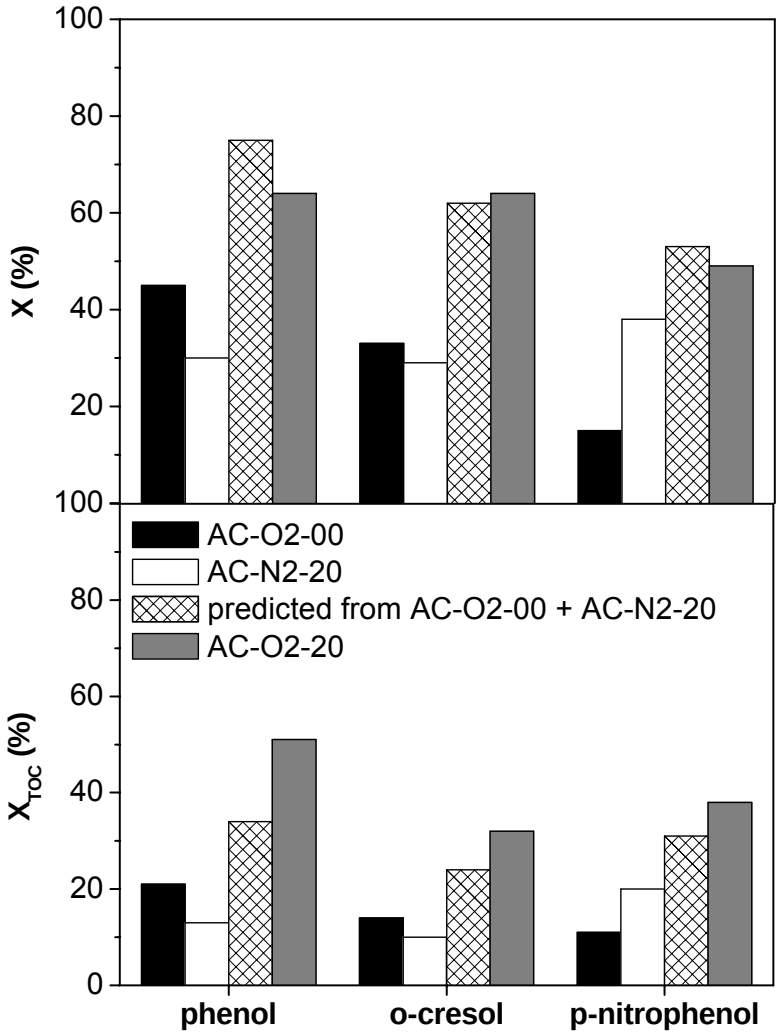

Figure 6.2. Promoting and synergic effect of H_2O_2 in the CWAO for phenol, o-cresol and p-nitrophenol.

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Regarding to the reaction intermediates, Figure 6.3 summarises the results for the effluents characterisation in terms of fraction of COD, in both processes: CWAO (AC-O2-00) and PP-CWAO (AC-O2-20). The theoretical COD of each identified intermediate was calculated and then grouped into remaining model compound, phenol (from o-cresol oxidation), quinone-like compounds (catechol, hydroquinone and p-benzoquinone), condensation products (4-hydroxybenzoic acid and salicylic acid), carboxylic acids (oxalic, formic, malonic, acetic, maleic, succinic, fumaric and propionic acids) and non-identified products. Then, the contribution of each group was compared to the experimental remaining COD obtained in the CWAO and PP-CWAO effluents.

As it can be observed from Figure 6.3, in all the cases, the biggest part of the remaining COD corresponds to the remaining model compound. Regarding to the quinone-like fraction, it is noticeable that quinone-like compounds only appeared in significant amounts in the phenol tests, being negligible for o-cresol and p-nitrophenol tests. The carboxylic acids fraction is higher in the PP- CWAO processes than in the CWAO process for o-cresol and p-nitrophenol, but the opposite is found in the case of phenol. Moreover, the intermediates occurrence in phenol PP-CWAO tests is lower than in phenol CWAO (approximately, 10 % and 20 % of the effluent COD, respectively), which confirms the higher degree of mineralisation achieved with PP-CWAO for phenol. In the case of o-cresol, the intermediates for the CWAO process represent less than 4 % of the effluent COD, due to the low conversion achieved, but, observing the PP-CWAO process, the intermediates occurrence increase to 30 % of the effluent COD, being phenol one of these intermediates (20 % of the effluent COD). Finally, for p-nitrophenol, both the intermediates occurrence and distribution were similar, although a higher COD removal was achieved when using H_2O_2 in the reaction media.

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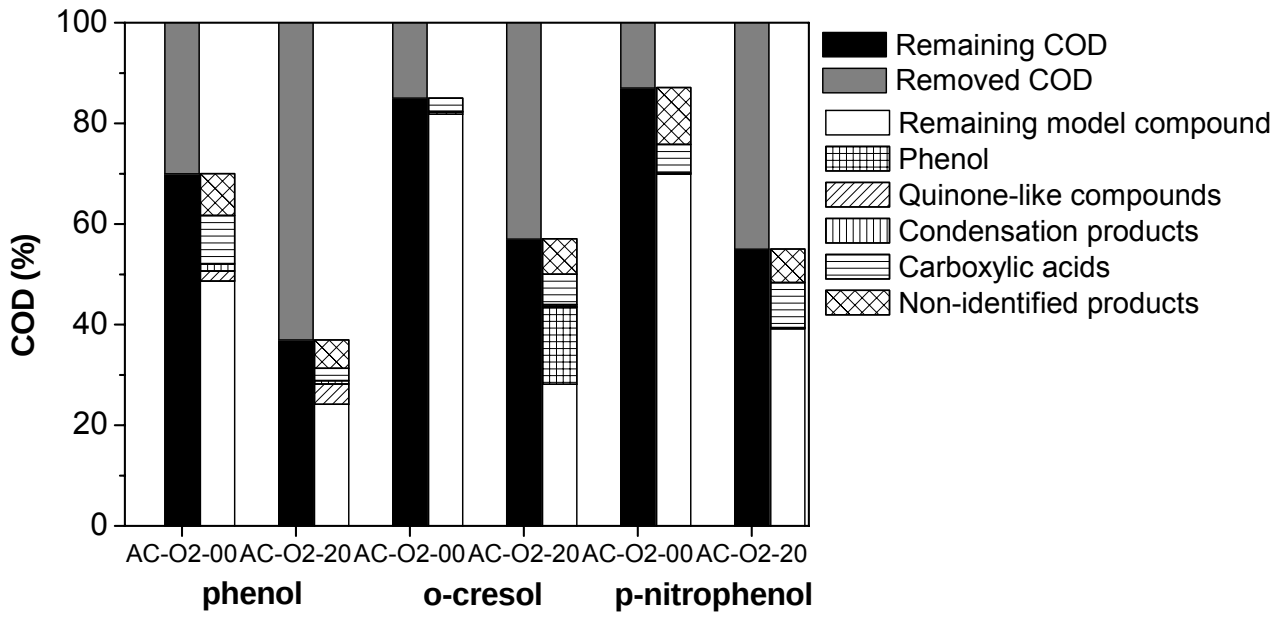

Figure 6.3. Distribution of oxidation products in the CWAO and PP-CWAO effluents using phenol, o-cresol or p-nitrophenol as target pollutants.

6.2. Activated carbon performance

The adsorption isotherms of each one of the studied compounds can be found in Figure 6.4 These isotherms were obtained at 20 ºC after the equilibration between AC and phenolic solution for 4 h in oxic conditions. Oxidative coupling reactions on AC surface are thought to be facilitated in the presence of dissolved oxygen. However, they could be neglected since, according to the literature [4], these reactions are only relevant for contact times between phenols and AC longer than 12 h. These isotherms were later fitted to the Freundlich Equation:

$$q = kc^{1/n} \qquad \text{Eq. 5.6}$$

where, *c* is the compound concentration in the bulk solution (mg L^{-1}), *q* the amount of substrate adsorbed in mg per g of AC and *k* and *1/n* are empirical parameters. This equation assumes that there is absence of chemical adsorption and that the adsorbent has a heterogeneous surface composed by different kinds of adsorption sites. Then, values of 1/n close to 0 mean heterogeneous adsorption, while values close to 1 indicate homogeneous adsorption [5].

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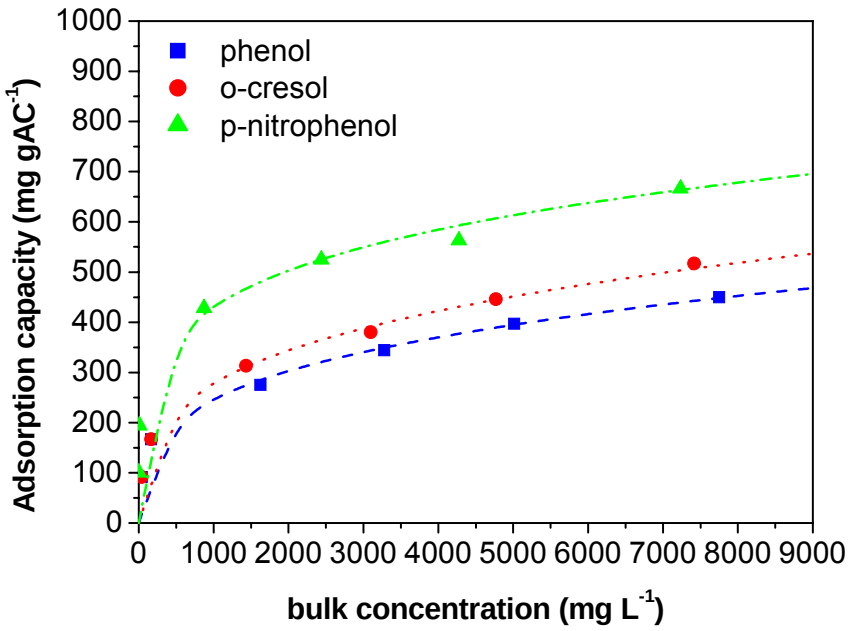

Figure 6.4. Adsorption isotherms of phenolic compounds studied. Symbols refer to experimental data, whereas lines correspond to the Freundlich Equation fitting.

Table 6.3 summarises the parameters obtained from the adsorption capacity calculated at 5 g L^{-1} and the Freundlich parameters of each compound, previously included in Suárez-Ojeda (2006) [6]. All correlation factors (R^2) found were over 0.98. The 1/n values found were below 1, indicating a favourable adsorption on AC surface.

It is noticeable that the adsorption capacity, following the order p-nitrophenol > o-cresol > phenol, follows the same trend found for the solubility in water and the molecular weight of the compounds (see Table 3.1), as previously found by different authors [1,7-8]. Therefore, also taking into account the reactivity order found in both CWAO and PP-CWAO, it can be said that the higher the adsorption capacity, the lower the removal obtained, which reinforces the theory that oxidation takes place in the liquid phase and not in the AC surface when the organic compounds are adsorbed [1].

Table 6.3. Parameters of the Freundlich equation and adsorption capacity at 5 g L^{-1}.

Compound	q (mg g_{AC}^{-1})	k (mg g_{AC}^{-1})	1/n (mg^{-1})
phenol	395 ± 20	34 ± 1	0.29 ± 0.02
o-cresol	451 ± 16	37 ± 1	0.29 ± 0.02
p-nitrophenol	613 ± 20	99 ± 1	0.21 ± 0.02

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According to the flow rate in the TBR experiments and the adsorption capacity calculated from the Freundlich equation, the AC bed saturation times should be 10 h for phenol, 11 for o-cresol and 15 for p-nitrophenol. The adsorption dominating period experimentally observed (Figure 6.1) closely matches these values. The differences with theoretical saturation times should be attributed to the higher temperature at which reaction takes place, since adsorption capacity decreases as temperature increases [9]. This deviation can be also due to competition of model organic compound with oxidation products that appear in the reaction media, since it is hardly difficult to assume constant concentration through the AC bed.

To study whether the organic compound used in the reaction has any effect on the stability of AC and on the formation of carbonaceous deposits, thermogravimetric analyses were performed on AC after each run. Table 6.4 summarises the weight changes recorded. The ΔW was positive for all the cases, which means that AC weight increased due to carbon deposits that could not be desorbed just by heating the samples at 400 ºC in an inert environment and not only to physisorbed compounds. The TWL was measured from TGA up to 900 ºC and can be used to assess the extent of oxidative coupling reactions giving irreversible adsorption of phenols over the AC. In general terms, the greater the TWL, the higher the development of oxidative coupling reactions and therefore the higher the loss in catalytic activity. It is worth mentioning that the AC, before being used in any oxidation process, gives a TWL around 5 % (see Table 5.8); therefore the difference with the used AC can be assumed to be mainly being due to oxidative coupling reactions, as stated before. From Table 6.4, the TWL in PP-CWAO for phenol is twice that obtained for the process not using H_2O_2, so the loss of AC surface by oxidative coupling seems to be greater in PP-CWAO than in CWAO. As it could be expected and as previously found when using high amounts of H_2O_2, this loss of catalytic surface affects the conversions profiles and can lead to a decrease in the steady state conversions. On contrary, the TWL for o-cresol and p-nitrophenol did not significantly change whether H_2O_2 was used or not in the oxidation process. Therefore, it has to be assumed that H_2O_2 was mainly used to oxidise the substituted phenols and did not influence the formation of carbonaceous deposits on the AC surface at the present conditions. Moreover, as also observed by Suárez-Ojeda et al. [1] for the CWAO of substituted phenols in the same reaction conditions that the ones used here, neither the ΔW nor the TWL can explain the reactivity order found, since it can not be related to the extent of oxidative coupling induced by the use of H_2O_2.

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Table 6.4. Weight loss of AC samples after reaction.

Target pollutant	CWAO (AC-O2-00)			PP-CWAO (AC-O2-20)		
	ΔW (%)	TWL (%)	m_{fAC} (g)	ΔW (%)	TWL (%)	m_{fAC} (g)
phenol	4	12	7.28	18	26	6.68
o-cresol	21	24	7.11	21	24	7.38
p-nitrophenol	11	23	6.58	9	20	6.43

Figures 6.5, 6.6 and 6.7 present TGA data for the AC samples after reaction. Original AC and AC saturated with phenol, o-cresol or p-nitrophenol are also included for comparison. As it can be seen, the weight change recorded for the used AC was notably higher than for the commercial AC, since for the latter the weight loss is only due to desorption of surface oxygen groups. Moreover, differences can be observed between the AC used in the CWAO process (AC-O2-00) and the samples from the PP-CWAO (AC-O2-20), depending on the model compound oxidised, as previously commented.

The first derivative of the thermograms points out the temperature ranges at which higher release of gaseous species occurred. The main peaks observed around 200 and 400 ºC in the AC saturated with phenol, o-cresol or p-nitrophenol correspond to thermal desorption of each phenolic compound. In the used AC, these peaks were less marked showing that some other compounds different from the phenolics were also adsorbed. However, these 200 and 400 ºC peaks are still predominant in p-nitrophenol profiles (Figure 6.7), indicating that probably the carbons used in these runs contain a high amount of phenolic compounds, which would agree with the lower conversions obtained.

The weight loss up to 400 ºC is believed [10-11] to correspond to phenol and its reaction intermediates physisorbed during the oxidation reaction, while the weight low up to 900 ºC includes de decomposition of chemisorbed species and the cracking of polymers from oxidative coupling reactions, as also observed by Suárez-Ojeda et al. (2005) [1] in AC samples used in the CWAO of different phenolic compounds in the same experimental installation and reaction conditions that the ones used here.

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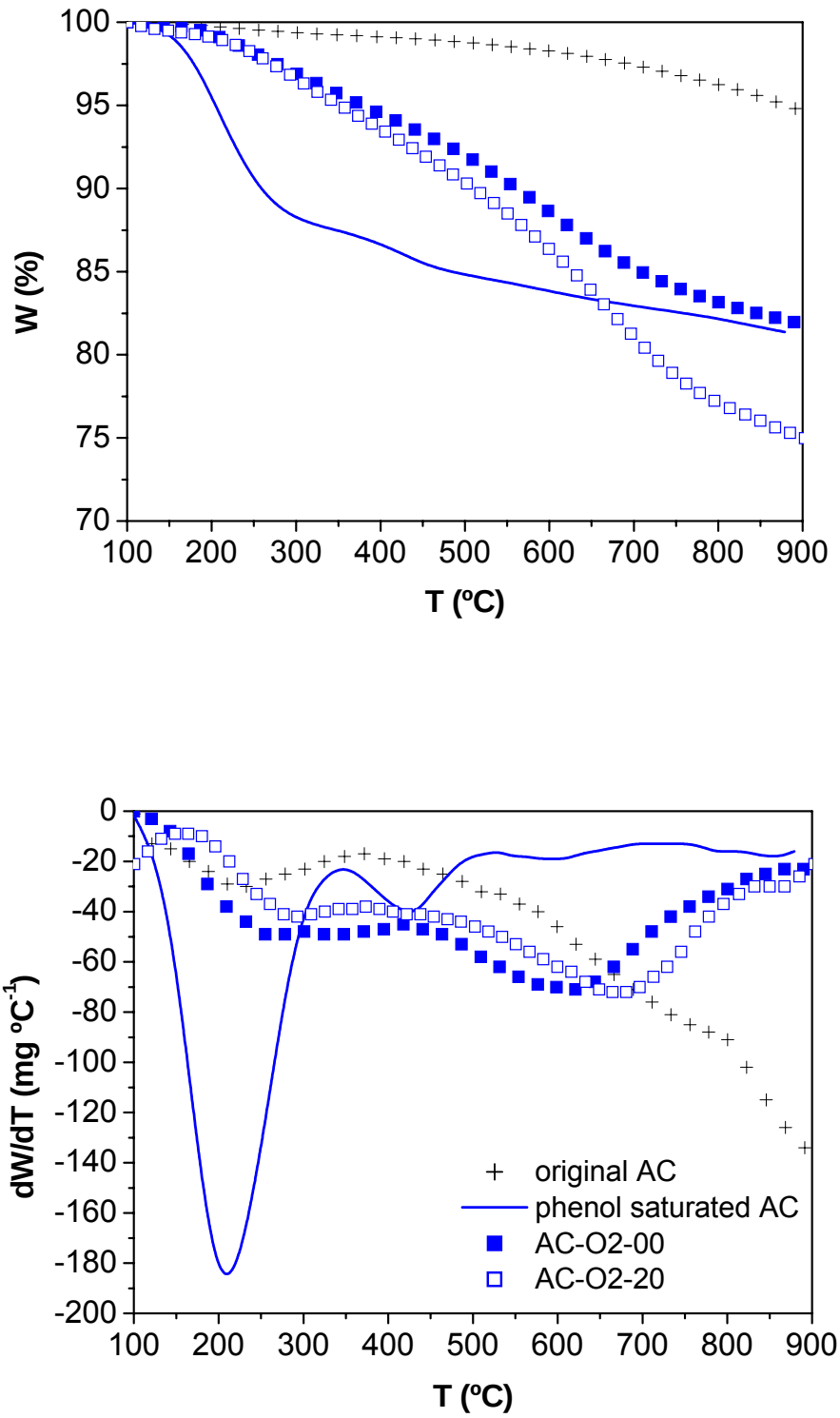

Figure 6.5. TGA data and first derivative of TGA data for phenol.

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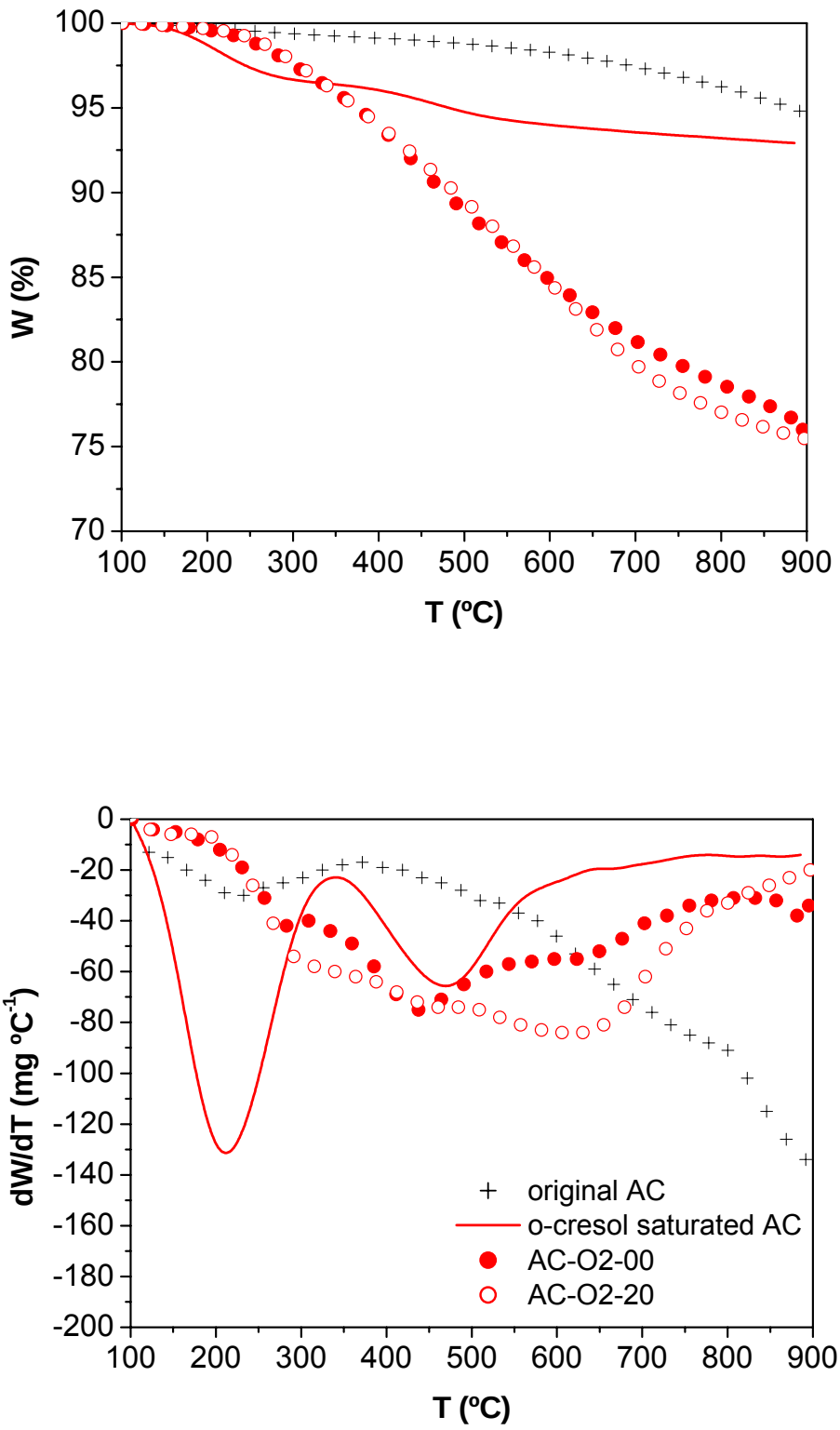

Figure 6.6. TGA data and first derivative of TGA data for o-cresol.

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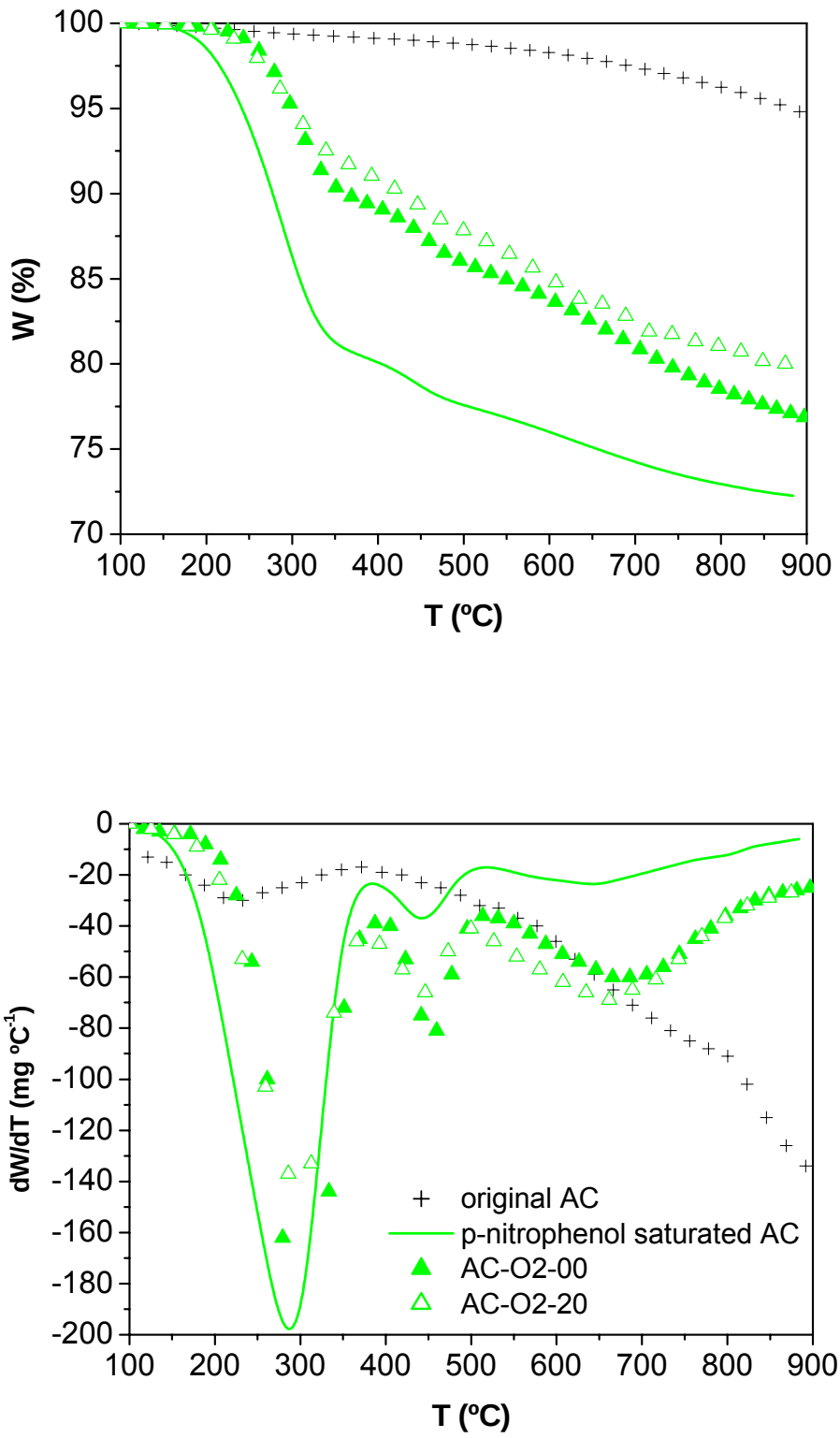

Figure 6.7. TGA data and first derivative of TGA data for p-nitrophenol.

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Trying to relate the catalyst mass change and the conversion, results were fitted to a first-order kinetic model as previously done in Section 5.5, applying Equation 5.5. The so calculated kinetic constants (k_{ap}) for the disappearance of each model compound are in Table 6.5.

Table 6.5. Kinetic constants for CWAO and PP-CWAO experiments at 140 ºC.

Experimental conditions	k_{ap} (mL h^{-1} g^{-1})		
	phenol	o-cresol	p-nitrophenol
AC-O2-00	4.71 ± 0.06	3.23 ± 0.05	1.42 ± 0.04
AC-O2-20	8.78 ± 0.10	7.95 ± 0.09	6.01 ± 0.07

As previously discussed, the reactivity order expected for these compounds is phenol > o-cresol > p-nitrophenol, which perfectly matches with the calculated values for the apparent kinetic constant. Still, what is observed is that using H_2O_2 doubles the reaction rate for phenol and o-cresol, but increases it as much as 4 times for p-nitrophenol. On the other hand, it is not possible to relate the catalyst mass after reaction (m_{fAC} in Table 6.4) neither with the kinetic constants obtained nor with the presence of H_2O_2 in the reaction, since different trends were found for experiments AC-O2-00 and AC-O2-20. Using H_2O_2 in the oxidation of phenol lead to a reduction of the final mass of AC, as also happened in the p-nitrophenol oxidation. On contrary, in the case of o-cresol oxidation, AC mass for the non-promoted process was higher than for the process using peroxide. In view of this, it can be concluded that in the oxidation of phenolic compounds using AC as catalyst many parallel reactions and adsorption processes are present, which cannot be uncoupled and studied separately.

6.3. Biodegradability enhancement

Once the biodegradability parameters (OUR and OC) are obtained by respirometry, the fraction of readily biodegradable COD (%COD_{rb}) of an effluent can be calculated as explained in the experimental section. The total biodegradable COD (COD_{tb}) fraction of an effluent is the sum of the readily (COD_{rb}) and the slowly (COD_{sb}) biodegradable fractions, therefore COD_{rb} is always lower than COD_{tb}. Determination of COD_{sb} requires long term experiments in a biological pilot plant configuration, which would be extremely time-consuming. Therefore, COD_{rb} can be used as a fast method to compare the biodegradability enhancement reached in an effluent from different oxidation treatments with respect to the initial phenol, o-cresol and p-nitrophenol solutions, which have an experimentally determined 0 % of COD_{rb}.

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Figure 6.8 shows the % COD_{rb} obtained from the respirometric tests performed to each effluent coming from CWAO and PP-CWAO experiments.

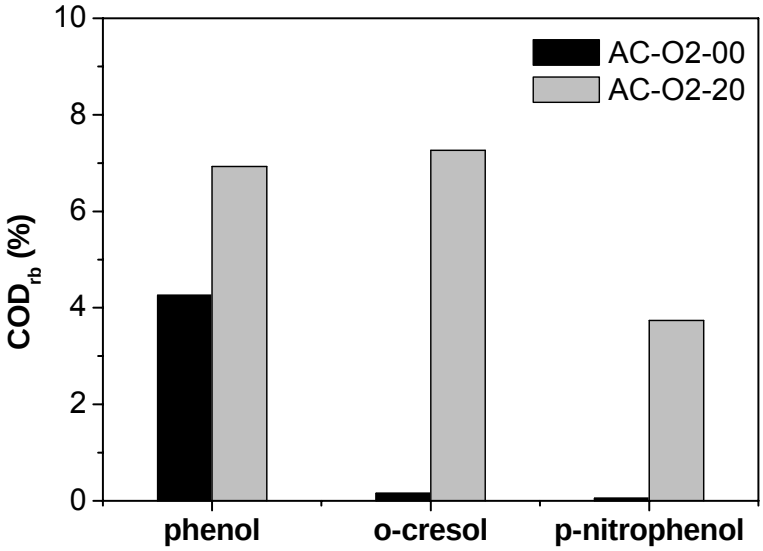

Figure 6.8. Fraction of COD readily biodegradable from the respirometric tests performed to effluents from CWAO (AC-O2-00) and PP-CWAO (AC-O2-20).

Figure 6.8 shows that PP-CWAO process gave more biodegradable effluents than CWAO, although the maximum %COD_{rb} was only 7.5 % for o-cresol PP-CWAO. In the case of o-cresol and p-nitrophenol after CWAO, the operating conditions selected were not severe enough to transform the pollutant into an effluent with a higher biodegradability. In this way, Arslan and Ayberk (2003) [12] found a %COD_{rb} between 3-24 % for wastewaters treated in the Izmit industrial and domestic WWTP that included pre-treated industrial wastewaters of various sectors such as tyre, drug or chemistry. The comparison of the values obtained in this work and the values presented by Arslan and Ayberk (2003) [12] shows that the effluents obtained in this work are difficult to handle in a context of integrated management of these pre-treated effluents as part of the total influent to a WWTP. Probably, the %COD_{rb} would be higher if the remaining model compounds fraction is lowered. For instance, from Figure 6.3, there are almost 6 % of carboxylic acids COD in the effluent of p-nitrophenol CWAO available for microorganisms' consumption, but a negligible experimental %COD_{rb} was obtained, probably because the 70 % of the remaining COD is in form of p-nitrophenol, which can have a toxic effect over the biomass.

Therefore, it can be concluded that the selected conditions of temperature, P_{O2} and space time (τ) in both CWAO and PP-CWAO are not effective enough to produce

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a suitable effluent that could be safely sent to a municipal WWTP, despite having a fraction of readily biodegradable compounds up to 7.5 %. Nevertheless, it has been proved the potential of H_2O_2 as oxidation promoter for CWAO process, since higher pollutant conversions and higher biodegradability was obtained.

6.4. Overview

Oxidation tests in a trickle bed reactor at mild total pressure (i.e. 2 bar of P_{O2}, 13.1 bar) and temperature (140 ºC) conditions, using small amounts of hydrogen peroxide validate the suitability of AC as catalyst to be used in the PP-CWAO of phenolic compounds.

The PP-CWAO process leads to higher pollutant removal conversions than the CWAO process. Besides, a synergistic effect was found when H_2O_2 is combined with O_2 which lead to higher mineralisation of the target pollutants.

The partial oxidation products found after phenol oxidation was lower for the PP-CWAO than for the classical CWAO (approximately, 10 % and 20 % of the effluent COD, respectively), which confirms the higher degree of mineralisation achieved when H_2O_2 is used. In the case of o-cresol, the intermediates occurrence increase to 30 % of the effluent COD from the PP-CWAO, although phenol was the predominant product. For p-nitrophenol, both the intermediates occurrence and distribution were similar, but higher COD removal was achieved when using H_2O_2 in the reaction media.

Regardless the use of H_2O_2 in the reaction, the experimental reactivity order in terms of pollutant conversion is phenol = o-cresol > p-nitrophenol, which agrees with the generally accepted nucleophilic aromatic substitution mechanism. The adsorption capacity followed the order p-nitrophenol > o-cresol > phenol, the same trend found for the solubility in water and the molecular weight of the compounds. Therefore, also taking into account the reactivity order obtained in both CWAO and PP-CWAO, it can be said that the higher the adsorption capacity, the lower the removal obtained, which reinforces the theory that oxidation takes place in the liquid phase and not in the AC surface when the organic compounds are adsorbed.

On the other hand, it is not possible to relate the catalyst mass after reaction neither with the kinetic constants calculated or with the presence of H_2O_2 in the reaction, since different trends were found for CWAO and PP-CWAO experiments.

Finally, PP-CWAO effluents improved their biodegradability more than CWAO effluents. Nevertheless, despite having a fraction of COD readily biodegradable up to

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7.5 %, reaction conditions still need to be improved to produce suitable effluents that could be safely sent to a municipal WWTP.

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7. PP-CWAO of phenol using FeAC materials

In this section, results form the characterisation of the iron containing AC prepared during a research stay in the *Grupo de Ingeniería Química y Ambiental* (GIQA) from *Universidad Rey Juan Carlos* in Móstoles (Spain) are presented. Following, a selected FeAC catalyst was applied in the PP-CWAO for testing its catalytic activity and stability for the oxidation of phenol in the TBR at 140 ºC and using 20 % of the stoichiometric demand of H_2O_2 for complete phenol mineralisation.

7.1. FeAC characterisation

FeAC materials were prepared according to the procedure described in the Methodology (Section 3.1.3.1), beginning with an acidic treatment previous to the iron wet impregnation and following by a thermal treatment to fix iron species on AC surface.

Characterisation of the carbon materials was performed by different conventional techniques. First of all, the changes on the surface oxygen groups after the oxidation treatments were determined by Boehm titration, NMR and ultimate analyses. After the wet impregnation with iron nitrate, the iron content was measured by ICP-AES and it was related to the density of acidic surface groups and the isoelectric point of charge developed by each carbon material due to the acidic treatments applied. Finally, textural changes induced by the chemical and thermal treatments were evaluated by means of N_2 adsorption/desorption isotherms.

7.1.1. Surface oxygen groups

In order to facilitate the iron anchoring on the AC surface, the demineralised AC (AC-L) was submitted to three different oxidation treatments following the procedures described by Salame et al (1999) [1].

Table 7.1 summarises the distribution of the surface oxygen groups identified on AC by Boehm titration after the three oxidation treatments tested. As expected, the oxidation treatment performed to AC increased the concentration of oxygenated

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functional groups. Treatment with $(NH_4)_2S_2O_8$ (AC-APS) leads to the highest rise in total acidic sites, while treatment with HNO_3 (AC-CN) and H_2O_2 (AC-HP) still render a significant increase with respect to the original AC. Demineralisation with HCl (AC-L) also produced an increase on the number of acidic groups, since although it was not the objective of this treatment it can be considered as an acidic treatment itself. Overall, treatment with $(NH_4)_2S_2O_8$ mostly generates carboxylic groups, whereas treatment with HNO_3 and H_2O_2 creates both lactones and carboxylic groups. Phenolic groups were less affected by the acidic treatments.

Boehm titration analysis reveals a considerable reduction of basic sites, except for AC-HP. The greatest destruction if observed for $(NH_4)_2S_2O_8$ followed by HNO_3 and H_2O_2, which is recognised to have the gentler oxidant character [2].

Table 7.1. Surface oxygen groups on the original and oxidised AC.

Carbon material	Density of surface oxygen groups (meq g^{-1} AC)				
	Acidic groups				Basic groups
	Carboxylic	Lactones	Phenolic*	Total acidic	
AC-M	0.106	0.072	0.035	0.213	0.290
AC-L	0.265	0.078	0.186	0.528	0.069
AC-CN	0.351	0.364	0.000	0.712	0.168
AC-HP	0.212	0.419	0.028	0.659	0.290
AC-APS	0.715	0.072	0.035	0.821	0.037

* also including carbonyls.

As it can be seen in Table 7.1, the amount of acidic groups increased following the order AC-APS > AC-CN > AC-HP. Although the effect of these treatments mainly depends on the activated carbon considered, these results are in close agreement with the existing literature [1-4] and were also verified by other techniques such as the Nuclear Magnetic Resonance (NMR) and ultimate analyses.

Figure 7.1 shows the NMR ^{13}carbon spectra of the different oxidised carbons, where two main bands are present. The one at 115 ppm corresponds to aromatic carbon links (C-C), via one double bound and two single bounds, whereas the band located between 120-130 ppm can be attributed to chemical shifts of carbon atoms in the AC grapheme sheets with bounded carboxylic ((C=O)OH) or lactonic groups (O(C=O)R) [5]. Therefore, it can be qualitatively observed that the ratio between signals of carbon from aromatic rings and carbon with oxygenated carbon groups decrease following the order AC-APS > AC-CN > AC-HP, which seems to be in fairly agreement with the amount of total acidic surface groups detected by Boehm titration.

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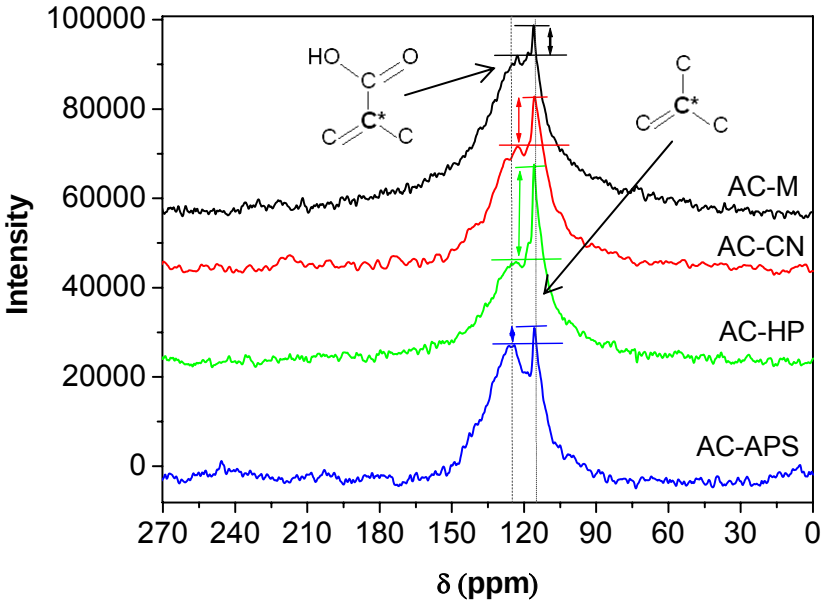

Figure 7.1. ^{13}C NMR spectra of commercial and oxidised AC.

The increase in surface oxygen groups is also demonstrated by ultimate analyses, which gives the composition of a given sample in terms of nitrogen, carbon, sulphur and hydrogen. The amount of oxygen is obtained by difference to 100 %. The corresponding results are summarised in Table 7.2. As expected, the oxygen content in the oxidised carbons increased and also followed the order found through the Boehm titration and the NMR spectra (AC-APS > AC-CN > AC-HP).

The relatively high amount of oxygen found in the samples accounts for the moisture that they still may content, although samples are dried before analyses. As it will be discussed later, the pores volume and the surface area are very similar for all carbons prior to the thermal treatments. Therefore, it can be assumed that moisture content will be also similar since they were all analysed under the same conditions. The higher nitrogen content found after HNO_3 treatment is probably due to the formation of nitrogen-containing species [2,4] which could not be accounted for using Boehm titrations due to its inability to dissociate. As expected, demineralisation with HCl did not introduce significant changes on the ultimate analysis with respect to the parent AC.

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Table 7.2. Ultimate analyses of original and oxidised AC.

Carbon material	C (%)	H (%)	N (%)	S (%)	O (%)*
AC-M	85.1	2.6	0.5	0.9	10.9
AC-L	83.5	2.2	0.5	0.9	12.9
AC-CN	72.5	2.0	1.1	0.6	23.8
AC-HP	80.0	2.6	0.5	0.7	16.3
AC-APS	58.4	2.3	0.4	0.5	38.4

* calculated by difference to 100 %.

7.1.2. Iron content

Table 7.3 summarises the iron content for the AC after wet impregnation with $Fe(NO_3)_3$, measured by ICP-AES, and its relationship with the density of acidic surface groups and the isoelectric point (IEP) of charge. Commercial AC (AC-M) and AC after demineralisation with HCl (AC-L) were also subjected to wet impregnation as reference samples, although the expected iron content was evidently lower than in the impregnated carbons.

Table 7.3. Iron loading of AC materials and its relationship with the amount of surface oxygen groups and the isoelectric point.

Carbon material	Fe (%)	acidic SOG (meq g^{-1} AC)	IEP
AC-M-Fe	0.84	0.213	8.87
AC-L-Fe	1.13	0.528	3.43
AC-CN-Fe	1.86	0.712	3.15
AC-HP-Fe	1.64	0.659	4.33
AC-APS-Fe	2.61	0.821	2.89

The percentage of iron and the amount of acidic SOG that the samples contained follow the same tendency, showing that there is some kind of relationship between them. Fixation of acidic groups on the surface of the AC makes it more hydrophilic [3,6], increasing the surface accessibility to the metal precursor. Therefore, since iron wet impregnation was performed using an iron nitrate aqueous solution, a lower hydrophobicity (i.e. a higher content of SOG) must facilitate the impregnation process leading to an iron content, as expected, in the order: AC-M-Fe < AC-L-Fe < AC-HP-Fe < AC-CN-Fe < AC-APS-Fe.

The IEP of a solid placed in an electrolyte corresponds to the pH value at which the surface of the solid is electrically neutral. When the pH of the solution is lower than the IEP the surface is positively charged and negatively charged species are adsorbed, for compensation. An opposite process proceeds at pH values higher than the IEP [7].

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Figure 7.2 schematically shows the distribution of charges on AC surface in the different situations possible (i.e. the amphoteric character) according to the relation between the IEP and the solution pH, for a better understanding of these phenomena.

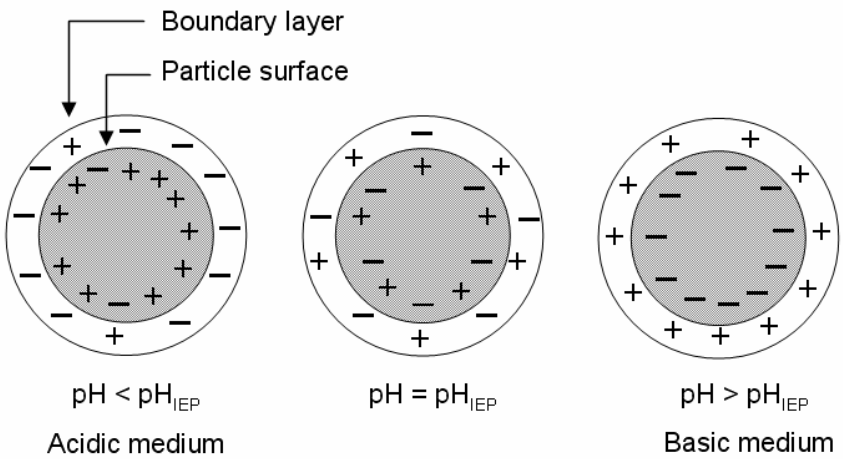

Figure 7.2. Illustration of the amphoteric character of carbon materials [8].

It can be expected than the amount of adsorbed species will be influenced by the IEP and therefore, its measurement is important for the preparation and analyses of catalysts by wet impregnation. Then, when the AC is placed in an acidic solution, as during the wet impregnation with iron nitrate, the surface gets positively charged, which in fact leads to the repulsion between the iron cations and the carbon surface. However, the lower difference between the IEP of the carbon and the pH during the wet impregnation, the highest the final iron content we should get, since the repulsion to the iron cations is reduced as the carbon is less positively charged. Taking into account that wet impregnation with iron nitrate took place at an initial pH of 0.80, the expected iron loading for the three oxidised AC was following the order AC-APS > AC-CN > AC-HP, which matches with the results found with ICP-AES.

7.1.3. Textural properties

Textural characterisation of carbon materials was performed by N_2 isotherms. N_2 isotherms were used to obtain information about the porosity and adsorption capacity of samples before and after the acidic treatments, iron wet impregnation and calcinations.

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Figure 7.3 shows the typical curves found in N_2 adsorption/desorption isotherms for microoporous materials. Also, some mesoporosity was present in the carbon materials analysed, as deduced by the little hysteris loops obtained on desorption. It has been found after analysis of many adsorption isotherms on carbon with different types and amounts of oxygen groups [6] that the total amount of surface groups controls the relative pressure at which the plateau of the isotherm start, whereas the type of surface groups conditions the slope of the isotherm in the initial portion up to the plateau. Accordingly, the specific surface area decreased after the three oxidation treatments in the same order that the increase of SOG was found to follow (AC-APS > AC-CN > AC-HP), although this effect can not be distinguished in the isotherms slope.

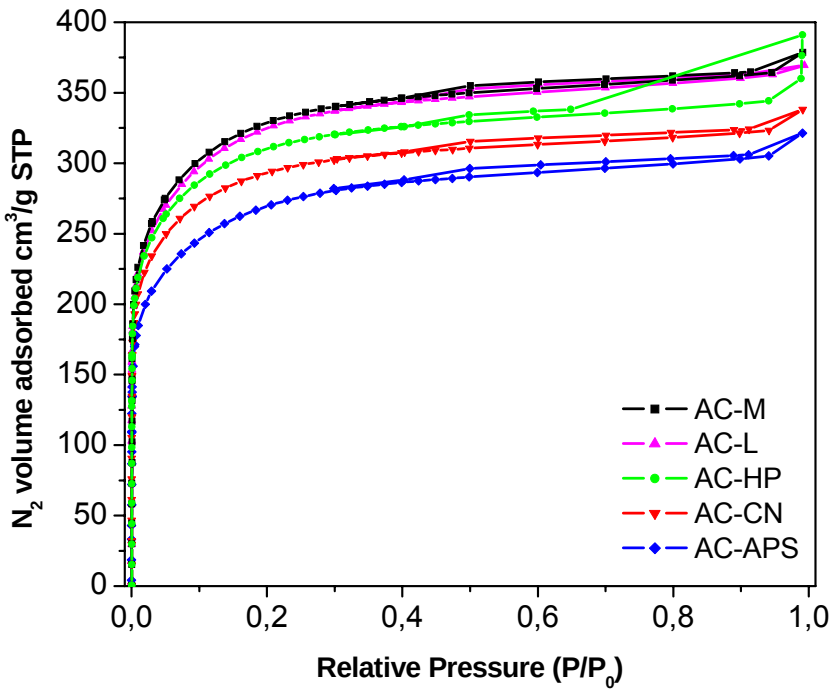

Figure 7.3. N_2 isotherms for commercial and oxidised AC.

Table 7.4 collects the results for the textural characterisation of the different carbon materials under study in terms of micropore volume, BET surface and changes in BET surface (ΔS_{BET}) with respect to the original AC (AC-M) surface. Then, a negative value of ΔS_{BET} means a loss of surface area, whereas a positive ΔS_{BET} means that surface area has increased. The acidic pretreatments lead to a slight decrease of surface area and pore volume. However, the most striking decrease of both BET surface and pore volume takes place as a result of the incorporation of iron into the microporous carbon matrix, reaching a 17 % loss after treatment with ammonium

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persulfate (AC-APS) and up to 34 % after Fe incorporation. Coming back to Table 7.3, it is noticeable that there is a concordance between the amount of SOG and iron incorporated and the loss of area.

Table 7.4. Textural characterisation of AC samples.

Carbon material	$V_{\mu pore}$ (cm^3)	S_{BET} (m^2g^{-1})	ΔS_{BET} (%)
AC-M	0.48	1140	--
AC-L	0.49	1151	0.96
AC-CN	0.44	1017	-10.79
AC-HP	0.46	1083	-5.00
AC-APS	0.40	943	-17.28
AC-CN-Fe	0.44	1014	-11.05
AC-HP-Fe	0.41	972	-14.74
AC-APS-Fe	0.32	757	-33.60
AC-CN-Fe-250	0.41	1017	-10.79
AC-CN-Fe-500	0.44	1014	-11.05
AC-HP-Fe-250	0.42	975	-14.47
AC-HP-Fe-500	0.46	1089	-4.47
AC-APS-Fe-250	0.24	607	-46.75
AC-APS-Fe-500	0.37	890	-21.93

The different calcination treatments at which the iron impregnated carbons were submitted pursued two different objectives. First, fixing iron on AC surface by facilitating the formation of iron oxides under the suitable atmosphere and temperature conditions, which is usually applied for the preparation of supported metal catalysts [9-10]. Second, the removal of the less stable oxygen surface groups [11] and nitrates from the $Fe(NO_3)_3$ used as precursor during wet impregnation, which could lead to some recovery of AC surface. The first objective was partly achieved since a higher percentage of iron was measured on the samples, i.e., the relative fraction of Fe increased with respect to the AC mass after calcination. However, this was possible due to loss of AC by direct combustion, when it was calcined in air, and because of the thermal removal of remaining nitrates and sulphates from acidic treatments. Generally speaking, air treatment lead to higher loss of area and this is attributed to desorption of afore mentioned remaining cations. Calcination under nitrogen atmosphere allowed using higher temperatures and some recovering of pores volume, while surface remains nearly invariable.

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7.1.4. Selection of the best FeAC obtained

After the preparation and characterisation of different FeAC materials, its performance as catalysts in the PP-CWAO of phenol was tested. For scheduling reasons, only one of the carbon materials was tested. The selection of such material was based in the following criteria:

1. high iron content
2. preservation of surface area and micropores volume

Keeping in mind the desired characteristics for a presumably good FeAC catalyst for the PP-CWAO process, the selected FeAC was the AC-APS-Fe-250. It is noticeable from Table 7.4 that this catalyst has the highest loss of surface area after oxidation, wet impregnation and calcination treatments. However, it was also the material that reached a higher iron content after calcination (i.e. 3.37 %), which must have a direct relation with the surface reduction. Finally, since only one FeAC material could be tested, it was preferred to be the one having more differences with respect to the original AC. Nonetheless, as extracted from the complete study of the PP-CWAO process in Chapter 5 and as also pointed out by Suárez-Ojeda et al. (2005) [12] there are evidences that oxidation reaction takes place in the liquid phase and not when the target organic compound is adsorbed on AC. Therefore, the high reduction on surface area and micropore volume registered for sample AC-APS-Fe-250 should not necessarily have a negative impact on the oxidation capacity of the system.

7.2. Catalytic activity of FeAC in the PP-CWAO

Once the best FeAC was selected based on the previous criteria, its catalytic activity for the PP-CWAO (140 ºC, 2 bar P_{O2}, 20 % H_2O_2) of high concentrated phenolic aqueous solutions (5 g L^{-1}) was tested in the TBR. In order to discriminate the possible homogenous effect that any iron leaching could have on the process, reaction using the non-modified AC and a fixed amount of iron (8 mg L^{-1}) diluted with the feed solution was also performed. These reaction conditions will be identified as FeAC-O2-20 and AC-O2-20+Fe^{3+}, respectively. At the end, the effect of initial phenol concentration on catalyst activity and stability was also tested.

7.2.1. FeAC performance as catalyst in the phenol PP-CWAO

Table 7.4, summarises the physicochemical properties of carbon materials used in these runs: commercial AC and AC-APS-Fe-250, which for simplicity is referred to as FeAC in this section. Boehm titrations could not be easily performed on FeAC since the

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formation of $Fe(OH)_3$ during the titration of the filtrates caused an increase in the amount of NaOH, required to reach the titration end point in the case of basic SOG [13]. This fact was also observed when FeAC was placed into basic solutions to determine the acidic SOG, as presence of iron was evidenced by a slight change in the solutions colour and was verified by ICP-AES measurement. Nevertheless, there is still no satisfactory explanation for the catalytic performance of AC depending on the nature of their SOG [2]. Therefore, it is expected that the increased Fe content on FeAC would be responsible for the catalytic properties that this material could show and not to rely on the amount and type of SOG present.

Table 7.5. Summary of physicochemical properties of AC materials used in the catalytic tests.

AC Materials	Surface groups density (meq/g AC)					S_{BET} ($m^2\ g^{-1}$)	$V_{micropore}$ ($cm^3\ g^{-1}$)	Fe (%)
	acidic				basic			
	carboxylic	lactone	phenolic*	total				
AC-M	0.106	0.072	0.035	0.213	0.290	1140	0.48	0.54
AC-APS	0.715	0.072	0.053	0.822	0.073	943	0.40	--
FeAC	--	--	--	--	--	607	0.24	3.37

* also including carbonyls.

The main monitored parameters in the outlet aqueous stream along the reaction, such as phenol removal, TOC conversion, iron concentration and pH solution are shown in Figures 7.4, 7.5 and 7.6, respectively. For comparison, the results for the CWAO (140 ºC, 2 bar P_{O2}) without using hydrogen peroxide (AC-O2-00) are also included in the figures.

As previously discussed in Chapter 5, it is clearly evident the important role of hydrogen peroxide as source of hydroxyl and oxygen radicals in the AC-O2-20 system as compared to the catalytic performance attained by the AC and oxygen alone (AC-O2-00). When using the iron containing catalyst, a high phenol and TOC conversion for the FeAC-O2-20 system was achieved during the first 24 h on stream. However, the continuous decrease in the conversion profiles is observed at longer times on stream. So, after 48 h, results of phenol or TOC conversion are even lower than those corresponding to the AC as direct catalyst in the PP-CWAO. This catalytic behaviour could be attributed to the intrinsic loss of AC initial activity because of the oxidation treatment. AC-APS used to get the FeAC has a much more oxidised surface than AC-M and it is expected to have a lower catalytic activity, as found by Santiago et al. (2005) [2]. These authors observed a reduction in phenol conversion when using oxidised carbons, which was related to the destruction of basic groups or the generation of carboxylic groups that could not be catalytically active.

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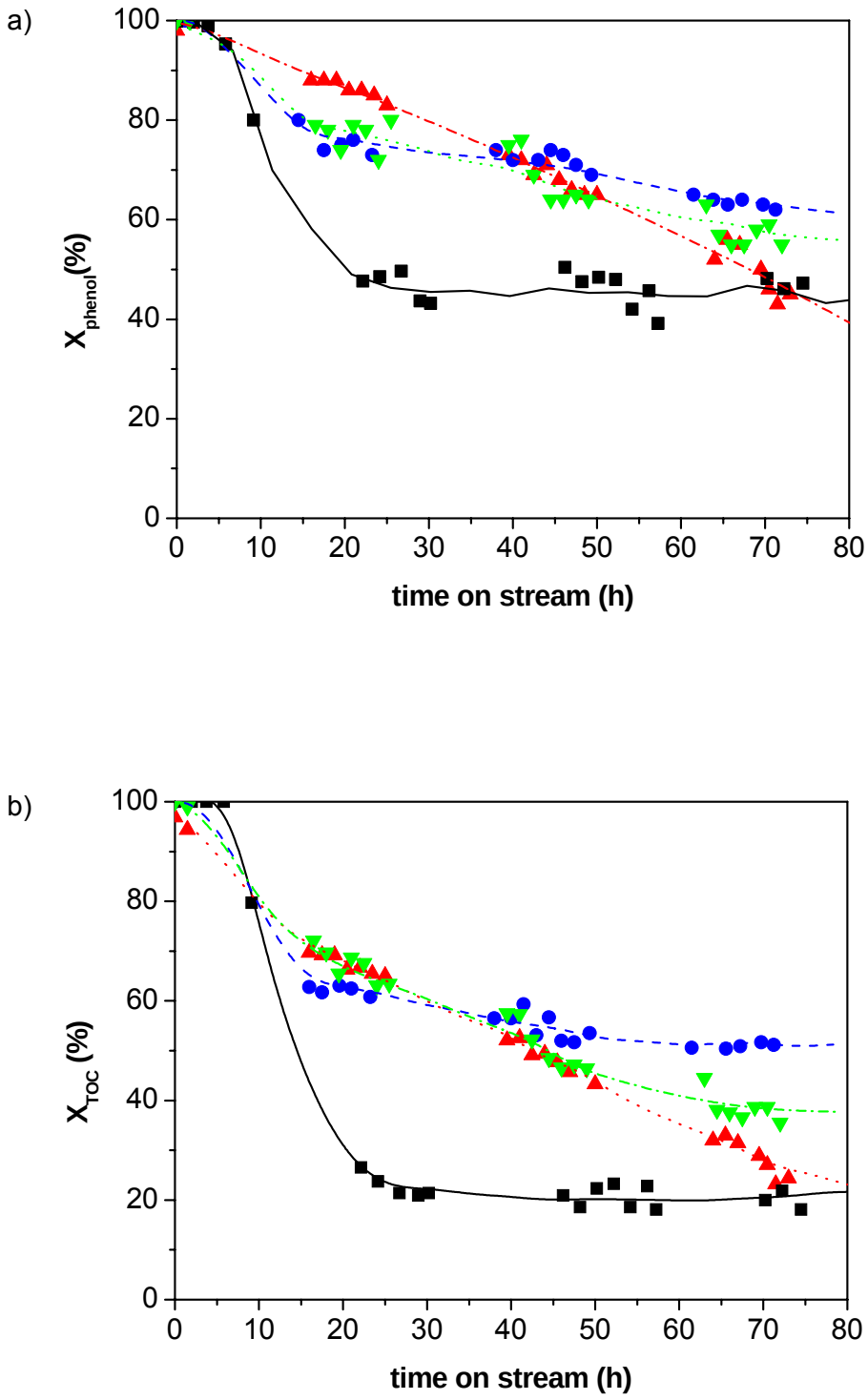

Figure 7.4. Catalytic performance of PP-CWAO process: a) phenol conversion and b) TOC conversion, for: (■) AC-O2-00, (●) AC-O2-20, (▲) FeAC-O2-20, (▼) AC-O2-20+Fe^{3+}.

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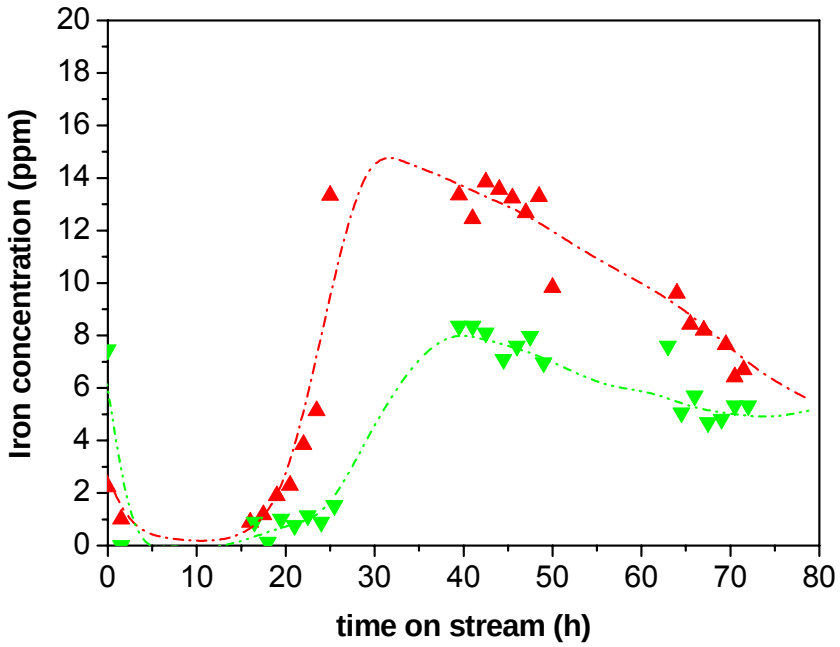

Figure 7.5. Iron concentration in the effluents form the PP-CWAO process, for: (▲) FeAC-O2-20, (▼) AC-O2-20+Fe^{3+}.

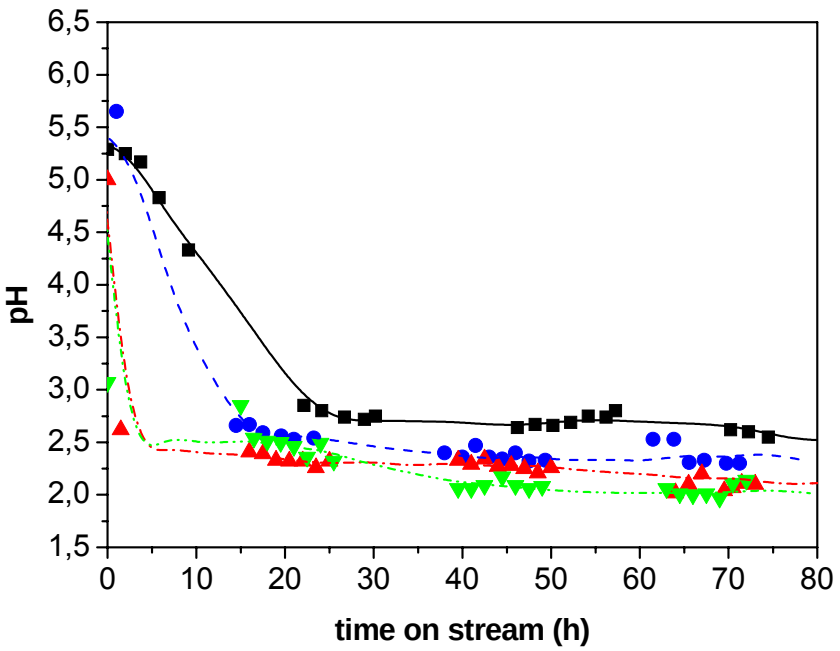

Figure 7.6. pH profiles obtained from the PP-CWAO process, for: (■) AC-O2-00, (●) AC-O2-20, (▲) FeAC-O2-20, (▼) AC-O2-20+Fe^{3+}.

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In addition, as it will be discussed later, it was found after TGA that FeAC suffered a high loss of mass as well as a significant degree of depositions of carbonaceous polymers that would also have a negative impact on its catalytic performance as time on stream proceed.

Another problem is the catalyst deactivation caused by the leaching of metal ions that, as can be observed in Figure 7.5, reached a maximum of 14 mg L^{-1} for FeAC-O2-20 which decreased until 8 mg L^{-1} after 72 h of reaction. The metal ions leached from the FeAC material act as homogeneous catalyst for the activation of hydrogen peroxide which makes it difficult to differentiate between homogeneous and heterogeneous catalytic effects. Still, an attempt was made by supplying 8 mg L^{-1} of Fe^{3+} solved with the phenol initial feed solution in the AC-O2-20 system. This iron concentration was chosen since it was the concentration found in the effluent from FeAC-O2-20 after 48 to 72 h of time on stream. Homogeneous presence of dissolved iron ions in the liquid phase (AC-O2-20+Fe^{3+}) does not promote an enhancement of phenol and TOC degradation. A similar decrease of activity is evidenced for the homogenous Fenton catalytic system (AC-O2-20+Fe^{3+}), even though less accentuated than that observed by the heterogeneous one. In this case, this fact can be accounted for the formation of carbonaceous deposits onto the catalyst surface by oxidative coupling reactions of phenol in the homogeneous liquid phase, observed after TGA as discussed later. Therefore, as reaction proceeds, the catalytic effect of AC in presence of homogeneous Fenton reagent would be inhibited by carbon depositions.

It is noticeable from Figure 7.5 that both profiles had a similar behaviour that leads to the increase of iron concentration in the effluent after 24 h of time on stream. This behaviour could be related to the AC adsorption capacity, especially for the case of AC-O2-20-Fe^{3+}, since it has been reported that AC can be used to remove iron ions from solution at pH close to 3 [14]. It seems that at the beginning of the reaction AC is capable to adsorb both organic compounds and iron, thus giving the low iron concentrations in the effluent until saturation is reached. At this point is when phenol and TOC conversions start lowering and for the case of AC-O2-20+Fe^{3+} it seems that iron concentration in the effluent could reach a stable value if eventually the iron adsorption/desorption on AC surface is equilibrated.

Therefore, from the different reaction systems in Figure 7.4, the adsorption capacity of AC should be of crucial importance in the oxidation rate overcoming the effect of Fenton reagent when using iron either homogeneous or heterogeneously. What is observed it that the greater the initial surface of the carbon catalyst, the higher the catalytic performance and more importantly, the higher the catalyst stability along the reaction.

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Phenol is a relatively strong acid, which confers acidic properties to the feed solution (i.e initial pH around 5.9). In addition, the reaction intermediates from the complex oxidation mechanism are mostly organic acids, which account for the decrease of pH up to 2.5-3 depending on the extension of the oxidation process, as plotted in Figure 5.20. At the same time, the iron species supported into AC are susceptible to be leached out due to the acid conditions that the degradation process involves, since leaching process is accelerated with decreasing pH [15]. If iron leaching is due to the acidic conditions of reaction, the control of pH can be an interesting issue in order to keep iron supported over the AC and so to avoid the catalyst deactivation by leaching phenomenon. However, as previously reported by Santos et al. (1999) [16] for the oxidation of phenol using a commercial copper catalyst in a basket stirred tank reactor, basic pH (pH_0 10 and 12) gave no benefits in terms of catalyst lixiviation. Moreover, assuming first order for phenol concentration, the calculated kinetic constant was one order of magnitude lower in basic media than that obtained in acid media (pH_0 3.6) [16]. Nevertheless, in a later work using a fixed bed reactor, Santos et al. (2005) [17] found that indeed using basic pH (pH_0 8) in the reaction media lead to negligible copper catalyst leaching, although phenol conversion obtained under acid conditions (pH_0 6) was still higher than that achieved at pH 8. On contrary, Miró et al. (1999) [18] who tested several copper-based catalyst for phenol oxidation in a TBR, observed that catalyst lixiviation and deactivation was largely reduced at basic pH (pH_0 8.3, 9 and 10), but the highest phenol conversions were also reached in these basic conditions. Therefore, it has to be concluded that metal leaching from supported catalyst could be prevented by using high pH, but its effect on the process performance in terms of organic load removal depends on other factors such as catalyst and reactor types.

At the present conditions, while the Fe concentration in the outlet effluent is increased, the catalyst performance in terms of phenol and TOC conversion is gradually reduced. This result could be attributed to deactivation of the catalyst by AC burning-off. Table 7.6 collects the AC weight changes recorded from TGA performed on all AC samples after reaction.

Table 7.6. Weight loss of original and AC samples after reaction.

AC materials	ΔW (%)	TWL (%)
original AC	--	5.36
AC-O2-00	3.61	12.20
AC-O2-20	17.63	26.40
FeAC-O2-20	-10.75	23.36
AC-O2-20+Fe^{3+}	29.14	24.27

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Values of AC mass change from TGA up to 400 ºC (ΔW) clearly evidence that AC burning and carbonaceous depositions due to oxidative coupling reactions occurred at very different extents depending on the reaction conditions. As previously discussed in Chapter 5, the presence of H_2O_2 in the reaction media promoted phenol polymerisation and chemisorption on AC surface leading to a positive ΔW. This phenomenon is also observed and even doubled when homogeneous iron is present in the reaction media (AC-O2-20+Fe^{3+}). In this case it seems to confirm the deactivation of AC by oxidative carbon polymers supported over the carbon surface which prevented its burning away in the oxidation process. On the other hand, for FeAC, the observed mass change after reaction is negative, which means that AC heavily suffered from combustion, although some carbonaceous deposits were also formed as a TWL of 23.36 % was obtained from TGA up to 900 ºC. This combustion of AC in the FeAC catalyst must be also responsible for the iron concentration found in the effluent, since the loss of metal from the catalyst is primarily related to the consumption of the support [19]. What is more, AC consumption is accompanied by a continuous decrease on the space time (τ), which also explains the observed fall in conversion.

Figure 7.7 shows the thermograms from AC samples after reaction. Thermogravimetric profiles for original AC and phenol saturated AC are also included, as reference samples. As expected from the close values found for the TWL, except for AC-O2-00, the initial difference in surface groups seems to vanish after reaction. This gradual homogenisation of carbon surface has been previously reported for the oxidation of phenol [2] and for the oxidative dehydrogenation of ethylbenzene [20]. From Figure 7.7.b it can be observed that the greatest release of gaseous species takes place around 300 and 650 ºC, except for AC-O2-00. These two peaks of maximal desorption correspond with those found for PP-CWAO experiments shown in Figures 5.7, 5.8 and 5.9. Then, it appears that the formation of carbonaceous deposits is mainly promoted by the presence of peroxide, being less affected by the addition of iron to the process. Nevertheless, the high loss of AC mass found for FeAC-O2-20 points out that simultaneous oxidative coupling of phenol and burning of AC surface took place during reaction, both phenomena being responsible of the low stability shown by FeAC on the PP-CWAO of phenol at 140ºC.

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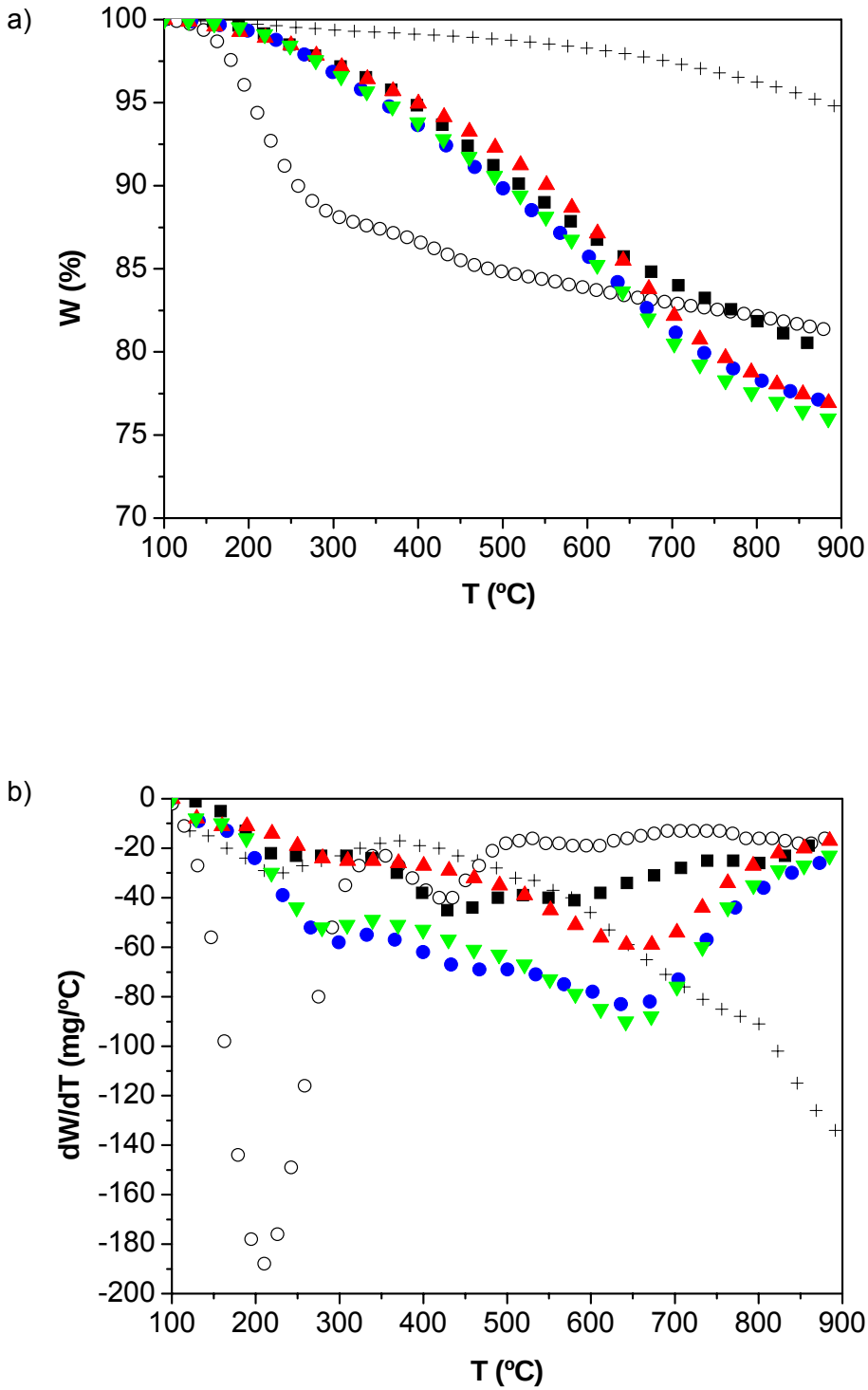

Figure 7.7. Thermogravimetric profiles (a) and first derivative of thermogravimetric profiles (b), for: (+) original AC; (o) phenol saturated AC, (■) AC-O2-00, (●) AC-O2-20, (▲) FeAC-O2-20, (▼) AC-O2-20+Fe^{3+}.

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Assuming that the reaction order with respect to phenol is one and the system follow an ideal plug-flow model, as previously done in Section 5.5 using Equation 5.5, the apparent kinetic constant (k_{ap}) for phenol disappearance can be estimated. The most relevant results at 72 h for the different catalytic systems tested as well as the calculated kinetic constants are summarized in Table 7.7. It is worth remembering that the catalyst weight used (m_{fAC}) in the calculations is that obtained for the spend carbon samples after TGA up to 900 ºC, when physisorbed and chemisorbed compounds are released and just the remaining AC is left (see Equation 3.18).

Table 7.7. Main results and estimation of apparent kinetic constants for each catalytic system.

Experiment	X_{phenol} (%)	X_{TOC} (%)	$[Fe]_{effluent}$ (mg L^{-1})	$[Fe]_{effluent}$ (%)*	m_{fAC} (g)	k_{ap} (mL g^{-1} h^{-1})
AC-O2-00	45	21	--	--	7.28	4.71 ± 0.06
AC-O2-20	64	51	--	--	6.68	8.78 ± 0.10
FeAC-O2-20	46	28	8	12.9	5.23	6.76 ± 0.08
AC-O2-20+Fe^{3+}	56	38	6	--	7.60	6.20 ± 0.07

* iron leaching degree with respect to the initial iron content of catalyst bed.

As previously commented in Section 5.1, addition of H_2O_2 to the CWAO process leads to a twofold increase in the phenol oxidation rate, which is accompanied by an increase on phenol conversion but also by a higher loss of AC after 72 h of time on stream. From the calculated kinetic constants, it is clear that adding iron, either homogeneous or heterogeneously, increases the reaction rate when compared to AC-O2-00, but not if compared to AC-O2-20. This is due, on one hand, to the enhanced decrease on AC mass for the FeAC-O2-20 system and the continuous lixiviation of iron that reduces the catalytic activity of FeAC. In addition, the lower oxidation rates for the FeAC-O2-20 system have to be also related to the poor catalytic activity of the oxidised AC (AC-APS) used to prepare the FeAC. It has been previously reported for the oxidation of phenol in similar reaction conditions that oxidised AC shows a worse catalytic activity with an overall kinetic constant of 3.5 mL g_{AC}^{-1} h^{-1} [2], which means a 60 % reduction in comparison with the original AC-M used in AC-O2-20. On the other hand, during the AC-O2-20+Fe^{3+} the build up of polymers on AC surface was doubled if compared to AC-O2-20, as deduced after observation of ΔW in Table 7.6. These carbonaceous deposits block the access to the pores and also hinders activated carbon's role as oxygen radical generator [2], negatively affecting the process performance.

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7.2.2. Influence of initial phenol concentration

In order to test whether the initial phenol concentration has any influence on the activity and stability of the selected FeAC catalyst, reactions using 5 and 1 g L^{-1} of phenol were compared. Figure 7.8 plots the obtained phenol and TOC conversions for the FeAC-O2-20 and AC-O2-20 systems.

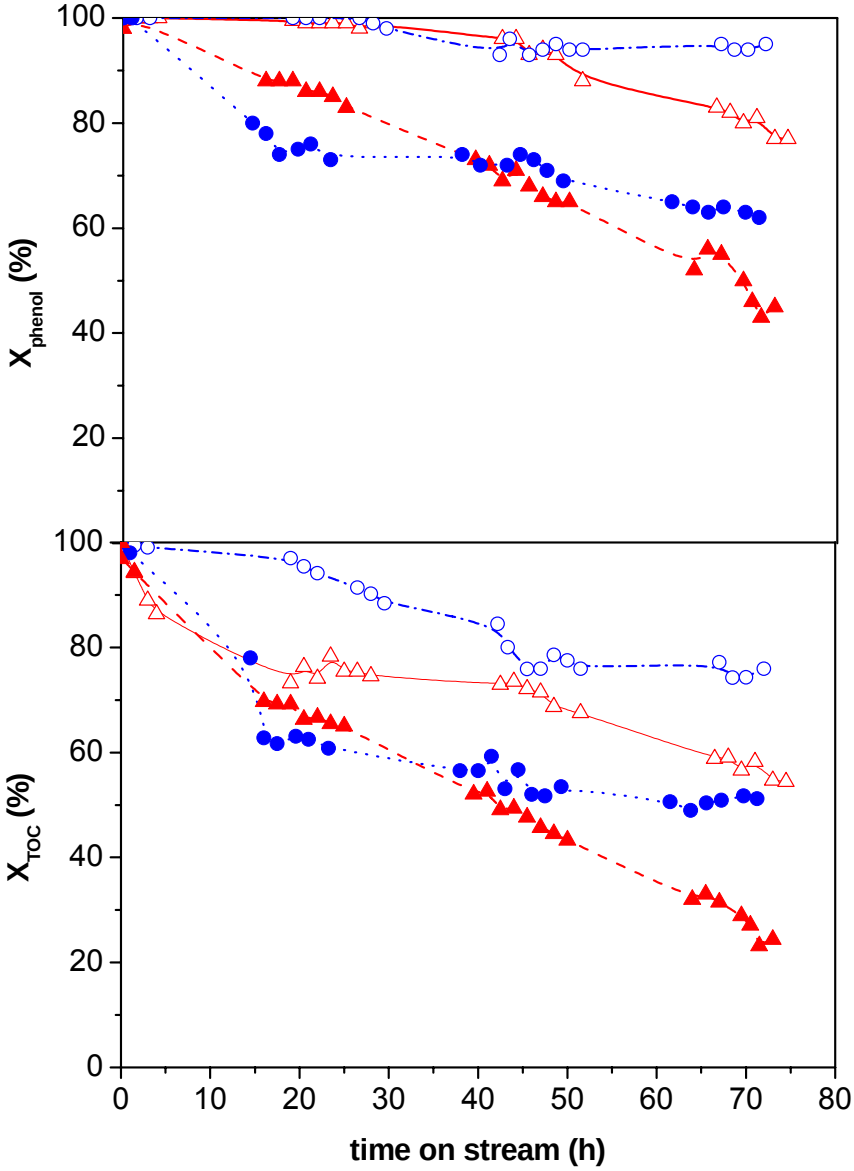

Figure 7.8. Influence of initial phenol concentration on phenol and TOC conversion, for: (▲) FeAC-O2-20, $[phenol]_0$= 5 g L^{-1}; (△) FeAC-O2-20, $[phenol]_0$= 1 g L^{-1}; (●) AC-O2-20, $[phenol]_0$= 5 g L^{-1}; (○) AC-O2-20, $[phenol]_0$= 1 g L^{-1}.

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It is easily seen in Figure 7.8 that oxidation of less concentrated phenolic solutions leads to higher phenol and TOC conversions. A similar effect of the initial phenol concentration has been reported for CWAO [21] and CWPO processes [22] using different metal based catalysts.

It can be noticed in Figure 7.8 that phenol conversions for both processes were similar for 50 h of reaction. After that, a continuous fall on phenol conversion begins for FeAC-O2-20. Meanwhile, as it can be seen in Figure 7.9, the leaching of iron is significantly reduced when dealing with 1 g L^{-1} of phenol as initial concentration, although a slight increase is also registered after 45-50 h on stream. This seems to point out that presence of soluble iron does not influence the oxidation of phenol as much as the chemical nature of the surface in the original AC. Therefore, using lower initial phenol concentration helped to highlight the importance of AC as a radical generator either from oxygen or hydrogen peroxide, as already observed by other authors [23-25].

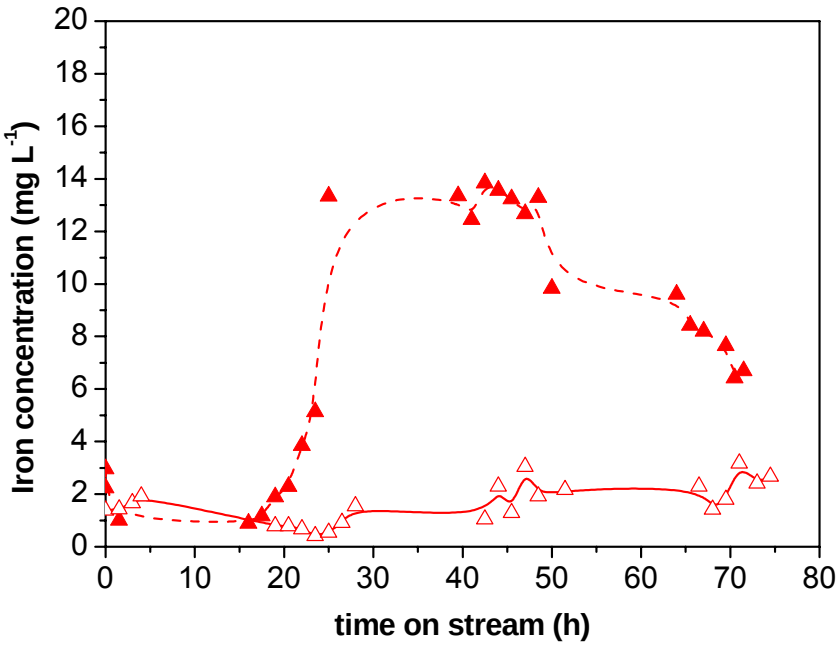

Figure 7.9. Influence of initial phenol concentration on iron leaching, for: (▲) FeAC-O2-20, $[phenol]_0$= 5 g L^{-1} and (△) FeAC-O2-20, $[phenol]_0$= 1 g L^{-1}.

In addition to the higher removals reached for the reactions with the lower initial phenol concentration, more stable conversion profiles were also obtained. Therefore, it seems that lower organic loads improved both catalyst activity and stability in terms of conversion, at the present reaction conditions

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Thermogravimetric analyses were performed on the used catalyst and the results are summarised in Table 7.8. It is noticeable that for the AC-O2-20 system, the main difference was in terms of phenol removal, since the AC mass change (ΔW or TWL) remain at similar levels. On contrary, for the FeAC-O2-20 system, the loss of AC was significantly enhanced during the oxidation of 1 g L^{-1} phenol solutions. The highly negative value for ΔW indicated that AC combustion prevailed over oxidative coupling, as confirmed by the low AC mass obtained after TGA up to 900 ºC (m_{fAC}, calculated according to Equation 3.18). Therefore, it can be concluded that at the present conditions the iron containing AC is not suitable for the PP-CWAO of phenol regardless the initial phenol concentration, since best results have been found for the non-modified AC.

Table 7.8. Influence of initial phenol concentration on the AC loss.

Experiment	$[phenol]_0$ (g L^{-1})	X_{phenol} (%)	ΔW (%)	TWL (%)	m_{fAC} (g)
AC-O2-20	5	64	17.63	26.40	6.68
	1	94	10.01	26.79	6.86
FeAC-O2-20	5	46	-10.75	23.36	5.23
	1	80	-51.64	25.38	2.79

A priori the last affirmation contradicts that postulated by Fortuny et al. (1998) and for similar reaction conditions in a TBR [26], who suggested that AC would be suitable for treating highly concentrated phenol solutions rather than dilute solutions. They had observed a faster carbon loss in the absence of phenol in the reaction media and concluded that the presence of phenol in the feed solution prevents the AC from being rapidly burned. Nevertheless, these authors did not use hydrogen peroxide in the reaction, which has been found to be a promoter of phenol polymerisation on the carbon surface. In the PP-CWAO process, the formation of a carbonaceous layer on the AC surface due to the presence of H_2O_2 could also have a role preventing the carbon from its own oxidation. At the same time, these carbonaceous deposits could also be susceptible of being burned. Therefore, it is again confirmed that carbon polymerisation and combustion can not be treated independently to clarify the preventing role that the initial phenol concentration may have on the process.

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7.3. Overview

It has been shown that by modification of the chemical nature of the surface of a given carbon, without altering the porosity, it is possible to change the impregnation stage of the catalyst preparation, leading to significant changes in the metal loading and the subsequent modification in the catalytic behaviour.

AC, Fe containing AC and homogeneous Fe^{3+} plus AC in the presence of hydrogen peroxide have been used for the CWAO degradation of phenolic aqueous solutions. The use of Fenton catalytic systems through FeAC or Fe^{3+} in PP-CWAO shows a negative effect on the life cycle of AC in the operation conditions under study (140 ºC, 2 bar P_{O2}, 20 % H_2O_2). The progressive loss of activity for the Fenton systems is attributed to the iron leaching in the case of heterogeneous FeAC catalysts, but also to the enhanced carbon consumption during the process. In addition, the poorer behaviour with respect to AC-M has to be related to the higher AC burning-off, which effectively reduces the space time, or to an intrinsic loss of AC initial activity because of the oxidation treatment. The promotion of oxidative coupling reactions in the liquid phase leading to carbonaceous deposits on the AC when Fe^{3+} is directly delivered to the catalyst bed is believed to be the reason for the lower performance obtained with respect to the process based on non modified AC.

Oxidation of less concentrated phenol solutions lead to higher phenol and TOC removals. Still, the process using non modified AC showed the best performance for the PP-CWAO process in terms of catalyst activity and stability.

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8. Conclusions and Open questions

8.1. Conclusions

The effects of operating variables such as pH, temperature and ratio of H_2O_2 to Fe^{2+} have been explored for the oxidation of phenol by the Fenton process and the most relevant conclusions are:

- Experimental results show that there is no need of adjusting initial pH when dealing with concentrated phenolic aqueous solutions, i.e., 5 g L^{-1}, since reaction products lead to a sufficient drop in pH for the reaction to proceed.
- It has been found that neither using double of the stoichiometric H_2O_2 dose for phenol mineralisation nor operating at temperatures higher than 30 ºC leads to significant benefits, since all reaction conditions tested reached similar results (i.e. complete phenol conversion in just 3 minutes of reaction and COD removals between 73 and 97 %, after 60 minutes of reaction).
- For an accurate kinetic modelling of the Fenton process, side reactions such as H_2O_2 thermal degradation and radical scavenging reactions must be considered at the temperature range studied (i.e. 30 to 85 ºC).
- When phenolic solutions were treated using low concentrations of iron catalyst (5-100 mg L^{-1}) it was found that a Fe^{2+} dosage above 50 mg L^{-1} does not increase phenol conversion, but there is an effect on the overall TOC removal.
- Residual H_2O_2 in the samples causes interference with conventional analytical procedures. Several methods were tested to remove it from the samples. H_2O_2 chemical decomposition to oxygen and water raising the pH to 11-12 was able to eliminate this interference.

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Peroxide Promoted Catalytic Wet Air Oxidation of phenolic aqueous solutions in the presence of heterogeneous catalytic systems is shown to be a promising alternative to the homogeneous system (Fenton Process) and also to the processes using air as an oxidant (CWAO). Additionally, the use of activated carbon as catalyst would be a good alternative, since it is a cheap material which does not introduce secondary pollution problems due to metal leaching. The most important conclusions derived from this part of the research work can be summarised as follows:

- Tests in a trickle bed reactor at mild total pressure (11-16 bar) and temperature (120-160 ºC) and feeding small amounts of hydrogen peroxide confirm that AC can be included among the catalysts able to be used in the PP-CWAO process.
- Activated carbon actually seems to act as a heterogeneous catalyst for the activation of hydrogen peroxide and can be used for the oxidation of organic substances.
- Simultaneous use of oxygen and hydrogen peroxide as oxidants leads to higher phenol, COD and TOC conversions. Although the improvement on the oxidation efficiency was not proportional to the amount of hydrogen peroxide added, a synergistic effect is outlined by the deepness in phenol mineralisation. This synergistic effect was predominant when using 20 % of the stoichiometric H_2O_2.
- Thermogravimetric analyses on samples after reaction reveal that AC suffers from partial burning-off and deactivation by formation of carbonaceous deposits that are favoured by the presence of H_2O_2, being less influenced by the reaction temperature.
- Partially oxidised products identified in PP-CWAO effluents indicate that the oxidation process evolves through a pathway similar to CWAO. Only a slight increase in hydroquinone and a reduction in p-benzoquinone concentrations are found in effluents from PP-CWAO.
- Respirometric analyses pointed out that although PP-CWAO leads to higher organic conversions, these were accompanied by higher fractions of COD readily biodegradable in the effluents, and an increase of toxicity and inhibition properties was also achieved. Therefore, longer tests on a pilot scale WWTP dealing with effluents from the PP-CWAO process would be recommended to ascertain the viability of such effluents for a biological end treatment.
- The activation energy values obtained ranged between 67.9 to 85.7 kJ mol^{-1} and were comparable to those frequently reported in the literature for the oxidation of phenol.

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- The lower activation energy was found for the process using 20 % of the stoichiometric demand for complete phenol mineralisation, confirming that the highest oxidation capacity was obtained for the AC-O2-20 system.
- PP-CWAO for the treatment of o-cresol and p-nitrophenol aqueous solutions at the selected conditions of 140 ºC and 20 % of H_2O_2 validate the process suitability to deal with different kind of phenolic compounds. Both higher target compound removal and degree of mineralisation can be obtained when H_2O_2 is combined with O_2. The fraction of COD readily biodegradable increased up to 7.5 %, although reaction conditions still need to be improved to produce effluents that could be safely sent to a municipal WWTP.
- The striking enhancement on p-nitrophenol removal for the PP-CWAO highlights the potential of H_2O_2 for the treatment of organic compounds refractory to CWAO.
- Regardless the use of H_2O_2 in the reaction, the experimental reactivity order in terms of pollutant conversion is phenol = o-cresol > p-nitrophenol, which agrees with the generally accepted nucleophilic aromatic substitution mechanism.
- The AC adsorption capacity followed the order p-nitrophenol > o-cresol > phenol, the same trend found for the solubility in water and the molecular weight of the compounds. Therefore, it can be said that the higher the adsorption capacity, the lower the removal obtained, which reinforces the theory that oxidation takes place in the liquid phase and not over the AC surface when the organic compounds are adsorbed.
- Modification of AC surface by acidic treatments and iron impregnation to produce an iron containing AC (FeAC) lead to significant changes in the catalytic behaviour.
- AC, FeAC and homogeneous Fe^{3+} plus AC (AC+ Fe^{3+}) in the presence of H_2O_2 have been compared for the CWAO degradation of phenolic aqueous solutions. The use of Fenton catalytic systems through FeAC or AC+Fe^{3+} in PP-CWAO shows a negative effect on the life cycle of AC in the operation conditions under study (140 ºC, 2 bar P_{O2}, 20% H_2O_2).
- The low efficiency of Fenton systems is attributed to the iron leaching in the case of heterogeneous FeAC catalysts, but also to the enhanced carbon consumption during the process. This AC combustion is accompanied by a continuous decrease on the space time (τ), which also explains the observed fall in conversion.
- The promotion of oxidative coupling reactions in the liquid phase leading to carbonaceous deposits on the AC when Fe^{3+} is directly delivered to the catalyst

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bed is believed to be the reason for the lower performance obtained with respect to the process based on non modified AC.

- Oxidation of less concentrated phenol solutions leads to higher phenol, COD and TOC removals. Still, the process using non modified AC showed the best performance for the PP-CWAO process in terms of catalyst activity and stability, since it gave more stable conversion profiles for longer time on stream.

8.2. Open questions

The Catalytic Wet Air Oxidation process promoted with hydrogen peroxide for the treatment of phenolic wastewater combines different areas of chemistry and chemical engineering, and obviously all of them can not be exhaustively treated in one PhD work. Several open research topics have aroused from this work, which are worth to be addressed in detail in order to improve understanding on the PP-CWAO process looking for its eventual industrial implementation.

The first question that rises is the economical implications of using H_2O_2 in the CWAO. Thus, a deeper study of the efficient use of H_2O_2 in order to economise the process would be very practical. In addition, an economic evaluation would be necessary for scaling up the process.

One important option is certainly the kinetic study over a variety of AC and organic pollutants to find out the complex mechanism and the role of oxygen surface groups on AC in the oxidation reaction. Besides, it would be interesting to test the process performance for the treatment of real industrial effluents since usually the destruction efficiencies obtained are lower than those achieved for single pollutants.

Another promising field is the tailored modification or manufacturing design of AC for its optimal catalytic performance and increased resistance to burning and deactivation during reaction.

In the context of process combination, efforts must be addressed to the study of coupling chemical oxidation followed by biological treatments or the use of combined adsorption-reaction cycles and different chemical oxidation stages working in series.

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Biographical note

Name: Alícia Rubalcaba Mauri

Place and date of birth: Tarragona, 15 July 1979

Education:

- 1997-2001: Diploma in Environmental Sciences, Universitat de Girona, Girona, Spain.
- 2002-2004: Research Sufficiency (Diploma d'Estudis Avançats, DEA), Universitat Rovira i Virgili, Tarragona, Spain.

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- A. Rubalcaba, R.R.N. Marques, A. Fortuny, R.M. Quinta-Ferreira, A. Fabregat, *Catalytic Wet Air Oxidation of Phenol over Activated Carbon Catalyst Promoted with Hydrogen Peroxide at Soft Temperature Conditions* (poster), accepted in the 8th International Conference on Gas-Liquid and Gas-Liquid-Solid Reactor Engineering, New Delhi (India), 2007.
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- September – December 2005, *Grupo de Ingeniería Química y Ambiental* from Universidad Rey Juan Carlos, Móstoles (Spain), under the supervision of Dr. Fernando Martínez and Dr. Juan A. Melero.
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